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*Supplement of*

## **Mixing state of oxalic acid containing particles in the rural area of Pearl River Delta, China: implications for the formation mechanism of oxalic acid**

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## Supplementary materials

### Table list:

Table S1. The SPAMS markers used to search for major groups of oxalic acid particles in this work.

### Figure caption:

Figure S1. The topography of Heshan sampling site (22.73N, 112.93E) and its surrounding areas.

Figure S2. The positive and negative mass spectra of oxalic acid measured by SPAMS through standard oxalic acid solution ( $400 \mu\text{g}\cdot\text{ml}^{-1}$ ).

Figure S3. The temporal variation of in-situ pH ( $pH_{is}$ ) of ambient  $\text{PM}_{2.5}$  particles during sampling period in summer.

Figure S4. The clustered 48 hr back trajectories of air masses arriving in Heshan during the sampling period: (a) summer (from July 18 to August 1, 2014), (b) winter (from January 27 to February 8, 2015).

Figure S5. The diurnal variations of in-situ pH ( $pH_{is}$ ), RH, nitrate, sulfate, ammonium and the aqueous phase concentration of  $\text{H}^+$  ( $\text{mol L}^{-1}$ ) in aerosols from July 28 to August 1 in 2014.

Figure S6. The diurnal variations of temperature (T), RH, wind speed (WS), oxalic acid particles, total EC particles, the EC type oxalic acid-containing particles and ambient  $\text{NO}_2$  concentrations from July 28 to August 1 in 2014.

Figure S7. Temporal variation of organosulfate ( $m/z=-155$ ) containing particles in total particles and in oxalic acid particles in Heshan, China.

Table S1. The SPAMS markers used to search for major groups of oxalic acid particles in this work.

Species	m/z	Marker Ion	Area	Relative Area	Function
Elemental Carbon	12±0.5	[C] <sup>+</sup>	50	0.005	or
	24±0.5	[C <sub>2</sub> ] <sup>+</sup>	50	0.005	or
	36±0.5	[C <sub>3</sub> ] <sup>+</sup>	50	0.005	or
	48±0.5	[C <sub>4</sub> ] <sup>+</sup>	50	0.005	or
	60±0.5	[C <sub>5</sub> ] <sup>+</sup>	50	0.005	or
	-12	[C] <sup>-</sup>	50	0.005	or
	-24	[C <sub>2</sub> ] <sup>-</sup>	50	0.005	or
	-36	[C <sub>3</sub> ] <sup>-</sup>	50	0.005	or
	-48	[C <sub>4</sub> ] <sup>-</sup>	50	0.005	or
	-60	[C <sub>5</sub> ] <sup>-</sup>	50	0.005	or
Organic Carbon	27	[C <sub>2</sub> H <sub>3</sub> ] <sup>+</sup>	50	0.005	or
	43	[C <sub>2</sub> H <sub>3</sub> O] <sup>+</sup>	50	0.005	or
Elemental Carbon and Organic Carbon	12	[C] <sup>+</sup>	50	0.005	or
	24	[C <sub>2</sub> ] <sup>+</sup>	50	0.005	or
	36	[C <sub>3</sub> ] <sup>+</sup>	50	0.005	or
	37	[C <sub>3</sub> H] <sup>+</sup>	50	0.005	or
	43	[C <sub>2</sub> H <sub>3</sub> O] <sup>+</sup>	50	0.005	or
Biomass Burning	39	[K] <sup>+</sup>	1500		and
	113,115	[K <sub>2</sub> Cl] <sup>+</sup>	50	0.005	or
	213	[K <sub>3</sub> SO <sub>4</sub> ] <sup>+</sup>	50	0.005	or
	-26	[CN] <sup>-</sup>	50	0.005	or
	-59	[C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ] <sup>-</sup>	50	0.005	or
Sec	-73	[C <sub>3</sub> H <sub>3</sub> O <sub>2</sub> ] <sup>-</sup>	50	0.005	or
	18	[NH <sub>4</sub> ] <sup>+</sup>	50	0.005	or
	39	[K] <sup>+</sup>	1500		and
	-62	[NO <sub>3</sub> ] <sup>-</sup>	100	0.05	
	-97	[HSO <sub>4</sub> ] <sup>-</sup>	100	0.05	
Heavy Metal	206-208	[Pb] <sup>+</sup>	50	0.005	or
	64,66	[Zn] <sup>+</sup>	50	0.005	or
	63,65	[Cu] <sup>+</sup>	50	0.005	or
	56	[Fe] <sup>+</sup>	50	0.005	or
	55	[Mn] <sup>+</sup>	50	0.005	or
	71	[MnO] <sup>+</sup>	50	0.005	or
	51	[V] <sup>+</sup>	50	0.005	or
	67	[VO] <sup>+</sup>	50	0.005	or
Dust	24	[Mg] <sup>+</sup>	1000		
	27	[Al] <sup>+</sup>	1500		
	40	[Ca] <sup>+</sup>	2500		
	56	[CaO] <sup>+</sup> /[Fe] <sup>+</sup>	100	0.05	

	-76	[SiO <sub>3</sub> ] <sup>-</sup>	500	0.05	
NaK	23	[Na] <sup>+</sup>	100	0.05	
	62	[Na <sub>2</sub> O] <sup>+</sup>	50	0.005	or
	63	[Na <sub>2</sub> OH] <sup>+</sup>	50	0.005	or
	81,83	[Na <sub>2</sub> Cl] <sup>+</sup>	50	0.005	or
	-35,-37	[Cl] <sup>-</sup>	100	0.05	
Ammonium	18	[NH <sub>4</sub> ] <sup>+</sup>	50	0.005	
Nitrate	-46	[NO <sub>2</sub> ] <sup>-</sup>	100	0.05	
	-62	[NO <sub>3</sub> ] <sup>-</sup>	100	0.05	
Sulfate	-80	[SO <sub>3</sub> ] <sup>-</sup>	100	0.05	
	-97	[HSO <sub>4</sub> ] <sup>-</sup>	100	0.05	

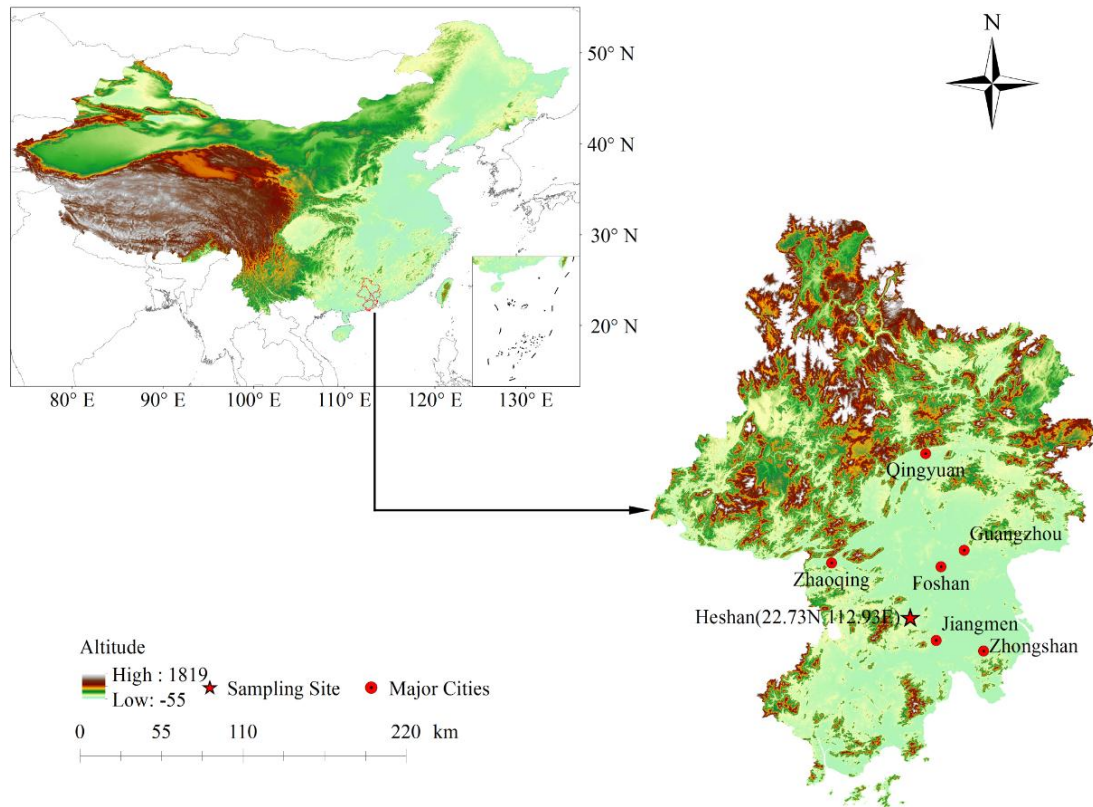


Figure S1. The topography of Heshan sampling site (22.73N, 112.93E) and its surrounding areas.

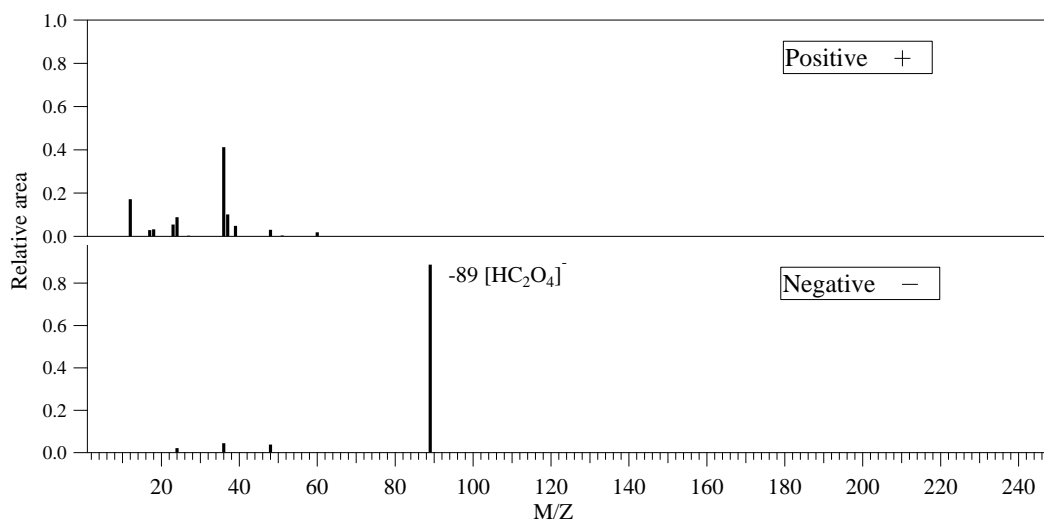


Figure S2. The positive and negative mass spectra of pure oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ , purity: 99.99%, Aladdin Industrial Corporation) measured by SPAMS through authentic oxalic acid solution ( $200 \mu\text{g}\cdot\text{ml}^{-1}$ ).

The relative area of each fragment refers to the abundance of each peak area in total signal of the mass spectra. The parent ion signal of oxalic acid at mass-to-charge ( $m/z$ ) -89 ( $\text{HC}_2\text{O}_4^-$ ) is significant in the negative mass spectrum. Carbon clusters of  $12[\text{C}]^+$ ,  $24[\text{C}_2]^+$ ,  $36[\text{C}_3]^+$  are observed in positive mass spectrum, and  $23[\text{Na}]^+$  and  $39[\text{K}]^+$  also show peaks due to extremely high sensitivity of SPAMS to these elements which are present as trace impurities ( $<0.01$ ).  $\text{HC}_2\text{O}_4^-$  ( $m/z$  -89) is selected as the marker ion for oxalic acid containing particles. In this work, oxalic acid particles are identified if the peak area of  $m/z$  -89 was larger than 0.5% of the total signal in the mass spectrum.

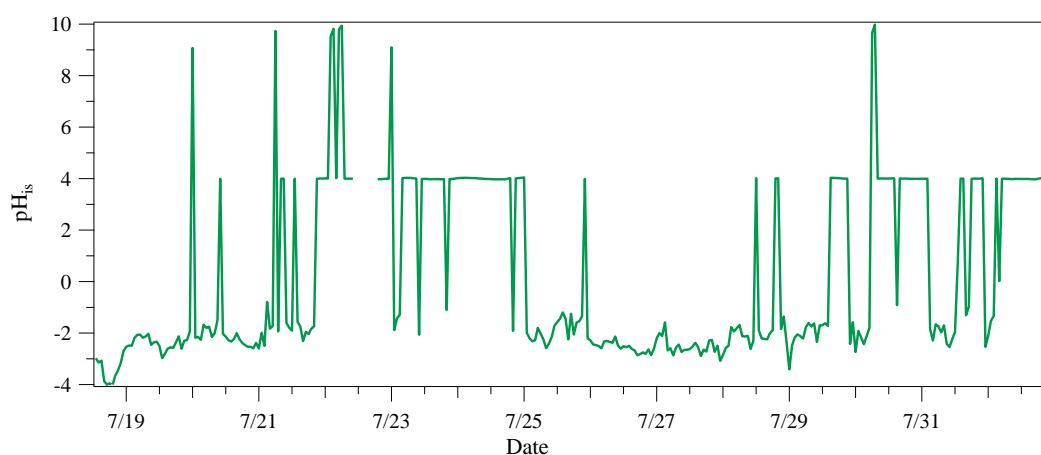


Figure S3. The temporal variation of in-situ pH ( $pH_{is}$ ) of ambient  $PM_{2.5}$  particles during sampling period in summer.

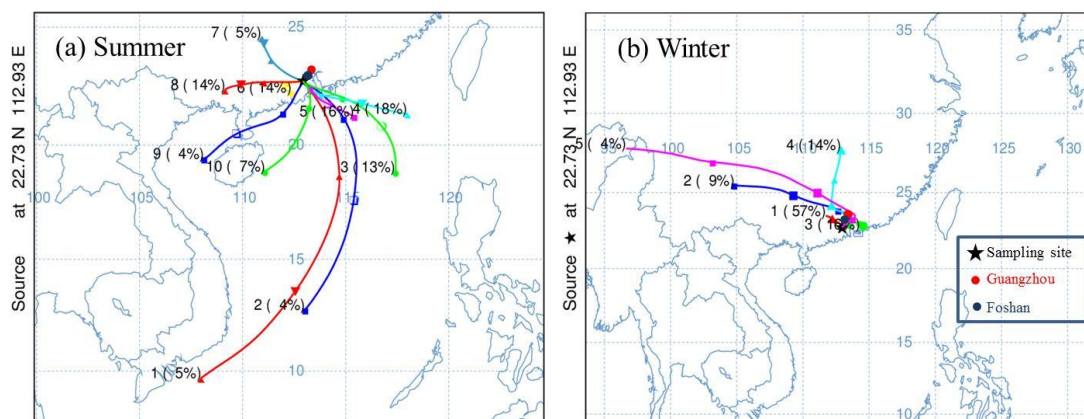


Figure S4. The clustered 48 hr back trajectories of air masses arriving in Heshan during the sampling period: (a) summer (from July 18 to August 1, 2014), (b) winter (from January 27 to February 8, 2015).

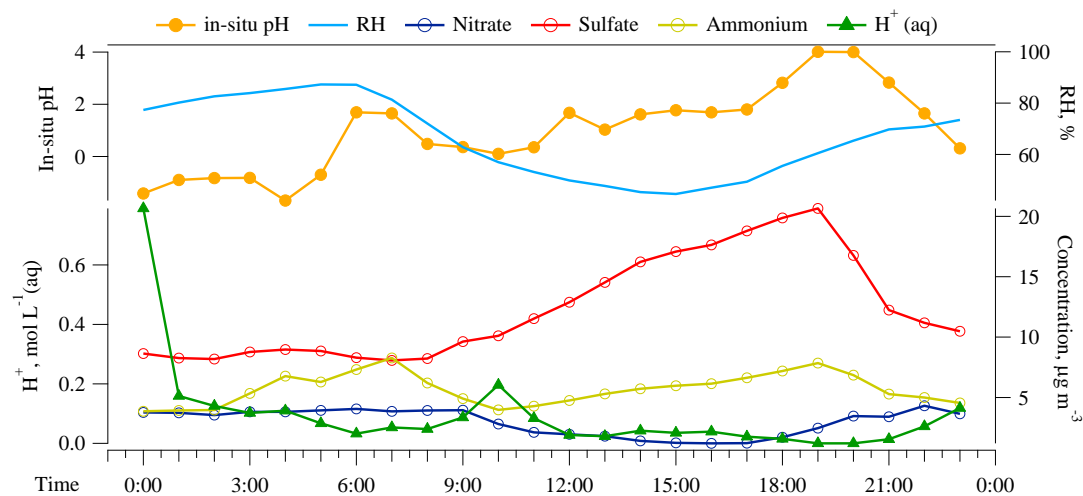


Figure S5. The diurnal variations of in-situ pH ( $pH_{is}$ ), RH, nitrate, sulfate, ammonium and the aqueous phase concentration of  $H^+$  ( $\text{mol L}^{-1}$ ) in aerosols from July 28 to August 1 in 2014.

The  $pH_{is}$  of ambient particles ranged from -1.42 to 4.01, which indicate that fine particles in the sampling site are highly acidic. These values are within the range of previous studies that investigated  $pH_{is}$  through filter-based and real-time measurements in the PRD area (Xue et al., 2011; Pathak et al., 2004; Yao et al., 2006). Based on the calculation equation, the  $pH_{is}$  is determined by the concentration of  $H^+$  and liquid water content (LWC) in the aerosols. LWC is strongly dependent on the ambient RH and water-soluble inorganic salts like sulfate, nitrate and ammonium in the aerosols. The aqueous phase concentration of  $H^+$  was lower from 12:00 to 21:00 compared to other time, which suggests a less acidity effect on the photochemical production of oxalic acid during this period.



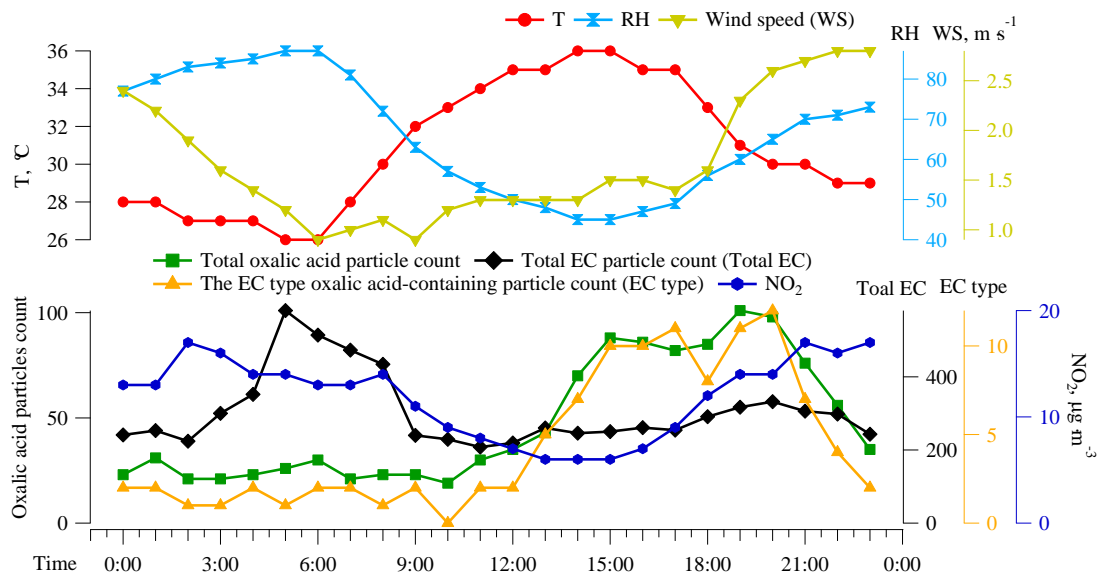


Figure S6. The diurnal variations of temperature (T), RH, wind speed (WS), oxalic acid particles, total EC particles, the EC type oxalic acid-containing particles and ambient NO<sub>2</sub> concentrations from July 28 to August 1 in 2014.

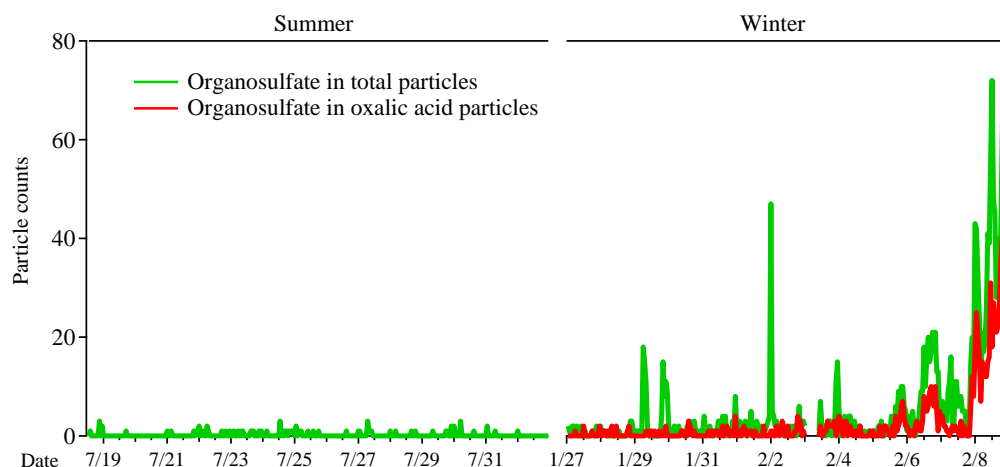


Figure S7. Temporal variation of organosulfate ( $m/z=-155$ ) containing particles in total particles and in oxalic acid particles in Heshan, China.

The organosulfate derived from reaction between glyoxal and sulfuric acid was identified at  $m/z=-155$  ( $[C_2H_3O_2SO_4]^-$ ) based on previous work conducted by Surratt (Surratt et al., 2007; Surratt et al., 2008) and Hatch (Hatch et al., 2011) in chamber and field measurements. In current work organosulfate-containing particles were identified if the relative peak area of  $m/z -155$  was larger than 0.5%. With this threshold, 78 and 1874 of organosulfate particles were obtained in summer and winter separately, accounting for 0.01% and 0.25% in each total detected particles. The temporal trend of organosulfate-containing oxalic acid particles in winter is also shown in Figure S8, which exhibited a similar pattern as the total oxalic acid particles. The percentage of organosulfate-containing oxalic acid particles in total oxalic acid particles ranged from 0 to 16.4% with the highest ratio observed on February 8.

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