



2011

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

Y Jiang

G Zhuang

Q Wang

T Liu

K Huang

See next page for additional authors

Follow this and additional works at: https://trace.tennessee.edu/utk_civipubs

 Part of the [Civil and Environmental Engineering Commons](#)

Recommended Citation

Atmos. Chem. Phys. Discuss., 11, 22075-22112, 2011 www.atmos-chem-phys-discuss.net/11/22075/2011/ doi:10.5194/acpd-11-22075-2011

This Article is brought to you for free and open access by the Engineering -- Faculty Publications and Other Works at TRACE: Tennessee Research and Creative Exchange. It has been accepted for inclusion in Faculty Publications and Other Works -- Civil & Environmental Engineering by an authorized administrator of TRACE: Tennessee Research and Creative Exchange. For more information, please contact trace@utk.edu.

Authors

Y Jiang, G Zhuang, Q Wang, T Liu, K Huang, Joshua S. Fu, J Li, Y Lin, R Zhang, and C Deng

Abstract

A total of 238 samples of PM_{2.5} 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⁻³ in PM_{2.5} and 0.10–0.48 μg m⁻³ in TSP, respectively. Oxalate displayed a seasonal variation of autumn>summer>winter>spring in both PM_{2.5} and TSP and was dominantly present in PM_{2.5} in all samples. Correlation between oxalate and K⁺ and high ratio of oxalate/K⁺ 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-SO₄²⁻, K⁺ and NO₃⁻, 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-SO₄²⁻ and K⁺, dominant residence of oxalate in droplet mode and result of favorable meteorological condition analysis. High correlation of oxalate and NO₃⁻ 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.

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 μm with MMAD (mass median aerodynamic diameters) at 1.0 μm (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

ACPD

11, 22075–22112, 2011

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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 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 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/PM₁₀/PM_{2.5})-2, flow rate: 76.67 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,

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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°C). All of those filters were weighed before and after sampling with an analytical balance (Sartorius 204 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°C in a clean tube for analysis. The concentrations of ten anions (F^{-} , $\text{CH}_3\text{COO}^{-}$, HCOO^{-} , MSA, Cl^{-} , NO_2^{-} , NO_3^{-} , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-}) and five cations (Na^{+} , NH_4^{+} , K^{+} , Mg^{2+} , Ca^{2+}) in the aqueous extracts were determined by Ion Chromatography (IC, Dionex 3000, USA). The gradient base eluent (76.2 mm NaOH + H_2O) was used for anion detection, while the weak acid eluent (20 mM MSA) for cation detection. The oxalate concentrations of the blanks were below detection

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



limit or under $0.02\mu\text{g m}^{-3}$ 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°C for 4 h in high-pressure Teflon digestion vessel with 3 ml concentrated HNO_3 , 1 ml concentrated HCl and 1 ml concentrated HF . After cooling, the solutions were dried, then added 0.1 ml concentrated 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

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



gaseous SO₂ and NO₂ 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° 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 SO₂ and 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 ~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 PM_{2.5} and TSP

Average concentrations of oxalate in Shanghai both in 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 0.07–0.41 μg m⁻³ in PM_{2.5} and 0.10–0.48 μg m⁻³ in TSP, respectively. The oxalate concentrations in PM_{2.5} were a little lower than the value measured in 1999–2000 by Yao

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 PM_{2.5} and TSP samples collected in 2007 were showed in Table 3. The average concentrations of oxalate indicated a seasonal variation of autumn>summer>winter>spring in both 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 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 PM_{2.5}/TSP of oxalate concentration reached its peak in summer, up to 0.88. According to the data from our online monitoring of PM_{2.5} and PM₁ in the same sampling site, the ratios of mass concentration of PM₁ to that of PM_{2.5} averaged at 80% in 2009 in Shanghai which suggested that aerosol oxalate probably dominated in finer particles (<1.0 μm). This is consistent with the results of previous studies, in which majority of aerosol oxalate was found appeared in the droplet mode (~0.7–2.0 μm) with a MMAD around 1.0 μm, while small fraction of it distributed in the coarse mode (>2.0 μm) and condensation mode (~0.1–0.7 μm) (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 PM_{2.5} rather than in TSP in all four seasons, with an exception of nitrate. The ratios of PM_{2.5} to TSP of nitrate concentration were

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 (HNO_3) and nitrate (NO_3^-) bound to aerosol particles coexist in the atmosphere. Nitrate in the aerosols can exist in the forms of NH_4NO_3 , 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 NaNO_3 (Dasgupta et al., 2007). Most of the newly formed 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

**Characteristics of
aerosol oxalate in an
Eastern Asia
megacity**

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 $PM_{2.5}/TSP$ 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 $PM_{2.5}$ 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 $PM_{2.5}/TSP$ 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, NO_2^- for vehicular emission, nss-SO_4^{2-} and NO_3^- for secondary formation through different pathways, and 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 ($r = 0.02\text{--}0.53$, 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).

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Previous researches suggested that combustion processes were important sources of atmospheric 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 (NO_2^-) associated with the atmospheric aerosol are proportional to HNO_2 concentrations in the gas phase according to the Henry's Law. Therefore, here we use aerosol NO_2^- as an indicator for primary vehicular emissions. From the very low correlation coefficients between oxalate and NO_2^- in every season ($r = 0.07\text{--}0.25$), 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 NO_3^- ($r = 0.49\text{--}0.90$) in $\text{PM}_{2.5}$, suggesting a similar source or formation pathway between these two species. The atmospheric precursors of NO_3^- and oxalate were 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 NO_3^- and oxalate provided evidence that vehicular emission was a major secondary source for these two compounds in Shanghai. Furthermore, the conversion of NO_2 to 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 ($1.0\text{--}2.5\ \mu\text{m}$). 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.

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 % SO₂ 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 ($r = 0.60\text{--}0.95$), 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_{2.5} 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 NH₃ 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.

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Since K^+ 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^+ observed in this work also showed that K^+ dominantly reside in $PM_{2.5}$ in every season in urban Shanghai ($\sim 80\%$). The results of correlation analysis presented a moderate correlation between oxalate and K^+ 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^+ 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^+ (oxalate/ K^+) 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^+ 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, SO_4^{2-} and NO_3^- , could give a hint to the secondary formation pathways of aerosol oxalate. As mentioned above, the oxidation of SO_2 to SO_4^{2-} in the atmosphere is mainly happened

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 behaved 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.

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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; Mysliwicz 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 NH_4^+ , SO_4^{2-} , and 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

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Characteristics of
aerosol oxalate in an
Eastern Asia
megacity**

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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 = $Al/0.08$; (2) secondary = $NH_4^+ + NO_3^- + SO_4^{2-}$; (3) sea salt = $2.54*(Na-0.3 Al)$; (4) smoke = $K-0.25 Al$; (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 H_2O , = aerosol mass – sum of ((1)~(5)); (7) $OC * 1.8 =$ carbonaceous species – 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 $PM_{2.5}$ in Shanghai, 2007 were shown in Fig. 6. Organic carbon was estimated contributing over 30 % of the total $PM_{2.5}$ 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 SO_4^{2-} , NO_3^- , NH_4^+ and K^+ took ~20 % of that of the total $PM_{2.5}$. 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 $PM_{2.5}$ 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

SO₄²⁻, 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 0.07–0.41 μg m⁻³ in PM_{2.5} and 0.10–0.48 μg 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 PM_{2.5} or even finer particle mode (<1.0 μm) in all samples, and the peak value of PM_{2.5}/TSP appeared in summer. Nss-SO₄²⁻, NH₄⁺ and K⁺ showed a dominant residence in PM_{2.5} as oxalate did while NO₃⁻ had obviously lower values of PM_{2.5}/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 PM_{2.5}/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 K⁺ and high ratio of oxalate/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

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Characteristics of
aerosol oxalate in an
Eastern Asia
megacity**

Y. Jiang et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

took place through an aqueous-phase oxidation pathway as aerosol SO_4^{2-} did. This conclusion was supported by the high correlation of oxalate with nss-SO_4^{2-} and 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 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).

References

- Blando, J. D. and Turpin, B. J.: Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility, *Atmos. Environ.*, 34, 1623–1632, 2000.
- Brooks, S. D., Wise, M. E., Cushing, M. and Tolbert, M. A.: Deliquescence behavior of organic/ammonium sulfate aerosol, *Geophys. Res. Lett.*, 29(19), 1917, doi:10.1029/2002GL014733, 2002.
- Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H., and Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, *Atmos. Environ.*, 41, 7588–7602, 2007.
- Chan, Y. C., Simpson, R. W., Mctainsh, G. H., Vowles, P. D., Cohen, D. D. and Bailey, G.

**Characteristics of
aerosol oxalate in an
Eastern Asia
megacity**

Y. Jiang et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

M.: Source apportionment of PM_{2.5} and PM₁₀ aerosols in Brisbane (Australia) by receptor modeling, *Atmos. Environ.*, 33, 3251–3268, 1999.

Chen, L. W. A., Chow, J. C., Doddridge, B. G., Dickerson, R. R., Ryan, W. F. and Mueller, P. K.: Analysis of a summertime PM_{2.5} and haze episode in the mid-Atlantic region, *J. Air Waste Manage. Assoc.*, 53, 946–956, 2003.

Chow, J. C., Watson, J. G., Doraiswamy, P., Chen, L. W. A., Sodeman, D. A., Lowenthal, D. H., Park, K., Arnott, W. P., and Motallebi, N.: Aerosol light absorption, black carbon, and elemental carbon at the Fresno Supersite, California, *Atmos. Res.*, 93, 874–887, 2009.

Clegg, S. L., Brimblecombe, P., and Khan, I.: The Henry's law constant of oxalic acid and its partitioning into the atmospheric aerosol, *IdÜjárás*, 100, 51–68, 1996.

Crahan, K. K., Hegg, D., Covert, D. S., and Jonsson, H.: An exploration of aqueous oxalic acid production in the coastal marine atmosphere, *Atmos. Environ.*, 38, 3757–3764, 2004.

Cruz, C. N. and Pandis, S. N.: The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol, *J. Geophys. Res.*, 103(D11), 13,111–13,123, 1998.

Dasgupta, P. K., Campbell, S. W., Al-Horr, R. S., Ullah, S. M. R., Li, J. Z., Amalfitano, C., and Poor, N. D.: Conversion of sea salt aerosol to and the production of HCl: Analysis fo temporal behavior of aerosol chloride /nitrate and gaseous HCl/HNO₃ concentrations with AIM, *Atmos. Environ.*, 41, 4242–4257, 2007.

Decesari, S., Facchini, M. C., Matta, E., Lettini, F., Mircea, M., Fuzzi, S., Tagliavini, E., and Putaud, J. P.: Chemical features and seasonal variation of water soluble organic compounds in the Po valley fine aerosol, *Atmos. Environ.*, 35, 3691–3699, 2001.

Decesari, S., Fuzzi, S., Facchini, M. C., Mircea, M., Emblico, L., Cavalli, F., Maenhaut, W., Chi, X., Schkolnik, G., Falkovich, A., Rudich, Y., Claeys, M., Pashynska, V., Vas, G., Kourtchev, I., Vermeylen, R., Hoffer, A., Andreae, M. O., Tagliavini, E., Moretti, F., and Artaxo, P.: Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds, *Atmos. Chem. Phys.*, 6, 375–402, doi:10.5194/acp-6-375-2006, 2006.

Deguillaume, L., Leriche, M., Desboeufs, K., Mailhot, G., George, C., and Chaumerliac, N.: Transition metals in atmospheric liquid phases: Sources, reactivity, and sensitive parameters, *Chem. Rev.*, 105, 3388–3431, 2005.

Dutton, M. V. and Evans, C. S.: Oxalate production by fungi: its role in pathogenicity and ecology in the soil environment, *Can. J. Microbiol.*, 42, 881–895, 1996.

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Facchini, M. C., Fuzzi, S., Zappoli, S., Andracchio, A., Gelencser, A., Kiss, G., Kriva'csy, Z., Mešzařos, E., Hansson, H. C., Alsberg, T. and Zebühr, Y.: Partitioning of the organic aerosol component between fog droplets and interstitial air, *J. Geophys. Res.*, 104(D21), 26,821–26,832, 1999a.
- 5 Facchini, M. C., Mircea, M., Fuzzi, S., and Charlson, R. J.: Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, 401, 257–259, 1999b.
- Falkovich, A. H., Graber, E. R., Schkolnik, G., Rudich, Y., Maenhaut, W., and Artaxo, P.: Low molecular weight organic acids in aerosol particles from Rondnia, Brazil, during the biomass-burning, transition and wet periods, *Atmos. Chem. Phys.*, 5, 781–797, doi:10.5194/acp-5-781-2005, 2005.
- 10 Finlayson-Pitts, B. J. and Pitts Jr., J. N.: *Chemistry of the Upper and Lower Atmosphere*, Academic Press, New York, USA, 2000.
- Fu, Q. Y., Zhuang, G. S., Wang, J., Xu, C., Huang, K., Li, J., Hou, B., Lu, T., and Streets, D. G.: Mechanism of formation of the heaviest pollution episode ever recorded in the Yangtze River Delta, China, *Atmos. Environ.*, 42, 2023–2036, 2008.
- 15 Gadd, G. M.: Fungal production of citric and oxalic acid: importance in metal speciation, physiology and biogeochemical processes, *Adv. Microb. Physiol.*, 41, 47–92, 1999.
- Geng, F. H., Tie, X. X., Xu, J. M., Zhou, G. Q., Peng, L., Gao, W., Tang, X. and Zhao, C. S.: Characterizations of ozone, NO_x, and VOCs measured in Shanghai, China, *Atmos. Environ.*, 42, 6873–6883, 2008.
- 20 Hennigan, C. J., Bergin, M. H., and Weber, R. J.: Correlations between water-soluble organic aerosol and water vapor: a synergistic effect from biogenic emissions, *Environ. Sci. Technol.*, 42, 9079–9085, 2008.
- Huang, X. F., Yu, J. Z., He, L. Y., and Yuan, Z. B.: Water-soluble organic carbon and oxalate in aerosols at a coastal urban site in China: Size distribution characteristics, sources, and formation mechanism, *J. Geophys. Res.*, 111, D22212, doi:10.1029/2006JD007408, 2006.
- 25 Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., Cao, J. J., Boyd, P. W., Duce, R. A., Hunter, K. A., Kawahata, H., Kubilay, N., laRoche, J., Liss, P. S., Mahowald, N., Prospero, J. M., Ridgwell, A. J., Tegen, I. and Torres, R.: Global iron connections between desert dust, ocean biogeochemistry, and climate, *Science*, 308, 67–71, 2005.
- 30 Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, 27, 2227–2235, 1993.

**Characteristics of
aerosol oxalate in an
Eastern Asia
megacity**

Y. Jiang et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

- Kawamura, K. and Kaplan, I. R.: Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air, *Environ. Sci. Technol.*, 21, 105–110, 1987.
- Kawamura, K. and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, 104(D3), 3501–3509, 1999.
- 5 Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: one year of observations, *Atmos. Environ.*, 30, 1709–1722, 1995.
- Kerminen, V. M., Ojanen, C., Pakkanen, T., Hillamo, R., Aurela, M., and Merilainen, J.: Low-molecular weight dicarboxylic acids in an urban and rural atmosphere, *J. Aerosol Sci.*, 31, 349–362, 2000.
- 10 Kerminen, V. M.: Relative roles of secondary sulfate and organics in atmospheric cloud condensation nuclei production. *J. Geophys. Res.*, 106(D15), 17321–17333, 2001.
- Kessler, C. and Platt, U.: Nitrous acid in polluted air masses – sources and formation pathways, in: *Physico-chemical Behaviour of Atmospheric Pollutants*, edited by: Versino, B. and Angeletti, G., Proceedings of the 3rd European Symposium, Varese, Italy, 412–421, Reidel, Dordrecht, The Netherlands, 1984.
- 15 Pradeep Kumar, P., Broekhuizen, K., and Abbatt, J. P. D.: Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species, *Atmos. Chem. Phys.*, 3, 509–520, doi:10.5194/acp-3-509-2003, 2003.
- Lefer, B. L. and Talbot, R. W.: Summertime measurements of aerosol nitrate and ammonium at northeastern U.S. site, *J. Geophys. Res.*, 106(D17), 20,365–20,378, 2001.
- Lim, H. J. and Turpin, B. J.: Origins of primary and secondary organic aerosol in Atlanta: Results of time-resolved measurements during the Atlanta supersite experiment, *Environ. Sci. Technol.*, 36, 4489–4496, 2002.
- 25 Limbeck, A., Puxbaum, H., Otter, L., and Scholes, M. C.: Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA), *Atmos. Environ.*, 35, 1853–1862, 2001.
- Mader, B. T., Yu, J. Z., Xu, J. H., Li, Q. F., Wu, W. S., Flagan, R. C., and Seinfeld, J. H.: Molecular composition of the water-soluble fraction of atmospheric carbonaceous aerosols collected during ACE-Asia, *J. Geophys. Res.*, 109, D06206, doi:10.1029/2003JD004105, 2004.
- 30 Martinelango P. K., Dasgupta, P. K., and Al-Horr R. S.: Atmospheric production of oxalic

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



acid/oxalate and nitric acid/nitrate in the Tampa Bay airshed: Parallel pathways, *Atmos. Environ.*, 41, 4258–4269, 2007.

McHenry, J. N. and Dennis, R. L.: The relative importance of oxidation pathways and clouds to atmospheric ambient sulfate production as predicted by the regional acid deposition model, *J. Appl. Meteorol.*, 33, 890–905, 1994.

Mysliwicz, M. J. and Kleeman, M. J.: Source apportionment of secondary airborne particulate matter in a polluted atmosphere, *Environ. Sci. Technol.*, 36, 5376–5384, 2002.

Novakov, T. and Corrigan, C. E.: Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Geophys. Res. Lett.*, 23(16), 2141–2144, 1996.

Okada, K., Ikegami, M., Zaizen, Y., Makino, Y., Jensen, J. B., and Gras, J. L.: The mixture state of individual aerosol particles in the 1997 Indonesian haze episode, *J. Aerosol Sci.*, 32, 1269–1279, 2001.

Pathak, R. K. and Chan, C. K.: Inter-particle and gas-particle interactions in sampling artifacts of PM_{2.5} in filter-based samplers, *Atmos. Environ.*, 39, 1597–1607, 2005.

Pitts Jr., J. N., Biermann, H. W., Winer, A. M., and Tuazon, E. C.: Spectroscopic identification and measurement of gaseous nitrous acid in dilute auto exhaust, *Atmos. Environ.*, 18, 847–854, 1984.

Rogers, C. F., Hudson, G. J., Zielinska, B., Tanner, R. L., Hallett, J. and Watson, J. G.: *Global Biomass Burning: Atmospheric, Climatic and Biophysical Implications*, 431–438, MIT Press, Cambridge, MA, 1991.

Saxena, P. and Hildemann, L. M.: Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, 24, 57–109, 1996.

Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics from Air Pollution to Climate Change*, John Wiley and Sons, New York, USA, 1998.

Sempere, R. and Kawamura, K.: Comparative distribution of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere, *Atmos. Environ.*, 28, 449–459, 1994.

Sorooshian, A., Varutbangkul, V., Brechtel, F. J., Ervens, B., Feingold, G., Bahreini, R., Murphy, S. M., Holloway, J. S., Atlas, E. L., Buzorius, G., Jonsson, H., Flagan, R. C. and Seinfeld, J. H.: Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004, *J. Geophys. Res.*, 111, D23S4, doi:10.1029/2005JD006880, 2006.

**Characteristics of
aerosol oxalate in an
Eastern Asia
megacity**

Y. Jiang et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Souza, S. R., Vasconcellos, P. C., and Carvalho, L. R. F.: Low molecular weight carboxylic acids in an urban atmosphere: winter measurements in São Paulo City, Brazil, *Atmos. Environ.*, 33, 2563–2574, 1999.

Sullivan R. C. and Prather, K. A.: Investigations of the diurnal cycle and mixing state of oxalic acid in individual particles in Asian aerosol outflow, *Environ. Sci. Technol.*, 41, 8062–8069, 2007.

Sun, Y., Zhuang, G., Wang, Y., Han, L., Guo, J. H., Dan, M., Zhang, W., and Wang, Z.: The airborne particulate pollution at Beijing—concentrations, composition, distribution, and sources of Beijing aerosol, *Atmos. Environ.*, 38, 5991–6004, 2004.

Sun, Y., Zhuang, G., Tang, A., Wang, Y. and An, Z.: Chemical characteristics of PM_{2.5} and PM₁₀ in haze-fog episodes in Beijing, *Environ. Sci. Technol.*, 41, 3148–3155, 2006.

Taha, G., Box, G. P., Cohen, D. D., and Stelcer, E.: Black carbon measurement using laser integrating plate method, *Aero. Sci. Technol.*, 41, 266–276, 2007.

Uchiyama, S.: The behavior of oxalic acid in atmospheric aerosols, *Taiki Kankyo Gakkaishi*, 31, 141–148, 1996.

Wang, H. B. and Shooter, D.: Coarse-fine and day-night differences of water-soluble ions in atmospheric aerosols collected in Christchurch and Auckland, New Zealand, *Atmos. Environ.*, 36, 3519–3529, 2002.

Wang, Y., Zhuang, G., Chen, S., An, Z., and Zheng, A.: Characteristics and sources of formic, acetic and oxalic acids in PM_{2.5} and PM₁₀ in Beijing, China, *Atmos. Res.*, 84, 169–181, 2007a.

Wang, Y., Zhuang, G., Tang, A., Zhang, W., Sun, Y., Wang, Z., and An, Z.: The evolution of chemical components of aerosols at five monitoring sites of China during dust storms, *Atmos. Environ.*, 41, 1091–1106, 2007b.

Warneck, P.: The relative importance of various pathways for the oxidation of sulphur dioxide and nitrogen dioxide in sunlit continental fair weather clouds, *Phys. Chem. Chem. Phys.*, 1, 5471–5483, 1999.

Warneck, P.: *Chemistry of the Natural Atmosphere*, Academic Press, London, UK, 2000.

Warneck, P.: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.*, 37, 2423–2427, 2003.

Warneck, P.: Multi-Phase Chemistry of C₂ and C₃ Organic Compounds in the Marine Atmosphere, *J. Atmos. Chem.*, 51, 119–159, 2005.

Yadav, A. K., Kumar, K., Kasim, A., Singh, M. P., Parida, S. K., and Sharan, M.: Visibility and

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



incidence of respiratory diseases during the 1998 haze episode in Brunei Darussalam, Pure Appl. Geophys., 160, 265–277, 2003.

Yamasoe, M. A., Artaxo, P., Miguel, A. H., and Allen, A. G.: Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water soluble species and trace elements, Atmos. Environ., 34, 1641–1653, 2000.

Yang, H., Yu, J. Z., Ho, S. S. H., Xu, J., Wu, W., Wan, C. H., Wang, X., Wang, X., and Wang, L.: The chemical composition of inorganic and carbonaceous materials in PM_{2.5} in Nanjing, China, Atmos. Environ., 39, 3735–3749, 2005.

Yao, X. H., Fang M., and Chan, C. K.: Size distributions and formation of dicarboxylic acids in atmospheric particles, Atmos. Environ., 36, 2099–2107, 2002a.

Yao, X. H., Chan, C. K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K., and Ye, B.: The water-soluble ionic composition of PM_{2.5} in Shanghai and Beijing, China. Atmos. Environ., 36, 4223–4234, 2002b.

Yao, X. H., Lau, A. P. S., Fang, M., Chan, C. K., and Hu, M.: Size distribution and formation of ionic species in atmospheric particulate pollutants in Beijing, China: 2-dicarboxylic acids, Atmos. Environ., 37, 3001–3007, 2003.

Yao, X. H., Fang, M., Chan, C. K., Ho, K. F. and Lee, S. C.: Characterization of dicarboxylic acids in PM_{2.5} in Hong Kong, Atmos. Environ., 38, 963–970, 2004.

Yin, J. and Tan, J.: Effect of surface wind direction on air pollutant concentrations in Shanghai, Meteorol. Sci. Technol., 31, 366–369 2003 (in Chinese).

Yu, J. Z., Huang, X. F., Xu, J. H., and Hu, M.: When aerosol sulfate goes up, so does oxalate: implication for the formation mechanisms of oxalate, Environ. Sci. Technol., 39, 128–33, 2005.

Yuan, H., Wang, Y., and Zhuang, G.: Simultaneous determination of organic acids, methane sulfonic acid and inorganic anions in aerosol and precipitation samples by ion chromatography, J. Instrum. Anal., 22, 11–14, 2003 (in Chinese).

Zhang, Q. and Jimenez, J.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophys. Res. Lett., 34, L13801, doi:10.1029/2007GL029979, 2007.

Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E., Tie, X., Molina, L., and Molina, M.: Atmospheric new particle formation enhanced by organic acids, Science, 304, 1487–1490, 2004.

Zhuang, H., Chan, C. K., Fang, M., and Wexler, A. S.: Size distributions of particulate sulfate,

nitrate, and ammonium at a coastal site in Hong Kong, *Atmos. Environ.*, 33, 843–853, 1999.
Zhuang, G., Guo, J., Yuan, H., and Zhao, C.: The compositions, sources, and size distribution of the dust storm from China in spring of 2000 and its impact on the global environment, *Chinese Sci. Bull.*, 46, 895–901, 2001.

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Table 1. Average aerosol pH values, ambient relative humidity, temperature, SO₂ and NO₂ concentrations in the four sampling seasons in Shanghai.

	pH		Relative humidity (%)	Temperature (°)	SO ₂ (mg m ⁻³)	NO ₂ (mg m ⁻³)
	PM _{2.5}	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.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

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 _{2.5}	0.07–0.41	This work
Shanghai	1999–2000	PM _{2.5}	0.50	Yao et al. (2002b)
Nanjing	2001	PM _{2.5}	0.22–0.30	Yang et al. (2005)
Hong Kong	Winter 2000	PM _{2.5}	0.35 ± 0.14	Yao et al. (2004)
Tokyo, Japan	1989	PM _{2.5}	0.27 ± 0.19	Kawamura and Ikushima (1993)
Beijing	2002–2003	PM _{2.5}	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 _{12.5}	0.29	Martinelango et al. (2007)
Los Angeles, USA	–	TSP	0.19 ± 0.78	Kawamura et al. (1987)
Beijing	2002–2003	PM ₁₀	0.38 ± 0.32	Wang et al. (2007a)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 _{2.5}	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%.

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Table 4. Segmented aerosol and oxalate mass concentrations in $PM_{2.5}$ 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)
		$PM_{2.5}$	TSP	$PM_{2.5}/TSP$	$PM_{2.5}$	TSP	$PM_{2.5}/TSP$		
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.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 5. The correlation coefficients between oxalate and several source indicating species in the PM_{2.5} aerosol samples collected in Shanghai in 2007.

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

^aCorrelation is significant at $p < 0.01$ level.

^bCorrelation is significant at $p < 0.05$ level.

^cNon sea salt sulfate.

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

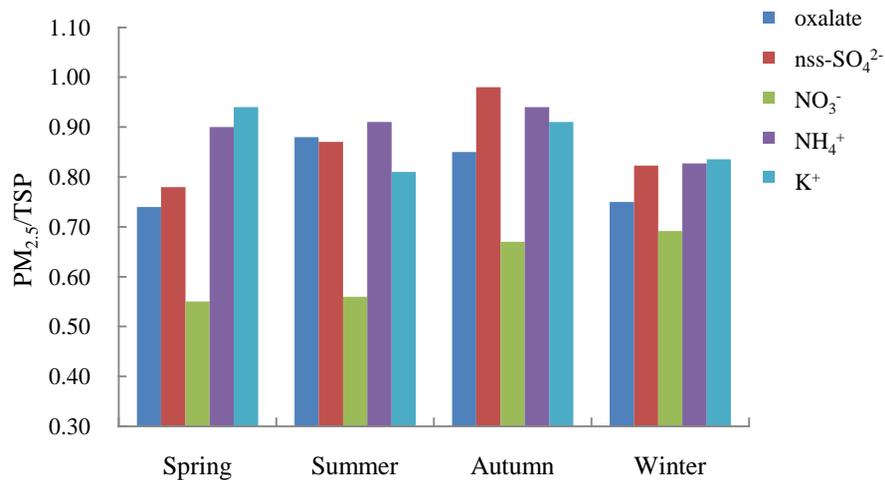


Fig. 1. Distribution of aerosol oxalate and selected inorganic ions between $PM_{2.5}$ and TSP in four seasons of Shanghai.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

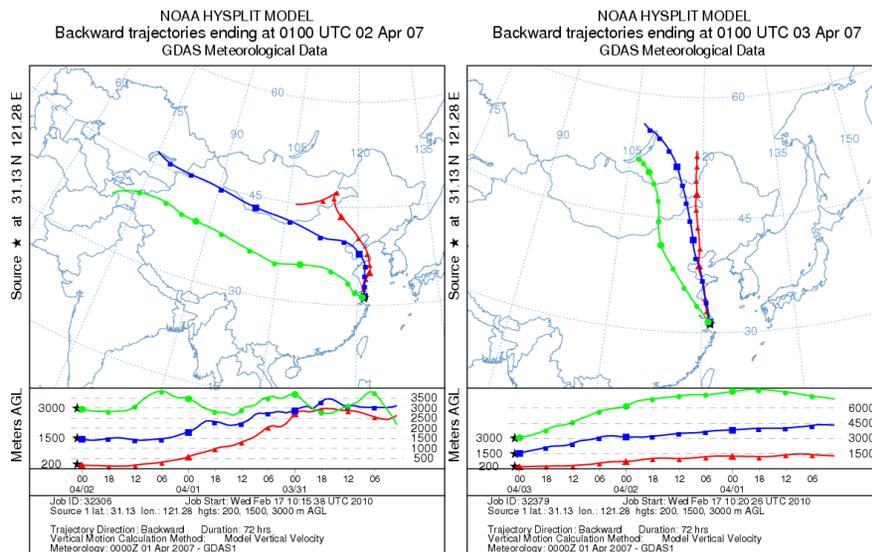


Fig. 2. Three-day back trajectories of the air masses at the beginning (left) and ending (right) of the dust day.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Characteristics of
aerosol oxalate in an
Eastern Asia
megacity**

Y. Jiang et al.

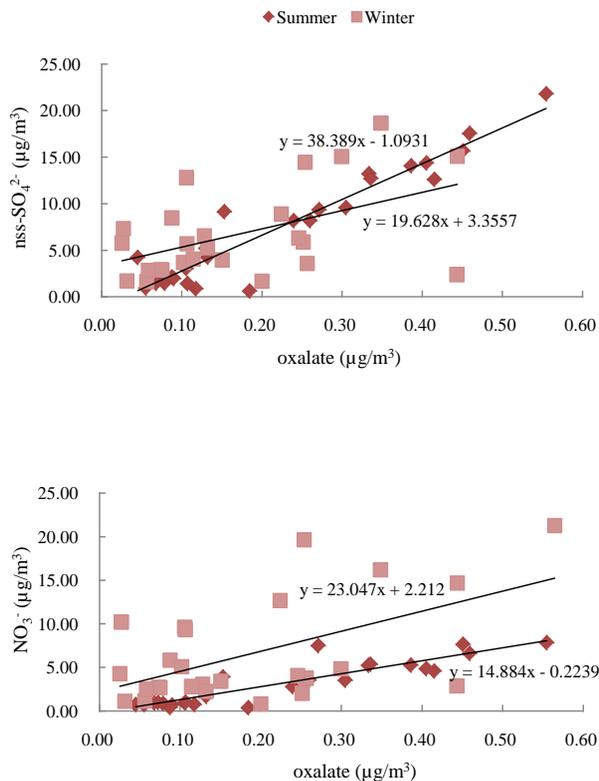


Fig. 3. The linear regression curves of oxalate- nss-SO_4^{2-} (up) and oxalate- NO_3^- (down) in summer and winter.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Characteristics of
aerosol oxalate in an
Eastern Asia
megacity**

Y. Jiang et al.

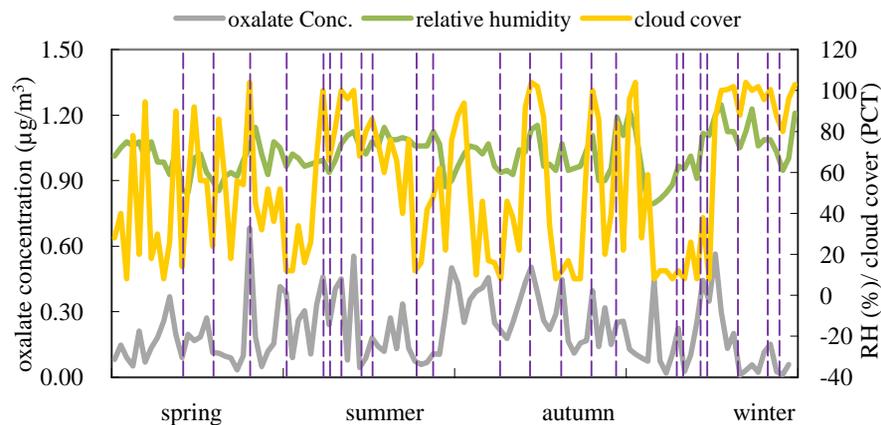
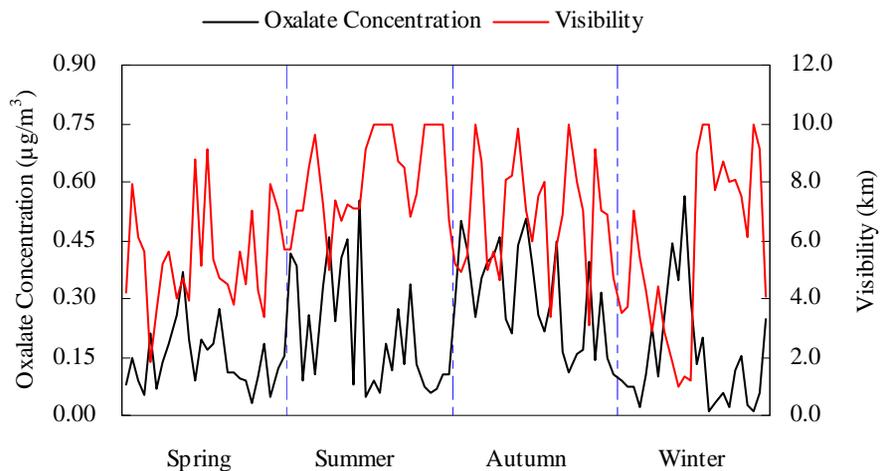


Fig. 4. Time series of oxalate concentration, relative humidity (RH) and cloud cover through the sampling period.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Characteristics of aerosol oxalate in an Eastern Asia megacity

Y. Jiang et al.

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

**Characteristics of
aerosol oxalate in an
Eastern Asia
megacity**

Y. Jiang et al.

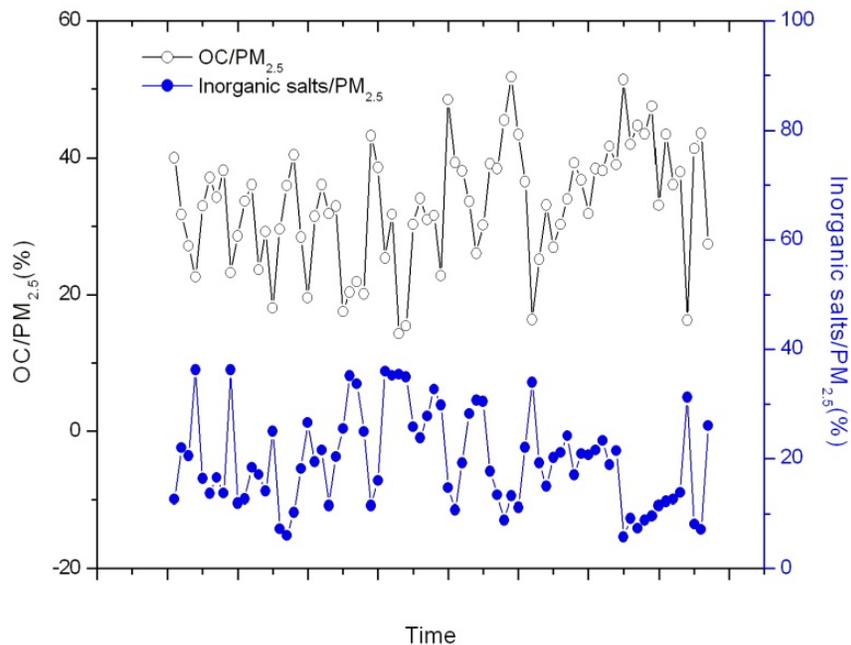


Fig. 6. Relative contributions of OC (estimated) and major inorganic salts (observed, SO_4^{2-} , NO_3^- , NH_4^+ and K^+) in $\text{PM}_{2.5}$ in Shanghai, 2007.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion