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Dicarboxylic acids, ketocarboxylic acids, α -dicarbonyls, fatty acids, and benzoic acid in urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006)

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[1] Ground-based studies of PM_{2.5} were conducted for determination of 30 water-soluble organic species, including dicarboxylic acids, ketocarboxylic acids and dicarbonyls, nine fatty acids, and benzoic acid, during the Campaign of Air Quality Research in Beijing 2006 (CAREBeijing-2006; 21 August to 4 September 2006) at urban (Peking University, PKU) and suburban (Yufa) sites of Beijing. Molecular distributions of dicarboxylic acids demonstrated that oxalic acid (C₂) was the most abundant species, followed by phthalic acid (Ph) and succinic acid (C₄) at both sites. The sum of three dicarboxylic acids accounted for 71% and 74% of total quantified water-soluble organics (327–1552 and 329–1124 ng m⁻³) in PKU and Yufa, respectively. Positive correlation was found between total quantified water-soluble species and water-soluble organic compounds (WSOC). On a carbon basis, total quantified dicarboxylic acids and ketocarboxylic acids and dicarbonyls account for up to 14.2% and 30.4% of the WSOC in PKU and Yufa, respectively, suggesting that they are the major WSOC fractions in Beijing. The distributions of fatty acids are characterized by a strong even carbon number predominance with maximum at hexadecanoic acid (C_{16:0}). The ratio of octadecanoic acid (C_{18:0}) to hexadecanoic acid (C_{16:0}) (0.39–0.85, with an average of 0.36) suggests that in addition to vehicular emissions, an input from cooking emissions is important, as is biogenic emission. Benzoic acid that has been proposed as a primary pollutant from vehicular exhaust and a secondary product from photochemical reactions was found to be abundant: 72.2 ± 58.1 ng m⁻³ in PKU and 78.0 ± 47.3 ng m⁻³ in Yufa. According to the 72 hour back trajectory analysis, when the air mass passed over the southern or southeastern part of Beijing (24–25 August and 1–2 September), the highest concentrations of organic compounds were observed. On the contrary, when the clean air masses came straight from the north during 3–4 September, the lowest levels of organic compounds were recorded. This study demonstrates that pollution episodes in Beijing were strongly controlled by wind direction; that is, air quality in Beijing is good when air masses originate from the north and northwest, whereas it deteriorates when the air mass originates from the south and southeast.

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1. Introduction

[2] Organic compounds comprise an important fraction of atmospheric aerosols. They have strong impacts to radiative

forcing of climate, human health effects, pollution transport, and visibility degradation [Penner and Novakov, 1996; Menon et al., 2002; Wilkening et al., 2000; Nel, 2005]. All

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these features are influenced by the aerosol concentrations and its chemical compositions. Organic compounds can be either directly emitted from sources, or formed in the atmosphere through photochemical reactions.

[3] Water-soluble organic compounds including dicarboxylic acids, ketocarboxylic acids, dicarbonyls are important components of atmospheric aerosols [Rogge *et al.*, 1993a; Jacobson *et al.*, 2000; Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005]. Owing to their hygroscopic property, they play a role in the global radiative balance [Saxena *et al.*, 1995; Facchini *et al.*, 1999; Kerminen, 2001]. Dicarboxylic acids are widely present in the urban, rural and marine atmospheres [Kawamura and Kaplan, 1987; Kawamura *et al.*, 1996a; Kawamura and Sakaguchi, 1999; Kerminen *et al.*, 2000]. Total dicarboxylic acids account for ~1%–3% of the total particulate carbon in urban areas and >10% in remote marine environments [Kawamura and Ikushima, 1993; Kawamura *et al.*, 1996b, 1996c; Kawamura and Sakaguchi, 1999; Kerminen *et al.*, 2000]. Oxalic acid (C_2), generally the most abundant dicarboxylic acid in the atmosphere [Kawamura and Sakaguchi, 1999], is formed from oxidation of volatile organic compounds (VOCs) and aqueous phase chemistry in aerosol/cloud/fog droplets, as well as from primary emissions from fossil fuel combustion and biomass burning [Kawamura and Kaplan, 1987; Narukawa *et al.*, 1999; Warneck, 2003].

[4] Oxidation of unsaturated fatty acid such as oleic acid ($C_{18:1}$) is one of the major sources of azelaic acid (C_9 dicarboxylic acid) and other shorter carbon chain dicarboxylic acids [Kawamura and Gagosian, 1987; Legrand *et al.*, 2007]. The unsaturated fatty acids are rich in marine phytoplankton and terrestrial higher plant leaves, and are emitted into atmosphere from anthropogenic sources such as meat cooking [Rogge *et al.*, 1991] and wood burning [Rogge *et al.*, 1998]. Phthalic acid (Ph) which can be derived from the oxidation of naphthalene or other polycyclic aromatic hydrocarbons (PAHs) [Fine *et al.*, 2004], is used as a surrogate for the contribution of secondary organic aerosol (SOA) to an ambient sample [Oliveira *et al.*, 2007]. It is not emitted from primary sources in significant quantities, but has been shown to roughly correlate with the unidentified organic mass in chemical mass balance model results that is often assumed to be secondary.

[5] Solvent extractable fatty acids were reported as the most abundant polar organic fraction of aerosols [Oliveira *et al.*, 2007]. They contribute 6%–53% of identified organic compounds from emission sources such as biomass burning [Rogge *et al.*, 1998; Fine *et al.*, 2002; Schauer *et al.*, 2001; Nolte *et al.*, 2001], cooking [Schauer *et al.*, 1999, 2002; Rogge *et al.*, 1991; He *et al.*, 2004], paved road dust [Nolte *et al.*, 2002], and automobiles [Rogge *et al.*, 1993a; He *et al.*, 2006]. The $<C_{20}$ homologues of fatty acids are ubiquitous. The dominant fatty acids in cooking emission are hexadecanoic acid ($C_{16:0}$) and octadecanoic acid ($C_{18:0}$) [He *et al.*, 2004; Zhao *et al.*, 2007a, 2007b]. However, knowledge of their composition and formation pathways is very limited. Fatty acids comprise 46%–80% of the solvent extractable organic compounds in particulate matter less than $2.5 \mu\text{m}$ in diameter ($PM_{2.5}$) at urban sites in China [Zheng *et al.*, 2000]. Benzoic acid is a secondary product from photochemical degradation of aromatic hydrocarbons (e.g., toluene) emitted

by automobiles [Suh *et al.*, 2003] that have also been measured as primary pollutant in the exhaust of motor vehicles [Kawamura and Kaplan, 1987; Rogge *et al.*, 1993b]. A significant increase of benzoic acid was observed in daytime in Beijing, possibly with relevance to stronger photochemical reaction [Li *et al.*, 2009].

[6] China has been facing serious air pollution problems due to huge usage of fossil fuels. One fourth of global primary anthropogenic organic aerosols is generated in China, approximately 70% of which origins from coal burning [Streets *et al.*, 2004]. Organic compositions are being received more attentions due to her rapid industrialization and urbanization. Beijing, the capital of China, locates on the northwest border of the North China Plain, with a total area of $16,807.8 \text{ km}^2$. It is surrounded by the Yanshan Mountains from the west to the northeast and has heavily industrialized areas from the southwest to the east [Chen *et al.*, 2007; Streets *et al.*, 2007]. Emissions from nearby sources possibly undergo chemical reactions during transport on the prevailing winds and affect the local air quality in Beijing [Han *et al.*, 2005; Hatakeyama *et al.*, 2005; Luo *et al.*, 2000; Mauzerall *et al.*, 2000]. In 2004, Beijing had a population of 15.4 million [Beijing Municipal Bureau of Statistics, 2006]. Owing to rapid increases of vehicle number and energy consumption, the air pollution problem has become severe. However, studies of organic aerosols are only limited on reporting their molecular levels [Zheng *et al.*, 2005; Feng *et al.*, 2006; Huang *et al.*, 2006; He *et al.*, 2006; Ho *et al.*, 2007]. Lack of further characterization works have been done.

[7] To better understand the distributions of organic compounds in Beijing, $PM_{2.5}$ samples were collected at an urban and rural site in the Beijing region in August–September 2006. Molecular compositions of low molecular weight (MW) dicarboxylic acids (C_2 – C_{12}), ketocarboxylic acids (ωC_2 – ωC_9 , pyruvic acid), α -dicarbonyls (C_2 – C_3), benzoic acid and fatty acids (C_{12} – C_{25}) were determined with gas chromatography (GC)/flame ionization detector (FID) and GC/mass spectrometry (MS). Samples were also analyzed for organic carbon (OC), elemental carbon (EC), and water-soluble organic carbon (WSOC) fractions. On the basis of extensive field measurements, the relative roles of primary emissions, long-range transport, and secondary formations in the atmosphere of Beijing were interpreted. Factors that control the molecular distributions of these organic species in the Beijing urban atmosphere were discussed. The temporal variability of the organic concentrations and the mass fractions in WSOC were presented.

2. Experiment

2.1. Sample Collection

[8] The annual emission rates of anthropogenic OC and black carbon (BC) over North China Plain estimated for the year 2006 were shown in Figure 1. They include emissions from power plants, industry, residential biofuel/fossil fuel combustion, and transportation. As Hebei Province and Tianjin Municipality are highly industrialized areas, anthropogenic OC and BC are strongly emitted from the south of Beijing area. When the winds come from these regions, the air quality in Beijing is greatly impacted [Xia *et al.*, 2007]. In order to evaluate the contribution from local

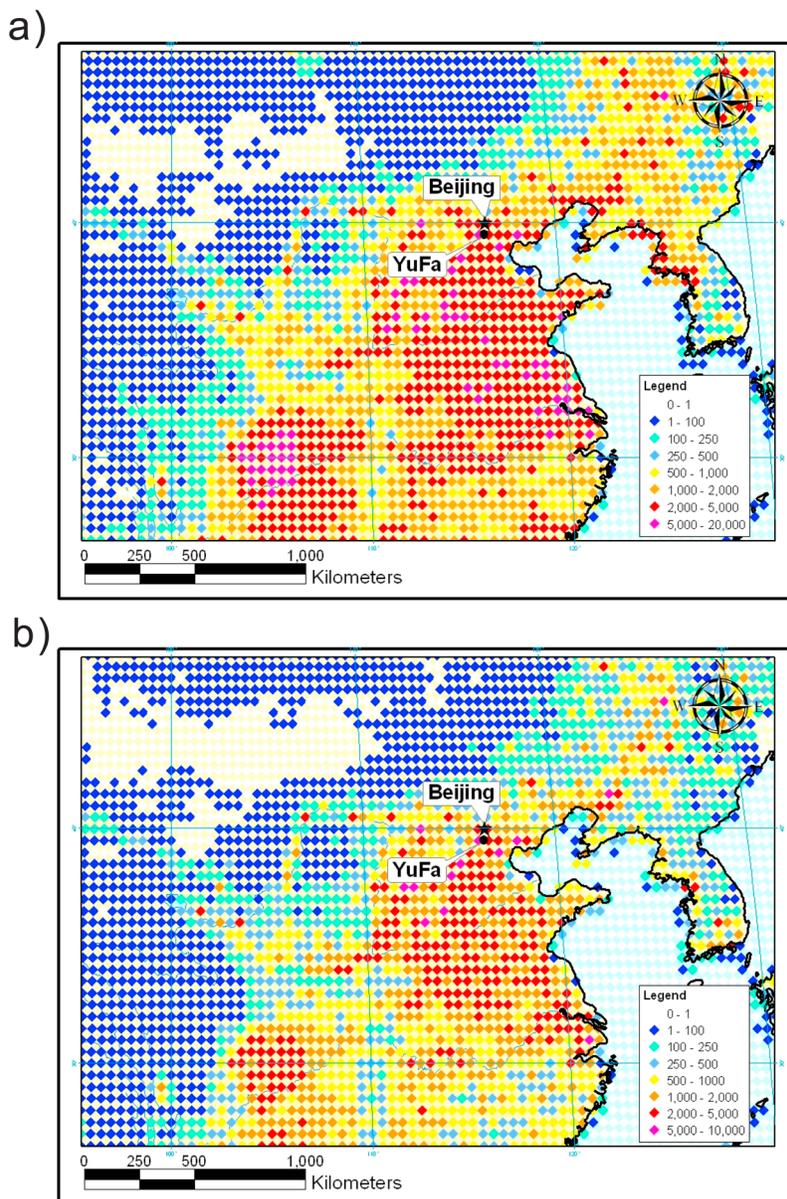


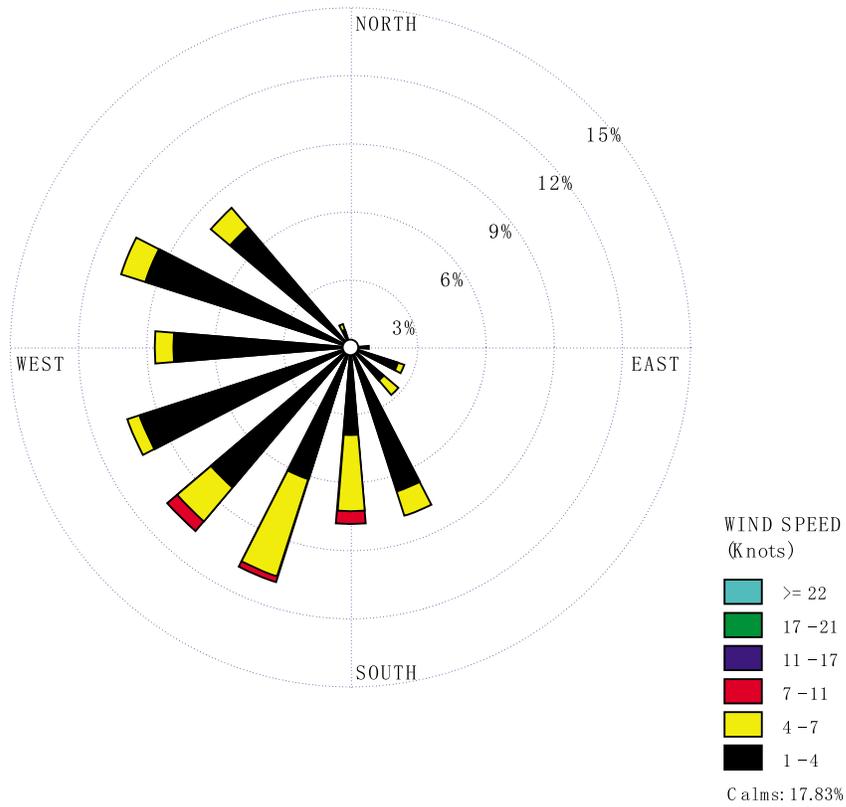
Figure 1. The annual emission rates of anthropogenic (a) organic carbon (OC) and (b) black carbon (BC) over the North China Plain estimated for the year 2006. Location of Beijing is shown as an asterisk (data available online at http://www.cgrer.uiowa.edu/EMISSION_DATA_new/data/intex-b_emissions).

emission and regional transportation, two sampling locations, including Huang Pu Military College in Yufa (Yufa) (39.51°N, 116.31°E) and Peking University in Beijing city (PKU) (39.98°N, 116.35°E), were selected to represent urban and suburban sites during CAREBeijing campaign, respectively. PKU is located in the northwest urban area of Beijing as shown in Figure 1. The observation site is about 600 m north of the fourth ring main road and ~220 m away from an eastern main road. Yufa is located at ~30 km south of Beijing. Yufa has population of 47,000, and there is a state highway at 1.5 km east of the site, and the vehicular emissions there may sometimes influence the site [Yuan *et al.*, 2009]. The samplers were located on the top floor of the buildings (at PKU, a six story building; at Yufa, a four story building). Simultaneously, meteorological parameters

including temperature, relative humidity, wind speed, and direction were continuously measured at the ground level of the measurement site. The average temperature and relative humidity in PKU and Yufa were 26°C, 64% and 24°C, 71%, respectively. Figure 2 presents the wind rose diagrams measured at PKU and Yufa. The wind from the south or southwest sector dominated during the sampling period. North and northwest part of Beijing is mainly surrounded by the mountains while south and southeast of Beijing are heavily populated, urbanized, and industrialized areas such as Tianjin and Hebei province.

[9] PM_{2.5} samples were collected on preheated (800°C, 3 hours) quartz-fiber filters (47 mm Whatman quartz microfibre filters) by minivolume air samplers (Airmetrics, Eugene, Oregon) at a flow rate of 5 L min⁻¹ for 24 hours. Sampling

a)



b)

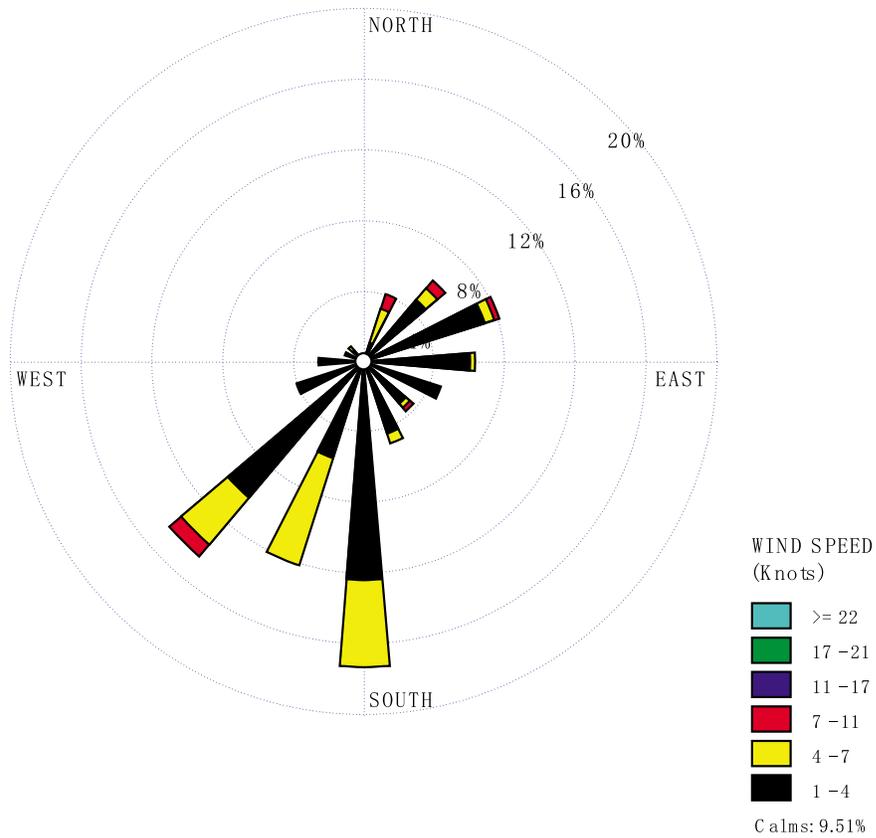


Figure 2. Wind rose diagrams during the sampling period at (a) Peking University (PKU) and (b) Yufa (21 August to 4 September 2006).

flows were checked before and after sampling with a DryCal DCLite flowmeter (BIOS International, Butler, New Jersey). Sampling was simultaneously conducted from 0900 to 0900 LT of the next day at the two sampling locations from 21 August to 4 September 2006. Sample-collected filters were properly stored at -20°C to avoid microbial degradation of organics and evaporation of semi-volatile components. One field blank filter was collected at each site to subtract the artifacts due to adsorption of gas-phase organic components onto the quartz-fiber filters during and/or after sampling. Totally 23 valid samples were collected in this study.

2.2. OC, EC, and WSOC Analysis

[10] OC and EC were measured on a 0.526 cm^2 punch from each filter by thermal optical reflectance (TOR) following the IMPROVE protocol on a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic, Calabasas, California) [Chow *et al.*, 2004, 2005; Cao *et al.*, 2003]. The minimum detection limit (MDL) for the carbon analysis is 0.8 and $0.4\ \mu\text{gC cm}^{-2}$ for OC and EC, respectively, with a precision better than 10% for total carbon (TC). For WSOC, five punches (total area of 2.63 cm^2) were taken from each filter and placed into a 15 mL screw-capped vial to which 5 mL of distilled deionized water (DDW) was added. Samples were extracted in a sonication bath for 1 hour. Filter debris and suspending insoluble particles were removed from the water extracts using a syringe filter (0.2 mm polytetrafluoroethylene (PTFE) membrane). Each filtered extract was then transferred into a clean autosampler fitted vial. One microliter of the extract was automatically injected into a high-sensitivity Shimadzu TOC-V CPH Total Carbon Analyzer (Columbia, Maryland) for determination of total organic carbon (TOC) content. Each extract was analyzed three times to take the mean TOC value. The MDL for the method is $15\ \mu\text{g L}^{-1}$, with a precision of $\pm 5\%$. Insufficient amount of OC, EC, and WSOC were determined in the field blanks.

2.3. Organic Acid Analysis

[11] The details of sample extraction, derivatization, and analytical procedures were documented elsewhere [Kawamura and Ikushima, 1993; Kawamura, 1993; Kawamura and Yasui, 2005]. For the determination of water-soluble organic compounds, briefly, aliquot of the filter sample was extracted with organic-free pure water ($10\text{ mL} \times 3$) to isolate low MW dicarboxylic acids, keto-carboxylic acids and α -dicarbonyls. After concentration, the extracts were reacted with 14% BF_3/n -butanol at 100°C to convert the carboxyl groups to butyl esters and the aldehyde groups to dibutoxy acetals. Field blank filters were also handled by the procedure described above. The results showed no sufficient contamination ($<5\%$ of real samples). The data reported here are all corrected for the blanks. The derivatized extracts were analyzed using a split/splitless Hewlett Packard 6890GC/FID (Palo Alto, California) with a HP-5 fused silica capillary column ($25\text{ m} \times 0.2\text{ mm i.d.} \times 0.5\ \mu\text{m}$ film thickness) column. Authentic standards were used for the peak identification based on GC retention times. Homologous series of fatty acids were determined as butyl esters [Mochida *et al.*, 2007]. Mass spectral confirmation of the compounds was achieved using ThermoQuest Trace MS (Austin, Texas) using a similar

GC conditions. Recoveries of the dicarboxylic acids, keto-carboxylic acids, α -dicarbonyls, and fatty acids were $>70\%$. The reproducibility of the methods for the determination of organic species was $<\pm 15\%$ [Kawamura and Yasui, 2005; Mochida *et al.*, 2007]. Levels of field blanks were below 15% of actual samples, except for phthalic acid (up to 30%). The data reported here were all corrected against the blanks.

3. Results and Discussion

3.1. Molecular Compositions of Dicarboxylic Acids, Ketocarboxylic Acids, and α -Dicarbonyls in $\text{PM}_{2.5}$

[12] Temporal variations of the mass concentrations of OC, EC and WSOC, total quantified water-soluble species in PKU and Yufa from 21 August to 4 September 2006 were shown in Figures 3a and 3b. Average concentrations of OC, EC, and WSOC were 10.9 ± 4.49 , 7.30 ± 3.35 , and $4.87 \pm 2.58\ \mu\text{gC m}^{-3}$ in PKU, and 8.66 ± 2.94 , 6.49 ± 3.19 , and $2.05 \pm 0.90\ \mu\text{gC m}^{-3}$ in Yufa, respectively (Table 1). The EC concentration at suburban site of Yufa (average $6.94\ \mu\text{g m}^{-3}$) is close to that at urban site of PKU (average $7.30\ \mu\text{g m}^{-3}$). It is well known that Yufa is located at south part of Beijing and near the border of Beijing Municipality and Hebei Province. Even though there is low local anthropogenic source, the regional pollution sources, mainly diesel engine emission, from nearby heavy urbanized and industrialized Tianjin city and Hebei province greatly influence the Yufa area. Yuan *et al.* [2009] have done a source analysis study with positive matrix factorization source apportionment model at PKU and Yufa in Beijing. They had similar observation and reported that the VOC concentrations contributed by diesel exhaust are higher at Yufa than that at PKU. This proves that the regional diesel engine emission has stronger impact than that from local Beijing center (PKU).

[13] The average WSOC concentration at PKU ($4.87\ \mu\text{g m}^{-3}$) is more than twice as that at Yufa ($2.05\ \mu\text{g m}^{-3}$). The WSOC accounted for $44\% \pm 12\%$ of OC in PKU and $24\% \pm 12\%$ of OC in Yufa. Our results are consistent to the WSOC/OC ratios, in a range of 20%–40%, in other urban sites in China [Yang *et al.*, 2005; Ho *et al.*, 2007]. As secondary organic aerosols (SOA) (e.g., Humic-like substances (HULIS)) are expected to be the major fraction of WSOC, our finding is thus opposite to the usual observation which lower WSOC/OC ratio would be determined in urban sites. However, according to the meteorological data, the air mass flow mainly came from south which brought primary industrialized and urbanized emission sources to Yufa during the sampling period. Along the long-distance transport of pollutants from southern areas, the formations of SOA became more dominant at PKU, where is at a downwind location. The local primary emission impact is less sufficient.

[14] Table 1 shows concentrations of dicarboxylic acids, ketocarboxylic acids, and α -dicarbonyls determined in PKU and Yufa. The concentrations of total dicarboxylic acids ranged from 294 to 1440 ng m^{-3} , with an average of $760 \pm 369\text{ ng m}^{-3}$ in PKU, and from 308 to 1064 ng m^{-3} , with an average of $725 \pm 282\text{ ng m}^{-3}$ in Yufa. These values are higher than those reported (90 – 1370 ng m^{-3} , average 480 ng m^{-3}) in urban Tokyo, Japan [Kawamura and Ikushima, 1993], but are close to those reported in Chinese cities [Ho *et al.*, 2007].

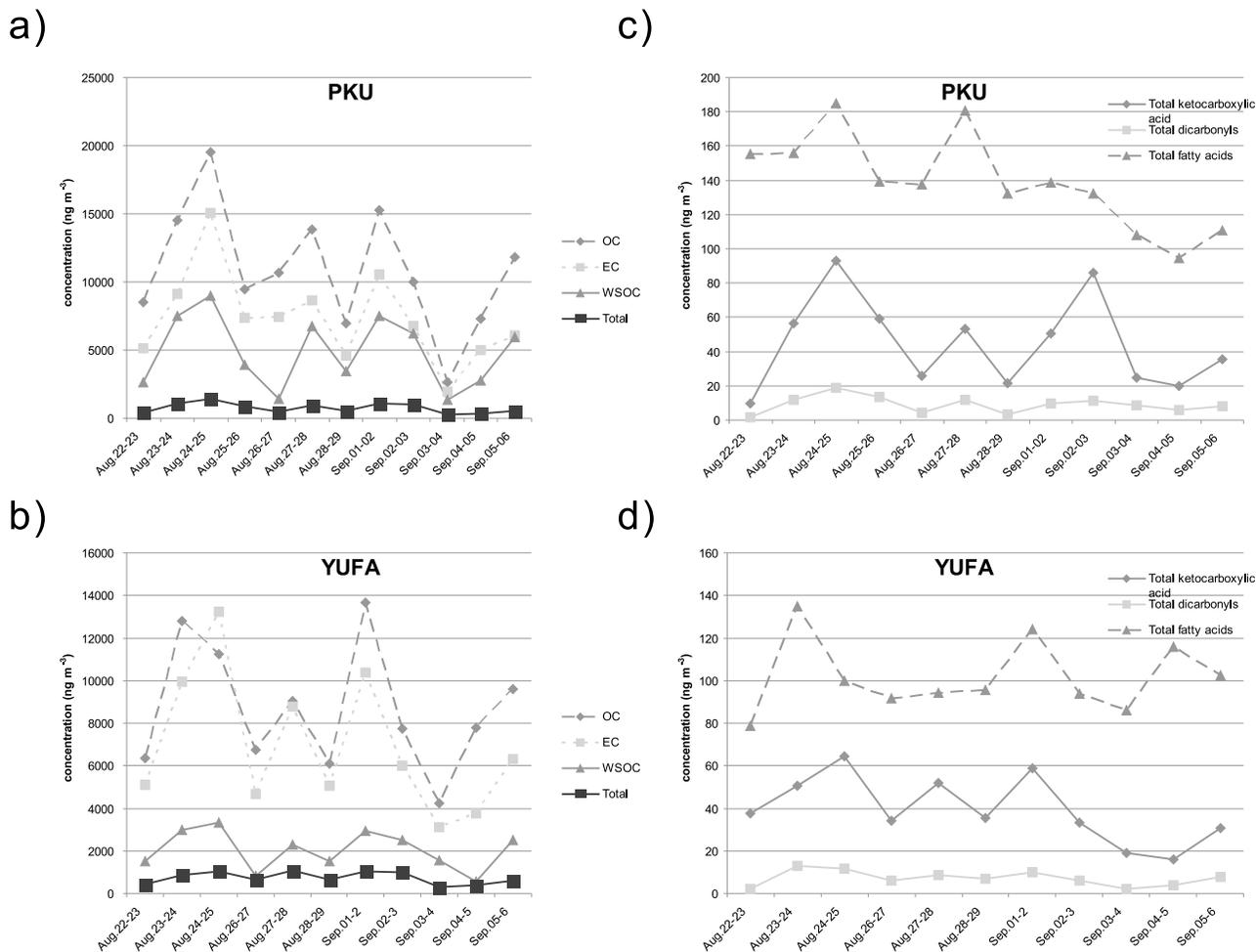


Figure 3. Temporal variations of OC, elemental carbon (EC), water-soluble organic carbon (WSOC), and various organic compound classes over PKU and Yufa during CAREBeijing-2006.

[15] Oxalic acid (C_2) was the most abundant dicarboxylic acid ($449 \pm 274 \text{ ng m}^{-3}$ and $455 \pm 219 \text{ ng m}^{-3}$), followed by phthalic acid (Ph) ($77.5 \pm 17.6 \text{ ng m}^{-3}$ and $68.3 \pm 14.7 \text{ ng m}^{-3}$), and succinic acid (C_4) ($49.9 \pm 19.5 \text{ ng m}^{-3}$ and $48.6 \pm 17.6 \text{ ng m}^{-3}$) at PKU and Yufa, respectively. On average, concentrations of these three species accounted for 71% and 74% of total quantified water-soluble species in PKU and Yufa, respectively. The average concentrations of phthalic acid (Ph) are substantially higher than those reported from urban Tokyo in summer (July, average 29 ng m^{-3}) [Kawamura and Yasui, 2005], but are close to those reported in Chinese cities [Ho et al., 2007].

[16] Ph can be derived from incomplete combustion of aromatic hydrocarbons (e.g., naphthalenes) in vehicular exhaust [Kawamura and Kaplan, 1987] or produced by atmospheric oxidation of aromatic hydrocarbons [Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005]. Abundant naphthalene (2000 ng m^{-3}) observed in urban area of Beijing [Liu et al., 2007] is a potential precursor to the large formation of Ph. Thus, the high concentration of Ph can prove that vehicle emission is one of the major sources resulting of poor air quality in Beijing. Three phthalic acids (Ph) (including *iso* and *tere* isomers) were detected in the aerosol samples. The isomer distribution was characterized by a

predominance of phthalic acid (Ph) followed by terephthalic acid, being consistent with those reported in the aerosols in Mt. Tai, China [Fu et al., 2008], and East China Sea [Simoneit et al., 2004]. In this study, phthalic acid (Ph) and isophthalic acid showed a strong correlation ($r^2 = 0.85$), but terephthalic acid did not correlate with the other two, indicating its different origin and/or different atmospheric lifetime.

[17] Azelaic acid (C_9) is generally more abundant than other higher MW homologues such as C_8 and C_{10} dicarboxylic acids. Since it is known as an oxidation product of unsaturated fatty acids [Kawamura and Gagosian, 1987], high abundance of azelaic acid (C_9) can indicate that urban aerosols have been subjected to significant atmospheric processing.

[18] Concentrations of total ketocarboxylic acids ranged from 9.54 to 93.3 ng m^{-3} , with an average of $44.7 \pm 26.6 \text{ ng m}^{-3}$ in PKU, and from 16.0 to 64.3 ng m^{-3} , with an average of $39.3 \pm 15.5 \text{ ng m}^{-3}$ in Yufa (Table 1). The concentration is similar to those reported at the Gosan site on Jeju Island, South Korea (53 ng m^{-3}) [Kawamura et al., 2004] and urban cities in China in summer (37 ng m^{-3}) [Ho et al., 2007]. Glyoxylic acid (ωC_2) is the dominant ketocarboxylic acids, followed by pyruvic acid (Pyr) and

Table 1. Concentrations of Dicarboxylic Acids, Benzoic Acid, and Fatty Acids in PM_{2.5} Samples During CAREBeijing-2006^a

Compounds (ng m ⁻³)	PKU (<i>n</i> = 12)			Yufa (<i>n</i> = 11)		
	Range	Average	SD	Range	Average	SD
<i>Dicarboxylic Acids</i>						
Oxalic, C2	115–954	449	274	153–703	455	219
Malonic, C3	17.6–39.8	28.1	7.99	13.2–27.0	20.8	4.46
Succinic, C4	31.1–89.0	49.9	19.5	27.1–75.4	48.6	17.6
Glutaric, C5	11.7–28.3	19.2	5.85	9.60–21.3	16.2	4.34
Adipic, C6	10.0–27.5	17.4	6.02	8.96–21.1	14.7	3.45
Pimelic, C7	1.06–9.86	5.05	3.15	1.00–5.49	3.10	1.47
Suberic, C8	0.46–1.43	0.85	0.31	0.43–1.00	0.77	0.18
Azelaic, C9	13.8–66.0	34.8	15.7	13.0–34.8	19.7	6.98
Sebacic, C10	0.70–7.49	3.45	2.14	0.72–4.35	2.07	1.31
Undecanedioic, C11	MDLs–5.05	1.43	1.90	MDLs–2.75	0.25	0.83
Dodecanedioic, C12	MDLs–1.83	0.77	0.59	0.10–1.06	0.48	0.33
Methylmalonic, iC4	MDLs–2.77	0.82	1.01	MDLs–1.55	0.91	0.62
Methylsuccinic, iC5	2.89–11.2	6.32	3.09	2.52–9.51	5.93	2.38
2-Methylglutaric, iC6	2.14–5.18	3.41	1.09	1.61–4.06	2.77	0.76
Maleic, M	4.05–7.39	5.55	1.00	4.16–9.40	6.21	1.69
Fumaric, F	0.69–10.5	2.43	2.61	0.96–3.12	1.78	0.68
Methylmaleic, mM	1.38–3.79	2.45	0.64	1.27–2.92	2.21	0.50
Phthalic, Ph	49.5–102	77.5	17.6	41.0–86.1	68.3	14.7
Isophthalic, iPh	2.44–8.97	5.11	1.99	2.11–6.99	4.08	1.58
Terephthalic, tPh	15.8–53.7	32.4	11.6	14.9–88.4	40.5	22.5
Malic, hC4	MDLs–2.29	0.72	0.73	MDLs–1.22	0.41	0.45
Ketomalonic, kC3	1.88–13.4	7.74	4.08	1.73–9.67	5.68	2.66
4-Ketopimelic, kC7	1.59–10.9	5.22	3.31	1.25–8.01	4.31	2.42
Total diacids	294–1440	760	369	308–1064	725	282
<i>Ketocarboxylic Acids</i>						
Pyruvic	MDLs–34.2	8.78	8.83	1.92–23.0	7.46	5.65
Glyoxylic, ωC2	7.01–55.2	25.1	13.9	7.68–38.0	20.6	9.75
3-Oxopropanoic, ωC3	0.36–1.56	1.08	0.43	0.35–1.40	0.87	0.35
4-Oxobutanoic, ωC4	1.79–11.7	5.61	3.22	1.79–11.9	4.89	3.10
9-Oxononoic, ωC9	MDLs–12.2	4.13	3.46	0.88–13.3	5.49	3.36
Total ketoacids	9.54–93.3	44.7	26.6	16.0–64.3	39.3	15.5
<i>α-Dicarbonyls</i>						
Glyoxal, Gly	1.07–11.3	4.66	2.87	1.11–6.05	3.31	1.50
Methylglyoxal, MeGly	MDLs–11.7	4.39	3.01	0.16–7.08	3.81	2.25
Total dicarbonyls	1.66–19.0	9.05	4.90	2.00–13.1	7.11	3.63
Sum of water-soluble species	327–1552	813	398	329–1124	771	298
<i>Fatty Acids</i>						
Tridecanoic acid, C _{13:0}	3.26–6.21	4.85	1.18	3.07–6.53	4.58	1.13
Tetradecanoic acid, C _{14:0}	13.9–33.2	25.4	6.49	14.1–32.2	19.8	5.12
Hexadecanoic acid, C _{16:0}	38.4–92.5	59.2	15.3	29.7–56.6	38.1	8.98
Heptadecanoic acid, C _{17:0}	1.24–16.7	3.29	4.35	0.81–1.59	1.08	0.22
Octadecanoic acid, C _{18:0}	23.8–43.7	32.3	6.47	18.6–31.3	24.4	3.79
Octadecenoic acid, C _{18:1}	2.25–9.93	6.84	2.06	4.43–6.67	5.75	0.71
Eicosanoic acid, C _{20:0}	1.05–5.72	2.78	1.45	1.35–5.87	3.48	1.50
Docosanoic acid, C _{22:0}	1.68–3.70	2.38	0.57	1.55–3.28	2.20	0.54
Tetracosanoic acid, C _{24:0}	1.71–3.20	2.24	0.45	1.57–2.64	2.10	0.37
Sum of fatty acids	94.7–185	139	27.3	78.5–135	102	16.8
Benzoic acid	11.1–212	72.2	58.1	21.3–163	78.0	47.3
PM _{2.5} (μg m ⁻³)	15.5–192	85.3	55.6	32.1–186	96.1	50.1
OC (μg m ⁻³)	2.61–19.5	10.9	4.49	4.23–13.6	8.66	2.94
EC (μg m ⁻³)	1.97–15.1	7.30	3.35	3.12–13.2	6.94	3.19
WSOC (μg m ⁻³)	1.37–9.00	4.87	2.58	0.57–3.32	2.05	0.90

^aAbbreviations are EC, elemental carbon; MDL, method detection limit; OC, organic carbon; PKU, Peking University; WSOC, water-soluble organic compounds.

4-oxobutanoic acid (ωC4). Their concentrations are similar to those reported in Tokyo, Japan [Kawamura and Yasui, 2005] and urban cities in China [Ho et al., 2007].

[19] Concentrations of α-dicarbonyls ranged from 1.66 to 19.0 ng m⁻³, with an average of 9.05 ± 4.90 ng m⁻³ in PKU, and from 2.00 to 13.1 ng m⁻³, with an average of 7.11 ± 3.63 ng m⁻³ in Yufa. The values are slightly higher than

those in urban Chinese sites in summer (average 5.2 ng m⁻³) [Ho et al., 2007]. Glyoxal and methylglyoxal are both gas-phase oxidation products of numerous VOCs such as benzene, toluene, xylene and alkenes [Volkamer et al., 2001]. They have been demonstrated to be precursors to the formation of SOA via heterogeneous processes [Kroll et al., 2005; Liggió et al., 2005]. For instance, photo-oxidation

Table 2. Comparison of Dicarboxylic Acid Concentrations in Fine Particles From Different Cities^a

Site/Type	Season	Size	Method	Oxalic Acid	Malonic Acid	Succinic Acid	Phthalic Acid
Shanghai, China/urban ^b	1 year average	PM _{2.5}	IC	500	40/100	200	
Beijing, China/urban ^b	1 year average	PM _{2.5}	IC	300	100	30/20	
Beijing, China/urban ^c	Summer and winter	PM _{2.5}	CE	218	39	39	
Beijing, China/urban ^d	1 year average	PM _{2.5}	IC	353			
Nanjing, China/urban ^e	Winter	PM _{2.5}	GC-MS	880	114	146	
	Spring	PM _{2.5}	GC-MS	440	63	80	
Nanjing, China/urban ^f	Summer, daytime	PM _{2.5}	GC-FID			55	39
	Summer, nighttime	PM _{2.5}	GC-FID			51	19
	Winter, daytime	PM _{2.5}	GC-FID			38	32
	Winter, nighttime	PM _{2.5}	GC-FID			55	20
Hong Kong/urban ^g	Summer	PM _{2.5}	IC	90	13	7	
	Winter	PM _{2.5}	IC	350	20	50	
Hok Tsui, Hong Kong/remote ^g	Summer	PM _{2.5}	IC	40	ND	ND	
	Winter	PM _{2.5}	IC	370	20	60	
14 cities in China/urban ^h	Winter, 14 cities	PM _{2.5}	GC-MS/FID	558	41	80	78
	Summer, 14 cities	PM _{2.5}	GC-MS/FID	519	55	71	102
Southern Taiwan/suburban ⁱ	Fall, normal	PM _{2.5}	IC	460	65	77	
	Fall, episode	PM _{2.5}	IC	795	51	61	
K-puszta/Hungary/forest ^j	Summer	PM _{2.5}	IC	264	29	21	
Aveiro/Portugal/coast ^j	Summer	PM _{2.5}	IC	290	28	17	
Azores/Portugal/coast ^j	Summer	PM _{2.5}	IC	75	7.9	2.3	
Sonnblick/Austria/mountain ^j	Summer	PM _{2.5}	IC	76	24	20	
Houston, Texas/urban ^k	Summer	PM _{2.5}	GC-MS	16	13	16	
Helsinki, Finland/suburban ^l	Spring	PM ₁	IC		6.7	6.0	
This study/PKU	Summer	PM _{2.5}	GC-FID	449	28	50	78
This study/Yufa	Summer	PM _{2.5}	GC-FID	455	21	49	68

^aAcid concentrations are in ng m⁻³. Abbreviations are CE, capillary electrophoresis; GC-FID, gas chromatography–flame ionization detector; IC, ion chromatography; ND, not detected; PKU, Peking University.

^bYao *et al.* [2002].

^cHuang *et al.* [2005].

^dWang *et al.* [2007].

^eWang *et al.* [2002].

^fWang and Kawamura [2005].

^gYao *et al.* [2004].

^hHo *et al.* [2007].

ⁱHsieh *et al.* [2008].

^jLegrand *et al.* [2007].

^kYue and Fraser [2004].

^lTimonen *et al.* [2008].

of glyoxal can lead the formation of oxalic acid (C₂). Glyoxal and methylglyoxal can also present in either gaseous or particulate phase subjected to atmospheric conditions. The average concentrations of glyoxal and methylglyoxal were 4.66 ± 2.87 and 4.39 ± 3.01 ng m⁻³ in PKU versus 3.31 ± 1.50 and 3.81 ± 2.25 ng m⁻³ in Yufa, respectively. The higher concentration of glyoxal and methylglyoxal may represent the greater potential of subsequent SOA formation processing in PKU.

[20] As shown in Table 1, total dicarboxylic acids, keto-carboxylic acids, and α -dicarbonyls concentrations were slightly higher in PKU than in Yufa. However, few individual compounds had very close abundances at the two sites. Concentrations of the most abundant dicarboxylic acids (C₂, C₃, C₄ and Ph) in PM_{2.5} are compared with those reported in different Asian, European and American cities (Table 2). Averagely, the concentrations of the dicarboxylic acids in this study are close to those previously reported in Beijing and also are comparable to other Chinese (e.g., Nanjing and Shanghai) and Asian locations (e.g., Hong Kong and Taiwan). However, their concentrations are up to 90 times higher than those reported in Austria, Finland and United States. The comparison can efficiently represent the air pollution problems in Beijing.

3.2. Molecular Distributions of Fatty Acids and Benzoic Acid in PM_{2.5}

[21] Figures 3c and 3d present the temporal variations of total fatty acids in PM_{2.5} collected in PKU and Yufa during summertime in 2006. A homologous series of straight chain fatty acids (C_{12:0}–C_{25:0}) and unsaturated oleic acid (C_{18:1}) were detected in the samples. Their distributions are characterized by a strong even carbon number predominance with maximum at hexadecanoic acid (C_{16:0}) (Table 1). Similar distribution patterns have been demonstrated in other urban and rural Chinese cities [Fu *et al.*, 2008; Hou *et al.*, 2006]. Concentrations of total fatty acids ranged from 94.7 to 185 ng m⁻³ (average 139 ng m⁻³) in PKU and 78.5–135 ng m⁻³ (average 102 ng m⁻³) in Yufa. Both biogenic and anthropogenic sources are the essential inputs of fatty acids into the atmosphere. Plant tissues and surface waxes consist of high fractions of fatty acids and can be thus emitted during biomass burning. Hexadecanoic acid (C_{16:0}), octadecanoic acid (C_{18:0}) and oleic acid (C_{18:1}) were the dominant compounds emitted from the meat cooking [Zhao *et al.*, 2007a, 2007b; Rogge *et al.*, 1991; Schauer *et al.*, 1999, 2002]. In addition, fossil fuel combustion is also an important source of hexadecanoic acid (C_{16:0}). Higher concentrations of the total fatty acids observed in PKU are

Table 3. Comparison of Fatty Acid Concentrations From Different Cities^a

Site/Type	Season	Size	Method	C _{14:0}	C _{16:0}	C _{18:0}	C _{18:1}
Mt. Tai/China/mountain ^b	Spring, daytime	TSP	GC/MS	13	56	20	2.8
	Spring, nighttime	TSP	GC/MS	17	63	18	3.2
Beijing/China/urban ^c	Spring	PM _{2.5}	GC/MS	5.8	23	12	7.1
Miyun/China/suburban ^c	Spring	PM _{2.5}	GC/MS	1.4	5.5	2.8	1.1
Yulin/China/sand land ^c	Spring	PM _{2.5}	GC/MS	7.0	74	34	40
Shanghai/China/urban ^c	Spring	PM _{2.5}	GC/MS	2.7	27	9.0	5.5
Qingdao/China/urban ^c	Spring	PM _{2.5}	GC/MS	2.8	28	12	5.2
Duolun/China/sand land ^c	Spring	PM _{2.5}	GC/MS	7.0	73	34	28
Nanjing, China/urban ^d	Summer, daytime	PM _{2.5}	GC-FID	2.8	36	18	10
	Summer, nighttime	PM _{2.5}	GC-FID	3.0	61	32	14
	Winter, daytime	PM _{2.5}	GC-FID	5.3	85	43	17
	Winter, nighttime	PM _{2.5}	GC-FID	6.8	114	52	97
Gent/Belgium/urban ^e	Winter	TSP	GC-MS/FID	6.9	59	30	32
	Summer	TSP	GC-MS/FID	3.6	24	15	5.2
Gosan/Korea/background ^f	Spring	TSP	GC/MS	1.0	7.2	5.1	2.7
Jülich/Germany/forest ^g	Jul	PM _{2.5}	GC/MS	9.6	27	11.3	4.5
Temuco/Chile/urban ^h	Sep	PM _{2.5}	GC/MS	112	175	46	
Santiago/Chile/urban ^h	Oct	PM _{2.5}	GC/MS	127	130	34	
Houston, USA/urban ⁱ	Summer	PM _{2.5}	GC/MS	4.9	15.4	31	6.6
This study/PKU	Summer	PM _{2.5}	GC-FID	25	59	32	6.8
This study/Yufa	Summer	PM _{2.5}	GC-FID	20	38	24	5.6

^aFatty acid concentrations are in ng m⁻³. Abbreviations are as follows: GC-FID, gas chromatography–flame ionization detector; GC-MS, gas chromatography–mass spectrometry; PKU, Peking University.

^bFu *et al.* [2008].

^cHou *et al.* [2006].

^dWang and Kawamura [2005].

^eKubátová *et al.* [2002].

^fWang *et al.* [2009].

^gKourchev *et al.* [2008].

^hTsapakis *et al.* [2002].

ⁱYue and Fraser [2004].

influenced by the mixture of regional and local emissions. Total quantified fatty acids/OC ratios were 1.0% in PKU and 0.6% in Yufa. The individual fatty acid concentrations in this study are compared with other cities which are shown in Table 3. Their average concentrations are at the same magnitude compared with other Chinese cities (e.g., Nanjing) but higher than other worldwide countries except Chile. The poor air quality in China can be further evidenced.

[22] The dominance of even carbon number fatty acid to odd carbon number fatty acid isomers is quantified by Carbon Preference Index (CPI) and is calculated as follows:

$$\text{CPI}_{\text{fatty acid}} = \sum \text{Even carbon number fatty acids.}$$

Here the CPI was calculated with homologous series of fatty acids (C_{12:0}–C_{25:0}). The CPI values of the fatty acids are 17.3 in PKU and 16.3 in Yufa. The large elevated CPI values indicate a significant influence from biological sources of aerosols such as epicuticular waxes of vascular plant [Simoneit, 1984]. Oleic acid (C_{18:1}) were detected in all the samples which can be directly emitted from automobile source [Rogge *et al.*, 1993b]. Its concentrations ranged from 2.25 to 9.93 ng m⁻³ (average 6.84 ng m⁻³) in PKU and from 4.43 to 6.67 ng m⁻³ (average 5.75 ng m⁻³) in Yufa. The low relative abundance of the unsaturated fatty acid in summer is possibly attributed to a higher atmospheric oxidation. Oxidation of unsaturated oleic acid (C_{18:1}) is one of the major sources of azelaic acid (C₉). The ratio of C₉/C_{18:1} was higher in PKU (with an average of 5.09) than Yufa (with an average of 3.42), suggesting the secondary formation of azelaic acid (C₉) is sufficient in PKU. The ratios of C_{18:1}/

C_{18:0} obtained during this sampling period were 0.21 in PKU versus 0.24 in Yufa, suggesting an enhanced photochemical degradation of unsaturated fatty acids in PKU [Wang *et al.*, 2006]. Lower values of C_{18:1}/C_{18:0} ratios demonstrate that the aerosols are aged, i.e., relatively longer residence time since its formation and probably superimposition of long-distance transport on local characteristics.

[23] The ratio of C_{18:0}/C_{16:0} has been used as a qualitative tool for source assessment. Ratios lower than 0.25 have been obtained in atmospheric PM_{2.5} resulting from foliar vegetation combustion, waxy leaf surface abrasions, and wood smoke; values between 0.25 and 0.5 were registered for car and diesel truck exhausts; proportions in the interval 0.5–1 were achieved for paved and unpaved road dust and for hamburger charbroiling [Oliveira *et al.*, 2007; Rogge *et al.*, 2006]. In PKU and Yufa, the ratios of C_{18:0}/C_{16:0} were in the range of 0.39–0.85 (with an average of 0.36), indicating that beside the contribution of vehicular emissions, a strong input from cooking emissions is not negligible.

[24] Benzoic acid was detected in almost all the samples. The average concentration of benzoic acid was 72.2 ± 58.1 ng m⁻³ in PKU and 78.0 ± 47.3 ng m⁻³ in Yufa. Benzoic acid has been proposed as a primary pollutant in the exhaust of motor vehicles [Kawamura *et al.*, 1985, 2000; Rogge *et al.*, 1993b] and a secondary product from photochemical degradation of aromatic hydrocarbons such as toluene emitted by automobiles [Suh *et al.*, 2003]. Semivolatile benzoic acid was mainly determined in gaseous phase [Fraser *et al.*, 2003] but also present in particulate phase by partitioning. High ambient level of toluene (11.4 μg m⁻³) was detected in Beijing in August 2006 during an ozone

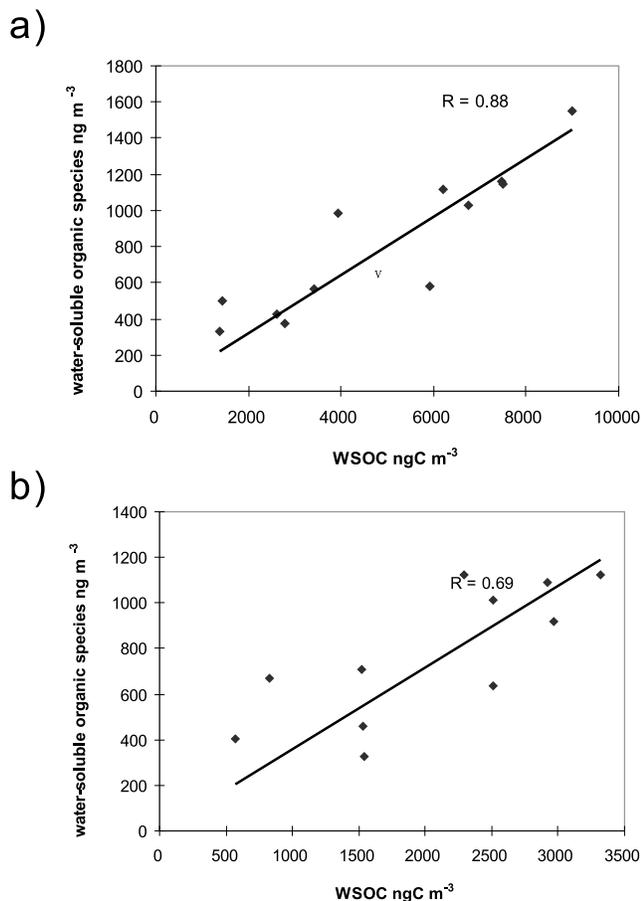


Figure 4. Relationship between the concentrations of total measured water-soluble organic species and total WSOC.

episode [Duan *et al.*, 2008], suggesting that benzoic acid is significantly produced by the oxidation of toluene in the atmosphere.

3.3. Correlation Analysis and the Ratios of Selected Species

[25] Low MW dicarboxylic acids are produced in the atmosphere by photochemical chain reactions of unsaturated hydrocarbons or fatty acids as well as their oxidation products [Kawamura and Sakaguchi, 1999; Kawamura *et al.*, 1996b]; however, their formation mechanisms are poorly understood. Other than anthropogenic emission, photochemical processes play an important role in controlling the atmospheric concentrations of dicarboxylic acids and related compounds. Therefore, the correlation coefficients were examined for selected species. Glyoxylic acid (ωC_2), the most abundant ketocarboxylic acid, can be further oxidized to oxalic acid (C_2). A good correlation was thus found between ωC_2 and C_2 ($r^2 = 0.94$, in PKU; $r^2 = 0.90$ in Yufa). In addition, malonic acid (C_3) and succinic acid (C_4) can be also oxidized to oxalic acid (C_2) [Kawamura and Ikushima, 1993]. The possible oxidation pathways explain why good correlations ($r^2 = 0.65$ – 0.93) were observed among the three dicarboxylic acids.

[26] Total quantified water-soluble organic compounds (TQWO), sum of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls, account for 6.5% (range from 4.1% to

14.2%) and 14.4% (range from 8.8% to 30.4%) of WSOC in PKU and Yufa, respectively. Meteorological data shows southern air mass flow was dominant during the sampling period. The pollutants from industrialized and urbanized Tianjin city and Hebei province, which were in primary form passing through Yufa, may have sufficient time to form SOA during the long-distance transport to the down-wind location of PKU. Higher SOA contribution can be thus explained a smaller ratio of TQWO to WSOC at PKU. Positive correlations ($r^2 = 0.88$, in PKU; $r^2 = 0.69$, in Yufa) were observed between the TQWO and WSOC at the two sampling locations (Figures 4a and 4b). These results again suggest that dicarboxylic acids, ketocarboxylic acids and dicarbonyls are the major water-soluble organic species in Beijing.

[27] The ratio of C_3/C_4 dicarboxylic acids is an indicator of enhanced photochemical production of dicarboxylic acids [Kawamura and Ikushima, 1993]. Succinic acid (C_4) can serve as a precursor in the formation of malonic (C_3) acid. In this study, the C_3/C_4 ratios ranged between 0.28 and 0.77 with an average of 0.53, which are slightly higher than those reported from vehicular emissions (0.3–0.5) [Kawamura and Kaplan, 1987], but slightly lower than those reported in Northern China in summer (0.61) [Ho *et al.*, 2007]. However, the C_3/C_4 ratios are much lower than those of the remote marine aerosols from the Pacific Ocean [Kawamura and Sakaguchi, 1999]. This result suggested that in addition to primary exhaust, secondary formation of particulate dicarboxylic acids by photo-oxidation reaction is also critical. The average C_3/C_4 ratio was higher in PKU (0.59) than in Yufa (0.46), being consistent with the enhanced degree of photochemical processing indicated by the higher WSOC/OC ratios in PKU.

3.4. Temporal Variations and Back Trajectory Analysis

[28] Figure 3a presents the temporal variations of OC, EC, WSOC and total dicarboxylic acids in $PM_{2.5}$ collected in PKU during summertime in 2006. Heavier air pollutions were observed during 23–25 August and 1–2 September. Concentrations of OC, EC, WSOC and total dicarboxylic acids generally increased during 23–25 August but rapidly decreased during 25–26 August. Another peak then appeared during 1–2 September. The lowest concentrations were observed during 3–4 September. Variations of total concentrations of ketocarboxylic acids, α -dicarbonyls, and fatty acids have the same trends in PKU during the sampling period (Figure 3c). In addition, temporal variations were observed in Yufa (Figures 3b and 3d) which are similar to the findings in PKU. In order to investigate the transport and the source region of air pollutants, air mass back trajectory analyses were conducted using National Oceanic and Atmospheric Administration Hybrid Single-Particle Lagrangian Integrated Trajectory with a starting elevation of 100 m. Figures 5a–5c show the typical trajectories for the event of the highest concentrations and lowest concentrations, respectively. It can be seen that there are large differences between the concentrations of air pollutants when the air mass came from the south versus the air mass from the north. North and northwest part of Beijing is mainly surrounded by the mountains without particular anthropogenic pollution sources while south and southeast of Beijing

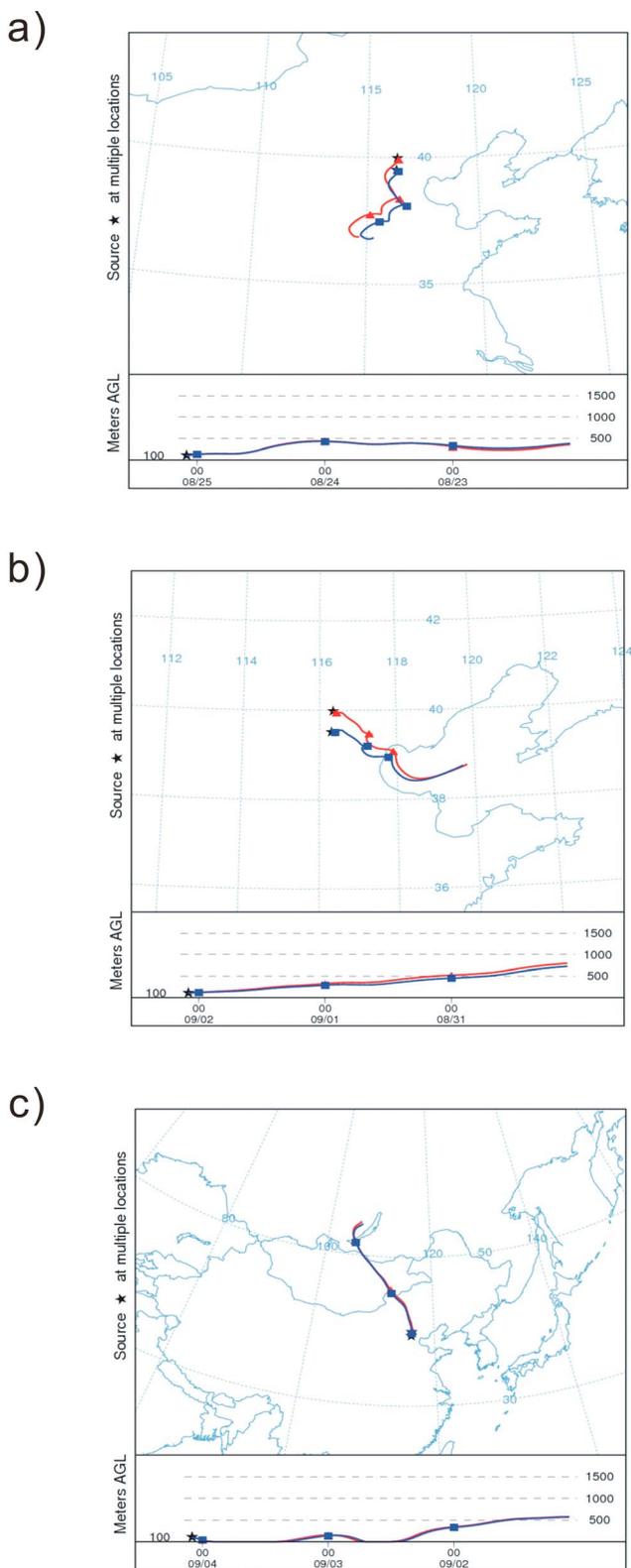


Figure 5. Three day air mass back trajectories on (a) 24–25 August, (b) 1–2 September, and (c) 4–5 September.

are heavily populated, urbanized, and industrialized areas such as Tianjin, Hebei province, and Shandong province. High emission of carbonaceous aerosols from southern part

of Beijing (Figure 1) is the major source for the episode during 24–25 August and 1–2 September. According to the 72 hour back trajectory analysis (Figures 5a and 5b), when the air mass passed over southern or southeastern part of Beijing (24–25 August and 1–2 September) (suggesting the influence by high OC emissions; Figure 1), higher concentrations of air pollutants were observed in PKU. The areas were influenced by the combination of regional and local emission sources. This indicates that the southerly inflow to Beijing has a higher aerosol loading than the outflow from the north. Lower ratios of TQWO to WSOC are observed in the two peak periods in PKU, suggesting the other water-soluble SOA formation products (e.g., HULIS or polymeric organic matter) were more dominant due to long-distance transport of the air pollutants from south or southeast. Highest C_3/C_4 dicarboxylic acid ratios (0.68 and 0.77) at the peak periods also represent that secondary formation of particulate dicarboxylic acids via photo-oxidation reaction. In addition, lower $C_{18:1}/C_{18:0}$ fatty acid ratios further demonstrate that the aerosols were aged from primary pollution sources from south or southeast.

[29] On the contrary, Figure 5c shows that the clean air masses came straightly from the north during 3–4 September when very low levels of organic compounds were observed. The local emission sources were more dominant, evidencing by lowest C_3/C_4 dicarboxylic acid ratio and highest $C_{18:1}/C_{18:0}$ fatty acid ratio was found in PKU. When the air mass came from the north of Beijing, higher concentrations of OC, EC, WSOC and oxalic acid (C_2) were observed in downwind location of Yufa than PKU. The air masses that were delivered from the north were collected at PKU before reaching Yufa. However, some precursor compounds such as malic acid (hC_4), methylmaleic acid (mM), glyoxal (Gly), and methylglyoxal (mGly) had lower concentrations in the downwind location of Yufa. They have been possibly oxidized in form of other compounds during the atmospheric transport. Unfortunately, influences from eastern part to PKU and Yufa cannot be interpreted as the air mass flow from the east is insufficient during the sampling period.

4. Summary and Conclusions

[30] During the Campaign of Air Quality Research in Beijing 2006 in summer (CAREBeijing-2006; 21 August to 4 September 2006), molecular compositions of low MW dicarboxylic acids (C_2 – C_{12}), ketocarboxylic acids (ωC_2 – ωC_9 , pyruvic acid), α -dicarbonyls (C_2 – C_3), fatty acids (C_{12} – C_{25}) and benzoic acid were determined at the urban (PKU) and suburban (Yufa) sites in Beijing. Among the quantified species, oxalic acid (C_2) (PKU = $449 \pm 274 \text{ ng m}^{-3}$; Yufa = $455 \pm 219 \text{ ng m}^{-3}$) was found as the most abundant dicarboxylic, followed by benzoic acid (PKU = $113 \pm 91.3 \text{ ng m}^{-3}$; Yufa = $123 \pm 74.2 \text{ ng m}^{-3}$) and phthalic (Ph) (PKU = $77.5 \pm 17.6 \text{ ng m}^{-3}$; Yufa = $68.3 \pm 14.7 \text{ ng m}^{-3}$). Low MW dicarboxylic acids, ketocarboxylic acids, α -dicarbonyls were found as major water-soluble organics, which account for more than 6.5% and 14.4% of WSOC in PKU and Yufa, respectively. Total quantified fatty acids accounted for 1.0% and 0.6% of OC in PKU and Yufa, respectively. Generally, concentrations in PKU were slightly higher than

in Yufa but the abundances of most species were quite similar in both sites.

[31] The $C_{18:1}/C_{18:0}$ ratios were used to point out the aged aerosols. The lower ratio (0.21) were observed in PKU than in Yufa (0.24), suggesting an enhanced photochemical degradation of unsaturated fatty acids in PKU. Moreover, the $C_{18:0}/C_{16:0}$ ratios have been used as a qualitative tool for source assessment. In PKU and Yufa, the ratios of $C_{18:0}/C_{16:0}$ were in the range of 0.39–0.85 (with an average of 0.36), suggesting that beside the contribution of vehicular emissions, a stronger input from cooking emissions is a possible source as well as plant emissions. Relatively high C_3/C_4 ratios (0.28–0.77 with an average of 0.53) were found for dicarboxylic acids in this study, further suggesting that in addition to primary emissions from motor exhausts, secondary formation of particulate dicarboxylic acids via photo-oxidation reaction is also important in Beijing.

[32] Two types of air mass with the highest and lowest concentrations were observed during 24–25 August and 1–2 September as well as 3–4 September. According to the back trajectory analysis, pollution episodes in Beijing were found to strongly relate with wind direction. The concentrations of air pollutants in Beijing can be increased up to 10 times higher than those obtained under air mass conditions associated with the north winds.

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References

- Beijing Municipal Bureau of Statistics (2006), *Beijing Statistical Yearbook 1998–2006*, China Stat. Press, Beijing.
- Cao, J. J., S. C. Lee, K. F. Ho, X. Y. Zhang, S. C. Zou, K. Fung, J. C. Chow, and J. G. Watson (2003), Characteristics of carbonaceous aerosol in Pearl River delta region, China during 2001 winter period, *Atmos. Environ.*, **37**, 1451–1460, doi:10.1016/S1352-2310(02)01002-6.
- Chen, D. S., S. Y. Cheng, L. Liu, T. Chen, and X. R. Guo (2007), An integrated MM5-CMAQ modeling approach for assessing trans-boundary PM10 contribution to the host city of 2008 Olympic summer games—Beijing, China, *Atmos. Environ.*, **41**, 1237–1250, doi:10.1016/j.atmosenv.2006.09.045.
- Chow, J. C., J. G. Watson, L.-W. A. Chen, W. P. Arnott, H. Moosmüller, and K. K. Fung (2004), Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols, *Environ. Sci. Technol.*, **38**, 4414–4422, doi:10.1021/es034936u.
- Chow, J. C., J. G. Watson, L.-W. A. Chen, G. Paredes-Miranda, M. C. Chang, D. Trimble, K. K. Fung, J. Zhang, and J. Z. Yu (2005), Refining temperature measures in thermal/optical carbon analysis, *Atmos. Chem. Phys.*, **5**, 2961–2972, doi:10.5194/acp-5-2961-2005.
- Duan, J. C., J. H. Tan, L. Yang, S. Wu, and J. M. Hao (2008), Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing, *Atmos. Res.*, **88**, 25–35, doi:10.1016/j.atmosres.2007.09.004.
- Facchini, M. C., M. Mircea, S. Fuzzi, and R. J. Charlson (1999), Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, **401**, 257–259, doi:10.1038/45758.
- Feng, J. L., M. Hu, C. K. Chan, P. S. Lau, M. Fang, L. Y. He, and X. Y. Tang (2006), A comparative study of the organic matter in $PM_{2.5}$ from three Chinese megacities in three different climatic zones, *Atmos. Environ.*, **40**, 3983–3994, doi:10.1016/j.atmosenv.2006.02.017.
- Fine, P. M., G. R. Cass, and B. R. T. Simoneit (2002), Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States, *Environ. Sci. Technol.*, **36**, 1442–1451, doi:10.1021/es0108988.
- Fine, P. M., B. Chakrabarti, M. Krudysz, J. J. Schauer, and C. Sioutas (2004), Diurnal variations of individual organic compound constituents of ultrafine and accumulation mode particulate matter in the Los Angeles Basin, *Environ. Sci. Technol.*, **38**, 1296–1304, doi:10.1021/es0348389.
- Fraser, M. P., G. R. Cass, and B. R. T. Simoneit (2003), Air quality model evaluation data for organics. 6. C–C organic acids, *Environ. Sci. Technol.*, **37**, 446–453, doi:10.1021/es0209262.
- Fu, P., K. Kawamura, K. Okuzawa, S. G. Aggarwal, G. Wang, Y. Kanaya, and Z. Wang (2008), Organic molecular compositions and temporal variations of summertime mountain aerosols over Mt. Tai, North China Plain, *J. Geophys. Res.*, **113**, D19107, doi:10.1029/2008JD009900.
- Han, Z., H. Ueda, and K. Matsuda (2005), Model study of the impact of biogenic emission on regional ozone and the effectiveness of emission reduction scenarios over eastern China, *Tellus, Ser. B*, **57**, 12–27, doi:10.1111/j.1600-0889.2005.00132.x.
- Hatakeyama, S., A. Takami, W. Wang, and D. Tang (2005), Aerial observation of air pollutants and aerosols over Bo Hai, China, *Atmos. Environ.*, **39**, 5893–5898, doi:10.1016/j.atmosenv.2005.06.025.
- He, L.-Y., M. Hu, X.-F. Huang, B.-D. Yu, Y.-H. Zhang, and D.-Q. Liu (2004), Measurement of emissions of fine particulate organic matter from Chinese cooking, *Atmos. Environ.*, **38**, 6557–6564, doi:10.1016/j.atmosenv.2004.08.034.
- He, L.-Y., M. Hu, X.-F. Huang, Y.-H. Zhang, and X.-Y. Tang (2006), Seasonal pollution characteristics of organic compounds in atmospheric fine particles in Beijing, *Sci. Total Environ.*, **359**, 167–176, doi:10.1016/j.scitotenv.2005.05.044.
- Ho, K. F., J. J. Cao, S. C. Lee, K. Kawamura, R. J. Zhang, J. C. Chow, and J. G. Watson (2007), Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in 14 cities of China, *J. Geophys. Res.*, **112**, D22S27, doi:10.1029/2006JD008011.
- Hou, X., G. Zhuang, Y. Sun, and Z. An (2006), Characteristics and sources of polycyclic aromatic hydrocarbons and fatty acids in $PM_{2.5}$ aerosols in dust season in China, *Atmos. Environ.*, **40**, 3251–3262, doi:10.1016/j.atmosenv.2006.02.003.
- Hsieh, L. Y., C. L. Chen, M. W. Wan, C. H. Tsai, and Y. I. Tsai (2008), Speciation and temporal characterization of dicarboxylic acids in $PM_{2.5}$ during a PM episode and a period of non-episodic pollution, *Atmos. Environ.*, **42**, 6836–6850, doi:10.1016/j.atmosenv.2008.05.021.
- Huang, X. F., M. Hu, L. Y. He, and X. Y. Tang (2005), Chemical characterization of water soluble organic acids in $PM_{2.5}$ in Beijing, China, *Atmos. Environ.*, **39**, 2819–2827, doi:10.1016/j.atmosenv.2004.08.038.
- Huang, X. F., L. Y. He, M. Hu, and Y. H. Zhang (2006), Annual variation of particulate organic compounds in $PM_{2.5}$ in the urban atmosphere of Beijing, *Atmos. Environ.*, **40**, 2449–2458, doi:10.1016/j.atmosenv.2005.12.039.
- Jacobson, M. C., H. C. Hanson, K. J. Noone, and R. J. Charlson (2000), Organic atmospheric aerosols: Review and state of the science, *Rev. Geophys.*, **38**, 267–294, doi:10.1029/1998RG000045.
- Kawamura, K. (1993), Identification of C2–C10 w-oxocarboxylic acids, pyruvic acid and C2–C3 a-dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC-MS, *Anal. Chem.*, **65**, 3505–3511, doi:10.1021/ac00071a030.
- Kawamura, K., and R. B. Gagosian (1987), Implications of ω -oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids, *Nature*, **325**, 330–332, doi:10.1038/325330a0.
- Kawamura, K., and K. Ikushima (1993), Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, **27**, 2227–2235, doi:10.1021/es00047a033.
- Kawamura, K., and I. R. Kaplan (1987), Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air, *Environ. Sci. Technol.*, **21**, 105–110, doi:10.1021/es00155a014.
- Kawamura, K., and F. Sakaguchi (1999), Molecular distribution of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, **104**, 3501–3509, doi:10.1029/1998JD100041.
- Kawamura, K., and O. Yasui (2005), Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, **39**, 1945–1960, doi:10.1016/j.atmosenv.2004.12.014.
- Kawamura, K., L.-L. Ng, and I. R. Kaplan (1985), Determination of organic acids (C_1 – C_{10}) in the atmosphere, motor exhausts, and engine oils, *Environ. Sci. Technol.*, **19**, 1082–1086, doi:10.1021/es00141a010.
- Kawamura, K., H. Kasukabe, and L. A. Barrie (1996a), Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in Arctic aerosols: One year of observations, *Atmos. Environ.*, **30**, 1709–1722, doi:10.1016/1352-2310(95)00395-9.
- Kawamura, K., R. Sempéré, Y. Imai, M. Hayashi, and Y. Fujii (1996b), Water soluble dicarboxylic acids and related compounds in Antarctic aerosols, *J. Geophys. Res.*, **101**, 18,721–18,728, doi:10.1029/96JD01541.
- Kawamura, K., S. Steinberg, and I. R. Kaplan (1996c), Concentrations of monocarboxylic and dicarboxylic acids and aldehydes in southern Cali-

- fomia wet precipitations: Comparison of urban and non-urban samples and compositional changes during scavenging, *Atmos. Environ.*, *30*, 1035–1052, doi:10.1016/1352-2310(95)00404-1.
- Kawamura, K., S. Steinberg, and I. R. Kaplan (2000), Homologous series of C1-C10 monocarboxylic acids and C1-C6 carbonyls in Los Angeles air and motor vehicle exhausts, *Atmos. Environ.*, *34*, 4175–4191, doi:10.1016/S1352-2310(00)00212-0.
- Kawamura, K., M. Kobayashi, N. Tsubonuma, M. Mochida, T. Watanabe, and M. Lee (2004), Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in *Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan*, edited by R. J. Hill et al., *Geochem. Soc. Publ.*, *9*, 243–265.
- Kerminen, V.-M. (2001), Relative roles of secondary sulfate and organics in atmospheric cloud condensation nuclei production, *J. Geophys. Res.*, *106*, 17,321–17,333, doi:10.1029/2001JD900204.
- Kerminen, V.-M., C. Ojanen, T. Pakkanen, R. Hillamo, M. Aurela, and J. Merilainen (2000), Low-molecular-weight dicarboxylic acids in an urban and rural atmosphere, *J. Aerosol Sci.*, *31*, 349–362, doi:10.1016/S0021-8502(99)00063-4.
- Kourtchev, I., J. Warnke, W. Maenhaut, T. Hoffmann, and M. Claeys (2008), Polar organic marker compounds in PM_{2.5} aerosol from a mixed forest site in western Germany, *Chemosphere*, *73*, 1308–1314, doi:10.1016/j.chemosphere.2008.07.011.
- Kroll, J. H., N. L. Ng, S. M. Murphy, V. Varutbangkul, R. C. Flagan, and J. H. Seinfeld (2005), Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, *J. Geophys. Res.*, *110*, D23207, doi:10.1029/2005JD006004.
- Kubátová, A., R. Vermeylen, M. Claeys, J. Cafmeyer, and W. Maenhaut (2002), Organic compounds in urban aerosols from Gent, Belgium: Characterization, sources, and seasonal differences, *J. Geophys. Res.*, *107*(D21), 8343, doi:10.1029/2001JD000556.
- Legrand, M., S. Preunkert, T. Oliveira, C. A. Pio, S. Hammer, A. Gelencsér, A. Kasper-Giebl, and P. La (2007), Origin of C₂–C₅ dicarboxylic acids in the European atmosphere inferred from year-round aerosol study conducted at a west-east transect, *J. Geophys. Res.*, *112*, D23S07, doi:10.1029/2006JD008019.
- Li, X. G., X. Q. Guo, X. R. Liu, C. S. Liu, S. S. Zhang, and Y. S. Wang (2009), Distribution and sources of solvent extractable organic compounds in PM_{2.5} during 2007 Chinese Spring Festival in Beijing, *J. Environ. Sci.*, *21*, 142–149, doi:10.1016/S1001-0742(08)62242-1.
- Liggio, J., S.-M. Li, and R. McLaren (2005), Reactive uptake of glyoxal by particulate matter, *J. Geophys. Res.*, *110*, D10304, doi:10.1029/2004JD005113.
- Liu, Y., S. Tao, Y. F. Yang, H. Dou, Y. Yang, and R. M. Coveny (2007), Inhalation exposure of traffic police officers to polycyclic aromatic hydrocarbons (PAHs) during the winter in Beijing, China, *Sci. Total Environ.*, *383*, 98–105, doi:10.1016/j.scitotenv.2007.05.008.
- Luo, C., J. C. St. John, X. Zhou, K. S. Lam, T. Wang, and W. L. Chameides (2000), A nonurban ozone air pollution episode over eastern China: Observations and model simulations, *J. Geophys. Res.*, *105*, 1889–1908, doi:10.1029/1999JD900970.
- Mauzerall, D. L., D. Narita, H. Akimoto, L. Horowitz, S. Walters, D. A. Hauglustaine, and G. Brasseur (2000), Seasonal characteristics of tropospheric ozone production and mixing ratios over East Asia: A global three-dimensional chemical transport model analysis, *J. Geophys. Res.*, *105*, 17,895–17,910, doi:10.1029/2000JD900087.
- Menon, S., J. Hansen, L. Nazarenko, and Y. Luo (2002), Climate effects of black carbon aerosols in China and India, *Science*, *297*, 2250–2253, doi:10.1126/science.1075159.
- Mochida, M., N. Umemoto, K. Kawamura, H. Lim, and B. J. Turpin (2007), Bimodal size distributions of various organic acids and fatty acids in the marine atmosphere: Influence of anthropogenic aerosols, Asian dusts, and sea spray off the coast of East Asia, *J. Geophys. Res.*, *112*, D15209, doi:10.1029/2006JD007773.
- Narukawa, M., K. Kawamura, N. Takeuchi, and T. Nakajima (1999), Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, *26*, 3101–3104, doi:10.1029/1999GL010810.
- Nel, A. (2005), Air pollution-related illness: Effects of particles, *Science*, *308*, 804–806, doi:10.1126/science.1108752.
- Nolte, C. G., J. J. Schauer, G. R. Cass, and B. R. T. Simoneit (2001), Highly polar organic compounds present in wood smoke and in the ambient atmosphere, *Environ. Sci. Technol.*, *35*, 1912–1919, doi:10.1021/es001420r.
- Nolte, C. G., J. J. Schauer, G. R. Cass, and B. R. T. Simoneit (2002), Trimethylsilyl derivatives of organic compounds in source samples and in atmospheric fine particulate matter, *Environ. Sci. Technol.*, *36*, 4273–4281, doi:10.1021/es020518y.
- Oliveira, C., et al. (2007), Seasonal distribution of polar organic compounds in the urban atmosphere of two large cities from the north and south of Europe, *Atmos. Environ.*, *41*, 5555–5570, doi:10.1016/j.atmosenv.2007.03.001.
- Penner, J. E., and T. Novakov (1996), Carbonaceous particles in the atmosphere: A historical perspective to the fifth international conference on carbonaceous particles in the atmosphere, *J. Geophys. Res.*, *101*, 19,373–19,378, doi:10.1029/96JD01175.
- Penner, J. E., R. Dickenson, and A. O'Neill (1992), Effects of aerosols from biomass burning on the global radiation budget, *Science*, *256*, 1432–1434, doi:10.1126/science.256.5062.1432.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1991), Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations, *Environ. Sci. Technol.*, *25*, 1112–1125, doi:10.1021/es00018a015.
- Rogge, W. F., M. A. Mazurek, L. M. Hildemann, G. R. Cass, and B. R. T. Simoneit (1993a), Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation, *Atmos. Environ., Part A*, *27*, 1309–1330.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1993b), Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy duty diesel trucks, *Environ. Sci. Technol.*, *27*, 636–651, doi:10.1021/es00041a007.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1998), Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces, *Environ. Sci. Technol.*, *32*, 13–22, doi:10.1021/es960930b.
- Rogge, W. F., P. M. Medeiros, and B. R. T. Simoneit (2006), Organic marker compounds for surface soil and fugitive dust from open lot dairies and cattle feedlots, *Atmos. Environ.*, *40*, 27–49, doi:10.1016/j.atmosenv.2005.07.076.
- Saxena, P., L. M. Hildemann, P. H. McMurry, and J. H. Seinfeld (1995), Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, *100*, 18,755–18,770, doi:10.1029/95JD01835.
- Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit (1999), Measurement of emissions from air pollution sources. 1. C₁ through C₂₉ organic compounds from meat charbroiling, *Environ. Sci. Technol.*, *33*, 1566–1577, doi:10.1021/es980076j.
- Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit (2001), Measurement of emissions from air pollution sources. 3. C₁–C₂₉ organic compounds from fireplace combustion of wood, *Environ. Sci. Technol.*, *35*, 1716–1728, doi:10.1021/es001331e.
- Schauer, J. J., M. R. Kleeman, and B. R. T. Simoneit (2002), Measurement of emissions from air pollution sources. 4. C₁–C₂₇ organic compounds from cooling with seed oils, *Environ. Sci. Technol.*, *36*, 567–575, doi:10.1021/es002053m.
- Simoneit, B. R. T. (1984), Organic matter of the troposphere—III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States, *Atmos. Environ.*, *18*, 51–67, doi:10.1016/0004-6981(84)90228-2.
- Simoneit, B. R. T., M. Kobayashi, M. Mochida, K. Kawamura, and B. J. Huebert (2004), 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.*, *109*, D19S09, doi:10.1029/2004JD004565.
- Streets, D. G., T. C. Bond, T. Lee, and C. Jang (2004), On the future of carbonaceous aerosol emissions, *J. Geophys. Res.*, *109*, D24212, doi:10.1029/2004JD004902.
- Streets, D. G., et al. (2007), Air quality during the 2008 Beijing Olympic Games, *Atmos. Environ.*, *41*, 480–492, doi:10.1016/j.atmosenv.2006.08.046.
- Suh, I., R. Zhang, L. T. Molina, and M. J. Molina (2003), Oxidation mechanism of aromatic peroxy and bicyclic radicals from OH-toluene reactions, *J. Am. Chem. Soc.*, *125*, 12,655–12,665, doi:10.1021/ja0350280.
- Timonen, H. J., S. K. Saarikoski, M. A. Aurela, K. M. Saarnio, and R. E. J. Hillamo (2008), Water-soluble organic carbon in urban aerosol: Concentrations, size distributions and contribution to particulate matter, *Boreal Environ. Res.*, *13*, 335–346.
- Tsapakis, M., E. Lagoudakia, E. G. Stephanou, I. G. Kavouras, P. Koutrakis, P. Oyolac, and D. von Baer (2002), The composition and sources of PM_{2.5} organic aerosol in two urban areas of Chile, *Atmos. Environ.*, *36*, 3851–3863, doi:10.1016/S1352-2310(02)00269-8.
- Volkamer, R., U. Platt, and K. Wirtz (2001), Primary and secondary glyoxal formation from aromatics: Experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene, and p-xylene, *J. Phys. Chem. A*, *105*, 7865–7874, doi:10.1021/jp010152w.

- Wang, G. H., and K. Kawamura (2005), Molecular characteristics of urban organic aerosols from Nanjing: A case study of a mega-city in China, *Environ. Sci. Technol.*, *39*, 7430–7438, doi:10.1021/es051055+.
- Wang, G. H., S. L. Niu, C. Liu, and L. S. Wang (2002), Identification of dicarboxylic acids and aldehyde of PM₁₀ and PM_{2.5} aerosols in Nanjing, China, *Atmos. Environ.*, *36*, 1941–1950, doi:10.1016/S1352-2310(02)00180-2.
- Wang, G. H., K. Kawamura, S. C. Lee, K. F. Ho, and J. J. Cao (2006), Molecular, seasonal and spatial distribution of organic aerosols from fourteen Chinese cities, *Environ. Sci. Technol.*, *40*, 4619–4625, doi:10.1021/es060291x.
- Wang, G. H., K. Kawamura, X. Zhao, Q. G. Li, Z. X. Dai, and H. Y. Niu (2007), Identification, abundance and seasonal variation of anthropogenic organic aerosols from a mega-city in China, *Atmos. Environ.*, *41*, 407–416, doi:10.1016/j.atmosenv.2006.07.033.
- Wang, G. H., K. Kawamura, and M. H. Lee (2009), Comparison of organic compositions in dust storm and normal aerosol samples collected at Gosan, Jeju Island, during spring 2005, *Atmos. Environ.*, *43*, 219–227, doi:10.1016/j.atmosenv.2008.09.046.
- Warneck, P. (2003), In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.*, *37*, 2423–2427, doi:10.1016/S1352-2310(03)00136-5.
- Wilkening, K. E., L. A. Barrie, and M. Engle (2000), Trans-Pacific air pollution, *Science*, *290*, 65–67, doi:10.1126/science.290.5489.65.
- Xia, X., H. Chen, and W. Zhang (2007), Analysis of the dependence of column-integrated aerosol properties on long-range transport of air masses in Beijing, *Atmos. Environ.*, *41*, 7739–7750, doi:10.1016/j.atmosenv.2007.06.042.
- Yang, H., J. Z. Yu, S. S. H. Ho, J. Xu, W. S. Wu, C. H. Wan, X. Wang, X. Wang, and L. Wang (2005), The chemical composition of inorganic and carbonaceous materials in PM_{2.5} in Nanjing, China, *Atmos. Environ.*, *39*, 3735–3749, doi:10.1016/j.atmosenv.2005.03.010.
- Yao, X. H., C. K. Chan, M. Fang, S. Cadle, T. Chan, P. Mulawa, K. B. He, and B. M. Ye (2002), The water-soluble ionic composition of PM_{2.5} in Shanghai and Beijing, China, *Atmos. Environ.*, *36*, 4223–4234, doi:10.1016/S1352-2310(02)00342-4.
- Yao, X. H., M. Fang, C. K. Chan, K. F. Ho, and S. C. Lee (2004), Characterization of dicarboxylic acids in PM_{2.5} in Hong Kong, *Atmos. Environ.*, *38*, 963–970, doi:10.1016/j.atmosenv.2003.10.048.
- Yuan, Z., A. K. H. Lau, M. Shao, P. K. K. Louie, S. C. Liu, and T. Zhu (2009), Source analysis of volatile organic compounds by positive matrix factorization in urban and rural environments in Beijing, *J. Geophys. Res.*, *114*, D00G15, doi:10.1029/2008JD011190.
- Yue, Z. W., and M. P. Fraser (2004), Polar organic compounds measured in fine particulate matter during TexAQS 2000, *Atmos. Environ.*, *38*, 3253–3261, doi:10.1016/j.atmosenv.2004.03.014.
- Zhao, Y. L., M. Hu, S. Slanina, and Y. H. Zhang (2007a), Chemical compositions of fine particulate organic matter emitted from Chinese cooking, *Environ. Sci. Technol.*, *41*, 99–105, doi:10.1021/es0614518.
- Zhao, Y. L., M. Hu, S. Slanina, and Y. H. Zhang (2007b), The molecular distribution of fine particulate organic matter emitted from Western-style food cooking, *Atmos. Environ.*, *41*, 8163–8171, doi:10.1016/j.atmosenv.2007.06.029.
- Zheng, M., M. Fang, F. Wang, and K. L. To (2000), Characterization of the solvent extractable organic compounds in PM_{2.5} aerosols in Hong Kong, *Atmos. Environ.*, *34*, 2691–2702, doi:10.1016/S1352-2310(99)00521-X.
- Zheng, M., L. G. Salmon, J. J. Schauer, L. Zeng, C. S. Kiang, Y. H. Zhang, and G. R. Cass (2005), Seasonal trends in PM_{2.5} source contributions in Beijing, China, *Atmos. Environ.*, *39*, 3967–3976, doi:10.1016/j.atmosenv.2005.03.036.

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