

Organic aerosols in East Asia and their impact on the downstream atmosphere: a review

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Abstract: In this paper primary (i.e., *n*-alkanes, PAHs, levoglucosan, and phthalates) and secondary organic aerosols (i.e., dicarboxylic acids) are reviewed on a molecular level for their spatial distribution of concentrations over East Asia. Differences in the abundances and sources of those organic aerosols between China and India are further presented, along with a discussion on climate effect (e.g., CCN activity and radiative forcing) of organic aerosols in the atmosphere.

Key words: atmospheric aerosols; organic tracer; molecular composition; source; seasonal and spatial distribution

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1 Introduction

Atmospheric aerosols are tiny liquid or solid matters suspended in the air, including mineral dust, spores, pollen, fungi, sulfate, nitrate, ammonium, elemental carbon and organic compounds (Seinfeld, 2004; Seinfeld and Pandis, 1998). Sizes of these aerosols vary from a few nanometers to hundreds of micrometers. Particles in the air with a diameter larger than 100 μm rapidly deposit into the earth surface, thus atmospheric aerosols are in generally referred to those with a diameter less than 100 μm (Hinds, 1999). These particles can be classified into three modes, i.e., Aitken mode, whose diameters are less than 100 nm, accumulation mode, whose diameters range from 100 nm to 2 μm , and coarse mode, whose diameters are larger than 2 μm . Coarse mode particles are produced by mechanical process. For example, sea salt aerosol is originated from sea wave splash, and mineral/soil dust particle is lofted by wind. Aitken mode particles are generated from transformation of gas phase to solid phase. These newly formed aerosols are of high surface-to-volume ratio and thus readily grow into large size, i.e., accumulation mode, by absorbing gaseous species and/or by coagulating with other particles (Hinds, 1999). Once emitted into the air, aerosols can

scatter and absorb solar radiation, which is called direct effect of radiative forcing. A fraction of the aerosols is hygroscopic and can be activated as cloud condensation nuclei (CCN), thus change the lifetime and forms of cloud and further alter the solar radiation onto ground surface, which is called indirect effect. Asian continent is the largest source of aerosols on the Earth. Much more soot derived from coal and biomass combustion in the region are emitted in some cases without strict emission control, adding more absorbing particles into the atmosphere, along with the frequent occurrence of dust storm, making the unique characteristics of Asian aerosols (Huebert et al, 2003; IPCC, 2007; Jacob et al, 2003). In this paper, I first gave a review on the spatial distributions of organic aerosols over East Asia on a molecular level, then discussed their sources based on organic compositions and correlation with inorganic components, and finally recognized the impact of anthropogenic pollutants from inland China on aerosol chemistry of the downwind atmosphere and the effect of organic aerosols on climate change.

2 Organic aerosols in the atmosphere over East Asia

2.1 *n*-Alkanes

Normal alkanes (*n*-alkanes) are a major class

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of organics with a carbon chain length up to forty. *n*-Alkanes are derived from natural plant wax and fossil fuel emissions. The plant wax derived *n*-alkane are characterized by a odd carbon number preference (carbon preference index, CPI), which is calculated as the sum of odd number divided by the sum of even number (Simoneit, 1999; Simoneit, 2002), and in general larger than 5; whereas fossil fuel derived *n*-alkanes are characterized by a CPI close to unity. Due to enhanced biogenic activities, plant wax derived *n*-alkanes are more abundant in summer. Oppositely, an increase in coal burning for house heating in winter results in a sharp increase in fossil fuel derived *n*-alkanes. Therefore, particulate *n*-alkanes from plant wax in China are higher in the south than in the north. As seen in Table 1, wintertime concentrations of *n*-alkanes in Xi'an and Chongqing are most abundant than other regions in China. *n*-Alkanes in east coastal China are comparable to those in New Delhi, India and 2 times higher than in Chennai, another Indian coastal mega-city. Recent satellite observation found that the annual averages of PM_{2.5} from 2001–2006 in North China Plain, Guangzhou Plain and Sichuan Basin in China are more than 80 $\mu\text{g}\cdot\text{m}^{-3}$ (van Donkelaar et al, 2010), which are the highest in the world, suggesting a severe aerosol pollution in the above three Chinese regions. CPI values in these Chinese mega-cities are

close to unity, indicating fossil fuel combustion as their major sources. *n*-Alkanes in New Delhi and Chennai are characterized by a higher value of CPI and larger molecular weight of the compounds, suggesting more plant wax emissions compared to those in Chinese mega-cities. Xi'an city is situated in Guanzhong Plain, a semi-arid region in China. Thus suspended soil/dust is more significant in the air and contribution of biogenic *n*-alkanes from soil/dust is pronounced, resulting in the CPI value higher than that in other regions. Another possible factor is the relatively lower level of emissions from vehicle exhausts in the Guanzhong Plain, because economic level in the region is relatively lower.

2.2 PAHs

Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion of materials containing carbon and ubiquitous in the atmosphere. PAH are harmful to human health due to their mutagenic and carcinogenic nature (Dockery et al, 1993). Biomass burning and fossil fuel combustion are the major sources of atmospheric PAHs. Major source of airborne PAHs in developed countries is traffic emission (e.g., diesel truck exhaust), although wood burning is an important source in heating season. In contrast, coal combustion is the most significant source of atmospheric PAHs in China (Wang et al, 2006b).

Fig.1 plots a spatial distribution of total PAHs

Table 1 Airborne particulate *n*-alkanes in mega-cities of China and India, $\text{ng}\cdot\text{m}^{-3}$

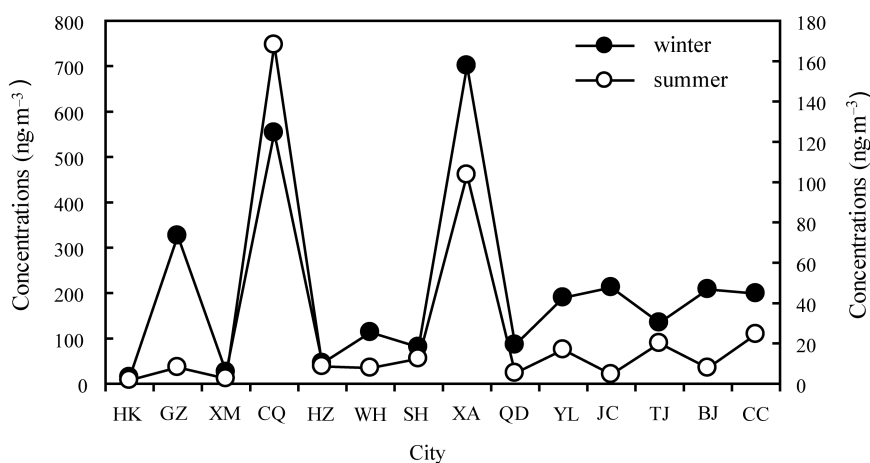
City	Size	Year	Season	<i>n</i> -alkanes	Cn-Cm	Cmax	CPI	Reference
Beijing	PM _{2.5}	2003	Winter	399	C ₁₆ -C ₃₃	C ₂₃	1.1	(Wang et al, 2006b)
Tianjin	PM _{2.5}	2003	Winter	297	C ₁₇ -C ₃₃	C ₂₂	1.1	(Wang et al, 2006b)
Qingdao	PM _{2.5}	2003	Winter	286	C ₁₇ -C ₃₃	C ₂₂	1.1	(Wang et al, 2006b)
Xi'an	PM _{2.5}	2003	Winter	1433	C ₁₈ -C ₃₄	C ₂₅	1.3	(Wang et al, 2006b)
Baoji	PM ₁₀	2007	Winter	1733	C ₁₈ -C ₃₃	C ₂₃	1.3	(Xie et al, 2009)
Shanghai	PM _{2.5}	2003	Winter	259	C ₁₆ -C ₃₃	C ₂₃	1.0	(Wang et al, 2006b)
Nanjing	PM _{2.5}	2003	Winter	250	C ₁₈ -C ₃₃	C ₂₂	1.0	(Wang et al, 2006b)
Chongqing	PM _{2.5}	2003	Winter	948	C ₁₈ -C ₃₅	C ₂₃	1.3	(Wang et al, 2006b)
Guangzhou	TSP	2003	Winter	300	C ₁₉ -C ₃₁	C ₂₃	na	(Bi et al, 2008)
Hong Kong	PM _{2.5}	2003	Winter	195	C ₁₆ -C ₃₃	C ₂₃	1.3	(Wang et al, 2006b)
II. India								
New Dehli	PM ₁₀	2001	Winter	382	C ₁₉ -C ₃₁	C ₂₉		(Sharma et al, 2003)
Chennai	PM ₁₀	2007	Winter	141	C ₁₈ -C ₄₀	C ₂₉	1.6	(Fu et al, 2010)

Cn-Cm is the carbon chain range; Cmax is the compound with a highest concentration; CPI is the carbon preference index calculated as the sum of odd number divided by even number.

in fine particles from fourteen cities in China during the winter and summer of 2003 (Original data are cited from (Wang et al, 2006b)). During winter, Xi'an, Chongqing and Guangzhou showed a much higher concentrations of PAHs, while in summer only Xi'an and Chongqing presented higher concentrations. Such a spatial difference is in good greement with the spatial distributions of particulate *n*-alkanes and fine particles discussed above, further demonstrating the more serious pollution in the two regions, i.e., Guanzhong Plain and Sichuan Basin in the country. Diagnostic ratios of PAHs are useful tool to recognize their sources (Oros and Simoneit, 1999; Oros and Simoneit, 2001; Simoneit, 2002). For example, the concentration ratios of indeno[1,2,3-*c,d*]pyrene to benzo(ghi)perylene (IP/BghiP) in the gasoline, diesel and coal combustion emissions are 0.22, 0.5 and 1.3 respectively, and

benzo(ghi)perylene/benzo(e)pyrene (BghiP/BeP) ratio in traffic emission and coal burning emission is 2.0 and 0.8, respectively. As seen in Table 2, during winter IP/BghiP was in the range of 1.0~1.4 for the fourteen Chinese cities, indicating the importance of coal burning emissions (Wang et al, 2006c).

Benzo(b)fluoranthene (BbF), a PAH congener with 5-ring, was dominant in the particulate PAHs detected in the fourteen Chinese cities. Moreover, we also found that BbF was the most abundant congener among the PAH class in our previous studies on aerosols from Nanjing (Wang et al, 2006a; Wang et al, 2007b) and Baoji (Xie et al, 2009), two cities located in east and central China. Coals are still commonly used in Chinese families for house cooking and heating in rural and urban areas especially in winter, in which lots of pollutants are emitted due to the low combustion



(HK: Hong Kong, GZ: Guangzhou, XM: Xiamen, CQ: Chongqing, HZ: Hangzhou, WH: Wuhan, SH: Shanghai, XA: Xi'an, QD: Qingdao, YL: Yulin, JC: Jinchang, TJ: Tianjin, BJ: Beijing, CC: Changchun)

Fig.1 Concentrations of PAHs in PM_{2.5} from Chinese cities (wintertime PAH concentrations are referred to left y-axis and summertime PAH concentrations are referred to right y-axis).

Table 2 Diagnostic ratios of PAHs in fourteen Chinese cities during winter and summer

	City														Source		
	HK	GZ	XM	CQ	HZ	WH	SH	XA	QD	YL	JC	TJ	BJ	CC	Gasoline	Diesel	Coal
Winter																	
IP/BghiP	1.0	1.2	1.0	1.2	1.2	1.1	1.1	1.3	1.0	1.4	1.0	1.2	1.2	1.3	0.22	0.5	1.3
BghiP/BeP	0.8	1.8	1.4	1.1	1.3	0.9	1.3	1.3	1.0	1.2	0.9	1.3	1.0	1.4	2.0		0.8
Summer																	
IP/BghiP	Na	0.9	1.6	1.1	2.7	0.9	1.0	1.0	1.0	1.0	0.8	1.2	1.0	0.9			
BghiP/BeP	0.0	2.4	2.0	1.3	0.5	1.5	2.0	1.2	1.3	1.3	1.9	1.4	1.6	1.7			

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efficiency of the stoves. It is estimated that around 5000 tons of PAHs were emitted annually in China due to the combustion of household honeycomb-briquette that are made of coal, in which BbF gives the highest emission factor (Chen et al, 2005). That is the reason why BbF is dominant in these Chinese urban regions. BbF is chemically stable in the air with a lifetime of about 7 days (Finlayson-Pitts and Pitts Jr, 2000), thus it is found to be a dominant PAH in Chinese coastal marine aerosols (Simoneit et al, 2004). Such a dominant BbF in the atmosphere over China is different from the cases in any other countries, where BghiP is the most abundant particulate PAH due to the emissions from vehicular engines. Seasonal changes in the PAH compositions obtained in Hong Kong showed that BbF is predominant in winter when PAHs are mostly derived from inland China and BghiP is dominated in summer when PAHs are largely derived from local vehicle exhausts (Zheng et al, 1997; Zheng and Fang, 2000), further confirming that BbF is a dominant PAH in Chinese aerosols, which can be thought as a fingerprint for coal burning in China. Spatially, PAHs and *n*-alkanes in Chinese urban areas is about 1~2 orders of magnitude higher than those in remote areas such as those in Mt. Hua and Mt. Tai, and 2~3 orders of magnitude higher than those in outflow regions of Asian continent (Wang et al, 2009). Similar to the fine

particle loadings observed by satellite, concentrations of PAHs and *n*-alkanes in the fourteen Chinese cities are around ten times higher than those in developed countries such as Tokyo (Kawamura et al, 1995), London (Baek et al, 1992; Finlayson-Pitts and Pitts Jr, 2000) and Los Angeles (Rogge et al, 1993).

2.3 Levoglucosan

Levoglucosan is a pyrolysis product of cellulose, and chemically stable in the atmosphere, thus has been recognized as a key tracer for biomass burning smoke (Simoneit et al, 1999). Fig.2 exhibits the spatial distribution of levoglucosan in the atmosphere over East Asia. The wintertime concentration of levoglucosan in Chinese urban areas ranged from 130 $\text{ng}\cdot\text{m}^{-3}$ in Hong Kong to 3200 $\text{ng}\cdot\text{m}^{-3}$ in Xi'an, which is 10~200 times higher than that in Asian continent outflow region such as East China Sea (15 $\text{ng}\cdot\text{m}^{-3}$), Japan Sea (29 $\text{ng}\cdot\text{m}^{-3}$) and Japanese Islands (100 $\text{ng}\cdot\text{m}^{-3}$) (Mochida et al, 2003a), indicating a significant biofuel combustion in Guanzhong Plain and Sichuan Basin. Except for Chongqing and Xi'an, levoglucosan in other Chinese cities is comparable to that (112 $\text{ng}\cdot\text{m}^{-3}$) in Chennai, a coastal megacity of India (Fu et al, 2010), but lower than that in Los Angeles and Amazonia, Brazil (Simoneit et al, 2004a). Such a difference between the Asian countries and the United States in winter is most likely due to the prevailing

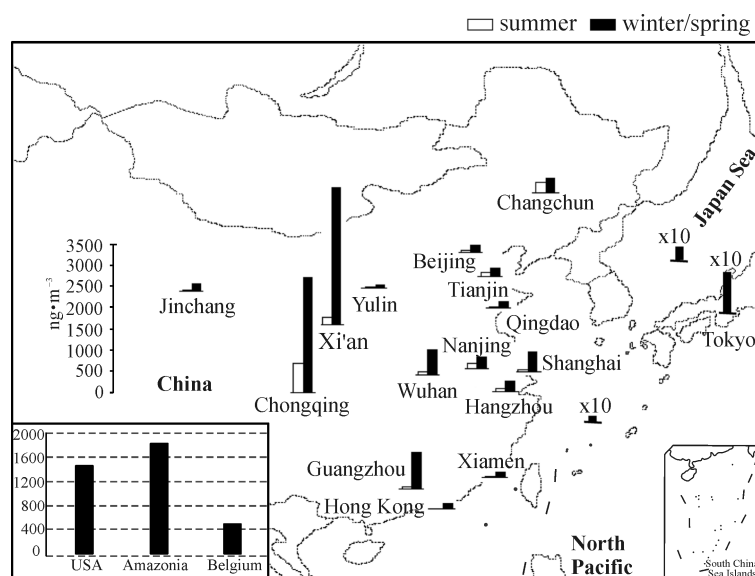


Fig.2 Spatial distribution of levoglucosan in East Asia

Black columns for Chinese cities represent winter while the three black columns for North Pacific represent spring (modified from Wang et al, 2006c).

combustion of wood for house heating in U.S.

2.4 Phthalates

Phthalates are widely used in industry and commerce; they are used in personal care (e.g., makeup, soaps, and shampoo), plastic products, paints and some pesticide formulations. Phthalates are ubiquitous in the environment. Several studies have reported that phthalates are carcinogenic and endocrine-disrupting. Experiments have demonstrated that prenatal phthalate exposure impairs testicular function and shortens anogenital distance in male rodents, thus supporting the hypothesis that prenatal phthalate exposure at environmental levels can adversely affect male reproductive development in humans. Moreover, phthalates in the atmosphere can be photochemically oxidized as dicarboxylic acids, thus can further activate into cloud condensation nuclei by uptake of water. The most frequently detected phthalates in the Chinese atmosphere are dimethyl-, diethyl-, diisobutyl-, dibutyl-, benzylbutyl-, bis(2-ethylhexyl)-, and di-n-octyl. Among them, diisobutyl, dibutyl and bis (2-ethylhexyl)phthalates are predominant. Phthalates are added into plastic products like polyvinyl chloride (PVC) and others as plastic materials but not chemically bonded onto the polymer, thus they may evaporate into the air from the matrix with an emission rate increasing

as a function of temperature, resulting in their airborne concentrations normally more abundant in summer than in winter. Table 3 lists the spatial distributions of major phthalates in fifteen cities in China and one city in India. During the winter of 2003, Xi'an had the highest concentrations ($439 \text{ ng}\cdot\text{m}^{-3}$ in total, Table 3), while Chongqing, Shanghai and Guangzhou showed a similar level (around $330 \text{ ng}\cdot\text{m}^{-3}$), followed by Nanjing ($262 \text{ ng}\cdot\text{m}^{-3}$), Hangzhou ($194 \text{ ng}\cdot\text{m}^{-3}$), indicating that industrial emissions at Changjiang Delta Region is also significant. In contrast, during the summer of 2003 phthalates in all the cities increased by a factor of 1~20 with Chongqing being the highest ($2193 \text{ ng}\cdot\text{m}^{-3}$), followed by Tianjin ($944 \text{ ng}\cdot\text{m}^{-3}$), Xi'an ($646 \text{ ng}\cdot\text{m}^{-3}$), Shanghai ($599 \text{ ng}\cdot\text{m}^{-3}$), and Hangzhou ($568 \text{ ng}\cdot\text{m}^{-3}$). More than 60% of the fifteen Chinese cities showed a higher concentration of phthalates than in Chennai, India, which may be due to less active economic activities in the India subcontinent.

2.5 Secondary organic aerosols (dicarboxylic acids)

Secondary organic aerosols (SOA) are produced by photochemical oxidation of organic precursors, which can occur in gas phase and subsequently transform into solid phase by a condensation process and/or occur in particle phase by an aqueous phase

Table 3 Phthalates in fine particles from cities in China and India, $\text{ng}\cdot\text{m}^{-3}$

	Year	Winter				Summer				Reference
		diisobutyl	dibutyl	Bis(2-ethylhexyl)	Total	diisobutyl	dibutyl	Bis(2-ethylhexyl)	Total	
I. China										
Hong Kong	2003	20	0	0	20	36	117	241	395	(Wang et al, 2006b)
Guangzhou	2003	31	37	262	330	104	121	202	427	(Wang et al, 2006b)
Xiamen	2003	30	30	76	137	43	52	102	197	(Wang et al, 2006b)
Hangzhou	2003	45	34	115	194	137	165	266	568	(Wang et al, 2006b)
Shanghai	2003	43	32	258	332	164	158	277	599	(Wang et al, 2007)
Nanjing	2004	14	14	234	262	12	20	202	234	(Wang et al, 2006b)
Wuhan	2003	36	29	63	129	130	131	198	459	(Wang et al, 2006b)
Chongqing	2003	35	53	244	332	175	270	1748	2193	(Wang et al, 2006b)
Xi'an	2003	79	48	313	439	236	185	225	646	(Wang et al, 2006b)
Qingdao	2003	19	28	44	92	44	64	55	164	(Wang et al, 2006b)
Yulin	2003	17	14	25	56	57	60	119	237	(Wang et al, 2006b)
Jinchang	2003	23	19	39	81	64	97	110	271	(Wang et al, 2006b)
Tianjing	2003	24	21	75	121	281	269	394	944	(Wang et al, 2006b)
Beijing	2003	22	21	130	173	122	135	130	387	(Wang et al, 2006b)
Changchun	2003	28	18	63	108	118	149	133	394	(Wang et al, 2006b)
II.India										
Chennai	2006	104	25	171	300	127	42	379	548	(Fu et al, 2010)

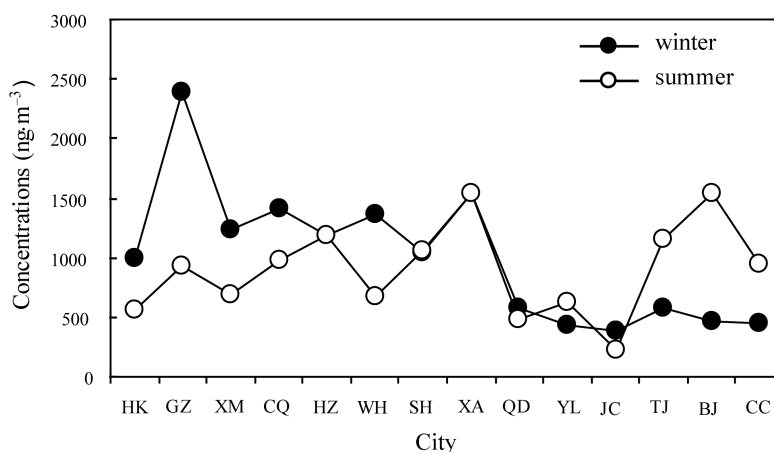
reaction. The SOA yield is dependent on concentrations of precursors and oxidants, temperature and chemical stability of the oxidized daughter products. Since SOA compounds are oxygenized, the product has more polar functional groups such as $-\text{CHO}$, $-\text{CH}_2\text{OH}$, $-\text{COOH}$, and $-\text{CO}-$, making the compound more water-soluble, and thus significantly increasing the ability of airborne particle to uptake water. Modeling studies estimated that global anthropogenic SOA precursors are annually 6.7, 4.5 and 0.8 Tg for toluene, xylene, and trimethylbenzene, respectively, accounting for about 10%~15% of all anthropogenic non-methane volatile organic compounds (NMVOC), and yielding about $1.4\sim 8.6 \text{ Tg}\cdot\text{a}^{-1}$ SOA (Hallquist et al, 2009; Henze et al, 2008).

Dicarboxylic acids are a major class of SOA in the atmosphere, and have been found from continental areas such as urban (Kawamura and Ikushima, 1993; Wang et al, 2002), rural (Limbeck et al, 2005; Limbeck et al, 2001), mountain (Wang et al, 2011), forest and savanna regions to marine areas (Kawamura and Sakaguchi, 1999; Mochida et al, 2003b) and even in remote Arctic region (Kawamura et al, 2005; Narukawa et al, 2002). Such a ubiquity nature may imply a significant climate effect as they are water-soluble. Diacids in the atmosphere are mostly produced secondarily from oxidation of natural and anthropogenic VOCs, although a minor fraction of the compounds in the atmosphere can be directly produced

from combustion process including fossil fuel and biofuel burnings. Fig.3 presents the concentrations of dicarboxylic acids in fine particles from fourteen cities in China. No clear trend in spatial distribution was found for the cities, but in most cases summertime showed a higher concentration compared to that in wintertime. Concentrations in summer varied from $350 \text{ ng}\cdot\text{m}^{-3}$ in Hong Kong to around $1500 \text{ ng}\cdot\text{m}^{-3}$ in Xi'an and Beijing, while the wintertime concentrations varied from $234 \text{ ng}\cdot\text{m}^{-3}$ in Hong Kong to around $2000 \text{ ng}\cdot\text{m}^{-3}$ in Guangzhou (Ho et al, 2007; Wang et al, 2006c), which is comparable to those ($227\sim 1030 \text{ ng}\cdot\text{m}^{-3}$) (Pavuluri et al, 2010) in the tropical city of Chennai in India but much lower than those in New Delhi, the India capital, where the diacids ranged from $800 \text{ ng}\cdot\text{m}^{-3}$ to $6030 \text{ ng}\cdot\text{m}^{-3}$ (Miyazaki et al, 2009). The high concentration of diacids in New Delhi is mostly like due to the enhanced biomass burning emissions.

3 Correlations of organic aerosols with mineral dust and their impact on the downstream atmosphere

Sulfate aerosol in China is mainly originated from coal burning emissions, which contain a significant amount of sulfur dioxide and further be transformed into sulfate by heterogeneous reactions and water uptake. In-cloud process is an important pathway of sulfate formation. Linear fit regression for fossil fuel derived *n*-alkanes and PAHs in the PM_{10} aerosols from Baoji, an inland city in China, showed a robust



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Fig.3 Concentrations of diacids in $\text{PM}_{2.5}$ from Chinese cities (modified from Wang et al, 2006b)

correlation with a high value of coefficient (Fig.4) (Wang et al, 2010). Moreover, sulfate, lead and PAHs in the PM_{10} samples also correlated well (Fig.5). Pb is a tracer of coal burning emission, thus the correlations further demonstrate that PAHs and sulfate in Baoji city are largely derived from coal combustion. Stable carbon isotope data showed that $\delta^{13}C$ % of TC (total carbon) in the Baoji samples increases as an increase of ratios of oxalic acid to OC (Wang et al, 2010), suggesting that organic aerosols are photochemically oxidized with a release of small molecules into the air during aging process, which is most likely CO_2 , (Aggarwal and Kawamura, 2009; Wang et al, 2006d). Primary organic carbon in the samples linearly correlated with Fe and Ca^{2+} (Fig.6), indicating that soil dust is an important source of primary organic compounds.

Anthropogenic aerosols have been found to be abundant in the outflow region of East Asia continent. In Cheju Island, Korea, the ambient concentrations of OC and EC during April 2001 were $3.9\sim 8.6 \mu g \cdot m^{-3}$ and $0.8\sim 2.0 \mu g \cdot m^{-3}$, respectively. While in the north Pacific region like Chichi-jima Island OC and EC at the same time were found to be $1.4 \mu g \cdot m^{-3}$ and $0.52 \mu g \cdot m^{-3}$, respectively (Simoneit et al, 2004c). Total fossil fuel derived n -alkanes in Cheju Island, Korea, ranged from $7.3 ng \cdot m^{-3}$ to $59 ng \cdot m^{-3}$ (data were calculated from Simoneit et al, 2004, thereafter), while PAHs was $0.6\sim 7.8 ng \cdot m^{-3}$. In the more remote area, i.e., Chichijima Island, Japan, fossil fuel derived n -alkanes and PAHs were about $0.08\sim 2.0 ng \cdot m^{-3}$. Levoglucosan decreased from $10\sim 74 ng \cdot m^{-3}$ in Cheju Island, Korea

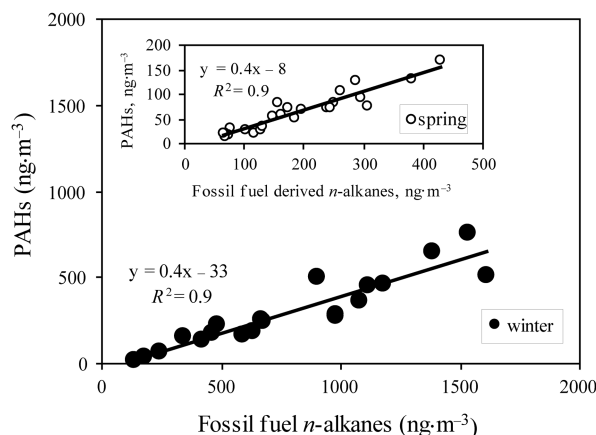


Fig.4 Linear fit regression of PAHs with fossil fuel derived n -alkanes in Baoji city, China during winter and spring of 2008 (modified from Xie et al, 2009)

to only $0.5 ng \cdot m^{-3}$ in Chichijima Island, Japan. To measure the vertical profile of organic aerosols in the north Pacific region, aircraft observation was performed along with the above ground measurement during the 2001 ACE-Asia campaign, during which vertical profiles of organic aerosols in the rim of North Pacific was observed by C-130 while that in the mid of north Pacific was observed by R/V Ronald H. Brown. Fossil fuel derived n -alkanes between the boundary layer and the 7 km height of free troposphere varied from $14 ng \cdot m^{-3}$ to $67 ng \cdot m^{-3}$ in East China Sea and Japan Sea area, and down to about $1.0 ng \cdot m^{-3}$ in Hawaii region (Simoneit et al, 2004b; Simoneit et al, 2004c), while airborne particulate PAHs was undetectable during the flight cruise and levoglucosan was $0.2\sim 1.3 ng \cdot m^{-3}$.

OC in the aircraft samples collected in Hawaii area during the ACE-Asia was $0.0\sim 0.5 \mu g \cdot m^{-3}$, while EC

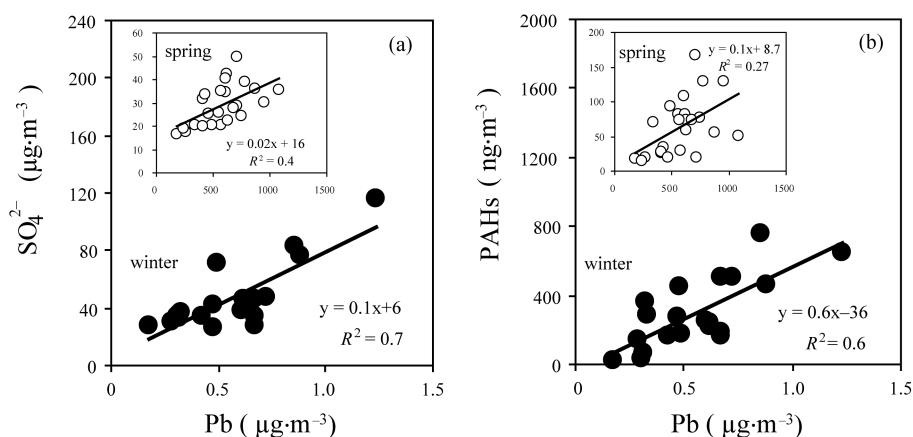


Fig.5 Linear fit regression for PAHs, Pb and sulfate in PM_{10} from Baoji city in China (modified from Wang et al, 2010)

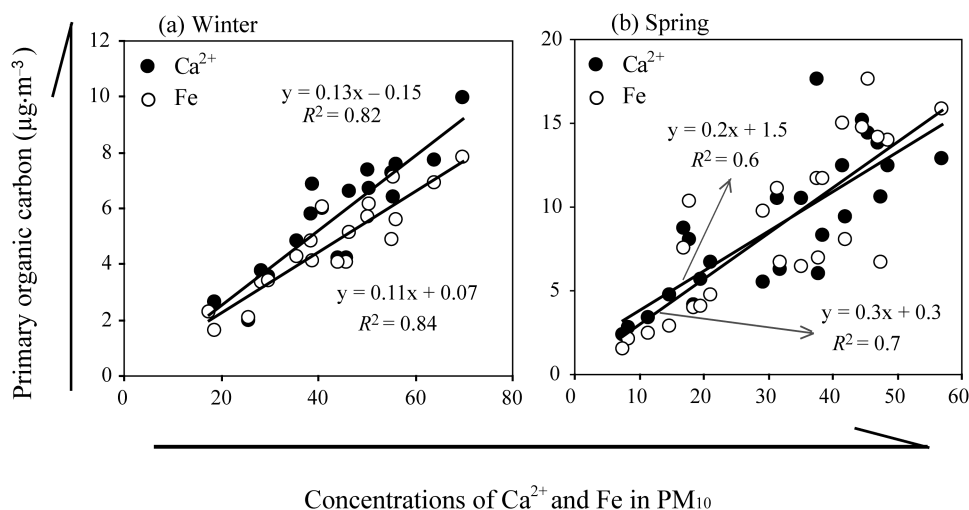


Fig.6 Linear regression for primary organic carbon with Fe and Ca^{2+} in PM_{10} from Baoji city located in Guanzhong Plain in China (modified from Wang et al, 2010)

was $0.0\sim 0.1 \mu\text{g}\cdot\text{m}^{-3}$. Aircraft measurement of organic aerosols in east coastal China showed that PAHs was $(24\pm 15) \text{ ng}\cdot\text{m}^{-3}$ and levoglucosan was $(47\pm 2.2) \text{ ng}\cdot\text{m}^{-3}$ (Wang et al, 2007a). Compared to those in Hawaii regions, levoglucosan in the free troposphere over east coastal China was 80 times higher. Since levoglucosan is chemically stable in the atmosphere, thus it is plausible that free tropospheric organic aerosols in China is about two orders of magnitude higher than in the mid north Pacific region. The extremely lower level of organic aerosol in the Hawaii atmosphere suggests that impact of anthropogenic organic pollutants from East Asia continent on the mid-region of North Pacific is insignificant.

However, impact of mineral dust, sulfate and nitrate from Asian continent on the western America atmosphere is significant (Seinfeld et al, 2004). For example, the INTEX-B 2006 near Whistler, BC, Canada found that trans-Pacific transport between 2 km and 5 km altitudes from 22 April 2006 to 15 May 2006 increased ozone by 10×10^{-9} and fine particulate sulfate by $0.2\sim 0.5 \mu\text{g}\cdot\text{m}^{-3}$ (Leaitch et al, 2009). A five-year (1996–2008) observation performed at Hawaii showed that 19% of CaCO_3 in dust particles from Asian continent has reacted into CaSO_4 , and 7% of the CaCO_3 has reacted into $\text{Ca}(\text{NO}_3)_2$, with minor amount of the CaCO_3 reacted as CaCl_2 (McNaughton et al, 2009). Size distribution results suggest that those chemical conversions mostly occur in coarse particles,

significantly increasing the dust particle hygroscopicity (Leaitch et al, 2009; Tobo et al, 2010), diminishing indirect radiative forcing of these compounds, but potentially increasing their direct radiative forcing (Seinfeld et al, 2004).

4 Climate effect of organic aerosols

Organic compounds in atmospheric aerosols can alter the water uptake of the particles. Such a physical property is related to chemical compositions and sizes of the particle. Water-soluble organic compounds (WSOC) constitute a substantial fraction of organic matter in the atmosphere, thus understanding the hygroscopicity of WSOC is very important in order to improve our knowledge on climate effects of atmospheric aerosols. In the past decades, a number of WSOC have been measured for their water uptake properties, including lower molecular dicarboxylic acids (Choi and Chan, 2002; Cruz and Pandis, 2000a; Hemming and Seinfeld, 2001), amino acids (Chan et al, 2005) and anhydrosaccharides (Chan et al, 2005; Mochida and Kawamura, 2004). Oxalic acid, a smallest dicarboxylic acid, is of a similar cloud condensation nuclei (CCN) activity to sulfate (Saxena et al, 1995). Prenni et al investigated the effect of low molecular weight diacids on cloud formation and found that ice formation occurs via homogenous nucleation for most of lower molecular weight (LMW) diacids ($\text{C}_2\text{--C}_6$), and that nucleation for these acids is not as efficient

as that for sulfate aerosol (Prenni et al, 2001). Cruz and Pandis found that LMW diacids like glutaric acid take up water at $RH > 85\%$, and may act as efficient CCN (Cruz and Pandis, 2000b). Mixing state of diacids with other species is also responsible for their hygroscopicity. For example, a glutaric acid coating on ammonium sulfate can increase the CCN activity of ammonium sulfate (Cruz and Pandis, 2000a; Saxena et al, 1995). Several studies have confirmed that highly water-soluble organic species have critical activation diameters near that of ammonium sulfate, while the less water-soluble WSOC has a significant larger activation diameter, suggesting an importance of their solubility. A substantial fraction of WSOC in the atmosphere is directly produced by biomass burning, including carboxylic acids, aldehydes, sugars and amino acids. Similar to carboxylic acids, amino acids like glycine, alanine, serine, glutamine and threonine take up water under a higher RH, and crystallize under a lower RH condition. In contrast, sugars like levoglucosan, mannosan and galactosan, three most abundant anhydrosaccharides found in biomass burning smokes, do not crystallize nor do deliquesce at either humid or dry conditions, and exist as highly concentrated liquid droplets at low RH (Chan et al, 2005; Mochida and Kawamura, 2004). Ability of these sugar compounds to absorb water increase with an increase in relative humidity (Mochida and Kawamura, 2004).

Global organic aerosol concentrations in the atmosphere are frequently observed to be comparable to sulfate. Bond et al (2004) reported that combustion derived organic aerosols in the world is about $5 \sim 17 \text{ TgC} \cdot \text{a}^{-1}$ with $2.4 \text{ TgC} \cdot \text{a}^{-1}$ from fossil fuel burning. Since industrial revolution in 1870 global emissions of organic aerosols from fossil fuel and biofuel combustion increased by a factor of three with present-day amounts of $2.2 \text{ TgC} \cdot \text{a}^{-1}$ and $7.5 \text{ TgC} \cdot \text{a}^{-1}$, respectively. Water is often associated with organic aerosols at low relative humidity and with inorganic aerosols at higher relative humidity. Thus, hygroscopicity of organic aerosols is larger than sulfate aerosols at low RH and considerably less than sulfate aerosols at high RH. Coating of organic aerosols on sulfate may lead to suppression of the rate

of water uptake during cloud activation (Xiong et al, 1998; Chuang, 2003). Field measurements showed that organic-containing aerosols are less abundant than sulfate-containing aerosols in ice cloud particles, indicating that organic aerosols do not preferentially freeze. These organic aerosols do not significantly affect the cirrus formation unless they are present at low temperature in a high concentration comparable to sulfate. Recent modeling results showed that organic aerosols from both fossil fuel and biofuel combustion generate a top of atmosphere (TOA) direct RF of $(-0.24 \pm 0.08) \text{ W} \cdot \text{m}^{-2}$ on a global scale. IPCC report also indicated that the TOA direct RF of organic aerosols from fossil fuel combustion is about $(-0.10 \pm 0.30) \text{ W} \cdot \text{m}^{-2}$ (IPCC, 2007), further confirming the important role of anthropogenic organic aerosols in the global climate system.

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