Science of the Total Environment 476–477 (2014) 485–495

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Comparison of abundances, compositions and sources of elements, inorganic ions and organic compounds in atmospheric aerosols from Xi'an and New Delhi, two megacities in China and India

Jianjun Li [a], Gehui Wang [a,*], Shankar G. Aggarwal [b], Yao Huang [a], Yanqin Ren [a], Bianhong Zhou [c], Khem Singh [b], Prabhat K. Gupta [b], Junji Cao [a], Rong Zhang [a]

[a] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China
[b] Analytical Chemistry Section, Council of Scientific and Industrial Research-National Physical Laboratory, New Delhi 110012, India
[c] Department of Geographical Science and Environmental Engineering, Baoji University of Arts and Sciences, Baoji 721013, China

HIGHLIGHTS

- ~100 organic tracers were compared for Chinese & Indian aerosols in a single study.
- The major sources are biomass & waste burning in India and coal burning in China.
- Organic aerosols are endocrine disrupting in India and carcinogenic in China.

ARTICLE INFO

Article history:
Received 28 August 2013
Received in revised form 1 January 2014
Accepted 5 January 2014
Available online xxxx

Keywords:
Chemical compositions
Organic aerosols
PAHs, phthalates and bisphenol A
Carcinogenicity and endocrine disrupting
Aerosol aging

ABSTRACT

Wintertime TSP samples collected in the two megacities of Xi'an, China and New Delhi, India were analyzed for elements, inorganic ions, carbonaceous species and organic compounds to investigate the differences in chemical compositions and sources of organic aerosols. The current work is the first time comparing the composition of urban organic aerosols from China and India and discussing their sources in a single study. Our results showed that the concentrations of Ca, Fe, Ti, inorganic ions, EC, PAHs and hopanes in Xi'an are 1.3–2.9 times of those in New Delhi, which is ascribed to the higher emissions of dust and coal burning in Xi'an. In contrast, Cl^-, levoglucosan, *n*-alkanes, fatty alcohols, fatty acids, phthalates and bisphenol A are 0.4–3.0 times higher in New Delhi than in Xi'an, which is attributed to strong emissions from biomass burning and solid waste incineration. PAHs are carcinogenic while phthalates and bisphenol A are endocrine disrupting. Thus, the significant difference in chemical compositions of the above TSP samples may suggest that residents in Xi'an and New Delhi are exposed to environmental hazards that pose different health risks.

Lower mass ratios of octadecenoic acid/octadecanoic acid ($C_{18:1}/C_{18:0}$) and benzo(a)pyrene/benzo(e)pyrene (BaP/BeP) demonstrate that aerosol particles in New Delhi are photochemically more aged. Mass closure reconstructions of the wintertime TSP indicate that crustal material is the most abundant component of ambient particles in Xi'an and New Delhi, accounting for 52% and 48% of the particle masses, respectively, followed by organic matter (24% and 23% in Xi'an and New Delhi, respectively) and secondary inorganic ions (sulfate, nitrate plus ammonium, 16% and 12% in Xi'an and New Delhi, respectively).

1. Introduction

Pollutants derived from increasing usage of fossil fuels and biofuels, along with emissions from waste incineration and dust have been causing serious air pollution problems in the urban areas of China and India. High loadings of airborne particulate matter and its precursors in both countries have a significant impact on atmospheric compositions (Aldhous, 2005; Ramana et al., 2010; Ramanathan et al., 2007; Rosenfeld et al., 2007). Anthropogenic aerosols emitted from China and India may alter regional atmospheric stability, and thus affect the hydrologic cycle on a large scale with significant regional climate effects (Menon et al., 2002).

China is the largest user of coal in the world and has consumed 1.0–2.4 billion tons of coal per year in the past decade (NBSC, 2001–2012), some of which are burned for household heating and cooking without efficient emission controls. In contrast, biomass burning is the most important source of aerosols in India, especially for carbonaceous aerosols (Gustafsson et al., 2009; Pavuluri et al., 2010; Venkataraman et al., 2005). Motor vehicle usage is growing rapidly in

---

* Corresponding author. Tel.: +86 29 8832 9320; fax: +86 29 8832 0456.
E-mail addresses: wanggh@ieecas.cn, gehuiwang@yahoo.com.cn (G. Wang).

0048-9697/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2014.01.011

both countries. For example, annual average growth rates of vehicle numbers are 20% in Shaanxi Province of China (NBSC, 2001–2012) and 5.9% in New Delhi of India (Perrino et al., 2011). Thus, traffic emissions are also important sources of atmospheric aerosols in the two countries. In addition, municipal solid waste (MSW) in both countries are growing and often combusted under open conditions without any emission controls (Kawamura and Pavuluri, 2010), releasing high amounts of pollutants into the atmosphere (Kumar et al., 2012).

As the two biggest developing countries in the world, China and India both have been facing serious air pollution problems. In the current study, a TSP (total suspended particle) winter sampling campaign was conducted in Xi'an and New Delhi, two megacities with high levels of airborne particles. We compared the differences in concentrations and compositions of elements, inorganic ions, carbonaceous species and organic compounds of the samples and investigated the aerosol sources in the two cities.

2. Experimental section

2.1. Sample collection

Xi'an (34.27° N, 108.90° E) is a megacity in northwestern China and situated in Guanzhong Basin, a semi-arid region in East Asia. TSP samples were collected on the rooftop (10 m above the ground) of a three-story building at the Institute of Earth Environment, Chinese Academy of Science, which is located in the urban center of Xi'an. The sampling was conducted from January to February 2009 on a day/night basis at an airflow rate of 100 L min^{-1}. New Delhi (28.37° N, 77.13° E) is the capital of India with a monsoon-influenced humid subtropical climate. The TSP samples were collected on a rooftop (15 m above the ground) of the building of CSIR-National Physical Laboratory (NPL) in New Delhi during November 2006 to February 2007 and January 2008. The samples were also collected on a day/night basis using a high-volume sampler at an airflow rate of 1200 L min^{-1}. Field blank samples were collected by mounting blank filters onto the sampler for about 10 min without pumping any air. All the samples were collected onto pre-baked (450 °C, 6–8 h) quartz fiber filters. After sampling, the sample filter was sealed in aluminum foil bags and stored in a freezer (−20 °C) prior to analysis.

2.2. Sample analysis

2.2.1. Elements

Elemental compositions of the TSP samples were determined by Energy Dispersive X-Ray Fluorescence (ED-XRF) spectrometry (Epsilon 5 ED-XRF, PANalytical B. V., Netherlands). The X-ray source is a side window X-ray tube with a gadolinium anode and operated at an accelerating voltage of 25e100 kV and a current of 0.5e24 mA (maximum power: 600 W). The characteristic X-ray radiation is detected by a germanium detector (PAN 32). Each sample was analyzed for 30 min to obtain a spectrum of X-ray counts versus photon energy with the individual peak energies matching specific elements and peak areas corresponding to elemental concentrations. The spectrometer was calibrated with thin-film standards obtained from MicroMatter Co. (Arlington, WA, USA). In this study, 15 elements (i.e., S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Mo, Pb) were determined. The element concentrations for blank quartz fiber filter are 0–0.658 μg cm^{-2} and less than 10% of those in the ambient samples.

2.2.2. Carbonaceous components and inorganic ions

OC (organic carbon) and EC (elemental carbon) were analyzed using a DRI Model 2001 Carbon Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol. Briefly, a size of 0.526 cm^2 sample filter was placed in a quartz boat inside the analyzer and stepwise heated to temperatures of 140 °C (OC1), 280 °C (OC2), 480 °C (OC3), and 580 °C (OC4) in a non-oxidizing helium (He) atmosphere, and 580 °C (EC1), 740 °C (EC2), and 840 °C (EC3) in an oxidizing atmosphere of 2% oxygen in helium. Pyrolyzed carbon (PC) is determined by reflectance and transmittance of 633 nm light. The analyzer was calibrated with a known quantity of CH_4 every day. One sample was randomly selected from every 10 samples and re-analyzed. Differences determined from the replicate analyses were <5% for TC, and <10% for OC and EC.

Inorganic ions, water-soluble organic carbon (WSOC) and water-soluble inorganic carbon (WSIC) of the samples were measured as follows. A portion of the filter was cut and extracted with 40 mL Milli-Q water under sonication (15 min each, repeated 3 times) and filtered through a PTFE filter to remove any particles and filter debris. Then the water-extract was divided into two parts. One part was used for inorganic ion analysis using ion chromatography (Dionex 600, Dionex, US). The detection limits were lower than 0.05 mg L^{-1} for both anions and cations. The second part of the water-extract was analyzed for WSOC and WSIC using a TOC analyzer (TOC-L CPH, Shimadzu, Japan). All carbonaceous components and inorganic ion data reported here were corrected by the field blanks.

2.2.3. Organic compounds

A 1.5–3.0 cm^{-2} punch of the sample/blank filter was cut and extracted with a mixture of dichloromethane and methanol (2:1, v/v) under ultrasonication. The extracts were concentrated using a rotary evaporator under vacuum conditions and then blow dried using pure nitrogen. After reacting with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) at 70 °C for 3 h, the derivatives were determined using gas chromatography/mass spectrometry (GC/MS).

GC/MS analysis of the derivatized fraction was performed using an Agilent 7890A GC coupled with an Agilent 5975C MSD. The GC separation was carried out using a DB-5MS fused silica capillary column with the GC oven temperature programmed from 50 °C (2 min) to 120 °C at 15 °C min^{-1} and then to 300 °C at 5 °C min^{-1} with a final isothermal hold at 300 °C for 16 min. The sample was injected in a splitless mode at an injector temperature of 280 °C, and scanned from 50 to 650 Da using an electron impact (EI) mode at 70 eV. GC–MS response factors were determined using authentic standards. Method detection limits (MDLs) for major compounds (i.e., nonacosane (C_{29} alkane), hexadecanoic ($C_{16:0}$), hexacosanol (C_{26} alcohol), levoglucosan, benzo(b)fluoranthene (BbF), bis(2-ethylhexyl)phthalate (BEHP), bishpenol A and 17α(H),21β(H)-30-norhopane($C_{29}\alpha\beta$)) were 0.16, 0.70, 0.27, 0.11, 0.016, 0.26, 0.57 and 0.77 ng m^{-3}, respectively. No significant contamination (<5% of those in the samples) was found in the blanks. Recoveries of all the target compounds ranged from 80% to 120%. Data presented were corrected for the field blanks but not corrected for the recoveries.

3. Results and discussion

Concentrations of TSP, elements, inorganic ions, carbonaceous species and meteorological parameters are summarized in Table 1 and Fig. 1. New Delhi is a monsoon-influenced humid subtropical region, where wintertime temperatures (17 ± 2.7 °C, Table 1) and relative humidities (60 ± 8.4%, Table 1) were higher than those in Xi'an (0.3 ± 4.4 °C and 53 ± 13%, Table 1). The average concentration of TSP in Xi'an during the winter is 531 ± 156 μg m^{-3} (Table 1), which is comparable to the results (587 μg m^{-3}) reported by Yu et al. (2003). As shown in Table 1, TSP concentrations in New Delhi (440 ± 95 μg m^{-3}) are lower than that in Xi'an.

3.1. Elements

As seen in Table 1 and Fig. 1a, a total of 15 elements in the Xi'an and New Delhi samples were determined with S, Ca, Fe and K being the most abundant. Ca, Fe and Ti are the tracers of soil and dust, which are 0.3–1.2

Table 1
Concentrations of elements, water-soluble inorganic ions and carbonaceous species of TSP in Xi'an and New Delhi during winter.

	Xi'an			New Delhi		
	Day (N = 8)	Night (N = 7)	24 h	Day (N = 7)	Night (N = 6)	24 h
T(°C)	3.6 ± 3.1	−2.7 ± 3.1	0.3 ± 4.4	17 ± 2.5	17 ± 2.8	17 ± 2.7
RH (%)	42 ± 7.0	63 ± 6.1	53 ± 13	60 ± 10	60 ± 6.8	60 ± 8.4
TSP (μg m^{-3})	544 ± 164	519 ± 148	531 ± 156	446 ± 96	433 ± 94	440 ± 95
(I) Elements (μg m^{-3})						
S	26 ± 14	23 ± 10	24 ± 12	11 ± 9.4	10 ± 3.9	11 ± 7.3
K	12 ± 3.8	12.65 ± 3.4	12 ± 3.6	6.7 ± 1.4	7.4 ± 0.58	7.0 ± 1.1
Ca	27 ± 6.7	22 ± 6.2	24 ± 6.8	12 ± 1.6	11 ± 2.5	11 ± 2.2
Ti	1.4 ± 0.2	1.3 ± 0.2	1.3 ± 0.2	0.87 ± 0.12	0.88 ± 0.17	0.88 ± 0.15
V	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
Cr	0.07 ± 0.03	0.05 ± 0.02	0.06 ± 0.03	0.09 ± 0.05	0.07 ± 0.02	0.08 ± 0.04
Mn	0.43 ± 0.10	0.38 ± 0.22	0.40 ± 0.17	0.35 ± 0.11	0.22 ± 0.12	0.28 ± 0.13
Fe	12 ± 2.1	10 ± 2.8	11 ± 2.7	8.7 ± 1.4	8.3 ± 1.8	8.5 ± 1.6
Ni	0.04 ± 0.04	0.04 ± 0.03	0.04 ± 0.03	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
Cu	0.19 ± 0.05	0.16 ± 0.06	0.17 ± 0.05	0.23 ± 0.08	0.21 ± 0.07	0.22 ± 0.08
Zn	3.1 ± 2.1	3.0 ± 2.7	3.1 ± 2.4	2.3 ± 1.7	1.8 ± 0.73	2.1 ± 1.3
As	0.16 ± 0.07	0.15 ± 0.08	0.15 ± 0.08	0.07 ± 0.11	0.03 ± 0.03	0.05 ± 0.08
Br	0.10 ± 0.06	0.14 ± 0.07	0.12 ± 0.07	0.31 ± 0.31	0.25 ± 0.13	0.28 ± 0.24
Mo	0.07 ± 0.06	0.12 ± 0.09	0.09 ± 0.08	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Pb	1.06 ± 0.49	0.93 ± 0.40	0.99 ± 0.45	0.97 ± 0.55	1.8 ± 1.01	1.4 ± 0.94
(II) Water-soluble inorganic ions (μg m^{-3})						
SO_4^{2-}	41 ± 22	36 ± 17	39 ± 20	24 ± 23	19 ± 11	22 ± 19
NO_3^-	36 ± 22	33 ± 19	34 ± 20	19 ± 7.4	21 ± 8.8	20 ± 8.2
NH_4^+	13 ± 7.2	13 ± 5.6	13 ± 6.4	12 ± 6.2	12 ± 7.8	12 ± 7.0
Cl^-	14 ± 7.9	17 ± 7.0	15 ± 7.6	34 ± 20	34 ± 32	34 ± 26
F^-	1.4 ± 0.7	1.2 ± 0.5	1.3 ± 0.6	0.3 ± 0.3	0.3 ± 0.2	0.3 ± 0.3
Ca^{2+}	13 ± 5.1	11 ± 3.8	12 ± 4.6	8.9 ± 2.7	7.9 ± 1.9	8.5 ± 2.4
Mg^{2+}	1.0 ± 0.3	0.9 ± 0.3	0.9 ± 0.3	0.6 ± 0.2	0.6 ± 0.1	0.6 ± 0.2
K^+	4.3 ± 2.4	5.0 ± 1.8	4.6 ± 2.1	2.9 ± 1	3.2 ± 0.9	3.0 ± 1.0
Na^+	2.9 ± 0.8	2.2 ± 0.6	2.5 ± 0.8	1.1 ± 0.3	1.0 ± 0.3	1.1 ± 0.3
subtotal	127 ± 67	118 ± 53	122 ± 60	102 ± 49	99 ± 54	101 ± 51
(III) Carbonaceous species (μg m^{-3})						
OC[a]	72 ± 33	88 ± 30	80 ± 32	60 ± 16.5	67 ± 23	63 ± 20
EC[a]	22 ± 4.1	22 ± 4.6	22 ± 4.4	7.1 ± 2.0	8.5 ± 1.5	7.7 ± 1.9
WSOC[b]	38 ± 17	38 ± 14	38 ± 15	29 ± 6.7	33 ± 12	31 ± 10
WSIC[b]	2.2 ± 0.4	1.7 ± 0.4	2.0 ± 0.4	2.2 ± 1.5	2.1 ± 1.3	2.2 ± 1.5

[a] OC and EC: organic (OC) and elemental carbon (EC).
[b] WSOC and WSIC: water-soluble organic (WSOC) and inorganic carbon (WSIC).

times higher in Xi'an than in New Delhi, indicating that dust emissions are more significant in the Chinese city. Br and Pb are the tracers of vehicle exhausts, which are about double in the New Delhi samples than those from Xi'an, suggesting that traffic emissions in New Delhi are more significant. It is important to note that the number of diesel powered vehicles is rapidly increasing over petrol powered vehicles in the National Capital Region (NCR) of Delhi (unpublished data provided by Shankar G. Aggarwal).

Enrichment factors (EFs) of elements of aerosols relative to the earth's upper crust can indicate the origins from crustal or non-crustal

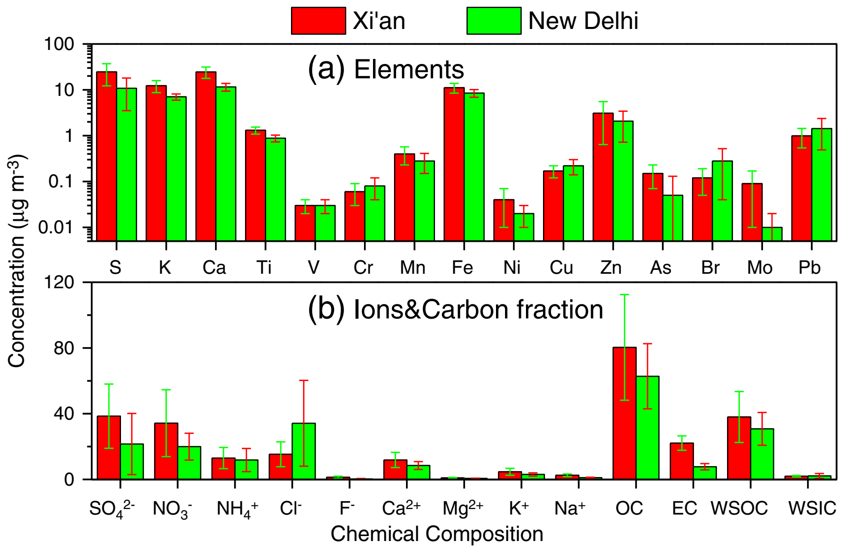

Fig. 1. Concentrations of elements, water-soluble inorganic ions and carbonaceous species in the TSP samples collected in Xi'an and New Delhi during winter.

sources (Taylor and McLennan, 1995; Wedepohl, 1995). EF was calculated as follows:

$$EF = \frac{(C_{element}/C_{reference})_{air}}{(C_{element}/C_{reference})_{crust}} \quad (1)$$

where $C_{element}$ and $C_{reference}$ are the concentrations of the target element and reference element, respectively. Typically, Al, Si, or Ti is chosen as the reference element because they are dominated by crustal sources (Cao et al., 2008). In the current study Ti is chosen as the reference element, because Al and Si were not determined by the XRF spectrometry. Concentrations of all the elements in the crust are quoted from Wedepohl (1995). The EF values of the 15 elements are shown in Fig. 2. V, Cr, and Cu are the catalysts of petroleum refining. These elements, along with Pb and Br, presented higher EF values for the New Delhi samples in comparison with those from Xi'an, further indicating more significant traffic emissions in the Indian capital. EF values of Fe, Mn and Ca in the samples are in the range of 1–5, suggesting that these elements are mainly derived from soil. Potassium in fine particles is usually emitted from biomass burning (Andreae et al., 1990; Li et al., 2011, 2012), while potassium in coarse particles mainly originates from dust (Li et al., 2008; Shen et al., 2009). Enrichment factors of K in Xi'an and New Delhi are 1.0 and 0.9, respectively, suggesting that potassium in the TSP samples from the two cities during winter is mainly of crustal origin.

3.2. Water-soluble inorganic ions

SO_4^{2-} and NO_3^- are the most abundant inorganic ions in the Xi'an TSP samples. In contrast, Cl^- is the highest one in the New Delhi samples. Sulfate and nitrate are mainly derived from photo-chemical oxidation of SO_2 and NO_x. In China, coal burning is the most important source of SO_2 and NO_x emission (Streets and Waldhoff, 2000; Wang et al., 2012c; Zhang et al., 2009). For example, Zhang et al. (2009) demonstrated that almost 90% of SO_2 and 70% of NO_x emissions in China during 2006 are from power plants and industry where coal is the main fuel. In the current study, SO_4^{2-} and NO_3^- are 1–2 times higher in Xi'an than in New Delhi (Table 1 and Fig. 1b), mainly due to the high emissions from coal combustion. The ratio of SO_4^{2-}/S would be 3.0 if the entire measured sulfur is oxidized to water-soluble sulfate. However, the ratios of SO_4^{2-}/S in Xi'an and New Delhi are 1.57 ± 0.11 and 2.10 ± 0.34, respectively, which imply that a substantial fraction of airborne particulate sulfur in both cities is water-insoluble. Xi'an is located at the south edge of the Loess Plateau, where dust emissions are significant. Aerosols derived from dust contain many water-insoluble and non-oxidized sulfur-containing compounds such as FeS and $CuFeS_2$ (Zhang et al., 2005). Thus, the ratio of SO_4^{2-}/S in the Xi'an aerosols is lower than that in New Delhi.

Cl^- in New Delhi is 34 ± 26 μg m^{-3}, about 1.3 times higher than that in Xi'an. Similar levels of Cl^- in Indian megacities were also reported by Perrino et al. (2011) and Tiwari et al. (2009), which are attributed to the local complicated source emissions such as biomass burning, waste incineration and vehicle exhaust (Perrino et al., 2011). Although SO_4^{2-} and NO_3^- in New Delhi are lower than those in Xi'an, concentrations of NH_4^+ in both megacities are comparable. Thus, it is expected that particulate ammonium chloride is an important species in the Indian atmosphere. Crustal ions such as Ca^{2+} and Mg^{2+} are abundant in soil dust and show higher concentrations in Xi'an, consisting with the ratio of SO_4^{2-}/S.

3.3. Carbonaceous species

OC in Xi'an (80 ± 32 μg m^{-3}) is only 0.3 times higher than that in New Delhi (63 ± 20 μg m^{-3}). However, EC in Xi'an (22 ± 4.4 μg m^{-3}) is nearly 2 times more than that in New Delhi (7.7 ± 1.9 μg m^{-3}). The high concentration of EC in Xi'an is probably due to household coal burning for heating, of which emissions are not efficiently controlled, especially in the surrounding rural areas. Previous studies reported that OC/EC ratios in the aerosols derived from motor vehicles, coal combustion and biomass burning are 1.1, 2.7 and 9.0 (Cachier et al., 1989; Watson et al., 2001), respectively. Mean ratios of OC/EC are 3.6 ± 1.0 (Table 2) for the Xi'an TSP samples and 8.7 ± 3.7 for the New Delhi samples, which further indicate that coal combustion and biomass burning are important aerosol sources in Xi'an and New Delhi, respectively. Concentrations of water-soluble organic and inorganic carbon (WSOC and WSIC) in the TSP of Xi'an (38 ± 15 and 2.0 ± 0.4 μg m^{-3}) and New Delhi (31 ± 10 and 2.2 ± 1.5 μg m^{-3}) are comparable.

3.4. Organic compounds

About one hundred organic species were detected in the TSP samples. Their concentrations are shown in Table 3 as eight classes of compounds based on differences in functional groups and their sources. The most abundant compounds in both megacities are fatty acids, followed by sugars, fatty alcohols and *n*-alkanes. All of these organic compounds had higher concentrations at night than in the day, which is most likely due to the accumulation effect caused by the decreased height of planetary boundary layer at night.

3.4.1. n-alkanes, fatty acids and alcohols

Total *n*-alkanes (C_{18}–C_{35}) in TSP are 874 ± 438 and 1379 ± 904 ng m^{-3} in Xi'an and New Delhi (Table 3), respectively. *n*-alkanes derived from terrestrial plants and fossil fuels are dominated by high (HMW, carbon number > 25) and low (LMW, carbon number ≤ 25) molecular weight species, respectively (Rogge et al., 1993; Simoneit et al., 2004b). As shown in Fig. 3a, *n*-alkanes in the range of $C_{18}-C_{36}$ were detected for the TSP samples with a peak at C_{29}/C_{31} in both cities,

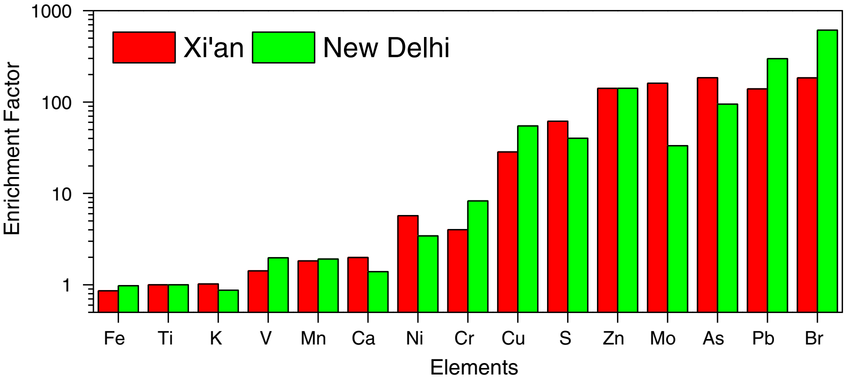

Fig. 2. Enrichment factors (EFs) for the 15 elements in the Xi'an and New Delhi TSP samples during winter.

Table 2
Diagnostic ratios of detected species in the TSP samples from Xi'an and New Delhi.

	Xi'an			New Delhi		
	Day (N = 8)	Night (N = 7)	24 h	Day (N = 7)	Night (N = 6)	24 h
OC/EC	3.2 ± 1.0	3.9 ± 0.8	3.6 ± 1.0	9.3 ± 4.1	8.1 ± 2.9	8.7 ± 3.7
Cl^-/Na^+	4.5 ± 1.3	7.6 ± 2.3	6.1 ± 2.5	32 ± 22	30 ± 22	31 ± 22
$HMW/LMW_{n\text{-alkanes}}$[a]	1.9 ± 0.2	1.8 ± 0.3	1.9 ± 0.3	5.1 ± 1.2	4.8 ± 1.4	4.9 ± 1.3
$C_{18:1}/C_{18:0}$	0.12 ± 0.01	0.60 ± 0.22	0.37 ± 0.29	0.08 ± 0.03	0.11 ± 0.08	0.09 ± 0.06
Levoglucosan/OC(‰)	8.7 ± 2.5	7.6 ± 2.7	8.1 ± 2.6	29 ± 5.4	33 ± 9.7	31 ± 8.0
IP/BghiP[b]	1.8 ± 1.1	1.8 ± 1.1	1.8 ± 1.1	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3
BghiP/BeP[b]	0.55 ± 0.05	0.55 ± 0.05	0.55 ± 0.05	1.1 ± 0.1	1.1 ± 0.1	1.1 ± 0.1
BaP/BeP[b]	0.73 ± 0.06	0.86 ± 0.09	0.80 ± 0.10	0.60 ± 0.15	0.68 ± 0.13	0.63 ± 0.15
$\sum$3,4-/5,6-rings PAHs	0.83 ± 0.11	0.92 ± 0.11	0.88 ± 0.12	0.42 ± 0.11	0.43 ± 0.08	0.42 ± 0.10

[a] $HMW/LMW_{n\text{-alkanes}}$: mass ratio of high molecular weight (HMW, carbon number > 25) to low molecular weight (LMW, carbon number ≤ 25) *n*-alkanes.

[b] Indeno(c,d)pyrenen (IP), benzo(ghi)perylene(BghiP), benzo(a)pyrene (BaP) and benzo(e)pyrene (BeP).

indicating that the organic compounds in both urban areas are significantly influenced by plant wax emissions. All the HMW *n*-alkanes are more abundant in New Delhi, in contrast to LMW *n*-alkanes, which are more abundant in Xi'an. The ratios of HMW/LMW *n*-alkanes in Xi'an and New Delhi are 1.9 ± 0.3 and 4.9 ± 1.3 (Table 2), respectively, further suggesting that fossil fuel emissions are relatively more significant in Xi'an.

Twenty-two fatty acids ($C_{12:0}$–$C_{32:0}$, $C_{34:0}$ and $C_{18:1}$) were detected in the TSP samples with a major peak at $C_{16:0}/C_{18:0}$ and a minor peak at $C_{30:0}$ (Fig. 3b). HMW fatty acids ($C_{20:0}$–$C_{34:0}$) largely originate from terrestrial higher plants, while LMW fatty acids ($C_{12:0}$–$C_{19:0}$) are mostly derived from microbe and marine phytoplankton (Mochida et al., 2003; Simoneit et al., 2004c; Wang et al., 2007). Thus, the high concentrations of $C_{28:0}$, $C_{30:0}$ and $C_{32:0}$ observed in the samples originate from direct emission/burning of terrestrial higher plants. In addition, the major peak of $C_{16:0}/C_{18:0}$ in the urban aerosols is attributed to cooking activities (Wang and Kawamura, 2005). Compared to octadecanoic acid ($C_{18:0}$), octadecenoic acid ($C_{18:1}$) is liable to photochemical degradation (Wang et al., 2012b), thus the mass ratio of $C_{18:1}/C_{18:0}$ can be used to compare the extent of aerosol oxidation. As shown in Fig. 4a, the ratio of $C_{18:1}/C_{18:0}$ shows a significant day–night variation in Xi'an. However, no clear day–night variation of $C_{18:1}/C_{18:0}$ was found in New Delhi (Fig. 4b). The lower $C_{18:1}/C_{18:0}$ values during daytime in Xi'an are probably due to the sunlight irradiation and higher oxidative capacity (such as O_3 concentration) of the atmosphere. Moreover, ambient temperatures in Xi'an also show a significant day–night variation (Fig. 4a), which may be another factor influencing the unsaturated fatty acid degradation. On the other hand, the ratios of $C_{18:1}/C_{18:0}$ exhibited lower values (0.09 ± 0.06) in New Delhi in comparison with those (0.37 ± 0.29) in Xi'an, which indicates that the Indian aerosol is more oxidized. The result is consistent with the ratio of oxalic acid to total diacids, which is also indicative of aerosol aging and was found to be 0.62 in New Delhi (Miyazaki et al., 2009) and 0.45 in Xi'an (Wang et al., 2012a), respectively. Similar results are also reported by a recent study on the aerosols from Mumbai, where the winter aerosols are found to be more oxidized (Aggarwal et al., 2013).

Fatty alcohols in the range of C_{22}–C_{32} were determined for the TSP samples. These components are dominated by C_{28} and C_{30} alcohols with an even-to-odd carbon number predominance (Fig. 3c). The HMW fatty alcohols ($\geq C_{20}$) are mainly derived from higher plants and loess deposits (Wang and Kawamura, 2005). As shown in Table 1, concentrations of total *n*-alkanes, fatty acids and fatty alcohols in New Delhi are 1.4–1.6 times of those in Xi'an, consistent with the reports that biomass burning and plant activities are very significant in India during winter (Gustafsson et al., 2009; Venkataraman et al., 2005).

3.4.2. Sugars and sugar alcohols

Concentration of total sugars and sugar alcohols are 1127 ± 297 ng m^{-3} and 3313 ± 1615 ng m^{-3} in Xi'an and New Delhi, respectively. Levoglucosan, a key tracer for combustion of cellulose-containing materials (Engling et al., 2009; Mochida et al., 2010; Oros et al., 2006; Simoneit et al., 2004a), was found to be the most abundant species in the sugar class in both cities (Fig. 5a). Levoglucosan in New Delhi (1978 ± 971 ng m^{-3}) is more than two times higher than that in Xi'an (576 ± 99 ng m^{-3}) (Table 3), and the ratio of levoglucosan/OC (31 ± 8.0‰) in New Delhi is nearly three times higher than that in Xi'an (8.1 ± 2.6‰) (Table 2), both demonstrating that biomass burning emissions in the Indian city are much higher. Such a phenomenon is reasonable, because many studies have reported that biomass burning is the most important source of carbonaceous aerosols in India (Gustafsson et al., 2009; Tiwari et al., 2009). For example, Venkataraman et al. (2005) found that based on emission factor calculations the relative contributions of residential biofuel combustion to OC and BC (black carbon) are 43% and 33% in India, respectively. Recently, Gustafsson et al. (2009) determined the radiocarbon abundance of winter monsoon aerosols from western India and the Indian Ocean and found that biomass combustion produced two-thirds of the bulk carbonaceous. Aggarwal et al. (2013) further reported that biomass burning is the most significant source for the Mumbai aerosols.

Galactosan and mannosan are also the tracers for smoke from biomass burning (Oros et al., 2006), and both exhibit higher concentrations in the atmosphere of New Delhi (261 ± 207 and 179 ± 156 ng m^{-3}) than those in Xi'an (172 ± 77 and 130 ± 69 ng m^{-3}). As shown in Fig. 5a, the three biomass burning derived sugars contribute over 70% of the total sugars and sugar alcohols in both cities. OC in the TSP samples showed a better linear relationship with levoglucosan in New Delhi ($R^2 = 0.77$) compared to that in Xi'an ($R^2 = 0.26$) (Fig. 6 a and c), again confirming that urban air quality in New Delhi is more significantly influenced by biomass burning.

Other sugars including monosaccharides (i.e., glucose and fructose), disaccharides (i.e., sucrose and trehalose) and sugar polyols (i.e., arabitol and mannitol) are the major forms of photosynthetically assimilated carbon in the biosphere, and their sources include soil microbiota, plants and animals (Medeiros et al., 2006; Simoneit et al., 2004a). The contribution of these compounds except sucrose to total sugars and sugar alcohols are very low in both cities. Sucrose is a photosynthesis product in the leaves of plants (Jaeger et al., 1999; Wang et al., 2011); thus it is more abundant (nearly 15% to total sugars and sugar alcohols) in New Delhi because of enhanced photosynthesis activity of plants.

3.4.3. Phthalates, bisphenol A and PAHs

Phthalates and bisphenol A are important products from manufacturing of plastics and have been considered endocrine disrupting chemicals (EDCs) (Flint et al., 2012; Larsen et al., 2007; Teil et al., 2006). In this study, five phthalate esters including diisobutyl (DiBP), butyl isobutyl (BiBP), di-*n*-butyl (DnBP), benzyl butyl (BBP) and bis-(ethyl hexyl) (BEHP) were detected in the urban aerosols. BEHP is the most abundant

Table 3
Concentrations of organic compounds in TSP from Xi'an and New Delhi (ng m^{-3}).

	Xi'an			New Delhi		
	Day (N = 8)	Night (N = 7)	24 h	Day (N = 7)	Night (N = 6)	24 h
(I) n-Alkanes						
Octadecane (C_{18})	4.8 ± 1.6	10 ± 4.3	7.5 ± 4.2	1.1 ± 0.4	2 ± 1.2	1.5 ± 1
Nonadecane (C_{19})	8.5 ± 5	19 ± 10	14 ± 9.8	1.4 ± 0.7	2.4 ± 1.5	1.9 ± 1.3
Icosane (C_{20})	19 ± 15	37 ± 18	29 ± 19	6.8 ± 5	10 ± 8.5	8.5 ± 7.1
Henicosane (C_{21})	37 ± 26	58 ± 24	48 ± 27	18 ± 11	29 ± 27	23 ± 21
Docosane (C_{22})	45 ± 28	63 ± 24	55 ± 27	23 ± 15	45 ± 38	33 ± 30
Tricosane (C_{23})	48 ± 28	66 ± 23	57 ± 27	36 ± 21	68 ± 55	51 ± 43
Tetracosane (C_{24})	41 ± 24	60 ± 21	51 ± 24	46 ± 24	79 ± 56	61 ± 45
Pentacosane (C_{25})	47 ± 29	64 ± 23	56 ± 28	57 ± 27	93 ± 59	74 ± 48
Hexacosane (C_{26})	32 ± 18	49 ± 18	41 ± 20	59 ± 25	99 ± 66	78 ± 52
Heptacosane (C_{27})	48 ± 27	65 ± 25	57 ± 27	86 ± 35	123 ± 67	103 ± 55
Octacosane (C_{28})	28 ± 16	43 ± 17	36 ± 18	75 ± 35	108 ± 64	90 ± 53
Nonacosane (C_{29})	95 ± 55	114 ± 42	105 ± 49	170 ± 61	237 ± 115	201 ± 96
Triacontane (C_{30})	26 ± 14	40 ± 17	34 ± 17	63 ± 33	89 ± 59	75 ± 48
Hentriacontane (C_{31})	84 ± 45	107 ± 42	96 ± 45	142 ± 57	235 ± 139	185 ± 113
Dotriacontane (C_{32})	29 ± 17	50 ± 22	40 ± 22	56 ± 32	90 ± 66	72 ± 53
Tritriacontane (C_{33})	52 ± 28	75 ± 30	64 ± 31	101 ± 45	159 ± 103	128 ± 83
Tetratriacontane (C_{34})	25 ± 15	42 ± 23	34 ± 21	56 ± 43	85 ± 68	69 ± 58
Pentatriacontane (C_{35})	27 ± 18	48 ± 28	38 ± 26	57 ± 38	99 ± 90	77 ± 70
Hexatriacontane (C_{36})	22 ± 19	41 ± 25	32 ± 25	38 ± 36	66 ± 64	51 ± 53
Subtotal	705 ± 416	1024 ± 401	874 ± 438	1090 ± 516	1716 ± 1118	1379 ± 904
(II) Fatty acids						
Dodecanoic ($C_{12:0}$)	15 ± 6.1	22 ± 9.2	19 ± 8.6	19 ± 7	26 ± 14	22 ± 11
Tridecanoic ($C_{13:0}$)	11 ± 5.3	14 ± 5.3	13 ± 5.4	8.8 ± 4.3	15 ± 8.9	11 ± 7.4
Tetradecanoic ($C_{14:0}$)	41 ± 21	58 ± 19	50 ± 22	83 ± 42	118 ± 68	99 ± 58
Pentadecanoic ($C_{15:0}$)	21 ± 12	29 ± 11	25 ± 12	34 ± 14	48 ± 25	40 ± 21
Hexadecanoic ($C_{16:0}$)	438 ± 168	587 ± 121	517 ± 163	889 ± 374	1239 ± 728	1051 ± 592
Heptadecanoic ($C_{17:0}$)	19 ± 13	27 ± 12	23 ± 13	26 ± 11	39 ± 19	32 ± 16
Octadecanoic ($C_{18:0}$)	228 ± 127	359 ± 121	297 ± 140	537 ± 202	839 ± 565	677 ± 438
Nonadecanoic ($C_{19:0}$)	17 ± 13	20 ± 9	19 ± 11	18 ± 8.2	25 ± 15	21 ± 12
Eicosanoic ($C_{20:0}$)	100 ± 64	137 ± 44	120 ± 57	78 ± 33	115 ± 71	95 ± 57
Heneicosanoic ($C_{21:0}$)	42 ± 29	54 ± 22	48 ± 26	28 ± 11	39 ± 23	33 ± 19
Docosanoic ($C_{22:0}$)	144 ± 92	207 ± 76	177 ± 90	109 ± 39	165 ± 90	135 ± 73
Tricosanoic ($C_{23:0}$)	77 ± 53	107 ± 49	93 ± 53	56 ± 21	88 ± 49	71 ± 40
Tetracosanoic ($C_{24:0}$)	179 ± 121	258 ± 99	221 ± 117	143 ± 53	219 ± 125	178 ± 101
Pentacosanoic ($C_{25:0}$)	48 ± 35	63 ± 29	56 ± 33	39 ± 18	59 ± 34	48 ± 28
Hexacosanoic ($C_{26:0}$)	120 ± 88	164 ± 72	143 ± 83	124 ± 48	193 ± 123	156 ± 97
Heptacosanoic ($C_{27:0}$)	36 ± 28	43 ± 23	40 ± 26	37 ± 16	49 ± 27	42 ± 23
Octacosanoic ($C_{28:0}$)	173 ± 128	236 ± 110	206 ± 123	246 ± 111	354 ± 194	296 ± 164
Nonacosanoic ($C_{29:0}$)	70 ± 48	78 ± 32	74 ± 41	64 ± 32	96 ± 63	79 ± 51
Triacontanoic ($C_{30:0}$)	368 ± 307	487 ± 252	431 ± 285	631 ± 251	952 ± 520	779 ± 429
Hentriacontanoic ($C_{31:0}$)	75 ± 61	95 ± 57	85 ± 60	73 ± 48	146 ± 110	107 ± 90
Dotriacontanoic ($C_{32:0}$)	124 ± 113	173 ± 110	150 ± 114	209 ± 98	338 ± 226	268 ± 181
Dotriacontanoic ($C_{342:0}$)	21 ± 22	27 ± 19	24 ± 20	36 ± 16	77 ± 80	55 ± 53
Octadecenoic ($C_{18:1}$)	28 ± 16	211 ± 94	125 ± 115	47 ± 27	97 ± 119	70 ± 87
Subtotal	2395 ± 1546	3457 ± 1306	2957 ± 1520	3536 ± 1340	5334 ± 3065	4366 ± 2471
(III) Fatty alcohols						
Eicosanol (C_{20})	6.9 ± 4.8	11 ± 4.5	8.9 ± 5	8.8 ± 5	14 ± 12	11 ± 9.1
Heneicosanol (C_{21})	6.7 ± 5.3	17 ± 26	12 ± 20	15 ± 17	43 ± 44	28 ± 35
Docosanol (C_{22})	18 ± 12	35 ± 14	27 ± 16	16 ± 8.6	19 ± 12	18 ± 10
Tricosanol (C_{23})	7.3 ± 4.5	23 ± 39	15 ± 30	7.2 ± 5	10 ± 6.3	8.4 ± 5.8
Tetracosanol (C_{24})	29 ± 17	46 ± 22	38 ± 21	25 ± 10	34 ± 12	29 ± 12
Pentacosanol (C_{25})	10 ± 8	33 ± 59	22 ± 45	7.1 ± 2.7	7.8 ± 4.5	7.4 ± 3.7
Hexacosanol (C_{26})	65 ± 43	81 ± 33	73 ± 39	40 ± 14	73 ± 38	55 ± 32
Heptacosanol (C_{27})	13 ± 9.1	30 ± 33	22 ± 26	6 ± 3.8	15 ± 13	10 ± 11
Octacosanol (C_{28})	163 ± 93	192 ± 100	179 ± 98	105 ± 33	171 ± 69	135 ± 62
Nonacosanol (C_{29})	30 ± 20	59 ± 57	45 ± 46	15 ± 5.4	29 ± 20	22 ± 16
Triacontanol (C_{30})	156 ± 95	195 ± 89	177 ± 94	326 ± 166	587 ± 289	446 ± 265
Hentriacontanol (C_{31})	33 ± 24	61 ± 68	48 ± 54	25 ± 12	36 ± 21	30 ± 18
Dotriacontanol (C_{32})	83 ± 72	86 ± 54	85 ± 63	210 ± 104	271 ± 138	238 ± 125
Subtotal	621 ± 401	869 ± 361	752 ± 400	807 ± 328	1310 ± 643	1039 ± 559
(IV) Sugars and sugar alcohols						
Galactosan	140 ± 79	201 ± 62	172 ± 77	195 ± 82	340 ± 271	262 ± 207
Mannosan	95 ± 53	161 ± 66	130 ± 69	127 ± 54	241 ± 206	179 ± 156
Levoglucosan	555 ± 82	596 ± 109	576 ± 99	1746 ± 649	2248 ± 1190	1977 ± 971
Arabitol	32 ± 18	43 ± 16	38 ± 18	43 ± 15	61 ± 25	51 ± 22
Fructose	41 ± 15	46 ± 19	44 ± 18	30 ± 22	59 ± 34	44 ± 31
Glucose	71 ± 36	77 ± 33	74 ± 35	157 ± 129	192 ± 86	173 ± 112
Mannitol	15 ± 8.4	20 ± 6.5	17 ± 7.9	36 ± 15	55 ± 28	45 ± 24
Inositol	4.3 ± 2.5	8.1 ± 3.2	6.3 ± 3.5	16 ± 6	25 ± 13	20 ± 11
Sucrose	45 ± 36	73 ± 77	60 ± 63	437 ± 472	541 ± 566	485 ± 520

Table 3 (*continued*)

	Xi'an			New Delhi		
	Day (N = 8)	Night (N = 7)	24 h	Day (N = 7)	Night (N = 6)	24 h
(IV) Sugars and sugar alcohols						
Trehalose	7.4 ± 3.1	11 ± 4.5	9.3 ± 4.3	68 ± 35	85 ± 52	76 ± 45
Subtotal	1005 ± 282.9	1235 ± 266	1127 ± 297	2855 ± 989	3847 ± 1995	3313 ± 1615
(V) Phthalates						
Diisobutyl	47 ± 11	48 ± 15	47 ± 13	92 ± 41	134 ± 69	112 ± 60
Isobutyl butyl	3.3 ± 0.6	3.4 ± 1.1	3.3 ± 0.9	7.6 ± 6.1	17 ± 15	12 ± 12
Dibutyl	34 ± 10	39 ± 12	37 ± 11	35 ± 16	77 ± 74	55 ± 55
Benzyl butyl	17 ± 6	17 ± 2.9	17 ± 4.6	14 ± 3	20 ± 5.4	17 ± 5.1
Bis-(ethyl hexyl)	124 ± 80	199 ± 59	164 ± 79	579 ± 162	817 ± 518	689 ± 390
Subtotal	226 ± 93	306 ± 87	268 ± 98	729 ± 154	1065 ± 630	884 ± 474
(VI) Bisphenol A						
Bisphenol A	9.4 ± 9.2	25 ± 12	18 ± 14	36 ± 30	60 ± 48	47 ± 41
(VII) PAHs						
Phenanthren (Phe)	33 ± 20	56 ± 22	45 ± 24	7.0 ± 5.0	9.2 ± 6.2	8.1 ± 5.7
Anthracene (Ant)	3.6 ± 1.6	4.3 ± 2.5	4.0 ± 2.2	0.6 ± 0.3	0.6 ± 0.3	0.6 ± 0.3
Fluoranthene (Flu)	31 ± 21	50 ± 23	41 ± 24	6.8 ± 3.8	12 ± 7.2	9.1 ± 6.2
Pyrene (Pyr)	30 ± 20	54 ± 24	43 ± 25	6.8 ± 3.9	11 ± 6.7	8.5 ± 5.7
Benz(*a*)anthracene (BaA)	27 ± 22	56 ± 23	42 ± 27	6.6 ± 3.5	14 ± 12	9.9 ± 9.3
Chrysene/triphenylene (Chr/TP)	32 ± 18	48 ± 15	40 ± 19	14 ± 6.6	25 ± 18	19 ± 14
Benzo(b)fluoranthene (BbF)	41 ± 28	62 ± 23	52 ± 28	24 ± 10	40 ± 27	31 ± 21
Benzo(k)fluoranthene (BkF)	10 ± 4.8	13 ± 4.4	11 ± 4.9	6.6 ± 2.3	12 ± 7.6	9.0 ± 6.0
Benzo(e)pyrene (BeP)	38 ± 25	55 ± 19	47 ± 24	15 ± 6.3	26 ± 18	20 ± 14
Benzo(a)pyrene (BaP)	28 ± 19	48 ± 18	39 ± 21	9.2 ± 4.4	20 ± 17	14 ± 13
Perylene (Pery)	6.5 ± 3.6	11 ± 4.2	9 ± 4.6	2.0 ± 1.1	4.2 ± 3.6	3.0 ± 2.8
Indeno[123-cd]pyrene (IP)	39 ± 28	56 ± 23	48 ± 27	23 ± 11	41 ± 31	31 ± 24
Dibenz(a,h)anthracene (DBA)	21 ± 15	31 ± 12	26 ± 14	16 ± 7.1	27 ± 18	21 ± 14
Benzo(ghi)perylene (BghiP)	7.4 ± 5.7	11 ± 4.3	9.4 ± 5.3	3.0 ± 1.4	6.1 ± 4.0	4.4 ± 3.3
Subtotal	347 ± 229	555 ± 210	457 ± 243	140 ± 62	248 ± 175	190 ± 138
(VIII) Hopanes						
17α(H)-22,29,30-trisnorhopane($C_{27\alpha}$)	4.7 ± 2.1	7.2 ± 2.4	6 ± 2.6	1.8 ± 1.1	3.4 ± 2.1	2.6 ± 1.8
17β(H)-22,29,30-trisnorhopane($C_{27\beta}$)	4.4 ± 2.7	4.7 ± 1.5	4.5 ± 2.1	1.1 ± 0.6	1.7 ± 1.1	1.4 ± 0.9
17α(H),21β(H)-30-norhopane($C_{29\alpha\beta}$)	9.8 ± 5	15 ± 5.7	13 ± 6.1	7.2 ± 5.0	11.1 ± 8.9	9.0 ± 7.4
17β(H),21α(H)-30-norhopane($C_{29\beta\alpha}$)	5.2 ± 2.6	7.4 ± 2.3	6.4 ± 2.7	1.1 ± 0.6	2.0 ± 1.5	1.5 ± 1.2
17α(H),21β(H)-hopane($C_{30\alpha\beta}$)	8.5 ± 3.7	14 ± 5.1	11 ± 5.2	5.6 ± 3.7	8.9 ± 6.7	7.1 ± 5.5
17β(H),21α(H)-hopane($C_{30\beta\alpha}$)	3.5 ± 1.5	4.6 ± 1.5	4.1 ± 1.6	1.1 ± 0.5	1.6 ± 0.9	1.3 ± 0.8
17α(H),21β(H)-22S-homohopane($C_{31\alpha\beta}S$)	5.0 ± 3.2	8.6 ± 3.4	6.9 ± 3.8	3.6 ± 2.2	5.7 ± 4.2	4.6 ± 3.4
17α(H),21β(H)-22R-homohopane($C_{31\alpha\beta}R$)	3.8 ± 1.7	5.7 ± 2.1	4.8 ± 2.1	2.9 ± 2.0	4.9 ± 3.5	3.8 ± 2.9
17β(H),21α(H)-homohopane($C_{31\beta\alpha}$)	2.8 ± 1.0	4.4 ± 1.9	3.7 ± 1.7	1.6 ± 0.8	2.5 ± 1.8	2.0 ± 1.5
17α(H),21β(H)-22S-bishomohopane($C_{32\alpha\beta}S$)	2.8 ± 1.0	4.4 ± 1.3	3.6 ± 1.4	2.3 ± 1.4	3.5 ± 2.4	2.9 ± 2
17α(H),21β(H)-22R-bishomohopane($C_{32\alpha\beta}R$)	3.3 ± 1.0	4.7 ± 1.4	4.0 ± 1.4	2.2 ± 1.4	3.3 ± 2.1	2.7 ± 1.8
Subtotal	54 ± 25	81 ± 28	68 ± 30	30 ± 19	49 ± 35	39 ± 29

phthalate in both cities, followed by DiBP and DnBP. Concentrations of total phthalates in New Delhi are 884 ± 474 ng m^{-3}, which are 2.3 times higher than those in Xi'an (268 ± 98 ng m^{-3}), indicating that plastic waste emissions are more significant in Indian urban areas. Bisphenol A showed the same pattern (47 ± 41 ng m^{-3} in New Delhi and in 18 ± 14 ng m^{-3} Xi'an), consisting with the results reported by Fu and Kawamura (2010).

Polycyclic aromatic hydrocarbons (PAHs) are the products of incomplete combustion of carbon-containing materials and are of high toxicity and carcinogenicity (Halek et al., 2008; Sultan et al., 2001). Grimmer et al. (1981) reported that diagnostic ratios of IP/BghiP are 0.2, 0.5, and 1.3 in the smokes from gasoline, diesel, and coal combustions, respectively. Ohura et al. (2004) further reported that BghiP/BeP is 2.0 and 0.8 in emissions from vehicle exhaust and coal burning. As

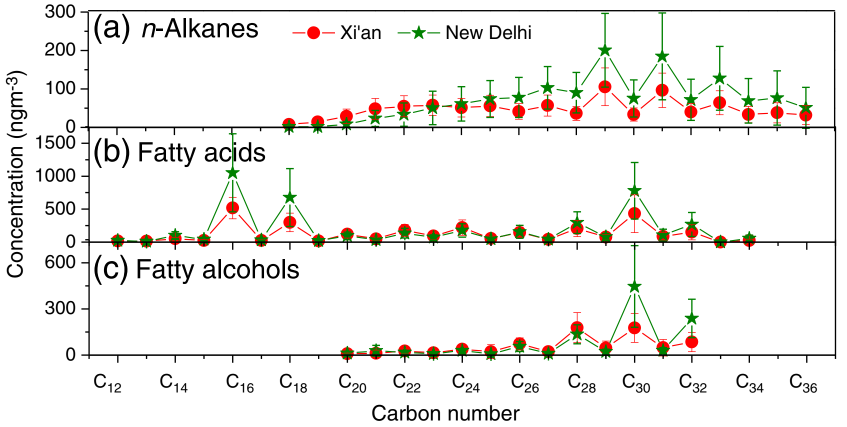

Fig. 3. Molecular compositions of *n*-alkanes, fatty acids and fatty alcohols.

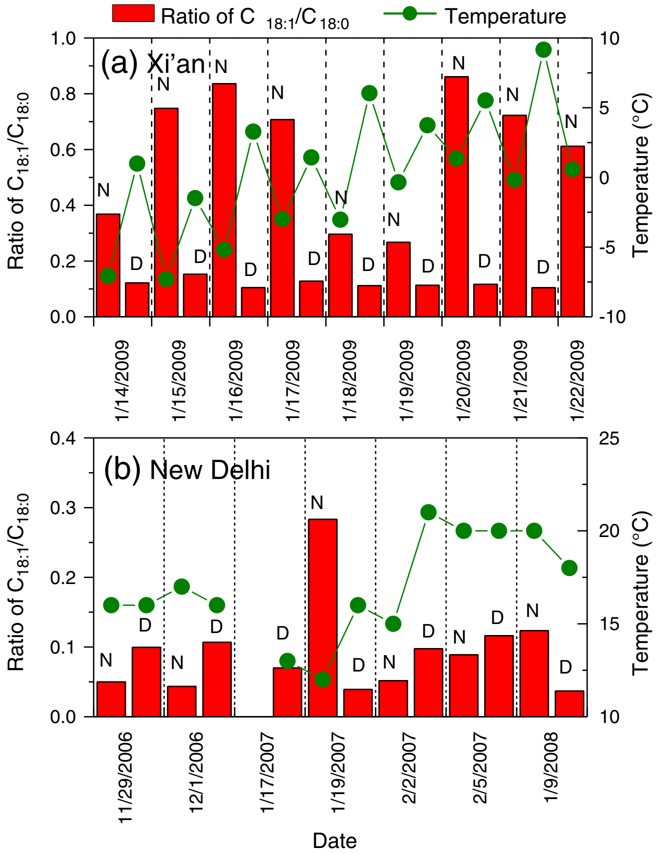

Fig. 4. Diurnal variations of the mass ratio of $C_{18:1}/C_{18:0}$ in the samples and ambient temperature in Xi'an and New Delhi during the sampling periods.

shown in Table 2, diagnostic ratios of IP/BghiP and BghiP/BeP of the Xi'an samples are 1.8 ± 0.1 and 0.55 ± 0.05, respectively, which are closer to those in coal burning smoke in comparison with those of the New Delhi samples. Concentration of total PAHs in Xi'an (457 ± 243 ng m^{-3}) is 2.4 times higher than that in New Delhi (198 ± 138). Such congener compositions and abundances of PAHs again demonstrate that coal combustion emissions are more significant in the Chinese city. As shown in Fig. 5b, relative abundance of LMW PAHs (mainly 3-/4-rings PAHs) in Xi'an is higher than that in New Delhi, in contrast to HMW PAHs (mainly 5-/6-rings PAHs), which are more abundant in New Delhi. Such a phenomenon can be explained by low ambient temperatures in Xi'an that may promote gas-to-particle partitioning of semi-volatile LMW PAHs. In contrast to the correlation of OC and levoglucosan, the relationship of OC and PAHs in Xi'an ($R^2 = 0.84$) is more significant than that in New Delhi ($R^2 = 0.69$) (Fig. 6b and d) due to more intensive emissions of coal burning in Xi'an. Similar to $C_{18:1}/C_{18:0}$, the ratios of benzo(a)pyrene/benzo(e)pyrene (BaP/BeP) also showed lower values in New Delhi (0.63 ± 0.15) than in Xi'an (0.80 ± 0.10), further indicating that aerosols in New Delhi are more oxidized.

3.4.4. Hopanes

A series of hopanes were detected in the urban samples with total concentrations of 68 ± 30 ng m^{-3} in Xi'an and 39 ± 29 ng m^{-3} in New Delhi, respectively. The dominant hopane is 17α(H),21β(H)-30-norhopane($C_{29\alpha\beta}$), followed by 17α(H),21β(H)-hopane($C_{30\alpha\beta}$) and 17α(H),21β(H)-22S-homohopane($C_{31\alpha\beta}S$) in the atmospheres of both cities (Fig. 5c). Hopanes are abundant in coal and crude oils and enriched in lubricant oil fraction (Oros and Simoneit, 2000; Kawamura et al., 1995). They can be emitted to the atmosphere from coal burning and/or internal combustion of fuel in engines. Thus, hopanes showed a robust liner relationship with PAHs ($R^2 = 0.89$ in Xi'an and $R^2 = 0.65$ in New Delhi).

3.5. Mass balance reconstruction of the TSP samples

The relative contributions of major chemical species to the TSP samples in Xi'an and New Delhi are shown in Fig. 7. The geological material (Geo, i.e., soil/dust) is roughly estimated from the concentrations of Fe (Cao et al., 2008; Wu et al., 2011) using the following formula:

$$C_{Geo} = C_{Fe}/4\% \qquad (2)$$

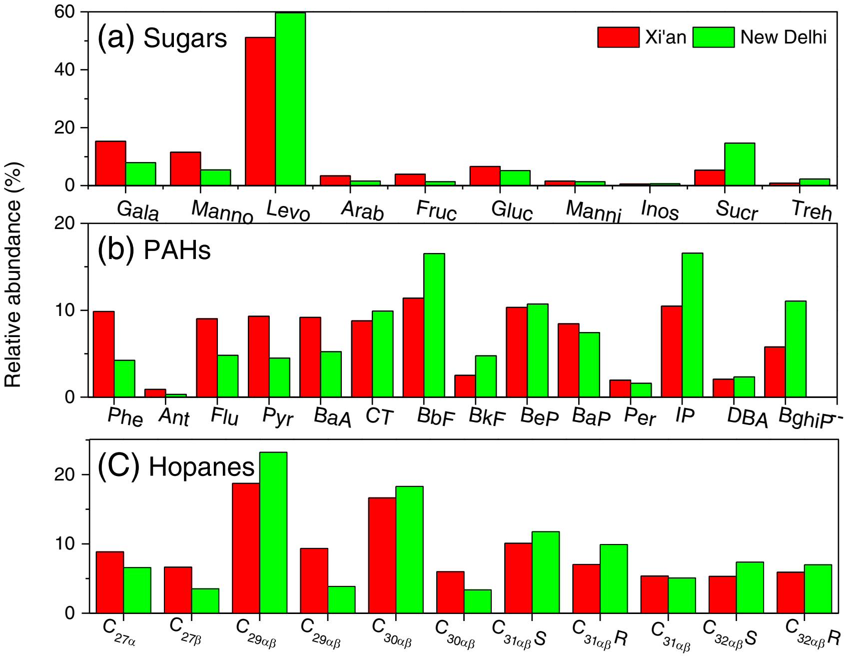

Fig. 5. Molecular compositions of sugars, PAHs and hopanes (relative abundance: [(concentration of individual compound) / (concentration of the total congeners)] × 100%).

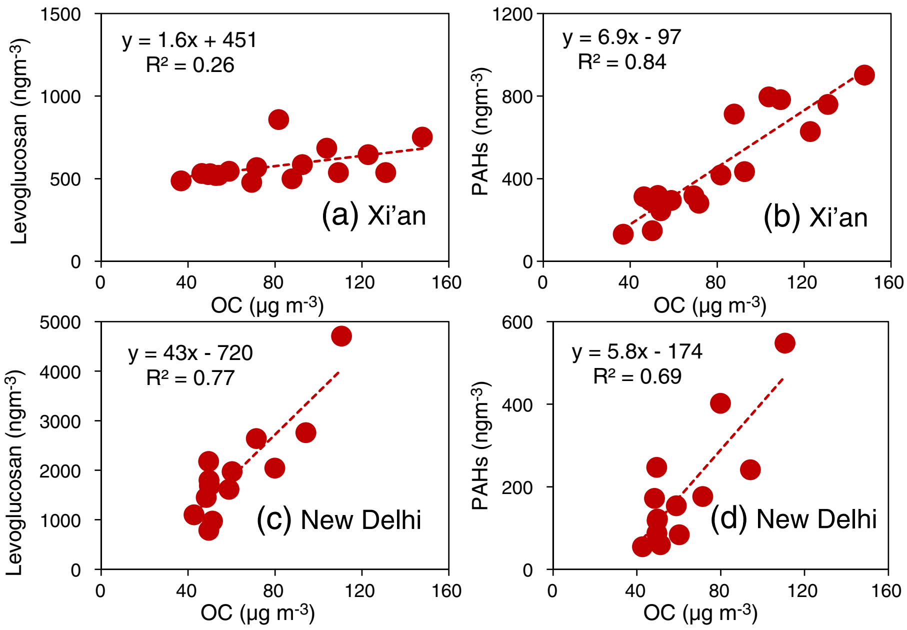

Fig. 6. Linear fit regressions for OC with levoglucosan and PAHs in the Xi'an and New Delhi TSP samples.

and the organic matter (OM) (Chen and Yu, 2007; El-Zanan et al., 2005, 2009) is calculated as:

$$C_{OM} = C_{OC} \times 1.6. \quad (3)$$

As shown in Fig. 7, the geological material is the most abundant component of the TSP samples in both cities, accounting for about half of the mass (52% in Xi'an and 48% in New Delhi, seen in Fig. 7). The second most abundant component in the TSP from Xi'an and New Delhi is the organic matter, which accounts for nearly one quarter of TSP concentration. Relative abundances of EC, SO_4^{2-} and NO_3^- in Xi'an (4.2%, 7.1% and 6.1%) are 0.4–1.3 times higher than those in New Delhi (1.8%, 4.9% and 4.5%), while that of Cl^- in New Delhi is around two times higher than that in Xi'an. The percentages of ammonium in the TSP samples in the two cities are comparable (2.3% in Xi'an and 2.7% in New Delhi). About 0.9 and 7.2% of the TSP in Xi'an and New Delhi are unidentified, probably due to the uncertainties of chemical analysis and geological material and organic matter estimation.

4. Conclusion

Concentrations of Br and Pb in the New Delhi samples are about two times of those in the Xi'an, suggesting that traffic emission in New Delhi is relatively more significant. SO_4^{2-} and NO_3^- in Xi'an are about twice as those in New Delhi, indicating that coal burning is more intensive in the Chinese megacity. High concentrations of Cl^- were found in the New Delhi TSP samples, which are due to local complicated source emissions such as biomass burning, waste incineration and coal combustion. The ratio of OC/EC in New Delhi is about two times of that in Xi'an due to the high loading of biomass burning emissions and strong photochemical oxidation. To the best of our knowledge, this is the first study in which about 100 organic compounds were determined and compared for Chinese and Indian aerosols in a single study. Levoglucosan in New Delhi is two times more abundant than in Xi'an due to a high level of biomass burning emission. PAHs present higher concentrations in the Xi'an TSP samples because of coal burning. In contrast, phthalates and bisphenol A are more abundant in New Delhi mostly due to high

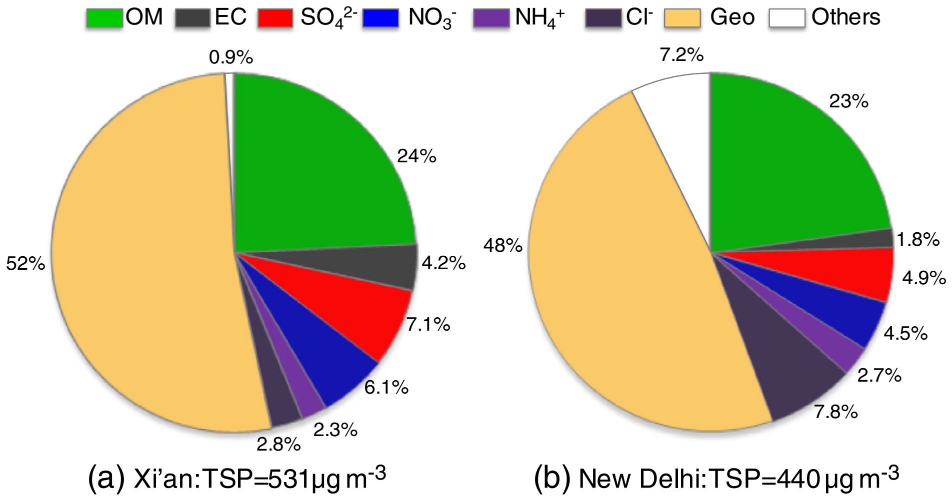

Fig. 7. Mass closure reconstructions of TSP in Xi'an and New Delhi during winter (OM: organic matter, estimated as 1.6 × OC (Chen and Yu, 2007; El-Zanan et al., 2005, 2009). Geo: geological material, estimated as Fe/4% (Cao et al., 2008; Wu et al., 2011)).

emissions from open burning of plastic and other solid wastes. The different concentrations of these harmful organic compounds suggest that residents in Xi'an and New Delhi are probably exposed to different health risks, because PAHs are carcinogenic while phthalates and bisphenol A are endocrine disrupting. Lower ratios of octadecenoic acid/octadecanoic acid and benzo(a)pyrene/benzo(e)pyrene (BaP/BeP) imply that aerosols in New Delhi are more oxidized.

Acknowledgments

This work was financially supported by the China National Science Funds for Distinguished Young Scholars (No. 41325014) and the “Strategic Priority Research Program” of the Chinese Academy of Sciences (Grant Nos. XDA05100103, XDB05020401). We thank the anonymous reviewers and Ms. Meiling Gao in the Department of Environmental Health Sciences, School of Public Health, UC-Berkeley for their comments on this work, which are very helpful for us to improve the paper quality.

References

Aggarwal SG, Kawamura K, Umarji GS, Tachibana E, Patil RS, Gupta PK. Organic and inorganic markers and Stable C-, N-isotopic compositions of tropical coastal aerosols from megacity Mumbai: sources of organic aerosols and atmospheric processing. Atmos Chem Phys 2013;13:4667–80.

Aldhous P. China's burning ambition. Nature 2005;435:1152–4.

Andreae MO, Talbot RW, Berresheim H, Beecher KM. Precipitation chemistry in central Amazonia. J Geophys Res Atmos 1990;95:16987–99.

Cachier H, Bremond MP, Buat-Menard P. Carbonaceous aerosols from different tropical biomass burning sources. Nature 1989;340:371–3.

Cao JJ, Chow JC, Watson JG, Wu F, Han YM, Jin ZD, et al. Size-differentiated source profiles for fugitive dust in the Chinese Loess Plateau. Atmos Environ 2008;42:2261–75.

Chen X, Yu JZ. Measurement of organic mass to organic carbon ratio in ambient aerosol samples using a gravimetric technique in combination with chemical analysis. Atmos Environ 2007;41:8857–64.

El-Zanan HS, Lowenthal DH, Zielinska B, Chow JC, Kumar N. Determination of the organic aerosol mass to organic carbon ratio in IMPROVE samples. Chemosphere 2005;60:485–96.

El-Zanan HS, Zielinska B, Mazzoleni LR, Hansen DA. Analytical determination of the aerosol organic mass-to-organic carbon ratio. J Air Waste Manage Assoc 2009;59:58–69.

Engling G, Lee JJ, Tsai YW, Lung SCC, Chou CCK, Chan CY. Size-resolved anhydrosugar composition in smoke aerosol from controlled field burning of rice straw. Aerosol Sci Tech 2009;43:662–72.

Flint S, Markle T, Thompson S, Wallace E. Bisphenol A exposure, effects, and policy: a wildlife perspective. J Environ Manage 2012;104:19–34.

Fu PQ, Kawamura K. Ubiquity of bisphenol A in the atmosphere. Environ Pollut 2010;158:3138–43.

Grimmer G, Jacob J, Naujack KW, Dettbarn G. Profile of the polycyclic aromatic hydrocarbons from used engine oil—inventory by GCGC/MS—PAH in environmental materials, part 2. Fresenius Z Anal Chem 1981;309:13–9.

Gustafsson O, Krusa M, Zencak Z, Sheesley RJ, Granat L, Engstrom E, et al. Brown clouds over South Asia: biomass or fossil fuel combustion? Science 2009;323:495–8.

Halek F, Nabi G, Kavousi A. Polycyclic aromatic hydrocarbons study and toxic equivalency factor (TEFs) in Tehran, IRAN. Environ Monit Assess 2008;143:303–11.

Jaeger CH, Lindow SE, Miller S, Clark E, Firestone MK. Mapping of sugar and amino acid availability in soil around roots with bacterial sensors of sucrose and tryptophan. Appl Environ Microbiol 1999;65:2685–90.

Kawamura K, Pavuluri CM. New directions: need for better understanding of plastic waste burning as inferred from high abundance of terephthalic acid in South Asian aerosols. Atmos Environ 2010;44:5320–1.

Kawamura K, Kosaka M, Sempere R. Distributions and seasonal changes in hydrocarbons in urban aerosols and rain waters. Chikyu Kagaku (Geochemistry) 1995;29:1–15. (In Japanese).

Kumar S, Aggarwal SG, Saxena RK, Gupta PK. Identify metals as source marker for open-waste burning aerosols. Indian Aerosol Science and Technology Association (IASTA-2012) Conference, 20 (1&2). IASTA bulletin; 2012. p. 156–9.

Larsen ST, Hansen JS, Hansen EW, Clausen PA, Nielsen GD. Airway inflammation and adjuvant effect after repeated airborne exposures to di-(2-ethylhexyl)phthalate and ovalbumin in BALB/c mice. Toxicology 2007;235:119–29.

Li J, Zhuang GS, Huang K, Lin YF, Xu C, Yu SL. Characteristics and sources of air-borne particulate in Urumqi, China, the upstream area of Asia dust. Atmos Environ 2008;42:776–87.

Li JJ, Wang GH, Zhou BH, Cheng CL, Cao JJ, Shen ZX, et al. Chemical composition and size distribution of wintertime aerosols in the atmosphere of Mt. Hua in central China. Atmos Environ 2011;45:1251–8.

Li JJ, Wang GH, Zhou BH, Cheng CL, Cao JJ, Shen ZX, et al. Airborne particulate organics at the summit (2060 m, a.s.l.) of Mt. Hua in central China during winter: implications for biofuel and coal combustion. Atmos Res 2012;106:108–19.

Medeiros PM, Conte MH, Weber JC, Simoneit BRT. Sugars as source indicators of biogenic organic carbon in aerosols collected above the Howland Experimental Forest, Maine. Atmos Environ 2006;40:1694–705.

Menon S, Hansen J, Nazarenko L, Luo YF. Climate effects of black carbon aerosols in China and India. Science 2002;297:2250–3.

Miyazaki Y, Aggarwal SG, Singh K, Gupta PK, Kawamura K. Dicarboxylic acids and water-soluble organic carbon in aerosols in New Delhi, India, in winter: characteristics and formation processes. J Geophys Res Atmos 2009;114:D19206.

Mochida M, Kawamura K, Umemoto N, Kobayashi M, Matsunaga S, Lim HJ, et al. Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: continental outflow of organic aerosols during the ACE-Asia campaign. J. Geophys Res Atmos 2003:108.

Mochida M, Kawamura K, Fu PQ, Takemura T. Seasonal variation of levoglucosan in aerosols over the western North Pacific and its assessment as a biomass-burning tracer. Atmos Environ 2010;44:3511–8.

NBSC. China Statistical Yearbook. Beijing: Chinese Statistics Press; 2001–2012.

Ohura T, Amagai T, Fusaya M, Matsushita H. Polycyclic aromatic hydrocarbons in indoor and outdoor environments and factors affecting their concentrations. Environ Sci Technol 2004;38:77–83.

Oros DR, Simoneit BRT. Identification and emission rates of molecular tracers in coal smoke particulate matter. Fuel 2000;79:515–36.

Oros DR, bin Abas MR, Omar N, Rahman NA, Simoneit BRT. Identification and emission factors of molecular tracers in organic aerosols from biomass burning: part 3. Grasses. Appl Geochem 2006;21:919–40.

Pavuluri CM, Kawamura K, Tachibana E, Swaminathan T. Elevated nitrogen isotope ratios of tropical Indian aerosols from Chennai: implication for the origins of aerosol nitrogen in South and Southeast Asia. Atmos Environ 2010;44:3597–604.

Perrino C, Tiwari S, Catrambone M, Dalla Torre S, Rantica E, Canepari S. Chemical characterization of atmospheric PM in Delhi, India, during different periods of the year including Diwali festival. Atmos Pollut Res 2011;2:418–27.

Ramana MV, Ramanathan V, Feng Y, Yoon SC, Kim SW, Carmichael GR, et al. Warming influenced by the ratio of black carbon to sulphate and the black-carbon source. Nat Geosci 2010;3:542–5.

Ramanathan V, Li F, Ramana MV, Praveen PS, Kim D, Corrigan CE, et al. Atmospheric brown clouds: hemispherical and regional variations in long-range transport, absorption, and radiative forcing. J Geophys Res Atmos 2007;112:D22S21.

Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of fine organic aerosols.4. Particulate abrasion products from leaf surfaces of urban plants. Environ Sci Technol 1993;27:2700–11.

Rosenfeld D, Dai J, Yu X, Yao ZY, Xu XH, Yang X, et al. Inverse relations between amounts of air pollution and orographic precipitation. Science 2007;315:1396–8.

Shen ZX, Cao JJ, Arimoto R, Han ZW, Zhang RJ, Han YM, et al. Ionic composition of TSP and PM2.5 during dust storms and air pollution episodes at Xi'an, China. Atmos Environ 2009;43:2911–8.

Simoneit BRT, Elias VO, Kobayashi M, Kawamura K, Rushdi AI, Medeiros PM, et al. Sugars — dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. Environ Sci Technol 2004a;38:5939–49.

Simoneit BRT, Kobayashi M, Mochida M, Kawamura K, Huebert BJ. Aerosol particles collected on aircraft flights over the northwestern Pacific region during the ACE-Asia campaign: composition and major sources of the organic compounds. J Geophys Res Atmos 2004b;109:D19S09.

Simoneit BRT, Kobayashi M, Mochida M, Kawamura K, Lee M, Lim HJ, et al. Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign. J Geophys Res Atmos 2004c;109:D19S10.

Streets DG, Waldhoff ST. Present and future emissions of air pollutants in China: SO_2, NO_x, and CO. Atmos Environ 2000;34:363–74.

Sultan C, Balaguer P, Terouanne B, Georget V, Paris F, Jeandel C, et al. Environmental xenoestrogens, antiandrogens and disorders of male sexual differentiation. Mol Cell Endocrinol 2001;178:99–105.

Taylor SR, McLennan SM. The composition of the continental crust. Rev Geophys 1995;33:241–65.

Teil MJ, Blanchard M, Chevreuil M. Atmospheric fate of phthalate esters in an urban area (Paris-France). Sci Total Environ 2006;354:212–23.

Tiwari S, Srivastava AK, Bisht DS, Bano T, Singh S, Behura S, et al. Black carbon and chemical characteristics of PM10 and PM2.5 at an urban site of North India. J Atmos Chem 2009;62:193–209.

Venkataraman C, Habib G, Eiguren-Fernandez A, Miguel AH, Friedlander SK. Residential biofuels in south Asia: carbonaceous aerosol emissions and climate impacts. Science 2005;307:1454–6.

Wang GH, Kawamura K. Molecular characteristics of urban organic aerosols from Nanjing: a case study of a mega-city in China. Environ Sci Technol 2005;39:7430–8.

Wang GH, Kawamura K, Hatakeyama S, Takami A, Li H, Wang W. Aircraft measurement of organic aerosols over China. Environ Sci Technol 2007;41:3115–20.

Wang GH, Chen CL, Li JJ, Zhou BH, Xie MJ, Hu SY, et al. Molecular composition and size distribution of sugars, sugar-alcohols and carboxylic acids in airborne particles during a severe urban haze event caused by wheat straw burning. Atmos Environ 2011;45:2473–9.

Wang GH, Kawamura K, Cheng CL, Li JJ, Cao JJ, Zhang RJ, et al. Molecular distribution and stable carbon isotopic composition of dicarboxylic acids, ketocarboxylic acids, and alpha-dicarbonyls in size-resolved atmospheric particles from Xi'an City, China. Environ Sci Technol 2012a;46:4783–91.

Wang GH, Li JJ, Cheng CL, Zhou BH, Xie MJ, Hu SY, et al. Observation of atmospheric aerosols at Mt. Hua and Mt. Tai in central and east China during spring 2009 — part 2: impact of dust storm on organic aerosol composition and size distribution. Atmos Chem Phys 2012b;12:4065–80.

Wang SW, Zhang Q, Streets DG, He KB, Martin RV, Lamsal LN, et al. Growth in NO_x emissions from power plants in China: bottom-up estimates and satellite observations. Atmos Chem Phys 2012c;12:4429–47.

Watson JG, Chow JC, Houck JE. PM2.5 chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in Northwestern Colorado during 1995. Chemosphere 2001;43:1141–51.

Wedepohl KH. The composition of the continental crust. Geochim Cosmochim Acta 1995;59:1217–32.

Wu F, Chow JC, An Z, Watson JG, Cao J. Size-differentiated chemical characteristics of Asian Paleo Dust: records from Aeolian deposition on Chinese Loess Plateau. J Air Waste Manage Assoc 2011;61:180–9.

Yu Y, Zhang Z, Li Y. Total suspended particulates in ambient air and their characteristics on metallic elements in Xi'an. J Environ Health 2003;20:359–60. (In Chinese).

Zhang X, Zhuang G, Chen J, Xue H. Speciation of the elements and compositions on the surfaces of dust storm particles: the evidence for the coupling of iron with sulfur in aerosol during the long-range transport. Chin. Sci. Bull. 2005;50:738–44.

Zhang Q, Streets DG, Carmichael GR, He KB, Huo H, Kannari A, et al. Asian emissions in 2006 for the NASA INTEX-B mission. Atmos Chem Phys 2009;9:5131–53.