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# Concentration and size distribution of particulate oxalate in marine and coastal atmospheres – Implication for the increased importance of oxalate in nanometer atmospheric particles

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## HIGHLIGHTS

- ~80% of particulate oxalate mass existed in atmospheric particles >100 nm.
- Oxalate in 0.01–0.056 μm particles were increased on the NPF-event days.
- The mass ratio of oxalate to sulfate were greatly increased in particles <56 nm.
- The study of particulate oxalate should concentrate in the nanometer size range.

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## ABSTRACT

In literature, particulate oxalate has been widely studied in the total suspended particles (TSP), particles <10 μm or 2.5 μm ($PM_{10}$ and $PM_{2.5}$) and size-segregated particles >100 nm. In this article, we measured oxalate's concentrations in size-segregated atmospheric particles down to 10 nm or 56 nm during eight campaigns performed at a semi-urban coastal site, over the marginal seas of China and from the marginal seas to the northwest Pacific Ocean (NWPO) in 2012–2015. When the sum of the oxalate's concentration in particles <10 μm was used for intercomparison, the lowest average values of 0.05–0.06 μg $m^{-3}$ were observed during the two campaigns performed at NWPO. The highest average value of 0.38 μg $m^{-3}$ was observed at the coastal site during a heavy pollution event. Mode analysis results of particulate oxalate and the correlation between oxalate and sulfate suggested that the elevated concentrations of oxalate in $PM_{10}$ were mainly related to enhanced in-cloud formation of oxalate via anthropogenic precursors. Size distribution data in the total of 136 sets of samples also showed approximately 80% of particulate oxalate's mass existing in atmospheric particles >100 nm. Consistent with previous studies, particulate oxalate in particles >100 nm was a negligible ionic component when comparing to particulate $SO_4^{2-}$ in the same size range. However, the mole ratios of oxalate/sulfate in particles <100 nm were generally increased by 1–2 orders of magnitude. In approximately 30% of the samples, the mole ratios in atmospheric particles <56 nm were larger than 0.5. Moreover, during Campaign 5, the oxalate's concentrations in <56 nm particles were substantially increased on the days in presence of new particle formation events. These results strongly imply the importance of oxalate in nanometer atmospheric particles, but not in >100 nm atmospheric particles such as $PM_{2.5}$, $PM_{10}$, TSP, etc.



## 1. Introduction

Oxalic acid is the most abundant dicarboxylic acid in the atmosphere (Legrand et al., 2007; Mochida et al., 2007; Wang et al., 2002), except in the Polar Regions where malonic acid dominates (Kawamura and Bikkina, 2016). Dicarboxylic acids and/or their salts

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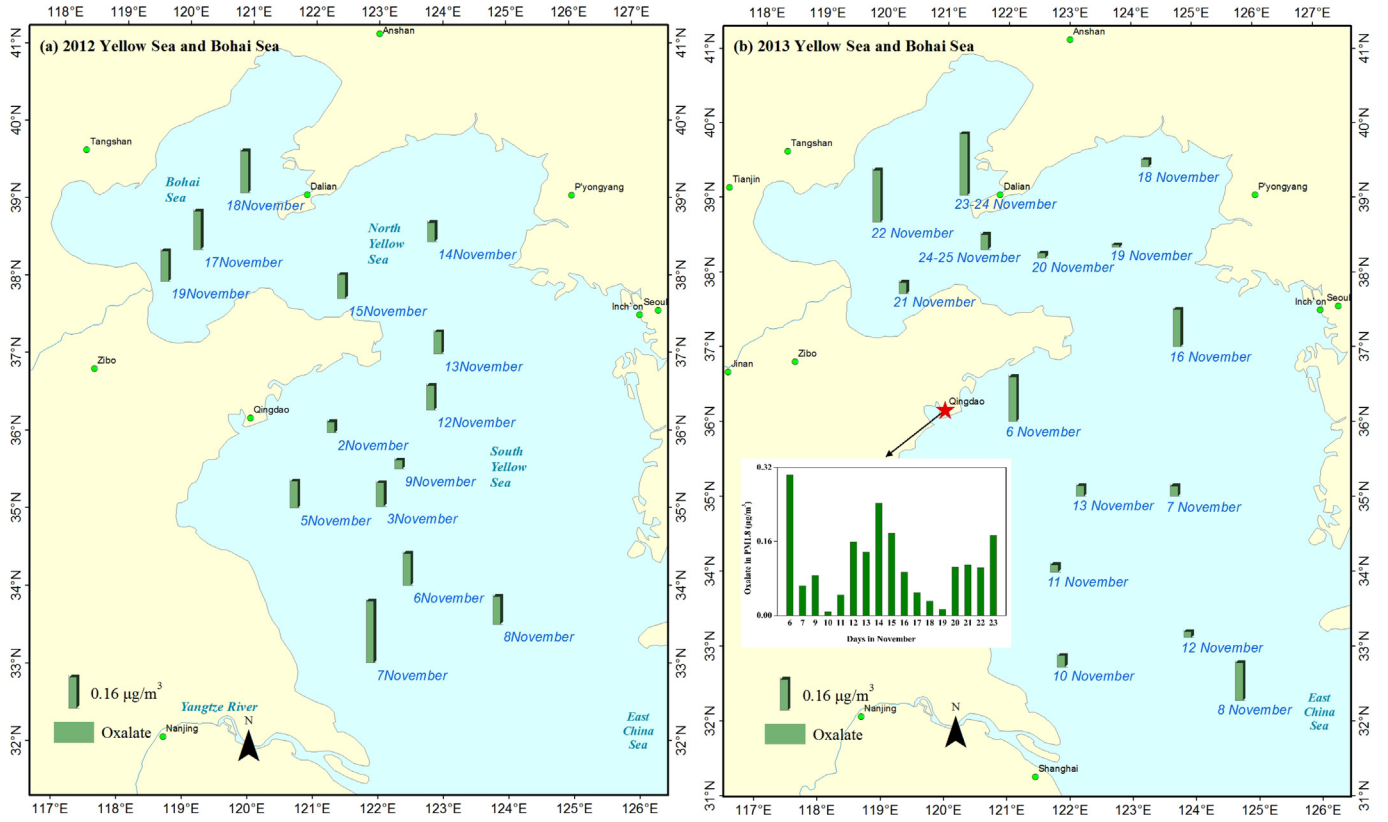


**Fig. 1.** Geographical distributions of oxalate in mass concentration in $PM_{1.8}$ measured over the SYS, NYS and BS in November 2012 and 2013 (a: Campaign 5; b: Campaign 6; red pentagram represented the semi-urban sampling site in Qingdao, Campaign 2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in atmospheric particles potentially play an important role as cloud condensation nuclei (CCN) in the global atmosphere (Kroll and Seinfeld, 2008; Ervens et al., 2011). Oxalic acid has also been reported to act as heterogeneous ice nucleus in the upper troposphere and to affect the climate (Zobrist et al., 2006). In the particle phase, most of oxalic acid was reported to be neutralized as oxalate salts (Yang and Yu, 2008). In this study, we used particulate oxalate to represent the measured oxalate salts and oxalic acid in atmospheric particles if not specified. Concentrations of particulate oxalate ranged from several tens of nanograms per cubic meter in clean marine atmospheres (Baboukas et al., 2000; Legrand et al., 2007; Miyazaki et al., 2010) to several thousands of nanograms per cubic meter in polluted atmospheres (Biswas et al., 2008; Li and Yu, 2010; Souza et al., 1999; Yang et al., 2014). Particulate oxalate can be derived from secondary formation and/or primary emissions in the atmosphere (Ervens, 2004a, b; Falkovich et al., 2005; Kawamura and Bikkina, 2016; Kawamura and Kaplan, 1987; Narukawa et al., 1999; Yang et al., 2014; Yao et al., 2002; Yu et al., 2005). Myriokefalitakis et al. (2011) recently modeled particulate oxalate in the global troposphere and proposed that in-cloud oxalate formation can well explain the observed particulate oxalate, except in urban atmospheres.

When we reviewed studies of particulate oxalate in literature, we found that most of studies focused on total suspended particles (TSP), particles in aerodynamic diameter less than 10 μm ($PM_{10}$), or less than 2.5 μm ($PM_{2.5}$) and size-segregated particles with aerodynamic diameter larger than 100 nm. Although particulate oxalate is highly hygroscopic, the concentration of particulate oxalate is much lower when comparing to those of sulfate and nitrate (Feng et al., 2012; Sorooshian et al., 2007; Wang et al., 2006; Yao et al., 2003a, b; Zhao and Gao, 2008; Zhou et al., 2015). For example, Zhou et al. (2015) recently summarized the mass ratio of oxalate/sulfate in $PM_{2.5}$ around the world, including urban, rural, marine atmospheres and aircraft observations. The maximum ratio value was only 0.12 with the median value of 0.06. The small ratio raises a concern on the importance of particulate oxalate in the atmosphere. However, Paciga et al. (2014) recently reported that ammonia dramatically lowered the vapor pressure of oxalic acid by several orders of magnitude. The result implies that ammonium oxalate can overcome Kelvin Effect and may stably exist in nanometer atmospheric particles. Hsieh et al. (2009) once reported a larger mass ratio of oxalate/sulfate (0.4–0.8) in particles less than 100 nm during high particulate pollution episodes in Taiwan. In addition, new particle formation is considered to be an important source of atmospheric particles in the nanometer size range. Previous experimental and theoretical studies show that carboxylic acids can reduce the nucleation barrier and enhance new particle formation (Zhang et al., 2012). The previous studies and the new findings by Hsieh et al. (2009) and Paciga et al. (2014) motivate an examination for the oxalate's concentrations in nanometer particles in various atmospheres.

In this study, we used two types of Micro-Orifice Uniform Deposition Impactors (MOUDI) samplers to collect atmospheric particles from 18 μm to 10 nm or from 18 μm to 56 nm. Particulate oxalate and inorganic ions were extracted by deionized water and chemically determined using ion chromatographs. Thus, particulate oxalate in nanometer, submicron meter and supermicron meter size ranges can be studied and compared. To investigate the importance of oxalate's concentrations in nanometer particles in various atmospheres, the data measured during eight campaigns,