

# Azaarenes in fine particulate matter from the atmosphere of a Chinese megacity

Benjamin A. Musa Bandowe<sup>1,2</sup> · Hannah Meusel<sup>3</sup> · Rujin Huang<sup>4,5,6,7</sup> ·  
Thorsten Hoffmann<sup>7</sup> · Junji Cao<sup>4</sup> · Kinfa Ho<sup>8</sup>

Received: 16 February 2016 / Accepted: 22 April 2016  
© Springer-Verlag Berlin Heidelberg 2016

**Abstract** Azaarenes (AZAs) are toxicologically relevant organic compounds with physicochemical properties that are significantly different from the well-studied polycyclic aromatic hydrocarbons (PAHs). However, little is known about their concentrations, seasonal variations, fate, and relationship with PAHs in air. This paper reports the temporal variations in the concentrations and composition patterns of AZAs in PM<sub>2.5</sub> that was

sampled once per 6 days from outdoor air of Xi'an, China from July 2008 to August 2009. The concentrations of the  $\Sigma$ AZAs, quinoline (QUI), benzo[h]quinoline (BQI), and acridine (ACR) in PM<sub>2.5</sub> were 213–6441, 185–520, 69–2483, and 10–3544 pg m<sup>-3</sup>, respectively. These concentrations were higher than those measured in urban areas of Western Europe. AZA compositional patterns were dominated by BQI and ACR. The high concentration of AZAs, high AZA/related PAH ratio, and the dominance of three-ring AZAs (BQI and ACR) in PM<sub>2.5</sub> of Xi'an are all in contrast to observations from Western European and North American cities. This contrast likely reflects differences in coal type and the more intense use of coal in China. The PM<sub>2.5</sub>-bound concentration of AZA in winter season (W) was higher than during the summer season (S) with W/S ratios of 5.7, 1.4, 4.1, and 13, for  $\Sigma$ AZAs, QUI, BQI, and ACR, respectively. Despite their significantly different physicochemical properties, AZAs were significantly ( $p < 0.05$ ) positively correlated with their related PAHs and pyrogenic elemental carbon. The changes in AZA concentrations were positively correlated with ambient pressure but negatively correlated with ambient temperature, wind speed, and relative humidity. This trend is similar to that observed for the related PAHs. We conclude that Xi'an and possibly other Chinese cities have higher emission of AZAs into their atmosphere because of the more pronounced use of coal. We also conclude that in spite of differences in physicochemical properties between AZAs and related PAHs, the atmospheric dynamics and relationships with meteorological factors of both compound groups are similar.

Responsible editor: Constantini Samara

**Electronic supplementary material** The online version of this article (doi:10.1007/s11356-016-6740-z) contains supplementary material, which is available to authorized users.

✉ Benjamin A. Musa Bandowe  
benjamin.bandowe@giub.unibe.ch

- <sup>1</sup> Institute of Geography, University of Bern, Hallerstrasse 12, 3012 Bern, Switzerland
- <sup>2</sup> Oeschger Centre for Climate Change Research, University of Bern, Falkenplatz 16, 3012 Bern, Switzerland
- <sup>3</sup> Multiphase Chemistry Department, Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
- <sup>4</sup> Key Laboratory of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, 10 Fenghui South Road, 710075 Xi'an, China
- <sup>5</sup> Centre for Atmospheric and Marine Sciences, Xiamen Huaxia University, Xiamen 361024, China
- <sup>6</sup> Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland
- <sup>7</sup> Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany
- <sup>8</sup> Jockey Club School of Public Health & Primary Care, The Chinese University of Hong Kong, Sha Tin, Hong Kong

**Keywords** Azaarenes · PAHs · PM<sub>2.5</sub> · Chinese megacity · Seasonal change · Meteorological conditions

## Introduction

Several published studies report a link between air particulate matter (PM) and the level of diseases borne by people living in or near cities and industrial zones (Pope and Dockery 2006; Cao et al. 2012). Higher levels of cardiovascular diseases, respiratory diseases, lung cancer, developmental and reproductive disorders, premature mortality and morbidity are all associated with inhalation of air contaminated with fine PM (Nel 2005; Millman et al. 2008; Cao et al. 2012). Economic growth, industrialization, and urbanization in China have all accelerated over the past few decades. These rapid transitions, which far outpace environmental protection measures, have resulted in severe cases of air pollution by PM and increased exposure of people to toxic air pollutants in many urban areas in China (Streets et al. 2006; Chan and Yao 2008; Huang et al. 2014). This situation has negative consequences for human health, general well-being (lower quality of life), and workplace productivity. These also result in high financial costs due to loss of working time and treatment of ailments (Zhang et al. 2009; Cao et al. 2012; Kan et al. 2012; Matus et al. 2012). The negative effects of exposure to fine PM are related to their small size, morphology, and high concentration of toxic chemicals bound to them (Harrison and Yin 2000). Polycyclic aromatic compounds (PACs) are prime suspects in the toxicity, mutagenicity, and estrogenicity of PM (Harrison and Yin 2000; Harrison et al. 2004; Gerlofs-Nijland et al. 2009; Wei et al. 2009). Previous studies that characterized the composition of toxic chemicals in PM were focused on polycyclic aromatic hydrocarbons (PAHs) or only benzo[a]pyrene probably because these are covered by air quality regulations in China, European Union, North America, and several other countries (European Union 2005; Wang et al. 2006; Ravindra et al. 2008; Ministry of Environmental Protection of The People's Republic of China 2012). However, other PACs like nitrogen-heterocyclic polycyclic aromatic compounds (azaarenes or AZAs) also show toxic effects. The toxic, mutagenic, carcinogenic, and estrogenic effects of some AZAs are higher than for some PAHs (Machala et al. 2001; Jung et al. 2001; IARC 2011). Several AZAs have been classified as probable/possible human carcinogens and assigned toxicity equivalence factors which are higher than those of some PAHs (Collins et al. 1998; IARC 2011). PM<sub>2.5</sub>, their bound AZAs, PAHs, and pyrogenic/elemental carbon (EC) are co-emitted into the atmosphere of urban environment from the combustion of fossil fuels (coal, oil) and biomass that take place during household heating, cooking, municipal waste incineration, transportation, industrial/power production, farming, and natural fires (Wilhelm et al. 2000; Bleeker et al. 2002; Boström et al. 2002; Bi et al. 2008; Junninen et al. 2009; Vicente et al. *in press*). Compared to PAHs with equal number of benzene rings (related PAHs), AZAs tend to have higher water

solubility, lower octanol-water ( $K_{OW}$ ), lower octanol-air partition coefficients ( $K_{OA}$ ), and lower vapor pressures (Table 1, Figure S1).

AZAs also have unpaired electrons, acid/base characteristics, and can exist in protonated (ionic forms) form under the right pH conditions (Kochany and Maguire 1994; Chen and Preston 2004; Reineke et al. 2007). AZAs might be washed out of the atmosphere by precipitation (especially with low pH) in more significant amounts than related PAHs because of their higher water solubility and acid/base properties (Osborne et al. 1997; Chen and Preston 2004). Furthermore, AZAs can be more strongly sorbed to charged surfaces of minerals and organic materials in atmospheric PM (by ionic and/or polar intermolecular forces) through their unpaired electrons and protonated ionic forms. Thus, the interactions of AZAs with sorbents in PM are different from those of their related PAHs whose sorption to PM is mainly by hydrophobic and weak van der Waal forces (Osborne et al. 1997; Chen and Preston 1997; Chen and Preston 2004; Bi et al. 2006; Arp et al. 2008). The above factor/properties could have enormous effects on the levels, temporal trends, gas/particle partitioning, particle size distribution, deposition patterns, and toxic effects of AZAs in air that are less predictable and different from their related but more hydrophobic PAHs (Chen and Preston 1997; Bandowe et al. 2014a). We therefore hypothesize that AZAs behave differently with respect to interaction with carbon fractions in atmospheric PM and meteorological conditions than related PAHs. However, up to now, not enough studies have been conducted on atmospheric AZAs with regards to their concentration levels, composition pattern, sources, fate, and behavior. The relationship of atmospheric AZAs with other co-emitted atmospheric pollutants (e.g., EC, PAHs) and meteorological conditions is sparsely investigated (Chen and Preston 1997; Lintelmann et al. 2010; Delhomme and Millet 2012). There are no studies on PM<sub>2.5</sub>-bound AZAs in China. However, the concentrations of AZAs in air of China could be very high because coal combustion (which is a significant source of AZAs) constitutes a large percentage of fuels currently used in China (Millman et al. 2008; Junninen et al. 2009; You and Xu 2010).

We recently reported the levels, temporal trends, composition pattern, and sources of a range of PACs (PAHs, oxygenated PAHs (OPAHs), nitrated-PAHs) in PM<sub>2.5</sub> (from Xi'an, China) sampled once per 6 days from July 2008 to August 2009. This previous study also evaluated the effects of seasonality and meteorological conditions on the levels, sources, composition pattern, and fate of the PACs groups listed above (Bandowe et al. 2014a). The current paper focuses on AZAs that was measured in the same samples as used in the previous paper with the following objectives: (1) to study the concentrations, temporal trends, and composition pattern of PM<sub>2.5</sub>-bound AZAs in the atmosphere of the Chinese megacity of Xi'an, (2) to compare the concentrations of AZAs in our study

**Table 1** Physicochemical properties of azaarenes (25 °C, 101.3 kPa) in comparison with related PAHs. All data were taken from the database of EPI-suiteTM 4.1 (<http://www.epa.gov/opptintr/exposure/pubs/episuitd1.htm>). Data in italics were estimated while all others were experimental data

Name	Mw [g/mol]	Water solubility [mg/L]	Log Kow	Vapor pressure [Pa]	Log Koa
<b>Azaarenes</b>					
Quinoline	129.16	6110	2.03	8	<i>6.19</i>
Benzo[h]quinoline	179.22	78.7	3.43	0.0291	<i>8.578</i>
Acridine	179.22	38.4	3.4	0.018	<i>8.961</i>
<b>Related PAHs</b>					
Naphthalene	128.18	31	3.3	11.3	5.19
Phenanthrene	178.24	1.15	4.46	0.016	7.57
Anthracene	178.24	0.0434	4.45	0.00087	7.55

to those reported in other studies, (3) to explore the relationship between AZAs, their related PAHs, and carbon fractions reported in earlier studies, (4) to study the relationship between ambient meteorological conditions and the temporal variation of PM<sub>2.5</sub>-bound AZAs, and (5) To draw conclusions on the drivers of PM<sub>2.5</sub>-bound AZAs concentrations in comparison to other related PACs measured in the same samples (Bandowe et al. 2014a).

## Materials and methods

### Sampling and laboratory analysis

Sampling location and procedures were described in the previous paper (Bandowe et al. 2014a). In brief, 65 and 24 h PM<sub>2.5</sub> samples were collected from the atmosphere of Xi'an (33.29°N–34.44°N and 107.40°E–109.49°E, Fig. 1), China.

The city of Xi'an which has a population of ca. 8 million is the administrative capital of Shaanxi province. The PM<sub>2.5</sub>

sampler was placed at the top of the roof of the building of the Institute of Earth Environment, Chinese Academy of Sciences. Xi'an city center is about 15 km away from the sampling location (Cao et al. 2005; Dai et al. 2012; Bandowe et al. 2014a). One 24-h sample (10:00 to the next day 10:00) was collected every sixth day from 5 July, 2008 to 8 August 2009 on pre-baked (780°C, 3 h) quartz-fiber filters (203 mm × 254 mm, Whatman QM-A, USA) using TE-6070MFC Hi-Vol PM<sub>2.5</sub> air samplers (Tisch, OH, USA). The sampler was operated at a flow rate of 1 m<sup>3</sup> min<sup>-1</sup>. All collected samples (filters with PM<sub>2.5</sub>) were immediately kept in cold storage (temperature < -15°C) until laboratory analysis. Ambient temperature (T), relative humidity (RH), pressure (P), wind speed (WS), and wind direction (WD) were recorded during sampling. Further details about the sampling location and the health impact of PM on inhabitants of Xi'an were discussed in previous papers (Cao et al. 2005; Cao et al. 2012; Dai et al. 2012; Bandowe et al. 2014a). Properties such as mass of PM<sub>2.5</sub>, total carbon (TC), organic carbon (OC), EC, and other PACs (OPAHs, PAHs, and nitrated-PAHs) have previously been determined in the same set of samples (Bandowe et al. 2014a), and the procedures and results reported previously (Chow et al. 2007; Chow et al. 2011; Dai et al. 2012; Bandowe et al. 2014a).

### Analysis of PM<sub>2.5</sub>-bound AZAs

The procedure for the analysis of PM<sub>2.5</sub>-bound AZAs was similar to those used for other PACs (PAHs and OPAHs) (Bandowe and Wilcke 2010; Bandowe et al. 2014a; Bandowe et al. 2014b; Lundstedt et al. 2014). In brief, AZAs (together with PAHs, OPAHs, and nitrated-PAHs) were extracted from the PM<sub>2.5</sub> samples (on filters) and blank filters by pressurized liquid extraction after being spiked with internal standards. Each sample was extracted twice using dichloromethane. After that, the two extracts from each sample were combined, spiked with toluene as keeper, rotary evaporated, and transferred to 2 ml GC vials. Analytes were then measured by gas chromatography mass spectrometry (GC-MS) in the



**Fig. 1** Location of the sampling site in Xi'an, China

selected ion monitoring mode. Target AZAs [quinoline (QUI), benzo[h]quinoline (BQI) and acridine (ACR)] were identified using their retention times, ratios of quantifying and qualifier ions as compared to those in calibration standards measured together with the samples in same GC-MS sequence. AZAs were quantified by the internal standard method. Target and qualifier ions (SIM ions) used during GC-MS measurements are same as in previous reports (Bandowe and Wilcke 2010; Bandowe et al. 2014a; Bandowe et al. 2014b; Lundstedt et al. 2014). The mass of target compounds measured in blanks (which was insignificant) was deducted from the mass measured in samples (to correct for artifacts).

To check for the accuracy and precision of the analytical procedures, we spiked blank filters ( $n=3$ ) with target AZAs (at ca. 1000 ng) and applied the entire analytical procedure to it and then calculated the recovery of the target compounds as indicator of accuracy and the relative standard deviation as indication of the precision of the measurements. The average recoveries of the AZAs were  $75 \pm 5$ ,  $87 \pm 6$ ,  $54 \pm 5$  % for QUI, BQI, and ACR, respectively. The relative standard deviation (RSD) for the replicate ( $n=3$ ) measurements of each target AZA compound was 7–10 % indicating the high precision of our measurements. The detection limit of our analytical method (LOD) was calculated as mass of target compound that produces a signal that is three times the baseline noise in the chromatogram. Concentrations lower than the LOD were designated as non-detected (n.d.).

### Data evaluation and statistical analyses

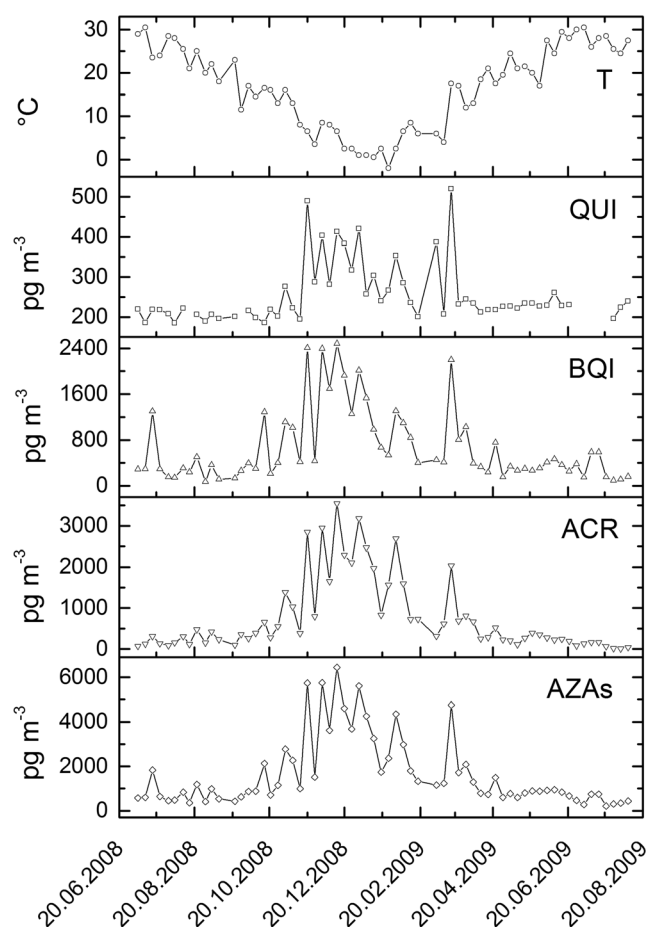
Based on the climate of Xi'an, the months of March, April, and May constitute the spring season; June, July, and August constitute the summer season; and September, October, and November constitute fall season while the months of December, January, and February constitute winter season (Dai et al. 2012). The sum of the three analyzed AZAs was called  $\Sigma$ AZAs. The sum of the concentration of all analyzed PAHs is designated as  $\Sigma$ 26PAHs. Naphthalene, phenanthrene, anthracene, and benzo[a]pyrene are symbolized by as NAPH, PHEN, ANTH, and BaP, respectively. The sum of fluoranthene, pyrene benzo[a]anthracene, chrysene, benzo[b+j+k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, and coronene which mainly originate from combustion sources are referred to as  $\Sigma$ COMB-PAHs (Bandowe et al. 2011). NAPH, PHEN, and ANTH are designated as PAHs related (related PAHs) to QUI, BQI, and ACR, respectively, because of their structural similarity (Fig SI, Table 1). Concentrations of all PAHs used in the current work were taken from the previously published paper (Bandowe et al. 2014a). Statistical evaluations (Pearson's correlation and regression analysis,  $t$  tests, ANOVA, and Tukey's HSD post hoc tests) were conducted on concentration data that have been mathematically transformed to improve their

normal distribution. Concentration data sets were transformed using the formula  $\log(x+1)$ , where  $x$  is concentration. Statistical analyses were done with SPSS 19.0. The statistical tests were deemed to be significant at  $p < 0.05$ .

## Results and discussion

### Temporal and seasonal variation in concentrations of PM<sub>2.5</sub>-bound AZAs

The concentration of the  $\Sigma$ AZAs in PM<sub>2.5</sub> for the 14 months sampling period were 213–6440  $\text{pg m}^{-3}$  (Fig. 2). The mean concentration of individual AZAs for the whole sampling period increased in the order QUI (mean 254  $\text{pg m}^{-3}$ , range 185–520  $\text{pg m}^{-3}$ ) < BQI (669  $\text{pg m}^{-3}$ , range 69–2480  $\text{pg m}^{-3}$ ) < ACR (757  $\text{pg m}^{-3}$  10–3540  $\text{pg m}^{-3}$ ) (Table S1). Very few studies have been conducted on AZAs in atmospheric PM<sub>2.5</sub> (Lintelmann et al. 2010; Table 2). Compared to the measurements from other cities, the concentrations of individual AZAs and  $\Sigma$ AZAs from this study were



**Fig. 2** Relationships between ambient temperature (T) and QUI, BQI, ACR, and  $\Sigma$ AZA concentrations in PM<sub>2.5</sub> of Xi'an sampled from 5 July 2008 to 8 August 2009



**Table 2** Concentrations [ $\text{pg m}^{-3}$ ] of particle-bound azaarenes in Xi'an, China in comparison with other geographic locations

Location	Date	Particle size	Typology	Quinoline	Benzo[h]quinoline	Acridine	$\Sigma$ AZA	Reference
Xi'an, China	Winter 08/09	PM <sub>2.5</sub>	Urban	201–420	402–2483	720–3544	1329–6411 ( $n=3$ )	This study
Xi'an, China	Summer 08/09	PM <sub>2.5</sub>	Urban	185–261	69–1304	10–477	213–1833 ( $n=3$ )	This study
Algiers, Algeria	Winter 05/06	PM <sub>10</sub>	Urban			290–420	570–1100 ( $n=2$ )	Ladji et al. 2009
Algiers, Algeria	Summer 05/06	PM <sub>10</sub>	Urban			nd-30	0.0–30 ( $n=2$ )	Ladji et al. 2009
NY, USA	Feb-Apr/75	TSP	Urban	69	10	41	1244 ( $n=21$ )	Dong et al. 1977
NY, USA	Jan-Mar/76	TSP	Urban	22	13	40	716 ( $n=21$ )	Dong et al. 1977
Copenhagen, Denmark	Winter 76–82	PM <sub>1.2</sub>	Residential	110	200		960 ( $n=11$ )	Nielsen et al. 1986
Copenhagen, Denmark	Winter 76–82	PM <sub>1.2</sub>	Traffic	400	300		1275 ( $n=11$ )	Nielsen et al. 1986
Münich, Germany	Winter 08	PM <sub>2.5</sub>	Suburban			356	120–600 ( $n=10$ )	Lintelmann et al. 2010
Upper Silesia, Poland	Summer 91	TSP	Industrial		390 (220–600)	678 (530–1000)	1190–2290 ( $n=5$ )	Warzecha 1993
Strasbourg, France	Annual 06/07	PM <sub>10</sub>	Urban				2800 ( $n=19$ )	Delhomme and Millet 2012
Besancon, France	Annual 06/07	PM <sub>10</sub>	Urban				1600 ( $n=19$ )	Delhomme and Millet 2012
Spicheren, Germany	Annual 06/07	PM <sub>10</sub>	Urban				1000 ( $n=19$ )	Delhomme and Millet 2012
Liverpool, UK	Annual 94–96	TSP	Urban		27 (6–152)	176 (22–523)	2800 ( $n=47$ )	Chen and Preston 1998
Liverpool, UK	Winter 94–96	TSP	Urban				6240 ( $n=47$ )	Chen and Preston 1998
Liverpool, UK	Summer 94–96	TSP	Urban				480 ( $n=47$ )	Chen and Preston 1998

either comparable or higher than at the other locations (Table 2, Table S1). The concentrations of AZAs in PM<sub>2.5</sub> samples have never been reported from any location in China. However, the fact that the concentrations of AZAs in Xi'an are higher than in urban areas of Western Europe and USA (Table 2) is in line with findings for other PACs. PACs such as PAHs, OPAHs, and nitrated-PAHs in air PM from Chinese cities are of similarly higher concentrations than in air PM sampled from Western Europe, Japan, and North America (Wang et al. 2006; Bandowe et al. 2014a).

The concentrations of  $\Sigma$ AZAs, individual AZAs, and their composition pattern showed a seasonal variation. Mean concentration of  $\Sigma$ AZAs was highest in winter and lowest in summer (i.e., winter > fall > spring > summer; Fig. 2). The mean concentration of  $\Sigma$ AZAs in winter was significantly higher than that in fall, summer, and spring (ANOVA with Tukey's HSD test). The ratio of the concentration of  $\Sigma$ AZAs in winter to that in summer (W/S) averaged 5.7. The concentrations of individual AZAs showed similar trend (i.e., highest concentration in winter and lowest concentration in summer) as the  $\Sigma$ AZAs (Fig. 2, Table S1). The average W/S was 1.4, 4.1, and 13 for QUI, BQI, and ACR, respectively. A previous study from Strasbourg (France) found the W/S ratio of 9.2, 7.3, 41, and 3.2 for two-, three-, four-, and five-ring AZAs, respectively, which is in line with our study (Delhomme and Millet 2012). The seasonal variation in our AZA concentration is consistent with most previous studies which also report higher average concentrations in winter seasons than in summer seasons (Chen and Preston 1998; Ladji et al. 2009;

Delhomme and Millet 2012). This trend reflect increased tendency of AZAs (like other PACs) to condense into the particle phase during the winter months because of the lower ambient temperature, a lower inversion layer height, higher mass of total suspended particles, higher PACs emissions (from increased household heating), and a lower photo degradation than in summer (Bandowe et al. 2014a; Chen and Preston 1998; Ladji et al. 2009; Delhomme and Millet 2012). Chen and Preston (1997) have shown that the percentage of AZAs in particulate phase of air was 30 % in summer and 70 % in winter hence strongly suggesting that larger partitioning into the particulate phase during winter is a reason for the increase in AZAs concentrations in winter. Elevated contribution of fine PM to the total atmospheric PM and lower redistribution of AZAs to larger particles in winter compared to summer fraction are further factors that contribute to the higher concentrations of PM<sub>2.5</sub>-bound AZAs in winter compared to summer (Chen and Preston 1997; Chen and Preston 1998; Albinet et al. 2008; Ringuet et al. 2012).

The average composition pattern of the AZA mixtures for the whole sampling period was dominated by BQI (mean 42 %, range 17–48 %) > ACR (38 %, 3–66 %) > QUI (21 %, 0–65 %). The seasonal contributions of the individual compounds to the  $\Sigma$ AZAs followed the order, ACR (54 %) > BQI (35 %) > QUI (6 %) in winter and BQI (49 %) > QUI (27 %) > ACR (24 %) in summer (Fig. 3). Hence, the composition pattern of AZAs in PM<sub>2.5</sub> of Xi'an's atmosphere was in all cases dominated by the three-ring AZAs, followed by the two-ring AZA.

In contrast, the composition pattern of AZAs from several European and North American cities (Liverpool, Strasbourg, Spicheren, Besancon, Copenhagen, and New York) showed increasingly lower contributions to  $\Sigma$ AZAs concentrations with increasing ring size (Dong et al. 1977; Chen and Preston 1998; Delhomme and Millet 2012). However, in an industrialized area of Upper Silesia, Poland (where coal is extensively used), the concentration of 3-ring AZAs (ACR and BQI) was also higher than those of two-ring AZAs (Warzecha 1993). We therefore attribute the dominance of three- over two-ring AZAs in the Xi'an samples compared to the other cities (Liverpool, Strasbourg, Spicheren, Besancon, Copenhagen, and New York) as indication of greater use of coal in Xi'an, where the fossil fuel used for energy (which amounts to 4.905.405 t of standard coal equivalent) includes 58 % of coal and 25 % of oil (Xi'an Municipal Statistics Bureau 2011). Coal combustion is known to produce both larger concentrations of AZAs as well as higher contributions of higher ring size AZAs to the total AZA concentration (Dong et al. 1977; Wakeham 1979; Warzecha 1993; Osborne et al. 1997; Chen and Preston 1998). The higher molecular weight and lower vapor pressure of ACR (Table 1, Figure S1) will also lead to its more pronounced partitioning into the particulate phase, hence its higher contribution to  $\Sigma$ AZAs concentrations than of the low molecular weight QUI. The seasonal change in the dominant AZA may also be an indication of the increased emission of ACR from household combustion of coal (for heating) during winter season.

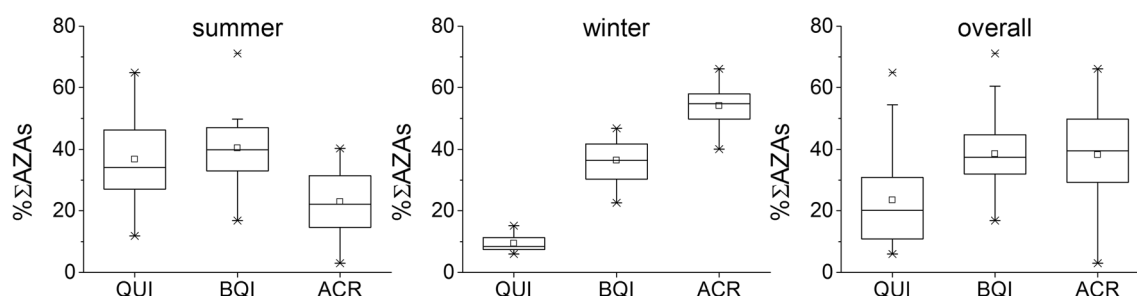
There was significant correlation ( $p < 0.05$ ) of the concentrations of individual AZAs with each other (Table S2). The correlation between QUI and BQI ( $r = 0.713$ ,  $p < 0.01$ ) and ACR ( $r = 0.653$ ,  $p < 0.01$ ) was weaker than the correlation between BQI and ACR ( $r = 0.849$ ,  $p < 0.01$ ). In comparison, the concentrations of the three-ring PAHs (PHEN and ANTH, taken from previous paper, Bandowe et al. 2014a) were correlated with each other ( $r = 0.966$ ,  $p < 0.01$ ) but not with the two-ring PAH, NAPH (Table S2). Correlations between two- and three-ring AZAs ( $r = 0.82$  and  $0.89$ ) were observed in the atmosphere of the Strasbourg region (France) and Liverpool (England), respectively (Chen and Preston 1998; Delhomme and Millet 2012). In Munich (Germany), the correlation

coefficient between individual  $PM_{2.5}$ -bound AZAs sampled in winter was  $> 0.9$  (Lintelmann et al. 2010). Such strong correlations between individual AZAs result from their common source, co-sorption, and/or similar fates in outdoor atmospheric environment (Osborne et al. 1997; Chen and Preston 1998; Chen et al. 2008). The weaker correlation between QUI and the three-ring AZAs could be explained by differences in their physicochemical properties and thus gas/particle partitioning (Table 1, Chen and Preston 1997, 1998 and 2004).

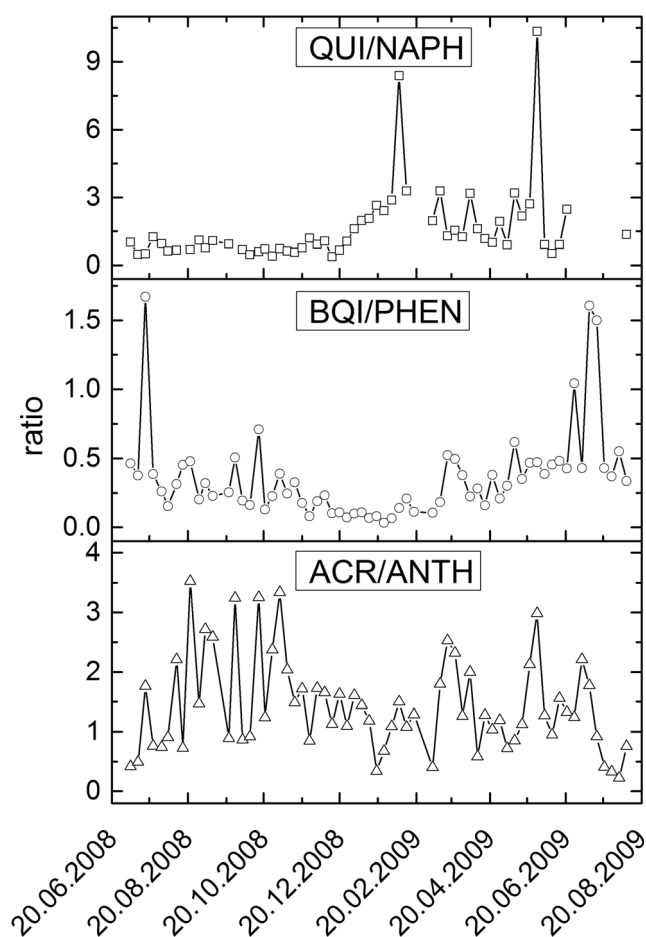
### Relationship between AZAs, PAHs, mass of $PM_{2.5}$ , and carbon

The average individual AZA/related PAH concentration ratios calculated in the current study were QUI/NAPH (mean 1.64, range 0.37–10), BQI/PHEN (mean 0.36, range 0.03–1.67), and ACR/ANTH (mean 1.43, range 0.23–3.5) (Fig. 4). This is in contrast to previous reports that suggest that the concentrations of AZAs in environmental media are frequently about 1–10 % of those of their related PAHs (Bleeker et al. 2002; Lintelmann et al. 2010).

The percent number of days for which the individual AZA/related PAH ratio was  $> 1$  and was 56, 6, and 68 % for QUI/NAPH, BQI/PHEN, and ACR/ANTH, respectively. These enhanced concentrations of AZAs relative to their related PAHs which are in contrast to studies from Western Europe and USA are an additional reflection of the higher proportion of coal in the fossil fuel use profile of Xi'an. Enhanced concentrations of AZAs relative to PAHs have also been observed in European regions where coal is dominantly used as industrial fuel or for power plants or in European cities with less efficient combustion of coal (e.g., Krakow, Poland) for residential heating (Warzecha 1993; Junninen et al. 2009). AZAs are considered as markers for coal combustion (Junninen et al. 2009). Bi et al. (2008) suggested that the higher concentrations of organic nitrogen in coal used in China might favor the formation and emission of high concentrations of AZAs during their combustion. Furthermore, there might also be a distinct influence of biomass burning which is more pronounced in China than most developed countries (Xu et al. 2006; Shen et al. 2013). Concentration of individual AZAs was higher



**Fig. 3** Composition pattern of AZAs in  $PM_{2.5}$  of Xi'an



**Fig. 4** Concentration ratio of AZAs to their related PAHs in  $PM_{2.5}$  of Xi'an

than their related PAHs in soils of Bangkok (Thailand) which could be related with enhanced biomass burning (Shen et al. 2013; Bandowe et al. 2014b).

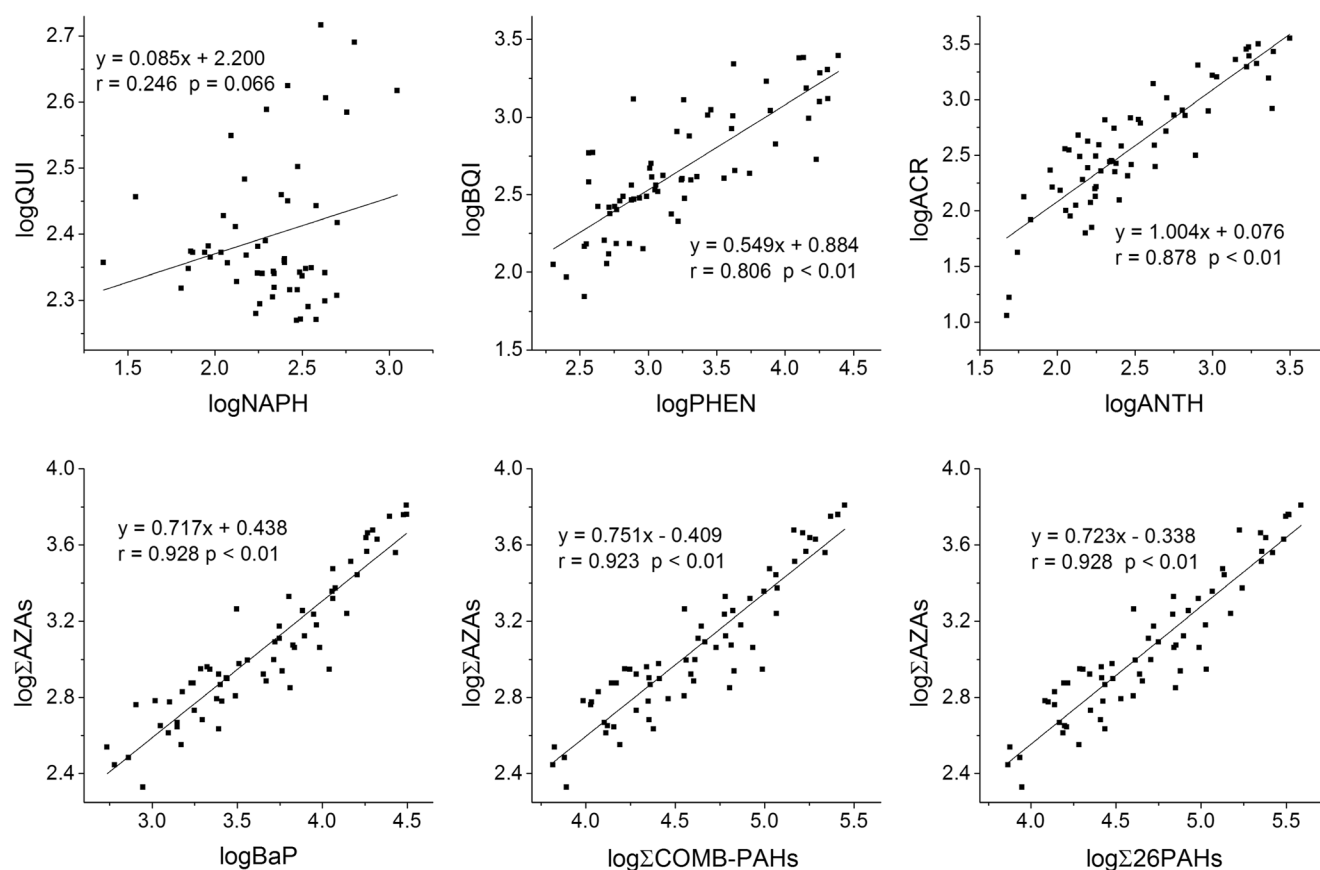
The concentrations of three-ring AZAs were correlated with their related PAHs [i.e., BQI vs PHEN ( $r=0.806$ ,  $p<0.01$ ) and ACR vs ANTH ( $r=0.878$ ,  $p<0.01$ )] while the two-ring QUI did not significantly correlate with NAPH (Fig. 5). The concentrations of individual AZAs and  $\Sigma$ AZAs also correlated significantly with the concentrations of  $\Sigma$ 26PAHs,  $\Sigma$ COMB-PAHs, and BaP (Fig. 5, Table S2) reported in Bandowe et al. (2014a). Such strong relationships between AZAs and related PAHs indicate common sources (pyrogenic combustion activities), and similarity in post-emission transport and environmental turnover. We previously found similar relationships between other polar PACs (OPAHs and nitrated PAHs) and PAHs in this same set of samples which were also attributed to their common source, similar transport mechanisms, and atmospheric turnover (Bandowe et al. 2014a).

The concentration of total carbon (TC), elemental carbon (EC), and organic carbon (OC) in atmospheric PM is frequently found to be strongly correlated with non-ionizable polar and

hydrophobic PACs because of their co-emission, co-sorption, transport, and similar fate (Pankow and Bidleman 1991; Cao et al. 2009; Li et al. 2009; Ma et al. 2013; Bandowe et al. 2014a). The concentrations of each AZA were correlated with EC, OC, and  $PM_{2.5}$  (Fig. 6, Table S2). Correlations between three-ring AZA and OC, EC, and  $PM_{2.5}$  were stronger than with those of the two-ring AZA (QUI) and OC, EC, and  $PM_{2.5}$ , which was also earlier observed for the related PAHs (Table S2, Bandowe et al. 2014a). This is attributable to the higher vapor pressure of QUI and the higher fraction of it in the gaseous phase compared to the three-ring AZAs (Chen and Preston 1997). Individual AZAs were more strongly correlated OC than with EC. Similar pattern was also observed for their related PAHs and other PACs (OPAHs and nitrated-PAHs, Bandowe et al. 2014a, Table S2). It was the working hypothesis of this study that there will be significant differences between AZAs and their related PAHs with regards to the relationship between each compound group and the components of atmospheric PM (mass of  $PM_{2.5}$ , EC, OC, and TC). This is because the physicochemical properties of AZAs (ability to form ions under changing atmospheric pH, ability to be sorbed to minerals because of their higher charge density/ionic forms which enables them to form specific bonds with minerals particle in atmospheric aerosols, and their higher water solubility) are different from the more hydrophobic and neutral PAHs (Götz et al. 2007; Arp et al. 2008; Bandowe et al. 2014a). In contrast to our hypothesis, our results strongly suggest that the relationships between AZAs and atmospheric sorbents ( $PM_{2.5}$  and carbonaceous matter) are similar to the relationship between hydrophobic PAHs and atmospheric sorbents ( $PM_{2.5}$  and carbonaceous matter). This finding strongly suggests that the physical, chemical, and ionic properties of AZAs do not significantly lead to a deviation in terms of their sorption properties compared to the neutral and more hydrophobic PACs. Further investigations on the relationships between atmospheric sorbents and higher molecular weight AZAs are warranted because the differences in sorption mechanism and extent of sorption could become more visible with increasing molecular weight. Previous studies have suggested that the sorption mechanisms and partitioning properties of AZAs might be similar to those of PAHs (Chen and Preston 1997).

### Relationship between ambient meteorological conditions and $PM_{2.5}$ -bound AZAs

The concentrations of QUI, BQI, ACR, and AZAs increased with decreasing ambient T and WS (significant negative correlation, Fig. 2, Table S2), but increased with increasing ambient P (significant positive correlation, Table S2). The concentration of QUI decreased with increasing RH (significant negative correlation, Table S2). There were slight differences between some individual AZAs and their related PAHs. For



**Fig. 5** Correlation of log (x + 1)-transformed concentration of AZAs and PAHs in PM<sub>2.5</sub> of Xi'an

instance, there was no significant relationship between NAPH concentrations in PM<sub>2.5</sub> and any meteorological parameter while the concentrations QUI (the NAPH-related AZA) were significantly correlated with T, P, RH, and WS (Table S2). Furthermore, there was no significant relationship between RH and BQI and ACR concentrations, but RH was negatively correlated with the concentrations of the BQI- and ACR-related PAHs (PHEN and ANTH). We previously also found significant correlations between several PAHs, OPAHs, nitrated-PAHs, and meteorological parameters for the same PM<sub>2.5</sub> samples (Bandowe et al. 2014a). Studies that investigated annual concentrations of AZAs in European cities (Liverpool, Strasbourg, Besançon, and Spicheren) found negative correlations between ambient T and concentrations of AZAs ( $r = -0.5$  to  $-0.88$ ) in PM (Chen and Preston 1998; Delhomme and Millet 2012). The inverse relationship between ambient T and AZAs concentrations can be attributed to higher AZAs emissions during colder periods because of enhanced household heating, less degradation because of lower heat and sunlight, lower average OH radical concentration in the atmosphere, enhanced partitioning onto atmospheric PM, and smaller redistribution to coarser particles (Yamasaki et al. 1982; Chen and Preston 1997; Chen and Preston 1998; Tsapakis and Stephanou 2005). The inverse relationship between WS and PM<sub>2.5</sub>-bound AZAs concentrations results

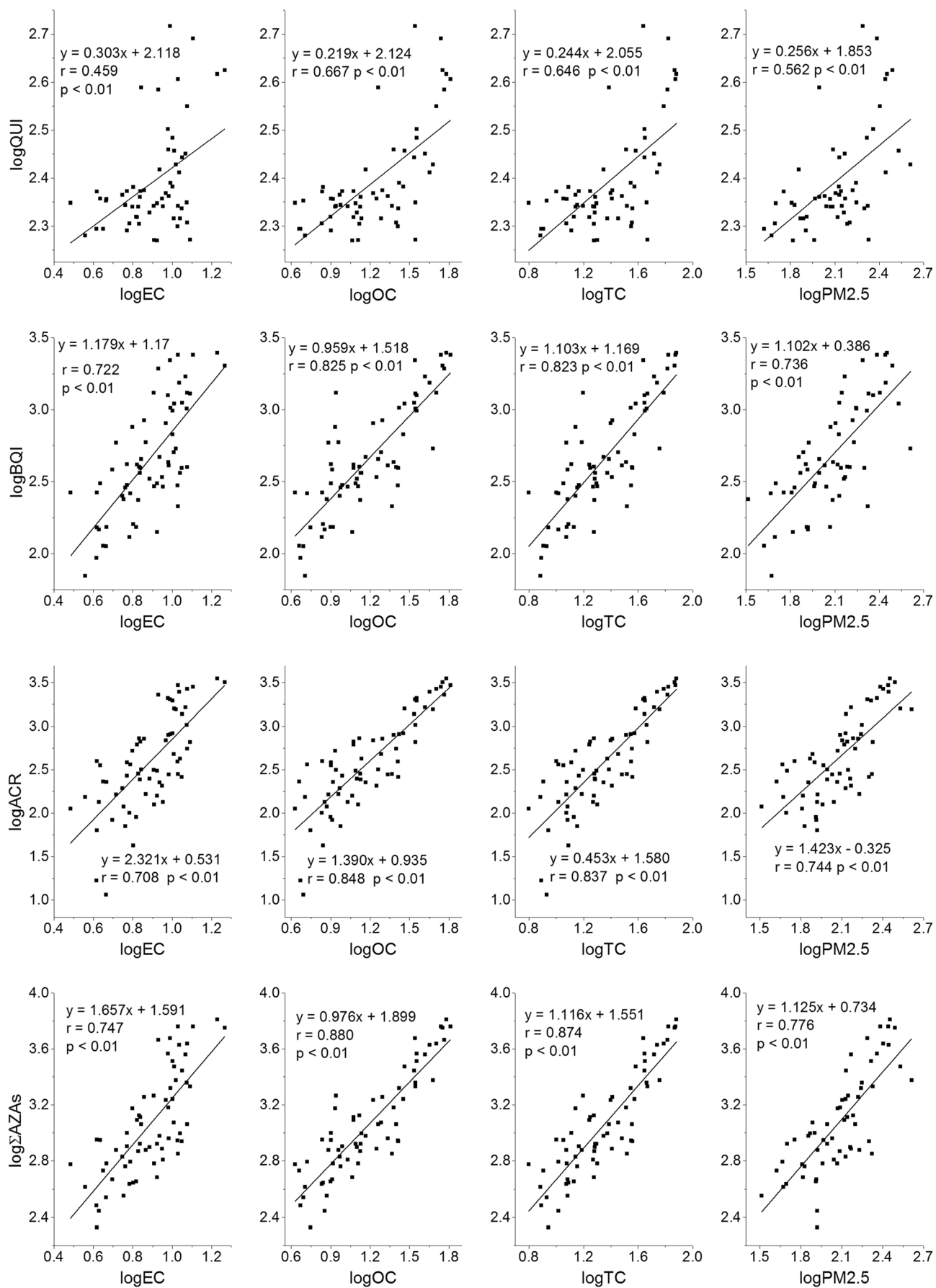
from the fact that higher WS dilutes and disperses AZAs (Mastral et al. 2003; Amodio et al. 2009; Cao et al. 2009; Gu et al. 2010; Bandowe et al. 2014a). High ambient P often results in stable and calm ambient atmospheric conditions such as low WS, stable atmospheric stratification, and narrower atmospheric mixing layer height (Tsai 2005; Akyüz and Çabuk 2009). These conditions results in lower dispersion of PM-bound AZAs and hence higher concentrations (Tsai 2005; Akyüz and Çabuk 2009; Zhou et al. 2013; Bandowe et al. 2014a; Li et al. 2015). A winter-time study in Munich found that AZAs concentrations were higher in days without rain or snow (Lintelmann et al. 2010).

## Conclusions

The PM<sub>2.5</sub>-bound concentrations of individual AZAs from Xi'an, China are higher than those reported from North American and Western European cities. Individual AZA concentrations were frequently higher than those of their regulated and related PAHs. There was a dominance of three-ring AZAs over two-ring AZAs. The more pronounced use of coal

**Fig. 6** Relationship between log (x + 1)-transformed carbon fractions and mass of PM<sub>2.5</sub> log (x + 1)-transformed concentrations of AZAs





in Xi'an compared to Western countries is a likely explanation for the contrasts between the results from Xi'an and Western countries. Concentrations of AZAs showed positive correlations with the concentrations of PM<sub>2.5</sub>, EC, OC, and their related PAHs, indicating similar sources and fates. Concentrations of AZAs in PM<sub>2.5</sub> also showed strong negative correlations with T, WS, and positive relationship with P which is related to enhanced emissions, enhanced gas/particle partition and retention onto PM<sub>2.5</sub>, lower degradation during colder months and lower dispersion/dilution during periods of lower WS, and stable atmospheric conditions. The findings strongly suggest that the fate of AZAs is similar to that of their related PAHs in spite of their significantly different physico-chemical properties.

**Acknowledgment** This project was funded with grants from the Swiss National Science Foundation (SNF 200021\_131938/1) and the Chinese Academy of Science "Strategic Priority Research Program" (XDB05060500). We thank Wolfgang Wilcke (Karlsruhe Institute of Technology (KIT), Germany) for his support. We thank Alexander Herrmann (Institute of Geography, University of Bern) for drawing Fig. 1.

## References

- Albinet A, Leoz-Garziandia E, Budzinski H, Villivave E, Jaffrezou J-L (2008) Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys part 2: particle size distribution. *Atmospheric Environment* 42:55–64
- Akyüz M, Çabuk H (2009) Meteorological variations of PM<sub>2.5</sub>/PM<sub>10</sub> concentrations and particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey. *Journal of Hazardous Materials* 170:13–21
- Amodio M, Caselli M, de Gennaro G, Tutino M (2009) Particulate PAHs in two urban areas of Southern Italy: impact of the sources, meteorological and background conditions on air quality. *Environmental Research* 109:812–820
- Arp HPH, Schwarzenbach RP, Goss KU (2008) Ambient gas/particle partitioning. 1. Sorption mechanisms of apolar, polar, and ionizable organic compounds. *Environmental Science & Technology* 42:5541–5547
- Bandowe BAM, Sobocka J, Wilcke W (2011) Oxygen-containing polycyclic aromatic hydrocarbons (OPAHs) in urban soils of Bratislava, Slovakia: patterns, relation to PAHs and vertical distribution. *Environmental Pollution* 159:539–549
- Bandowe BAM, Wilcke W (2010) Analysis of polycyclic aromatic hydrocarbons and their oxygen-containing derivatives and metabolites in soils. *Journal of Environmental Quality* 39:1349–1358
- Bandowe BAM, Meusel H, Huang R-J, Ho KF, Cao JJ, Hoffmann T, Wilcke W (2014a) PM<sub>2.5</sub>-bound oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: seasonal variation, sources and cancer risk assessment. *Science of the Total Environment* 473–474:77–87
- Bandowe BAM, Lueso MG, Wolfgang W (2014b) Oxygenated polycyclic aromatic hydrocarbons and azaarenes in urban soils: a comparison of a tropical city (Bangkok) with two temperate cities (Bratislava and Gothenburg). *Chemosphere* 107:407–414
- Bi E, Schmidt TC, Haderlein SB (2006) Sorption of heterocyclic organic compounds to reference soils: column studies for process identification. *Environmental Science & Technology* 40:5962–5970
- Bi X, Simoneit BRT, Sheng G, Fu J (2008) Characterization of molecular markers in smoke from residential coal combustion in China. *Fuel* 87:112–119
- Bleeker EAJ, Wiegman S, de Voogt P, Kraak M, Leslie HA, de Haas, Admiraal W (2002) Toxicity of azaarenes. *Reviews of Environmental Contamination and Toxicology* 173:39–83
- Boström CE, Gerde P, Hanberg A, Jernström B, Johansson C, Kyrklund T, Rannug A, Tornqvist M, Victorin K, Westerholm R (2002) Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environmental Health Perspectives* 110:451–488
- Cao J, Wu F, Chow JC, Lee SC, Li Y, Chen SW, An ZS, Fung KK, Watson JG, Zhu CS, Liu SX (2005) Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. *Atmospheric Chemistry & Physics* 5:3127–3137
- Cao JJ, Zhu CS, Chow JC, Watson JG, Han YM, Wang GH, Shen ZX, An ZS (2009) Black carbon relationships with emissions and meteorology in Xi'an, China. *Atmospheric Research* 94:194–202
- Cao JJ, Xu HM, Xu Q, Chen BH, Kan HD (2012) Fine particulate matter constituents and cardiopulmonary mortality in a heavily polluted Chinese city. *Environmental Health Perspectives* 120:373–378
- Chan CK, Yao X (2008) Air pollution in megacities in China. *Atmos Environ* 42:1–42
- Chen HY, Preston MR (1997) Gas/particle partitioning behaviour of azaarenes in an urban atmosphere. *Environmental Pollution* 97:289–298
- Chen HY, Preston MR (1998) Azaarenes in the aerosol of an urban atmosphere. *Environment Science & Technology* 32:577–583
- Chen HY, Preston MR (2004) Dissolution of azaarenes from urban aerosols. *Atmospheric Environment* 38:1023–1028
- Chen HY, Su CC, Hung CC, Yeh TC, Shen YH, Tsai CH, Chen LD, Gong GC (2008) Occurrence of azaarenes in Sediments of the Danshuei River, Taiwan - the use of azaarenes as indicator of anthropogenic source to the estuarine system. *Environ Toxicol* 23:25–35
- Chow JC, Watson JG, Chen LWA, Chang MCO, Robinson NF, Trimble D, Kohl S (2007) The IMPROVE-A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database. *Journal of Air & Waste Management Association* 57:1014–1023
- Chow JC, Watson JG, Robles J, Wang XL, Chen LWA, Trimble DL, Kohl SD, Tropp RJ, Fung KK (2011) Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon. *Analytical and Bioanalytical Chemistry* 401:3141–3152
- Collins J, Brown J, Alexeeff G, Salmon A (1998) Potency equivalency factors for some polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbon derivatives. *Regulatory Toxicology and Pharmacology* 28:45–54
- Dai WT, Ho SSH, Ho KF, Cao JJ (2012) Characterization of particulate-phase high molecular weight mono-carbonyls (C<sub>#</sub> > 5) and dicarbonyls in urban atmosphere of Xi'an, China. *Aerosol and Air Quality Research* 12:892–901
- Delhomme O, Millet M (2012) Azaarenes in atmospheric particulate matter samples of three different urban sites in east of France. *Atmospheric Environment* 47:541–545
- Dong MW, Locke DC, Hoffmann D (1977) Characterization of azaarenes in basic organic portion of suspended particulate matter. *Environmental Science & Technology* 11:612–618
- European Union (2005) Directive 2004/107/EC of the European Parliament and the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. *Off J Eur Union* 23:3–16
- Gerlofs-Nijland ME, Rummelhard M, Boere AJF, Leseman DLAC, Duffin R, Schins RPF, Borm, Paul JA, Sillanpää M, Salonen RO,

- Cassee FR (2009) Particle induced toxicity in relation to transition metal and polycyclic aromatic hydrocarbon contents. *Environmental Science & Technology* 43:4729–4736
- Götz CW, Scheringer M, Macleod M, Roth CM, Hungerbuehler K (2007) Alternative approaches for modeling gas-particle partitioning of semivolatile organic chemicals: model development and comparison. *Environmental Science & Technology* 41:1272–1278
- Gu Z, Feng J, Han W, Li L, Wu M, Fu J, Sheng G (2010) Diurnal variations of polycyclic aromatic hydrocarbons associated with PM<sub>2.5</sub> in Shanghai, China. *Journal of Environmental Science* 22: 389–396
- Harrison RM, Smith DJT, Kibble AJ (2004) What is responsible for the carcinogenicity of PM<sub>2.5</sub>? *Occupational and Environmental Medicine* 61:799–805
- Harrison RM, Yin J (2000) Particulate matter in the atmosphere: which particle properties are important for its effects on health? *The Science of the Total Environment* 249:85–101
- Huang RJ, Zhang YL, Bozzetti C, Ho KF, Cao JJ, Han YM, Daellenbach KR, Slowik JG, Platt SM, Canonaco F, Zotter P, Wolf R, Pieber SM, Brunns EA, Crippa M, Ciarelli G, Piazzalunga A, Schwikowski M, Abbaszade G, Schnelle-Kreis J, Zimmermann R, An ZS, Szidat S, Baltensperger U, El Haddad I, Prevot ASH (2014) High secondary aerosol contribution to particulate pollution during haze events in China. *Nature* 514:218–222
- IARC (2011) Bitumens and bitumen emissions, and some N- and S-heterocyclic aromatic hydrocarbons. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans 103:1–311
- Jung DJK, Klaus T, Fent K (2001) Cytochrome P450 induction by nitrated polycyclic aromatic hydrocarbons, azaarenes, and binary mixtures in fish hepatoma cell line PLHC-1. *Environmental Toxicology and Chemistry* 20:149–159
- Junninen H, Monster J, Rey M, Cancelinha J, Douglas K, Duane M, Forcina V, Müller A, Lagler F, Marelli L, Borowiak A, Niedzialek J, Paradiz B, Mira-Salama D, Jimenez J, Hansen U, Astorga C, Stanczyk K, Viana M, Querol X, Duvall RM, Norris GA, Tsakovski S, Wahlin P, Horak J, Larsen BR (2009) Quantifying the impact of residential heating on the urban air quality in a typical European coal combustion region. *Environmental Science & Technology* 43:7964–7970
- Kan H, Chen R, Tong S (2012) Ambient air pollution, climate change, and population health in China. *Environment International* 42:10–19
- Kochany J, Maguire RJ (1994) Abiotic transformations of polynuclear aromatic hydrocarbons and polynuclear aromatic nitrogen heterocycles in aquatic environments. *The Science of the Total Environment* 144:17–31
- Ladji R, Yassaa N, Balducci C, Cecinato C, Meklati BY (2009) Annual variation of particulate organic compounds in PM<sub>10</sub> in the urban atmosphere of Algiers. *Atmospheric Research* 92:258–269
- Li Y, Chen QL, Zhao HJ, Wang L, Tao R (2015) Variations in PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1.0</sub> in an urban area of the Sichuan Basin and their relation to meteorological factors. *Atmosphere* 6:150–163
- Li Z, Sjödin A, Porter EN, Patterson DG Jr, Needham LL, Lee S, Russell AG, Mulholland JA (2009) Characterization of PM<sub>2.5</sub>-bound polycyclic aromatic hydrocarbons in Atlanta. *Atmospheric Environment* 43:1043–1050
- Lintelmann J, França MH, Hubner E, Matuschek G (2010) A liquid chromatography-atmospheric pressure photoionization tandem mass spectrometric method for the determination of azaarenes in atmospheric particulate matter. *Journal of Chromatography A* 1217:1636–1646
- Lundstedt S, Bandowe BAM, Wilcke W, Boll E, Christensen JH, Vila J, Grifoll M, Faure P, Biache C, Lorgeoux C, Larsson M, Frech Irgum K, Ivarsson P, Ricci M (2014) First intercomparison study on the analysis of oxygenated PAHs and nitrogen heterocyclic compounds (N-PACs) in contaminated soil. *Trends in Analytical Chemistry* 57: 83–92
- Ma J, Chen ZY, Wu MH, Feng JL, Horii Y, Ohura T, Kannan K (2013) Airborne PM<sub>2.5</sub>/PM<sub>10</sub>-associated chlorinated polycyclic aromatic hydrocarbons and their parent compounds in a suburban area in Shanghai, China. *Environmental Science & Technology* 14:7615–7623
- Machala M, Ciganek M, Blaha L, Minksova K, Vondrack J (2001) Aryl hydrocarbon receptor-mediated and estrogenic activities of oxygenated polycyclic aromatic hydrocarbons and azaarenes originally identified in extracts of river sediments. *Environmental Toxicology and Chemistry* 20:2736–2743
- Mastral AM, López JM, Callén MS, García T, Murillo R, Navarro MV (2003) Spatial and temporal PAH concentrations in Zaragoza, Spain. *Science of the Total Environment* 307:111–124
- Matus K, Nam KM, Selin NE, Lamsal LN, Reily JM, Paltsev S (2012) Health damages from air pollution in China. *Global Environmental Change* 22:55–66
- Millman A, Tang D, Perera FP (2008) Air pollution threatens the health of children in China. *Pediatrics* 122:620–628
- Ministry of Environmental Protection of The People's Republic of China (2012) Ambient air quality standards (GB-3095-2012, in Chinese). <http://kjs.mep.gov.cn/hjbhbz/bzwb/dqhjbh/dqhjzlbz/201203/W020120410330232398521.pdf>
- Nel A (2005) Air pollution-related illness: effects of particles. *Science* 308:804–806
- Nielsen T, Clausen P, Jensen FP (1986) Determination of basic azaarenes and polynuclear aromatic hydrocarbons in airborne particulate matter by gas chromatography. *Analytical Chimica Acta* 187:223–231
- Osborne PJ, Preston MR, Chen HY (1997) Azaarenes in sediment, suspended particles and aerosol associated with the River Mersey estuary. *Marine Chemistry* 58:73–83
- Pankow JF, Bidleman TF (1991) Effects of temperature, TSP and percent non-exchangeable material in determining the gas-particle partitioning of organic compounds. *Atmospheric Environment* 25: 2241–2249
- Pope III CA, Dockery DW (2006) Health effects of fine particulate air pollution: lines that connect. *J Air Waste Manage Assoc* 56:709–742
- Ravindra K, Sokhi R, Van Grieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmospheric Environment* 42:2895–2921
- Reineke A-K, Göen T, Preiss A, Hollender J (2007) Quinoline and derivatives at tar oil contaminated site: hydroxylated products as indicator for natural attenuation? *Environmental Science & Technology* 47: 5314–5322
- Ringuet J, Leoz-Garziandia E, Budzinski H, Villinave E, Albinet A (2012) Particle size distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs and OPAHs) on traffic and suburban sites of a European megacity: Paris (France). *Atmospheric Chemistry and Physics* 12:8877–8887
- Shen HZ, Huang Y, Wang R, Zhu D, Li W, Shen GF, Wang B, Zhang YY, Chen YC, Lu Y, Chen H, Li TC, Sun K, Li BG, Liu WX, Liu JF, Tao S (2013) Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. *Environmental Science & Technology* 47:6415–6424
- Streets DG, Yu C, Bergin MH, Wang XM, Carmichael GR (2006) Modeling study of air pollution due to the manufacture of export goods in China's Pearl River Delta. *Environmental Science & Technology* 40:2099–2107
- Tsai YI (2005) Atmospheric visibility trends in an urban area in Taiwan 1961–2003. *Atmospheric Environment* 39:5555–5567
- Tsapakis M, Stephanou EG (2005) Occurrence of gaseous and particulate polycyclic aromatic hydrocarbons in the urban atmosphere: study of sources and ambient temperature effect on the gas/particle concentration and distribution. *Environmental Pollution* 133:147–156

- Vicente ED, Vicente AM, Bandowe BAM, Alves CA (in Press) Particulate phase emission of parent polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, azaarenes and nitrated-PAHs) from manually and automatically fired combustion appliances. *Air Quality, Atmosphere & Health*. Doi: 10.1007/s11869-015-0364-1
- Wakeham SG (1979) Azaarenes in recent lake sediments. *Environ Sci Technol* 13:1118–1123
- Wang G, Kawamura K, Lee S, Ho K, Cao JJ (2006) Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities. *Environmental Science & Technology* 40:4619–4625
- Warzecha L (1993) Separation and analysis of azaarenes from Upper-Silesia airborne particulate matter. *Chemia Analityczna* 38:571–583
- Wei YJ, Han IK, Shao M, Hu M, Zhang JF, Tang XY (2009) PM<sub>2.5</sub> constituents and oxidative DNA damage in humans. *Environmental Science & Technology* 43:4757–4762
- Wilhelm M, Matuschek G, Kettrup A (2000) Determination of basic nitrogen-containing polynuclear aromatic hydrocarbons formed during thermal degradation of polymers by high performance liquid chromatography-fluorescence detection. *Journal of Chromatography A* 878:171–181
- Xi'an Municipal Statistics Bureau (2011) Xi'an statistic yearbook. China Statistics Press, Beijing
- Xu SS, Liu WX, Tao S (2006) Emission of polycyclic aromatic hydrocarbons in China. *Environmental Science & Technology* 40:702–708
- Yamasaki H, Kuwata K, Miyamoto H (1982) Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environmental Science & Technology* 16:189–194
- You CF, Xu XC (2010) Coal combustion and its pollution control in China. *Energy* 35:4467–4472
- Zhang Y, Tao S, Shen H, Ma J (2009) Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population. *Proceedings of the National Academy of Science of the USA* 106:21063–21067
- Zhou CZ, Zhu XH, Wang Z, Ma XD, Chen JP, Ni YW, Wang W, Mu J, Li XX (2013) Gas-particle partitioning of PAHs in the urban air of Dalian, China: measurements and assessments. *Polycyclic Aromatic Compounds* 33:31–51