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Polycyclic aromatic hydrocarbons (PAHs) in the air of Chinese cities†

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Polycyclic aromatic hydrocarbons (PAHs) were determined in the air of 37 cities and 3 rural
locations across China during the winter, spring, summer and autumn of 2005, using
polyurethane foam (PUF) disks as passive air samplers (PAS). Winter and autumn concentrations
in cities exceeded spring and summer values. Concentrations were amongst the highest in the
world; seasonally averaged autumn/winter values in some cities in the north and north-west of
China exceeded proposed European Union air quality standards. Several factors, acting in
combination, influenced air concentrations. A significant negative correlation was found between
average annual city concentrations and the annual average temperature, while winter time PAH
concentrations correlated with estimated coal consumption. The highest total PAH concentrations
and loadings of high molecular weight compounds generally occurred in major cities located on
higher land (500–2000 m), where relatively cold winters and higher coal consumption occurs.
Lower values occurred in cities located in the south and east China and along the coastal regions.
Molecular markers indicated incomplete combustion of fossil fuels dominated the urban air and
gave evidence for photo-decomposition of selected compounds.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed during
incomplete combustion; several are known mutagens or carci-
nogens. Although they may be released to the environment by
natural processes,[1,2] it is believed that anthropogenic sources
dominate national or regional atmospheric source inven-
tories.[3–5] Concerns about their potential adverse health effects
have led to air quality standards being set for these com-
pounds;[6] PAHs are also the subject of international atmo-
spheric emission reduction efforts.[6,7] Key emission sources
may include: burning of coal or wood for domestic space
heating; coal burning for large-scale power generation; vehicle
emissions; waste incineration and accidental fires.[5,8,9] In urban
areas and indoor environments, these may be further supple-
mented by cooking and smoking. PAH emissions depend on
the efficiency of combustion; coal burned in domestic settings
may produce much higher PAH emission factors than coal
burned in large-scale power plants, for example.

The economy of China—the world's most populated
country—is undergoing massive expansion, and there have
been shifts recently in population distribution, leading to an
increased proportion of people living in cities or 'mega-cities'.
China is now the largest coal consumer in the world
and its consumption is still increasing rapidly; vehicle owner-
ship and use is also increasing. This study was therefore
undertaken to provide a large-scale assessment of PAH levels
in urban China.

China extends longitudinally from E73°–135° and latitudin-
ally from N4°–53° (see Fig. 1). There are also major regional
differences in population density, which is generally greatest in
the coastal zones, and along the major riverine catchments,
rather than the high plateau to the west. In 2005, there were
661 cities in China; 8 had >10 million people and 57 of them
>5 million. These most populated cities are generally located
on the regions <500 m (China's 'third elevation', consisting
of: the northwest plain, the north plain, the plain and lakes
region of the Yangtze River middle and low reaches, and the
hilly regions to the south of the Yangtze River) and 500–
2000 m (China's 'second elevation': the inner Mongolia
Plateau, Sinkiang Province, Sichuan Basin, Yun Gui plateau,
etc.), rather than the land >2000 m above sea level
(China's 'first elevation'—the 'roof of the world': Qinghai–
Tibet plateau). These latitudinal and altitudinal gradients
clearly strongly affect climate. This in turn affects fuel con-
sumption and the environmental conditions which may affect
ambient PAH loadings (e.g. sunlight, precipitation). For
example, from the southeast to the northwest, the climate is
divided into tropical, sub-tropical, warm temperate, middle
temperate, and cold temperate zones (see ESI Fig. SI1†). An
important aspect of the study was therefore to compare
different cities in different regions, and over different seasons.

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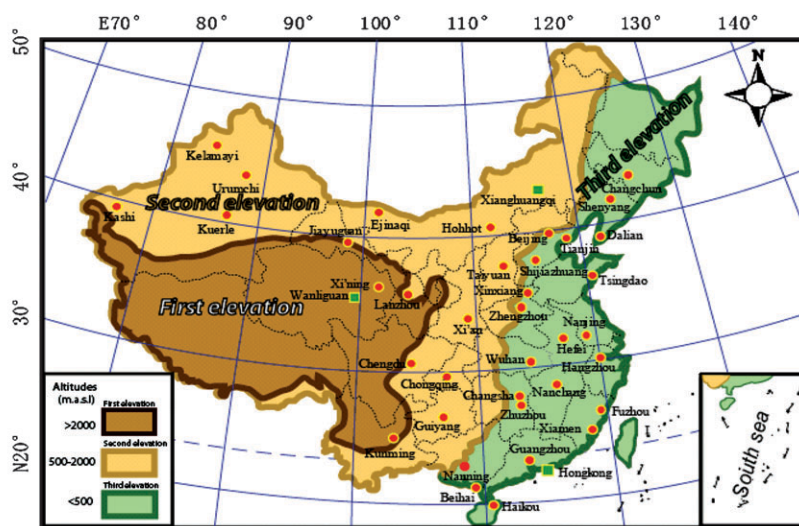
Fig. 1 Locations of PUF passive sampling sites, together with information on topography in China.

Conducting an ambient air sampling campaign across a country the size of China represents a major logistical challenge; it would also be extremely expensive, if conventional active air sampling methods were used. A co-ordinated passive air sampling (PAS) campaign was therefore undertaken in 2005, with polyurethane foam (PUF) sampling disks deployed in 36 cities and 3 background locations over the 4 seasons. Such an approach has been conducted successfully before in Europe[10,11] and across global background sites.[12] Indeed, this study follows a previous campaign in which PAS was undertaken across China and other Asian countries in 2004, to sample for polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs).[13]

Materials and methods

Site locations and air sampling

Thirty seven cities (provincial capitals and major regional centres) and 3 background stations were selected (see Fig. 1 and ESI Table SI1†). In the cities, the PAS were deployed in open areas, such as schools, hospitals or parks, >3 m above the ground. The background stations were: (i) the Wanliguan mountain observatory (36°17′N, 100°54′E, 3810 m.a.s.l), a global atmosphere watch (GAW) site on the Tibetan plateau. This is the only inland baseline station of the World Meteorological Organization (WMO) in Asia; (ii) Xianghuangqi, a prairie site in inner-Mongolia (42°14′N, 113°49′30″E), north China, located 30 km from any human activity; (iii) the Hok Tsui background station (22°12′N,114°15′E) of the National Oceanic and Atmospheric Administration (NOAA), situated at the tip of southern Hong Kong island, south China.

The PUF disk PAS system has been used and described several times previously (*e.g.* ref. 11, 14 and 15). All the PUF disks were pre-extracted with dichloromethane (DCM) and acetone at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), and transferred by express mail service to sampling sites in sealed containers. Four separate deployments of 8 weeks each were made in 2005: winter (Feb. 1 to Mar. 28), spring (Apr. 1 to May 28), summer (Jul. 5 to Aug. 30) and autumn (Sep. 15 to Nov. 11), respectively.

Analysis

The PAS disks were Soxhlet extracted for 24 h with DCM and the extract then cleaned on a column (7 mm i.d.) packed with 1 g anhydrous sodium sulfate, 1 g aluminum oxide and 1 g silica gel, eluted with an 8 mL mixture of hexane and DCM (V : V = 1 : 1). Before extraction, a known mixture of naphthalene-d8, acenaphthane-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 was added, to act as surrogates. Samples were prepared for GC-MS in a final volume of 0.2 mL. PAH compounds were separated on a 30 m × 0.25 mm i.d. HP-5 capillary column (film thickness 0.25 μm) and analyzed using an Agilent 6890N gas chromatography system and 5975 mass selective detector (GC-MSD) operated in the electron impact mode (70 eV). The instrumental conditions were as follows: injector temperature, 280 °C; ion source temperature, 180 °C; temperature program: 60 °C (2 min), 60–290 °C at 3 °C min^{-1}, 290 °C (30 min). The carrier gas was helium at a constant flow rate of 1.2 mL min^{-1}. A 1 μL sample was injected in splitless mode. Mass range m/z 50 to 500 was used for quantitative determinations. Data acquisition and processing was controlled by Agilent MSD Productivity Chemstation software. The following 20 PAH compounds were quantified: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), carbazole (CAR), fluoranthene (FLA), pyrene (PYR), benzo[*a*]anthracene (BAA), chrysene (CHR), benzo[*b*]fluoranthene (BBF), benzo[*k*]fluoranthene (BKF), benzo[*a*]pyrene (BAP), benzo[*e*]pyrene (BEP), perylene (PER), indeno[123-cd]pyrene (INP), dibenzo[*ah*]anthracene (DAC), benzo[*ghi*]perylene (BGP) and coronene (COR).

Quality assurance/quality control (QA/QC)

No target compounds were detected in the method blanks. Four field blanks were analyzed using the same procedure as for real samples and were low for all compounds. Mean recoveries for the surrogates were as follows: naphthalene-d8: 77.5%, acenaphthane-d10: 93.1%, phenanthrene-d10: 98.9%, chrysene-d12: 98.2%, perylene-d12: 95.8%. The GC-MSD instrument detection limit ranged between 0.13–0.92 ng.

Results and discussion

Summary remarks on PAHs in Chinese city air

Data derived from PAS can be presented in different ways. Commonly, this is as the compound mass detected per sampler for a given deployment (*e.g.* ng per sampler), or as a time-normalised mass per sampler (*e.g.* ng sampled per day). Either of these approaches highlight spatial and seasonal differences. Alternatively, the data can be converted to an estimate of the compound mass per unit volume of air (*e.g.* ng m^{-3}), using information from uptake calibration studies and permeation compounds.[14] Depending on the configuration of the sampler, uptake rates using the sampler design here are typically 3–5 m^3 day^{-1}.[14] In this paper, where the focus is on spatial and seasonal comparisons, the data are presented as ng day^{-1}, to allow for slight differences in deployment time between locations and sampling occasions. However, some estimates of

typical air concentrations are made later in this section, to give some international context to the levels measured. Derived concentration data will generally be within a factor of 2 of data taken with conventional active samplers.

A summary of the average PAH composition of city air by season and region (northwest China [NW], north [N], southwest [SW], central [M], south [S], east and coastal region [EC]) is given in Table 1; background [BG] site data are also included. Most compounds were regularly detected in the city samples. Generally, city air gave a trend for total PAH where winter > autumn > spring/ summer. Levels at the BG sites were typically lower by a factor of ∼10, with several high molecular weight (MW) compounds being non-detectable.

As observed elsewhere (*e.g.* ref. 11), the samples were dominated by the lower MW compounds, which exist primarily in the gas phase. PHE, NAP, FLU, FLA and PYR typically accounted for ∼80–90% of the total concentrations, while the particle-dominated 5 + 6 ring compounds only constituted *ca.* 2–3% of the total (see ESI Fig. SI2† for details). Issues concerning the times to reach gas phase–PUF disk equilibrium and sampling/trapping efficiency of gas and particle phase compounds have been discussed elsewhere; lighter compounds equilibrate more quickly, while studies show fine particles trapped in the PUF matrix, giving similar uptake rates for gas/particle phase compounds.[10–15] However, these do not substantially affect the mixture of compounds detected in the PAS as opposed to the ambient air (*i.e.* the sampler

Table 1 Summary data of PAHs in PAS deployed in the Chinese cities and background sites (ng day^{-1})

Season	Group	NAP	ACY	ACE	FLU	PHE	ANT	CAR	FLA	PYR	BAA	CHY	BBF	BKF	BEP	BAP	PER	INP	DAC	BGP	COR	∑PAH20
Winter	NW	113	7.4	14	118	378	27	13	113	74	4.9	8.6	9	2.3	4.4	2.2	0.5	3.3	0.9	2.8	0.9	898
	N	148	5.6	11	70	229	9.7	11	81	47	3.7	8.5	8.2	2.3	4.8	2.1	0.6	3.5	1.0	3.1	0.9	652
	SW	93	3.9	6.9	45	160	5.8	15	52	30	1.6	4	2.5	0.7	1.6	0.7	0.2	0.9	0.3	0.8	0.2	425
	M	63	2.6	3.6	28	131	2.2	5.6	49	27	1.5	5	4.3	1.3	2.5	0.8	0.2	1.7	0.4	1.5	0.4	332
	S	44	7.2	2	20	117	5.1	4.4	58	43	2.2	5.3	2.4	0.8	1.2	0.4	0.2	0.7	0.2	0.8	0.3	315
	EC	80	3.8	3.3	19	61	2.5	1.7	21	15	0.8	2	1.1	0.5	0.6	0.3	0.1	0.4	0.1	0.4	0.1	215
	BG	2.9	1.5	3.7	24	1	0.7	5.6	8.6	0.3	0.8	0.4	0.2	0.2	0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	50
	Mean	103	4.8	7.4	50	174	7.6	8.6	61	37	2.5	5.8	5	1.4	2.8	1.2	0.3	2	0.6	1.8	0.5	477
Spring	NW	68	3.6	5.9	36	153	6.7	10	65	36	2.7	7.2	6.5	1.7	3.7	1.1	0.3	2.3	0.8	2.1	0.6	411
	N	48	2	3.2	25	124	3.8	8.7	66	34	2.4	7.8	6.1	1.6	3.4	1.5	0.3	2.5	0.6	2.2	0.6	345
	SW	38	1.4	2.8	26	116	2.9	7.4	35	19	0.8	3.5	1.7	0.5	1	0.4	<0.1	0.5	0.1	0.5	0.1	258
	M	35	1.2	1.7	15	112	2.1	10	60	35	1.9	6.5	3.7	1.1	2.1	0.6	0.2	1.3	0.3	1.1	0.4	291
	S	24	1.7	0.9	7	63	2.2	4.2	46	32	2.2	6.9	3	0.9	1.5	0.3	0.1	0.7	0.2	0.7	0.2	197
	EC	55	0.8	1.7	11	46	1.4	1.9	16	9.3	0.5	2	1	0.4	0.6	0.2	0.1	0.3	<0.1	0.4	<0.1	148
	BG	26	0.3	1	2.1	4.6	0.2	0.2	1.6	0.7	<0.1	0.3	0.4	0.2	0.2	<0.1	<0.1	0.1	<0.1	0.1	<0.1	38
	Mean	44	1.6	2.5	20	103	2.9	6.6	48	27	1.6	5.3	3.6	1	1.9	0.7	0.1	1.2	0.3	1.1	0.3	273
Summer	NW	142	5	5.7	34	153	7.5	11	69	42	3.8	10	4	1.3	1.9	0.6	0.2	1.3	0.3	1.1	0.2	495
	N	55	3.2	4.1	21	117	3.8	9.7	61	34	3.1	12	3.8	1	2.1	0.8	0.2	1.4	0.4	1.2	0.2	335
	SW	34	2	2.1	17	72	4.6	4.3	24	14	0.8	3.3	0.8	0.2	0.5	0.1	<0.1	0.2	<0.1	0.2	<0.1	180
	M	22	1.5	1.1	9.2	100	3.2	18	52	28	1.3	5.5	1.7	0.9	0.9	0.6	<0.1	0.4	<0.1	0.4	<0.1	248
	S	17	2.4	0.8	6.2	48	1.6	2	23	12	1.1	3.4	1.2	0.4	0.5	0.5	<0.1	0.4	<0.1	0.3	<0.1	121
	EC	25	2.5	1.8	12	54	2.7	3.9	24	15	0.7	2.7	1.2	0.4	0.6	0.2	<0.1	0.4	0.1	0.3	<0.1	148
	BG	16	1	2	3.7	16	0.9	1	6.7	4.1	0.2	0.9	0.5	0.2	0.3	<0.1	<0.1	<0.1	<0.1	0.0	<0.1	53
	Mean	58.5	3	3.3	19.8	103.8	4.3	9	49.6	28.4	2.3	8	2.7	0.8	1.4	0.5	0.1	0.9	0.3	0.8	0.1	298
Autumn	NW	80	12	8.7	68	206	23	6.5	81	56	5.4	9.9	5.8	1.5	3	1.3	0.4	2.3	0.7	2	0.4	574
	N	122	11	12	68	222	14	10	96	57	6.4	19	9.2	2.5	5.6	2.5	0.7	4	1.4	3.5	0.6	667
	SW	54	5.9	5.7	39	148	7.4	5.5	49	32	2.5	7.2	2.6	0.7	1.5	0.6	0.2	0.8	0.3	0.8	0.1	364
	M	33	2.6	4.9	24	124	3.6	7	57	33	2.1	6.8	3.3	1	1.9	0.6	0.2	1.3	0.3	1.1	0.1	308
	S	65	8.5	6.6	43	170	10	7.3	87	59	5.4	13.5	5.8	1.6	3.1	1.1	0.3	2.1	0.6	1.7	0.3	493
	EC	30	3.4	2.5	18	71	5	1.9	33	24	2.4	5.3	2.6	0.8	1.3	0.5	0.1	0.9	0.2	0.7	0.1	204
	BG	30	0.5	2.3	3.9	6.7	0.3	0.4	3.9	1.8	0.2	1.3	0.9	0.3	0.5	0.1	<0.1	0.3	<0.1	0.2	<0.1	54
	Mean	69	7.7	7.1	46	161	11	6.4	68	44	4.2	11	5.2	1.4	2.9	1.2	0.4	2.0	0.7	1.8	0.3	450

composition reflects the ambient profile), for the deployment times used here.

It is important to set the levels here in a broader international context. The European Commission recently set an air quality standard for BAP, at 0.25 ng m^{-3},[6,16] to safeguard human health. If a sampling rate of 3 m^3 day^{-1} is assumed, it appears that this limit is exceeded on a seasonally averaged basis in many of the cities in NW, N and M China during the autumn and winter. The highest values were for Taiyuan (the centre of the largest coal using region in China), where the derived concentrations in autumn and winter averaged $\sim$2–2.5 ng m^{-3}. By comparison, the BAP limit is generally only exceeded in UK cities under quite unusual meteorological events (*e.g.* winter temperature inversions). The total air concentrations obtained in this study also exceed values reported for Thailand, Malaysia, Japan, Europe, São Paulo in Brazil, and Toronto in recent surveys.[10,17,18] It is clear that the levels of PAHs in many Chinese cities are amongst the highest in the world. The health implications of these high levels need further investigation.

Statistical evaluations of the dataset

The air concentration data (expressed as an annual average) was compared against a number of variables. This included total suspended particulates and PM-10, coal consumption, temperature, precipitation, humidity and sunshine.[19–24] The data used is summarized in ESI Table SI1† and a correlation coefficient matrix is given in ESI Table SI2†. In summary, PAH concentrations were strongly positively correlated ($p < 0.01$) with coal consumption and PM-10 (see Fig. 2 as an illustration), and with altitude. They were strongly negatively correlated ($p < 0.01$) with temperature (see Fig. 3), precipitation and humidity. An initial interpretation of these results indicates the importance of combustion sources used for space heating (*i.e.* greatest when temperatures are lower) in controlling the ambient levels of PAHs across China's cities. Once released from such combustion sources, precipitation appears to enhance removal/scavenging of these compounds from air, while photo-decomposition appears relatively unimportant (compared to the overwhelming influence of source inputs).

Geographical and seasonal distribution patterns of PAHs

Analysis of the variables above provides context to the geographical differences noted in the data. As noted above, regionally averaged data are given in Table 1. Site-specific data are presented in Fig. 4 (and in a different way in ESI Fig. SI2†). The geographical distribution of selected individual compounds is shown in Fig. 4. Further information on PAH seasonality is presented in ESI Table SI3† (seasonal ratios of compounds in different regions). The high molecular weight (particle-dominated) compounds (CHY, BAP, BGP) show the strongest signal in the northern second elevation, and the lowest levels in the south and east. This closely mirrors data for total suspended particulates and PM-10.[19] Some of the lighter, gas phase dominated compounds (FLA, PYR and PHE) are generally more evenly distributed.

The highest concentrations were generally observed in cities in the second elevation regions (*i.e.* between 500–2000 m). This
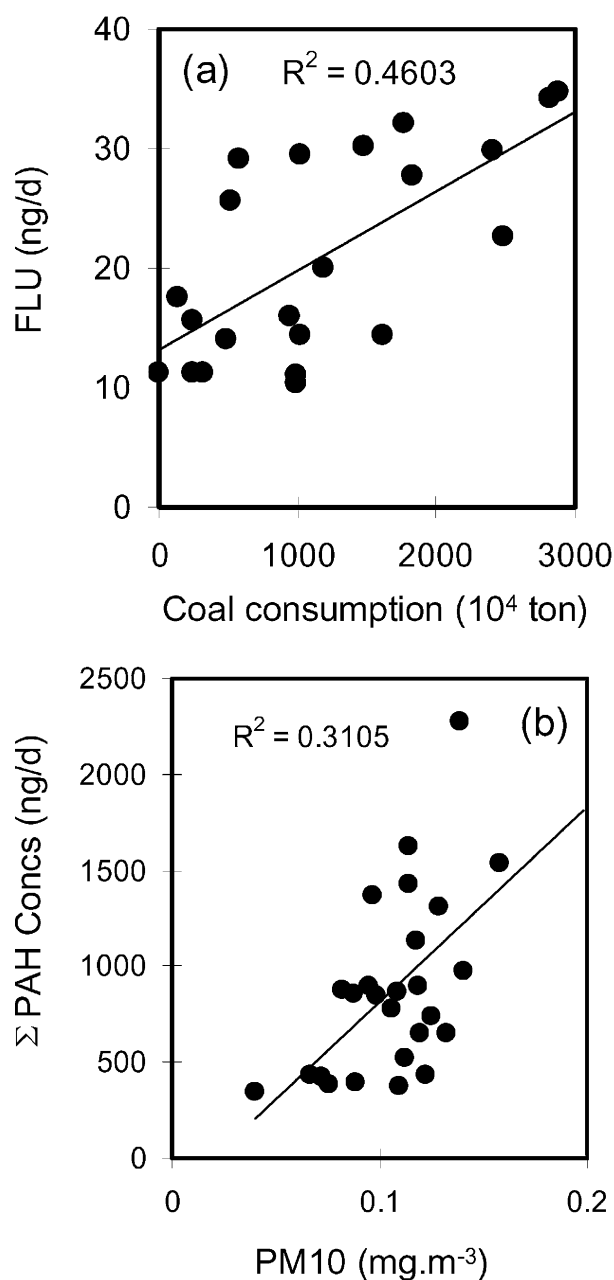

Fig. 2 Correlations of estimated coal consumption and PM10 with the PAH air concentrations in the city region for 2005.

is shown most clearly in Fig. 4 and ESI Fig. SI2†, where the cities generally located in the N, NW, and SW regions of China (*e.g.* Taiyuan, Xi'an, Hohhot, Lanzhou, Urumqi, Kunming) appear prominently. Each is characterized by colder and longer winters than regions to the south and east, resulting in greater requirements for space heating. However, for some cities, elevated levels occur across all seasons (*e.g.* Taiyuan; ESI Fig. SI2†), indicating ongoing sources (*e.g.* power generation; factories/industry). These observations are broadly consistent with predicted emissions distributions made by Xu *et. al*, with the Heibei (N), Shanxi (N) and Guizhou (SW) provinces being particularly high.[9] Coastal cities, where space heating needs are less and where cleaner
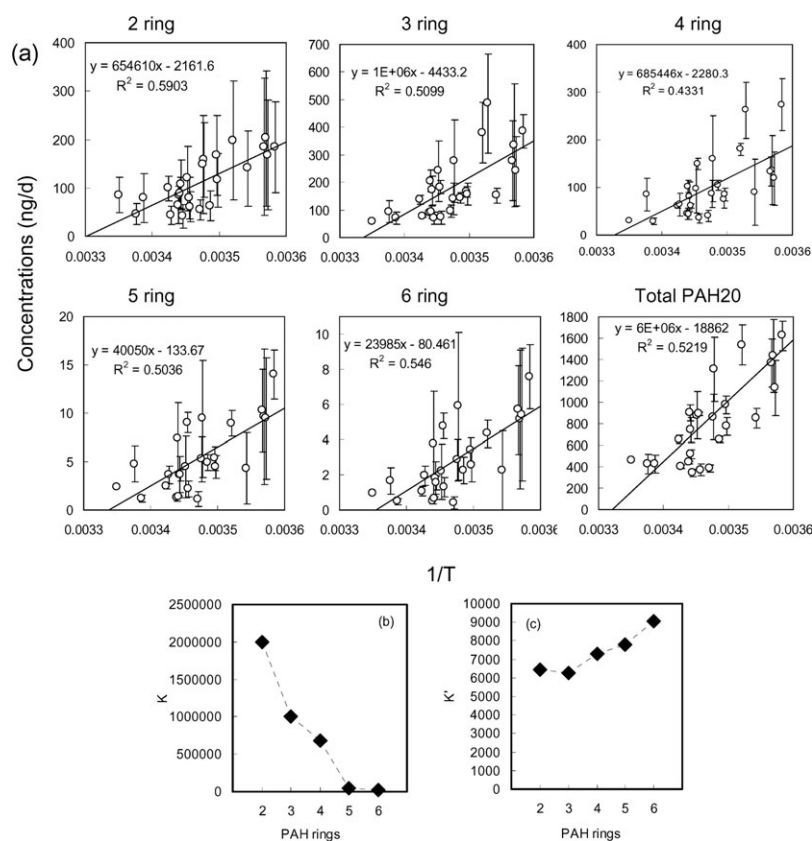
Fig. 3 Correlations of PAH concentrations with annual mean temperature in Chinese cities.

air arriving from the Pacific at certain times of the year helps to dilute emissions, gave the lowest values.

Further comments on sources, seasonality and environmental processes

As just seen, the general trend was for winter > autumn > spring/summer, with primary emissions sources clearly implicated as an important reason for the elevated winter levels in several cities. However, in this section, these trends and sources are examined in more detail, to better assess their implications for sources and environmental processes. One simple way to do this was to calculate the ratios of selected PAHs in the air, which may be markers of incomplete combustion sources. These are presented in Table 2 (more detailed information is presented in ESI Table SI4†). In brief, this shows that PAHs in urban air mainly result from incomplete combustion of fossil fuel.[25–28] However, several combustion source types are potentially important in China. Domestic space heating in rural areas typically relies on combustion of coal or wood—depending on the region. In urban areas, space heating is often provided by coal used to generate piped hot water/steam, for particular accommodation blocks; or by electricity, which may be generated by coal burning, nuclear or hydro-power, with the former most important. Clearly, space heating requirements are driven by the inverse of T and—as such—would give marked seasonality to emissions if coal or wood is used as the fuel. In contrast, coal-fired power generation for industrial activity or traffic would exhibit less seasonally dependent demand.

Effects of temperature. As noted earlier, Fig. 3 plots the correlations between sampler PAH loadings and the reciprocal of the mean annual temperature recorded in the different cities. Fig. 2 suggests that much of this relationship is simply a function of source strength; estimated coal usage for the city regions in 2005 was positively correlated with PAH compound concentration. However, ambient temperature may be important in influencing factors other than just source strength. For example, it influences emissions from secondary sources (*e.g.* re-emission from plants, soils, water bodies), gas–particle partitioning and atmospheric reaction rates. In Fig. 3, heavier compounds exhibited stronger temperature dependence than lighter compounds (K is the concentration dependent slope and K' the concentration independent slope in Fig. 3). This may be an indication that gas–particle partitioning, and hence atmospheric loss processes, also have some influence on the mixture of compounds sampled from the air in different seasons. In addition, the more frequently developed inversion layers may also contribute to the higher PAH loadings in colder cities.

There is evidence in the dataset that other seasonally variable factors also influence ambient levels.

Data from the background sites. Unlike the general picture in the cities, the BG stations sometimes actually had higher summer concentrations of some compounds than winter concentrations (see ESI Fig. SI3a and Table SI4†). This occurred at the southern coastal station (Hok Tsui) and the north western high plateau station (Waliguan), although the factors
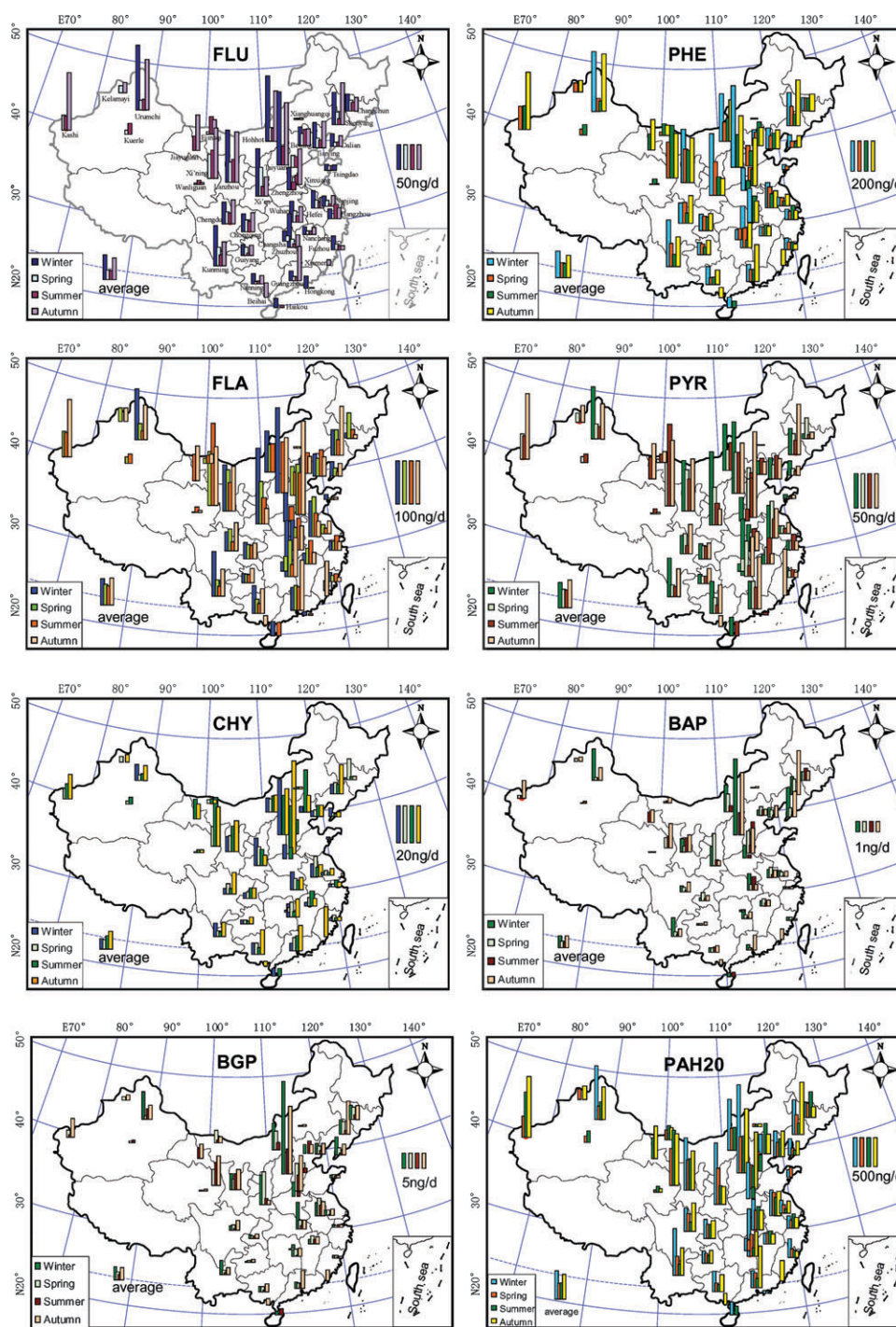
Fig. 4 Geographical distributions of selected and total PAHs in Chinese city air in 2005.

Table 2 Selected PAH ratios in the urban air of China

Season	M-PHE : PHE	PHE : ANT	FLA : PYR	BAP : BGP	BAP : CHR	BEP : BAP	INP : BGP	O = FLU : FLU[a]	O = ANT = O : ANT[b]
Winter	0.43	31	1.6	0.72	0.21	2.4	1.1	2.3	4.9
Spring	0.49	39	1.8	0.63	0.13	3.8	1.1	3.9	15
Summer	0.47	36	1.8	0.81	0.08	2.9	1.2	3.5	25
Autumn	0.5	20	1.6	0.69	0.12	2.5	1.2	2.1	6.3

[a] O = FLU: 9-Fluorenone. [b] O = ANT = O: 9,10-Anthracenedione.

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influencing these trends may be very different at the two sites. The seasonal ratios showed very similar patterns for spring/summer (ESI Fig. SI3b†) and autumn/summer (ESI Fig. SI3c†). Possible explanations for the elevated summer levels include:

(i) Seasonal differences in air mass origin—at Wanliguan, in summer, warmer air moves from the more contaminated east, while in winter it originates from the cold, mountainous areas to the west and may have been cleansed by cold condensation and scavenging processes.[29,30] The inner-Mongolian BG station, at Xianghuangqi (BGN), receives more significant contributions of PAHs *via* long-range atmospheric transport (LRAT). Dry and cold monsoon conditions dominated in cold weather, giving relatively clean air, while more contaminated air is brought from the south and east in summer and autumn. As a result, autumn concentrations were higher than summer ones for most compounds, except some light PAHs (ACY and ACE) (ESI Fig. SI3b and c†).

(ii) Emissions from secondary sources—soils and vegetation—is likely to be greater in summer[31,32] and minimized by snow cover and frozen surfaces in cold weather.

(iii) Some PAHs (notably NAP, PHE, PER) have been reported to have natural biogenic sources, which again would make a greater contribution during the summer.[1,33]

Photo-oxidation. In addition to measuring parent PAHs, possible atmospheric photo-oxygenation products were also studied. The compounds 9-fluorenone (O = FLU) and 9,10-anthracenedione (O = ANT = O), products of FLU and ANT, respectively, were quantified. Table 2 shows that the ratios of O = FLU : FLU) and O = ANT = O : ANT were greater in spring and summer than autumn and winter, indicating that seasonality is also influenced by compound loss processes, not only source processes.

Precipitation. Precipitation also plays an important role in cleansing the air (see ESI Table SI2†). For example, on the Yun Gui plateau in SW China, low concentrations are observed in the rainy seasons of spring and summer.

Further studies

Given the high PAH concentrations observed in many cities, further research is needed to better discriminate PAH sources: *e.g.* use PAS across selected cities, to better identify local sources and source types, and to assess exposures to PAHs. One approach may be to use compound-specific stable isotopes of PAHs, to better attribute sources at local and regional scales. This would help to unravel the different sources which have been implicated by this study as making a contribution to the ambient loadings of PAHs in Chinese cities, namely coal, traffic and natural sources.[34]

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References

1 W. Wilcke, W. Amelung, C. Martius and V. B. Z. Garcia, *J. Plant Nutr. Soil Sci.*, 2000, **163**, 27–30.
2 M. B. Yunker, R. W. Macdonald, D. Goyette, D. W. Paton, B. R. Fowler, D. Sullivan and J. Boyd, *Sci. Total Environ.*, 1999, **225**, 181–209.
3 S. R. Wild and K. C. Jones, *Environ. Pollut.*, 1995, **88**, 91–108.
4 K. Breivik, V. Vestreng, O. Rozovskaya and J. M. Pacyna, *Environ. Sci. Policy*, 2006, **9**, 663–674.
5 K. Breivik, R. Alcock, Y.-F. Li, R. E. Bailey, H. Fiedler and J. M. Pacyna, *Environ. Pollut.*, 2004, **128**, 3–16.
6 E. C., position paper, Luxembourg, European Commission, 2001.
7 United Nations Economic Commission for Europe (UNECE), 1998, ECE/EB.Air/60.
8 T. Nielsen, H. E. Jorgensen, J. C. Larsen and M. Poulsen, *Sci. Total Environ.*, 1996, **189–190**, 41–49.
9 S. Xu, W. Liu and S. Tao, *Environ. Sci. Technol.*, 2006, **40**, 702–708.
10 F. M. Jaward, N. J. Farrar, T. Harner, A. J. Sweetman and K. C. Jones, *Environ. Toxicol. Chem.*, 2004, **23**, 1355–1364.
11 F. M. Jaward, N. J. Farrar, T. Harner, A. J. Sweetman and K. C. Jones, *Environ. Sci. Technol.*, 2004, **38**, 34–41.
12 K. Pozo, T. Harner, F. Wania, D. C. G. Muir, K. C. Jones and L. A. Barrie, *Environ. Sci. Technol.*, 2006, **40**, 4867–4873.
13 F. M. Jaward, G. Zhang, J. J. Nam, A. J. Sweetman, J. P. Obbard, Y. Kobara and K. C. Jones, *Environ. Sci. Technol.*, 2005, **39**, 8638–8645.
14 M. Shoeib and T. Harner, *Environ. Sci. Technol.*, 2002, **36**, 4142–4151.
15 T. Harner, M. Shoeib, M. Diamond, G. Stern and B. Rosenberg, *Environ. Sci. Technol.*, 2004, **17**, 4474–4483.
16 K. Prevedouros, E. Brorstrom-Lunden, C. J. Halsall, K. C. Jones, R. G. M. Lee and A. J. Sweetman, *Environ. Pollut.*, 2004, **128**, 17–27.
17 K.-F. Chang, G.-C. Fang, J.-C. Chen and Y.-S. Wu, *Environ. Pollut.*, 2006, **142**, 388–396.
18 A. Motelay-Massei, T. S. Harner, M. S. Diamond and G. B. Rosenberg, *Environ. Sci. Technol.*, 2005, **39**, 5763–5773.
19 NBSC, *China Statistical Yearbook*, China Statistics Press, Beijing, 2006.
20 D. L. Poster and J. E. Baker, *Environ. Sci. Technol.*, 1996, **30**, 349–354.
21 P. Sun, I. Basu and R. A. Hites, *Environ. Sci. Technol.*, 2006, **40**, 1178–1183.
22 P. Sun, P. Blanchard, K. A. Brice and R. A. Hites, *Environ. Sci. Technol.*, 2006, **40**, 6221–6227.
23 M. Jang and R. M. Kamens, *Environ. Sci. Technol.*, 1998, **32**, 1237–1243.
24 Z. Fan, R. M. Kamens, J. Hu, J. Zhang and S. McDow, *Environ. Sci. Technol.*, 1996, **30**, 1358–1364.
25 P. M. Gschwend and R. A. Hites, *Geochim. Cosmochim. Acta*, 1981, **45**, 2359–2367.
26 H. Budzinski, I. Jones, J. Bellocq, C. Pierard and P. Garrigues, *Mar. Chem.*, 1997, **58**, 85–97.
27 M. B. Yunker, R. W. Macdonald, R. Vingarzan, R. H. Mitchell, D. Goyette and S. Sylvestre, *Org. Geochem.*, 2002, **33**, 489–515.
28 Z. Wang, M. Fingas, Y. Y. Shu, L. Sigouin, M. Landriault, P. Lambert, R. Turpin, P. Campagna and J. Mullin, *Environ. Sci. Technol.*, 1999, **33**, 3100–3109.
29 J. O. Grimalt, F. Borghini, J. C. Sanchez-Hernandez, R. T. G. Barra and C. J. S. Focardi, *Environ. Sci. Technol.*, 2004, **38**, 5386–5392.
30 X. Liu, G. Zhang, K. C. Jones, X. Li, X. Peng and S. Qi, *Atmos. Environ.*, 2005, **39**, 5490–5499.
31 S. N. Meijer, M. Shoeib, K. C. Jones and T. Harner, *Environ. Sci. Technol.*, 2003, **37**, 1300–1305.
32 T. Gouin, G. O. Thomas, I. Cousins, J. Barber, D. Mackay and K. C. Jones, *Environ. Sci. Technol.*, 2002, **36**, 1426–1434.
33 W. Wilcke, W. Amelung, M. Krauss, C. Martius, A. Bandeira and M. Garcia, *Org. Geochem.*, 2003, **34**, 1405–1417.
34 M. Krauss, W. Wilcke, C. Martius, A. Bandeira and W. Amelung, *Environ. Pollut.*, 2005, **135**, 143–154.