Dicarboxylic Acids, Ketocarboxylic acids, α-Dicarbonyls, Fatty Acids and Benzoic Acid in $PM_{2.5}$ aerosol collected during CAREBeijing-2007: an effect of traffic restriction on air quality

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Abstract

Thirty water-soluble organic species, including dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls, fatty acids, and benzoic acid were determined as well as organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC) in $PM_{2.5}$ samples collected during the Campaign of Air Quality Research in Beijing 2007 (CAREBeijing-2007) in the urban and suburban areas of Beijing. The objective of this study is to identify the influence of traffic emissions and regional transport to the atmosphere in Beijing during summer. $PM_{2.5}$ samples collected with or without traffic restriction in Beijing are selected to evaluate the effectiveness of local traffic restriction measure on air pollution reduction. The average concentrations of the total quantified bifunctional organic compounds (TQBOC), total fatty acids and benzoic acid during the entire sampling period were 1184 ± 241 ng m^{-3}, 597 ± 159 ng m^{-3} and 1496 ± 511 ng m^{-3} in PKU, and 1050 ± 303 ng m^{-3}, 475 ± 114 ng m^{-3} and 1278 ± 372 ng m^{-3} in Yufa. Oxalic acid (C_2) was found as the most abundant dicarboxylic acid at PKU and Yufa, followed by phthalic acid (Ph). A strong even carbon number predominance with the highest level at palmitic acid ($C_{16:0}$), followed by stearic acid ($C_{18:0}$) was found for fatty acids. According to the back trajectories modeling results, the air masses were found to originate mainly from northeast, passing over southeast or south of Beijing (heavily populated, urbanized and industrialized areas), during heavier pollution events, whereas they are mainly from north or northwest sector (mountain areas without serious anthropogenic pollution sources) during less pollution events. The data with wind only from the same sector (minimizing the difference from regional contribution) but with and without traffic restriction in Beijing were analyzed to evaluate the effectiveness of local traffic restriction measure on the reduction of local air pollution in Beijing. The results suggested that the “traffic restriction” measure can reduce the air pollutants, but the decrease of pollutants is generally smaller in Yufa compared to that in PKU. Moreover, an enhancement of elemental carbon (EC) value indicates elevated primary emissions in Yufa during restriction period than non-restriction period. This study demonstrates that even when primary exhaust was controlled by traffic restriction, the contribution of secondary organic species formed from photochemical processes was critical with long-range atmospheric transport of pollutants.

Keywords: dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls, fatty acids, secondary organic carbon, Chinese aerosols

1. Introduction

Organic aerosol (OA) typically constitutes 20–90% of submicron aerosol (Jimenez et al., 2009; Huang et al., 2014) and is influencing Earth's climate directly by absorbing and scattering radiation and indirectly by acting as cloud condensation. OA also adversely affects air quality and human health. However, uncertainties exist in the effect of OA on health and climate, due in large part to the complexity of the OA composition (Hallquist et al., 2009; Poschl, 2005; Hoffmann et al., 2011) . OA can be primary emitted, or secondary produced by photochemical reactions of gas-phase precursors. Due to polar functional groups formation (e.g., carbonyl, carboxyl and hydroxyl), a major fraction of the SOA is thought to be water-soluble which, together with some water-soluble POA, accounts for about 40–80% of the OA (Jaffrezo et al., 2005; Saxena and Hildemann, 1996) .

Despite the dominant presence of WSOC in the atmosphere, there exist large uncertainties associated with sources, the chemical composition, removal mechanisms and atmospheric formation processing of aerosol WSOC. This is particularly evident in polluted megacities where multiple sources of local and regional origins may significantly change the chemical and physical properties of aerosol and therefore influence the air quality, climate and human health. Dicarboxylic acids (diacids) are the most abundant organic compounds in OA, which can be derived from primary emissions and/or secondary formation from different precursor species via photochemical reactions (Glasius et al., 2000; Kawamura et al., 1996; Kundu et al., 2010; Legrand et al., 2007). Fossil fuel combustion and biomass burning (Falkovich et al., 2005; Ho et al., 2006; Kundu et al., 2010; Huang et al., 2014) are the major primary sources whereas photochemical oxidation of volatile organic compounds (VOCs) from biogenic and anthropogenic emissions (Kawamura et al., 1996; Mkoma and Kawamura, 2013) are the major secondary sources.

Beijing is one of the largest metropolitan cities in Asia and has become a heavily polluted area due to the fast urbanization and industrialization over the past two decades. In 2009, more than 17.5 million residents and 4.0 million vehicles were reported in Beijing (BMBS, 2010). Besides local emissions, the air flowed into Beijing from polluted neighboring regions can have significant impact to the air quality in Beijing (Hatakeyama et al., 2005; Luo et al., 2000; Mauzerall et al., 2000). Especially, the gas-to-particle partitioning of semi-volatile organic compounds (SVOCs) and their subsequent aging via photochemical processing during transport has been recognized to be a major air pollution source (Ding et al., 2008; Guttikunda et al., 2005). Atmospheric aerosols have been investigated extensively in China (An et al., 2007; Cao et al., 2003; Xu et al., 2008; Huang et al., 2014). However, relevant studies on organic acids are still very scarce. With such limited information available on organic acids despite the rapid urbanization and development (especially the increase in traffic density), it is essential to seek a better understanding of organic acids in Beijing. For the promised "Green Olympic Game" in 2008, many pollution control measures, such as controlling traffic, halting industrial/construction activities, and sweeping roads, was taken to improve the air quality. The 'traffic restriction' measure, which only allowed vehicles to be on road in alternative business days according to their even and odd plate numbers, was proposed to reduce air pollution.

To investigate the effects of the traffic restriction on the air quality of Beijing and to accumulate experience and scientific evidence for the preparation of the 2008 Olympic game, we conducted aerosol ($PM_{2.5}$) monitoring at two sites in Beijing during August 3−31, 2007. In this study, $PM_{2.5}$ samples collected were analyzed by gas chromatography flame ionization detector (GC-FID) and gas chromatography mass spectrometry (GC-MS) to determine the composition of low molecular weight (MW) diacids (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}). Moreover, OC, EC, and WSOC were also analyzed. Through the intensive sampling campaign, the roles of regional transport, local emissions and secondary formations of particulate matter in the atmosphere of Beijing were investigated.

2. Experiment

2.1 $PM_{2.5}$ sampling

Two sampling locations, Peking University (PKU) (39.98°N, 116.35°E) and Yufa (39.51°N, 116.31°E) were selected in this study. The detailed descriptions of the sampling locations were reported elsewhere (Ho et al., 2010). The air samplers were placed on the top floor of the buildings (PKU: a 6-story building; Yufa: 4-story building).The meteorological data such as wind speed, wind direction, relative humidity, and temperature were collected during the sampling period. North and northwest of PKU are enclosed by mountains whereas south and southeast of Yufa are surrounded by heavily industrialized and urbanized areas such as Hebei province and Tianjin city.

Pre-heated (800 ℃, 3h) quartz-fiber filters (47 mm QM-A Whatman quartz filters) were used to collect 24 h integrated $PM_{2.5}$ samples by Airmetrics mini-volume $PM_{2.5}$ samplers at a flow rate of 5 L min^{-1}. A DryCal® flow meter (BIOS International, Butler, NJ, USA) was used to calibrate the sampling flows before and after the sampling. Sampling was carried out simultaneously from 09:00 a.m. to 09:00 a.m. local time at the two sampling locations from 3rd to 31st August, 2007. The samples were properly kept in a freezer (–20°C) to prevent evaporation of semi volatile components and microbial degradation of organics.

2.2 Chemical analysis

OC and EC were analyzed (on a 0.526 cm^2 punch) by thermal analysis with optical detection following the IMPROVE protocol on a Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) (Cao et al., 2003; Chow et al., 2005). The method detection limit (MDL) of OC and EC analysis is 0.8 and 0.4 $\mu gC\ cm^{-2}$, respectively. Todetermine the WSOC, a total area of 2.63 cm^2 of the sample filter was cut from each filter and 5 ml of Milli-Q water (18 MΩ) was added into a 15 ml vial where the sample was placed. Ultra-sonic water bath was used to extract the particles on the filter for 1 hr. Syringe filters (0.2 μm PTFE membrane) were used to remove the insoluble particles from the extracts. Filtered extract was then transferred into clean vials and analyzed total organic carbon (TOC) by using a Shimadzu TOC-V CPH Total Carbon Analyzer (Columbia, MD, USA). The MDL is 0.01 $\mu gC\ m^{-3}$, with a precision of ±5%. The data reported in this study were all corrected by the blanks.

The analytical procedures for water-soluble organic species were well reported elsewhere (Kawamura and Yasui, 2005). Briefly, the sample was extracted with organic-free water (10 ml × 3) to isolate bifunctional organic compounds as well as fatty acids and benzoic acid. After the extracts were concentrated using a vacuum rotary evaporator, 14% BF_3/*n*-butanol were added at 100 °C to convert the aldehyde groups to dibutoxy acetals and carboxyl groups to butyl esters. Homologous series of fatty acids were analyzed as butyl esters (Mochida et al., 2007). No serious contamination (< 5% of real samples) was observed in our analysis. The data reported in this study were corrected by the field blanks. The derivatized samples were determined by a Agilent 6890GC/FID (Palo Alto, CA, USA) equipped with a split/splitless injector, HP-5 fused silica capillary column (25 m × 0.2 mm i.d. x 0.5 μm film thickness) and an FID detector. Peak identifications were relied on the retention times of authentic standards. ThermoQuest Trace MS (Austin, TX, USA) with a similar GC conditions was used for mass spectral confirmation of the compounds. The reproducibility of the methods was < ±15%; recoveries of the bifunctional organic compounds fatty acids and benzoic acid were > 70% (Kawamura and Yasui, 2005; Mochida et al., 2007). Field blanks concentrations were < 15% of real samples, except for phthalic acid (up to 30%). The results shown in this study were all corrected by the field blanks.

3. Results and discussion

3.1 Overview of molecular compositions of bifunctional organic compounds in PKU and Yufa

Average OC, EC, and WSOC concentrations in PKU and Yufa are illustrated in Table 1 and their levels during the entire sampling period were 14.9 ± 2.47, 6.21 ± 1.90 and 5.59 ± 1.49 μgC m^{-3} in PKU, and 11.1 ± 3.68, 5.6 ± 1.83 and 4.55 ± 1.79 μgC m^{-3} in Yufa, respectively. The WSOC accounted for 37 ± 7% and 40 ± 7% of OC in PKU and Yufa, respectively. It was consistent with the WSOC/OC ratios (20–40%) at other metropolitan cities (Ho et al., 2007; Yang et al., 2005), suggesting that WSOC is one of the main components in OA in China. Yufa is located at southern Beijing, which is close to the border of Beijing Municipality and Hebei Province. Regional pollution from heavy industrialized and urbanized areas, like Hebei province and Tianjin city, have a great impact to the air quality of Yufa area.

The concentrations of bifunctional organic compounds measured in PKU and Yufa are presented in Table 1. The concentrations of total quantified bifunctional organic compounds (TQBOC) varied from 730 to 1455 ng m^{-3} (average concentration: 1184 ± 241 ng m^{-3}) in PKU, and from 554 to 1621 ng m^{-3} (average concentration: 1050 ± 303 ng m^{-3}) in Yufa. The results are higher than measurements (average 813 ng m^{-3} in PKU; average 771 ng m^{-3} in Yufa) reported in 2006 in same sampling locations (Ho et al., 2010), reflecting that there were continuous increases of primary emissions and more aging of aerosols in Beijing. However, the concentrations are close to those megacities studied recently (Ho et al., 2007).

Oxalic acid (C_2) was the most abundant diacid (435 ± 124 ng m^{-3} and 418 ± 130 ng m^{-3} at PKU and Yufa, respectively) determined in this study, followed by phthalic acid (Ph) (209 ± 28.8 ng m^{-3} and 176.3 ± 91.5 ng m^{-3}), and succinic acid (C_4) (89.9 ± 27.7 ng m^{-3} and 80.9 ± 26.9 ng m^{-3}). These three species accounted for 65% of TQBOC in PKU and Yufa, respectively. Oxalic acid was also recognized as predominant diacid in previous studies in China (Ho et al. 2010, 2011). C_2 can be either released from combustion processes (e.g., fossil fuel and biomass burning) (Kawamura and Kaplan, 1987; Narukawa et al., 1999) or secondary produced by the oxidation of VOCs (Carlton et al., 2006; Warneck, 2005).

The average phthalic acid (Ph) concentrations measured in this study are higher than those reported by other studies (Ho et al., 2007; Wang and Kawamura, 2005). Three phthalic acids (phthalic acid (*o*-isomer), terephthalic acid (*p*-isomer) and isophthalic acid (*m*-ismoer)) were determined and these isomer species distribution was dominated by *o*-isomer, followed by *p*-isomer and *m*-isomer, which are consistent with studies measured in Mt. Tai, China and Pearl River Delta region (Fu et al., 2008; Ho et al., 2011). The abundant phthalic acid (Ph) can be released from incomplete combustion processes or secondary formed by oxidation of aromatic compounds (e.g., naphthalenes, NAP) (Kawamura and Kaplan, 1987; Kawamura and Yasui, 2005). In some previous studies, high levels of NAP were found in Beijing urban areas (Liu et al., 2007; Tao et al., 2007) and it can be thus one of the potential precursors to phthalic acid (Ph) formation (Ho et al., 2007).

Besides diacids (C_2-C_4), azelaic acid (C_9) was the most abundant species among the saturated diacids in both sampling locations (71.4 ± 8.91 ng m^{-3} in PKU; 49.2 ± 8.99 ng m^{-3} in Yufa). C_9 is recognized as a photochemical reaction product of biogenic unsaturated fatty acids, such as oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids [the first number is carbon number and the latter one refers to the amount of double bond] (Kawamura and Gagosian, 1987) and is generally abundance in the high molecular weight homologues. The unsaturated fatty acids are commonly determined in marine micro-organism or higher plant leaves. However, these acids could be released by meat charbroiling also (Rogge et al., 1991). During long range transport, photochemical oxidation of $C_{18:1}$ to C_9 via oxidants (e.g., ozone and/or OH radicals) may occur in the air (Stephanou and Stratigakis, 1993). The $C_9/C_{18:1}$ ratio determined was lower in Yufa (average value: 2.1) than that in PKU (average value: 5.1) suggesting that significant secondary production of C_9 occurred in urban area of Beijing.

Diacids can be formed when ketocarboxylic acids, which are regarded as intermediate product of mono-carboxylic acids oxidation, react with other pollutants in the air (He et al., 2013; Kawamura et al., 1996). The concentrations of total measured ketocarboxylic acids varied from 87.4 to 169 ng m^{-3}, (average value: 122 ± 28.8 ng m^{-3}) in PKU and from 52.0 to 131 ng m^{-3} (average value: 97.0 ± 22.9 ng m^{-3}) in Yufa (Table 1). The concentrations in both sampling sites are higher than those measured in rural site in Gosan, South Korea (53 ng m^{-3}) and megacities in China (summer: 37 ng m^{-3}) (Ho et al., 2007; 2010; Kawamura et al., 2004). These results reveal that the organic aerosols in PKU and Yufa were likely more photochemically aged than that in other urban sites caused by photochemical reaction during transportation (He et al., 2013). Glyoxylic acid (ωC_2) was found as the most abundant ketocarboxylic acid, followed by pyruvic acid (Pyr). Their concentration levels are similar to previous measurement in Tokyo, Japan (Kawamura and Yasui, 2005).

Concentrations of total measured α-dicarbonyls varied from 35.5 to 99.5 ng m^{-3} (average value: 51.8 ± 17.9 ng m^{-3}) in PKU and from 29.0 to 61.4 ng m^{-3} (average value: 44.2 ± 10.3 ng m^{-3}) in Yufa. The two simplest α-dicarbonyl compounds (Glyoxal and methylglyoxal) have recently attracted much attention as potential SOA precursors. These compounds are formed by photochemical oxidation of both biogenic (e.g., isoprene and terpenes) and anthropogenic VOCs (e.g., toluene, xylene) (Fick et al., 2004; Volkamer et al., 2001). They have been identified as the significant precursors in the heterogeneous processes for SOA formation (Kroll et al., 2005). High concentrations of glyoxal and methylglyoxal observed indicate the greater SOA formation potential in this region. α-Dicarbonyls levels measured in PKU and Yufa were higher than previous results in other cities of China (average value: 12 ng m^{-3}) (Ho et al., 2007). It indicates that the biogenic sources such as oxidation of isoprene are more important than other urban cities in China.

3.2 Overview of molecular compositions of fatty acids and benzoic acid in PKU and Yufa

Table 1 presents the average concentrations of straight chain saturated fatty acids ($C_{12:0}$-$C_{25:0}$, the first number is carbon-number and the latter one refers to the amount of double bonds), unsaturated fatty acid and benzoic acid. Total measured fatty acids concentrations varied from 459 to 1003 ng m^{-3} (average value: 597 ± 159 ng m^{-3}) in PKU and from 375 to 684 ng m^{-3} (average value: 475 ± 114 ng m^{-3}) in Yufa. The distributions of fatty acids were dominated by even carbon number with maximum at palmitic acid ($C_{16:0}$), followed by stearic acid ($C_{18:0}$). This finding is consistent with previous measurements reported in megacities of China (Fu et al., 2008; Ho et al., 2010). Both natural biogenic and anthropogenic emissions represent the major sources of fatty acids, whereas, homologs $< C_{20}$ are partially released from microbial sources (Simoneit and Mazurek, 1982). Additionally, low MW fatty acids ($< C_{18}$) can be emitted by tire wear debris and traffic exhaust. Biomass burning also produces high fractions of fatty acids which are the major components of plant tissues and surface waxes. $C_{16:0}$ and $C_{18:0}$ were also the major organic compounds emitted from the meat cooking (Schauer et al., 1999, 2002; Zhao et al., 2007a, b). Higher concentrations of fatty acids observed in PKU can be explained by the mixed contributions of regional and local emissions in urban area. Interestingly the contributions of total quantified fatty acids to OC are similar in both sites (3.1% in PKU and 3.2% in Yufa, respectively).

The even-over-odd carbon number preference in fatty acid ($C_{12:0}$ to $C_{25:0}$) is measured by Carbon Preference Index (CPI) :

$$\mathrm{CPI}_{\text{fatty acid}} = \frac{\Sigma \text{ Even carbon number fatty acids}}{\Sigma \text{ Odd carbon number fatty acids}}$$

CPI is a measure to differentiate anthropogenic and biogenic sources and the values are 43.3 in PKU and 45.9 in Yufa, respectively. High CPI values observed in this study indicate that biological sources such as vascular plant has significant influence in this region (Simoneit, 1984).

In this study, $C_{18:1}$ was detected in all samples which can be directly emitted from higher plants and soils. In urban areas, biomass burning and cooking are likely to be the main anthropogenic sources for this acid (Rogge et al., 1993). Its concentrations varied from 2.9 to 33.0 ng m^{-3} (average value: 24.3 ± 8.9 ng m^{-3}) and from 13.0 to 47.9 ng m^{-3} (average value: 24.6 ± 9.2 ng m^{-3}) in PKU and Yufa, respectively. Oleic acid is a good tracer for unsaturated organic aerosol and a representative compound for reactivity model (Rudich et al., 2007). The diagnostic ratio of $C_{18:1}/C_{18:0}$ was used to determine the level of aerosol aging in this study. Low values indicate that the air masses are more aged. The ratios in PKU and Yufa were 0.12 and 0.14, respectively, which suggests that unsaturated fatty acids are depleted by the enhanced photochemical degradation in PKU (Wang et al., 2006). Moreover, the diagnostic ratio of $C_{18:0}/C_{16:0}$ was applied as an indicator for source evaluation. Low ratios observed (< 0.25) in $PM_{2.5}$ were likely originated from wood smoke, waxy leaf surface abrasions, and foliar vegetation combustion; ratios that ranged between 0.25-0.5 were indicated for vehicle exhausts; while ratios that ranged between 0.5–1 were obtained from hamburger charbroiling and paved/unpaved road dust (Oliveira et al., 2007; Rogge et al., 2006). The $C_{18:0}/C_{16:0}$ ratios observed in this study had a range between 0.64 – 1.17 (average value: 0.85 in both locations) in PKU and Yufa, indicating that the contribution of cooking emissions and paved/unpaved road dust cannot be ruled out.

Almost all $PM_{2.5}$ samples collected contained benzoic acid which has been identified as a direct pollutant from the traffic emissions (Kawamura et al., 1985) and a indirect pollutant produced from photo-degradation of aromatic compounds (e.g., toluene) released from traffic exhausts (Suh et al., 2003). The average benzoic acid concentrations were 1496 ± 511 ng m^{-3} in PKU and 1278 ± 372 ng m^{-3} in Yufa, respectively. Although, benzoic acid is semi-volatile organic species and is mainly found in gas phase (Fraser et al., 2003), it can be formed in particulate phase via gas-to-particle partitioning. During ozone episode in August 2006, high concentration of toluene was determined in Beijing (11.4 µg m^{-3}) (Duan et al., 2008), which suggests that oxidation of toluene is one of the significant sources of benzoic acid in the air.

3.3 Less polluted air versus pollution events

Figure 1a and 1b show the temporal variation of mass concentrations of EC, OC and WSOC in PKU and Yufa from 3 to 31 August 2007, respectively. Heavier air pollution events were observed during 3, 5, 9, 15 and 31 August, as reflected by the elevated $PM_{2.5}$ concentrations (i.e., range 96-191 µg m^{-3}, average 124 µg m^{-3} in PKU and range 100-127 µg m^{-3}, average 110 µg m^{-3} in Yufa, respectively). The concentrations of OC, EC, and WSOC significantly increased during these pollution events, but generally decreased for the less polluted air mass events on 7, 13, 21 and 27 August, consistent with lower $PM_{2.5}$ concentrations (i.e., a range of 65-77 µg m^{-3}, average 71 µg m^{-3} in PKU and a range of 39-179 µg m^{-3}, average 62 µg m^{-3} in Yufa, respectively). Similar temporal variations in total quantified bifunctional organic compounds and fatty acids were observed in both PKU and Yufa (Figure 1c and 1d). However, the temporal variation of benzoic acid is different from the other compounds measured, indicating a different source or atmospheric processing for benzoic acid.

Ensemble 3 day air mass back trajectory analysis shows that the pollutants were mainly from northeast, passing over southeast or south of Beijing, during heavier pollution events, whereas they were mainly from north or northwest sector during less pollution events (see Figure 2). South and southeast areas of Beijing are located close to the heavily industrialized areas (e.g., Tianjin city, Shandong and Hebei province) whereas north and northwest areas of Beijing are enclosed by the massive mountain ranges without impact of anthropogenic pollution sources (Ho et al., 2010). As seen in Figures 3a and b, the concentration levels of EC, OC, WSOC, diacids and ketocarboxylic acids in PKU and Yufa are higher for heavier pollution episodes compared to the less polluted air events, suggesting that high emission of carbonaceous aerosols and their precursor gases from neighboring provinces and the subsequent transport to Beijing is one of the major sources responsible for the elevated particulate pollutants in Beijing.

The OC to EC ratio (OC/EC) was used to estimate the transformation and emission properties of carbonaceous aerosol. The average OC/EC ratios at less polluted air (PKU: 2.63; Yufa: 2.19) events were slightly higher those found at the pollution episodes (PKU: 2.52; Yufa: 2.05) at both sites. The slightly lower OC/EC ratio during pollution episodes is likely associated to high combustion emissions, especially from traffic exhaust. The slightly higher OC/EC ratios observed during less polluted air events suggest that secondary formation of OA was critical during less polluted air event. Bendle et al. (2007) reported that the unsaturated-over-saturated C_{18} fatty acids ($C_{18:n}/C_{18:0}$) ratio could be used as a good indicator to estimate the freshness of OM in marine samples. In this study, high ratios were recorded in samples associated with pollution episode, whereas low ratios were observed in less polluted air event with air masses originated from the north and northwest of Beijing. Low ratios observed in less polluted air event represent an aged air mass, indicating longer residence time for particle transformation and transportation (Alves et al., 2007).

Moreover, malonic acid (C_3) can be a byproduct of photochemical breakdown of succinic acid (C_4) in the air. The C_3/C_4 ratio, which was used as a tracer of the enhanced photochemical aging of OA (Kawamura and Ikushima, 1993), observed during less polluted air event was higher than pollution episode in both sites (0.66 versus 0.58 in PKU and 0.57 versus 0.52 in Yufa). Higher C_3/C_4 ratios in less polluted air event suggest that secondary formation of diacids are more significant in less polluted air event, which further indicates secondary photochemical formation of particulate diacids is also critical during less polluted air event.

It should be noted, however, that the concentrations of α-dicarbonyls and benzoic acid in both PKU and Yufa are higher during less polluted air episodes compared to pollution episodes. This indicates that local production or secondary formation could be important source for these compounds. It is known that α-dicarbonyls are intermediate reaction products (via photochemical oxidation) of a wide range of biogenic and anthropogenic VOCs (Galloway et al., 2009). More distant sources lead to longer transport time and therefore to increase chemical oxidation of glyoxal and methylglyoxal to their corresponding acids and further reaction products. This potentially reduces the local contribution of α-dicarbonyls in Beijing. Positive correlation was observed between α-dicarbonyls and benzoic acid ($R^2 = 0.82$ in PKU and $R^2 = 0.65$ in Yufa) at both sites (Figure 4a and 4b), which further suggests that a major fraction of α-dicarbonyls and benzoic acid are most likely produced in the local atmosphere of Beijing through photochemical processing.

3.4 Influence of local traffic on air quality between restriction and non-restriction periods

One goal of this sampling campaign is to study the traffic controls influence on the air quality in Beijing given the use of a large number of vehicles and the resulting high emission of particulate matter and precursor gases. As described above, the level of particulate pollutants in Beijing is significantly influenced by regional transport depending on the wind sector. Therefore, in the following discussion, only events with wind from the same sector (minimizing the difference from regional contribution) but with and without traffic restriction in Beijing are selected to evaluate the effectiveness of local traffic restriction measure on air pollution reduction. Measurements taken on 17 and 19 August represent the restriction events and those taken on 3, 5, 9, 15 and 31 August represent the non-restriction events.

The concentration ratios of the restriction to the non-restriction periods (R/N) are shown in Figure 5. A value of close to unity represents that the restriction does not have any impact in the pollution controls. In PKU, the R/N ratios of EC, OC, WSOC, total diacids, total ketocarboxylic acids and total α-dicarbonyls are much lower than 1, suggesting that these pollutants or their precursors are closely related to the traffic emissions and that the "traffic restriction" measure can reduce primary pollutants (e.g., EC) and the precursors of secondary pollutants (e.g., diacids and α-dicarbonyls). A previous study (Zhang et al., 2011) also indicated the reduction of anthropogenic elements in Beijing during the traffic restriction period of August, 2007. The average OC/EC ratios observed at traffic restriction period (PKU: 2.69) was slightly higher than that found at non-restriction period (PKU: 2.52). The slightly lower OC/EC ratio during non-restriction period was mainly due to the higher EC emissions from traffic exhaust, while EC emissions were reduced during traffic restriction period. However, the R/N ratios of benzoic acid and total fatty acids are higher than 1. A possible explanation for this elevated R/N ratios is that these organics are mainly derived from regional emissions. An alternative is that they are mainly produced from sources other than vehicle emissions. For example, cooking emission that was not controlled under traffic restriction period is a significant source of fatty acids in the air. More household cooking activities can be found if the residents trended to stay home during the restriction period.

The profile of R/N ratio in Yufa is different from that in PKU. The concentrations of OC, WSOC, total diacids and total fatty acids were lower during restriction period than those during non-restriction period, suggesting that the "traffic restriction" measure indeed reduced particulate pollutants. However, the decrease is generally smaller in Yufa compared to that in PKU, indicating that the contribution of local traffic emission to air pollution in Yufa is smaller. The R/N value >1 occurred to EC, total ketocarboxylic acids, total α-dicarbonyls and benzoic acid. An enhanced EC value indicates elevated primary emissions in Yufa during restriction period than non-restriction period. The potential contribution could be local rural emissions (e.g., biomass burning and coal burning) and/or regional transport from polluted neighboring provinces that are closer to Yufa. The average OC/EC ratios at traffic non-restriction period (Yufa: 2.05) events were slightly higher than those found at restriction period (Yufa: 1.89). The lower OC/EC ratios during restriction period further suggest the elevated emissions of EC from sources other than traffic at Yufa.

3.5 Ratios of selected species

The C_3/C_4 ratios measured in this study varied from 0.28 to 0.84 (average value: 0.59) which are close to those measured in Northern China (0.61) (Ho et al., 2007), but higher than that observed from traffic exhausts (0.3-0.5) (Kawamura and Kaplan, 1987). However, the ratios determined in this study are much lower than the marine particles measured from Pacific Ocean, where photochemical processing is commonly more intensive (Kawamura and Sakaguchi, 1999). Higher C_3/C_4 ratios were observed in PKU (0.62) than in Yufa (0.56), additionally, the ratios observed during traffic restriction period were higher than non-restriction periods in both sites (0.65 versus 0.58 in PKU and 0.61 versus 0.52 in Yufa). This result suggests that C_3 is vigorously produced in traffic restriction period by photochemical reaction of C_4 (Kawamura and Ikushima, 1993). Even though variations of the ratio were small, these are sufficiently representatives to any minor rotations and vibrations of emission sources. The results also suggested that secondary formation of diacids by photochemical oxidation was critical during traffic restriction period despite primary exhaust was controlled.

Adipic acid (C_6) is considered as a reaction product of the photochemical oxidation of cyclohexene, whereas C_9 is mainly emitted from unsaturated fatty acids (Hatakeyama et al., 1987; Kawamura and Gagosian, 1987). Therefore C_6/C_9 ratio has been applied to evaluate the abundances of biogenic and anthropogenic sources to OA (Kawamura and Yasui, 2005). C_6/C_9 ratios show higher values in non-restriction period (PKU: 0.40; Yufa: 0.61) than in restriction period (PKU: 0.36; Yufa: 0.38) in this study. Higher C_6/C_9 ratios observed in non-restriction period support that anthropogenic organic compounds, especially from vehicles, are the major source of OA during that period of time.

EC is a major component of vehicle exhaust, whereas C_2 is a major secondary organic species in the air. Therefore, C_2/EC ratio can be used to assess the aging of the air mass. The average C_2/EC ratios were 0.075 and 0.078 at PKU and Yufa, respectively, (which has a range of 0.044 to 0.113), which are much higher than previously reported traffic exhaust ratio (0.0022), but similar to those measured in the air over Shenzhen (0.063 in summer) (Huang and Yu, 2007). The C_2/EC ratios generally showed higher values in restriction period (PKU: 0.081; Yufa: 0.077) than in non-restriction period (PKU: 0.067; Yufa: 0.074). The results are consistent with the notion that the “traffic restriction” measure can reduce primary pollutants (e.g., EC).

Moreover, C_2/total diacids ratio can be applied as an indicator to assess the aging of OA (Kawamura and Sakaguchi, 1999). In this study, the abundances of C_2 in total diacids varied from less than 30% to 54%. Interestingly, the ratios of C_2/total diacids generally showed higher values in restriction period than in non-restriction period. The result indicates that oxalic acid is preferentially formed in restriction period by the oxidation of its precursors (other than anthropogenic VOCs, biogenic VOCs and their oxidation products may serve as important precursors in restriction period) in the atmosphere. Further, ωC_9 is generated by biogenic unsaturated fatty acids oxidation, revealing higher concentrations in restriction period (PKU: 3.47 ng m^{-3}; Yufa: 2.49 ng m^{-3}) than in non-restriction period (PKU: 1.82 ng m^{-3}; Yufa: 2.12 ng m^{-3}) (Yokouchi and Ambe, 1986). This result indicates that biogenic emissions are important source for the formation of ωC_9 in restriction period, which can further breakdown to produce lower molecular weight diacids including C_4, C_3, and C_2. The results further indicate that secondary formation of diacids by atmospheric oxidation was also critical during traffic restriction period despite primary exhaust was controlled.

4. Summary and Conclusions

During the CAREBeijing-2007 in summer, molecular compositions of bifunctional organic compounds, fatty acids and benzoic acid were studied in Beijing. Oxalic acid (C_2) was detected as the most abundant diacid followed by phthalic (Ph) acid. Low MW bifunctional organic compounds were found as the major water-soluble organic fraction, accounting for more than 8.9% and 10.3% of WSOC in PKU and Yufa, respectively. Additionally, total fatty acids and benzoic acid contributed 3.1% and 7.2% of OC in PKU and 3.2% and 9.3% of OC in Yufa, respectively. Bifunctional organic compounds can be released from primary emissions (e.g., traffic exhaust and biomass burning) or formed by atmospheric oxidation of VOCs in the Beijing atmosphere. Both natural biogenic (e.g., microbial) and anthropogenic (e.g., traffic exhaust, cooking) sources provide the major inputs of fatty acids, whereas benzoic acid was mainly formed by the photodegradation of aromatic compounds such as toluene from traffic emission.

The concentrations of OC, EC and WSOC significantly increased during the heavy pollution events, but generally decreased during the less pollution events. Results of back trajectory analyses indicated that the air masses were originated mainly from northeast, passing over heavily populated, urbanized and industrialized areas during the heavy pollution events, whereas they were mainly from mountain clean areas during less pollution events.

In PKU, the restriction to non-restriction period (R/N) ratios of OC, EC, WSOC, total diacids, total ketocarboxylic acids and total α-dicarbonyls were much lower than 1, suggesting that the "traffic restriction" measure can reduce primary pollutants (e.g., EC) and the precursors of secondary pollutants (e.g., diacids and α-dicarbonyls). The R/N ratios of OC, WSOC, total diacids and total fatty acids in Yufa were lower than 1, however, the values are generally larger than those in PKU. Moreover, the R/N value >1 occurred to EC, total ketocarboxylic acids, total α-dicarbonyls and benzoic acid, indicating that there are higher contribution of local emissions (e.g., coal and biomass burning) and/or regional transport from polluted neighboring provinces than local traffic emission in Yufa.

The C_3/C_4, C_2/EC and C_2/total diacids ratios observed during traffic restriction period were higher than those of non-restriction periods at both sites. This result suggests that C_2 and C_3 are secondarily more produced in traffic restriction period by the photochemical oxidation of their precursors, indicating that even when primary exhaust was controlled, secondary photochemical formation of particulate diacids was not controlled during traffic restriction period. This study demonstrates that atmospheric oxidizing capability (photochemical aging) is enhanced by the reduction of atmospheric loading of aerosol particles during the traffic restriction period possibly due to the increased solar radiation reaching to the ground surface.

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Table 1. Concentrations of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls, fatty acids and benzoic acid in $PM_{2.5}$ samples during CAREBeijing 2007.

Compounds	PKU (n=10)			Yufa (n=10)		
(ng m^{-3})	Range	Average	S.D.	Range	Average	S.D.
Dicarboxylic acids						
Oxalic, C2	212-586	435	124	226-632	418	130
Malonic, C3	30.0-73.5	54.9	14.0	17.1-68.6	43.5	15.0
Succinic, C4	52.8-147	89.9	27.7	44.8-129	80.9	26.9
Glutaric, C5	13.7-59.2	36.0	14.4	16.0-168	41.3	46.2
Adipic, C6	15.1-35.1	26.7	6.03	10.8-73.1	24.5	18.1
Pimeric, C7	MDLs-6.44	2.79	2.56	MDLs-3.38	0.34	1.07
Suberic, C8	MDLs	MDLs		MDLs	MDLs	
Azelaic, C9	58.8-85.8	71.4	8.91	37.5-64.6	49.2	8.99
Sebacic, C10	MDLs-3.91	0.69	1.47	MDLs-2.78	0.28	0.88
Undecanedioic, C11	MDLs	MDLs		MDLs	MDLs	
Dodecanedioic, C12	MDLs	MDLs		MDLs	MDLs	
Methylmalonic, iC4	MDLs	MDLs		MDLs	MDLs	
Methylsuccinic, iC5	MDLs-10.6	3.82	2.75	MDLs-5.21	3.05	2.22
2-Methylglutaric, iC6	MDLs-10.5	6.09	2.79	MDLs-8.92	4.80	2.40
Maleic, M	9.18-20.5	15.6	3.39	9.69-17.2	13.5	2.03
Fumaric, F	MDLs	MDLs		MDLs	MDLs	
Methylmaleic, mM	7.52-12.2	9.60	1.40	5.75-8.83	7.21	0.92
Phthalic, Ph	171-250	209	28.9	80.6-415	176	91.5
Isophthalic, iPh	MDLs-15.1	7.27	5.76	MDLs-12.8	4.65	5.22
Terephthalic, tPh	12.2-51.8	30.4	10.1	6.83-53.2	30.9	13.8
Malic, hC4	MDLs-3.21	0.32	1.02	MDLs	MDLs	
Ketomalonic, kC3	2.79-11.8	6.56	2.79	MDLs-10.4	6.67	3.07
4-Ketopimelic, kC7	MDLs-13.0	3.71	5.06	MDLs-11.0	3.21	4.33
Total diacids	599-1287	1010	220	473-1429	909	278
Ketocarboxylic acids						
Pyruvic	17.9-70.2	30.3	15.9	12.7-27.3	20.1	4.18
Glyoxylic, ωC2	49.2-105	72.9	16.1	32.8-81.7	59.7	14.5
3-Oxopropanoic, ωC3	MDLs-3.29	1.53	1.23	MDLs-1.31	0.59	0.62
4-Oxobutanoic, ωC4	5.91-25.0	15.8	5.55	6.59-23.3	15.0	4.83
9-Oxononaoic, ωC9	MDLs-7.28	1.70	2.50	MDLs-5.03	1.61	2.19
Total ketoacids	87.4-169	122	28.8	52.0-131	97.0	22.9
α-Dicarbonyls						
Glyoxal, Gly	1.40-21.4	13.1	5.72	2.93-17.3	11.5	4.04
Methylglyoxal, MeGly	23.3-81.3	38.7	16.2	21.3-51.3	32.7	8.76
Total dicarbonyls	35.5-99.5	51.8	17.9	29.0-61.4	44.2	10.3
Sum of bifunctional species	730-1455	1184	241	554-1621	1050	303
Fatty acids						
Tridecanoic acid, $C_{13:0}$	5.08-16.4	10.8	3.92	MDLs-11.8	7.56	3.31
Tetradecanoic acid, $C_{14:0}$	54.5-97.9	68.7	13.6	36.5-74.0	50.0	13.6
Hexadecanoic acid, $C_{16:0}$	199-393	249	57.0	149-310	201	48.9
Heptadecanoic acid, $C_{17:0}$	MDLs-13.3	4.32	4.53	MDLs-12.8	3.90	5.06
Octadecanoic acid, $C_{18:0}$	134-462	219	94.0	122-237	170	36.6
Octadecenoic acid, $C_{18:1}$	2.91-33.0	24.3	8.93	13.0-47.9	24.6	9.23
Eicosanoic acid, $C_{20:0}$	MDLs-7.84	4.01	3.51	MDLs-7.71	3.28	3.50
Docosanoic acid, $C_{22:0}$	5.69-13.6	9.24	2.43	MDLs-15.4	7.01	4.95
Tetracosanoic acid, $C_{24:0}$	MDLs-10.5	6.51	3.59	MDLs-12.1	7.11	3.09
Sum of fatty acids	459-1003	597	159	375-684	475	114
Benzoic acid	933-2754	1496	511	724-1930	1278	372
$PM_{2.5}$ (µg m^{-3})	64.9-191	103	35.1	38.6-160	98.3	34.1
OC (µg m^{-3})	12.1-19.3	14.9	2.47	4.63-17.0	11.1	3.68
EC (µg m^{-3})	4.48-11.0	6.21	1.90	2.96-8.62	5.57	1.83
WSOC (µg m^{-3})	2.69-8.20	5.59	1.49	1.72-7.16	4.55	1.79

MDL: Method Detection Limit

Figure Captions

Figure 1. Temporal variations of EC, OC, WSOC and various organic compound classes at PKU and Yufa during CAREBeijing-2007 [Note the difference in start time at PKU and Yufa (i.e., the first three days)].

Figure 2. 3-day air mass back trajectories on a) 05 August b) 13 August and c) 17 and 19 August.

Figure 3. Pollution events versus less polluted air at PKU (a and b) and Yufa (c and d), showing the variation of particulate pollutants.

Figure 4. Positive correlation between α-dicarbonyls and benzoic acid observed at PKU (a) and Yufa (b).

Figure 5. The R/N ratio of particulate compounds observed at PKU (a) and Yufa (b)

Figure 1

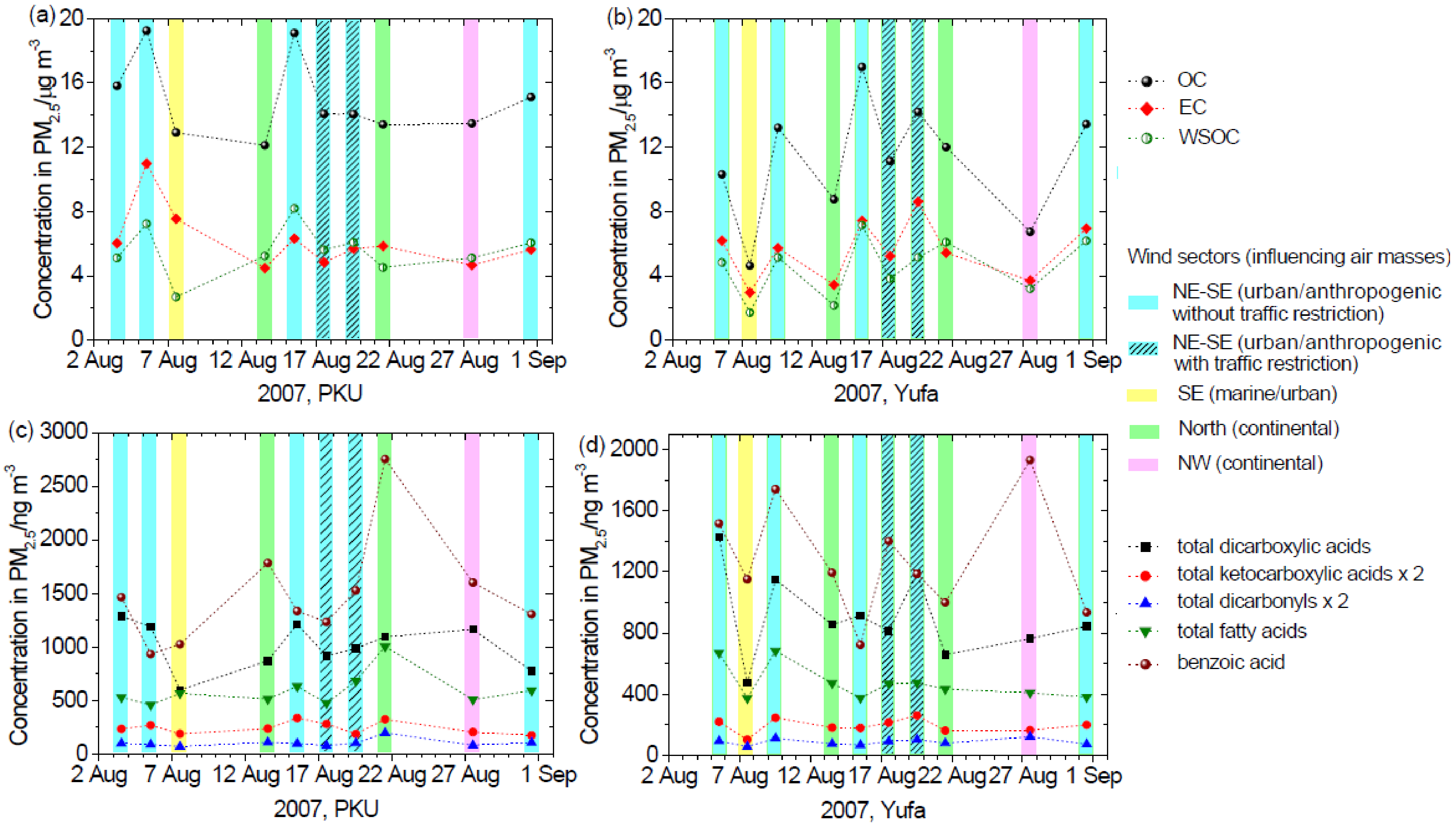

(a)
Concentration in PM$_{2.5}$/µg m^{-3}
0
4
8
12
16
20
2 Aug
7 Aug
12 Aug
17 Aug
22 Aug
27 Aug
1 Sep
2007, PKU
(b)
Concentration in PM$_{2.5}$/µg m^{-3}
0
4
8
12
16
20
2 Aug
7 Aug
12 Aug
17 Aug
22 Aug
27 Aug
1 Sep
2007, Yufa
(c)
Concentration in PM$_{2.5}$/ng m^{-3}
0
500
1000
1500
2000
2500
3000
2 Aug
7 Aug
12 Aug
17 Aug
22 Aug
27 Aug
1 Sep
2007, PKU
(d)
Concentration in PM$_{2.5}$/ng m^{-3}
0
400
800
1200
1600
2000
2 Aug
7 Aug
12 Aug
17 Aug
22 Aug
27 Aug
1 Sep
2007, Yufa
OC
EC
WSOC
Wind sectors (influencing air masses)
NE-SE (urban/anthropogenic without traffic restriction)
NE-SE (urban/anthropogenic with traffic restriction)
SE (marine/urban)
North (continental)
NW (continental)
total dicarboxylic acids
total ketocarboxylic acids x 2
total dicarbonyls x 2
total fatty acids
benzoic acid

Figure 2

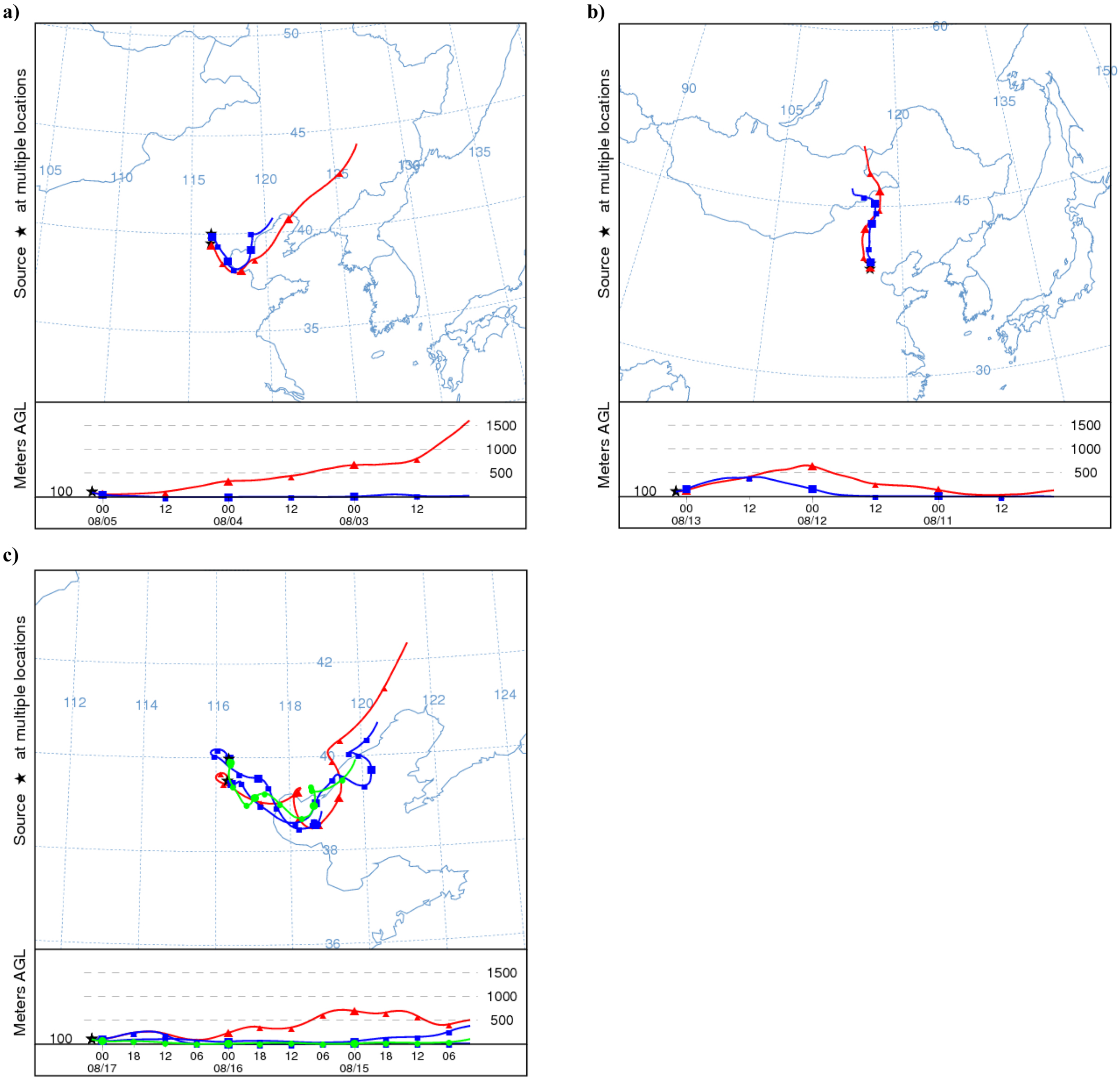

a)
Source ★ at multiple locations
50
45
40
35
105
110
115
120
125
130
135
Meters AGL
1500
1000
500
100
00
12
00
12
00
12
08/05
08/04
08/03
b)
Source ★ at multiple locations
60
45
30
90
105
120
135
150
Meters AGL
1500
1000
500
100
00
12
00
12
00
12
08/13
08/12
08/11
c)
Source ★ at multiple locations
42
40
38
36
112
114
116
118
120
122
124
Meters AGL
1500
1000
500
100
00
18
12
06
00
18
12
06
00
18
12
06
08/17
08/16
08/15

Figure 3

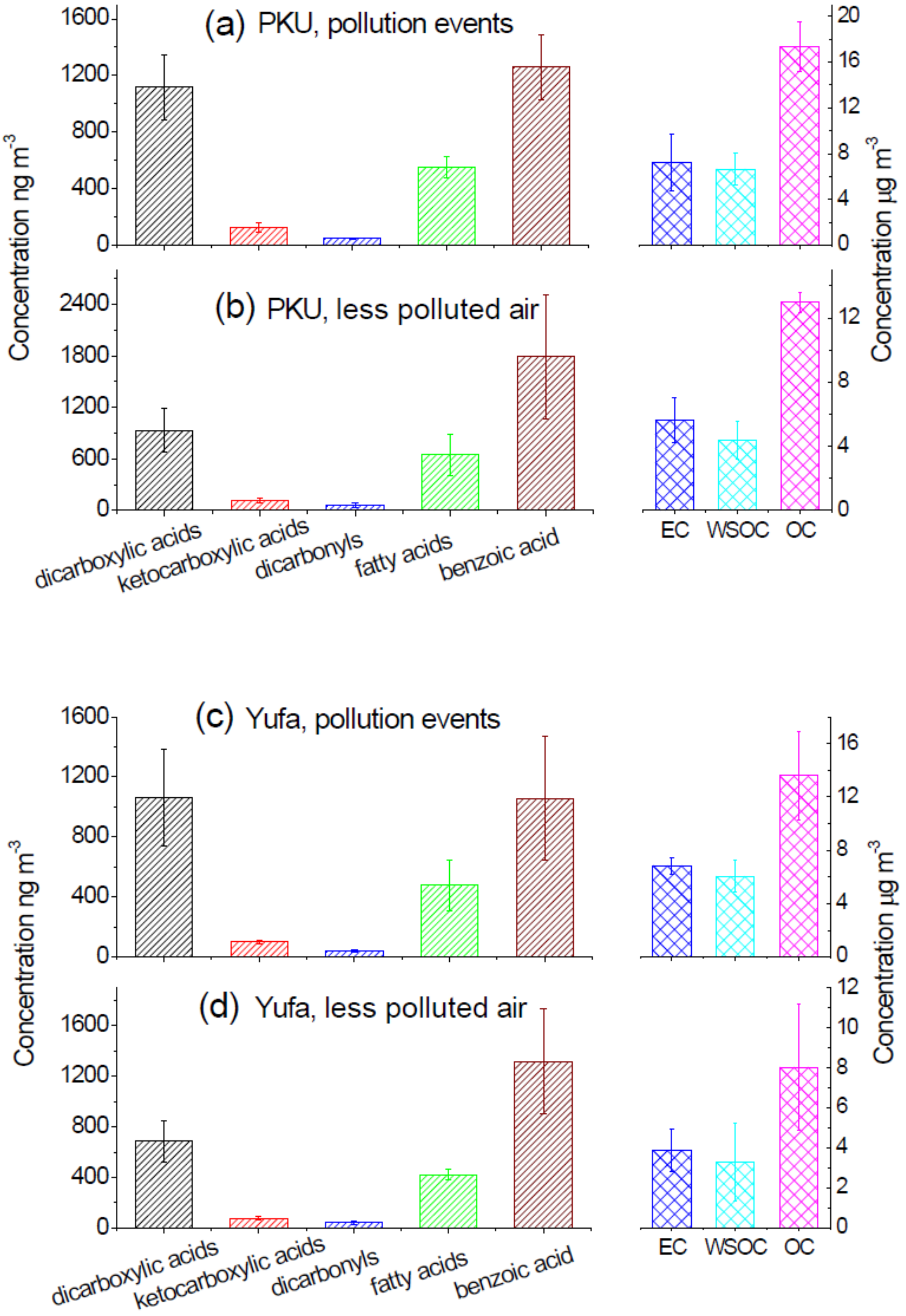

(a) PKU, pollution events
(b) PKU, less polluted air
(c) Yufa, pollution events
(d) Yufa, less polluted air
Concentration ng m-3
Concentration µg m-3
0
400
800
1200
1600
600
1800
2400
4
8
12
16
20
2
6
10
dicarboxylic acids
ketocarboxylic acids
dicarbonyls
fatty acids
benzoic acid
EC
WSOC
OC

Figure 4

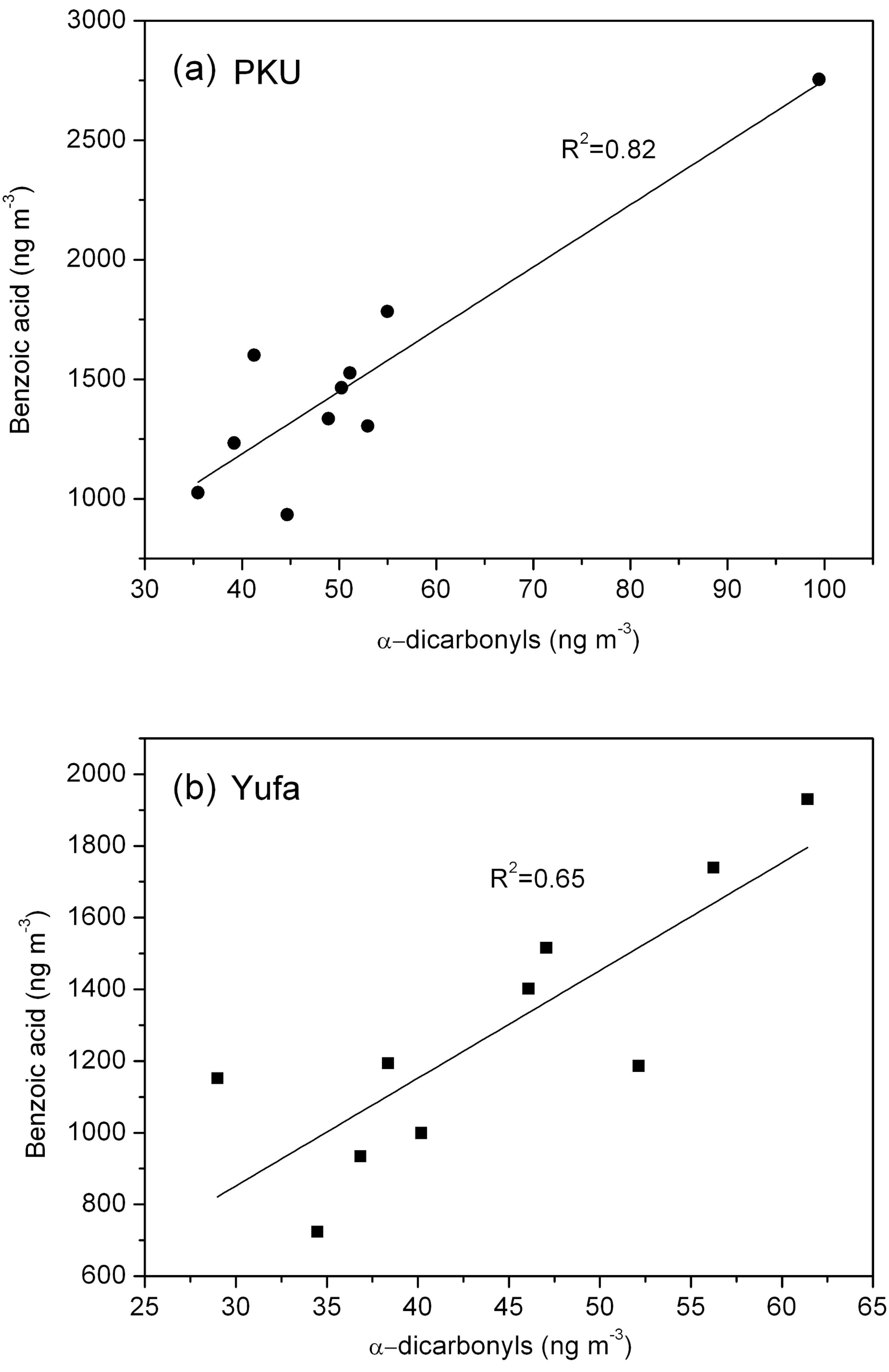
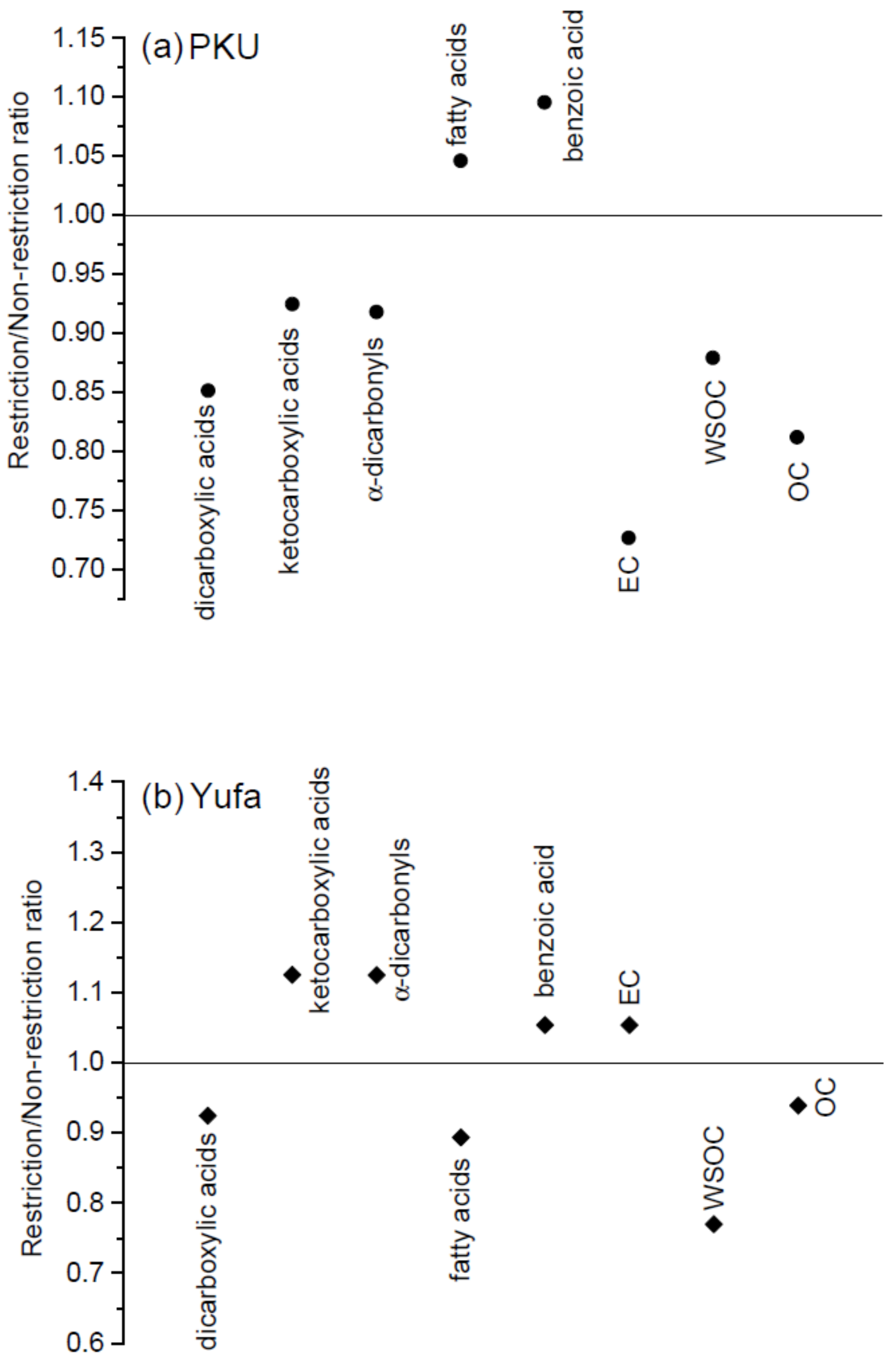

(a) PKU
R^2=0.82
Benzoic acid (ng m^{-3})
1000
1500
2000
2500
3000
30
40
50
60
70
80
90
100
α−dicarbonyls (ng m^{-3})
(b) Yufa
R^2=0.65
Benzoic acid (ng m^{-3})
600
800
1000
1200
1400
1600
1800
2000
25
30
35
40
45
50
55
60
65
α−dicarbonyls (ng m^{-3})

Figure 5


(a) PKU
Restriction/Non-restriction ratio
1.15
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
dicarboxylic acids
ketocarboxylic acids
α-dicarbonyls
fatty acids
benzoic acid
EC
WSOC
OC
(b) Yufa
Restriction/Non-restriction ratio
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
dicarboxylic acids
ketocarboxylic acids
α-dicarbonyls
fatty acids
benzoic acid
EC
WSOC
OC