

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

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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/m³ in PM_{2.5} and 0.10-0.48 μg/m³ 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 major source of secondary oxalate aerosol 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). As a major water-soluble organic compound

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29 in aerosols, concentration of oxalate showed a distinct negative correlation to the atmospheric
30 visibility, which implied that aerosol organic compounds could play an important role in haze
31 pollution as well as in air quality in Shanghai.

32

33 **1. Introduction**

34 Oxalic acid, with oxalate, has attracted a great deal of attention as the most abundant
35 dicarboxylic acid in the tropospheric aerosols (Kawamura and Ikushima, 1993; Facchini et al.,
36 1999a; Mader et al., 2004). As a major identified water-soluble organic compound in aerosol,
37 oxalate could affect hygroscopic properties of aerosol particles (Cruz and Pandis, 1998; Brooks et
38 al., 2002; Kumar et al., 2003). It can act as cloud condensation nuclei (CCN) or reduce the surface
39 tension of particles to form CCN (Facchini et al., 1999b; Kerminen, 2001); the refractive index of
40 aerosol particles can be influenced by the presence of oxalate and further their radiative forcing
41 estimates. Oxalate may also play a role in solubility, photochemistry and bioavailability of
42 transition metals in aerosols (Deguillaume et al., 2005; Jickells et al., 2005).

43 The sources and formation pathways of aerosol oxalate are still under investigation. Oxalate
44 can be emitted directly from fossil fuel combustion, biomass burning, and biogenic activity.
45 However, many studies suggested the existence of a global secondary source in addition to the
46 primary sources of the compound (Kawamura et al., 1995; Kawamura and Sakaguchi, 1999;
47 Kerminen et al., 2000; Yao et al., 2002a). A large fraction of aerosol oxalate is considered to be
48 produced from radical involved chemical/photochemical oxidation of volatile organic compounds
49 (VOCs) like ethene, toluene, isoprene, etc. (Warneck, 1999; Carlton et al., 2007a; Sullivan et al.,
50 2007). Based on some observations, the maximum oxalate concentrations appeared in the droplet
51 mode at 0.54-1.0 μm with MMAD (mass median aerodynamic diameters) at 1.0 μm (Yao et al.,
52 2002a; Huang et al., 2006). In-cloud process and oxidation of gaseous precursors followed by
53 condensation are the two major suggested secondary formation pathways of aerosol oxalate in the
54 fine particle mode (Seinfeld and Pandis, 1998; Blando and Turpin, 1999; Yao et al., 2002a; Yao et
55 al., 2003; Crahan et al., 2004). A close tracking of oxalate and sulfate in the atmosphere has been
56 observed in some studies, which suggested a similar dominant formation pathway of the two
57 chemically distinct species (Yu et al., 2005; Sorooshian et al., 2006). Martinelango et al. (2007)
58 discovered parallel formation pathways of oxalate and nitrate in a coastal atmosphere.

59 Shanghai (31° 13' N, 121.° 28'E) is located in the western coast of the North Pacific Ocean,
60 east front of the Yangtze River Delta, China. It is one of the largest, urbanized and motorized cities
61 in China with a population of ~19, 000, 000. Shanghai has the marine monsoon subtropical
62 climate with an annual average precipitation of ~1,100 mm (<http://cdc.cma.gov.cn>). Under the
63 influence of the monsoon system, one year in Shanghai is usually divided into the hiemal half-year
64 from November to April with prevailing northwesterly continental wind and the estival half-year
65 from May to October with prevailing southeasterly wind from the North Pacific Ocean (Yin and Tan,
66 2003). For the past decade the air quality has been terribly degraded due to the rapid motorization,
67 and the heavy haze has been the frequent weather pattern in Shanghai. Organic acids, including
68 oxalic acid, with the organic aerosol have been considered as one of major components of haze. In
69 this paper we report the concentration levels, seasonal variation and relative distribution of aerosol
70 oxalate in PM_{2.5} and TSP, as well as the possible sources and formation pathways of aerosol
71 oxalate. The relationships between oxalate, meteorological factors and the regional haze pollution
72 are also discussed. This is the first time the sources and the formation pathway of aerosol oxalate
73 in Shanghai, the eastern Asian megacity, were systematically investigated. The role of organic
74 aerosol in urban atmospheric haze pollution was explored through this water-soluble organic acid
75 in aerosols.

76

77 **2. Experiment**

78 **2.1. Sampling**

79 Aerosol samples of PM_{2.5} and TSP were collected in four seasons in 2007 in Shanghai. The
80 sampling site was on the roof (~15m) of a building at Fudan University, located in the urban area
81 of Shanghai. Samples were collected on Whatman[®] 41 polycarbonate filters (Whatman Inc.,
82 Maidstone, UK, diameter: 90 mm) by a medium-volume sampler (Model: (TSP/PM₁₀/PM_{2.5})-2,
83 flow rate: 76.67 L min⁻¹). Sampling was carried out approximately in 24-h intervals. The sampling
84 period were chosen to represent the different seasons: (1) 20 March-20 April 2007, spring; (2) 23
85 July-19 August 2007, summer; (3) 1 November-29 November 2007, autumn; (4) 24 December
86 2007-26 January 2008, winter. Polycarbonate filters were put in the sampler at the sampling site
87 for 24 hr (without pumping) and used as the blanks. Four blanks were collected in every season.
88 Samples were placed in polyethylene plastic bags with artificial parchment lining bags right after

89 sampling and reserved in a refrigerator ($-18\text{ }^{\circ}\text{C}$). All of those filters were weighed before and after
90 sampling with an analytical balance (Sartorius 2004 MP, reading precision $10\text{ }\mu\text{g}$) after stabilizing
91 under constant temperature ($20\pm 1\text{ }^{\circ}\text{C}$) and humidity ($40\pm 2\%$). A total of 238 aerosol samples were
92 collected and used in this study. All the procedures were strictly quality-controlled to avoid any
93 possible contamination of the samples.

94 Black carbon (BC) measurement was conducted before series of chemical analysis. The
95 concentration of BC in the aerosol samples was measured by a smoke stain reflectometer (model
96 43D, Diffusion Systems Ltd., London, UK). Five spots on each complete sample filter were
97 selected randomly and evenly as possible for the measurement of BC contents which were
98 calculated from comparing the reflectance of the sample filter with that of a clean filter (Taha et al.,
99 2007).

100

101 **2.2. Chemical Analysis**

102 **2.2.1. Ion Analysis and pH Measurement**

103 One-fourth of each aerosol sample filter and blank filter was extracted ultrasonically by 10
104 ml water, which was deionized to the resistivity of $18\text{ M}\Omega\text{ cm}^{-1}$. After passing through the
105 microporous membranes (mixed cellulose, pore size, $0.45\text{ }\mu\text{m}$; diameter, 25 mm), each filtrate was
106 stored at $4\text{ }^{\circ}\text{C}$ in a clean tube for analysis. The concentrations of ten anions (F^{-} , $\text{CH}_3\text{COO}^{-}$,
107 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+} ,
108 Ca^{2+}) in the aqueous extracts were determined by Ion Chromatography (IC, Dionex 3000, USA).
109 The gradient base eluent ($76.2\text{ mM NaOH}+\text{H}_2\text{O}$) was used for anion detection, while the weak
110 acid eluent (20 mM MSA) for cation detection. The oxalate concentrations of the blanks were
111 below detection limit or under $0.02\text{ }\mu\text{g}/\text{m}^3$ and had been deducted from the observation values.
112 The recovery of ions was in the range of 80%–120% by adding standard reference material of
113 each ion component into the filtrates for ion chromatography analysis. Reproducibility test
114 showed that relative standard deviation was less than 5% by calculating from the results of ion
115 chromatography detections of one sample at different times (under same analytical condition). The
116 quality assurance was routinely carried out by using Standard Reference Materials produced by
117 National Research Center for Certified Reference Materials, China. A pH meter (model: LIDA
118 PHS-2C) combined with a glass electrode was used for pH measurement of the filtrates for ion

119 chromatography analysis. The pH meter was calibrated before measurement using standard buffer
120 solutions with pH values of 4.00 and 6.86. Detailed procedures were given elsewhere (Yuan et al.,
121 2003).

122

123 **2.2.2. Element Analysis**

124 Half of the sample and blank filter was digested at 170 °C for 4 h in high-pressure Teflon
125 digestion vessel with 3 ml concentrated HNO₃, 1 ml concentrated HCl and 1 ml concentrated HF.
126 After cooling, the solutions were dried, then added 0.1 ml concentrated HNO₃ and diluted to 10 ml
127 with MilliQ water (resistivity of 18 MΩ cm⁻¹). A total of 19 elements (Al, Fe, Mn, Mg, Ti, Sc, Na,
128 Sr, Ca, Co, Cr, Ni, Cu, Pb, Zn, Cd, V, S and As) were determined by inductively coupled plasma
129 atomic emission spectroscopy (ICP-AES, Model: ULTIMA, JOBIN-YVON Company, France).
130 The detailed analytical procedures were given elsewhere (Zhuang et al., 2001; Sun et al., 2004). Al
131 was used as the reference element of crustal source in this study.

132

133 **2.3. Meteorological Conditions and Sampling Artifact**

134 The meteorological data, including temperature, relative humidity (RH), cloud cover, wind
135 speed, visibility and atmospheric pressure were downloaded from <http://www.arl.noaa.gov> and
136 <http://www.wunderground.com>. The daily average concentrations of ambient gaseous SO₂ and
137 NO₂ in Shanghai were obtained from <http://www.semc.gov.cn>.

138 The extent of the sampling artifact strongly depended on the volatility of the compounds, the
139 aerosol acidity, the ambient temperature and relative humidity (Clegg et al., 1996; Souza et al.,
140 1999; Limbeck et al., 2001; Pathak and Chan, 2005). The vapor pressure of oxalate is <20 mm Hg
141 at 20°C which reflects a low volatility of this compound. Low ambient temperature, low aerosol
142 acidity and high relative humidity would make oxalate in the atmosphere be more associated with
143 particles. The aerosols in Shanghai are known to be acidic due to the high concentration of SO₂
144 and NO_x (Fu et al., 2008). Results of our measurement also showed that the pH of aerosol filtrates
145 in Shanghai averaged at 3.96-5.41 (Table 1). However, the temperature of the ambient atmosphere
146 in Shanghai was moderate except in summer and the average RH was above ~65% throughout the
147 year. Consequently, the oxalate detected in the aerosol samples are expected to be able to represent
148 the characteristics of the majority of the atmospheric oxalate and its measurement in this work is

149 considered not affected by sorption or desorption artifacts under the local condition of Shanghai.

150

151 **3. Results and Discussion**

152 **3.1. Characteristics of Aerosol Oxalate in Shanghai**

153 **3.1.1. Concentration Level, Seasonal Variation and Relative Distribution of Oxalate in** 154 **PM_{2.5} and TSP**

155 Average concentrations of oxalate in Shanghai both in PM_{2.5} and TSP were presented in Table
156 2. For comparison, oxalate mass concentrations of some other sites over the world were also listed
157 in Table 2.

158 The oxalate concentrations in Shanghai in 2007 sampling year were 0.07-0.41 μg/m³ in PM_{2.5}
159 and 0.10-0.48 μg/m³ in TSP, respectively. The oxalate concentrations in PM_{2.5} were a little lower
160 than the value measured in 1999-2000 by Yao et al. (2002b). Table 2 showed that the
161 concentrations of oxalate in Shanghai were lower than those in Beijing and Hong Kong, but
162 comparable to those in Nanjing, Tokyo, Chiba, Tampa Bay and LA. The higher levels of oxalate in
163 Beijing may be explained by its heavy traffic emissions and winter heating system, while the high
164 relative humidity and thick cloud cover may be responsible for the high values in Hong Kong.

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

173 The relative distribution of oxalate and several selected inorganic ions between PM_{2.5} and
174 TSP in each season were analyzed. As shown in Figure 1, oxalate was mainly present in the fine
175 particle mode. The value of PM_{2.5}/TSP of oxalate concentration reached its peak in summer, up to
176 0.88. According to the data from our online monitoring of PM_{2.5} and PM₁ in the same sampling
177 site, the ratios of mass concentration of PM₁ to that of PM_{2.5} averaged at 80% in 2009 in Shanghai
178 which suggested that aerosol oxalate probably dominated in finer particles (< 1.0μm). This is

179 consistent with the results of previous studies, in which majority of aerosol oxalate was found
180 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
181 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.,
182 2002a; Huang et al., 2006; Martinelango et al., 2007).

183 It could also be seen clearly in Figure 1 that nss-sulfate (non sea salt sulfate), ammonium and
184 potassium reside dominantly in $\text{PM}_{2.5}$ rather than in TSP in all four seasons, with an exception of
185 nitrate. The ratios of $\text{PM}_{2.5}$ to TSP of nitrate concentration were near to 0.5 which may be
186 explained by the high volatility of nitric acid/nitrate and the coastal environment of Shanghai.
187 Gaseous nitric acid (HNO_3) and nitrate (NO_3^-) bound to aerosol particles coexist in the atmosphere.
188 Nitrate in the aerosols can exist in the forms of NH_4NO_3 , NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, etc., depending on
189 the category and concentration of gaseous and aerosol species which nitric acid can obtain to
190 combine with. In the coastal area, the abundant atmospheric sea salt aerosols can partition
191 gas-phase nitric acid to particle- or aqueous-phase NaNO_3 (Dasgupta et al., 2007). Most of the
192 newly formed NaNO_3 still reside in coarse particles of sea salt which consequently increased the
193 $\text{PM}_{2.5}/\text{TSP}$ ratio of nitrate in Shanghai. Martinelango et al. (2007) indicated a high ratio of
194 $\text{PM}_{10}/\text{PM}_{2.5}$ of nitrate in a coastal environment, while studies carried in Hong Kong (Zhuang et al.,
195 1999; Yao et al., 2002a) also observed a dominant coarse mode of nitrate. More nitric acid would
196 partition to gas phase under hot and acidic ambient environment, which means more coarse mode
197 nitrate could be produced from the gas phase through the sea salt conversion. From our
198 observation, the two lowest $\text{PM}_{2.5}/\text{TSP}$ ratios of nitrate appeared in spring, the most acidic season,
199 and in summer, the season with highest temperature, lend more support to this viewpoint.

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

203

204 **3.1.2. Case Study: Aerosol Oxalate in A Dust Event**

205 In an ever-recorded dust day in April.2nd 2007, sampling was segmented to five periods
206 (Table 4) to avoid possible overload of the filters and to gain a more lucid profile of the dust event.
207 The most intensive input of the dust occurred in the morning time (09:29-12:10) in which the mass
208 concentration of TSP and oxalate in TSP rushed to $1340.4\ \mu\text{g}/\text{m}^3$ and $1.14\ \mu\text{g}/\text{m}^3$ respectively. At

209 the same time, the $PM_{2.5}/TSP$ ratio of mass and oxalate concentration decreased to 0.29 and 0.38,
210 which was nearly half of the values in normal days. The three-day back trajectories exhibited the
211 air mass movements at the beginning of the dust day (Figure 2, left). The dust air mass originated
212 from west/northwest China, where is a major source area of Asian dust, crossed the continent to
213 the coastal regions, over the Bo Sea and Yellow Sea and finally arrived at Shanghai. The transport
214 heights of the air mass were at 2,500 m to 3,500 m, which were typical of the high altitude
215 transport pattern of a dust event. The aerosols arrived at Shanghai were mixed aerosols formed by
216 interactions between the dust particles, the anthropogenic pollutants entrained along the transport
217 pathway and at local area, and the gaseous species and sea salts over the seas. However, dust
218 particles still took the bulk of the total mass of the ambient aerosols on the dust day in Shanghai
219 (Table 4).

220 During the transport of the dust aerosols, atmospheric oxalate and its precursors over the
221 continent and the seas could be entrained and reacted with the alkaline/neutral components in the
222 dust aerosols, which led to increase in the absolute content of oxalate in the dust plume as well as
223 redistributions of atmospheric oxalate from gaseous phase or fine particle mode to the
224 predominant and more alkaline coarse particle mode. This could explain the distinct decrease of
225 $PM_{2.5}/TSP$ ratio of oxalate concentration during the dust episode compared to the value of spring
226 average.

227 Intensity of the dust lessened gradually along the time which could be concluded from the
228 aerosol mass concentrations in the five successive sampling periods. The mass concentrations of
229 both $PM_{2.5}$ and TSP in the fifth period (22:29 Apr.2nd - 09:11 Apr.3rd) displayed an obvious decline,
230 suggesting the ending of this dust event. Air masses observed largely came from north China
231 instead and the transport heights were obviously lower than those at the beginning of the dust
232 event (Figure 2, right). The cloud cover, which was believed to be influenced by the Asian brown
233 cloud (ABC) arisen by the dust air mass to a great extent in this case, also decreased from 104 to
234 66.7 PCT at the ending. However, the $PM_{2.5}/TSP$ ratio of aerosol mass and oxalate concentration
235 changed differently to the concentrations themselves. They both reached the minimums at the
236 third period (15:19-19:42) of the sampling, in which the ratios were 0.11 for mass concentration
237 and 0.31 for oxalate concentration respectively. Then in the fourth and fifth periods, the ratios kept
238 rising back to the normal day level. This was in accordance with the fact that dust aerosol was

239 mainly composed of coarse particles and the relative concentration of the coarse particles
240 measured in downwind area would decrease with the weakening of the dust event. Less input of
241 coarse mode particles meant that the aerosol oxalate from local primary/secondary sources, which
242 was mainly resided in fine particle mode in Shanghai, began taking up the predominance.

243

244 **3.2. Possible Sources and Formation Pathways of Aerosol Oxalate in Shanghai**

245 **3.2.1. Source Identification by Correlation Analysis**

246 To explore the possible sources and formation pathways, oxalate together with some species,
247 which could be the indicator or the tracer of the various sources, was subjected to correlation
248 analysis. We selected Al as the indicator for the crustal source, NO_2^- for vehicular emission,
249 nss-SO_4^{2-} and NO_3^- for secondary formation through different pathways, and K^+ for biomass
250 burning. The correlation coefficients between these source-indicating species and oxalate in $\text{PM}_{2.5}$
251 were listed in Table 5.

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

262 Previous researches suggested that combustion processes were important sources of
263 atmospheric HNO_2 and the most effective source of this type was the automobile engine (Kessler
264 and Platt, 1984; Pitts et al., 1984; Wang et al., 2007a). The concentrations of nitrite (NO_2^-)
265 associated with the atmospheric aerosol are proportional to HNO_2 concentrations in the gas phase
266 according to the Henry's Law. Therefore, here we use aerosol NO_2^- as an indicator for primary
267 vehicular emissions. From the very low correlation coefficients between oxalate and NO_2^- in every
268 season ($r=0.07-0.25$), we concluded that the vehicular emission made a very limited contribution

269 to the total amount of aerosol oxalate in Shanghai as a primary source. Hence, the secondary
270 formation in the atmosphere should account for the majority of this compound.

271 A high correlation was found between oxalate and NO_3^- ($r=0.49-0.90$) in $\text{PM}_{2.5}$, suggesting a
272 similar source or formation pathway between these two species. The atmospheric precursors of
273 NO_3^- and oxalate were NO_x and volatile organic matters (eg. alkenes) respectively, a characteristic
274 source of which in urban city was vehicular exhausts. The good correlation between aerosol NO_3^-
275 and oxalate provided evidence that vehicular emission was a major secondary source for these two
276 compounds in Shanghai. Furthermore, the conversion of NO_2 to NO_3^- , which is activated by ozone
277 or radicals like OH and the formation of oxalate from alkenes which was also supposed to be a
278 radical involved oxidation process, could be parallel and internally linked to each other through
279 gaseous or aqueous radicals. For oxalate resided in particle size range larger than droplet mode ($>$
280 $1.0\mu\text{m}$), it could be produced by surface reactions of gaseous oxalic acid or its precursors with
281 alkaline coarse particles or from the evaporation of oxalate in smaller size range (Kerminen et al.,
282 2000; Yao et al., 2002b). These could be two possible formation pathways for oxalate in higher
283 fine particle mode ($1.0-2.5\mu\text{m}$). However, more nitric acid evaporated from fine particles and
284 absorbed by alkaline coarse particles compared to oxalic acid due to their different volatility. This
285 provided a reasonable explanation for the high correlation and distinct size distribution between
286 these two compounds.

287 As a result of a number of the previous studies, the formation of sulfate in the atmosphere
288 through aqueous-phase oxidation is well established. Some researchers concluded from
289 simulations that in-cloud process could convert up to 80% SO_2 to sulfate in troposphere (McHenry
290 and Dennis, 1994; Warneck, 1999). Evidences were found in recent studies that the secondary
291 formation of oxalate in the troposphere also requires the aqueous medium, with glyoxylate as a
292 key aqueous-phase precursor (Yao et al., 2002a; Sorooshian et al., 2006; Carlton et al., 2007a). In
293 Shanghai, aerosol oxalate showed a strong correlation with nss-sulfate in all four seasons
294 ($r=0.60-0.95$), especially in summer ($r=0.95$), suggesting a common formation pathway between
295 these two species. The similarity in oxalate and sulfate's distribution between $\text{PM}_{2.5}$ and TSP also
296 offered support to this hypothesis. As mentioned in the size distribution analysis and a number of
297 studies, aerosol oxalate and sulfate mainly resided in fine particles and both probably represented
298 a dominant droplet particle mode ($< 1.0\mu\text{m}$). Based on plenty of previous studies, aqueous phase

299 reactions were necessary to droplet mode sulfate as well as droplet mode secondary organic
300 aerosol productions to occur (Blando and Turpin, 2000). That is to say, attributed to the particle
301 size distribution, in cloud process was suggested to be the most possible common formation
302 pathway of aerosol oxalate and sulfate.

303 Ammonium also showed an obvious positive correlation with oxalate, with the correlation
304 coefficients of 0.52-0.80. One possible explanation of this phenomenon is that ammonium in the
305 atmosphere is mainly produced by the reaction between gaseous NH_3 and acidic sulfate particles
306 (Finlayson-Pitts and Pitts, 2000) and therefore its high correlation with oxalate might be affected
307 (or brought) by sulfate. On the other hand, it could be explained by the presence of ammonium
308 oxalate in aerosols. Lefer and Talbot (2001) suggested that ammonium oxalate aerosol may be
309 directly formed from the gaseous ammonia and oxalic acid. Combined with the result of size
310 distribution analysis, the high correlation between ammonium and oxalate indicated a possible
311 form of existence for aerosol oxalate rather than an evidence for a common source.

312 Since K^+ is an essential nutrient element for the growth of plants, it has been used as an
313 effective indicator for the source of atmospheric particulates from biomass burning, especially in
314 the fine particle mode (Yamasoe et al., 2000; Yao et al., 2004; Falkovich et al., 2005; Huang et al.,
315 2006). The size distribution characteristics of K^+ observed in this work also showed that K^+
316 dominantly reside in $\text{PM}_{2.5}$ in every season in urban Shanghai (~80%). The results of correlation
317 analysis presented a moderate correlation between oxalate and K^+ with a peak value in autumn
318 ($r=0.65$), being consistent with the fact that the events of biomass burning happened most
319 frequently in this season. If an oxalate/ K^+ correlation suggested the contribution of biomass
320 burning to the aerosol oxalate concentrations, here is a question needed to be addressed: is
321 biomass burning just a primary source or also a secondary source for aerosol oxalate since
322 biogenic VOCs could be released to the atmosphere through the biomass burning activity? The
323 ratio of oxalate to K^+ (oxalate/ K^+) in this work averaged at 0.26 in autumn, which was apparently
324 larger than the reported values for the oxalate directly measured in biomass burning plumes
325 (0.03-0.1) (Yamasoe et al., 2000). On the other hand, the high content of water soluble compounds
326 (inorganic salts and water-soluble organic matters) in biomass burning aerosols made majority of
327 them could act as CCN (Rogers et al., 1991; Novakov and Corrigan, 1996). Hence, the high
328 oxalate/ K^+ ratio suggested a secondary formation of oxalate from biomass burning emitted VOCs

329 and probably through an in-cloud pathway as well. This is exactly the reason that VOCs
330 precursors of oxalate had a characteristic source from biomass burning in autumn that could
331 partially explain the observation of the highest oxalate concentration and the lowest correlation
332 coefficient between oxalate, nitrate and sulfate in this season.

333

334 **3.2.2. Linear Relationship of Oxalate with Sulfate/Nitrate**

335 The relationships of aerosol oxalate with the two source-indicating species, nss-SO_4^{2-} and
336 NO_3^- , could give a hint to the secondary formation pathways of aerosol oxalate. As mentioned
337 above, the oxidation of SO_2 to SO_4^{2-} in the atmosphere is mainly happened in aqueous phase,
338 where the dissolved SO_2 forms HSO_3^- and SO_3^{2-} and then oxidized by ozone or hydroperoxides at
339 significant rates. Meanwhile, aqueous phase formation was regarded necessary for droplet mode
340 secondary organic aerosol production to occur (Blando and Turpin, 2000), which was applicable
341 to the majority of aerosol oxalate in Shanghai based on previous discussions. Differently, the
342 oxidation of NO_2 to nitric acid in the atmosphere mostly occurs in the gaseous phase, either
343 oxidized by OH radical directly or by ozone through two intermediates, NO_3 radical and nitrogen
344 pentoxide (Warneck, 2000). Previous studies (Warneck, 2003; Warneck, 2005; Carlton et al.,
345 2007a; Martinelango et al., 2007) suggested that atmospheric oxalate is dominantly produced
346 through aqueous oxidation by OH radical with glyoxylic acid, the most immediate precursor,
347 which derived from either gaseous or aqueous oxidation of various primary precursors, ethene,
348 acetylene, isoprene from biogenic source, etc. It was noticed that OH radical was involved in
349 secondary formations of both NO_3^- and oxalate in the atmosphere. That is to say, the productions
350 of NO_3^- and oxalate would be limited by the availability of OH radical. From this point of view,
351 the secondary formations of these two species were internally related.

352 As shown in Figure 3, in summer and winter there was a significantly linear relationship of
353 oxalate with both sulfate and nitrate, which reflected the good correlations between aerosol
354 oxalate and the two inorganic salts. Further information could be obtained from the slope values of
355 the sulfate-oxalate and nitrate-oxalate linear regression curves, which both were higher in winter
356 than in summer. The seasonal variation of the average concentrations of SO_2 and NO_2 may explain
357 the difference. As shown in Table 1, the observed average concentrations of SO_2 and NO_2 in
358 winter were higher than those in summer in Shanghai. However, concentrations of VOCs (alkenes

359 and aldehydes) in Shanghai were much lower (< 5 ppbv) than the two inorganic pollutant gases
360 and showed no clear seasonal variation (Geng et al., 2008). Therefore, as compounds formed
361 through common or related formation pathways, the increased slope values in winter could be
362 partially attributed to the enhanced difference between the concentrations of SO_2 and NO_2 and
363 those of the VOCs precursors involved in the formation of aerosol oxalate.

364

365 **3.2.3. Meteorological Evidences for the Formation Pathway of Aerosol Oxalate**

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

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

387

388 **3.3. Aerosol Oxalate and Haze Pollution**

389 One of the meteorological factors, visibility, was selected for the further study on aerosol
390 oxalate due to its strong relationship with haze pollution. Haze is defined as the weather
391 phenomenon which leads to atmospheric visibility less than 10 km due to the moisture, dust,
392 smoke, and vapor in the atmosphere. Haze pollution has drawn great attention in the past decade
393 for its impact on visibility, public health and even climate change (Okada et al., 2001; Wang and
394 Shooter, 2002; Chen et al., 2003; Yadav et al., 2003). The characteristics and formation
395 mechanism of haze may vary in different regions. However, many studies on haze pollution (Chan
396 et al., 1999; Mysliwiec and Kleeman, 2002; Sun et al., 2006; Fu et al., 2008), including study in
397 Shanghai and its surrounding areas, indicated that high mass fractions of water soluble inorganic
398 ions, such as NH_4^+ , SO_4^{2-} , and NO_3^- in $\text{PM}_{2.5}$ were observed during the haze episodes. The
399 increases of mass fractions of these hygroscopic species were characteristic during haze episodes,
400 suggesting that contribution of these hygroscopic species to the degradation of visibility were
401 greater than other species in the aerosols. As a water-soluble organic compound (WSOC), the role
402 of oxalate in haze formation was investigated by comparing the variation of oxalate concentration
403 and daily visibility of Shanghai in four seasons. As shown in Figure 5, visibility of the city showed
404 a strong negative correlation with the oxalate concentration levels in each season. The correlation
405 coefficient r between visibility and oxalate concentration was -0.32 in average and -0.42 at peak
406 value.

407 In general, aerosol oxalate comprises less than 1% of the aerosol mass as a water soluble
408 organic compound. The mass relationship between oxalate-WSOC and OC-aerosol was examined
409 to illustrate what the negative correlation between oxalate concentration and atmospheric visibility
410 implied. WSOC usually accounted for 20-70% of aerosol OC (Decesari et al., 2001, 2006). This
411 percentage would be near the high end of the range in large urban center as Shanghai where more
412 hygroscopic secondary organic aerosol (SOA) comprised a large fraction of ambient aerosol OC,
413 due to the increase in polarity that accompanies the oxidizing formation pathway of SOA (Saxena
414 and Hildemann, 1996; Lim and Turpin, 2002; Hennigan et al., 2008). Without direct measurement,
415 the OC content of the aerosol was estimated by the measured concentrations of ions, elements, and
416 black carbon (BC). The method of the calculation was shown below (Wang et al., 2007b): (1) crust
417 = $\text{Al}/0.08$; (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 = $\text{K} -$
418 0.25Al ; (5) metals = the sum of the mass of all detected non-crustal/non-sea-salt elements by

419 ICP-AES; (6) aerosol carbonaceous species, roughly estimated with a mass balance, = aerosol
420 mass – sum of ((1), (2), (3), (4), (5)), neglecting those minor components and H₂O;; (7) OC * 1.8
421 = carbonaceous species – EC, here BC was used to represent EC for a rough estimate (Chow et al.,
422 2009). The relative contributions of OC and major inorganic salts in PM_{2.5} in Shanghai, 2007 were
423 shown in Figure 6. Organic carbon was estimated contributing over 30% of the total PM_{2.5} mass
424 concentration in average, which was consistent with results of studies carried in a worldwide
425 range suggesting that ~20-80% of fine particle mass was organic (Zhang et al., 2007). Comparably,
426 the sum of the mass concentrations of SO₄²⁻, NO₃⁻, NH₄⁺ and K⁺ took ~20% of that of the total
427 PM_{2.5}. If the OM (organic matter)/OC ratio of 1.8 and WSOC/OC ratio of 50% was applied in this
428 study, averagely 27% of the PM_{2.5} mass concentration would be occupied by water soluble organic
429 compounds, which was larger than the portion those major inorganic salts took.

430 The existence of WSOC in aerosol would make the aerosol be more hygroscopic and thus
431 be more easily to act as condensation nuclei. Being the most abundant identified dicarboxylic acid
432 in the tropospheric aerosol and a water soluble compound, oxalate could be taken as a
433 representative compound of the WSOC in the aerosols. Raise of aerosol oxalate concentration in
434 the atmosphere reflected the raise of WSOC content to a certain extent, which would be more
435 favorable to the formation of haze. In addition, studies (Myhre and Nielsen, 2004; Garland et al.,
436 2007) found that in areas where the portion of OC in atmospheric aerosol is significant and the
437 ambient RH is high, the change of extinction coefficient due to water uptake by the aerosol
438 organic compounds is an important factor influencing the aerosol optical properties. Aerosol
439 organic compounds were proved to be able to scatter similar solar radiation as sulfate aerosol did.
440 And these changes in aerosol extinction coefficient aroused by the organic fraction were not
441 dependent on either the concentration or the specific composition of it. Research carried out in
442 south China also reported that the extinction and scattering efficiencies (α_{ep} , α_{sp}) of aerosol organic
443 matter were rather high and close to those of aerosol sulfate and nitrate (Cheng et al., 2008).
444 Observation at Fudan sampling site in early spring 2009 (January 15 to February 4) confirmed that
445 organic matter (OM), sulfate and nitrate were the main light scattering components in aerosols
446 which accounted for 50.6%, 23.8% and 15.1% of the light the aerosol scattered, respectively
447 (Huang et al., 2010). Such high content and extinction efficiency made aerosol organic
448 compounds be the key components contributing to the degradation of atmospheric visibility in

449 Shanghai. Furthermore, some of the water-insoluble organics in aerosols can interact with certain
450 water-soluble inorganic compounds, such as SO_4^{2-} , to form an organic-inorganic complex and
451 promote efficient new formation of the both parties in aerosols (Zhang et al., 2004). Therefore, the
452 distinct negative correlation of atmospheric visibility with aerosol oxalate concentration, together
453 with the high percentage of WSOC and/or OC in the aerosols in Shanghai implied that oxalate
454 being the representative compound in this study, aerosol organic compounds played an important
455 role in the formation of haze as well as in shaping the characteristics of aerosol and air quality in
456 megacities.

457

458 **4. Conclusions**

459 The mass concentrations of oxalate in 2007 sampling year were 0.07-0.41 $\mu\text{g}/\text{m}^3$ in $\text{PM}_{2.5}$ and
460 0.10-0.48 $\mu\text{g}/\text{m}^3$ in TSP, respectively. The oxalate concentrations displayed a seasonal variation of
461 autumn > summer > winter > spring in both particle modes. Oxalate was dominantly present in
462 $\text{PM}_{2.5}$ or even finer particle mode ($< 1.0\mu\text{m}$) in all samples, and the peak value of $\text{PM}_{2.5}/\text{TSP}$
463 appeared in summer. Nss-SO_4^{2-} , NH_4^+ and K^+ showed a dominant residence in $\text{PM}_{2.5}$ as oxalate did
464 while NO_3^- had obviously lower values of $\text{PM}_{2.5}/\text{TSP}$ in all four seasons. In a recorded dust day, it
465 was observed that invading dust brought gaseous or particulate oxalate to Shanghai as well as
466 made local oxalate partitioning more to the coarse particle mode. As a result, a sharply increased
467 oxalate level and decreased $\text{PM}_{2.5}/\text{TSP}$ ratio of oxalate concentration was obtained during the dust
468 episode.

469 Based on the correlation analysis between aerosol oxalate and source-indicating species,
470 crustal source and vehicular emission was found minor contributors to the total amount of oxalate
471 as primary sources. Considering the good correlation between oxalate and K^+ and high ratio of
472 oxalate/ K^+ , biomass burning was proved to be a major source of secondary oxalate aerosol in
473 Shanghai, in addition to urban VOCs sources (vehicular and industrial emissions), especially in
474 autumn. Secondary formation accounted for the majority of aerosol oxalate in each season of
475 Shanghai and mainly took place through an aqueous-phase oxidation pathway as aerosol SO_4^{2-} did.
476 This conclusion was supported by the high correlation of oxalate with nss-SO_4^{2-} and K^+ , dominant
477 residence of oxalate in droplet mode and result of favorable meteorological condition analysis, in
478 which high oxalate concentration was observed when relatively high ambient RH and high cloud

479 cover happened simultaneously. However, since gaseous-phase oxidations happened in the early
480 stages of the production of oxalate from alkenes in the atmosphere, the high correlation of oxalate
481 and NO_3^- suggested that the formation of these two compounds were internally linked through the
482 radicals involved. Due to the large fraction of WSOC in $\text{PM}_{2.5}$ in Shanghai, oxalate as
483 representative compound of it, its contribution to the haze pollution and visibility degradation of
484 the local environment was comparable to that of the water-soluble inorganic species in the
485 aerosols. The role of oxalate together with other aerosol organic compounds in the haze pollution
486 and urban air quality needs to be further studied.

487

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

719

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

721

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

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725 Table 4. Segmented aerosol and oxalate mass concentrations in $\text{PM}_{2.5}$ and TSP, the ambient
726 temperature and the cloud cover in April.2nd 2007

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728 Table 5. The correlation coefficients between oxalate and several source indicating species in the
729 $\text{PM}_{2.5}$ aerosol samples collected in Shanghai in 2007

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736 **Table 1.** Average aerosol pH values, ambient relative humidity, temperature, SO_2 and NO_2
737 concentrations in the four sampling seasons in Shanghai

	pH		Relative humidity (%)	Temperature ($^{\circ}\text{C}$)	$\text{SO}_2(\text{mg}/\text{m}^3)$	$\text{NO}_2(\text{mg}/\text{m}^3)$
	$\text{PM}_{2.5}$	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)

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

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

Site	Sampling period	Size	Concentration $\mu\text{g}/\text{m}^3$	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)

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

		Spring	Summer	Autumn	Winter	Dust Day Apr.2, 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	
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	

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Level of significance: 95%.

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774 **Table 4.** Segmented aerosol and oxalate mass concentrations in PM_{2.5} and TSP, the ambient
775 temperature and the cloud cover in April.2nd 2007

Date	Time (UTC+0800)	Mass Concentration ($\mu\text{g}/\text{m}^3$)			Oxalate Concentration ($\mu\text{g}/\text{m}^3$)			Ambient Temperature ($^{\circ}\text{C}$)	Cloud Cover (PCT)
		PM _{2.5}	TSP	PM _{2.5} /TSP	PM _{2.5}	TSP	PM _{2.5} /TSP		
April.2 nd 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

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

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783 **Table 5.** The correlation coefficients between oxalate and several source indicating species in
784 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

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

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

787 ^cNon sea salt sulfate.

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801 **Figure captions**

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

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

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809 Figure 3. The linear regression curves of oxalate-nss-SO₄²⁻ (up) and oxalate-NO₃⁻ (down) in
810 summer and winter.

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

814

815 Figure 5. Variations of oxalate concentrations in PM_{2.5} and visibilities in four seasons of
816 Shanghai.

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818 Figure 6. Relative contributions of OC (estimated) and major inorganic salts (observed, SO₄²⁻,
819 NO₃⁻, NH₄⁺ and K⁺) in PM_{2.5} in Shanghai, 2007.

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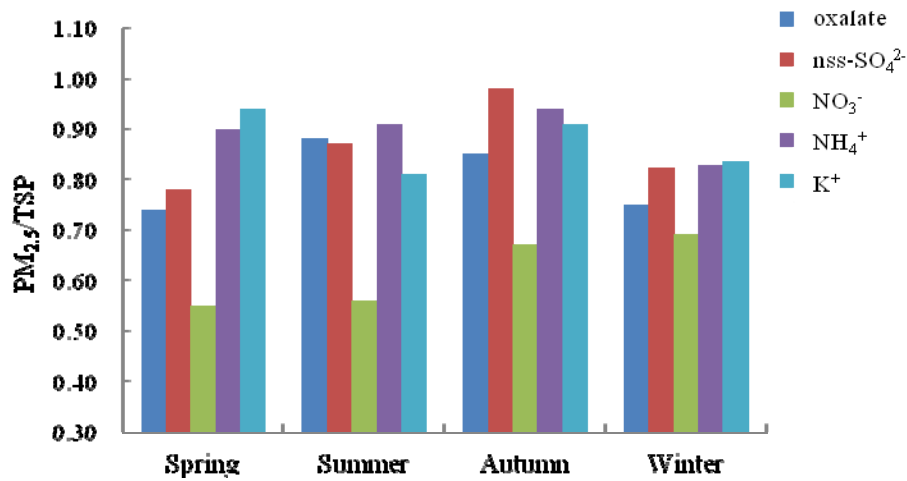
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844 Figure 1. Distribution of aerosol oxalate and selected inorganic ions between PM_{2.5} and TSP in
 845 four seasons of Shanghai.

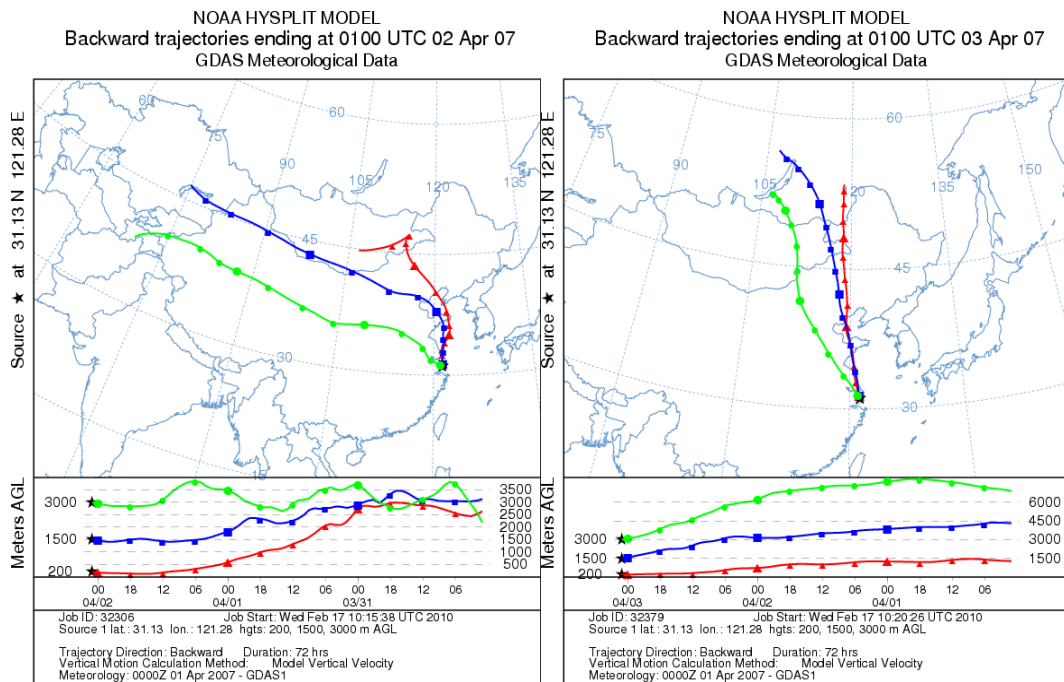
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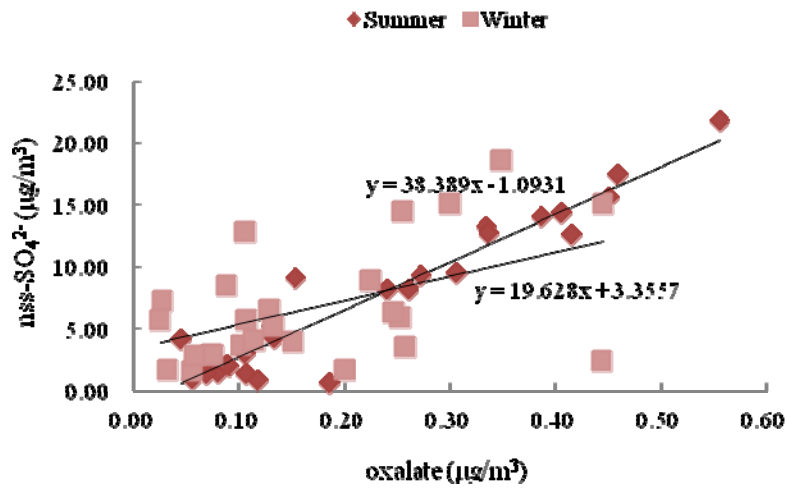
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 854 the dust day.

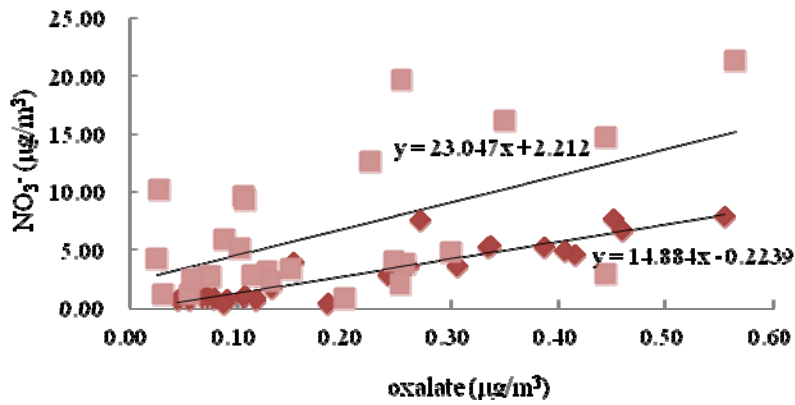
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860 Figure 3. The linear regression curves of oxalate- nss-SO_4^{2-} (up) and oxalate- NO_3^- (down) in
 861 summer and winter.

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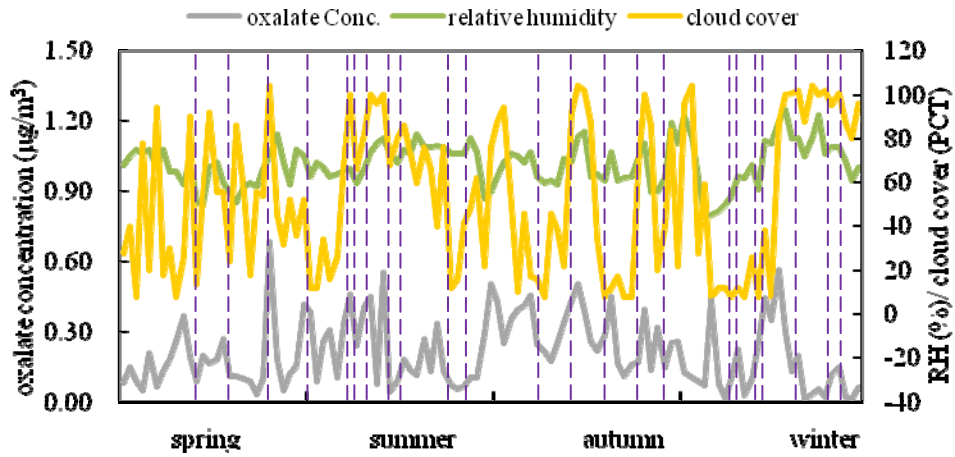
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878 Figure 4. Time series of oxalate concentration, relative humidity (RH) and cloud cover through the
 879 sampling period.

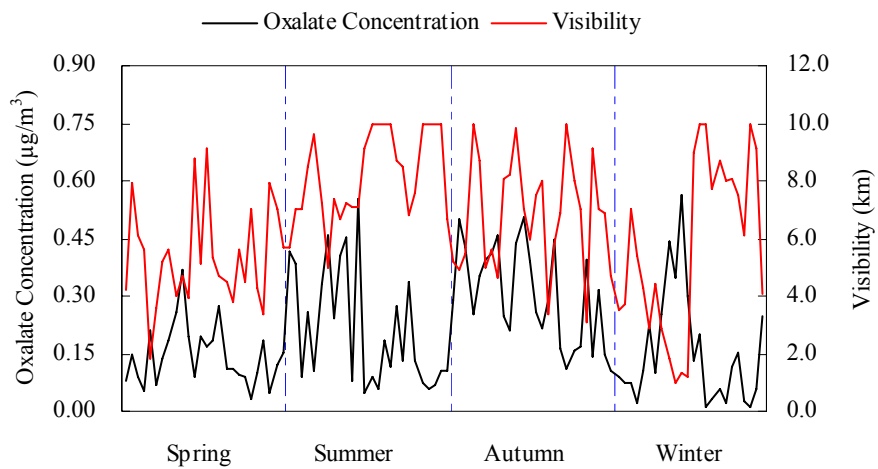
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886 Figure 5. Variations of oxalate concentrations in PM_{2.5} and visibilities in four seasons of
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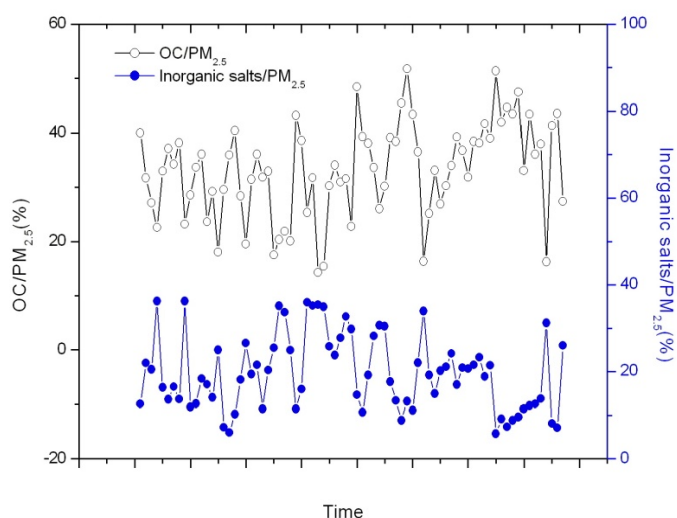
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897 Figure 6. Relative contributions of OC (estimated) and major inorganic salts (observed, SO_4^{2-} ,
 898 NO_3^- , NH_4^+ and K^+) in $\text{PM}_{2.5}$ in Shanghai, 2007.

899

900 **Appendix: Response to the reviewers' comments**

901

902 Response to the comments from **Anonymous Referee #1**

903

904 The paper presents the result of oxalate, inorganic ions, and some metal elements of $\text{PM}_{2.5}$ and
 905 TSP aerosols collected during one year in Shanghai, China. The authors analyzed the data,
 906 focusing on oxalate, in terms of season variations and correlation with some tracers of aerosol
 907 sources, and discussed the contribution of water-soluble organic carbon (WSOC) to visibility
 908 degradation.

909 The data set is quite extensive (with a total of 238 sets of samples), and the paper is well written
 910 and easy to follow. Unfortunately, the data analysis and interpretation lack depth, as such the paper
 911 gives neither new insights in science nor an advance in methodology. Significant revisions are
 912 needed to unravel the scientific value of the data before its publication.

913

914 [We would like to thank the referee for a thorough comment on this manuscript. In the revised](#)
 915 [manuscript, we have corrected the paper according to the comments point by point. Below are the](#)
 916 [responses to all the comments.](#)

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919 My specific comments are listed below.

920 (1) In the introduction, please state what knowledge gap this paper attempts to fill in. For example,
 921 what is new of the present work compared to previous studies in Shanghai and other cities
 922 mentioned in the introduction?

923

924 [Yes, thanks for the good suggestion of illustrating the meaning and new findings of the present](#)

925 work at the introduction part. Please see the Introduction in the revised manuscript.

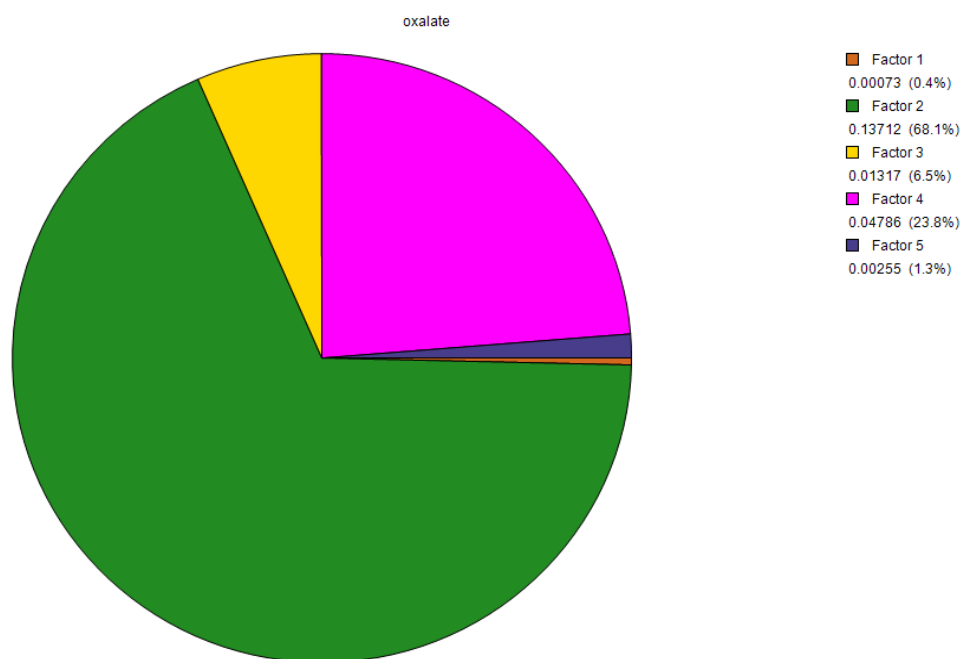
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928 (2) The results and discussion section contains a lot of general discussions, but they give few new
929 findings in term of the sources and processes of oxalate. These general discussions can be
930 shortened, and more in-depth analysis of the data should be included. The large part of the
931 discussions replies on simple analysis of correlation of oxalate with other parameters. I suggest the
932 authors consider use a multi-variate analysis such as PMF to examine the relationship of oxalate
933 with other tracers of aerosol sources and meteorological parameters.

934

935 Thanks for the advice. PMF analysis had been tried to apply to the PM_{2.5} data set involving 119
936 samples and seven variates, which were the concentration of oxalate and the aerosol source tracers.
937 Five factors were obtained contributing to the atmospheric oxalate in Shanghai as shown in the
938 figure below. Factor 1 had a high loading of potassium, representing the biomass burning source.
939 Factor 2 had a high loading of oxalate itself. Factor 3 had a high loading of nitrite, representing the
940 primary source of urban vehicle emission. Factor 4 had a high loading of nitrate, sulfate and
941 ammonium, representing the secondary formation pathway through gaseous-phase/aqueous-phase
942 oxidations. Factor 5 had a high loading of aluminum, representing the crustal source.



943

944

945 Basically, the result of PMF analysis was in accordance with that of the oxalate source
946 identification by correlation analysis. Secondary formation from VOCs precursors contributed
947 most to the aerosol oxalate in Shanghai, while direct vehicle emission and crustal sources
948 contributed limitedly.

949

950 However, such multi-variate analysis may not be the best solution for examining the relationship
951 of oxalate with other tracers of aerosol sources in this case. First, the variates themselves were the
952 aerosol source tracers' concentration and the amount of the variates was not so much that made it

953 was not so meaningful to apply such an analysis. Correlation analysis with statistical tests could
954 do the work. Second, the PMF analysis based on the data of 119 all-year-round samples obscured
955 the seasonal distinction of the sources. For example, biomass burning was a special secondary
956 source of oxalate with a seasonal stamp of autumn which could not be seen from the PMF result.
957 (Number of the samples in each season was not enough to run the PMF model and to make the
958 result significantive.)

959

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961 (3) The discussion on the contribution of oxalate and WSOC to haze lacks sufficient support from
962 the data collected in the present study. The good correlation of oxalate does not necessarily
963 indicate the importance of WSOC in visibility decrease. To quantify the contribution of each
964 aerosol component to visibility reduction, these components should be individually measured. The
965 mass extinction confident should be considered, so does the hygroscopic property of each
966 component. For example, the IMPROVE program in the US adopts the following formula:
967 $Bext (Mm^{-1}) = 3f(rh)[Sulfate] + 3f(rh)[Nitrate] + 4[Organic] + 1[Soil] + 0.6[Coarse Mass] + 10[EC]$
968 $+ 10$

969 Where: $Bext (Mm^{-1})$ is the extinction coefficient, which is proportional to the inverse of virual
970 range; $[Sulfate] = (NH_4)_2SO_4$; $[Nitrate] = NH_4NO_3$, $[Organic] = 1.4[OC]$; $[Soil] = 2.2[Al] +$
971 $2.19[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti]$; $[Coarse Mass] = [RSP] - [FSP]$; $f(rh)$ = hygroscopic
972 species growth function

973 Alternatively, the authors may apply a multiple linear regression to $Bext$ and the contributing
974 aerosol components.

975

976 Thank you for the advice. The objective of this study was aerosol oxalate in Shanghai as well as
977 the organic matter in aerosols the compound could represent. The content of calculated OC and
978 observed main inorganic ions in $PM_{2.5}$ was compared, reflecting the two categories were equated
979 to each other in amount. However, as you suggested, the optical property of the components
980 should be taken into account when the atmospheric visibility was concerned. Support from
981 literature and result of our relevant study was added in the revised version. Please see Section 3.3
982 in the revised manuscript.

983

984 Response to the comments from **Anonymous Referee #2**

985

986 General comments:

987 This paper presents aerosol oxalate variation in Shanghai in 2007, and tries to give some
988 information on oxalate formation. But little new insights can be taken from the Abstract. The main
989 idea in this manuscript is the formation pathway of oxalate, however, it is mainly from the
990 correlation analysis between oxalate and K^+ , NO_3^- , $nss-SO_4^{2-}$. This is apparently not enough as
991 there are no solid evidences and such suggestions have been published in many other papers. Most
992 of the conclusions in the manuscript are from speculations and some seem incorrect. I agree with
993 the other reviewer that deep analyses are needed before the publication.

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995 We'd like to thank for the reviewer's hard work and we have addressed the comments point by
996 point in the followings. Comments on same issues were replied together.

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Specific comments:

Abstract, Page 22076, Line 13, why K^+ is an evidence for secondary formation? Isn't it is an evidence for biomass burning as what you said in Line 8? In fact, in the manuscript the secondary formation is from relatively high ratio of oxalate/ K^+ , although this point seems also incorrect. Page 22088, the discussion about "the high oxalate/ K^+ ratio suggested a secondary formation of oxalate formation from biomass burning". I cannot get such information from the discussion. With the only discussion about relatively higher ratio of oxalate/ K^+ ratio in ambient atmosphere than that in biomass plume, such conclusion cannot be reasonably inferred. The higher ratio can also originate from the mixing of biomass burning emissions with other sources. Only when you can prove that there is only one kind of emission in this area (biomass burning), you can made such conclusion. But this is definitely not the truth.

Thank you for the advice. Indeed, higher oxalate/ K^+ ratio in the ambient atmosphere than in the biomass burning plume suggested possibilities of a secondary formation of oxalate from the biomass burning source and/or the existence of other emission sources. In this study, the correlation coefficients of oxalate with sulfate, nitrate and ammonium in autumn were all found to be the lowest among the four seasons (Table 5), which reflected that the contribution from the other sources to oxalate concentration was less important compared to that in the other seasons. Based on these, we came to the inference that biomass burning was an outstanding source of aerosol oxalate in autumn and probably experienced a secondary formation.

Page 22076, Line 21-25. It is not easy to determine that "aerosol oxalate contributed to the haze pollution and visibility" just based on the correlation analysis. Although it shows good correlation between aerosol oxalate and visibility, it is hard to say that oxalate contributes to visibility since oxalate accounts for only very small amount in aerosol mass compared with sulfate and nitrate. In the manuscript it has been suggested that both oxalate and sulfate and nitrate are associated with the secondary formation and they have good correlations. It is also the possibility that sulfate and nitrate contribute to visibility, which influence the correlation between oxalate and visibility. So this is just from a speculation. Don't say such exactly.

Page 22091, Lines 19-21, I would like to see the correlation coefficient between oxalate with other ions such as sulfate, nitrate. Such information lend itself to the understanding the comparison of relative contribution of oxalate, as well as the ions contribution to the visibility in this city.

The correlation coefficients between oxalate with other ions such as sulfate, nitrate were listed in Table 5. The linear relationship of oxalate with sulfate and nitrate was further discussed in Section 3.2.2. In this paper, oxalate was used as a representative compound of WSOC and/or OC in aerosols, as mentioned times in the manuscript, to indicate the role of aerosol OC in atmospheric visibility reduction and urban air quality. Besides hygroscopic property of the aerosol components, discussion on their optical property was added in the revised manuscript to support the viewpoint from another aspect. Please see Section 3.3 in the revised manuscript.

1041

1042 Page 22093, the first paragraph, you just suggest the contribution of organics in the formation of
1043 haze. I cannot see any message as what you state in the Abstract “Aerosol oxalate contributed to
1044 the haze pollution and visibility degradation of the local environment.” The contribution of
1045 organics on haze pollution is not directly equal to the contribution of oxalate to haze pollution.

1046

1047 Yes, thanks for pointing out the mistake in the Abstract. We agree that “The contribution of
1048 organics on haze pollution is not directly equal to the contribution of oxalate to haze pollution.”
1049 which is exactly what this paper tried to elucidate. Aerosol oxalate was used as a representative
1050 compound to show the role of aerosol WSOC and/or OC, which took a large fraction of aerosol
1051 mass, in the haze pollution. The statement in the Abstract was not accurate. Please see the
1052 modified content in the revised manuscript.

1053

1054

1055 I would like to suggest more references in the manuscript when these works are based on other
1056 researches. For example, when discussing about the formation of aerosol oxalate, there are lots of
1057 sentences, which have been reported by other works and cannot be inferred from your own study.
1058 Such sentences should be referenced. Not just limited to this part, as well as other parts.

1059

1060 We think all the referenced literatures had been cited properly in this paper. Please refer to the
1061 “Similarity Report” of this manuscript provided by the iThenticate which had been shown to the
1062 handling editor before the ACPD publication. The similarities it found are all in the following
1063 three kinds of content: (1) signature part of the authors and affiliations as well as the references
1064 part; (2) the experimental section. Concerning our research group have been doing the aerosol
1065 observation and study over years, lots of research papers applying the similar sampling and
1066 analysis methods have been published and cited; and (3) use of common terms and expressions,
1067 such as “...can be attributed to...”, “...were lower than those in...and...but...”, etc.

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