

# Field observation on secondary organic aerosols during Asian dust storm periods: Formation mechanism of oxalic acid and related compounds on dust surface



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## HIGHLIGHTS

- High concentration of oxalic acid observed during the dust events.
- Oxalic acid, glyoxal and methylglyoxal dominated in coarse particles.
- Aqueous-phase formation of oxalic acid on dust surface.

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## ABSTRACT

Chemical evolution of East Asian dust during transpacific transport has been given much attention for inorganic species such as sulfate, nitrate and ammonium. However, the role of organic species during the transport has almost entirely been ignored. To understand the formation mechanism of secondary organic aerosols (SOA) on dust surfaces, this study investigated the concentrations and compositions of dicarboxylic acids, keto-carboxylic acids,  $\alpha$ -dicarbonyls and inorganic ions in size-segregated aerosols (9-stages) collected in Xi'an, central China during the two dust storm episodes in the springs of 2009 and 2011 and compared with those in nondust storm periods. During the events the ambient particulate dicarboxylic acids were 932–2240 ng m<sup>-3</sup>, which are comparable and even higher than those in nondust periods. Molecular compositions of the above SOA are similar to those in nondust periods with oxalic acid being the leading species. In the presence of the dust storms, all the above mentioned SOA species in Xi'an were predominantly enriched on the coarse particles (>2.1  $\mu$ m), and oxalic acid well correlated with NO<sub>3</sub><sup>-</sup> (R<sup>2</sup> = 0.72,  $p$  < 0.001) rather than SO<sub>4</sub><sup>2-</sup>. This phenomenon differs greatly from the SOA in any other nondust period that is usually characterized by an enrichment of oxalic acid in fine mode and a strong correlation of oxalic acid with SO<sub>4</sub><sup>2-</sup>. We propose a formation pathway to explain these observations, in which nitric acid and/or nitrogen oxides react with dust to produce Ca(NO<sub>3</sub>)<sub>2</sub> and form a liquid phase on the surface of dust aerosols via water vapor-absorption of Ca(NO<sub>3</sub>)<sub>2</sub>, followed by a partitioning of the gas-phase water-soluble organic precursors (e.g. glyoxal and methylglyoxal) into the aqueous-phase and a subsequent oxidation into oxalic acid. To the best of our knowledge, we found for the first time the enrichment of glyoxal and methylglyoxal on dust surface. Our data suggest an important role of nitrate in the heterogeneous formation process of SOA on the surface of dust.

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## 1. Introduction

Dicarboxylic acids are a major class of secondary organic aerosol (SOA) species in the atmosphere and ubiquitously found from the ground surface to the free troposphere (Fu et al., 2008;

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Myriokefalitakis et al., 2011; Wang et al., 2006). A pervasive layer of dicarboxylic acids have been observed as residual particles from evaporated droplets above cumulus clouds over the Gulf of Mexico and Houston, Texas regions (Sorooshian et al., 2007), indicating that dicarboxylic acids are important cloud condensation nuclei (CCN). Oxalic acid is a leading species of dicarboxylic acids. Global tropospheric loading of oxalic acid is 0.2–0.3 Tg, contributing to 5–9% of the atmospheric water-soluble organic carbon burden (Myriokefalitakis et al., 2011). Dicarboxylic acids from primary emission sources such as biomass burning (Meng et al., 2013) and vehicle exhausts (Huang and Yu, 2007) are relatively low, while those in the atmosphere originate largely from photochemical oxidation (Meng et al., 2014; Plath, 2009; Wang et al., 2002, 2010). Dicarboxylic acids can be produced via gas-phase oxidation of volatile organic compounds (VOC) such as aromatics and cyclic alkenes (Hallquist et al., 2009; Kawamura et al., 1996, 2003), but other studies have reported that aqueous-phase chemistry is the predominant formation mechanism for oxalic acid (Carlton et al., 2007; Myriokefalitakis et al., 2011; Warneck, 2003; Yu et al., 2005). For example, Myriokefalitakis et al. (2011) used a 3-D model embedded with an aqueous-phase chemical scheme to simulate global distribution of oxalic acid and concluded that most oxalic acid is formed in-cloud. However, on the ground surface oxalic acid is largely formed in aerosol aqueous-phase (Hallquist et al., 2009). Under this condition water-soluble precursors such as glyoxal and methylglyoxal partition into the aqueous-phase and subsequently oxidize into oxalic acid (Ervens and Volkamer, 2010; Ervens et al., 2011). In addition, larger molecular weight dicarboxylic acids (e.g., malonic and succinic acids) and other compounds in the aqueous-phase can also be photochemically oxidized into oxalic acid (Agarwal et al., 2010; Carlton et al., 2007; Miyazaki et al., 2009; Mochida et al., 2003, 2007; Wang et al., 2012).

Taklimakan and Gobi deserts are the major sources of dust storms in East Asia (McNaughton et al., 2009; Peltier et al., 2008; Uno et al., 2009). Surface dust in these regions can be lofted into the troposphere during spring and early summer by cold front systems and the Mongolia cyclic depression and are transported eastward into the North Pacific (Fairlie et al., 2010; Formenti et al., 2011; Leaitch et al., 2009). During the long-range transport, mineral dust can internally mix with sulfate, nitrate, ammonium, amine and other organic compounds via heterogeneous reaction and/or adsorption (Bahadur et al., 2012; Hanisch and Crowley, 2001a,b; Leaitch et al., 2009; McNaughton et al., 2009; Seinfeld et al., 2004; Wang et al., 2014; Zamora et al., 2011, 2013). Sullivan and Prather (2007) reported a diurnal cycle of oxalic acid in mineral dust in East Asian outflow regions and proposed that the mixing state of oxalic acid was resulted from photochemical oxidation of volatile organic compounds (VOCs), followed by partitioning of the diacids and precursors to the Asian dust with subsequent heterogeneous and aqueous oxidation. Here we present new evidence on the heterogeneous formation of SOA on dust surfaces by investigating dicarboxylic acids ( $C_2$ – $C_{11}$ ) and their precursors (i.e., keto-carboxylic acids and  $\alpha$ -dicarbonyls) in size-segregated particles collected in Xi'an, China during three dust storm events. We first investigate molecular compositions of the diacids and the precursors, as well as inorganic ions, in the samples. Then we identify the changes in their size distributions in the presence of dust via a comparison with those previously observed in nondust periods. Finally, we propose a new mechanism on how the heterogeneous formations of oxalic acid and other related SOA proceed on the dust surface based on the results above and verify the mechanism through the correlation analysis of the species in the dust samples.

## 2. Experimental section

### 2.1. Sample collection

Three sets of size-resolved particles were collected using a 9-stage air sampler equipped with pre-combusted quartz fiber filters at an airflow rate of  $28.3 \text{ L min}^{-2}$ . The cutoff points of particles are 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8, and  $9.0 \mu\text{m}$ , respectively. The air sampler was set on the rooftop of a three-story building (about 12 m above ground) in the urban center of Xi'an, China (Fig. 1). Two massive dust storm episodes occurred in Xi'an on April 24th, 2009 (named DSI) and on March 29th–30th, 2011 (named DSII). One set of the size-resolved samples was collected during the DSI event for 10 h (8:00–18:00), and the other two sets of the samples were collected during the DSII periods each lasting for 12 h (18:00–6:00 named DSII-1 and 7:00–19:00 named DSII-2). Two sets of field blank samples were collected after the sampling and treated similarly as the dust samples. The mass of particles on each filter was determined by weighing the filter mass before and after sampling using a Sartorius MC5 electronic microbalance (Sartorius, Göttingen, Germany) with  $\pm 1 \mu\text{g}$  sensitivity after 48 h equilibration in a glass chamber ( $25 \pm 0.5 \text{ }^\circ\text{C}$ ,  $35 \pm 2\% \text{ RH}$ ). All the sample filters were sealed individually in an aluminum foil bag and stored at  $-20 \text{ }^\circ\text{C}$  prior to analysis. Meteorological parameters were measured hourly (Table 1). Based on the 72h-backward trajectories of air masses arriving in Xi'an at the mid-time point of the three sampling periods (Fig. 1) (Calculated by the US NOAA Hysplit Model), we found that air masses during the DSI event originated from the eastern part of the Gobi desert and traveled across the North China Plain (NCP), while air masses during the DSII-1 and DSII-2 periods originated from the Taklimakan desert and the western part of the Gobi desert, respectively, and moved eastward.

### 2.2. Sample analysis

#### 2.2.1. Inorganic ions, water-soluble organic carbon (WSOC) and water-soluble inorganic carbon (WSIC)

Analytical methods for inorganic ions, WSOC and WSIC were reported elsewhere (Wang et al., 2010, 2011). Briefly, one fourth of each filter was cut into pieces and extracted with Milli-Q pure water for three times each in 15 min under ultrasonication. Then the combined extracts were determined for inorganic ions using an ion chromatograph (Dionex-600) and for WSOC and WSIC using a Shimadzu TOC/N-5000 analyzer.

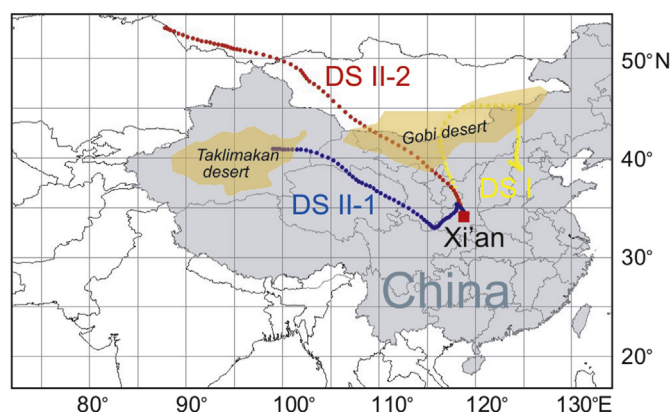


Fig. 1. A map description of the location of Xi'an, central China and 72h-backward trajectories of air masses arriving in Xi'an during the dust events.

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