High loadings and source strengths of organic aerosols in China

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Abstract: Nation-wide studies of organic aerosols were conducted on a molecular level in 15 Chinese cities. The results showed strikingly high levels of organic compounds (e.g., annual concentrations of polycyclic aromatic hydrocarbons, phthalates, sugars and diacids are 110, 370, 400 and 830 ng m^{-3}, respectively), especially in the mid-west region during winter (up to 125 μg m^{-3} organic carbon). Fossil fuel combustion and/or biomass burning products are 3–30 times more abundant in winter than in summer. In contrast, significant quantity of phthalates (168–2200 ng m^{-3}) was detected in summer. Concentrations of the pollutants are generally 1–3 orders of magnitude higher than those in developed countries. Their source strengths are characterized in winter by fossil fuel combustion, followed by secondary oxidation, plant wax emissions and biomass burning, whereas in summer by secondary oxidation, followed by fossil fuel combustion and plastic emissions.

1. Introduction

One fourth of primary anthropogenic organic aerosols on the globe is generated in China [*Cooke et al.*, 1999]. A steep increase in the concentrations of NOx, volatile organic compounds, particles, and ozone has been considered as the result of heavy usage of coals and the rapid growth of the number of vehicles in the urban areas, especially in the mega-cities [*Akimoto*, 2003; *Richter et al.*, 2005]. China is the largest user of coal in the world, consuming 1.2 billion tons of coal in 2002, most of which are burned without efficient controls. Its annual usage is predicted to increase by 3 times in 2020 [*Aldhous*, 2005]. Traditional Chinese style of domestic energy utilization (i.e., coal and biofuel usage) combined with its vigorous expansion of economy and number of motor vehicles make its air pollution problems different from those of any other countries in the world.

To better understand the current status of air pollution in China, a nation wide survey of organic aerosols was conducted on molecular levels in its 15 cities during summer and winter. Here, we highlight the anthropogenic compounds (i.e., polycyclic aromatic hydrocarbons (PAHs), phthalates, and biomass burning products) and photochemical oxidation products (i.e., dicarboxylic acids) and discuss their molecular compositions, seasonal and spatial distributions, and source strengths.

2. Experiment

$PM_{2.5}$ atmospheric aerosols were collected for 24hr using pre-combusted quartz filter. Two days of the samplings in 14 Chinese cities except Nanjing were simultaneously performed on January 13th and 14th, 2003 for winter campaign, but on different days for summer campain in June/July, 2003 to avoid any wet deposition. While a week term of aerosol collection in Nanjing was conducted in summer and winter 2004, respectively. The filter aliquot was extracted with a mixture of methanol/dichloromethane

(2:1, v/v), followed by concentration, and derivatization with N,O-bis-(trimethylsilyl)trifluoroacetamide prior to GC/MS determination. Another aliquot of the sample was extracted with pure water to isolate low molecular weight dicarboxylic acids, which were concentrated and reacted with BF_3/*n*-butanol before GC analysis. More details about the sample collection and determination can been seen in the previous papers [*Kawamura and Yasui*, 2005; *Wang et al.*, 2006a; *Wang et al.*, 2006b].

3. Results and discussion

A total of 129 organic compounds were detected, including *n*-alkanes (C_{16}–C_{31}), PAHs (18 species), hopanes (C_{27}–C_{32}), phthalates (6 species), fatty acids (C_{10}–C_{34}), fatty alcohols (C_{12}–C_{32}), sterols (4 species), lignin and resin products (3 species), sugars (8 species), polyols/polyacids (4 species), and dicarboxylic acids (C_2–C_{11}). Levoglucosan was found as the dominant species in winter, followed by oxalic, octadecenoic and hexadecanoic acids, whereas oxalic acid was found as the dominant in summer, followed by bis(2-ethylhexyl)phthalate, hexadecanoic acid and dibutyl phthalate. Concentrations of the organic compounds detected in Chinese aerosols are 1–3 orders of magnitude higher than those in developed countries, especially in cold seasons due to the usage of coal for house heating (Table 1).

Concentrations of ∑PAHs were found to be significantly higher in winter (14–701 ng m^{-3}, average 198 ng m^{-3}) than in summer (2–168 ng m^{-3}, average 29 ng m^{-3}) (Figure 1a). Their concentrations are generally 1–2 orders of magnitude higher than those reported in Los Angeles (12 ng m^{-3}) [*Rogge et al.*, 1993b], London (17 ng m^{-3}) [*Baek et al.*, 1992], and Tokyo (20 ng m^{-3}) [*Kawamura*, 1989]. The highest concentrations were obtained in the mid-west China, i.e., Xi'an and Chongqing (Figure 1a). In winter, benzo[*b*]fluoranthene (BbF) was found as the dominant PAH in all the cities studied (56.8 ± 53.4 ng m^{-3}), accounting for 30.1 ± 4.9 % of ∑PAHs. In summer, BbF was also the most abundant (9.3 ± 14.3 ng m^{-3}), except for Hong Kong, Xiamen and Jinchang. Indeno[1,2,3-*cd*]pyrene (IP) and benzo[*ghi*]perylene (BghiP) were the second most abundant PAHs in both seasons.

Coals are commonly used in China for heating and cooking, in which combustion efficiency is very low. Around 5000 tons of PAHs were emitted in 2000 from combustion of Chinese household honeycomb-briquette that are made of coal, in which BbF gives the highest emission factor [*Chen et al.*, 2005]. BbF was found as the dominant PAH in the soot deposits from coal-burning stoves in China [*Wornat et al.*, 2001]. Previous PAH studies also showed the predominance of BbF in Chinese continental [*Guo et al.*, 2003; *Wang et al.*, 2006a] and coastal marine aerosols [*Simoneit et al.*, 2004b]. All the data including those in this study (except the Hong Kong summer samples) demonstrated that BbF is the most abundant PAH in aerosols all over China mainly due to incomplete combustion of coals. This is different from the cases in other countries, where PAHs are largely derived from incomplete combustion of petroleum, and IP or BghiP is the dominant PAH [*Menichini et al.*, 1999; *Rogge et al.*, 1993a]. PAHs ratios are also used to discuss the sources of combustion-derived PAHs [*Yunker et al.*, 2002]. Ratio of BbF/(IP + BghiP) in the 15 Chinese cities was 1.2 ± 0.4 in summer and 1.8 ± 0.4 in winter. They are much higher than those reported in developed countries (e.g., 0.3 ± 0.2 in USA) [*Rogge et al.*, 1993a], further suggesting the difference in the PAH sources between China and other countries.

Extremely high levels of phthalates (up to 2200 ng m^{-3}) dominated by bis(2-ethylhexyl), dibutyl and diisobutyl phthalates are detected in the aerosols, especially in hot seasons (Table 1), probably due to an enhanced evaporative release from plastics, followed by adsorptive deposition on pre-existing particles (Figure 1b). Phthalate concentrations in Chinese aerosols are 1–3 orders of magnitude higher than those in Belgium [*Kubátová et al.*, 2002], Sweden [*Thuren and Larsson*, 1990] and France [*Teil et al.*, 2006] (Table 1 and Figure 1b). Phthalates are carcinogenic and endocrine-disrupting, and PAHs are mutagenic/carcinogenic as well. Their ubiquitous and abundant occurrences in the Chinese atmosphere may have a significant adverse impact on the local human health.

Levoglucosan (dehydrated sugar) is a major burning product of cellulose, whereas dehydroabietic acid is produced by burning conifer resin. Concentrations of these biomass burning products in winter were found to be several times greater than those in summer (see Figure 1c, only for levoglucosan). In mid-west cities (Chongqing and Xi'an), their wintertime concentrations are much higher than those reported in USA, Belgium and Amazonia [*Simoneit et al.*, 2004a]. This study clearly shows that biofuel combustion is another important source for organic aerosols in China.

Homologous dicarboxlylic acids (C_2-C_{11}) were detected in the aerosol, dominated with oxalic acid followed by malonic and succinic acids. Their concentrations (200–2150 ng m^{-3}, average 840 ng m^{-3}) are lower than those from Los Angeles in 1984 [*Kawamura and Kaplan*, 1987], but are similar to those from Amazonia in 1999 [*Graham et al.*, 2002] and Tokyo in 1989 [*Kawamura and Yasui*, 2005] (Table 1 and Figure 1d). Diacids are more abundant in summer than in winter in most north cities and vice versa in most south cities. Diacids can be produced primarily from vehicular exhaust, but the major portion is secondary oxidation products of the organic precursors [*Kawamura and Kaplan*, 1987; *Kawamura and Yasui*, 2005]. Ratios of total diacids on a carbon basis to organic carbon in the 15 cities were all higher in summer (6.8 ± 2.5%) and lower in winter (4.0 ± 2.0%), indicating the enhanced photochemical oxidation in summer. The more abundant wintertime diacids in the south cities were probably caused by the accumulation within the inversion layers that are frequently developed in winter. Diacids and sugars are water-soluble, and thus have been recognized as active cloud condensation and ice formation nuclei [*Sun and Ariya*, 2006].

Based on the organic tracers mentioned above and the classification by Simoneit et al [*Simoneit et al.*, 2004b], averaged source strengths of organic matter in aerosols from the 15 cities are evaluated as follows. Firstly, contribution of fossil fuel usage (coal and petroleum) was defined as the sum of coal and petroleum derived *n*-alkanes, UCM, PAHs and hopanes. Polyacids and dicarboxylic acids were classified as secondary oxidation. Terrestrial natural background was defined as the sum of plant wax alkanes and higher molecular weight (HMW) fatty acids ($C \geq 15$) and alcohols ($C \geq 22$). The biomass burning contribution was calculated as the sum of levoglucosan, lignin and resin products, and sterols (e.g., β-sitosterols and ergosterol). Phthalates were categorized as plastics, while primary saccharides and reduced sugars were classified into the soil category. Finally, contribution of marine natural background was defined as the sum of lower molecular weight (LMW) fatty acids and alcohols, since the LMW fatty acids and alcohols were undetectable in most cases for the inland samples.

We found that fossil fuel usage is the dominant source in winter (Figure 2), contributing to nearly 50 % of total identified compound mass (TCM), followed by secondary oxidation products, terrestrial plant emissions, and biomass burning (Figure 2). As discussed above, coal burning is the overwhelming source of organic aerosols in winter, although numbers of automobiles have rapidly increased these days. In contrast, secondary oxidation (i.e., diacids) were found as the most important source of summer organic aerosols, contributing one third of TCM, followed by fossil fuel combustion, plastic evaporation, and terrestrial plant emissions. The important contributions of photochemical oxidation of organic precursors have been reported on urban aerosols from Tokyo and Los Angels [*Kawamura and Yasui*, 2005; *Schauer et al.*, 1996]. Large contribution of plastic materials to summer organic aerosols may be characteristic to Chinese aerosols.

4. Conclusions

A heavy loading of organic pollutants has been confirmed as a common phenomenon in many regions of China, not only in the economically developed areas near the coast but also in the mid and western regions. However, it was found to be different from the satellite observation of tropospheric nitrogen dioxide over China [*Richter et al.*, 2005], whose column concentrations maximized in the economically developed eastern part mainly due to the intensified emissions of vehicular exhaust. The ground surface observations demonstrated that the Chinese organic aerosols are characterized by fossil fuel and biofuel burning in winter and secondary oxidation products in summer. The high loadings of Chinese organic aerosols probably influence the local human health and regional/global climate in a significant manner.

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Figure Captions

Figure 1. Seasonal and spatial distributions of organic compounds in the aerosols from 15 Chinese cities (ng m^{-3}).

Figure 2. Source strengths of organic matter in aerosols from 15 Chinese cities.

Table 1. Concentrations of organic compounds in aerosols ($PM_{2.5}$) from 15 Chinese cities, and comparison with other cities and regions in the world (ng m^{-3})

Compound	winter		summer		Comparison with other cities and regions
	range	mean	range	mean	
n-Alkanes(C_{16}-C_{31})	195-1430	516	10-328	138	69, Los Angeles [*Rogge et al.*, 1993a]
UCM[a]	784-6050	2200	37-1520	586	880, Tokyo [*Kawamura et al.*, 1995]
PAHs	14-701	198	2-168	29	12, Los Angeles [*Rogge et al.*, 1993a] 17, London [*Baek et al.*, 1992] 20, Tokyo [*Kawamura*, 1989]
Hopanes(C_{27}-C_{32})	3-60	18	0-15	3.1	2.6, Miami, Florida [*Lang et al.*, 2002]
Phthalates	62-445	196	168-2200	551	8.2, Paris [*Teil et al.*, 2006]
Fatty acids (C_{10}-C_{34})	318-3240	1020	155-876	457	317, Los Angeles [*Rogge et al.*, 1993a] 330, Tokyo [*Kawamura et al.*, 2003]
Fatty alcohols (C_{12}-C_{32}) [b]	6-527	91	3-42	21	
Sterols	11-1450	297	0-81	19	
Lignin & resin products	5-333	63	1-53	9	
Sugars	64-3240	675	9-735	130	1920, Amazonia [*Graham et al.*, 2002]
Polyols & polyacids	33-439	120	41-195	110	
Diacids (C_2-C_{11})	315-1920	867	198-2150	796	1870, Los Angeles [*Kawamura and Kaplan*, 1987] 678, Amazonia [*Graham et al.*, 2002] 636, Tokyo [*Kawamura and Yasui*, 2005]

[a]UCM: unresolved complex mixture of hydrocarbons; [b]fatty alcohols with even carbon number.

Figure 1. (Wang et al.)

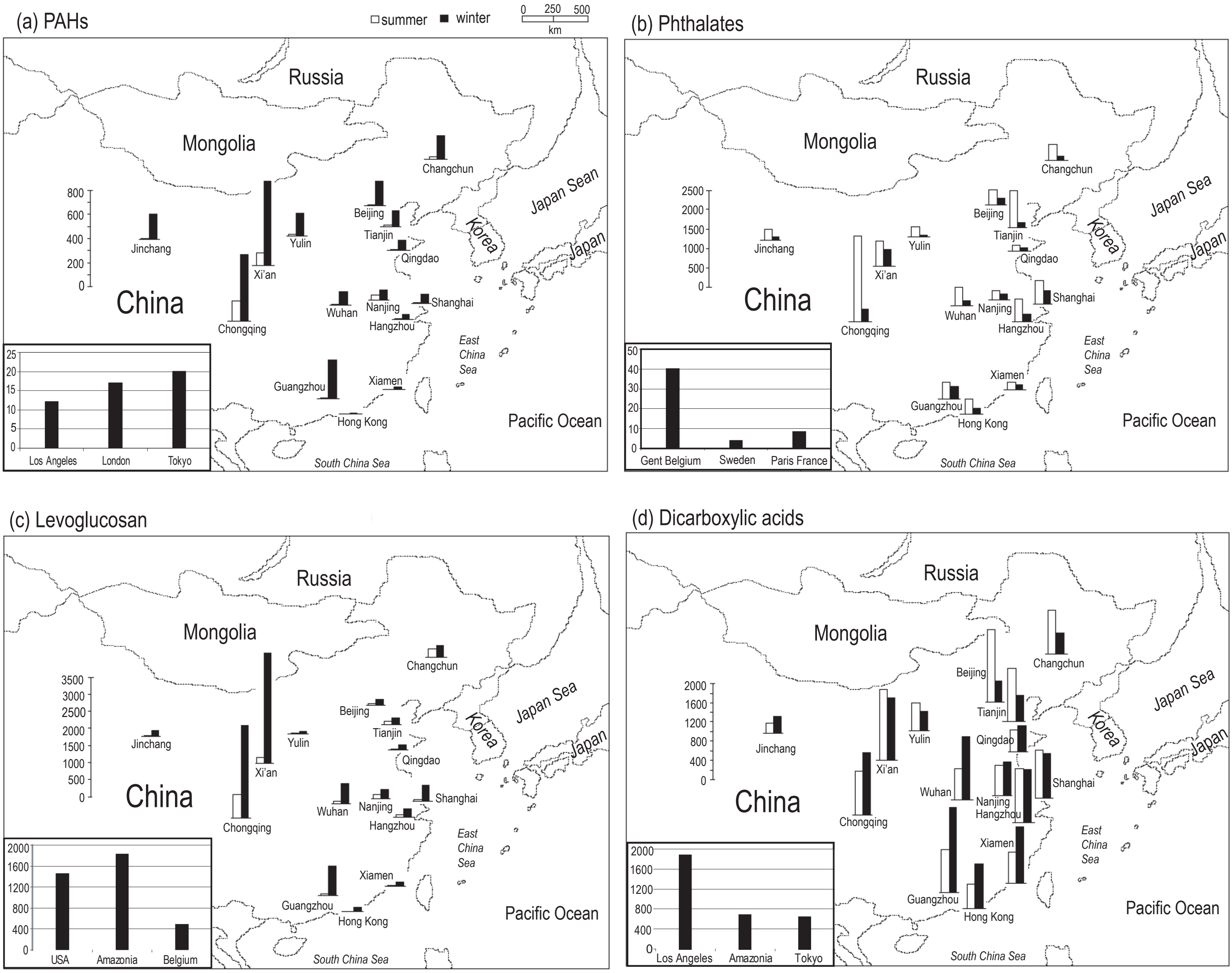

Figure 2 (Wang et al.)