Supplementary materials

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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	$[C]^+$	50	0.005	or
	24±0.5	$[C_2]^+$	50	0.005	or
	36±0.5	$[C_3]^+$	50	0.005	or
	48±0.5	$[C_4]^+$	50	0.005	or
	60±0.5	$[C_5]^+$	50	0.005	or
	-12	$[C]^-$	50	0.005	or
	-24	$[C_2]^-$	50	0.005	or
	-36	$[C_3]^-$	50	0.005	or
	-48	$[C_4]^-$	50	0.005	or
	-60	$[C_5]^-$	50	0.005	or
Organic Carbon	27	$[C_2H_3]^+$	50	0.005	or
	43	$[C_2H_3O]^+$	50	0.005	or
Elemental Carbon and Organic Carbon	12	$[C]^+$	50	0.005	or
	24	$[C_2]^+$	50	0.005	or
	36	$[C_3]^+$	50	0.005	or
	37	$[C_3H]^+$	50	0.005	or
	43	$[C_2H_3O]^+$	50	0.005	or
Biomass Burning	39	$[K]^+$	1500		and
	113,115	$[K_2Cl]^+$	50	0.005	or
	213	$[K_3SO_4]^+$	50	0.005	or
	-26	$[CN]^-$	50	0.005	or
	-59	$[C_2H_3O_2]^-$	50	0.005	or
	-73	$[C_3H_3O_2]^-$	50	0.005	or
Sec	18	$[NH_4]^+$	50	0.005	or
	39	$[K]^+$	1500		and
	-62	$[NO_3]^-$	100	0.05	
	-97	$[HSO_4]^-$	100	0.05	
Heavy Metal	206-208	$[Pb]^+$	50	0.005	or
	64,66	$[Zn]^+$	50	0.005	or
	63,65	$[Cu]^+$	50	0.005	or
	56	$[Fe]^+$	50	0.005	or
	55	$[Mn]^+$	50	0.005	or
	71	$[MnO]^+$	50	0.005	or
	51	$[V]^+$	50	0.005	or
	67	$[VO]^+$	50	0.005	or
Dust	24	$[Mg]^+$	1000		
	27	$[Al]^+$	1500		
	40	$[Ca]^+$	2500		
	56	$[CaO]^+/[Fe]^+$	100	0.05	

	-76	[SiO$_3$]$^-$	500	0.05	
NaK	23	[Na]$^+$	100	0.05	
	62	[Na$_2$O]$^+$	50	0.005	or
	63	[Na$_2$OH]$^+$	50	0.005	or
	81,83	[Na$_2$Cl]$^+$	50	0.005	or
	-35,-37	[Cl]$^-$	100	0.05	
Ammonium	18	[NH$_4$]$^+$	50	0.005	
Nitrate	-46	[NO$_2$]$^-$	100	0.05	
	-62	[NO$_3$]$^-$	100	0.05	
Sulfate	-80	[SO$_3$]$^-$	100	0.05	
	-97	[HSO$_4$]$^-$	100	0.05	
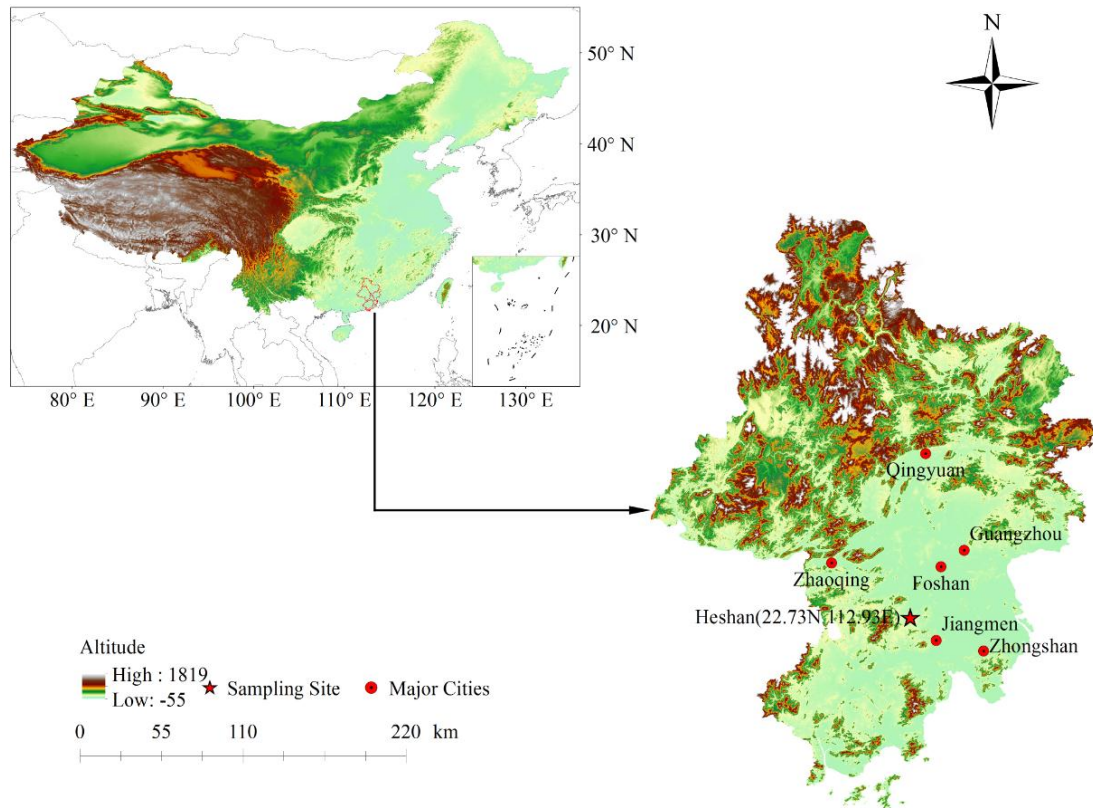
Figure S1. The topography of Heshan sampling site (22.73N, 112.93E) and its surrounding areas.
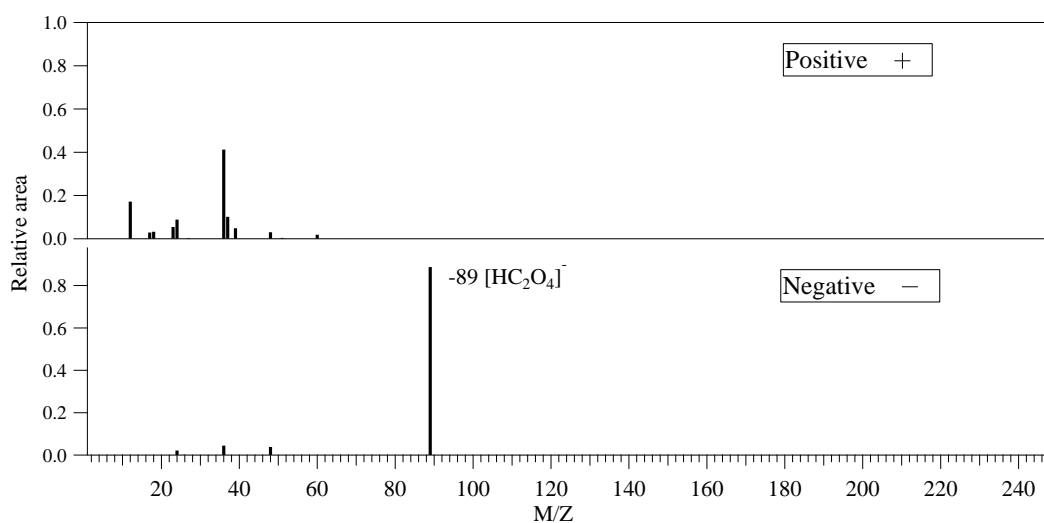
Figure S2. The positive and negative mass spectra of pure oxalic acid ($H_2C_2O_4$, purity: 99.99%, Aladdin Industrial Corporation) measured by SPAMS through authentic oxalic acid solution (200 μg•ml^{-1}).

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 ($HC_2O_4^-$) is significant in the negative mass spectrum. Carbon clusters of $12[C]^+$, $24[C_2]^+$, $36[C_3]^+$ are observed in positive mass spectrum, and $23[Na]^+$ and $39[K]^+$ also show peaks due to extremely high sensitivity of SPAMS to these elements which are present as trace impurities (<0.01). $HC_2O_4^-$ (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.
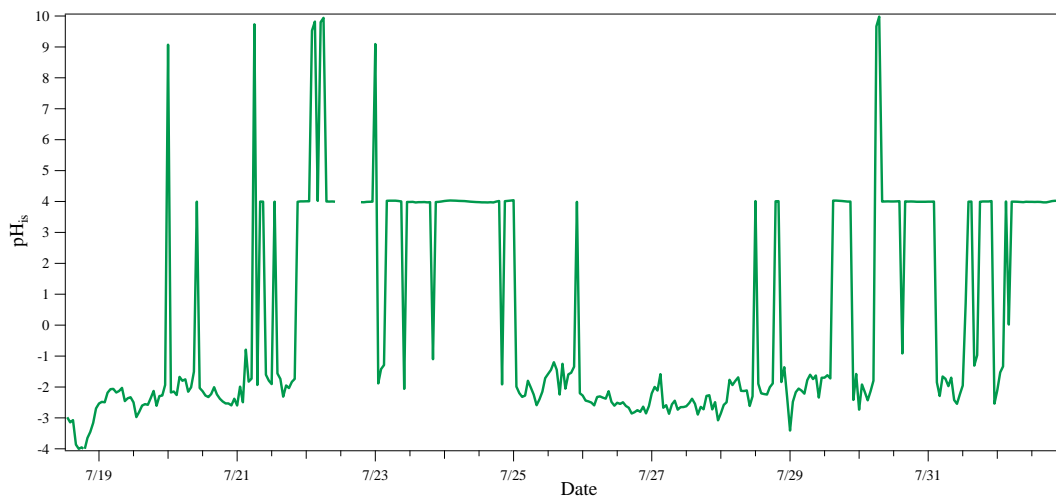
Figure S3. The temporal variation of in-situ pH (pH_{is}) of ambient $PM_{2.5}$ particles during sampling period in summer.
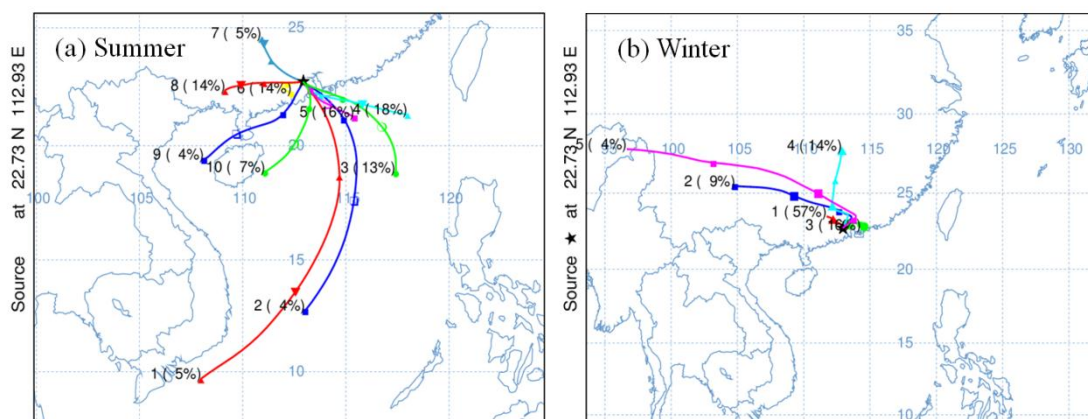
Figure S4. The clustered 48 hr back trajectories of air masses arriving in Heshan during the sampling period: (a) summer (from July 18 to August 1, 2014), (b) winter (from January 27 to February 8, 2015).
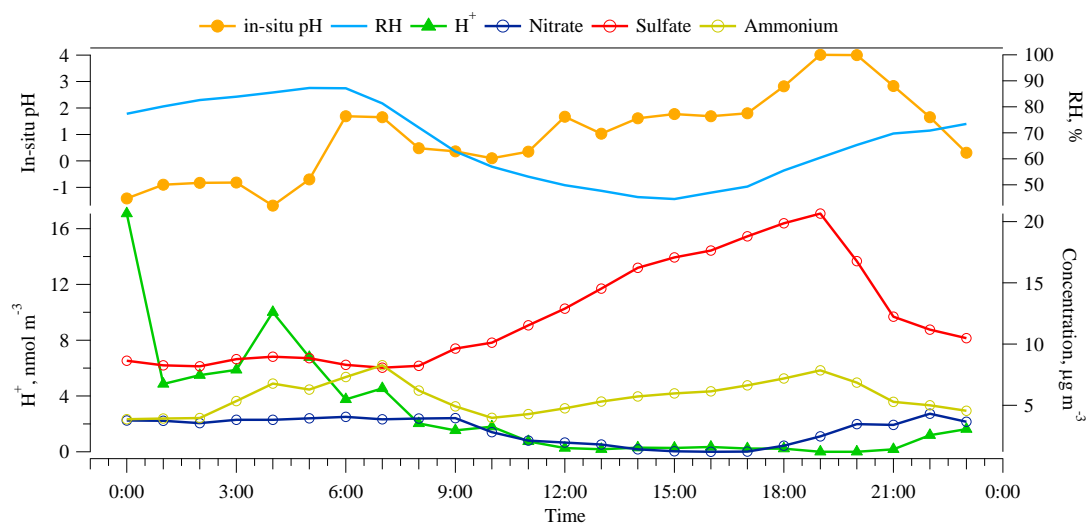
Figure S5. The diurnal variations of in-situ pH (pH_{is}), RH, nitrate, sulfate, ammonium and the free amount of H^+ in aerosols from July 28 to August 1 in 2014.

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 free amount of H^+ and liquid water content (LWC) in the aerosols. LWC is strongly dependent on the ambient RH and affected by water-soluble composition in the aerosols. Thus we investigate the diurnal patterns of RH, major inorganic ions and the free amount of H^+ in Figure S5. Although RH increased from 0:00 to 7:00, H^+ had higher concentration during this period than the other time, which resulted the lower value of pH_{is} (between -1.42 and 0) from 0:00 to 5:00. Thus more acidic aerosols with pH_{is} below 0 were observed due to the combined effects of the RH and relative abundance of H^+ in aerosols.
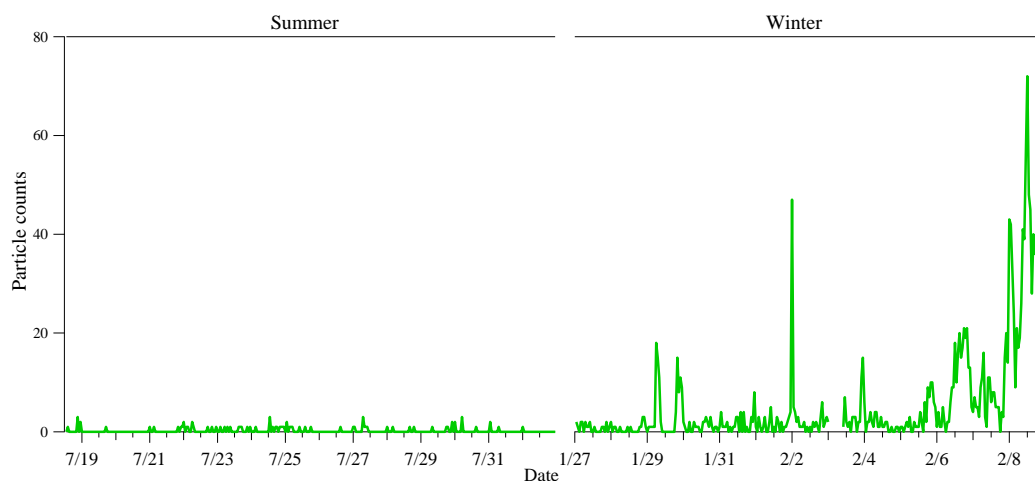
Figure S6. Temporal variation of organosulfate (m/z=-155) containing particles during whole sampling periods in Heshan, China.

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.

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