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PM$_{2.5}$-bound oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: Seasonal variation, sources and cancer risk assessment

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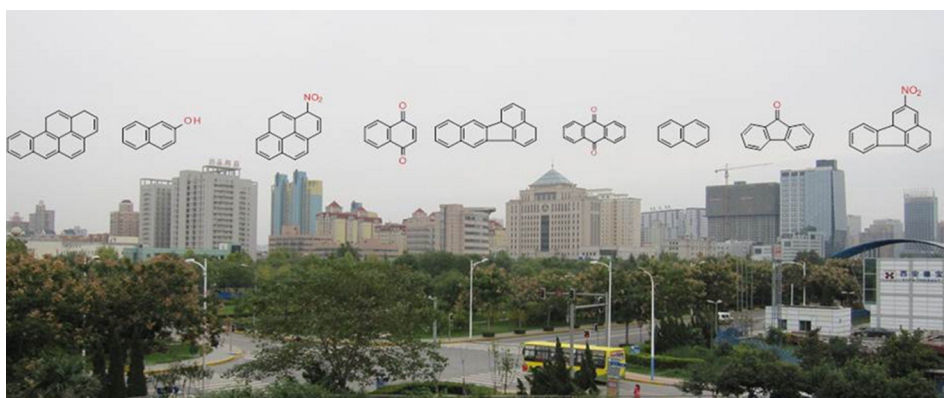[d] School of Public Health & Primary Care, Chinese University of Hong Kong, Hong Kong
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HIGHLIGHTS

- 24-h PM$_{2.5}$ samples were collected every sixth day for 13 months from the atmosphere of a Chinese megacity.
- Concentrations of PAHs, OPAHs and nitro-PAHs were measured in the PM$_{2.5}$
- Levels of PM$_{2.5}$-bound PAHs, OPAHs and nitro-PAHs were higher than in most Western cities.
- Excess inhalation cancer risk was six fold higher in winter compared to summer

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Polycyclic aromatic compounds (PACs) in air particulate matter contribute considerably to the health risk of air pollution. The objectives of this study were to assess the occurrence and variation in concentrations and sources of PM$_{2.5}$-bound PACs [Oxygenated PAHs (OPAHs), nitro-PAHs and parent-PAHs] sampled from the atmosphere of a typical Chinese megacity (Xi'an), to study the influence of meteorological conditions on PACs and to estimate the lifetime excess cancer risk to the residents of Xi'an (from inhalation of PM$_{2.5}$-bound PACs). To achieve these objectives, we sampled 24-h PM$_{2.5}$ aerosols (once in every 6 days, from 5 July 2008 to 8 August 2009) from the atmosphere of Xi'an and measured the concentrations of PACs in them. The PM$_{2.5}$-bound concentrations of Σcarbonyl-OPAHs, $\sum$ hydroxyl $+$carboxyl-OPAHs, Σnitro-PAHs and Σalkyl $+$ parent-PAHs ranged between 5–22, 0.2–13, 0.3–7, and 7–387 ng m^{-3}, respectively, being markedly higher than in most western cities. This represented a range of 0.01–0.4% and 0.002–0.06% of the mass of organic C in PM$_{2.5}$ and the total mass of PM$_{2.5}$, respectively. The sums of the concentrations of each compound group had winter-to-summer ratios ranging from 3 to 8 and most individual OPAHs and nitro-PAHs had higher concentrations in winter than in summer,

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suggesting a dominant influence of emissions from household heating and winter meteorological conditions. Ambient temperature, air pressure, and wind speed explained a large part of the temporal variation in PACs concentrations. The lifetime excess cancer risk from inhalation (attributable to selected PAHs and nitro-PAHs) was six fold higher in winter (averaging 1450 persons per million residents of Xi'an) than in summer. Our results call for the development of emission control measures.

1. Introduction

The negative effects of particulate matter (PM) especially those with aerodynamic diameter ≤ 2.5 μm (i.e. $PM_{2.5}$) on the health of urban dwellers is well documented. Such negative health effects can be attributed to the total mass and sizes of the PM, carbonaceous content as well as specific chemicals that are bound to the particulate matter (Harrison and Yin, 2000; Huang et al., 2012; Pöschl, 2005). In China, rapid economic and industrial development has resulted in severe air pollution problems in its major cities with negative consequences for the health of its population, high health care costs and associated loss of economic productivity. The effect of air pollution includes an estimated 300,000 premature deaths per year and costs of treatment of illnesses caused by air pollution amounting to 4% of China's gross domestic product in 2003 (Cao et al., 2012; Huang et al., 2012; Jia et al., 2011; Millman et al., 2008; World Bank, 2007). Previous studies have focused on the sources, fate, and toxic effects of PM-bound polycyclic aromatic hydrocarbons (PAHs) because these compounds are toxic, mutagenic, and carcinogenic and are regulated air toxicants in many countries including China (IARC, 2010; Jia et al., 2011; Ravindra et al., 2008; Wang et al., 2006; J. Wang et al., 2012; Zhang et al., 2009). Some of these studies have shown that as much as 1.6% of lung cancer cases in China can be attributed to inhalation of PAHs from polluted air (Zhang et al., 2009).

PAHs in urban atmosphere are products of incomplete combustion processes, which in the specific case of China is attributed mainly to emissions from coal and oil combustion, biomass burning, coke and aluminum production, vehicular transport, and waste incineration (Okuda et al., 2010; Zhang and Tao, 2009; Zhang et al., 2007). Besides parent-PAHs, combustion processes also release significant concentrations of OPAHs and nitro-PAHs (Jakober et al., 2007; Karavalakis et al., 2010; Shen et al., 2012). Additionally, OPAHs and nitro-PAHs are formed during photochemical transformation of emitted parent-PAHs by atmospheric oxidants and possibly microorganisms (Burrows et al., 2009; Vione et al., 2004; WHO, 2003; Yu, 2002). OPAHs and nitro-PAHs are known to have toxic, carcinogenic, mutagenic and estrogenic properties which are frequently more pronounced than those of their corresponding parent-PAHs. Furthermore, OPAHs and nitro-PAHs are direct acting mutagens and also produce reactive oxygen species both of which are responsible for toxicity (Benbrahim-Tallaa et al., 2012; Bolton et al., 2000; Chung et al., 2006; Pedersen et al., 2005; Wenger et al., 2009; WHO, 2003; Yu, 2002).

Several studies have indicated that over 90% of parent-PAHs, OPAHs and nitro-PAHs in atmospheric aerosols can be associated with PM with aerodynamic diameter ≤ 2.5 μm (Albinet et al., 2008b; Allen et al., 1996, 1997; Ringuet et al., 2012c). However, very little is known about the concentrations, sources and fate of OPAHs and nitro-PAHs in the atmosphere. The contribution of primary and secondary sources to atmospheric OPAHs and nitro-PAHs loads, which is influenced by the primary emission sources and intensity, atmospheric oxidation capacity, and meteorological conditions, remains unknown. We are not aware of any year-round simultaneous measurements of PAHs, OPAHs, and nitro-PAHs concentrations in $PM_{2.5}$ at high temporal resolution from China. Time series of PAHs, OPAHs and nitro-PAHs concentrations in atmospheric aerosols extending over a few years are only available from western industrialized economies (Barrado et al., 2012a,b; Lee et al., 2012; Pietrograndae et al., 2011; Schnelle-Kreis et al., 2007). The results from western urban areas cannot be easily compared to the situation in China, because the current energy profile of urban Chinese emissions is more influenced by burning of coal-based fuels than in the western world (Zhang and Tao, 2009; Zhang et al., 2007). Furthermore, the fate of OPAHs and nitro-PAHs in the urban atmosphere might be more susceptible to climatic variations because of their reactivity (Ringuet et al., 2012b).

PAHs, OPAHs, and nitro-PAHs (collectively called polycyclic aromatic compounds, PACs) are a fraction of total carbon (TC). TC is a prominent constituent of atmospheric PM (Pöschl, 2005). TC is a mixture of elemental carbon (EC) originating from primary combustion sources and organic carbon (OC) from both, combustion sources and transformation of organic constituents such as PAHs by secondary aerosol formation (Pöschl, 2005). Because the formation of secondary organic aerosols (SOA) may involve photochemical degradation of parent-PAHs and formation of OPAHs and nitro-PAHs, correlation of OPAHs and nitro-PAHs with the mass of SOA, their relationship with parent-PAHs (e.g., expressed as concentration ratios of OPAHs and nitro-PAHs to parent-PAHs) might be used to determine which OPAHs or nitro-PAHs are formed during secondary transformation processes (Chan et al., 2009; Lee et al., 2012; Shakya and Griffin, 2010).

The objectives of our work were (1) to determine the temporal course and seasonal variation of the $PM_{2.5}$-bound concentrations and composition pattern of PAHs, OPAHs, and nitro-PAHs, EC, and OC from a typical urban site in China for a whole year, (2) to assess the sources and influence of meteorological conditions on the $PM_{2.5}$-bound concentrations of these PACs, and (3) to estimate the potential health impact (inhalation cancer risk) on the inhabitants of this urban center from inhalation of $PM_{2.5}$ and how this varies temporally and seasonally. We selected Xi'an as a representative megacity in China (>8.1 million inhabitants) where several recent epidemiological studies have linked $PM_{2.5}$ to increased mortality, although the chemical constituents in $PM_{2.5}$ were not yet sufficiently characterized (Cao et al., 2012; Huang et al., 2012).

2. Materials and methods

2.1. Sampling

Xi'an (33.29°N–34.44°N and 107.40°E–109.49°E) is the capital city of the Shaanxi province in China (Fig. S1). Xi'an is the largest city in northwest China with an area of 9983 km^2 and a population of >8.1 million. This megacity is located on the Guanzhong Plain at the south edge of the Loess Plateau about 400 m above sea level. In summer, the weather is wet and hot with an average ambient temperature of 26 °C and relative humidity (RH) of 70%. In winter, the weather is cold and dry with an average ambient temperature of −1.3 °C and RH of 50% (http://www.weather.com.cn, Fig. S2). Xi'an experiences considerable air pollution problems which have been frequently linked to increased health problems and mortality (Cao et al., 2005, 2012; Dai et al., 2012; Huang et al., 2012).

The $PM_{2.5}$ sampler was located at the rooftop of the two-story building hosting the Institute of Earth Environment of the Chinese Academy of Science (approximately 10 m above the ground) in the southeast part of downtown Xi'an (34 14′ 0″/108 52′ 50″) (Fig. S1). The surrounding of the sampling station consisted of a mixture of urban, industrial, commercial and traffic areas. $PM_{2.5}$ (24-h samples) were collected every 6 days (from 10:00 am to 10:00 am on the next day) on pre-baked

(780 °C for 3 h) quartz-fiber filters (203 mm × 254 mm, Whatman QM-A, USA) using a TE-6070 MFC high volume $PM_{2.5}$ air sampler (Tisch, OH, USA) at a flow rate of 1 m^3 min^{-1} from 5 July 2008 to 8 August 2009. A total of 65 samples were collected. $PM_{2.5}$ masses were determined on Teflon filters simultaneously collected with the high-volume filters by weighing before and after sampling with an electronic microbalance (MC5, Sartorius, Göttingen, Germany, with a sensitivity of ±1 μg) under constant temperature (25 °C) and humidity (50%) (Ho et al., 2003). Field blanks were collected to eliminate passive adsorption of gas-phase organic compounds onto the filter during and/or after sampling. All sampled filters were stored at <−15 °C after sampling until analysis. Meteorological data (ambient temperature, pressure, relative humidity, wind speed and direction, Fig. S2) were recorded during sampling (Cao et al., 2005, 2012; Dai et al., 2012; Huang et al., 2012).

2.2. Organic and elemental carbon analyses

Organic carbon (OC) and elemental carbon (EC) were determined on a 0.56 cm^2 punch from each filter by a DRI model 2001 carbon analyzer (Atmoslytic, Inc., Calabasas, CA, USA) following the IMPROVE-A thermal/optical reflectance (TOR) protocol (Cao et al., 2005; Chow et al., 2007, 2011). Further details of this procedure, analytical quality measures and some of the results of EC and OC have been reported in previous studies (Dai et al., 2012).

2.3. PAHs, OPAHs and nitro-PAHs analyses

The concentration of 27 alkyl-, parent-PAHs and biphenyl, 15 carbonyl-OPAHs, 8 hydroxyl- and carboxyl-OPAHs, 2-hydroxybiphenyl and biphenyl-2′,2′-dicarboxylic acid, 9 nitro-PAHs and 2-nitrobiphenyl were analyzed in all samples and blanks (Table 1 which contains all abbreviations used hereafter). A punch of filter sample (filter size 8.68 cm^2) was placed in the 33 mL accelerated solvent extractor (ASE) extraction cell and spiked with a mixture of 11 deuterated-PAHs (NAP-D_8, AC-D_{10}, PHE-D_{10}, PYR-D_{10}, BaA-D_{12}, CHR-D_{12}, BkF-D_{12}, BaP-D_{12}, PER-D_{12}, DahA-D_{12} and BghiP-D_{12}), 2 deuterated-OPAHs (BP-D_5 and 9,10-ANQ-D_8) and 4 deuterated nitro-PAHs (1-NN-D_7, 5-NFL-D_9, 3-NFLT-D_9, 6-NC-D_{11}) as internal standards for the alkyl + parent-PAHs, carbonyl-OPAHs, and nitro-PAHs, respectively. After spiking the filters with the internal standards, the extra space in extraction cells was filled up with inert bulk sorbent (Isolute HMN, Biotage, Uppsala, Sweden) and extracted twice using pressurized liquid extraction (ASE 200, Dionex, Sunnyvale, CA, USA) and dichloromethane as the extraction solvent. The ASE extraction conditions were the same as in Bandowe and Wilcke (2010). Extracts from each sample were combined and dried on Na_2SO_4. They were then spiked with 3 drops of toluene, rotary evaporated to about 0.5 mL and then spiked with 20 μL of 5 μg mL^{-1} FLT-D_{10} (100 ng in toluene) which served as internal standard for the hydroxyl + carboxyl-OPAHs and recovery standard for the deuterated internal standards spiked to filters before extraction of PAHs and carbonyl-OPAHs. The analyte from each sample was then split into two and transferred into separate GC/MS vials. In one portion we determined PAHs, carbonyl-OPAHs and nitro-PAHs and in the other portion we measured hydroxyl + carboxyl-OPAHs (after derivatization).

We used an Agilent 7890 N gas chromatograph coupled to an Agilent 5975 C mass selective detector for our measurements. Compounds were separated on a HP-5MS column (5% phenyl–95% methyl-polysiloxane, 30 m × 0.25 mm i.d. × 0.25 μm film thickness). One half was measured directly with GC/MS in the EI-mode to quantify the carbonyl-OPAHs and parent-PAHs. From this same fraction the nitro-PAHs concentrations were measured with GC/MS using the negative chemical ionization mode with CH_4 as the ionization gas. The hydroxyl + carboxyl-OPAHs were also measured with GC/MS in the EI-mode after derivatization of target compounds into their silyl derivatives with N,O-bis-(trimethylsilyl)-trifluoroacetamide [BSTFA:TMCS (99:1)]. Derivatization was realized by adding 150 μL of BSTFA: TMCS (99:1)

Table 1
List of target compounds and their abbreviations measured in this study.

	Abbreviation
Alkyl + parent-PAHs	
1,2,3,4-Tetrahydronaphthalene	TH-NAP
Naphthalene	NAP
2-Methylnaphthalene	2-MNAP
1-Methylnaphthalene	1-MNAP
Biphenyl	BiPHEN
1,3-Dimethylnaphthalene	1,3-DMNAP
Acenaphthylene	ACY
Acenaphthene	AC
Fluorene	FLO
Phenanthrene	PHE
Anthracene	ANT
1-Methylphenanthrene	1-MPHE
3,6-Dimethylphenanthrene	3,6-DMPHE
Fluoranthene	FLT
Pyrene	PYR
Retene	RET
Benzo[a]anthracene	BaA
Chrysene	CHR
Benzo[b + j + k]fluoranthenes	BbjkF
Benzo[e]pyrene	BeP
Benzo[a]pyrene	BaP
Perylene	PER
Indeno[1,2,3-cd]pyrene	IcdP
Dibenzo[a,h]anthracene	DahA
Benzo[ghi]perylene	BghiP
Coronene	COR
Carbonyl-OPAHs	
1-Indanone	1-IND
1,4-Naphthalenedione	1,4-NQ
1-Naphthaldehyde	1-NALD
2-Biphenylcarboxaldehyde	2-BPCA
9-Fluorenone	9-FLU
1,2-Acenaphthenedione	1,2-ACNQ
9,10-Anthracenedione	9,10-ANQ
4H-Cyclopenta[d,e,f]phenanthrene-4-one	CpPHEone
1,8-Naphthalic anhydride	1,8-NANH
2-Methyl-9,10-anthracenedione	2-MANQ
Benzo[a]fluorenone	BaFLU
7H-Benz[d,e]anthracene-7-one	BANTone
Benzo[a]anthracene-7,12-dione	BANTdione
5,12-Naphthacenedione	5,12-NACQ
6H-Benzo[c,d]pyrene-6-one	BPYRone
Hydroxyl + carboxyl-OPAHs	
2-Hydroxynaphthalene	2-HNAP
2-Hydroxybiphenyl	2-HBP
1-Hydroxyacenaphthene	1-HAC
2-Naphthoic acid	2-NAA
5,6,7,8-Tetrahydro-2-naphthoic acid	TH-2-NAA
9-Hydroxyfluorene	9-HFL
2,3-Dihydroxynaphthalene	2,3-DiHNAP
1-Hydroxy-2-naphthoic acid	1-H-2-NAA
Biphenyl-2′,2′-dicarboxylic acid	BPA
9-Hydroxphenanthrene	9-HPHE
Nitro-PAHs	
1-Nitronaphthalene	1-NN
2-Nitrobiphenyl	2-NBP
5-Nitroacenaphthene	5-NAC
2-Nitrofluorene	2-NFL
9-Nitroanthracene	9-NANT
9-Nitrophenanthrene	9-NPHE
3-Nitrofluoranthene	3-NFLT
1-Nitropyrene	1-NPYR
2,7-Dinitrofluorene	2,7-DNF
6-Nitrochrysene	6-NC

to the extract, followed by homogenization, and heating (at 60 °C for 15 min). The mixture was then left at room temperature for 60 min to complete the derivatization of hydroxyl- and carboxyl-OPAHs before GC/MS measurements (Bandowe and Wilcke, 2010). Hydroxyl and

carboxyl-OPAHs were measured in 22 of the 65 samples chosen to represent all seasons. The GC/MS EI conditions used for the measurement of OPAHs and parent-PAHs were the same as specified previously (Bandowe and Wilcke, 2010; Bandowe et al., 2011). Further details of GC-MS parameters are shown in Supplementary Information. In brief, 1 μL of each sample was injected in splitless mode at injection port temperature of 280 °C and pressure of 80 kPa. The MS was operated in single ion monitoring mode (SIM) with two ions monitored for each compound with dwell times ranging between 25 to 50 ms (Table S1). The operating conditions for the MS were: electron energy 70 eV, emission current 36 μA, ion source temperature 230 °C and quadrupole temperature 150 °C. For the analysis of nitro-PAHs, we injected (1 μL) of analyte in pulsed splitless mode (pressure = 250 kPa) with an injection port temperature of 240 °C. The temperature program for the nitro-PAHs was adopted from Bezabeh et al. (2003). First, the initial temperature of 60 °C was held constant for 2 min. Then it was increased to 150 °C at a rate of 45 °C min^{-1}, held for 10 min and increased to 300 °C at a rate of 5 °C min^{-1}, held for 15 min. The transfer line temperature was 280 °C. The operating parameters of the mass spectrometer were electron energy 207 eV, emission current 49 μA, source temperature 150 °C, and quadrupole temperature 150 °C with CH$_4$ (5.5 quality) used as the ionizing gas. Target compounds were detected in SIM mode with two monitored ions per compound at dwell times between 25 and 50 ms (Tables S1-3). We detected target compounds in analytes by comparison of their retention time and ratios of quantifier and qualifier ions with those in standards measured simultaneously with samples. A compound was deemed to have been identified in a sample analyte only when the retention time was within ± 0.2 min and ratios of monitored ions within ± 20% of those in the standard. Target compounds were quantified by the internal standard technique using ten calibration standards with concentration of 10–2000 ng mL^{-1} for parent-PAHs and carbonyl-OPAHs and 10–500 ng mL^{-1} for nitro-PAHs, each spiked with a constant concentration of internal standard. All data recording and processing was done with the Agilent MSD ChemStation software package.

2.4. Quality assurance, quality control, and method quality

We used high purity solvents of pesticide residue grade (Carlo Erba, Milan, Italy) for all our extractions, rinsings and standard preparation. All glassware and metallic parts used during analysis were rinsed, machine washed and baked at 300 °C overnight. Immediately before use, they were rinsed with appropriate high purity residue grade solvents. We checked the accuracy of our measurements by spike and recovery experiments in which blank filters (n = 3) were spiked with a known amount (ca. 1000 ng of each) of the target parent-PAHs, OPAHs, and nitro-PAHs. The spiked filters were then extracted and quantified with the method above, the recovery and relative standard deviations were calculated as an indication of the accuracy and precision of our entire method. The recoveries of target alkyl/parent-PAHs, carbonyl-OPAHs, hydroxyl + carboxyl-OPAHs and nitro-PAHs averaged 102% (range: 67–154), 96% (range: 64–152), 22% (range: 4–51), and 85% (range: 40–113), respectively. The probable causes of the low recoveries of hydroxyl- and carboxyl-OPAHs were discussed in Bandowe and Wilcke (2010). The relative standard deviations (RSD) for the analysis of replicates of spiked filters (n = 3) were 5% (range: 0.7–10), 9% (2–31), 6% (0.3–26) and 8% (4–15) for alkyl + parent-PAHs, carbonyl-OPAHs, hydroxyl + carboxyl-OPAHs and nitro-PAHs, respectively.

To check for potential sample contamination during laboratory analysis we included several blank filters of same size and origin as used to sample PM$_{2.5}$ (n = 4) in our analysis and applied the same analytical procedures as above to determine the concentrations of our target compounds. Target compounds were either not detected in the blanks or the detected amounts were much lower than in the samples (except for 1,4-naphthalenedione [1,4-NQ] with 409 ng, Table S1-3). The mean masses of target compounds in the blank filters were subtracted from the masses measured in ambient PM$_{2.5}$ as correction for laboratory and field contamination. Target compounds in samples with mass below the limits of detection (LOD, defined as amount of target compound that produces a signal to noise ratio of 3:1) were assigned a value of non-detected (n.d).

2.5. Calculation of excess cancer risk

We used the recommended and widely applied procedures of the Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency (CalEPA) to calculate the lifetime excess cancer risk from inhalation (ECR) of PM$_{2.5}$-bound PACs in ambient air of Xi'an (Jia et al., 2011; OEHHA, 2003; Ramírez et al., 2011). In this point estimate-based approach, the [BaP]$_{eq}$ is calculated from the individual PM$_{2.5}$-bound concentration in each sample and the toxicity equivalency factor (TEF) of individual target compounds by using Eq. (1).

$$\sum [BaP]_{eq} = \sum_{i}^{n=1}(C_i \times TEF_i) \tag{1}$$

C_i is the concentration of the ith target compound (ng m^{-3}), TEF$_i$ is the toxic equivalency factor of the ith target compound (alkyl + parent-PAHs and nitro-PAHs); TEF$_i$ values (for 17 PAHs and 3 nitro-PAHs, Table S4) were taken from the literature (Collins et al., 1998; Nisbet and Lagoy, 1992). ECR was calculated using Eq. (2), where UR$_{BaP}$ is the inhalation cancer unit risk factor of BaP.

$$ECR = \sum [BaP]_{eq} \times UR_{BaP} \tag{2}$$

The UR$_{[BaP]}$ (unit risk) is defined as the number of people at risk of contracting cancer from inhalation a BaP equivalent concentration of 1 ng m^{-3} within their lifetime of 70 years. The World Health Organization (WHO) value of UR$_{[BaP]}$ is 8.7×10^{-5} and the value from the CalEPA UR$_{[BaP]}$ is 1.1×10^{-6} (OEHHA, 1994; WHO, 2000).

2.6. Data evaluation and statistical analysis

The sum of the concentrations of all analyzed 28 alkyl- and parent-PAHs, 15 carbonyl-OPAHs, 10 hydroxyl + carboxyl-OPAHs and 11 nitro-PAHs are reported as $\sum$ alkyl + parent-PAHs, $\sum$ carbonyl-OPAHs, $\sum$ hydroxyl + carboxyl-OPAHs and $\sum$ nitro-PAHs, respectively. The sum of the concentrations of 4–6 ring high molecular weight parent-PAHs (i.e. FLT, PYR, BaA, CHR, BbjkF, BeP, BaP, PER, IcdP, DahA, BghiP and COR) was referred to as $\sum$ HMW-PAHs and the sum of 2–3 low ring molecular weight parent-PAHs (NAP, ACY, AC, FLO, PHE and ANT) as $\sum$ LMW-PAHs. Concentrations of target compounds were generally log-transformed to approximate normal distribution before correlation and regression analyses, Student's t-tests or ANOVA and Tukey's HSD post-hoc tests were conducted. All statistical analyses were conducted with IBM SPSS 19.0 (IBM Corp., Armonk, NY, USA). Significance was set at $p < 0.05$.

3. Results and discussion

3.1. Seasonal changes of PACs concentrations in PM$_{2.5}$

The average concentration of PM$_{2.5}$ in ambient air (of Xi'an) for the entire sampling period was 140 μg m^{-3} (range: 32–408 μg m^{-3}). This value exceeded the yearly average limit of 35 μg m^{-3} set by the Chinese Government. Furthermore, the daily concentration limit set by the Chinese Government (i.e. 24-h PM$_{2.5}$ < 75 μg m^{-3}) was exceeded on 54 out of the 65 sampling days (Ministry of Environmental Protection of The People's Republic of China, 2012). The OC and EC concentrations in the PM$_{2.5}$ ranged between 3–64 μg m^{-3} and 2–17 μg m^{-3},

respectively. The mass of $PM_{2.5}$, OC and EC showed seasonal trends with higher concentrations in the cold period compared to the warm period. The mean winter (14 November to 23 March) to summer (10 May to 27 September) concentration ratios were 3, 3 and 2 for $PM_{2.5}$, OC and EC, respectively. The differences between winter and summer concentrations were significant (Student's t test). The concentrations of PACs compound groups in $PM_{2.5}$ showed the following trend: $\sum$ alkyl + parent-PAHs (mean: 87 ng m^{-3}, range: 7–387 ng m^{-3}) > $\sum$ carbonyl-OPAHs (mean: 44 ng m^{-3}, 5–215 ng m^{-3}) > $\sum$ hydroxyl + carboxyl-OPAHs (mean: 3.4 ng m^{-3}, 0.2–13 ng m^{-3}) > $\sum$ nitro-PAHs (mean: 2 ng m^{-3}, range: 0.5–7 ng m^{-3}). These concentrations levels were similar to other urban centers of China, but higher than in most west European cities (Table 2). Wang et al. (2006) reported a sum concentration of 18 PAHs in $PM_{2.5}$ from Xi'an (in 2003) of 104 ng m^{-3} (summer) and 701 ng m^{-3} (winter) which is about double of our results. The lower $PM_{2.5}$-bound PAH concentrations in the current study compared to the previous study of Wang et al. (2006) might be attributed to random effects of the weather and/or some efforts to improve air quality which includes stricter emission control measures and banning certain types of fuel combustion (Cao et al., 2005; Shen et al., 2008).

Further monitoring studies are needed to confirm that the lower concentrations from the current study are a trend related to emission control measures. The daily $PM_{2.5}$-bound BaP concentrations exceeded the 24-h average limit value (for China) of 2.5 ng m^{-3} on 42 of the 65 days monitored. The average $PM_{2.5}$-bound BaP concentration for the whole sampling period (5 July 2008 to 8 August 2009) from Xi'an was 8 ng m^{-3} (range: 0.5–31 ng m^{-3}) and also far exceeded the average year-round limit value of 1 ng m^{-3} for the mean annual BaP concentration in PM_{10} set by the European Union and the Chinese government (European Union, 2005; Ministry of Environmental Protection of The People's Republic of China, 2012). This suggests that Xi'an faces severe air pollution problems from PAHs which might have negative health effects.

The mean sum concentrations of all four compound groups showed a seasonal trend (Fig. 1, Fig. S3). Concentrations in fall (3 October to 8 November) and winter (14 November to 23 March) were significantly higher than in spring (29 March to 4 May) and summer (10 May to 27 September) (Tukey's HSD test). For all compound groups, the winter (14 November to 23 March) concentrations were significantly higher than the summer (10 May to 27 September) concentrations (Student's

Table 2

$PM_{2.5}$-bound $\sum$ alkyl + parent-PAHs, $\sum$ carbonyl-OPAHs, $\sum$ hydroxyl + carboxyl-OPAHs and $\sum$ nitro-PAHs concentrations (ng m^{-3}) at selected geographic locations. [U] denotes urban, [SU] suburban, [T] traffic, and [I] industrial areas.

Region	Sampling year	Particle size	# of samples	Summer	Winter	# of compounds	Reference
$\sum$ alkyl + parent-PAHs (ng m^{-3})							
Augsburg, Germany [U]	2007/2008	$PM_{2.5}$	63	1.34 ± 0.73	11 ± 10	11	Pietrogrande et al. (2011)
Athens, Greece [U]	2003/2004	$PM_{2.5}$	58	1.2 ± 1.5	28 ± 33–32 ± 29	18	Andreou and Rapsomanikis (2009)
Umea, Sweden [T]	2009	$PM_{2.5}$	8	0.9–7.9		15	Wingfors et al. (2011)
Madrid, Spain [U]	2008	$PM_{2.5}$	35	0.01–2	0.2–2	10	Barrado et al. (2012a)
Florence, Italy [U]	2008/2009	$PM_{2.5}$	NA[a]	0.5–10	0.8–24	16	Martellini et al. (2012)
Atlanta, USA [U + T + I]	2004	$PM_{2.5}$	120[b]	0.38–0.98	2.12–6.85	28	Li et al. (2009)
Mexico Valley [U + T]	2006	$PM_{2.5}$	189[c]	5.8–7.1		21	Amador-Muñoz et al. (2011)
Zonguldak, Turkey [U]	2007	$PM_{2.5}$	93	3.3 ± 4.4	153 ± 118	14	Akyüz and Çabuk (2008)
Tiruchirappalli, India [U + SU]	2009/2010	$PM_{2.5}$	48[d]	171–321	136–372	9	Mohanraj et al. (2011)
Hongkong, China [U + T]	2000/2001	$PM_{2.5}$	30	3.2–6.9	3.1–330	16	H. Guo et al. (2003)
Qingyuan, China [I]	2009/2010	$PM_{2.5}$	70[e]	7–33	42–113	17	Wei et al. (2012)
Nanjing, China [U]	2004	$PM_{2.5}$	28[f]	12–96	26–178	17	Wang et al. (2007)
Beijing, China [U + SU]	2002	$PM_{2.5}$	28	15–51	33–547	28	Feng et al. (2005)
Xi'an, China [U]	2003	$PM_{2.5}$	4	104	701	18	Wang et al. (2006)
Xi'an, China[U]	2008/2009	$PM_{2.5}$	65	7–71	51–387	28	This work
$\sum$ carbonyl-OPAHs (ng m^{-3})							
Paris region, France [SU + T]	2009/2010	PM_{10}	15[f]	0.1–1.4		9	Ringuet et al. (2012a)
Athens, Greece [U]	2003/2004	$PM_{2.5}$	58	3.5 ± 2.6	7 ± 11	14	Andreou and Rapsomanikis (2009)
Umea, Sweden [T]	2009	$PM_{2.5}$	8	0.09–1.8		12	Wingfors et al. (2011)
Augsburg, Germany [U]	2003/2004	$PM_{2.5}$	638[g]	0.41	7.4	6	Schnelle-Kreis et al. (2007)
Augsburg, Germany [U]	2007/2008	$PM_{2.5}$	63	0.66 ± 1.1	3.2 ± 2.9	7	Pietrogrande et al. (2011)
Kabul, Afganistan [U]	2009	$PM_{2.5}$	14		48–210	12	Wingfors et al. (2011)
Beijing, China [U]	2008	$PM_{2.5}$	63	0.2–2.2		5	Wang et al. (2011)
Qingyuan, China [I]	2009/2010	$PM_{2.5}$	70[e]	0.5–0.9	0.7–1.3	6	Wei et al. (2012)
Xi'an, China[U]	2008/2009	$PM_{2.5}$	65	5–40	29–208	15	This work
$\sum$ hydroxyl + carboxyl-OPAHs (ng m^{-3})							
Madrid, Spain [U]	2008	$PM_{2.5}$	35	0.02–0.1	0.02–0.3	2	Barrado et al. (2012a)
Nanjing, China[U]	2004	$PM_{2.5}$	28[f]	0.03–0.17	0.013–0.42	10	Wang et al. (2007)
Xi'an, China[U]	2008/2009	$PM_{2.5}$	22	0.3–3.2	3–13	10	This work
$\sum$ nitro-PAHs (ng m^{-3})							
Paris region, France [SU + T]	2009/2010	PM_{10}	15[f]	0.03–0.18		19	Ringuet et al. (2012a)
Madrid, Spain [U]	2008/2009	PM_{10}	55	0.11	0.16	5	Barrado et al., 2013
Sao Paulo, Brazil [U]	2002/2003	PM_{10}	22	0.2–1.2		16	de Castro Vasconcellos et al. (2008)
Mexico Valley[U + T + I]	2006	$PM_{2.5}$	134[c]	0.11–0.12		9	Amador-Muñoz et al. (2011)
Qingyuan, China [I]	2009/2010	$PM_{2.5}$	70[e]	0.04–0.2	0.3–0.7	13	Wei et al. (2012)
Beijing, China[U]	2008	$PM_{2.5}$	63	0.07–3		11	Wang et al. (2011)
X i'an, China[U]	2008/2009	$PM_{2.5}$	65	0.3–2.5	1.5–7	12	This work

[a] NA: Means not provided.
[b] Sum from two sites.
[c] Sum from 4 sites.
[d] Sum from 4 sites.
[e] Sum of separate day and night samples.
[f] Sum of separate day and night samples.
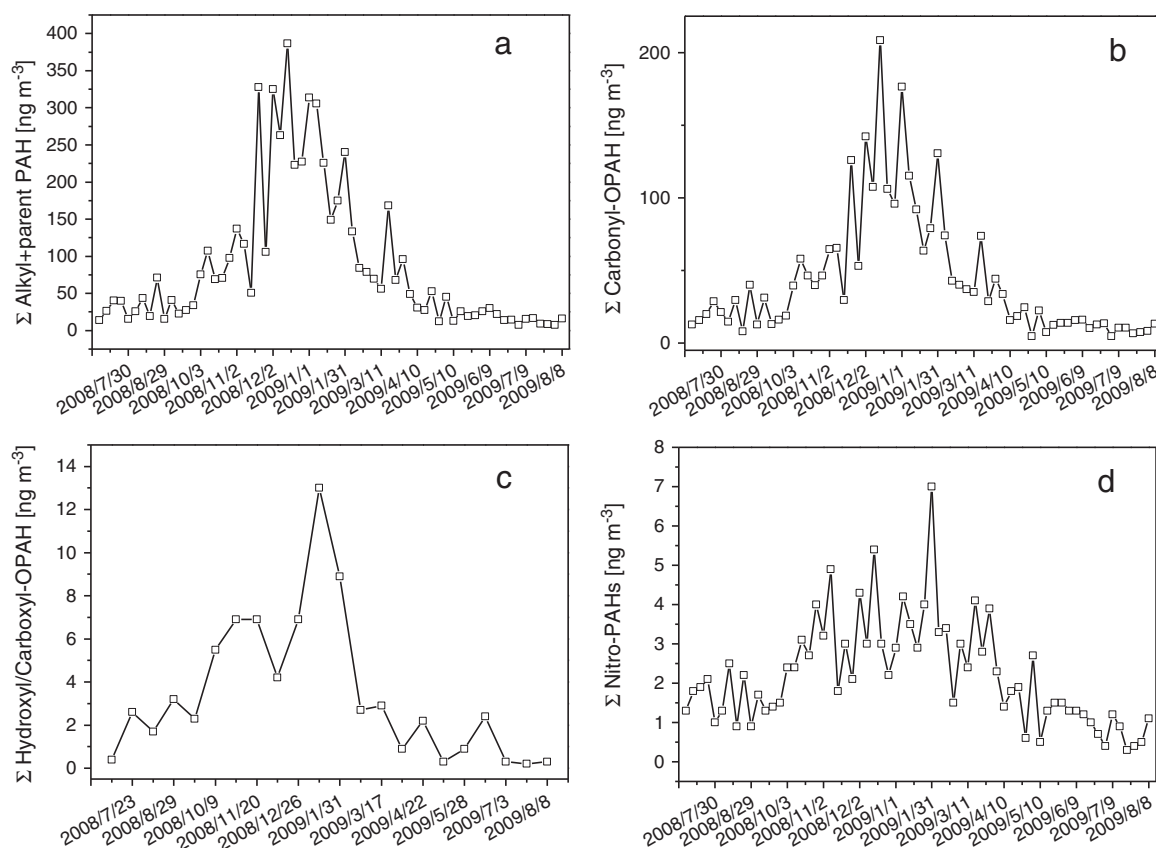[g] Sum of daily samples for 2 years.

Fig. 1. The $\sum$ alkyl + parent-PAHs, $\sum$ carbonyl-OPAHs, $\sum$ hydroxyl + carboxyl-OPAHs, and $\sum$ nitro-PAHs concentrations in PM$_{2.5}$ of Xi'an sampled from 5 July 2008 to 8 August 2009.

t test). The ratios of mean concentrations in winter divided by mean concentrations in summer were 8, 6, 5 and 3 for the $\sum$ alkyl + parent-PAHs, $\sum$ carbonyl-OPAHs, $\sum$ hydroxyl + carboxyl-OPAHs and $\sum$ nitro-PAHs, respectively. Similar seasonal trends for PAHs were reported in previous studies from China and other geographical regions and attributed to elevated alkyl + parent-PAH emissions in winter because of increased residential heating (Table 2) (Akyüz and Çabuk, 2008; H. Guo et al., 2003; Ramírez et al., 2011; Schauer et al., 2003; Tan et al., 2006; Tsapakis and Stephanou, 2005). The same seems to be true for OPAHs and nitro-PAHs (Albinet et al., 2008a; Barrado et al., 2012a,b; Lee et al., 2012; Schnelle-Kreis et al., 2007; Wei et al., 2012). Furthermore, the condensation of organic compounds on particles is favored under the lower temperature in winter (Fig. S2, Table S5) and the lower atmospheric mixing height in winter likely contributed to our finding of higher PACs concentrations in PM$_{2.5}$ in winter than in summer (Pankow and Bidleman, 1991; Pankow et al., 1993; Tsapakis and Stephanou, 2005; Yamasaki et al., 1982). An additional reason for the high concentrations of alkyl + parent-PAH concentrations in winter is the reduced degradation because of less radiation and therefore lower concentrations of atmospheric oxidants (e.g., OH, O$_3$, NOx, N$_2$O$_5$) than in summer (Atkinson and Arey, 1994; Vione et al., 2004; X. Wang et al., 2012). The $\sum$ alkyl + parent-PAHs, $\sum$ carbonyl-OPAHs, and $\sum$ nitro-PAHs concentrations correlated significantly with each other throughout the year (n = 65, r = 0.89–0.98, Table S6) but not with those of $\sum$ hydroxyl + carboxyl-OPAHs indicating a joint source of alkyl + parent-PAHs, carbonyl-OPAHs and nitro-PAHs (Karavalakis et al., 2010; Shen et al., 2012).

Many of the individual alkyl + parent-PAHs, carbonyl-OPAHs and nitro-PAHs concentrations correlated significantly with mass of PM$_{2.5}$, OC and EC. The $\sum$ alkyl + parent-PAHs, $\sum$ carbonyl-OPAHs, and $\sum$ nitro-PAHs concentrations correlated significantly with PM$_{2.5}$ (r = 0.37–0.43, p < 0.01), OC (r = 0.84–0.92, p < 0.01) and with EC (r = 0.81–0.83, p < 0.01) but there was no correlation with the

$\sum$ hydroxyl + carboxyl-OPAHs concentrations. The similar variations in concentrations of PACs and the PM, OC and EC are indications of both their common origin and the fact that these materials (PM, OC and EC) serve as sorbent for the PACs.

Ambient temperature (T) and wind speed (WS) correlated negatively (p < 0.01) with $\sum$ alkyl + parent-PAHs (T: r = −0.84., WS: r = −0.47), $\sum$ carbonyl-OPAHs (T: r = −0.81., WS: r = −0.46) and $\sum$ nitro-PAHs concentrations in PM$_{2.5}$ (T: r = −0.67., WS: r = −0.46). Ambient pressure (P), however showed a strong positive correlation (p < 0.01) with $\sum$ alkyl + parent-PAHs (r = 0.75), $\sum$ carbonyl-OPAHs (r = 0.73) and $\sum$ nitro-PAHs concentrations (r = 0.63). Relative humidity (RH) was negatively correlated to some few individual compounds and not with the overall sums while wind direction had no influence (Tables S5, S6). Similar correlations between PACs and meteorological factors have been reported in previous studies (Amodio et al., 2009; Barrado et al., 2012a,b; Gu et al., 2010; Tan et al., 2006; Tsapakis and Stephanou, 2005; Mastral et al., 2003). When it is cold, more alkyl + parent-PAHs, OPAHs and nitro-PAHs are emitted because of residential heating (Shen et al., 2012; Zhang and Tao, 2008). Temperature and pressure have also a direct influence on the gas/particle partition. In winter, when the temperature is lower than in summer the concentration of the compounds in particle phase increases because of more pronounced condensation. With increasing temperature, compounds evaporate into the gaseous phase or evaporate and condense in the coarse fraction (and therefore are not measured in PM$_{2.5}$). On the contrary, a higher ambient pressure leads to reduced volatilization (from particle surfaces) together with enhanced condensation of semi-volatile organic compounds on particles. The overall effect explains the positive relationship between ambient pressure and concentrations of PACs in PM$_{2.5}$ (Albinet et al., 2008a; Duan et al., 2007; Tsapakis and Stephanou, 2005; Walgraeve et al., 2010). In winter 2008/2009, when the analyzed samples were collected, both effects leading to higher particle concentrations (lower temperature and

higher pressure) were observed (Figures S3, S4). The RH possibly influenced the concentrations of some PACs in PM$_{2.5}$ by suppressing sorption of gas-phase organic species on particulate matter surfaces. Alternatively, the correlation between RH and PACs concentrations in PM$_{2.5}$ could just be a side effect of the relationship between relative humidity and ambient temperature (Gu et al., 2010; Mastral et al., 2003; Pankow et al., 1993). Strong wind tends to disperse and thus dilute particulate pollutants in air (Amodio et al., 2009).
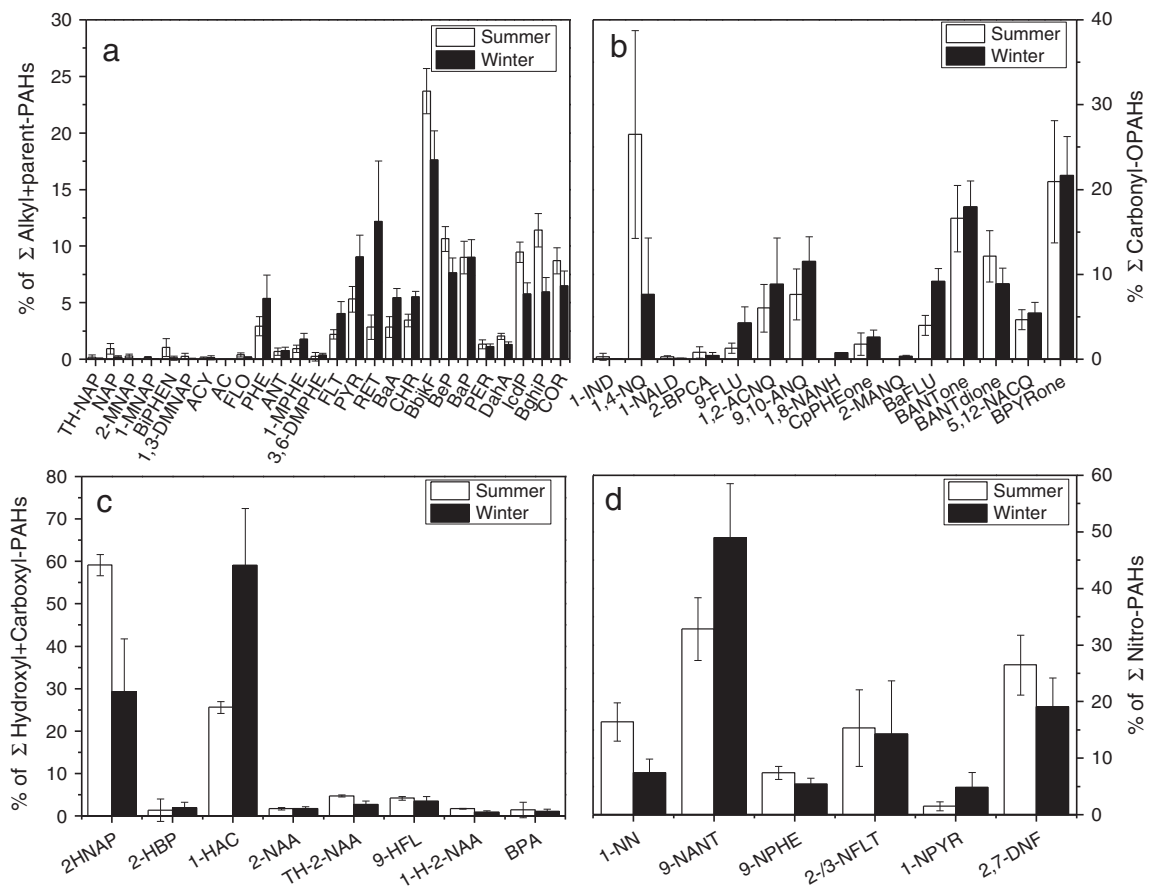
3.2. Composition pattern of PACs in PM$_{2.5}$

The $\sum$ alkyl + parent-PAHs contributed most to the sum of all PACs concentrations in PM$_{2.5}$ throughout the year followed by $\sum$ carbonyl-OPAHs, $\sum$ hydroxyl + carboxyl-OPAHs and $\sum$ nitro-PAHs (Fig. 1). In winter, $\sum$ alkyl + parent-PAHs contributed more to the sum of all PACs concentrations than in summer because of a higher emission and reduced atmospheric transformation of alkyl + parent-PAHs to the other compound groups. During the whole sampling period, the composition of the alkyl + parent-PAH mixture was dominated by BbjkF (mean: 22%, range: 14–28%) > BaP (10%, 6–13%) > BghiP (9%, 4–14%, Fig. 2a). On average of the whole observation period, the composition of the carbonyl-OPAH mixture was quantitatively dominated by BPYRone (mean: 23%, range: 10–35%) > BANTone (18%, 7–28%) > 1,4-NQ (17%, 7–64%). The winter mixture of the carbonyl-OPAHs was dominated by BPYRone (22%, 15–32%) > BANTone (18%, 13–25%) > 9,10-ANQ (12%, 7–14%). In summer, 1,4-NQ (26%, 7–64%) > BPYRone (21%, 9–35%) > BANTone (17%, 7–24%) contributed most to the Σcarbonyl-OPAHs concentrations (Fig. 2b). The contributions of 1,4-NQ, 1-NALD, and 22-BPCA to the Σcarbonyl-OPAHs concentrations

were significantly higher in summer than winter while other less volatile compounds showed the reverse.

The Σhydroxyl + carboxyl-OPAHs concentrations were dominated by 2-HNAP and 1-HAC contributing on average of the whole observation period 49% (18–62%) and 38% (23–71%), respectively (Fig. 2c). The contributions of 2-HNAP, TH-2-NAA, and 1-H-2-NAA to the $\sum$ hydroxyl + carboxyl-OPAHs concentrations were significantly higher in summer than in winter while 1-HAC, the most abundant compound in winter, had significantly higher contributions to $\sum$ hydroxyl + carboxyl-OPAHs concentrations in winter than in summer (Student's t-test). The Σnitro-PAHs concentrations were dominated by 9-NANT (mean: 39%, range: 22–68%), 2,7-DNF (22%, 10–37%), and 3-NLFT (18%, 2–40%) (Fig. 2d). This pattern is similar to that observed for nitro-PAHs in PM$_{2.5}$ of Beijing while in Longtang town (Qingyuan, China), 3-NLFT, 9-NANT, and 7-nitrobenz[a]anthracene (which is not included in our study) were the dominating nitro-PAHs in PM$_{2.5}$ (Wang et al., 2011; Wei et al., 2012). The contributions of 1-NN, 9-NPHEN and 2, 7-DNF and 2 + 3-NFLT were higher in summer than winter, while 9-NANT and 1-NPYR showed the opposite. The largest change in contributions of a single compound to the Σnitro-PAHs concentrations between the two seasons occurred for 1-NPYR.

Factors such as their relative proportions in emissions, higher relative formation from atmospheric transformation, photo stability and differences in extent of gas/particle partition and particle-size distribution may explain the seasonal variations of the composition of the nitro-PAHs mixture in PM$_{2.5}$. Furthermore, we cannot entirely rule out an artifact of our sampling method which might lead to the revolatilization of low molecular weight compounds especially in summer. It is also possible that the higher proportion in summer than in winter of 1,4-NQ, 1-NALD, and 2-BPCA, 2-HNAP, TH-2-NAA and 1-H-2-NAA was attributable

Fig. 2. Mean contributions of a) individual alkyl and parent-PAHs to the $\sum$ alkyl + parent-PAHs concentrations, b) individual carbonyl-PAHs to the $\sum$ carbonyl-OPAHs concentrations c) individual hydroxyl and carboxyl-OPAHs to the $\sum$ 10 hydroxyl + carboxyl-OPAHs concentrations, and d) individual nitro-PAHs to the $\sum$ nitro-PAHs concentrations in PM$_{2.5}$ of Xi'an in summer (10 May 2008–27 September 2008) and winter (14 November 2008–23 March 2009). Error bars indicate standard deviations.

to photochemical transformation from their parent-PAHs, or other OPAHs as part of enhanced SOA formation in summer (Chan et al., 2009; Kautzman et al., 2010; Lee and Lane, 2009; Mihele et al., 2002; Shakya and Griffin, 2010). We suggest that compounds like 9-NPHEN, 2-NLFT, and 2,7-DNF are more favored by summer-time meteorological conditions and atmospheric reactions (photo stability, secondary formation) while winter-time meteorological conditions and enhanced primary emissions from household-heating favor 9-NANT and 1-NPYR. This suggestion is supported by the fact that 1-NPYR is known to be mainly produced by combustion while 2-NLFT is from secondary reactions (Atkinson and Arey, 1994; Ciccioli et al., 1996; Reisen and Arey, 2005; Ringuet et al., 2012b).

3.3. Molecular ratios and correlations of PACs concentrations in PM$_{2.5}$

The ratio of HMW-PAHs to LMW-PAHs averaged 19 for the whole sampling period (range: 6–39). The observation of a HMW-PAHs/ LMW-PAHs concentration ratio > 1 is similar to previous reports from various urban areas in China and other geographical regions (Akyüz and Çabuk, 2008; Z. Guo et al., 2003; Li et al., 2009; Ramírez et al., 2011; Tan et al., 2006; Tsapakis and Stephanou, 2005). This finding can be explained by gas/particle partition (which favor HMW-PAHs in particulate phase), particle-size distribution (which favor the dominance of HMW-PAHs in finer particles) and the dominance of combustion sources in the atmosphere of Xi'an (Okuda et al., 2010). Lower vapor pressures of HMW-PAHs than LMW-PAHs favor the stronger association and co-condensation of HMW-PAHs with finer particles (aerodynamic diameter ≤ 2.5). In contrast, LMW-PAHs have higher vapor pressures which favor their occurrence in the gaseous phase and redistribution to the coarser fraction of aerosols than PM$_{2.5}$ (Allen et al., 1997; Walgraeve et al., 2010). Similar to other cities in China, the HMW-PAHs/LMW-PAHs in our Xi'an PM$_{2.5}$ samples were significantly higher in summer (mean: 21, range: 10–39) than in winter (14, 6–29, Student's *t* test) (Gu et al., 2010; Z. Guo et al., 2003; Tan et al., 2006). The driving role of gas-particle partitioning for HMW-PAHs/ LMW-PAHs ratios in PM$_{2.5}$ is supported by significant correlations of these ratios with T (r = 0.44, p < 0.05, Fig. S4), RH (r = 0.35, p < 0.05) and P (r = −0.29, p < 0.05).

The fact that the concentrations of both ∑ OPAHs and ∑ nitro-PAHs and all individual compounds were higher in winter than in summer (Fig. 1), suggested a significant contribution of primary emissions to the concentration of these compounds in PM$_{2.5}$ and also the favorable effects of winter ambient conditions on the enrichment of these compounds in PM$_{2.5}$. This is consistent with the findings from most previous studies and the known theoretical relationships between gas/particle partitioning and particle size distribution and ambient meteorological conditions (Atkinson and Arey, 1994; Finizio et al., 1997; Galarneau et al., 2006; Ligocki and Pankow, 1989; Pankow and Bidleman, 1991; Pankow et al., 1993; Walgraeve et al., 2010; Yamasaki et al., 1982; X. Wang et al., 2012). However, the concentration ratio of ∑ carbonyl-OPAHs/∑ alkyl + parent-PAHs in our samples was significantly higher in summer (mean: 0.7, range: 0.44–1.2) than in winter (0.5, 0.39–0.64; Student's *t*-test, Fig. S5). Similarly, ∑ nitro-PAHs/∑ alkyl + parent-PAHs concentration ratios were significantly higher in summer (0.056, 0.031-0.093) than in winter (0.022, 0.009–0.044). The mean ∑ hydroxyl + carboxyl-OPAHs/∑ alkyl + parent-PAHs concentration ratio in summer was, only at the p = 0.06 level significantly higher than the winter mean. The influence of gas-particle redistribution factors on the seasonal changes in these ratios cannot be fully accounted for in our study because we did not measure PACs concentrations in the gaseous phase. We, however, suggest that these increases in ∑ OPAH/alkyl + parent-PAH and ∑ nitro-PAH/∑ alkyl + parent-PAHs concentration ratios may be an indication of increasing formation of OPAHs and nitro-PAHs from photochemical degradation of parent-PAHs. This is in line with the finding that the concentration ratio of OPAHs to parent-PAHs in particulate matter is in general higher in

summer than in winter, which was mainly attributed to increased photo-chemical activity in summer than in winter (Walgraeve et al., 2010). In our study, the ratios of 9,10-ANQ/ANT, 9-FLU/FLO and BANTdione/BaA for the whole sampling period averaged 9 (range: 0.6–23), 6 (range: 1–20) and 2 (0.4–7), respectively.

The ratio of the concentration of 2-NFLT/1-NPYR has been used to differentiate primary from secondary photochemical sources of nitro-PAHs. This is because 2-NFLT is mainly formed by atmospheric photochemical reactions while 1-NPYR originates mainly from primary emissions. A 2-NFLT/1-NPYR concentration ratio > 5 indicates that secondary formation of nitro-PAHs dominates while 2-NFLT/1-NPYR < 5 indicates that primary emissions are the main source of the atmospheric nitro-PAHs (Albinet et al., 2007, 2008a; Bamford and Baker, 2003; Ciccioli et al., 1996). In our study, 2-NFLT and 3-NFLT were quantified together because our GC-column and analytical procedure did not allow for separation of these two compounds. Hence instead of the original concentration ratio of 2-NFLT/1-NPYR our ratio is 2 + 3-NFLT/ 1-NPYR. However this ratio is valid because several studies have shown that the atmospheric concentration of 3-NFLT is much lower than that of 2-NFLT (Bamford and Baker, 2003). The concentration ratio of 2 + 3-NFLT/1-NPYR in our samples ranged between 0.4 and 6.5 in winter while in the remaining time the ratios ranged between 2 and 50 which illustrated a dominating atmospheric formation of 2-NFLT (Fig. 3). Consequently, in winter primary sources were dominating the nitro-PAH concentrations while in summer there was a larger contribution of photochemical reactions of PAHs.

There were highly significant correlations between concentrations of ANT and 9,10-ANQ (r = 0.98), FLO and 9-FLU (r = 0.82), PYR and 1-NPYR (r = 0.91), and BaA and BANTdione (r = 0.91, Fig. S6–7, Table S6), in contrast, 1,4-NQ, 1-NALD, 2 + 3-NFLT did not significantly correlate or showed much weaker significant correlations with their related parent-PAHs, NAP, 1-MNAP, and FLT, respectively (Fig. S6-7, Table S6). This may be an indication that 9,10-ANQ, 9-FLU,1-NPYR, 2,7-DNF and 9-NANT the concentrations of which were closely correlated with those of their parent-PAHs originated together with their parent-PAHs from primary combustion emission sources (Chung et al., 2006; Shen et al., 2011, 2012), while 2-NFLT mainly originated from atmospheric photochemical reactions. This contrasting origin of 1-NPYR and 2-NFLT is in line with previous studies (Atkinson and Arey, 1994; Ciccioli et al., 1996; Reisen and Arey, 2005). The interpretation of the origin of 1,4-NQ and 1-NALD is complicated by the high blank values for the 1,4-NQ and their general susceptibility to sampling artifacts. It is, however, entirely possible that 1,4-NQ and 1-NALD are products of gas-phase heterogeneous reactions of their parent-PAHs or other OPAHs leading to the anti-correlation with their related parent-PAHs.
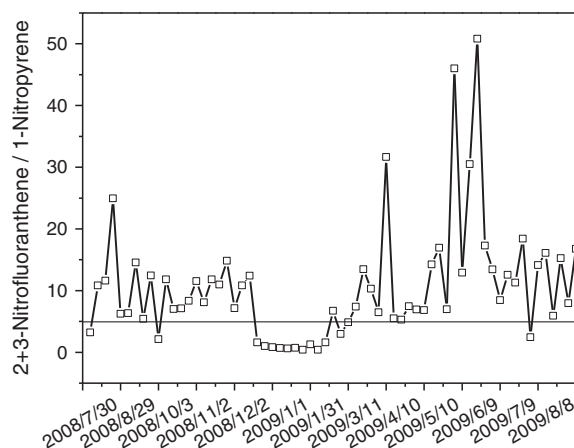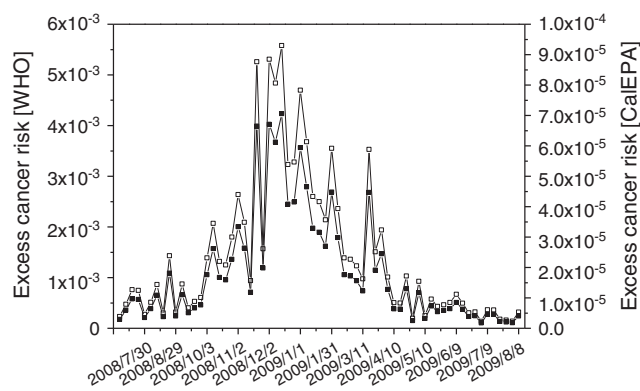

Fig. 3. The ratio of 2 + 3-nitrofluoranthene/1-nitropyrene in PM$_{2.5}$ of Xi'an sampled from 5 July 2008 to 8 August 2009.

Fig. 4. Estimated excess inhalation cancer risk attributed to measured concentrations of 17 alkyl + parent-PAHs and 3 nitro-PAHs in PM$_{2.5}$ of Xi'an sampled from July 2008 to 8 August 2009. Open square data points refer to excess cancer risk calculated according to the WHO procedure, and closed square points refer to excess cancer risk calculated according to the CalEPA procedure.

3.4. Toxicity and carcinogenic risk of polycyclic aromatic compounds in PM$_{2.5}$

The mean $\sum[\mathrm{BaP}]_{eq}$ for the whole monitoring period was 17 ng m^{-3} (range: 2–64 ng m^{-3}) and was higher in winter than in summer. These values were comparable to ranges of PM$_{2.5}$-bound $\sum \mathrm{BaP}_{eq}$ of 3–26 ng m^{-3} and 0.72–23 ng m^{-3} previously reported for Beijing and Zonguldak (Turkey), respectively, but again consistently higher than values in west European cities e.g., Florence: 0.34–0.79 ng m^{-3} (Jia et al., 2011; Akyüz and Çabuk, 2008; Martellini et al., 2012). The ECR for a lifetime of 70 years averaged 1.8×10^{-5} (range: 1.7×10^{-6} to 7×10^{-5}, CalEPA method) and 1.45×10^{-3} (range: 1.4×10^{-4} to 5.6×10^{-3}, WHO method) (Fig. 4). Hence, an estimated mean excess (for a lifetime of 70 years) of 20 (range: 2–70) per million people (CalEPA) or 1450 (range: 140–5600) per million people cancer cases (WHO) of the adult inhabitants of Xi'an will be attributable to inhalation of PM$_{2.5}$-bound 17 PAHs and 3 nitro-PAHs. ECR calculated with similar methods have produced comparable results for Beijing (range: 6.5 to 964 cases per million) and south China (9-1198 cases per million) all of which are much higher than those estimated for the surroundings of Taragona, Spain and the Chamonix and Maurienne valleys, France (Albinet et al., 2008a; Jia et al., 2011; Ramírez et al., 2011; J. Wang et al., 2012). Lower ECR in west European cities are likely attributable to cleaner energy sources, more efficient industrial technology, lower population, and better emission control measures. The average ECR in winter was six times higher than in summer. Our study also indicated a higher proportion of the highly toxic OPAHs and nitro-PAHs relative to the alkyl + parent-PAHs for which, however, no TEF values are available (Lübcke-von Varel et al., 2011; Wang et al., 2011).

4. Conclusions

The PM$_{2.5}$-bound PACs concentrations from the atmosphere of Xi'an were much higher than in most cities in Western Europe and North America but similar to those in other cities in China, Asia and Turkey. The concentrations of all studied PACs in PM$_{2.5}$ of Xi'an showed a seasonal variation with higher concentrations in winter than in summer. Higher emissions for residential heating, lower photochemical transformation, favorable meteorological factors and favorable gas/particle portioning in winter than in summer explained this seasonal variation. The concentrations of $\sum$ OPAHs and $\sum$ nitro-PAHs were strongly correlated with those of $\sum$ alkyl + parent-PAHs. Furthermore, the concentrations of several individual OPAHs and nitro-PAHs were also strongly correlated with their related parent-PAHs. These results suggest a dominant influence of primary combustion emissions on the sources of all PACs groups.

Concentration ratios of $\sum$ OPAHs and $\sum$ nitro-PAHs to the $\sum$ alkyl + parent-PAH were higher in summer than in winter. The concentration ratio of 2 + 3-NFLT/1-NPYR was also higher in summer than in winter. Besides sampling artifacts and different gas/particle partitioning, these ratios may indicate increasing contributions of the more dangerous OPAHs and nitro-PAHs to the total concentrations of PACs in PM$_{2.5}$ of Xi'an in summer because of their secondary formation by atmospheric photochemical reactions. The ECR associated with inhalation of PM$_{2.5}$ from Xi'an was among the highest ECRs reported in the world, particularly in winter, confirming potential negative health effects resulting from China's rapid industrialization and insufficient emission control measures.

Conflict of interest

The authors hereby declare that there are no actual or potential conflicts of interest that could inappropriately influence or be perceived to influence the contents of this manuscript.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.11.108.

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