

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

# Characteristics, sources and formation of aerosol oxalate in an Eastern Asia megacity and its implication to haze pollution

Y. Jiang<sup>1</sup>, G. Zhuang<sup>1</sup>, Q. Wang<sup>1</sup>, T. Liu<sup>1</sup>, K. Huang<sup>1,2</sup>, J. S. Fu<sup>2</sup>, J. Li<sup>1</sup>, Y. Lin<sup>1</sup>, R. Zhang<sup>1</sup>, and C. Deng<sup>1</sup>

<sup>1</sup>Center for Atmospheric Chemistry Study, Department of Environmental Science and Engineering, Fudan University, Shanghai, 200433, China

<sup>2</sup>Department of Civil and Environmental Engineering, The University of Tennessee, Knoxville, TN 37996, USA

Received: 15 July 2011 – Accepted: 28 July 2011 – Published: 4 August 2011

Correspondence to: G. Zhuang (gzhuang@fudan.edu.cn),  
J. S. Fu (jsfu@utk.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

A total of 238 samples of PM<sub>2.5</sub> and TSP were analyzed to study the characteristics, sources, and formation pathways of aerosol oxalate in Shanghai in four seasons of 2007. The concentrations of oxalate were 0.07–0.41 μg m<sup>-3</sup> in PM<sub>2.5</sub> and 0.10–0.48 μg m<sup>-3</sup> in TSP, respectively. Oxalate displayed a seasonal variation of autumn>summer>winter>spring in both PM<sub>2.5</sub> and TSP and was dominantly present in PM<sub>2.5</sub> in all samples. Correlation between oxalate and K<sup>+</sup> and high ratio of oxalate/K<sup>+</sup> suggested that biomass burning was a secondary source of aerosol oxalate in Shanghai, in addition to urban VOCs sources (vehicular and industrial emissions), especially in autumn. Secondary formation accounted for the majority of aerosol oxalate in Shanghai, which was supported by the high correlation of oxalate with nss-SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup> and NO<sub>3</sub><sup>-</sup>, proceeding from different mechanisms. Relatively high ambient RH together with high cloud cover was found benefiting the secondary formation of aerosol oxalate. The in-cloud process (aqueous-phase oxidation) was proposed to be likely the major formation pathway of aerosol oxalate in Shanghai, which was supported by the high correlation of oxalate with nss-SO<sub>4</sub><sup>2-</sup> and K<sup>+</sup>, dominant residence of oxalate in droplet mode and result of favorable meteorological condition analysis. High correlation of oxalate and NO<sub>3</sub><sup>-</sup> reflected the OH radical involved oxidation chemistry of the two species in the atmosphere and also suggested that gas-particle surface reactions and evaporation-condensation process were both possible secondary formation pathways of aerosol oxalate in coarser particle mode (>1.0 μm). Aerosol oxalate contributed to the haze pollution and visibility degradation of the local environment. As a major water-soluble organic compound in aerosols, concentration of oxalate showed a distinct negative correlation to the atmospheric visibility, which implied that aerosol organic compounds could play an important role in air quality in Shanghai.

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## 1 Introduction

Oxalic acid, with oxalate, has attracted a great deal of attention as the most abundant dicarboxylic acid in the tropospheric aerosols (Kawamura and Ikushima, 1993; Facchini et al., 1999a; Mader et al., 2004). As a major identified water-soluble organic compound in aerosol, oxalate could affect hygroscopic properties of aerosol particles (Cruz and Pandis, 1998; Brooks et al., 2002; Kumar et al., 2003). It can act as cloud condensation nuclei (CCN) or reduce the surface tension of particles to form CCN (Facchini et al., 1999b; Kerminen, 2001); the refractive index of aerosol particles can be influenced by the presence of oxalate and further their radiative forcing estimates. Oxalate may also play a role in solubility, photochemistry and bioavailability of transition metals in aerosols (Deguillaume et al., 2005; Jickells et al., 2005).

The sources and formation pathways of aerosol oxalate are still under investigation. Oxalate can be emitted directly from fossil fuel combustion, biomass burning, and biogenic activity. However, many studies suggested the existence of a global secondary source in addition to the primary sources of the compound (Kawamura et al., 1995; Kawamura and Sakaguchi, 1999; Kerminen et al., 2000; Yao et al., 2002a). A large fraction of aerosol oxalate is considered to be produced from radical involved chemical/photochemical oxidation of volatile organic compounds (VOCs) like ethene, toluene, isoprene, etc. (Warneck, 1999; Carlton et al., 2007a; Sullivan et al., 2007). Based on some observations, the maximum oxalate concentrations appeared in the droplet mode at 0.54–1.0  $\mu\text{m}$  with MMAD (mass median aerodynamic diameters) at 1.0  $\mu\text{m}$  (Yao et al., 2002a; Huang et al., 2006). In-cloud process and oxidation of gaseous precursors followed by condensation are the two major suggested secondary formation pathways of aerosol oxalate in the fine particle mode (Seinfeld and Pandis, 1998; Blando and Turpin, 1999; Yao et al., 2002a, 2003; Crahan et al., 2004). A close tracking of oxalate and sulfate in the atmosphere has been observed in some studies, which suggested a similar dominant formation pathway of the two chemically distinct species (Yu et al., 2005; Sorooshian et al., 2006). Martinelango et al. (2007) discovered parallel formation

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pathways of oxalate and nitrate in a coastal atmosphere.

Shanghai (31° 13' N, 121.° 28' E) is located in the western coast of the North Pacific Ocean, east front of the Yangtze River Delta, China. It is one of the largest, urbanized and motorized cities in China with a population of ~19 000 000. Shanghai has the marine monsoon subtropical climate with an annual average precipitation of ~1100 mm (<http://cdc.cma.gov.cn>). Under the influence of the monsoon system, one year in Shanghai is usually divided into the hiemal half-year from November to April with prevailing northwesterly continental wind and the estival half-year from May to October with prevailing southeasterly wind from the North Pacific Ocean (Yin and Tan, 2003). For the past decade the air quality has been terribly degraded due to the rapid motorization, and the heavy haze has been the frequent weather pattern in Shanghai. Organic acids, including oxalic acid, with the organic aerosol have been considered as one of major components of haze. In this paper we report the concentration levels, seasonal variation and relative distribution of aerosol oxalate in  $\text{PM}_{2.5}$  and TSP, as well as the possible sources and formation pathways of aerosol oxalate. The relationships between oxalate, meteorological factors and the regional haze pollution are also discussed.

## 2 Experiment

### 2.1 Sampling

Aerosol samples of  $\text{PM}_{2.5}$  and TSP were collected in four seasons in 2007 in Shanghai. The sampling site was on the roof (~15 m) of a building at Fudan University, located in the urban area of Shanghai. Samples were collected on Whatman 41 polycarbonate filters (Whatman Inc., Maidstone, UK, diameter: 90 mm) by a medium-volume sampler (Model: (TSP/ $\text{PM}_{10}$ / $\text{PM}_{2.5}$ )-2, flow rate: 76.67  $\text{l min}^{-1}$ ). Sampling was carried out approximately in 24-h intervals. The sampling period were chosen to represent the different seasons: (1) 20 March–20 April 2007, spring; (2) 23 July–19 August 2007,

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summer; (3) 1 November–29 November 2007, autumn; (4) 24 December 2007–26 January 2008, winter. Polycarbonate filters were put in the sampler at the sampling site for 24 h (without pumping) and used as the blanks. Four blanks were collected in every season. Samples were placed in polyethylene plastic bags with artificial parchment lining bags right after sampling and reserved in a refrigerator ( $-18^{\circ}\text{C}$ ). All of those filters were weighed before and after sampling with an analytical balance (Sartorius 2004 MP, reading precision  $10\ \mu\text{g}$ ) after stabilizing under constant temperature ( $20 \pm 1^{\circ}\text{C}$ ) and humidity ( $40 \pm 2\%$ ). A total of 238 aerosol samples were collected and used in this study. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

Black carbon (BC) measurement was conducted before series of chemical analysis. The concentration of BC in the aerosol samples was measured by a smoke stain reflectometer (model 43D, Diffusion Systems Ltd., London, UK). Five spots on each complete sample filter were selected randomly and evenly as possible for the measurement of BC contents which were calculated from comparing the reflectance of the sample filter with that of a clean filter (Taha et al., 2007).

## 2.2 Chemical analysis

### 2.2.1 Ion analysis and pH measurement

One-fourth of each aerosol sample filter and blank filter was extracted ultrasonically by 10 ml water, which was deionized to the resistivity of  $18\ \text{M}\Omega\ \text{cm}^{-1}$ . After passing through the microporous membranes (mixed cellulose, pore size,  $0.45\ \mu\text{m}$ ; diameter, 25 mm), each filtrate was stored at  $4^{\circ}\text{C}$  in a clean tube for analysis. The concentrations of ten anions ( $\text{F}^{-}$ ,  $\text{CH}_3\text{COO}^{-}$ ,  $\text{HCOO}^{-}$ , MSA,  $\text{Cl}^{-}$ ,  $\text{NO}_2^{-}$ ,  $\text{NO}_3^{-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) and five cations ( $\text{Na}^{+}$ ,  $\text{NH}_4^{+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) in the aqueous extracts were determined by Ion Chromatography (IC, Dionex 3000, USA). The gradient base eluent ( $76.2\ \text{mm}\ \text{NaOH} + \text{H}_2\text{O}$ ) was used for anion detection, while the weak acid eluent ( $20\ \text{mM}\ \text{MSA}$ ) for cation detection. The oxalate concentrations of the blanks were below detection

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limit or under  $0.02\ \mu\text{g}\ \text{m}^{-3}$  and had been deducted from the observation values. The recovery of ions was in the range of  $80\%$ – $120\%$  by adding standard reference material of each ion component into the filtrates for ion chromatography analysis. Reproducibility test showed that relative standard deviation was less than  $5\%$  by calculating from the results of ion chromatography detections of one sample at different times (under same analytical condition). The quality assurance was routinely carried out by using Standard Reference Materials produced by National Research Center for Certified Reference Materials, China. A pH meter (model: LIDA PHS-2C) combined with a glass electrode was used for pH measurement of the filtrates for ion chromatography analysis. The pH meter was calibrated before measurement using standard buffer solutions with pH values of 4.00 and 6.86. Detailed procedures were given elsewhere (Yuan et al., 2003).

### 2.2.2 Element analysis

Half of the sample and blank filter was digested at  $170^{\circ}\text{C}$  for 4 h in high-pressure Teflon digestion vessel with 3 ml concentrated  $\text{HNO}_3$ , 1 ml concentrated  $\text{HCl}$  and 1 ml concentrated  $\text{HF}$ . After cooling, the solutions were dried, then added 0.1 ml concentrated  $\text{HNO}_3$  and diluted to 10 ml with MilliQ water (resistivity of  $18\ \text{M}\Omega\ \text{cm}^{-1}$ ). A total of 19 elements (Al, Fe, Mn, Mg, Ti, Sc, Na, Sr, Ca, Co, Cr, Ni, Cu, Pb, Zn, Cd, V, S and As) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Model: ULTIMA, JOBIN-YVON Company, France). The detailed analytical procedures were given elsewhere (Zhuang et al., 2001; Sun et al., 2004). Al was used as the reference element of crustal source in this study.

### 2.2.3 Meteorological conditions and sampling artifact

The meteorological data, including temperature, relative humidity (RH), cloud cover, wind speed, visibility and atmospheric pressure were downloaded from <http://www.arl.noaa.gov> and <http://wunderground.com>. The daily average concentrations of ambient

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gaseous  $\text{SO}_2$  and  $\text{NO}_2$  in Shanghai were obtained from <http://www.semc.gov.cn>.

The extent of the sampling artifact strongly depended on the volatility of the compounds, the aerosol acidity, the ambient temperature and relative humidity (Clegg et al., 1996; Souza et al., 1999; Limbeck et al., 2001; Pathak and Chan, 2005). The vapor pressure of oxalate is  $<20$  mm Hg at  $20^\circ$  which reflects a low volatility of this compound. Low ambient temperature, low aerosol acidity and high relative humidity would make oxalate in the atmosphere be more associated with particles. The aerosols in Shanghai are known to be acidic due to the high concentration of  $\text{SO}_2$  and  $\text{NO}_x$  (Fu et al., 2008). Results of our measurement also showed that the pH of aerosol filtrates in Shanghai averaged at 3.96–5.41 (Table 1). However, the temperature of the ambient atmosphere in Shanghai was moderate except in summer and the average RH was above  $\sim 65\%$  throughout the year. Consequently, the oxalate detected in the aerosol samples are expected to be able to represent the characteristics of the majority of the atmospheric oxalate and its measurement in this work is considered not affected by sorption or desorption artifacts under the local condition of Shanghai.

### 3 Results and discussion

#### 3.1 Characteristics of aerosol oxalate in Shanghai

##### 3.1.1 Concentration Level, seasonal variation and relative distribution of oxalate in $\text{PM}_{2.5}$ and TSP

Average concentrations of oxalate in Shanghai both in  $\text{PM}_{2.5}$  and TSP were presented in Table 2. For comparison, oxalate mass concentrations of some other sites over the world were also listed in Table 2.

The oxalate concentrations in Shanghai in 2007 sampling year were  $0.07\text{--}0.41 \mu\text{g m}^{-3}$  in  $\text{PM}_{2.5}$  and  $0.10\text{--}0.48 \mu\text{g m}^{-3}$  in TSP, respectively. The oxalate concentrations in  $\text{PM}_{2.5}$  were a little lower than the value measured in 1999–2000 by Yao

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et al. (2002b). Table 2 showed that the concentrations of oxalate in Shanghai were lower than those in Beijing and Hong Kong, but comparable to those in Nanjing, Tokyo, Chiba, Tampa Bay and LA. The higher levels of oxalate in Beijing may be explained by its heavy traffic emissions and winter heating system, while the high relative humidity and thick cloud cover may be responsible for the high values in Hong Kong.

The seasonal variation of oxalate concentrations in  $\text{PM}_{2.5}$  and TSP samples collected in 2007 were showed in Table 3. The average concentrations of oxalate indicated a seasonal variation of autumnsummerwinterspring in both  $\text{PM}_{2.5}$  and TSP. Their contributions to the total mass of the aerosols displayed in a slightly different order as summer>autumn>spring>winter. Since the production of aerosol oxalate in the atmosphere is generally a radical (mainly hydroxyl radical) related photo-oxidation or chemical oxidation process (Warneck, 1999; Sorooshian et al., 2006; Martinelango et al., 2007), the high concentrations of oxalate in summer and autumn can be attributed to the generally high ambient temperature and more solar radiation in these two seasons.

The relative distribution of oxalate and several selected inorganic ions between  $\text{PM}_{2.5}$  and TSP in each season were analyzed. As shown in Figure 1, oxalate was mainly present in the fine particle mode. The value of  $\text{PM}_{2.5}/\text{TSP}$  of oxalate concentration reached its peak in summer, up to 0.88. According to the data from our online monitoring of  $\text{PM}_{2.5}$  and  $\text{PM}_1$  in the same sampling site, the ratios of mass concentration of  $\text{PM}_1$  to that of  $\text{PM}_{2.5}$  averaged at 80% in 2009 in Shanghai which suggested that aerosol oxalate probably dominated in finer particles ( $<1.0 \mu\text{m}$ ). This is consistent with the results of previous studies, in which majority of aerosol oxalate was found appeared in the droplet mode ( $\sim 0.7\text{--}2.0 \mu\text{m}$ ) with a MMAD around  $1.0 \mu\text{m}$ , while small fraction of it distributed in the coarse mode ( $>2.0 \mu\text{m}$ ) and condensation mode ( $\sim 0.1\text{--}0.7 \mu\text{m}$ ) (Yao et al., 2002a; Huang et al., 2006; Martinelango et al., 2007).

It could also be seen clearly in Figure 1 that nss-sulfate (non sea salt sulfate), ammonium and potassium reside dominantly in  $\text{PM}_{2.5}$  rather than in TSP in all four seasons, with an exception of nitrate. The ratios of  $\text{PM}_{2.5}$  to TSP of nitrate concentration were

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near to 0.5 which may be explained by the high volatility of nitric acid/nitrate and the coastal environment of Shanghai. Gaseous nitric acid ( $\text{HNO}_3$ ) and nitrate ( $\text{NO}_3^-$ ) bound to aerosol particles coexist in the atmosphere. Nitrate in the aerosols can exist in the forms of  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ , etc., depending on the category and concentration of gaseous and aerosol species which nitric acid can obtain to combine with. In the coastal area, the abundant atmospheric sea salt aerosols can partition gas-phase nitric acid to particle- or aqueous-phase  $\text{NaNO}_3$  (Dasgupta et al., 2007). Most of the newly formed  $\text{NaNO}_3$  still reside in coarse particles of sea salt which consequently increased the  $\text{PM}_{2.5}/\text{TSP}$  ratio of nitrate in Shanghai. Martinelango et al. (2007) indicated a high ratio of  $\text{PM}_{10}/\text{PM}_{2.5}$  of nitrate in a coastal environment, while studies carried in Hong Kong (Zhuang et al., 1999; Yao et al., 2002a) also observed a dominant coarse mode of nitrate. More nitric acid would partition to gas phase under hot and acidic ambient environment, which means more coarse mode nitrate could be produced from the gas phase through the sea salt conversion. From our observation, the two lowest  $\text{PM}_{2.5}/\text{TSP}$  ratios of nitrate appeared in spring, the most acidic season, and in summer, the season with highest temperature, lend more support to this viewpoint.

The probable dominant droplet mode oxalate and similarity in size distribution between oxalate and the inorganic ions also gave suggestion on the sources and formation pathways of aerosol oxalate which would be discussed further in the following sections.

### 3.1.2 Case study: aerosol oxalate in a dust event

In an ever-recorded dust day in 2 April 2007, sampling was segmented to five periods (Table 4) to avoid possible overload of the filters and to gain a more lucid profile of the dust event. The most intensive input of the dust occurred in the morning time (09:29–12:10) in which the mass concentration of TSP and oxalate in TSP rushed to  $1340.4 \mu\text{g m}^{-3}$  and  $1.14 \mu\text{g m}^{-3}$  respectively. At the same time, the  $\text{PM}_{2.5}/\text{TSP}$  ratio of mass and oxalate concentration decreased to 0.29 and 0.38, which was nearly half of the values in normal days. The three-day back trajectories exhibited the air mass

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movements at the beginning of the dust day (Fig. 2, left). The dust air mass originated from west/northwest China, where is a major source area of Asian dust, crossed the continent to the coastal regions, over the Bo Sea and Yellow Sea and finally arrived at Shanghai. The transport heights of the air mass were at 2500 m to 3500 m, which were typical of the high altitude transport weather pattern of a dust event. The aerosols arrived at Shanghai were mixed aerosols formed by interactions between the dust particles, the anthropogenic pollutants entrained along the transport pathway and at local area, and the gaseous species and sea salts over the seas. However, dust particles still took the bulk of the total mass of the ambient aerosols on the dust day in Shanghai (Table 4).

During the transport of the dust aerosols, atmospheric oxalate and its precursors over the continent and the seas could be entrained and reacted with the alkaline/neutral components in the dust aerosols, which led to increase in the absolute content of oxalate in the dust plume as well as redistributions of atmospheric oxalate from gaseous phase or fine particle mode to the predominant and more alkaline coarse particle mode. This could explain the distinct decrease of  $\text{PM}_{2.5}/\text{TSP}$  ratio of oxalate concentration during the dust episode compared to the value of spring average.

Intensity of the dust lessened gradually along the time which could be concluded from the aerosol mass concentrations in the five successive sampling periods. The mass concentrations of both  $\text{PM}_{2.5}$  and TSP in the fifth period (22:29, 2 April–09:11, 3 April) displayed an obvious decline, suggesting the ending of this dust event. Air masses observed largely came from north China instead and the transport heights were obviously lower than those at the beginning of the dust event (Fig. 2, right). The cloud cover, which was believed to be influenced by the Asian brown cloud (ABC) arisen by the dust air mass to a great extent in this case, also decreased from 104 to 66.7 PCT at the ending. However, the  $\text{PM}_{2.5}/\text{TSP}$  ratio of aerosol mass and oxalate concentration changed differently to the concentrations themselves. They both reached the minimums at the third period (15:19–19:42) of the sampling, in which the ratios were 0.11 for mass concentration and 0.31 for oxalate concentration respectively.

Then in the fourth and fifth periods, the ratios kept rising back to the normal day level. This was in accordance with the fact that dust aerosol was mainly composed of coarse particles and the relative concentration of the coarse particles measured in downwind area would decrease with the weakening of the dust event. Less input of coarse mode particles meant that the aerosol oxalate from local primary/secondary sources, which was mainly resided in fine particle mode in Shanghai, began taking up the predominance.

### 3.2 Possible sources and formation pathways of aerosol oxalate in Shanghai

#### 3.2.1 Source identification by correlation analysis

To explore the possible sources and formation pathways, oxalate together with some species, which could be the indicator or the tracer of the various sources, was subjected to correlation analysis. We selected Al as the indicator for the crustal source,  $\text{NO}_2^-$  for vehicular emission,  $\text{nss-SO}_4^{2-}$  and  $\text{NO}_3^-$  for secondary formation through different pathways, and  $\text{K}^+$  for biomass burning. The correlation coefficients between these source-indicating species and oxalate in  $\text{PM}_{2.5}$  were listed in Table 5.

Aerosol oxalate exhibited a poor correlation with aluminum with a peak value in spring ( $r = 0.02$ – $0.53$ , Table 5). This suggested the contribution from crust or soil to the atmospheric oxalate mass in Shanghai was relatively small. A moderate correlation coefficient of 0.53 between oxalate and Al in spring could be brought by the larger amount of dust/soil aerosol input from north/northwest areas of China to the coastal region in this season. Emissions of oxalate or its precursors from the metabolic processes of various soil fungal species could be another explanation for such a trend of correlation coefficients between oxalate and Al along the seasons (Dutton and Evans, 1999; Gadd, 1999). Obviously higher values were observed in spring ( $r = 0.53$ ) and summer ( $r = 0.36$ ) than in autumn ( $r = 0.02$ ) and winter ( $r = 0.10$ ), which was the inactive period of the metabolic processes of plants (Table 5).

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Previous researches suggested that combustion processes were important sources of atmospheric  $\text{HNO}_2$  and the most effective source of this type was the automobile engine (Kessler and Platt, 1984; Pitts et al., 1984; Wang et al., 2007a). The concentrations of nitrite ( $\text{NO}_2^-$ ) associated with the atmospheric aerosol are proportional to  $\text{HNO}_2$  concentrations in the gas phase according to the Henry's Law. Therefore, here we use aerosol  $\text{NO}_2^-$  as an indicator for primary vehicular emissions. From the very low correlation coefficients between oxalate and  $\text{NO}_2^-$  in every season ( $r = 0.07$ – $0.25$ ), we concluded that the vehicular emission made a very limited contribution to the total amount of aerosol oxalate in Shanghai as a primary source. Hence, the secondary formation in the atmosphere should account for the majority of this compound.

A high correlation was found between oxalate and  $\text{NO}_3^-$  ( $r = 0.49$ – $0.90$ ) in  $\text{PM}_{2.5}$ , suggesting a similar source or formation pathway between these two species. The atmospheric precursors of  $\text{NO}_3^-$  and oxalate were  $\text{NO}_x$  and volatile organic matters (e.g. alkenes), respectively, a characteristic source of which in urban city was vehicular exhausts. The good correlation between aerosol  $\text{NO}_3^-$  and oxalate provided evidence that vehicular emission was a major secondary source for these two compounds in Shanghai. Furthermore, the conversion of  $\text{NO}_2$  to  $\text{NO}_3^-$ , which is activated by ozone or radicals like OH and the formation of oxalate from alkenes which was also supposed to be a radical involved oxidation process, could be parallel and internally linked to each other through gaseous or aqueous radicals. For oxalate resided in particle size range larger than droplet mode ( $> 1.0 \mu\text{m}$ ), it could be produced by surface reactions of gaseous oxalic acid or its precursors with alkaline coarse particles or from the evaporation of oxalate in smaller size range (Kerminen et al., 2000; Yao et al., 2002b). These could be two possible formation pathways for oxalate in higher fine particle mode ( $1.0$ – $2.5 \mu\text{m}$ ). However, more nitric acid evaporated from fine particles and absorbed by alkaline coarse particles compared to oxalic acid due to their different volatility. This provided a reasonable explanation for the high correlation and distinct size distribution between these two compounds.

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As a result of a number of the previous studies, the formation of sulfate in the atmosphere through aqueous-phase oxidation is well established. Some researchers concluded from simulations that in-cloud process could convert up to 80% SO<sub>2</sub> to sulfate in troposphere (McHenry and Dennis, 1994; Warneck, 1999). Evidences were found in recent studies that the secondary formation of oxalate in the troposphere also requires the aqueous medium, with glyoxylate as a key aqueous-phase precursor (Yao et al., 2002a; Sorooshian et al., 2006; Carlton et al., 2007a). In Shanghai, aerosol oxalate showed a strong correlation with nss-sulfate in all four seasons ( $r = 0.60$ – $0.95$ ), especially in summer ( $r = 0.95$ ), suggesting a common formation pathway between these two species. The similarity in oxalate and sulfate's distribution between PM<sub>2.5</sub> and TSP also offered support to this hypothesis. As mentioned in the size distribution analysis and a number of studies, aerosol oxalate and sulfate mainly resided in fine particles and both probably represented a dominant droplet particle mode ( $< 1.0 \mu\text{m}$ ). Based on plenty of previous studies, aqueous phase reactions were necessary to droplet mode sulfate as well as droplet mode secondary organic aerosol productions to occur (Blando and Turpin, 2000). That is to say, attributed to the particle size distribution, in cloud process was suggested to be the most possible common formation pathway of aerosol oxalate and sulfate.

Ammonium also showed an obvious positive correlation with oxalate, with the correlation coefficients of 0.52–0.80. One possible explanation of this phenomenon is that ammonium in the atmosphere is mainly produced by the reaction between gaseous NH<sub>3</sub> and acidic sulfate particles (Finlayson-Pitts and Pitts, 2000) and therefore its high correlation with oxalate might be affected (or brought) by sulfate. On the other hand, it could be explained by the presence of ammonium oxalate in aerosols. Lefer and Talbot (2001) suggested that ammonium oxalate aerosol may be directly formed from the gaseous ammonia and oxalic acid. Combined with the result of size distribution analysis, the high correlation between ammonium and oxalate indicated a possible form of existence for aerosol oxalate rather than an evidence for a common source.

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Since K<sup>+</sup> is an essential nutrient element for the growth of plants, it has been used as an effective indicator for the source of atmospheric particulates from biomass burning, especially in the fine particle mode (Yamasoe et al., 2000; Yao et al., 2004; Falkovich et al., 2005; Huang et al., 2006). The size distribution characteristics of K<sup>+</sup> observed in this work also showed that K<sup>+</sup> dominantly reside in PM<sub>2.5</sub> in every season in urban Shanghai (~80%). The results of correlation analysis presented a moderate correlation between oxalate and K<sup>+</sup> with a peak value in autumn ( $r = 0.65$ ), being consistent with the fact that the events of biomass burning happened most frequently in this season. If an oxalate/K<sup>+</sup> correlation suggested the contribution of biomass burning to the aerosol oxalate concentrations, here is a question needed to be addressed: is biomass burning just a primary source or also a secondary source for aerosol oxalate since biogenic VOCs could be released to the atmosphere through the biomass burning activity? The ratio of oxalate to K<sup>+</sup> (oxalate/K<sup>+</sup>) in this work averaged at 0.26 in autumn, which was apparently larger than the reported values for the oxalate directly measured in biomass burning plumes (0.03–0.1) (Yamasoe et al., 2000). On the other hand, the high content of water soluble compounds (inorganic salts and water-soluble organic matters) in biomass burning aerosols made majority of them could act as CCN (Rogers et al., 1991; Novakov and Corrigan, 1996). Hence, the high oxalate/K<sup>+</sup> ratio suggested a secondary formation of oxalate from biomass burning emitted VOCs and probably through an in-cloud pathway as well. This is exactly the reason that VOCs precursors of oxalate had a characteristic source from biomass burning in autumn that could partially explain the observation of the highest oxalate concentration and the lowest correlation coefficient between oxalate, nitrate and sulfate in this season.

### 3.2.2 Linear relationship of oxalate with sulfate/nitrate

The relationships of aerosol oxalate with the two source-indicating species, nss-SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, could give a hint to the secondary formation pathways of aerosol oxalate. As mentioned above, the oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> in the atmosphere is mainly happened

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in aqueous phase, where the dissolved  $\text{SO}_2$  forms  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  and then oxidized by ozone or hydroperoxides at significant rates. Meanwhile, aqueous phase formation was regarded necessary for droplet mode secondary organic aerosol production to occur (Blando and Turpin, 2000), which was applicable to the majority of aerosol oxalate in Shanghai based on previous discussions. Differently, the oxidation of  $\text{NO}_2$  to nitric acid in the atmosphere mostly occurs in the gaseous phase, either oxidized by OH radical directly or by ozone through two intermediates,  $\text{NO}_3$  radical and nitrogen pentoxide (Warneck, 2000). Previous studies (Warneck, 2003, 2005; Carlton et al., 2007a; Martinelango et al., 2007) suggested that atmospheric oxalate is dominantly produced through aqueous oxidation by OH radical with glyoxylic acid, the most immediate precursor, which derived from either gaseous or aqueous oxidation of various primary precursors, ethene, acetylene, isoprene from biogenic source, etc. It was noticed that OH radical was involved in secondary formations of both  $\text{NO}_3^-$  and oxalate in the atmosphere. That is to say, the productions of  $\text{NO}_3^-$  and oxalate would be limited by the availability of OH radical. From this point of view, the secondary formations of these two species were internally related.

Summer and winter as representative seasons (Fig. 3), oxalate demonstrated a significantly linear relationship with both sulfate and nitrate, which reflected the good correlations between aerosol oxalate and the two inorganic salts. Further information could be obtained from the slope values of the sulfate-oxalate and nitrate-oxalate linear regression curves, which both were higher in winter than in summer. The seasonal variation of the average concentrations of  $\text{SO}_2$  and  $\text{NO}_2$  may explain the difference. As shown in Table 1, the observed average concentrations of  $\text{SO}_2$  and  $\text{NO}_2$  in winter were higher than those in summer in Shanghai. However, concentrations of VOCs (alkenes and aldehydes) in Shanghai were much lower (<5 ppbv) than the two inorganic pollutant gases and showed no clear seasonal variation (Geng et al., 2008). Therefore, as compounds formed through common or related formation pathways, the increased slope values in winter could be partially attributed to the enhanced difference between the concentrations of  $\text{SO}_2$  and  $\text{NO}_2$  and those of the VOCs precursors involved in the

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formation of aerosol oxalate.

### 3.2.3 Meteorological evidences for the formation pathway of aerosol oxalate

Meteorological factors were taken into account for the formation of aerosol oxalate in Shanghai. The variation of temperature, relative humidity (RH), cloud cover, wind speed (WS) and wind direction (WD) in the sampling period were compared with that of the oxalate concentrations. Based on the daily average observation values, no significant quantitative correlation was found between oxalate and any of these meteorological factors. However, the oxalate concentration did increase under such weather conditions: (1) clear days with clouds; (2) days with haze, mist or fog and (3) rain or shower or thunderstorm happened in the sampling days. Should the concentration level of aerosol oxalate be simultaneously influenced by multiple meteorological parameters? The time series of relative humidity (RH), cloud cover and oxalate concentration through the sampling period were shown in Fig. 4. It could be concluded from the temporal trends that whenever both the relative humidity and cloud cover declines compared to the values in the preceding day, a decrease of oxalate concentration was observed accordingly and vice versa (see the dash lines in purple in Fig. 4). That is to say, simultaneous increases in ambient RH and cloud cover would indicate raises in oxalate concentration in the same days.

The influence brought by the variations of meteorological conditions and the differences between the sources and concentration levels of VOCs precursors of oxalate in such a time scale could be reduced to a large extent by comparing the data of every two neighboring days. These two positive contributing meteorological factors to the ambient concentration of the compound implied that a secondary formation of aerosol oxalate in aqueous medium did exist in Shanghai and probably through an in-cloud pathway.

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### 3.3 Aerosol oxalate and haze pollution

One of the meteorological factors, visibility, was selected for the further study on aerosol oxalate due to its strong relationship with haze pollution. Haze is defined as the weather phenomenon which leads to atmospheric visibility less than 10 km due to the moisture, dust, smoke, and vapor in the atmosphere. Haze pollution has drawn great attention in the past decade for its impact on visibility, public health and even climate change (Okada et al., 2001; Wang and Shooter, 2002; Chen et al., 2003; Yadav et al., 2003). The characteristics and formation mechanism of haze may vary in different regions. However, many studies on haze pollution (Chan et al., 1999; Mysliwiec and Kleeman, 2002; Sun et al., 2006; Fu et al., 2008), including study in Shanghai and its surrounding areas indicated that high mass fractions of water soluble inorganic ions, such as  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  in  $\text{PM}_{2.5}$  were observed during the haze episodes. The increases of mass fractions of these hygroscopic species were characteristic during haze episodes, suggesting that contribution of these hygroscopic species to the degradation of visibility were greater than other species in the aerosols. As a water-soluble organic compound (WSOC), the role of oxalate in haze formation was investigated by comparing the variation of oxalate concentration and daily visibility of Shanghai in four seasons. As shown in Fig. 5, visibility of the city showed a strong negative correlation with the oxalate concentration levels in each season. The correlation coefficient  $r$  between visibility and oxalate concentration was  $-0.32$  in average and  $-0.42$  at peak value.

In general, aerosol oxalate comprises less than 1 % of the aerosol mass as a water soluble organic compound. The oxalate-WSOC-aerosol OC-aerosol mass relationship was examined to illustrate what the negative correlation between oxalate concentration and atmospheric visibility implied. WSOC usually accounted for 20–70 % of aerosol OC (Decesari et al., 2001, 2006). This percentage would be near the high end of the range in large urban center as Shanghai where more water soluble secondary organic aerosol (SOA) comprised a large fraction of ambient aerosol OC, due to the

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increase in polarity that accompanies the oxidizing formation pathway of SOA (Saxena and Hildemann, 1996; Lim and Turpin, 2002; Hennigan et al., 2008). This also suggested that the secondary formation mechanism of aerosol oxalate was the common and principal formation mechanism of the WSOC in aerosols. Without direct measurement, the OC content of the aerosol was estimated through the concentrations of ions, elements and black carbon (BC). The method of the calculation was shown below (Wang et al., 2007b): (1) crust =  $\text{Al}/0.08$ ; (2) secondary =  $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$ ; (3) sea salt =  $2.54 * (\text{Na} - 0.3 \text{Al})$ ; (4) smoke =  $\text{K} - 0.25 \text{Al}$ ; (5) metals = the sum of the mass of all detected non-crustal/non-sea-salt elements by ICP-AES; (6) aerosol carbonaceous species, roughly estimated with a mass balance, neglecting those minor components and  $\text{H}_2\text{O}$ , = aerosol mass – sum of ((1)~(5)); (7)  $\text{OC} * 1.8 = \text{carbonaceous species} - \text{EC}$ , here BC was used to represent EC for a rough estimate (Chow et al., 2009). The relative contributions of OC and major inorganic salts in  $\text{PM}_{2.5}$  in Shanghai, 2007 were shown in Fig. 6. Organic carbon was estimated contributing over 30 % of the total  $\text{PM}_{2.5}$  mass concentration in average, which was consistent with results of studies carried in a worldwide range suggesting that ~20–80 % of fine particle mass was organic (Zhang et al., 2007). Comparably, the sum of the mass concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  took ~20 % of that of the total  $\text{PM}_{2.5}$ . If the OM (organic matter)/OC ratio of 1.8 and WSOC/OC ratio of 50 % was applied in this study, averagely 27 % of the  $\text{PM}_{2.5}$  mass concentration would be occupied by water soluble organic compounds, which was larger than the portion those major inorganic salts took.

The existence of WSOC in aerosol would make the aerosol be more hygroscopic and thus be more easily to act as condensation nuclei. Being the most abundant identified dicarboxylic acid in the tropospheric aerosol and a water soluble compound, oxalate could be taken as a representative compound of the WSOC in the aerosols. Raise of aerosol oxalate concentration in the atmosphere reflected the raise of WSOC content to a certain extent, which would be more favorable to the formation of haze and, in turn, the degradation of visibility. Furthermore, some of the water-insoluble organics in aerosols can interact with certain water-soluble inorganic compounds, such as

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$\text{SO}_4^{2-}$ , to form an organic-inorganic complex and promote efficient new formation of the both parties in aerosols (Zhang et al., 2004). Therefore, the distinct negative correlation of atmospheric visibility with aerosol oxalate concentration, together with the high percentage of WSOC in the aerosols in Shanghai implied that oxalate being the representative compound in this study, aerosol organic compounds played an important role in the formation of haze as well as in shaping the characteristics of aerosol and air quality in urban cities.

#### 4 Conclusions

The mass concentrations of oxalate in 2007 sampling year were  $0.07\text{--}0.41 \mu\text{g m}^{-3}$  in  $\text{PM}_{2.5}$  and  $0.10\text{--}0.48 \mu\text{g m}^{-3}$  in TSP, respectively. The oxalate concentrations displayed a seasonal variation of autumn>summer>winter>spring in both particle modes. Oxalate was dominantly present in  $\text{PM}_{2.5}$  or even finer particle mode ( $<1.0 \mu\text{m}$ ) in all samples, and the peak value of  $\text{PM}_{2.5}/\text{TSP}$  appeared in summer.  $\text{Nss-SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  showed a dominant residence in  $\text{PM}_{2.5}$  as oxalate did while  $\text{NO}_3^-$  had obviously lower values of  $\text{PM}_{2.5}/\text{TSP}$  in all four seasons. In a recorded dust day, it was observed that invading dust brought gaseous or particulate oxalate to Shanghai as well as made local oxalate partitioning more to the coarse particle mode. As a result, a sharply increased oxalate level and decreased  $\text{PM}_{2.5}/\text{TSP}$  ratio of oxalate concentration was obtained during the dust episode.

Based on the correlation analysis between aerosol oxalate and source-indicating species, crustal source and vehicular emission was found minor contributors to the total amount of oxalate as primary sources. Considering the good correlation between oxalate and  $\text{K}^+$  and high ratio of oxalate/ $\text{K}^+$ , biomass burning was proved to be a secondary source of aerosol oxalate in Shanghai, in addition to urban VOCs sources (vehicular and industrial emissions), especially in autumn. Secondary formation accounted for the majority of aerosol oxalate in each season of Shanghai and mainly

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took place through an aqueous-phase oxidation pathway as aerosol  $\text{SO}_4^{2-}$  did. This conclusion was supported by the high correlation of oxalate with  $\text{nss-SO}_4^{2-}$  and  $\text{K}^+$ , dominant residence of oxalate in droplet mode and result of favorable meteorological condition analysis, in which high oxalate concentration was observed when relatively high ambient RH and high cloud cover happened simultaneously. However, since gaseous-phase oxidations happened in the early stages of the production of oxalate from alkenes in the atmosphere, the high correlation of oxalate and  $\text{NO}_3^-$  suggested that the formation of these two compounds were internally linked through the radicals involved. Due to the large fraction of WSOC in  $\text{PM}_{2.5}$  in Shanghai, oxalate as representative compound of it, its contribution to the haze pollution and visibility degradation of the local environment was comparable to that of the water-soluble inorganic species in the aerosols. The role of oxalate together with other aerosol organic compounds in the haze pollution and urban air quality needs to be further studied.

*Acknowledgements.* This work was supported by the great international collaboration project of MOST, China (2010DFA92230), the National Key Project of Basic Research of China (Grant Nos. 2006CB403704), and National Natural Science Foundation of China (Grant Nos. 20877020, 20977017).

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**Table 1.** Average aerosol pH values, ambient relative humidity, temperature, SO<sub>2</sub> and NO<sub>2</sub> concentrations in the four sampling seasons in Shanghai.

	pH		Relative humidity (%)	Temperature (°)	SO <sub>2</sub> (mg m <sup>-3</sup> )	NO <sub>2</sub> (mg m <sup>-3</sup> )
	PM <sub>2.5</sub>	TSP				
Spring	3.96 (2.92–4.57)	4.35 (3.61–5.97)	66.0 (50–87)	15.5 (8–22)	0.070 (0.026–0.173)	0.060 (0.022–0.091)
Summer	5.25 (3.77–6.04)	6.22 (5.91–6.33)	71.4 (60–80)	30.8 (28–34)	0.056 (0.020–0.119)	0.042 (0.013–0.096)
Autumn	5.41 (4.00–5.99)	6.41 (6.16–6.65)	65.6 (53–83)	13.7 (8–18)	0.051 (0.022–0.096)	0.058 (0.023–0.103)
Winter	5.25 (3.81–6.06)	5.44 (4.24–6.33)	70.6 (44–90)	5.5 (0–12)	0.075 (0.011–0.203)	0.059 (0.014–0.130)

The ranges of all parameters in the brackets were based on daily average values.

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**Table 2.** Aerosol oxalate concentrations measured at different sampling sites around the world.

Site	Sampling period	Size	Concentration $\mu\text{g m}^{-3}$	References
Shanghai	March 2007–January 2008	PM <sub>2.5</sub>	0.07–0.41	This work
Shanghai	1999–2000	PM <sub>2.5</sub>	0.50	Yao et al. (2002b)
Nanjing	2001	PM <sub>2.5</sub>	0.22–0.30	Yang et al. (2005)
Hong Kong	Winter 2000	PM <sub>2.5</sub>	0.35 ± 0.14	Yao et al. (2004)
Tokyo, Japan	1989	PM <sub>2.5</sub>	0.27 ± 0.19	Kawamura and Ikushima (1993)
Beijing	2002–2003	PM <sub>2.5</sub>	0.35 ± 0.26	Wang et al. (2007a)
Shanghai	March 2007–January 2008	TSP	0.10–0.48	This work
Tokyo, Japan	February 1992	TSP	0.27 ± 0.19	Sempere et al. (1994)
Chiba, Japan	April 1987–March 1993	TSP	0.38	Uchiyama et al. (1996)
Tampa Bay, USA	2002	PM <sub>12.5</sub>	0.29	Martinelango et al. (2007)
Los Angeles, USA	–	TSP	0.19 ± 0.78	Kawamura et al. (1987)
Beijing	2002–2003	PM <sub>10</sub>	0.38 ± 0.32	Wang et al. (2007a)

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**Table 3.** Seasonal variations of the oxalate concentrations ( $\mu\text{g m}^{-3}$ ) and their contributions (%) to the total mass of the aerosols.

	Spring	Summer	Autumn	Winter	Dust Day 2 Apr 2007	
PM <sub>2.5</sub>	Mean	0.14	0.20	0.31	0.15	0.26
	Median	0.12	0.13	0.29	0.11	
	contribution	0.59	0.80	0.77	0.13	0.21
TSP	Mean	0.19	0.27	0.37	0.25	0.67
	Median	0.12	0.25	0.36	0.15	
	contribution	0.19	0.49	0.38	0.10	0.09

Level of significance: 95%.

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**Table 4.** Segmented aerosol and oxalate mass concentrations in PM<sub>2.5</sub> and TSP, the ambient temperature and the cloud cover in 2 Apr 2007.

Date	Time (UTC + 08:00)	Mass Concentration ( $\mu\text{g m}^{-3}$ )			Oxalate Concentration ( $\mu\text{g m}^{-3}$ )			Ambient Temperature ( $^{\circ}$ )	Cloud Cover (PCT)
		PM <sub>2.5</sub>	TSP	PM <sub>2.5</sub> /TSP	PM <sub>2.5</sub>	TSP	PM <sub>2.5</sub> /TSP		
2 Apr 2007	09:29–12:10	383.3	1340.4	0.29	0.43	1.14	0.38	11.9	104
	12:14–15:14	223.8	1221.0	0.18	0.32	0.99	0.32	13.1	104
	15:19–19:42	101.5	913.9	0.11	0.24	0.76	0.31	11.7	104
	19:46–22:21	92.0	449.4	0.20	0.19	0.35	0.55	8.6	104
	22:29–09:11	35.4	106.2	0.33	0.10	0.12	0.85	6.8	66.7
Spring Average*		47.9	95.6	0.50	0.14	0.19	0.74	15.5	47.7

\*: Based on daily average values in spring sampling campaign, the dust day not included.

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**Table 5.** The correlation coefficients between oxalate and several source indicating species in the PM<sub>2.5</sub> aerosol samples collected in Shanghai in 2007.

	Sample Numbers	Al	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	nss-SO <sub>4</sub> <sup>2-</sup> c	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>
Spring	34	0.53 <sup>a</sup>	0.19	0.80 <sup>a</sup>	0.85 <sup>a</sup>	0.60 <sup>a</sup>	0.53 <sup>a</sup>
Summer	28	0.36 <sup>b</sup>	0.21	0.90 <sup>a</sup>	0.95 <sup>a</sup>	0.80 <sup>a</sup>	0.51 <sup>a</sup>
Autumn	27	0.02	0.25 <sup>b</sup>	0.49 <sup>a</sup>	0.60 <sup>a</sup>	0.52 <sup>a</sup>	0.65 <sup>a</sup>
Winter	31	0.10	0.07	0.60 <sup>a</sup>	0.67 <sup>a</sup>	0.59 <sup>a</sup>	0.29 <sup>b</sup>

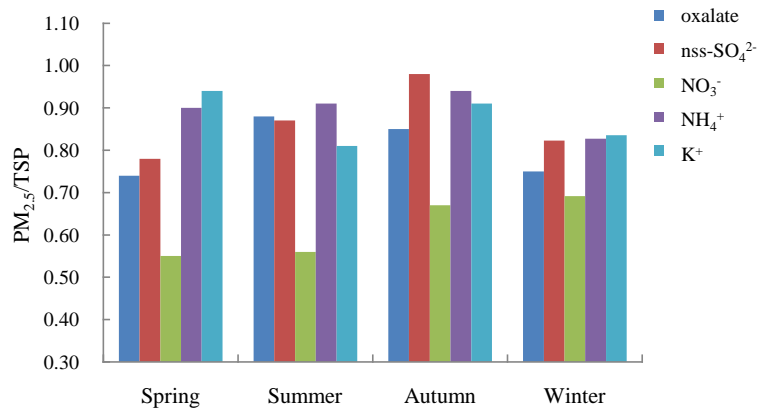
<sup>a</sup>Correlation is significant at  $p < 0.01$  level.

<sup>b</sup>Correlation is significant at  $p < 0.05$  level.

<sup>c</sup>Non sea salt sulfate.

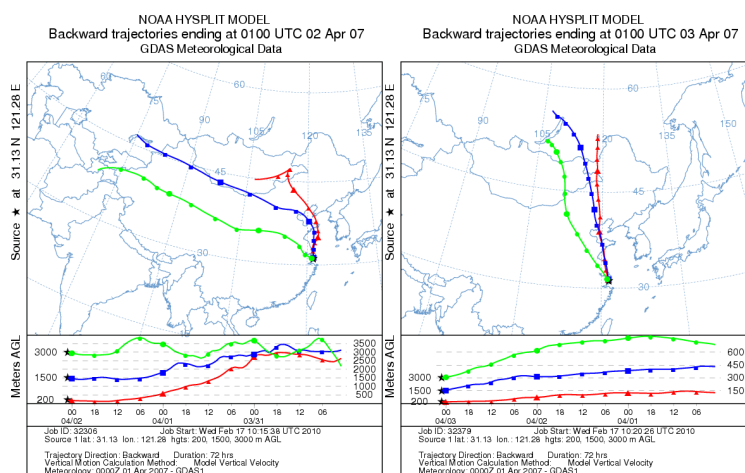
22106





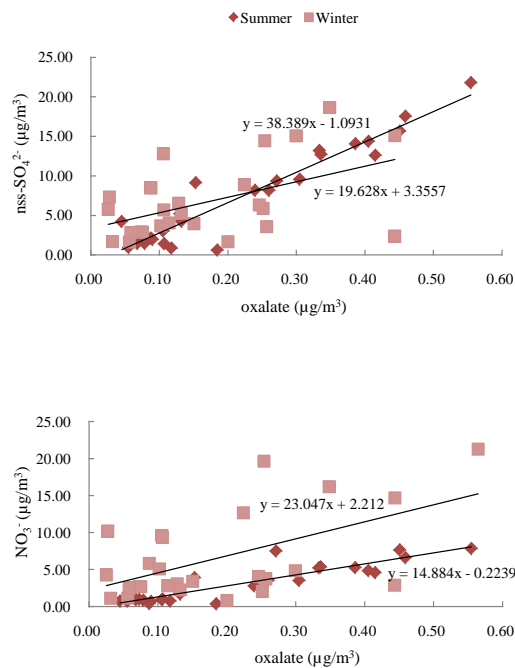
**Fig. 1.** Distribution of aerosol oxalate and selected inorganic ions between PM<sub>2.5</sub> and TSP in four seasons of Shanghai.

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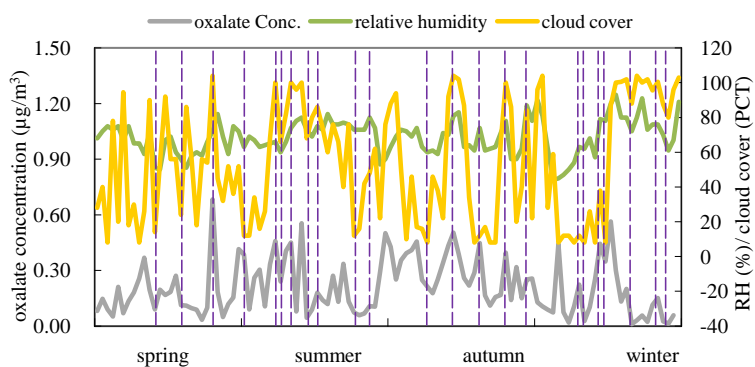
**Fig. 2.** Three-day back trajectories of the air masses at the beginning (left) and ending (right) of the dust day.

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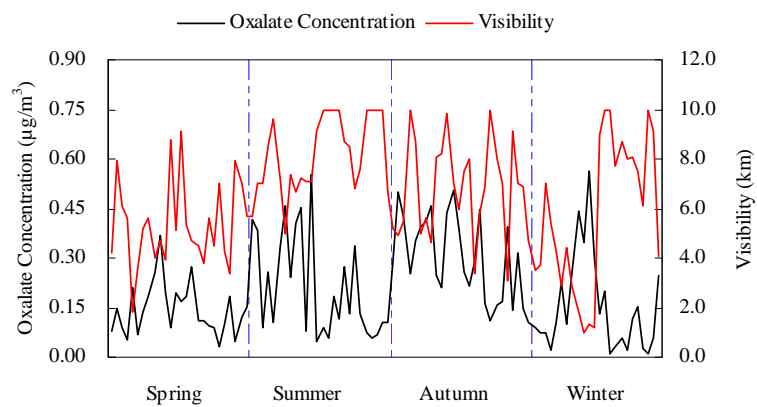
**Fig. 3.** The linear regression curves of oxalate-nss-SO<sub>4</sub><sup>2-</sup> (up) and oxalate-NO<sub>3</sub><sup>-</sup> (down) in summer and winter.

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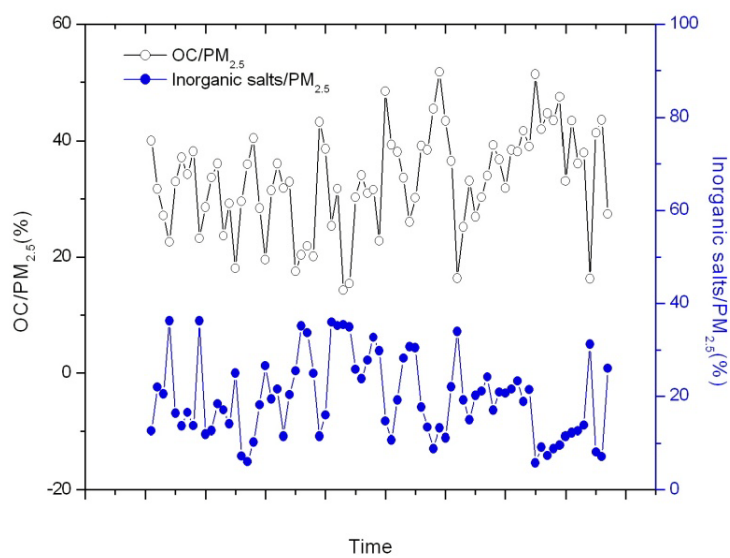
**Fig. 4.** Time series of oxalate concentration, relative humidity (RH) and cloud cover through the sampling period.

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**Fig. 5.** Variations of oxalate concentrations in  $\text{PM}_{2.5}$  and visibilities in four seasons of Shanghai.

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**Fig. 6.** Relative contributions of OC (estimated) and major inorganic salts (observed,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{K}^+$ ) in  $\text{PM}_{2.5}$  in Shanghai, 2007.

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