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Concentrations and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before, during, and after the 2014 APEC

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Abstract. To ensure good air quality for the 2014 Asia-Pacific Economic Cooperation (APEC) summit, stringent emission controls were implemented in Beijing and its surrounding regions, leading to a significant reduction in $PM_{2.5}$ loadings. To investigate the impact of the emission controls on aerosol chemistry, high-volume $PM_{2.5}$ samples were collected in Beijing from 8 October to 24 November 2014 and determined for secondary inorganic aerosols (SIA, i.e., SO_4^{2-}, NO_3^-, and NH_4^+), dicarboxylic acids, keto-carboxylic acid, and α-dicarbonyls, as well as stable carbon isotope composition of oxalic acid (C_2). Our results showed that SIA, C_2, and related secondary organic aerosols in $PM_{2.5}$ during APEC were 2–4 times lower than those before APEC, which is firstly ascribed to the strict emission control measures and secondly attributed to the relatively colder and drier conditions during the event that are unfavorable for secondary aerosol production.

C_2 in the polluted air masses, which mostly occurred before APEC, are abundant and enriched in ^{13}C. On the contrary, C_2 in the clean air masses, which mostly occurred during APEC, is much less abundant but still enriched in ^{13}C. In the mixed type of clean and polluted air masses, which mostly occurred after APEC, C_2 is lower than that before APEC but higher than that during APEC and enriched in lighter ^{12}C. A comparison on chemical composition of fine particles and $\delta^{13}C$ values of C_2 in two events that are characterized by high loadings of $PM_{2.5}$ further showed that after APEC SIA and the total detected organic compounds (TDOC) are much less abundant and fine aerosols are enriched with primary organics and relatively fresh, compared with those before APEC.

1 Introduction

Atmospheric aerosols profoundly impact the global climate directly by scattering and absorbing solar radiation and indirectly by affecting cloud formation and distribution via acting as cloud condensation nuclei (CCN) and ice nuclei (IN). Moreover, atmospheric aerosols exert negative effects on human health because of their toxicity. Due to fast urbanization and industrialization, high levels of atmospheric fine particle ($PM_{2.5}$) pollution have been a persistent problem in many cities of China since the 1990s (van Donkelaar et al., 2010). As the capital of China and one of the largest megacities in the world, Beijing has suffered from frequent severe

haze pollution, especially in winter, affecting more than 21 million people by the end of 2014 (Beijing Municipal Bureau of Statistics, 2015) and causing billions in economic losses (Mu and Zhang, 2013). To improve the air quality, the Beijing government has made many efforts to reduce the pollutant emissions (i.e., SO_2, NO_x, dust, and volatile organic compounds (VOCs)) from a variety of sources. The 2014 Asia-Pacific Economic Cooperation (APEC) summit was hosted in Beijing from 5 to 11 November. To ensure good air quality for the summit, a joint strict emission control program was conducted from 3 November 2014 in Beijing and its neighboring provinces including Inner Mongolia, Shanxi, Hebei, and Shandong provinces. During this period thousands of factories and power plants with high emissions were shut down and/or halted, all the construction activities were stopped, and the numbers of on-road vehicles were reduced. These strict emission controls resulted in the air quality of Beijing during the APEC period being significantly improved, leading to a decrease in $PM_{2.5}$ concentration by 59.2 % and an increase in visibility by 70.2 % in Beijing during the summit compared with those before the APEC (Tang et al., 2015; Z. Wang et al., 2015) and a term of "APEC blue" being created to refer to the good air quality. Such strong artificial intervening not only reduced $PM_{2.5}$ and its precursors' loadings in Beijing and its surrounding areas but also affected the composition and formation mechanisms of the fine particles (Sun et al., 2016).

A number of field measurements have shown that particle compositions in Beijing during wintertime haze periods are dominated by secondary aerosols (Guo et al., 2014; Huang et al., 2014; Xu et al., 2015). Rapid accumulation of particle mass in Beijing during the haze formation process is often accompanied by continuous particle size growth (Guo et al., 2014; Zhang et al., 2015), which is in part due to the coating of secondary organic aerosols (SOA) on pre-existing particles (Li et al., 2010). Several studies have found that SOA production during the 2014 Beijing APEC periods significantly reduced and ascribed this reduction to the efficient regional emission control (Sun et al., 2016; Xu et al., 2015). However, up to now information on the SOA decrease on a molecular level has not been reported.

Dicarboxylic acids are the major class of SOA species in the atmosphere and ubiquitously found from the ground surface to the free troposphere (Fu et al., 2008; Myriokefalitakis et al., 2011; Sorooshian et al., 2007; Sullivan and Prather, 2007). Previous studies have suggested that organic acids including dicarboxylic acids could take part in atmospheric particle nucleation (Zhang et al., 2004; Zhao et al., 2009) and growth processes (Zhang et al., 2012). Furthermore, organic acids may play a central role in the aging of black carbon particles (Xue et al., 2009; Ma et al., 2013), enhancing their roles in air pollution accumulation, and direct radiative forcing (Peng et al., 2016). In the current work we measured molecular distributions of dicarboxylic acids, keto-carboxylic acids and α-dicarbonyls and stable carbon isotope composition of oxalic acid in $PM_{2.5}$ aerosols collected in Beijing before, during, and after the APEC event in order to explore the impact of the APEC emission control on SOA in Beijing. We first investigated the changes in concentration and composition of dicarboxylic acids and related compounds during the three periods, then recognized the difference in stable carbon isotope composition of oxalic acid in different air masses in Beijing during the APEC campaign. Finally we compared the differences in chemical compositions of $PM_{2.5}$ during two heaviest pollution episodes.

2 Experimental section

2.1 Sample collection

$PM_{2.5}$ samples were collected by using a high-volume sampler (TISCH, USA) from 8 October to 24 November 2014 on the rooftop of a three-storey building located on the campus of the China Research Academy of Environmental Sciences, which is situated in the north part of Beijing and close to the fifth ring road. All the $PM_{2.5}$ samples were collected onto pre-baked (450 °C for 8 h) quartz fiber filters (Whatman 41, USA). The duration of each sample collection is 23 h from 08:00 LT of the previous day to 07:00 LT of the next day. Field blanks were also collected before and after the campaign by mounting a pre-baked filter onto the sampler for 15 min without pumping air. After collection, all the filter samplers were individually sealed in aluminum foil bags and stored in a freezer (−18 °C) prior to analysis. Daily values of SO_2, NO_x, and meteorological parameters were cited from the website of Beijing Environmental Protection Agency.

2.2 Sample analysis

2.2.1 Elemental carbon (EC), organic carbon (OC), water-soluble organic carbon (WSOC), inorganic ions, aerosol liquid water content (ALWC) and aerosol acidity

Detailed methods for the analysis of EC, OC, WSOC, and inorganic ions in aerosols were reported elsewhere (Wang et al., 2010). Briefly, EC and OC in the $PM_{2.5}$ samples were determined by using DRI Model 2001 Carbon analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al., 2007). WSOC and inorganic ions in the samples were extracted with Milli-Q pure water and measured by using a Shimadzu TOC-L CPH analyzer and Dionex-600 ion chromatography, respectively (Wang et al., 2010). In the current work, aerosol liquid water content (ALWC) and acidity (i.e., liquid H^+ concentrations, $[H^+]$) of the samples were calculated by using ISORROPIA-II model, which treated the $Na^+-NH_4^+-K^+-Ca^{2+}-Mg^{2+}-Cl^--NO_3^--SO_4^{2-}$ system (Hennigan et al., 2015; Weber et al., 2016).