

1 **Temporal and spatial variation in major ion chemistry and source**
2 **identification of inorganic aerosols in northern Zhejiang Province, China**

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27 **Abstract**

28 To investigate the seasonal and spatial variations of ion chemistry on fine particles in northern
29 Zhejiang Province (NZIP), China, a year-long field study was carried out at 4 representative sites
30 (2 urban, 1 suburb and 1 rural sites) in both Hangzhou and Ningbo cities from November 2014 to
31 November 2015. Twelve water soluble inorganic ions (WSII) have been characterized in this
32 study. In NZP, the annual averaged $PM_{2.5}$ concentration was $66.2 \pm 37.7 \mu\text{g m}^{-3}$ and urban sites
33 were observed with more severe $PM_{2.5}$ pollution than the suburban and rural sites; the annual
34 averaged total WSII concentration was $29.1 \pm 19.9 \mu\text{g m}^{-3}$, dominated by SO_4^{2-} ($10.3 \mu\text{g m}^{-3}$),
35 NO_3^- ($8.9 \mu\text{g m}^{-3}$), NH_4^+ ($6.6 \mu\text{g m}^{-3}$), Cl^- ($1.3 \mu\text{g m}^{-3}$) and K^+ ($0.7 \mu\text{g m}^{-3}$). NH_4^+ was highly
36 correlated with NO_3^- and SO_4^{2-} (r : 0.8~1.0) throughout the sampling period at 4 sites and the
37 annual averaged molar ratio of $[NH_4^+]/[SO_4^{2-}]$ of 4 sites were all above 3.3, indicating NH_4^+
38 existed predominantly as $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3 in aerosols, which was also the
39 predominant neutralizing cation with the highest neutralization factor (NF). The seasonal
40 patterns of SOR and NOR values were opposite to each other, which seemed influenced by
41 seasonal weather conditions and inter-relationships of $SO_2 - SO_4^{2-}$ and $NO_2 - NO_3^-$
42 transformations. Principal component analysis (PCA) showed that the predominant sources of
43 WSII in NZP were industrial emissions, biomass burning, and secondary inorganic aerosols; in
44 addition, transboundary transport of polluted aerosols also contributed based on air mass
45 backward trajectory.

46 **Keywords**

47 Northern Zhejiang Province, $PM_{2.5}$, inorganic ions, temporal and spatial variability, PCA

48 1. Introduction

49 Atmospheric aerosols, especially fine particles (aerodynamic diameter of $\leq 2.5 \mu\text{m}$, $\text{PM}_{2.5}$),
50 comprising a complex mixture of suspended solid particles and liquid droplets, have received a
51 lot of attention over the recent decades due to their important roles in affecting ecology, climate
52 change, visibility and public health, such as respiratory diseases, cardiopulmonary mortality and
53 lung cancer (Pope et al., 2002; Pope and Dockery, 2006; Fang et al., 2011; He et al., 2011; Xu et
54 al., 2016a). In terms of the sources and formation processes, they are basically classified as
55 primary and secondary aerosols; the former are emitted directly from various sources; while the
56 latter are formed through gas-particle transformation. For example, gaseous SO_2 and NO_2
57 emitted mostly from coal-fired power plants and vehicles can be oxidized and converted to SO_4^{2-}
58 and NO_3^- in the atmosphere through heterogeneous and homogeneous reactions (Kang et al.,
59 2010; Lin et al., 2009). Then these inorganic species can be converted to secondary aerosol
60 particles such as $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , and NH_4NO_3 through the neutralization reactions with
61 NH_4^+ , which is originated from gas-phase NH_3 . It is reported secondary inorganic aerosols
62 (sulfate, nitrate and ammonium (SNA)) are one of the most significant contributors to particulate
63 matters (Waldman et al., 1991; He and Balasubramanian, 2008), accounting for one third or
64 more of fine particles (Meng et al., 2016; Tsai and Chen, 2006; Wang et al., 2006); and they are
65 also reported to be one of the most important factors leading to visibility impairment (Kang et
66 al., 2004; Tian et al., 2014). Their formation greatly depends on the characteristics of pre-
67 existing aerosols, occurrence levels of the gaseous precursors, relative humidity (RH) and
68 atmospheric oxidants etc. (Baek et al., 2004; Deng et al., 2015; Pathak et al., 2009).

69 In China, due to the significantly decreasing air quality during recent decades across the
70 country, the pollution characteristics of aerosols have been widely studied. Among various

71 components of atmospheric aerosols, water-soluble components are of great interest in urban
72 atmosphere due to their impact on controlling the aerosol acidity and environmental acidification
73 (Deng et al., 2015). The earliest studies on WSII can be traced back to 1990s in China (Waldman
74 et al., 1991), and after that a number of researches have been conducted in many cities to
75 investigate the characteristics of water-soluble inorganic ions, such as Xiamen (Zhao et al., 2011),
76 Handan (Meng et al., 2016), Guangzhou (Hu et al., 2008), Jinan (Gao et al., 2011) and Beijing
77 (Hu et al., 2014; Huang et al., 2016), etc. Yangtze River Delta (YRD) is one of the largest city-
78 clusters and economically well-developed regions in China, and WSII characteristics of severe
79 aerosol pollution in this region have also been reported to some extent. In a western city of YRD-
80 Nanjing, Wang et al. (2016b) studied the seasonal and diurnal variations and sources of water-
81 soluble inorganic ions based on one-year online measurement data. Qiao et al. (2015)
82 investigated the seasonal variation of WSII in PM_{10} and their effects on haze episodes in
83 Shanghai. Hua et al. (2015) studied the ion characteristics of $PM_{2.5}$ during a severe haze episode
84 by a joint field observations at five cities in YRD and the source apportionment indicated that
85 $PM_{2.5}$ was predominantly from secondary pollutants and primary emissions of vehicles and
86 biomass burning. In an offshore site at east coastal line of Jiangsu Province, Kong et al. (2014)
87 investigated the ion chemistry including the ion mass concentration, ion balance and sea salt
88 contributions of size-segregated aerosols in autumn 2012 and found the sea salt contribution
89 could be ignored despite its geographical closeness to the East China Sea. Most of the previous
90 studies of ionic chemistry in fine aerosols in this region have been either based on a particular
91 haze episode or a particular sampling site, which may not represent the seasonal ion pollution
92 characteristics of the YRD region well. Due to the absence of long-term observation of
93 atmospheric inorganic ions in this region, Wang et al. (2015a) investigated the seasonal

94 variations and sources of water-soluble inorganic ions in size-fractionated aerosols of 5 urban
95 sites in YRD, but their data lacked the comparisons among the ion chemistry in urban, suburban
96 and rural areas in YRD. In this respect, the investigation of the seasonal ion chemistry and
97 sources in fine particles of urban, suburban and rural sites in YRD should be valuable to filling
98 such a gap and gain further knowledge of how ion chemistry in fine particles of various
99 representative sites in this region might differ from one another.

100 Due to the limited study of WSII on fine aerosols in northern Zhejiang Province (NZZP), 12
101 ionic species (F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) from 4 different
102 representative sites in this area located in the southern YRD were investigated, including two
103 urban, one suburban and one rural site. The main objectives of this work were to characterize the
104 temporal and spatial variations of fine aerosols and above mentioned ionic species profiles in
105 NZZP, compare the ionic chemistry at sites with different urbanization gradients and explore the
106 potential sources of these fine inorganic aerosols in this region.

107 **2. Experimental**

108 2.1. Sampling site

109 In order to investigate the ion chemistry of $PM_{2.5}$ and their possible sources in NZZP, different
110 types of representative sampling sites have been selected in both cities of Hangzhou and Ningbo,
111 which are presented in Fig. 1 and briefly introduced as below.

112 1) The University of Nottingham Ningbo, China (UNNC; suburban site; $29.80^\circ N$, $121.56^\circ E$)
113 is located at the University Park in the south of Ningbo city, less than 10km away from the
114 central business district (CBD). It can be characterized as an intermediate transition zone which
115 is affected by the pollution from both urban and rural anthropogenic activities.

116 2) Ningbo Meteorological Bureau (NMB; urban site; 29.86°N, 121.52°E) is located by the
117 side of a main road– Qixiang Road in Ningbo urban center and adjacent to a high school and
118 residential area. It is also only approximately 1km away from the airport highway elevated
119 bridge and 500m from a provincial highway. Therefore, it is expected to be influenced more by
120 traffic emissions.

121 3) Lin'an Regional Atmospheric Background Station (LRABS; rural site; 30.30°N,
122 119.73°E) , at the outskirts of Lin'an county within Hangzhou municipality, is a background
123 monitoring station for the World Meteorological Organization (WMO) global atmospheric
124 observation network. It is surrounded by agricultural fields and woods, and less affected by
125 urban, industrial and vehicular emissions.

126 4) Hangzhou Meteorological Bureau (HMB; urban site; 30.22°N, 120.17°E) is one of the
127 national atmospheric and meteorological monitoring stations in China. It is located at the urban
128 center of a densely populated city– Hangzhou, and close to a few heavy traffic roads with
129 distance around 200m.

130 2.2. Sample collection

131 The collection of PM_{2.5} was started simultaneously at 9 AM (1 UTC) at four above
132 mentioned sites every 6 days from 12 November 2014 to 12 November 2015. The 24-hour
133 sampling was conducted by medium volume PM_{2.5} samplers (Model: TH-150CIII, Tianhong
134 Instrument CO., Ltd. Wuhan, China), operating at a flow rate of 80 L min⁻¹ and PM_{2.5} aerosols
135 were captured on 90 mm quartz fiber filters (QMA, Whatman, UK). All filters were pre-baked in
136 muffle furnace for 5 hours at 550°C prior to any other treatments or usage. Blank samples were
137 obtained monthly at four sites.

138 2.3. Acquisition of PM_{2.5} mass, meteorological data and air mass backward trajectories

139 Prior to any gravimetric measurement, filters were equilibrated in a micro-balance room with
140 constant temperature ($22^{\circ}\text{C} \pm 1^{\circ}\text{C}$) and relative humidity ($30\% \pm 5\%$) for 24h before and after
141 the sampling events. The PM_{2.5} mass on 90mm quartz fiber filters were measured by an ultra-
142 microbalance (Model: SE2-F, Sartorius, precision 0.1 μg). After that, filters were wrapped in
143 prebaked aluminum foil and stored in refrigerator under -20°C until analysis.

144 Meteorological data (wind speed, precipitation, temperature and relative humidity) and
145 concentrations of gaseous pollutants (SO_2 , NO_2 , O_3) applied in this study were obtained from the
146 corresponding local air quality monitoring stations closest to each sampling site (less than 500m
147 distance) during the same aerosol sampling periods.

148 The air mass backward trajectories were computed from archived global data assimilation
149 system (GDAS1, 2006-present) meteorological data. 96 hours air mass backward trajectories
150 were started at 9:00 AM local time (1 UTC) with 6 hours intervals at a height of 500 m above
151 ground level (AGL) on each sampling day and calculated separately for each sampling site.
152 Achieved trajectories were then clustered by season using the air resources laboratory (ARL) of
153 National Ocean and Atmospheric Administration (NOAA) Hybrid Single-Particle Integrated
154 Trajectory (HYSPLIT 4.9) model (Draxler, 2013; Rolph, 2013), and those trajectories with
155 similar sources were merged. Clusters can reduce errors that might be related to a single
156 trajectory and indicate more accurate origins of those pollutants.

157 2.4. Ionic analysis

158 One eighth 90mm quartz fiber filters were used for ion analysis, which were extracted
159 ultrasonically using 20 mL of deionized water for 30 min, filtered with the $0.45\mu\text{m}$ PTFE
160 microporous membrane and stored in a refrigerator at 4°C until chemical analysis within two

161 weeks. In total, 6 anions (F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) and 6 cations (Li^+ , Na^+ , NH_4^+ , K^+ ,
162 Mg^{2+} , Ca^{2+}) were investigated by Ion Chromatograph (ICS-1600, Dionex, USA). Detailed
163 information about the detection system and methods could be found elsewhere (Xu et al., 2016b).
164 Ion concentrations were calculated through the external calibration ($r^2 \geq 0.99$) with authentic
165 standards purchased from Sigma-Aldrich and corrected by subtracting blank values obtained
166 from field blank samples.

167 **3. Results and discussion**

168 3.1. Air mass backward trajectory analysis

169 The air mass backward trajectories are very useful to identify the source origins of the
170 particulate pollutants measured at the sampling sites. Fig. 2 shows the clusters of air mass
171 backward trajectories during each season at different representative sampling sites of NCP,
172 which exhibited distinctive seasonal variations.

173 In winter, clusters at four sites were very similar to each other in this region; 75%-97% of the
174 air masses were coming through northwest and north China before arriving at the sampling sites
175 and part of them were originated from Russia and Kazakhstan. In spring, 13%-37% were
176 originated from northwestern Asia; at UNNC and NMB, 20%-30% were from northwestern
177 China and the rest were from either a mixed oceanic and terrestrial source or local origins in
178 YRD; at LRABS and HMB, around 50% of air masses were from central China and local YRD
179 region, respectively. In summer, 45%-64% of the air masses were originated from Chinese Bohai
180 Sea and Pacific Ocean and another part was from South China Sea and passing through southern
181 China to reach the studied sites with both oceanic and terrestrial source characteristics; the rest
182 10-29% was from the central China. In autumn, the clusters at UNNC and NMB showed similar
183 origins due to their geographical closeness to each other; approximately 40% of the trajectories

184 were originated from Russia and Inner Mongolia and the rest were from oceanic origin; at
185 LRABS and HMB, around 20% of trajectories were coming from north China, the rest were with
186 mixed origins of both ocean and land, among of which 10~20% were transported through south
187 China to sampling sites.

188 3.2. Spatial and temporal variability of meteorological conditions and PM_{2.5} concentrations in 189 NZP

190 Continuous hourly measured meteorological data were converted to give daily averaged
191 values from 9 AM on the sampling day to the same time next day. The seasonal mean
192 meteorological parameters (calculated as the daily average of sampling days during each season),
193 including wind speed (m s^{-1}), precipitation (mm), temperature ($^{\circ}\text{C}$) and relative humidity (RH, %)
194 at four sampling sites throughout the sampling campaign are summarized in Table 1.

195 The seasonal averaged temperature and RH at four sampling sites followed the same pattern:
196 Summer > Autumn > Spring > Winter. This is most likely due to the typical marine monsoon
197 subtropical climate in NZP of YRD region, thus all sampling sites in this region are featuring
198 cool dry winters and hot humid summers (Haas and Ban, 2014). The seasonal mean highest
199 temperature in NZP was 26.7°C during summer and the lowest was 6.3°C during winter. Winter
200 was also recorded as the driest season with RH of 64.1% and summer was recognized as the
201 most humid season with RH of 77.8%. The wind speeds of winter, spring and summer were very
202 similar, but that in autumn was obviously lower than the other seasons, implying a more stagnant
203 meteorological condition and weaker advection for dispersion.

204 The annual average PM_{2.5} concentration in this region (calculated as the average of PM_{2.5} at
205 four sampling sites) was $66.2 \pm 37.7 \mu\text{g m}^{-3}$, which is nearly twice the National Ambient Air
206 Quality Standards of China– Grade II ($35 \mu\text{g m}^{-3}$ for annual PM_{2.5} concentration), applicable to

207 residential, commercial, industrial and rural areas (MEP, 2012). To compare this result with
208 those in other cities of YRD, it is higher than the 3-year average PM_{2.5} concentration (47 μg m⁻³)
209 measured in Shanghai (Wang et al., 2016c), but comparable with the annual PM_{2.5} occurrence
210 levels in Hangzhou (64 ± 47 μg m⁻³) and Nanjing (75 ± 50 μg m⁻³) (Wang et al., 2014). The
211 annual average concentration of PM_{2.5} at four sites ranked as: UNNC (51.2 ± 29.1 μg m⁻³) <
212 LRABS (66.3 ± 36.6 μg m⁻³) < NMB (70.4 ± 40.6 μg m⁻³) < HMB (80.0 ± 39.6 μg m⁻³). Clearly,
213 the annual average PM_{2.5} concentrations in urban sites (NMB & HMB) were higher than the
214 other two suburban and rural sites (UNNC & LRABS), possibly indicating stronger
215 anthropogenic sources could contribute more to the higher occurrence levels of fine aerosol
216 particles in urban areas. Among four sites, UNNC was observed with the lowest annual PM_{2.5}
217 concentration and the highest average wind speed throughout the sampling period. Besides the
218 reasons such as less local emission impact that could be beneficial to the lower occurrence of
219 PM_{2.5} levels at this site, the easier dispersion of aerosol by the stronger wind speed and smoother
220 terrain feature surrounding the sampling site could also be one of them.

221 The averaged seasonal variations of PM_{2.5} concentrations at two urban sites (NMB & HMB)
222 showed the following pattern: Winter > Spring > Autumn > Summer, which is consistent with
223 that in an urban site of Shanghai (Wang et al., 2016c); while the occurrence levels of PM_{2.5} in
224 suburban and rural sites (UNNC & LRABS) showed slightly different: Winter > Autumn >
225 Spring > Summer, the same as that observed in a western downtown sampling area in Nanjing
226 of YRD (Li et al., 2015).

227 Among four seasons, the highest average PM_{2.5} concentration was observed in winter while
228 the lowest in summer. Heavy particle pollution in winter could be the synergetic effect of
229 increased emission from fuel burning and accumulation of pollutants under stagnant weather

230 conditions. Lower temperature in winter would lead to the increasing consumption of fuel, such
231 as biomass burning in rural areas and coal combustion in power plants, to meet the increased
232 energy demands for domestic house heating (Behera et al., 2015), resulting in more intensive
233 exhaust of air pollutants (Han et al., 2016). Meanwhile, these air pollutants would accumulate
234 under more calm and static atmospheric environment in winter as this season in this region is
235 normally characteristic of low wind speed, weak solar radiation and strong surface inversion,
236 which would lead to low planetary boundary layer (PBL) height and poor air dispersion (Behera
237 et al., 2015; Seidel et al., 2010). While in summer, wind mostly blows from the East China Sea
238 where less polluted air mass is transported to YRD; in addition, higher mixing layer during hot
239 summer could induce stronger vertical diffusion and dispersion of air pollutants.

240 It is noteworthy that the seasonal averaged PM_{2.5} concentrations in autumn were lower than
241 those in spring of two urban sites (NMB and HMB), but they were opposite at the other two
242 suburb and rural sites. These findings could be the result of various wet precipitation rates during
243 the different seasons and stronger precipitation favored to increase the scavenging of aerosols. In
244 addition, at suburban and rural sites, more open burning events for land clearing tend to occur
245 during autumn harvest season, mainly in October and November (Yin et al., 2017). Therefore, at
246 UNNC and LRABS, more emissions from biomass burning were expected to contribute to the
247 higher PM_{2.5} concentrations in autumn than in spring.

248 3.3. Characteristics of water-soluble inorganic ions (WSII)

249 3.3.1. Annual occurrence level of total WSII

250 The annual average concentration of total WSII in NZP was $29.1 \pm 19.9 \mu\text{g m}^{-3}$, constituting
251 44.0% of the annual average PM_{2.5} concentration. Sulfate, nitrate and ammonium (SNA) ranked
252 as the top three ions with highest concentrations in this study, and the sum of them was $25.6 \pm$

253 18.4 $\mu\text{g m}^{-3}$, accounting for 88.0% of total WSII and 38.7% of $\text{PM}_{2.5}$ concentration in this region,
254 respectively.

255 In order to better understand the fine aerosol pollution in YRD, intra- and inter-city
256 comparisons have been conducted as presented in Table 2 and other polluted areas in China
257 including North China Plain (NCP), Northwest China (NWC) and Pearl River Delta (PRD).

258 Cities in NCP such as Handan, Hefei and Tianjin were observed with much higher $\text{PM}_{2.5}$ and
259 total WSII concentrations, but the mass ratio of WSII in $\text{PM}_{2.5}$ is comparable to those found in
260 this study (Deng et al., 2015; Meng et al., 2016; Zhou et al., 2016). In addition to the effects of
261 stagnant meteorological conditions leading to high accumulation or trans-boundary transport of
262 pollutants originated from other regions, it seems that the aerosol pollution in different regions
263 also have its own characteristics. Higher particle pollution level in NCP is most likely due to the
264 numerous anthropogenic emissions from heavy industries and strong traffic emissions in this
265 region, as a result of its rapid population growth and economic development in past few decades
266 (Ran et al., 2016). Cities like Xi'an and Weinan in NWC were also observed with higher aerosol
267 concentrations, but the one in Xi'an had a relatively lower WSII/ $\text{PM}_{2.5}$ ratio compared to this
268 study (Niu et al., 2016; Zhang et al., 2011), which might be due to its higher mineral dust
269 contribution as it occurs frequently in this area (Zhang et al., 2011). The occurrence levels of fine
270 aerosols in urban PRD area seem very comparable to those in this study (Tao et al., 2009; Zhou
271 et al., 2016). In Shanghai a two-year (2012-2013) sampling campaign found out that the average
272 $\text{PM}_{2.5}$ concentration was lower than those reported in other cities in YRD, but WSII/ $\text{PM}_{2.5}$ ratio
273 was over 60% indicating a strong contribution of secondary inorganic ions to fine aerosols in this
274 urban area (Wang et al., 2016c).

275 3.3.2. Spatial and temporal variability of WSII in northern Zhejiang Province

276 The annual total WSII concentrations at four sampling sites followed such an order: UNNC
277 ($21.0 \pm 10.8 \mu\text{g m}^{-3}$) < NMB ($26.7 \pm 18.8 \mu\text{g m}^{-3}$) < LRABS ($29.6 \pm 18.2 \mu\text{g m}^{-3}$) < HMB ($41.3 \pm$
278 $25.5 \mu\text{g m}^{-3}$), contributed to 38.6% ~ 49.2% of $\text{PM}_{2.5}$, as shown in Table 2. Similar to the
279 occurrence levels of $\text{PM}_{2.5}$ and WSII, SNA exhibited much higher concentrations in NCP and
280 NWC than those in this study, which however seemed comparable to the reported values in YRD
281 and PRD. The annual SNA concentration at UNNC, the suburban site of Ningbo, was $17.4 \mu\text{g m}^{-3}$
282 ³, accounting for 81.9% of total WSII concentration and 35.8% of $\text{PM}_{2.5}$; while at NMB, the
283 urban site of Ningbo, higher annual SNA concentration of $23.0 \mu\text{g m}^{-3}$ was observed with higher
284 mass ratio of 83.3% in total WSII but lower proportion of 32.9% in $\text{PM}_{2.5}$. Higher annual SNA
285 concentrations of $27.2 \mu\text{g m}^{-3}$ (90.5% of total WSII concentration and 40.5% of $\text{PM}_{2.5}$) and 37.0
286 $\mu\text{g m}^{-3}$ (88.8% of total WSII concentration and 44.5% of $\text{PM}_{2.5}$) were observed at LRABS and
287 HMB in Hangzhou, respectively, suggesting the secondary aerosol formations at both sites were
288 more significant than Ningbo.

289 Table 3 illustrates the seasonal and annual averaged WSII concentrations at four sampling
290 sites. Among the investigated ions at all sites, NH_4^+ , NO_3^- , SO_4^{2-} and Cl^- were of predominance
291 and the first three are known to be the dominant secondary particles with their abundances
292 mainly dependent on the concentrations of their precursor gases and transformation rates. As
293 shown in Table 3, winter was observed with the highest ionic concentrations while summer was
294 observed with the lowest. The concentrations of both ammonium and nitrate in winter were 2~6
295 times higher than those in summer. This could be related to the low temperature in winter that
296 favors a conversion from nitric acid and ammonia gases to the particulate ammonium nitrate and
297 also that most nitrate would prefer to be gaseous at temperature higher than 30°C (Deng et al.,

298 2015). The seasonal variation of nitrate concentration could also be attributed to the seasonality
299 of NO_x emission (Li and Han, 2016). It is known that both HCl and SO₂ are the typical pollutants
300 emitted from coal combustion (Xue et al., 2016); hence, the highest abundance of both sulfate
301 and chloride in winter could be likely due to the increased coal consumption during heating
302 period combined with poor dispersion (He et al., 2001). In addition to the local emissions, during
303 winter in YRD, the prevalent north or northwest winds can bring atmospheric pollutants from
304 NCP, where more consumption of coal for domestic heating also occurs in this season (Wang et
305 al., 2016c), to the sampling sites in this study via long-range transport, which was supported by
306 air mass backward trajectory analysis in Section 3.1 that 75%-97% of the air masses were
307 coming through northwest and north China before arriving at the sampling sites.

308 Apart from NH₄⁺, Cl⁻, NO₃⁻ and SO₄²⁻, the concentration of K⁺ was the highest among the rest
309 ions. The highest concentration of K⁺ occurred in winter as well, it is around 2~4 times higher
310 than summer at four sites. As it is predominantly generated from biomass burning, such as wood,
311 grass and crop straw burning (Xu et al., 2016b), suggesting biomass burning is an important
312 contributor to the fine particles in the NZP, which can be supported by the high level of non-sea
313 salt (nss) K⁺ during winter (1.0 μg m⁻³) and spring (0.9 μg m⁻³) in a rural site- LRABS.

314 3.3.3. Aerosol acidity

315 (1) Ion balance

316 Water-soluble inorganic ions play important roles in controlling the aerosol acidity and
317 environmental acidification. Therefore, the aerosol acidity is also investigated in this study by
318 ion balance, which is determined by both anion equivalence (AE) and cation equivalence (CE),
319 calculated by following equations:

$$320 \quad AE = F^{-}/19 + Cl^{-}/35.5 + NO_3^{-}/46 + Br^{-}/80 + NO_2^{-}/62 + PO_4^{3-}/31.7 + SO_4^{2-}/48 \quad (1)$$

321
$$CE = Li^+/7 + Na^+/23 + NH_4^+/18 + K^+/39 + Mg^{2+}/12 + Ca^{2+}/20 \quad (2)$$

322 Where, F⁻, Cl⁻, NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ refer to their
 323 mass concentrations (μg m⁻³). Through calculations by the above equations, the anion and cation
 324 concentrations (μg m⁻³) were converted into their corresponding micro-equivalents (μ mol m⁻³)
 325 and the relationships between AE and CE in four seasons of the sampling sites are plotted in Fig.
 326 3.

327 As shown in Fig. 3, good correlations and very small intercepts between AE and CE were
 328 found in 4 seasons; therefore, the anion/cation equivalent ratios (AE/CE) were defined as the
 329 slopes of linear regressions in this study. At 4 sites, the correlation coefficients of AE and CE
 330 were in the range of 0.77~0.99, similar to the results in another study of YRD (0.72~0.94) (Wang
 331 et al., 2015a). At UNNC and HMB, the AE/CE ratios in four seasons were mostly above 1.0,
 332 except the ratio close to 1 in the summer of UNNC. These results indicated a deficiency in
 333 cations of PM_{2.5} samples in UNNC and HMB, anions were not fully neutralized and caused
 334 acidic nature of fine particles at these two sites. When using the equivalent ratio of [NH₄⁺]/
 335 [NO₃⁻+SO₄²⁻] to evaluate the aerosol acidity (Wang et al., 2016a), the ratio at HMB was 0.99,
 336 indicating a good neutralization relationship between the major secondary species at this site
 337 during the sampling period. At UNNC, the annual averaged equivalent ratio of [NH₄⁺]/ [NO₃⁻
 338 +SO₄²⁻] was only 0.89, while the annual averaged equivalent ratio of [NH₄⁺+Ca²⁺]/ [NO₃⁻+SO₄²⁻]
 339 of UNNC could be up to 0.98, suggesting Ca²⁺ might be another main cation affecting the
 340 neutralization of NO₃⁻ and SO₄²⁻. This could be explained by the fact that a number of
 341 construction sites existed around UNNC during this sampling campaign, which might be the
 342 dominant sources of Ca²⁺ at this site showing strong influence on the ionic chemistry here.

343 In LRABS, during winter and spring, it had lower AE/CE value (<1) and the seasonal
344 averaged equivalent ratio of $[\text{NH}_4^+]/[\text{NO}_3^-+\text{SO}_4^{2-}]$ of winter and spring were 1.13 and 1.36,
345 respectively, implying the aerosol samples during these two seasons were alkaline, probably due
346 to the increased biomass burning in winter and more usage of ammonia containing fertilizer in
347 spring for cultivation at this rural site (Whitburn et al., 2015). The aerosol collected in autumn at
348 Lin'an had shown higher AE/CE ratio ($=1.09$), indicating these aerosols were more acidic, which
349 could be attributed to the higher occurrence level of NO_3^- in autumn, which was 2.8 times that
350 during summer when ammonium nitrate is more easily volatilized as mentioned before. The
351 AE/CE ratio during summer at Lin'an was close to 1 and the averaged equivalent ratio of
352 $[\text{NH}_4^+]/[\text{NO}_3^-+\text{SO}_4^{2-}]$ was 0.95, indicating anions and cation maintained a good neutralization
353 relationship.

354 The AE/CE slope of the linear regression for NMB were all lower than 0.9 in the whole
355 sampling campaign; since most of the anions were analyzed but not the carbonate and
356 bicarbonate due to the limitation of the Ion Chromatogram (IC) method, the anion deficits in
357 aerosol samples of NMB could be partially attributed to the absence of both ions (Meng et al.,
358 2016). The annual averaged equivalent ratio of $[\text{NH}_4^+]/[\text{NO}_3^-+\text{SO}_4^{2-}]$ of NMB was 1.11, also
359 suggesting NH_4^+ was over-sufficient to neutralize NO_3^- and SO_4^{2-} . The excess of NH_4^+ could be
360 associated with anions like chloride and carbonate. Moreover, since NMB is located by the side
361 of a main road and near a couple of highways, it is expected to be influenced heavily by traffic
362 emissions, an important source of urban NH_3 derived from urea used in the selective catalytic
363 reduction (SCR) in vehicular engines (Pan et al., 2016), which seems supported by the higher
364 annual concentration of NH_4^+ at urban site NMB ($6.6 \mu\text{g m}^{-3}$) than suburban site UNNC ($3.9 \mu\text{g}$
365 m^{-3}) in Ningbo.

366 (2) Neutralization Factors (NF)

367 In order to further find out the significance of each cation in neutralizing aerosol acidity, the
368 neutralization capacities of major cations (nss-Ca²⁺, Mg²⁺, nss-K⁺ and NH₄⁺) were individually
369 estimated by applying the Neutralization Factors (NFs). SO₄²⁻ and NO₃⁻ were considered as the
370 dominant acidifying anions. Na⁺ and Cl⁻ were considered negligible in past few studies for
371 calculation of NF, as they existed mostly in the form of neutral sea salt (Safai et al., 2010;
372 Satsangi et al., 2013). However, in this study, poor correlation of Na⁺ and Cl⁻ (r² < 0.5) were
373 found at all four sites, suggesting possible different origins of Cl⁻. Moreover, the Na⁺/ Cl⁻
374 equivalent ratios of UNNC, NMB, LRABS and HMB were 0.47, 0.53, 0.91 and 0.51,
375 respectively, lower than that in seawater (1.1) (Xu et al., 2014), implying Cl⁻ could also have
376 other sources such as coal combustion and waste incineration in addition to sea salt (Xue et al.,
377 2016). LRABS had the highest Na⁺/ Cl⁻ equivalent ratio (0.91) and lowest Cl⁻/ PM_{2.5} mass ratio
378 (0.9%) among four sites (HMB: 1.8%; NMB: 2.2%; UNNC: 2.9%), suggesting relatively more
379 marine effect yet less contribution of other combustion processes at this rural site. Therefore, the
380 role of Cl⁻ in neutralization could not be neglected in this study. As Na⁺ was assumed to be all
381 derived from the ocean (Kong et al., 2014), and it predominantly existed as NaCl in sea salts
382 (Ueda et al., 2014), hence non-sea salt [Cl⁻] can be calculated by subtracting [Na⁺] from [Cl⁻] and
383 NFs were calculated by Equation (3-6):

384
$$NF (nss - Ca^{2+}) = [nss - Ca^{2+}] / ([nss - SO_4^{2-}] + 2[NO_3^-] + 2[Cl^-] - 2[Na^+]) \quad (3)$$

385
$$NF (Mg^{2+}) = [Mg^{2+}] / ([nss - SO_4^{2-}] + 2[NO_3^-] + 2[Cl^-] - 2[Na^+]) \quad (4)$$

386
$$NF (nss - K^+) = [nss - K^+] / (2[nss - SO_4^{2-}] + [NO_3^-] + [Cl^-] - [Na^+]) \quad (5)$$

387
$$NF (NH_4^+) = [NH_4^+] / (2[nss - SO_4^{2-}] + [NO_3^-] + [Cl^-] - [Na^+]) \quad (6)$$

388 [X] represents the molar concentration of ions, and nss-SO_4^{2-} , nss-K^+ and nss-Ca^{2+} were
389 estimated in section 3.4.1.

390 Fig. 4 depicts the NFs of nss-Ca^{2+} , Mg^{2+} , nss-K^+ and NH_4^+ in $\text{PM}_{2.5}$ at 4 sites of northern
391 Zhejiang Province. As expected, NH_4^+ was the predominant neutralizing cation with the highest
392 NF, and the average annual NF of NH_4^+ at 4 sites were LRABS (1.12) > NMB (1.08) > HMB
393 (0.95) > UNNC (0.83). The annual NF of NH_4^+ in LRABS and NMB were above 1, indicating
394 the excess of NH_4^+ after neutralizing nss-SO_4^{2-} , NO_3^- and Cl^- , which might also be explained by
395 those reasons discussed in Section 3.3.3 for part of AE/CE ratios smaller than unity at these two
396 sites. The NF values of nss-Ca^{2+} , nss-K^+ and Mg^{2+} were lower than 0.2, implying relatively
397 minor impact of these ions in the neutralization of aerosol acidity. On an annual basis, the
398 neutralization capacities of ions in UNNC and NMB ranked as: NH_4^+ > nss-Ca^{2+} > nss-K^+ >
399 Mg^{2+} . nss-Ca^{2+} was the second dominant neutralizing cation at both sites of Ningbo, possibly
400 due to the strong dust effect from the nearby construction areas and main roads as discussed
401 before. In LRABS, the annual averaged NF of nss-K^+ was the second highest after NH_4^+ , which
402 is reasonable since biomass burning is a common activity in rural area for land clearance and
403 house heating possibly to contribute more nss-K^+ to the local atmosphere. In HMB, NFs of nss-
404 K^+ during both winter and autumn were the second highest among four cations, possibly due to
405 the enhanced local biomass burning for house heating in winter and open crop residue burning in
406 autumn (Chen et al., 2016). Additionally, as shown in Fig. 2, the majority of air masses reaching
407 HMB were coming through highly polluted NCP, rural site- LRABS (located at the northwest of
408 HMB) and agriculture lands dominated western and northern suburban areas of Hangzhou
409 (Sheng et al., 2017), hence, elevated K^+ could be expected at HMB due to medium- and short-
410 range transport.

411 3.4. Ion chemistry and source identification

412 3.4.1. Marine contribution of the aerosol composition

413 As located at the east coast of China, bordering the East China Sea and Yellow Sea, marine
414 effects seemed not to be ignored in this work. Therefore, the non-sea salt (Toledano et al., 2012)
415 contribution to aerosols has been evaluated. Na^+ was assumed to be all derived from the sea and
416 non-sea salts were calculated using following equation (Kong et al., 2014):

$$417 \quad \text{nss-X} = X_i - \text{Na}^+_i \times (\text{X/Na}^+)_{\text{sea}} \quad (7)$$

418 where, X_i and Na^+_i represent the ion and Na^+ concentration in aerosol samples respectively.
419 $(\text{X/Na}^+)_{\text{sea}}$ is ratio of ion and Na^+ in seawater. The $(\text{X/Na}^+)_{\text{sea}}$ ratios for Ca^{2+} , K^+ and SO_4^{2-} are
420 0.0385, 0.037 and 0.2516, respectively, based on the seawater composition (Balasubramanian et
421 al., 2003).

422 Fig. 5 depicts the concentrations of nss- SO_4^{2-} , nss- K^+ , nss- Ca^{2+} and the respective nss- SO_4^{2-}
423 / SO_4^{2-} , nss- K^+/K^+ and nss- $\text{Ca}^{2+}/\text{Ca}^{2+}$ ratios. High ratios (≥ 0.86) of nss- $\text{SO}_4^{2-}/\text{SO}_4^{2-}$, nss- K^+/K^+
424 and nss- $\text{Ca}^{2+}/\text{Ca}^{2+}$ were found at all four sites, indicating minor marine contribution ($\leq 14\%$) to
425 these ions. In LRABS and HMB, the nss- $\text{SO}_4^{2-}/\text{SO}_4^{2-}$ of all seasons was up to 0.99, indicating the
426 marine influence on sulfate concentration is negligible. The trend of nss- $\text{SO}_4^{2-}/\text{SO}_4^{2-}$ during all
427 seasons in UNNC and NMB were quite similar and the ratios in winter, spring and autumn were
428 around 0.98-0.99; while marine source affected UNNC and NMB more in summer with a
429 contribution of non-sea salt to total sulphate up to 97%, which could be attributed to the slightly
430 elevated air mass from the sea compared to the other two sites, as shown in the trajectory clusters
431 of Fig. 2.

432 Nss- K^+ has been revealed as a tracer of biomass burning (Chow et al., 2004), the nss- K^+
433 concentration in winter were more than twice that in summer and the highest nss- K^+/K^+ also

434 occurred in winter at all four sites, indicating the heaviest biomass burning contribution to the
435 high level of fine particles in winter and minimum marine influence while most significant
436 biomass burning impact on K^+ during this season. Relatively higher nss- K^+ in autumn and spring
437 could also be the result of biomass burning during these two seasons, especially the straw
438 burning during both harvest periods in this region. However, in the summer at UNNC and NMB,
439 more sea salt contribution to K^+ with lowest nss- K^+/K^+ was observed, possibly due to the
440 stronger air masses transported from oceanic origins in this season. The high value of nss-
441 Ca^{2+}/Ca^{2+} indicate Ca^{2+} was not majorly related to marine origin but more of continental
442 contribution.

443 3.4.2. Correlations between WSII

444 The correlation between WSII mass concentrations is a good way to investigate the possible
445 sources and associations among various ionic species. Correlation results, shown as the
446 correlation coefficients (r), are provided in Supplemental Table S1-S16.

447 The secondary species, ammonium sulfate ($(NH_4)_2SO_4$), ammonium bi-sulfate (NH_4HSO_4)
448 and ammonium nitrate (NH_4NO_3), namely secondary inorganic aerosol (SIA), are generated
449 through both homogeneous and heterogeneous reactions of gaseous precursors (SO_2 , NO_2 , NH_3).
450 Their formation depends on the availability of their corresponding precursor gases and the
451 atmospheric conditions. It is reported that ammonia would first neutralize with sulphuric acid to
452 form NH_4HSO_4 and $(NH_4)_2SO_4$, then the remaining ammonia would react with nitric acid to
453 generate NH_4NO_3 (Squizzato et al., 2012). NH_4^+ was found out significantly correlated with
454 NO_3^- and SO_4^{2-} throughout the sampling period at 4 sites, and most of their correlation
455 coefficients were in the range of 0.80~0.99; moreover, the annual averaged molar ratio of
456 $[NH_4^+]/[SO_4^{2-}]$ at 4 sites were above 3.3, indicating the coexistence of $(NH_4)HSO_4$, $(NH_4)_2SO_4$

457 and NH_4NO_3 . Higher correlations between NH_4^+ and SO_4^{2-} than NH_4^+ and NO_3^- were found in
458 summer at 4 sites, indicating the primary formation of sulfates instead of nitrates during the
459 summer in NZP, which is also supported by the molar ratio of $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ with an average of
460 2.2 throughout the summer at all sites.

461 In winter, except the strong correlations between major secondary ionic species, NO_2^- was
462 found to correlate highly with Mg^{2+} ($r = 0.80$) and Ca^{2+} ($r = 0.88$) in UNNC (Table S1), implying
463 the major existence of NO_2^- was $\text{Mg}(\text{NO}_2)_2$ and $\text{Ca}(\text{NO}_2)_2$. Since it has been reported that NO_2^-
464 can be formed through heterogeneous conversion of NO_2 on wet particle surface (Wang et al.,
465 2015b), good correlations between NO_2^- and Mg^{2+} and Ca^{2+} could possibly be due to the efficient
466 conversion from NO_2 to NO_2^- on these mineral particles. Mg^{2+} and Ca^{2+} was found to correlate
467 well ($r = 0.85$) in winter at Lin'an (Table S9), likely attributed to their common sources such as
468 soil dust from the surrounding agricultural environment under dry and windy condition during
469 winter (Satsangi et al., 2013). The ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$ is 0.34 during winter in Lin'an, higher
470 than 0.12 in sea salt aerosol (Deng et al., 2015), reconfirming sea salt was not a major
471 contributor. As mentioned before, K^+ is treated as a tracer for biomass or biofuel emissions,
472 which is observed to correlate well with $\text{PM}_{2.5}$ in Lin'an ($r = 0.84$) (Table S9) and Hangzhou ($r =$
473 0.88) (Table S13), indicating the significant contributions from biomass burning to the
474 occurrence levels of aerosol at these two sites. Since biomass burning is reported as the second
475 largest emission source of NH_3 from land clearing activity (Whitburn et al., 2015), good
476 correlations between K^+ and NH_4^+ ($r=0.80$, Table S13) also supported the above statement on
477 contribution of biomass burning to high aerosol concentrations at Hangzhou.

478 In spring at UNNC, K^+ and NH_4^+ ($r = 0.82$), Cl^- and NO_2^- ($r = 0.87$) were also found
479 correlated (Table S2), suggesting their common source like coal combustion and biomass

480 burning (Pei et al., 2016; Whitburn et al., 2015). Even though Na^+ and Cl^- correlated very well (r
481 = 0.88), the equivalent ratio of Na^+/Cl^- was only 0.44, much lower than their equivalent ratio in
482 seawater (1.1), suggesting marine source was only one of its major origins and regional soil
483 could also be partially responsible for their tight correlation (Xu et al., 2014). As NO_x is also
484 emitted from biomass burning (Chen et al., 2016), good correlations ($r = 0.83$ and 0.87 ,
485 respectively, Table S10) between K^+ and NO_3^- may imply their common source of biomass
486 burning at NMB and Lin'an. In Hangzhou (Table S14), Mg^{2+} correlated with Ca^{2+} ($r = 0.85$) and
487 NO_2^- ($r = 0.81$), which might be due to the efficient heterogeneous conversion of NO_2 to NO_2^-
488 on mineral surface as explained, which is also supported by the highest concentration of Ca^{2+} in
489 spring of HMB. High correlation between Cl^- and NO_3^- ($r = 0.84$) suggested their common
490 sources such as coal combustion and waste incineration (Pei et al., 2016).

491 In summer, no tight correlations were found among these ions in Ningbo and Lin'an, apart
492 from SNA. While in summer of Hangzhou (Table S15), in addition to that, K^+ correlated very
493 well with Cl^- ($r = 0.90$) and SO_4^{2-} ($r = 0.88$), and Cl^- also correlated well with NO_3^- ($r = 0.83$) and
494 SO_4^{2-} ($r = 0.80$), indicating they may share part of the combustion related sources including fossil
495 fuel combustion, waste incineration and biomass burning, etc.

496 In autumn in this region, K^+ is found to correlate very well with $\text{PM}_{2.5}$, NO_3^- and NH_4^+ at all
497 sampling sites ($r > 0.80$) (Table S4, S8, S12, S16). As discussed above, in this season these
498 components could be affected heavily by agricultural activities (livestock waste volatilization
499 and nitrogen containing fertilizer) as well as land clearing practice. Besides, high correlations of
500 Na^+ and Cl^- ($r = 0.80$), Ca^{2+} and NO_2^- (0.88) were observed in HMB (Table S16). Na^+ is also
501 found to correlate well with NO_2^- ($r = 0.87$) at UNNC (Table S4), and K^+ is found to correlate
502 with both primary Ca^{2+} ($r = 0.80$) and secondary SO_4^{2-} ($r = 0.87$) in NMB (Table S8), possibly

503 due to the similar transport pathways of air masses or mixture of both primary and secondary
504 aerosols (Xu et al., 2014).

505 3.4.3. Chemical conversions of species– sulfur and nitrogen oxidation ratios

506 The oxidation of $\text{SO}_2 - \text{SO}_4^{2-}$ and $\text{NO}_2 - \text{NO}_3^-$ has two mechanisms: homogeneous and
507 heterogeneous reactions (Liu et al., 2016). The former involves gas-phase SO_2 and NO_2
508 oxidation reactions with $\text{OH}\cdot$ radical; the latter for $\text{SO}_2 - \text{SO}_4^{2-}$ transformation includes $\text{H}_2\text{O}_2/\text{O}_3$
509 oxidation or metal catalyzed sulfur and in-cloud process, closely associated with RH and aerosol
510 mass concentration (Wang et al., 2006), and heterogeneous reactions for $\text{NO}_2 - \text{NO}_3^-$ is the
511 hydrolysis of N_2O_5 on pre-existing particulate matter, such as sulfate aerosols (Meng et al., 2016;
512 Zhang et al., 1995). Therefore, to investigate the conversion of above species in this study, sulfur
513 oxidation ratio (SOR) and nitrogen oxidation ratio (Xie et al.) were applied and they are
514 calculated as follows (Lin, 2002):

$$515 \quad \text{SOR} = \frac{[\text{nss-SO}_4^{2-}]}{([\text{nss-SO}_4^{2-}] + [\text{SO}_2])} \quad (8)$$

$$516 \quad \text{NOR} = \frac{[\text{NO}_3^-]}{([\text{NO}_3^-] + [\text{NO}_2])} \quad (9)$$

517 Where $[\text{nss-SO}_4^{2-}]$, $[\text{SO}_2]$, $[\text{NO}_3^-]$ and $[\text{NO}_2]$ represent their respective molar concentrations;
518 higher SOR and NOR indicate greater oxidation of SO_2 and NO_2 , and more secondary aerosols
519 would be produced. The seasonal averaged SO_2 , NO_2 , O_3 concentrations and SOR, NOR values
520 at four sampling sites during the sampling campaign are presented in Supplemental Table S17.

521 It has been reported the photochemical oxidation of SO_2 to SO_4^{2-} could occur when
522 $\text{SOR} > 0.1$ (Ohta and Okita, 1990). The SOR values of all seasons at the 4 sampling sites were
523 above 0.1, indicating the oxidation of SO_2 occurred throughout the whole sampling campaign in
524 NZP. In four seasons, summer was observed with the highest SOR values at all sampling sites,
525 suggesting a considerable conversion of SO_2 to sulfate. As the homogeneous reaction of SO_2 and

526 OH• radical is a strong function of solar irradiation and ambient temperature (Meng et al., 2016),
527 homogeneous transition of SO₂ – SO₄²⁻ may have contributed to the highest SOR in hot summer.
528 High presence of O₃ in summer may have also helped the oxidation of SO₂ (Meng et al., 2016).
529 Additionally, more efficient heterogeneous aqueous reaction of SO₂ and NO₂ could also occur
530 under high RH in summer to generate sulfate and gas-phase HONO significantly (Wang et al.,
531 2016a). It is noteworthy that the highest SOR value and lowest SO₂ concentration were observed
532 simultaneously during the summer at all sites in NZP, very possibly due to 1) strong oxidation
533 of SO₂ to SO₄²⁻; 2) the highest precipitation rate favorable for the efficient scavenging of SO₂
534 and 3) high PBL height during the summer beneficial to dispersion of SO₂. The SOR in other
535 seasons ranked as autumn > spring > winter. Lowest SOR in highly polluted winter could be
536 caused by: 1) the intensive emission of SO₂ from enhanced coal combustion, which was inclined
537 to be accumulated greatly under stagnant weather condition during cold winter with poor air
538 dispersion and circulation; 2) under stagnant weather, low solar radiation reduced the
539 photochemical activity which could not provide sufficient oxidants and hindered the
540 homogeneous reaction of SO₂ – SO₄²⁻ (Hua et al., 2008; Liu et al., 2016); 3) lowest RH reduced
541 the possibility of heterogeneous aqueous reaction of SO₂ – SO₄²⁻, and eventually caused the
542 lowest SOR value in winter.

543 The NOR values in UNNC, LRABS and HMB shared a similar seasonal pattern: Winter >
544 Spring > Autumn > Summer. The NOR values in highly-polluted winter and less polluted
545 summer are consistent with those reported in Shanghai, where the NOR during hazy days and
546 clean days were 0.18 and 0.08, respectively (Hua et al., 2015). As discussed, the seasonal
547 variation of nitrate has shown an inverse relationship with the seasonal mean air temperature
548 variations. Low temperature (< 15°C) could favor the transformation of gaseous NO₂ to

549 particulate NO_3^- (Squizzato et al., 2012; US EPA, 1999). NOR in winter at these sampling sites
550 have shown the highest value (> 0.1), which implies the greatest oxidation degree of NO_2 to
551 NO_3^- occurred in the coldest season.. This is opposite to SOR trend, which shows the highest
552 during summer. As mentioned earlier, high RH can increase the possibility of heterogeneous
553 aqueous reaction of SO_2 and NO_2 to generate sulfate and gas-phase HONO, while less NO_2
554 might be converted into gas-phase HONO and more converted to particulate nitrate during the
555 dry winter. Also, lowest NOR in summer could be the result of the highest temperature in this
556 season favorable for the volatilization of nitrate when temperature $> 30^\circ\text{C}$ (Deng et al., 2015).
557 The NOR pattern in NMB showed slightly different from the other sites: Autumn (0.12) $>$
558 Winter (0.10) $>$ Spring (0.07) $>$ Summer (0.04). The highest NOR in autumn here might be
559 attributed to the greater increase of NO_3^- concentration ($10.28 \mu\text{g m}^{-3}$, in Table 3).

560 3.4.4. Principal component analysis

561 In order to investigate the possible sources of these ionic species in NZP, principal
562 component analysis (PCA, SPSS version 19.0, IBM Corp.) has been applied in this work and the
563 result is presented in Table 4. During the analysis, Varimax rotation was chosen to give a clearer
564 pattern of variables loading in factors, and this feature can make the loadings of obvious
565 variables close to 1 and non-obvious variables close to 0 (Meng et al., 2016). However, only
566 those loadings > 0.3 are shown in Table 4, and those variables with loading > 0.5 are considered
567 to be the indicators of the factors (Callén et al., 2009).

568 Nine ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_2^- , NO_3^- , SO_4^{2-}) in NZP were selected for PCA
569 analysis. Li^+ , F^- and PO_4^{3-} were undetectable in most of the aerosol samples due to their low
570 presence level in the atmosphere; therefore, they were not included in PCA analysis.

571 In winter, the variables resulted in 3 sources of eigenvalue > 1 and they explained 72.9% of
572 variance in total. Factor 1 (Component 1) covered 42.8% of total variance, and is heavily loaded
573 with NH_4^+ , K^+ , Cl^- , NO_3^- , SO_4^{2-} , suggesting the contributions from secondary inorganic aerosols,
574 coal combustion and biomass burning. Factor 2, explaining 17.1% of the data variance, is loaded
575 with Na^+ , Ca^{2+} and Cl^- , possibly indicating their marine and dust sources, along with coal
576 combustion as well as factor 1. Factor 3 is responsible for 13.0% of the variance, mainly affected
577 by Mg^{2+} and NO_2^- . Since NO_2 on wet crustal particle surface can form NO_2^- through
578 heterogeneous reaction (Wang et al., 2015b) and crustal originated Mg^{2+} ($r = 0.80$) and Ca^{2+} ($r =$
579 0.88) were also found correlated well with NO_2^- during winter at UNNC, therefore, Mg^{2+} and
580 NO_2^- loaded factor 3 could be the result of heterogeneous conversion of NO_2 .

581 In spring, 2 factors were obtained from PCA model. Factor 1, explaining 37.6% of variables,
582 is loaded with Na^+ , NH_4^+ , K^+ , NO_3^- and SO_4^{2-} , indicating likely sources from sea salts, biomass
583 burning and secondary aerosols. Factor 2 explains 18.6% of the variables, is affected by Mg^{2+} ,
584 Ca^{2+} and Cl^- , suggesting the contributions of suspending dust and coal combustion to the fine
585 particles in the atmosphere.

586 The PCA results in summer also have 2 factors, similar with those in spring. Factor 1,
587 accounting for 38.6% of the variables, is loaded with NH_4^+ , K^+ , Cl^- , NO_3^- , SO_4^{2-} , suggesting
588 contributions from industrial emissions, biomass burning and coal burning. Factor 2 explains
589 20.0% of the variance with loading of Na^+ , Mg^{2+} and Ca^{2+} , which are likely from sea salts and
590 dust particles. This is consistent with the cluster results in Fig. 2 that most of the air masses were
591 originated from the ocean, passed through mainland to reach studied sites and 10-29% was from
592 central China. Therefore, the aerosols were characterized with both oceanic and terrestrial
593 properties.

594 In autumn, 3 PCA factors were calculated, explaining 75.0% of the total variance. Factor 1
595 explained 44.5% of the variance, dominated by NH_4^+ , K^+ , NO_3^- and SO_4^{2-} with obvious loading
596 above 0.8, and K^+ is found to correlate very well with $\text{PM}_{2.5}$, NO_3^- and NH_4^+ at this region ($r >$
597 0.80), strongly suggesting emissions from industrial areas and biomass burning. Factor 2,
598 responsible for 16.2% of the total variance, is loaded with Na^+ , Mg^{2+} , Ca^{2+} and Cl^- , indicating
599 sources like sea salt, dust particles and coal burning. Only NO_2^- in Factor 3 has loading above 0.5,
600 indicating the origin from vehicle exhaust.

601 4. Conclusions

602 The seasonal variations of ion chemistry and sources of WSII were studied through a one-
603 year sampling campaign at 4 representative sites in both Hangzhou and Ningbo of NZP. The
604 annual averaged $\text{PM}_{2.5}$ and total WSII concentrations in NZP were $66.2 \pm 37.7 \mu\text{g m}^{-3}$ and $29.1 \pm$
605 $19.9 \mu\text{g m}^{-3}$, respectively. WSII in this region were dominated by SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- and K^+ .
606 SNA ranked as the top three ions, accounting for 88.0% of total WSII and 38.7% of $\text{PM}_{2.5}$
607 occurrence levels. The seasonal average WSII exhibited the highest in winter and lowest in
608 summer and spatially the annual total WSII at sites in Ningbo were relatively lower than those in
609 Hangzhou, indicating the aerosol ionic pollution was more severe within the provincial capital
610 municipality.

611 Aerosol acidity was also studied through ion balance. At UNNC and HMB, NO_3^- and SO_4^{2-}
612 were mostly neutralized by Ca^{2+} and NH_4^+ . In winter and spring at LRABS, the alkaline nature
613 of aerosols could be possibly due to the increased biomass burning emission and volatilization of
614 ammonia containing fertilizer; but the alkaline nature of aerosol in NMB could be the result of
615 enhanced traffic emitted NH_3 . Among all cations, NH_4^+ was the predominant neutralizing ion

616 with the highest neutralization factor (NF); while the NFs of nss-Ca^{2+} , nss-K^+ and Mg^{2+} were
617 lower than 0.2, implying minor impact of these ions in the neutralization of aerosol acidity.

618 High ratios of $\text{nss-SO}_4^{2-}/\text{SO}_4^{2-}$, $\text{nss-K}^+/\text{K}^+$ and $\text{nss-Ca}^{2+}/\text{Ca}^{2+}$ at all four sites of NZP indicated
619 minor marine contribution to these ions. High correlations of NH_4^+ with NO_3^- and SO_4^{2-} (r :
620 0.8~1.0) were observed throughout the sampling period at 4 sites and the annual averaged molar
621 ratio of $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ of 4 sites were all above 3.3, indicating NH_4^+ existed predominantly as
622 ammonium sulfates, ammonium bi-sulfates and ammonium nitrates in aerosols. The SOR value
623 in all seasons of NZP were above 0.1, indicating $\text{SO}_2 - \text{SO}_4^{2-}$ transformation dominantly
624 occurred throughout the year in NZP, and it was the highest in summer and lowest in winter;
625 however, the NOR seasonal pattern was the opposite to that of SOR. The seasonal values of SOR
626 and NOR seem to be significantly affected by both homogeneous and heterogeneous reactions
627 for the gaseous precursors converted to secondary ions and volatilization of nitrates under high
628 ambient temperature.

629 The sources of WSII were also investigated by PCA and the results showed that they were
630 predominantly from industrial emissions, biomass burning, secondary inorganic aerosols,
631 moderately from dust and soil originated particles and minorly from sea salts. In addition, the air
632 mass backward trajectory analysis also showed that the contribution from transboundary
633 transport of aerosols from highly polluted north China may not be negligible.

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643 **Conflict of interests**

644 The authors declare no conflict of interests at personal and/or organizational level.

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857 **Figure captions**

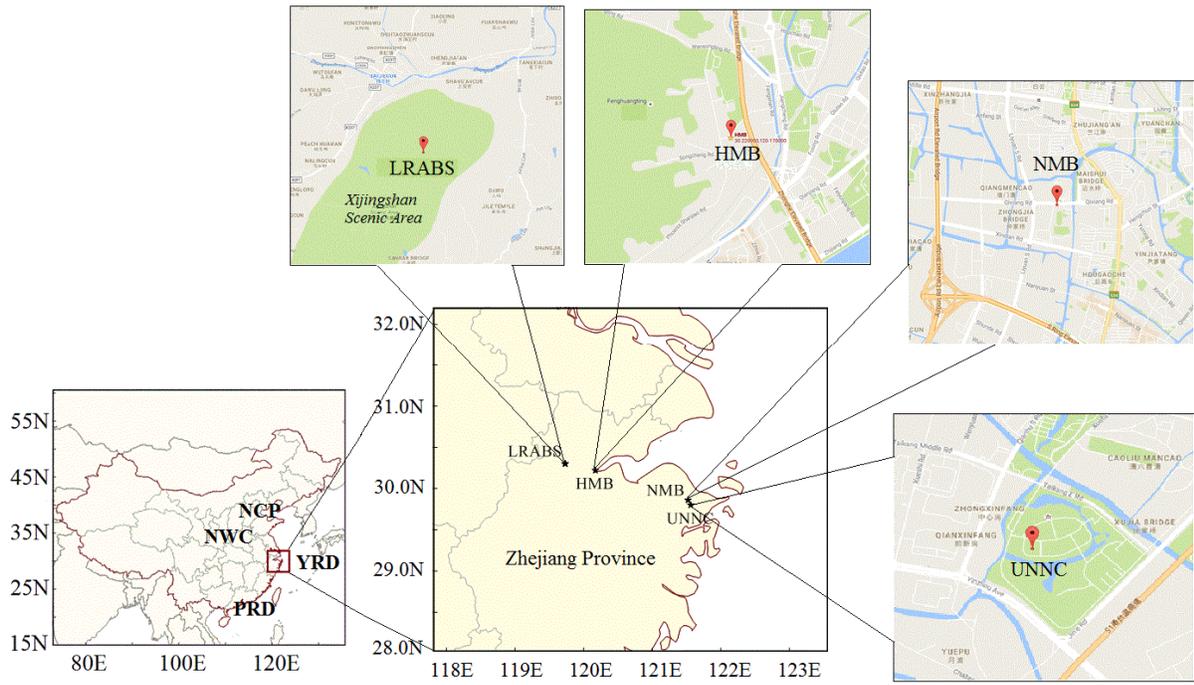
858 **Fig. 1** Locations of sampling sites in NZP, China (NCP: North China Plain; NWC: Northwest
859 China; PRD: Pearl River Delta; YRD: Yangtze River Delta)

860 **Fig. 2** Clusters of air mass backward trajectories during each season in sampling sites of NZP

861 **Fig. 3** Plot of anion equivalents (AE) vs cation equivalents (CE) in four seasons of NZP

862 **Fig. 4** The neutralization factors of nss-Ca^{2+} , Mg^{2+} , nss-K^{+} and NH_4^{+} in $\text{PM}_{2.5}$ at 4 sites of NZP

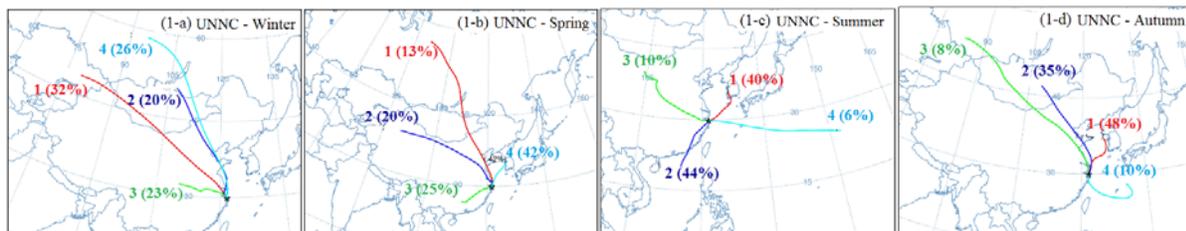
863 **Fig. 5** Concentration of non-sea salts and their respective non-sea salt ionic fractions at sampling
864 sites of NZP



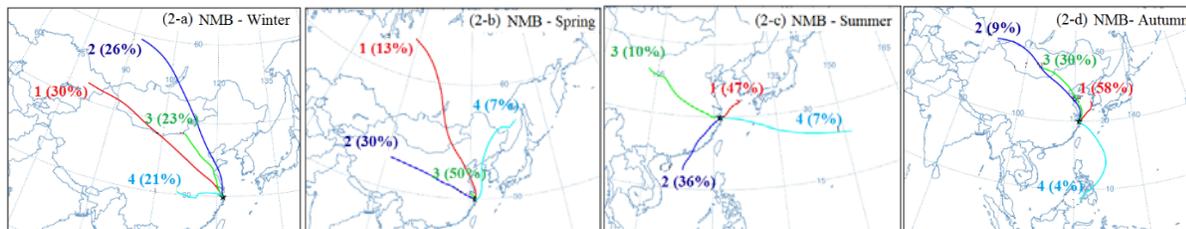
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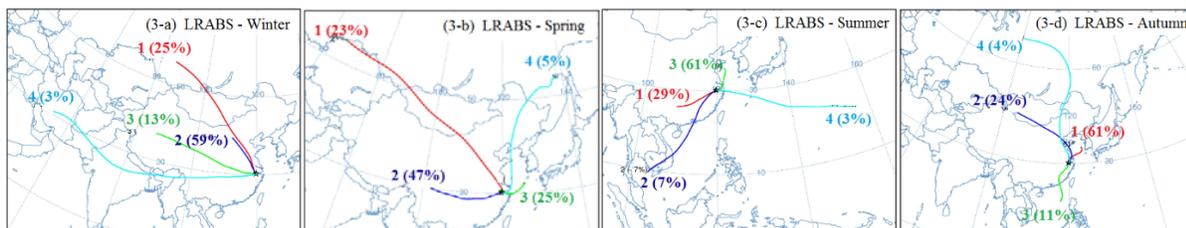
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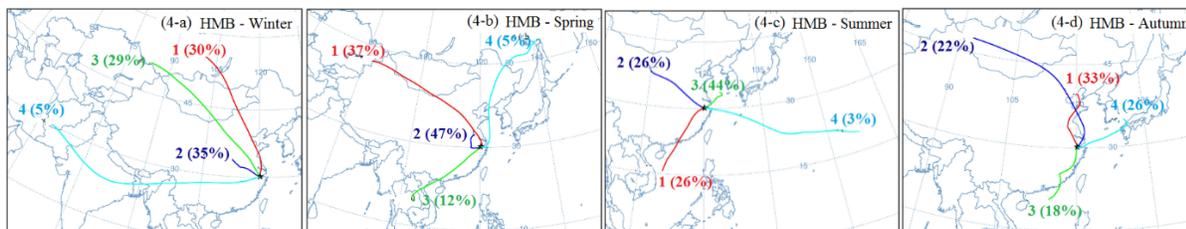
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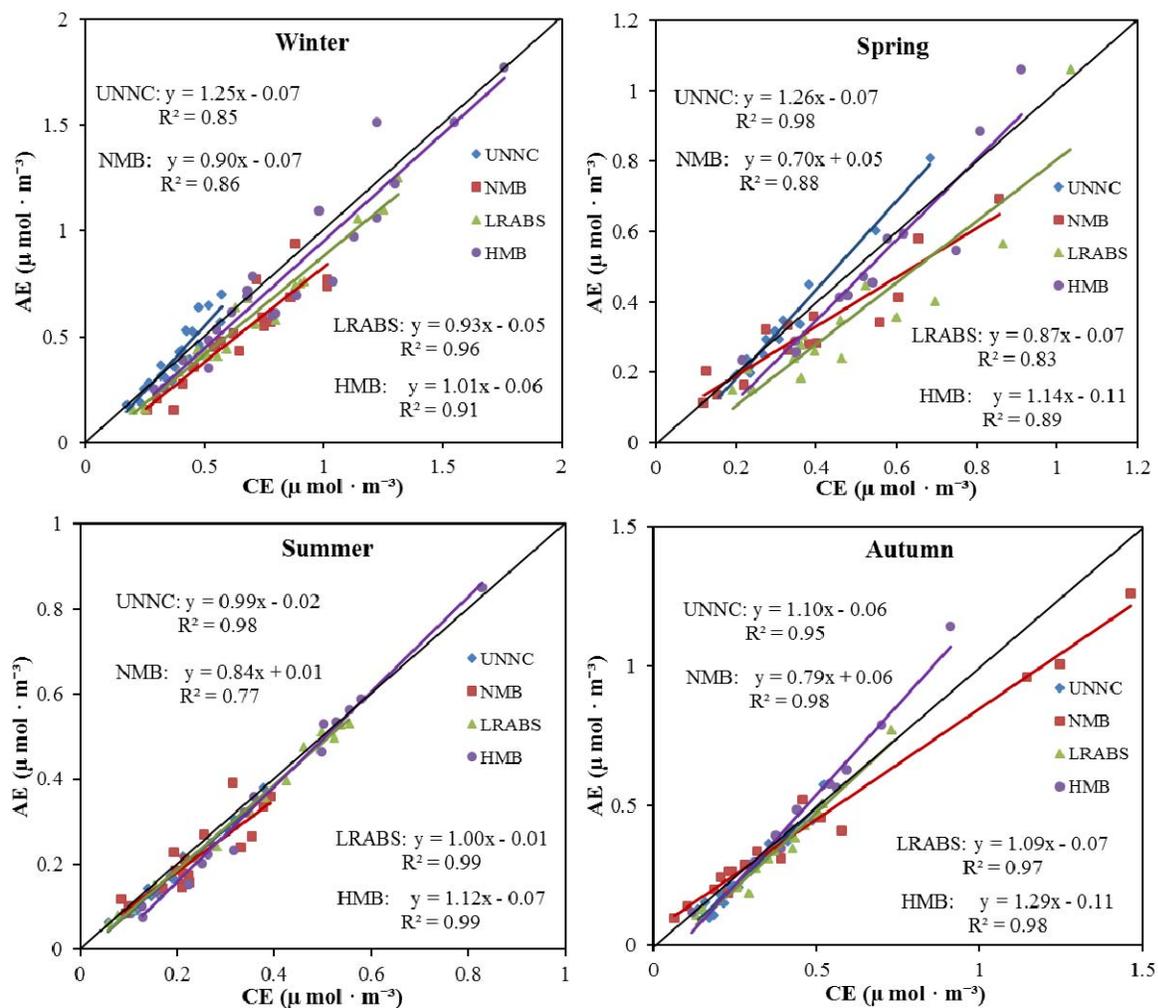


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Fig. 3. Plot of anion equivalents (AE) vs cation equivalents (CE) in four seasons of NZP

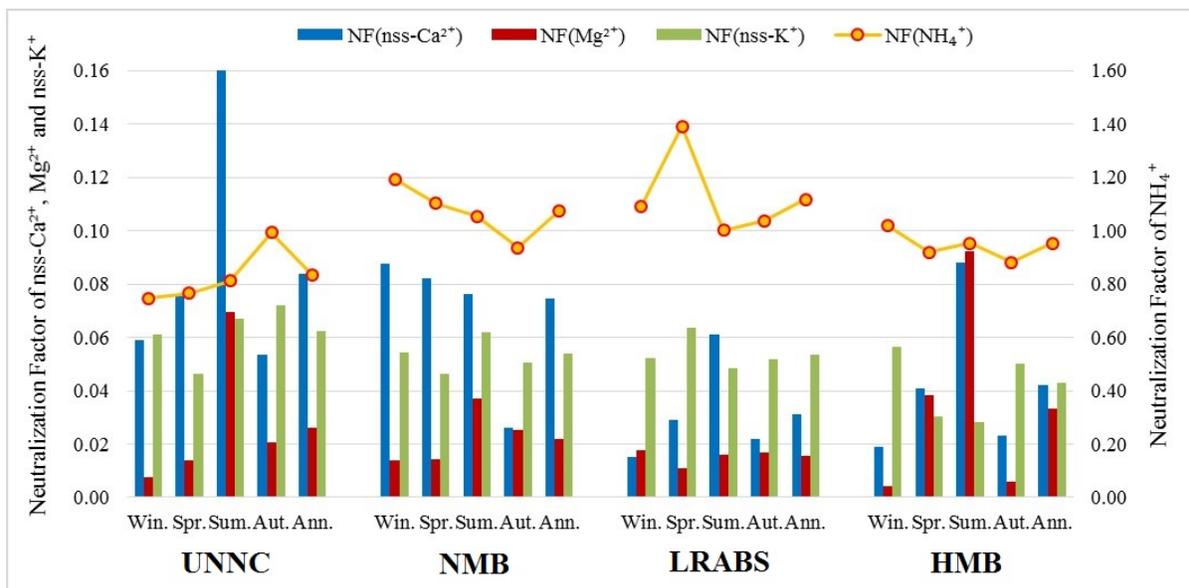
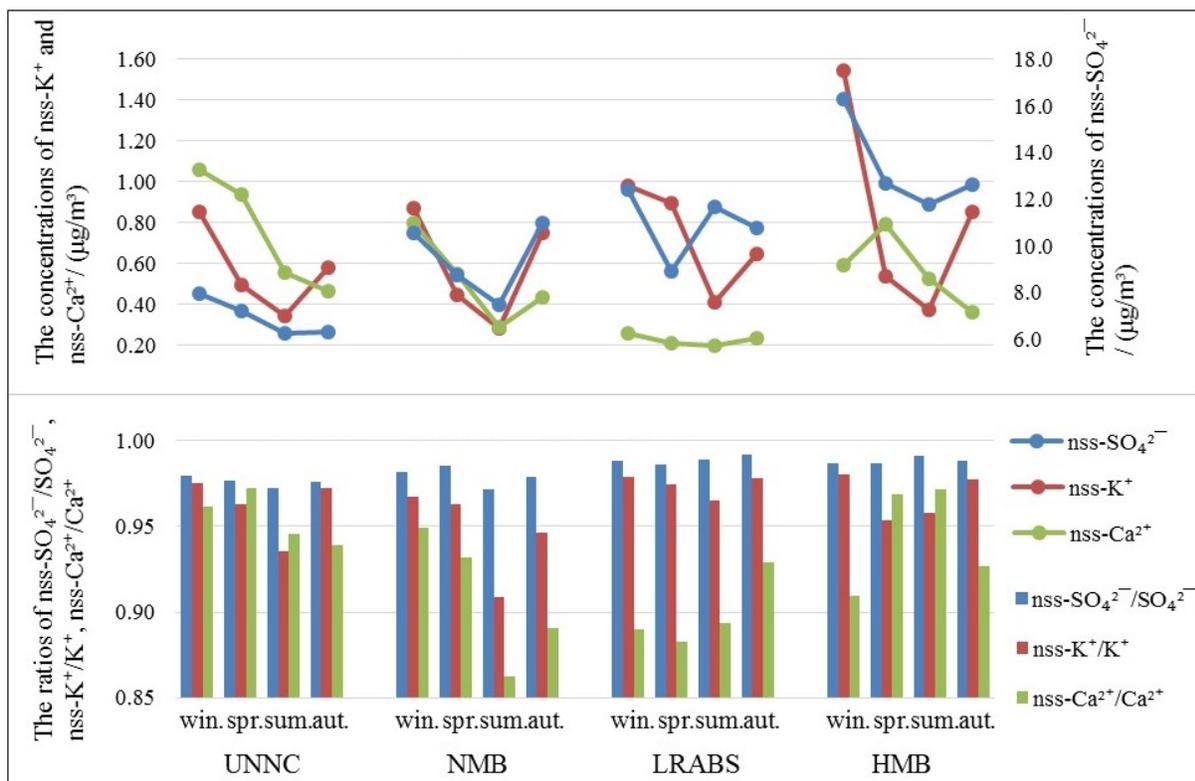


Fig. 4. The neutralization factors of nss-Ca²⁺, Mg²⁺, nss-K⁺ and NH₄⁺ in PM_{2.5} at 4 sites of NZP

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883 **Fig. 5.** Concentration of non-sea salts and their respective non-sea salt ionic fractions at sampling sites of NZP

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889 (YRD) of China

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893 of NZP

894 **Table 1**

895 Seasonal averaged PM_{2.5} concentrations and meteorological data at four sampling sites during the 2014-2015
 896 sampling campaign

| | | PM _{2.5} concentrations ($\mu\text{g m}^{-3}$) | Wind Speed (m s^{-1}) | Precipitation (mm) | Temperature ($^{\circ}\text{C}$) | Relative Humidity (%) |
|-------|----------------|--|-------------------------------------|-----------------------|---------------------------------------|--------------------------|
| UNNC | Winter-2014 | 74.4 \pm 30.3 | 2.4 | 0.052 | 6.5 | 64.2 |
| | Spring-2015 | 44.0 \pm 17.4 | 2.4 | 0.052 | 15.6 | 76.1 |
| | Summer-2015 | 27.7 \pm 8.5 | 2.4 | 0.110 | 26.5 | 80.1 |
| | Autumn-2015 | 50.1 \pm 27.7 | 2.2 | 0.038 | 18.0 | 76.5 |
| | Annual average | 51.2 \pm 29.1 | 2.3 | 0.063 | 16.6 | 74.2 |
| NMB | Winter-2014 | 98.1 \pm 36.4 | 1.5 | 0.030 | 6.1 | 65.1 |
| | Spring-2015 | 79.3 \pm 26.7 | 1.7 | 0.069 | 15.9 | 71.6 |
| | Summer-2015 | 33.6 \pm 11.0 | 1.6 | 0.198 | 26.7 | 79.4 |
| | Autumn-2015 | 71.2 \pm 47.5 | 1.4 | 0.166 | 18.2 | 77.6 |
| | Annual average | 70.4 \pm 40.6 | 1.6 | 0.116 | 16.7 | 73.4 |
| LRABS | Winter-2014 | 93.7 \pm 36.4 | 2.1 | 0.173 | 5.8 | 65.2 |
| | Spring-2015 | 59.0 \pm 36.4 | 2.0 | 0.299 | 15.5 | 72.6 |
| | Summer-2015 | 42.6 \pm 18.5 | 2.1 | 0.479 | 26.0 | 79.3 |
| | Autumn-2015 | 60.7 \pm 29.7 | 1.8 | 0.221 | 17.2 | 77.9 |
| | Annual average | 66.3 \pm 36.6 | 2.0 | 0.293 | 16.1 | 73.7 |
| HMB | Winter-2014 | 108.4 \pm 44.2 | 2.1 | 0.014 | 6.9 | 62.1 |
| | Spring-2015 | 82.6 \pm 24.5 | 2.2 | 0.051 | 15.8 | 64.1 |
| | Summer-2015 | 48.4 \pm 17.6 | 2.1 | 0.165 | 27.7 | 72.5 |
| | Autumn-2015 | 68.0 \pm 29.7 | 1.9 | 0.052 | 19.1 | 72.1 |
| | Annual average | 80.0 \pm 39.6 | 2.1 | 0.070 | 17.4 | 67.7 |
| NZP* | Winter-2014 | 93.1 \pm 38.4 | 2.0 | 0.067 | 6.3 | 64.1 |
| | Spring-2015 | 65.1 \pm 30.9 | 2.1 | 0.118 | 15.7 | 71.1 |
| | Summer-2015 | 37.8 \pm 16.2 | 2.0 | 0.238 | 26.7 | 77.8 |
| | Autumn-2015 | 61.3 \pm 34.5 | 1.8 | 0.119 | 18.1 | 76.0 |
| | Annual average | 66.2 \pm 37.7 | 2.0 | 0.136 | 16.7 | 72.3 |

897 NZP*: Data of NZP were calculated as the average values of those in four sampling sites of NZP

898 **Table 2**899 Literature data of averaged PM_{2.5}, WSII, SO₄²⁻, NO₃⁻ and NH₄⁺ concentrations in North China Plain (NCP), Northwest China (NWC), Pearl River Delta (PRD)
900 and Yangtze River Delta (YRD) of China

| Locations | Sampling period | Mass Concentrations ($\mu\text{g m}^{-3}$) | | | | | References |
|------------------------------|-------------------|--|---|-------------------------------|------------------------------|------------------------------|----------------------|
| | | PM _{2.5} | Total WSII (Total WSII/ PM _{2.5}) | SO ₄ ²⁻ | NO ₃ ⁻ | NH ₄ ⁺ | |
| Handan, NCP | 2013 – 2014 | 139.4 ± 98.5 | 63.1 ± 35.3 (45.3%) | 25.2 ± 13.5 | 20.6 ± 12.2 | 13.0 ± 8.1 | (Meng et al., 2016) |
| Hefei, NCP | 09/2012 – 11/2013 | 86.29 | 46.71 (54.1%) | 15.56 | 15.14 | 7.82 | (Deng et al., 2015) |
| Tianjin, NCP | 10/2012 – 08/2013 | 148.9 ± 91.1 | 64.2 (41%) | 24.2 ± 21.8 | 19.6 ± 16.5 | 8.5 ± 5.9 | (Zhou et al., 2016) |
| Xi'an, NWC | 03/2012 – 03/2013 | 169.3 ± 101.7 | 61.6 (36.4%) | 22.2 ± 16.8 | 17.1 ± 17.3 | 9.6 ± 8.7 | (Niu et al., 2016) |
| Weinan, NWC | 03/2012 – 03/2013 | 135.5 ± 70.0 | 60.2 (44.4%) | 24.7 ± 16.8 | 18.0 ± 17.5 | 10.0 ± 9.1 | (Niu et al., 2016) |
| Xi'an, NWC | 03/2006 – 03/2007 | 194.1 ± 78.6 | 76.5 (39.4%) | 35.6 ± 19.5 | 16.4 ± 10.1 | 11.4 ± 6.8 | (Zhang et al., 2011) |
| Guangzhou, PRD | 04/2007 | 79.2 ± 34.2 | 44.4 (55%) | 21.6 ± 10.7 | 9.5 ± 6.0 | 7.3 ± 3.9 | (Tao et al., 2009) |
| Zhongshan, PRD | 10/2012 – 08/2013 | 60.5 ± 46.5 | 22.4 (33%) | 9.8 ± 6.3 | 6.4 ± 7.7 | 2.8 ± 2.8 | (Zhou et al., 2016) |
| Shanghai, YRD | 01/2011 – 12/2013 | 47.0 ± 2.0 | 29.7 (63.2%) | 10.2 ± 0.6 | 9.2 ± 1.1 | 6.0 ± 0.7 | (Wang et al., 2016c) |
| Haining, YRD | 10/2012 – 08/2013 | 109.6 ± 59.4 | 42.0 (37%) | 16.5 ± 9.9 | 13.9 ± 12.0 | 6.1 ± 4.3 | (Zhou et al., 2016) |
| UNNC, Ningbo, this study | 11/2014 – 11/2015 | 51.2 ± 29.1 | 21.0 ± 10.8 (44.1%) | 7.1 ± 3.8 | 6.5 ± 4.9 | 3.9 ± 2.0 | This study |
| NMB, Ningbo, this study | 11/2014 – 11/2015 | 70.4 ± 40.6 | 26.7 ± 18.8 (38.6%) | 9.6 ± 4.8 | 7.3 ± 8.3 | 6.6 ± 5.1 | This study |
| LRABS, Lin'an, this study | 11/2014 – 11/2015 | 66.3 ± 36.6 | 29.7 ± 18.2 (44.9%) | 11.2 ± 6.3 | 8.7 ± 8.5 | 7.3 ± 4.5 | This study |
| HMB, Hangzhou, this study | 11/2014 – 11/2015 | 80.0 ± 39.6 | 41.3 ± 25.5 (49.2%) | 13.8 ± 7.6 | 14.2 ± 11.3 | 9.1 ± 5.7 | This study |

901 **Table 3**

902 Seasonal and annual averaged WSII concentrations at four sampling sites during the 2014-2015 sampling campaign

| Ion concentrations ($\mu\text{g m}^{-3}$) | Li ⁺ | Na ⁺ | NH ₄ ⁺ | K ⁺ | Mg ²⁺ | Ca ²⁺ | F ⁻ | Cl ⁻ | NO ₂ ⁻ | NO ₃ ⁻ | PO ₄ ³⁻ | SO ₄ ²⁻ | Sum of total WSII | |
|---|-----------------|-----------------|------------------------------|----------------|------------------|------------------|----------------|-----------------|------------------------------|------------------------------|-------------------------------|-------------------------------|-------------------|-------------|
| UNNC | Winter-2014 | 0.0 ± 0.0 | 0.5 ± 0.1 | 5.0 ± 1.8 | 0.9 ± 0.3 | 0.1 ± 0.0 | 1.1 ± 1.1 | 0.1 ± 0.1 | 2.5 ± 1.6 | 0.0 ± 0.0 | 10.6 ± 5.2 | 0.0 ± 0.0 | 8.1 ± 4.1 | 28.9 ± 9.7 |
| | Spring-2015 | 0.0 ± 0.0 | 0.5 ± 0.3 | 4.0 ± 2.0 | 0.5 ± 0.3 | 0.1 ± 0.1 | 0.9 ± 0.7 | 0.1 ± 0.1 | 2.2 ± 3.2 | 0.1 ± 0.1 | 6.6 ± 3.4 | 0.0 ± 0.0 | 7.4 ± 4.1 | 22.3 ± 11.0 |
| | Summer-2015 | 0.0 ± 0.0 | 0.5 ± 0.2 | 2.4 ± 1.4 | 0.4 ± 0.1 | 0.1 ± 0.1 | 0.5 ± 0.4 | 0.0 ± 0.0 | 0.4 ± 0.7 | 0.1 ± 0.1 | 2.3 ± 1.3 | 0.0 ± 0.0 | 6.4 ± 3.4 | 13.0 ± 6.2 |
| | Autumn-2015 | 0.0 ± 0.0 | 0.4 ± 0.1 | 3.8 ± 1.7 | 0.6 ± 0.3 | 0.1 ± 0.1 | 0.5 ± 0.4 | 0.0 ± 0.0 | 0.8 ± 0.9 | 0.0 ± 0.0 | 5.4 ± 3.9 | 0.0 ± 0.0 | 6.4 ± 3.5 | 17.9 ± 8.7 |
| | Annual average | 0.0 ± 0.0 | 0.5 ± 0.2 | 3.9 ± 2.0 | 0.6 ± 0.3 | 0.1 ± 0.1 | 0.8 ± 0.8 | 0.0 ± 0.1 | 1.5 ± 2.0 | 0.0 ± 0.1 | 6.5 ± 4.9 | 0.0 ± 0.0 | 7.1 ± 3.8 | 21.0 ± 10.8 |
| NMB | Winter-2014 | 0.0 ± 0.0 | 0.7 ± 0.3 | 9.4 ± 4.4 | 0.9 ± 0.4 | 0.1 ± 0.0 | 0.8 ± 0.8 | 0.0 ± 0.0 | 3.5 ± 2.3 | 0.1 ± 0.2 | 10.3 ± 7.6 | 0.0 ± 0.0 | 10.7 ± 4.0 | 36.4 ± 16.3 |
| | Spring-2015 | 0.0 ± 0.0 | 0.4 ± 0.1 | 5.9 ± 3.8 | 0.5 ± 0.2 | 0.1 ± 0.0 | 0.5 ± 0.4 | 0.1 ± 0.4 | 0.9 ± 0.8 | 0.7 ± 0.7 | 5.5 ± 4.0 | 0.1 ± 0.4 | 8.8 ± 4.6 | 23.4 ± 12.4 |
| | Summer-2015 | 0.0 ± 0.0 | 0.7 ± 0.5 | 3.2 ± 1.8 | 0.3 ± 0.3 | 0.1 ± 0.0 | 0.2 ± 0.3 | 0.2 ± 0.5 | 0.3 ± 0.3 | 0.2 ± 0.3 | 1.7 ± 1.4 | 0.0 ± 0.0 | 7.6 ± 3.1 | 14.5 ± 5.7 |
| | Autumn-2015 | 0.0 ± 0.0 | 0.6 ± 0.2 | 7.5 ± 7.2 | 0.8 ± 0.7 | 0.0 ± 0.0 | 0.2 ± 0.4 | 0.0 ± 0.0 | 1.1 ± 0.9 | 0.3 ± 0.3 | 10.3 ± 12.4 | 0.0 ± 0.0 | 11.2 ± 6.7 | 32.0 ± 27.0 |
| | Annual average | 0.0 ± 0.0 | 0.6 ± 0.4 | 6.6 ± 5.1 | 0.6 ± 0.5 | 0.1 ± 0.0 | 0.4 ± 0.5 | 0.1 ± 0.3 | 1.5 ± 1.8 | 0.3 ± 0.4 | 7.0 ± 8.3 | 0.0 ± 0.2 | 9.6 ± 4.8 | 26.7 ± 18.8 |
| LRABS | Winter-2014 | 0.1 ± 0.1 | 0.5 ± 0.2 | 10.2 ± 5.6 | 1.0 ± 0.4 | 0.2 ± 0.2 | 0.3 ± 0.2 | 0.1 ± 0.1 | 1.3 ± 1.1 | 0.1 ± 0.1 | 15.2 ± 8.7 | 0.2 ± 0.1 | 12.5 ± 7.1 | 41.6 ± 20.9 |
| | Spring-2015 | 0.0 ± 0.1 | 0.4 ± 0.2 | 7.5 ± 3.9 | 0.9 ± 1.5 | 0.1 ± 0.1 | 0.2 ± 0.1 | 0.0 ± 0.1 | 0.5 ± 0.6 | 0.2 ± 0.1 | 8.5 ± 9.3 | 0.0 ± 0.1 | 9.0 ± 4.8 | 27.4 ± 17.4 |
| | Summer-2015 | 0.0 ± 0.0 | 0.3 ± 0.1 | 4.9 ± 3.2 | 0.4 ± 0.2 | 0.0 ± 0.0 | 0.2 ± 0.1 | 0.0 ± 0.0 | 0.2 ± 0.1 | 0.2 ± 0.2 | 2.4 ± 2.0 | 0.1 ± 0.2 | 11.8 ± 7.4 | 20.6 ± 12.5 |
| | Autumn-2015 | 0.0 ± 0.1 | 0.3 ± 0.1 | 5.9 ± 2.5 | 0.7 ± 0.3 | 0.1 ± 0.1 | 0.2 ± 0.2 | 0.0 ± 0.0 | 0.3 ± 0.3 | 0.1 ± 0.1 | 6.7 ± 5.3 | 0.0 ± 0.0 | 10.9 ± 4.7 | 25.1 ± 11.6 |
| | Annual average | 0.0 ± 0.1 | 0.4 ± 0.2 | 7.3 ± 4.5 | 0.8 ± 0.7 | 0.1 ± 0.1 | 0.2 ± 0.2 | 0.0 ± 0.1 | 0.6 ± 0.8 | 0.1 ± 0.1 | 8.7 ± 8.5 | 0.1 ± 0.2 | 11.2 ± 6.3 | 29.6 ± 18.2 |
| HMB | Winter-2014 | 0.0 ± 0.0 | 0.7 ± 0.3 | 13.5 ± 6.7 | 1.6 ± 0.7 | 0.1 ± 0.0 | 0.6 ± 0.5 | 0.2 ± 0.0 | 3.4 ± 2.3 | 0.0 ± 0.1 | 21.9 ± 12.6 | 0.1 ± 0.1 | 16.5 ± 9.6 | 58.5 ± 29.7 |
| | Spring-2015 | 0.0 ± 0.0 | 0.5 ± 0.2 | 7.7 ± 3.2 | 0.6 ± 0.3 | 0.5 ± 0.3 | 0.8 ± 0.4 | 0.0 ± 0.1 | 1.0 ± 0.8 | 0.2 ± 0.3 | 13.3 ± 8.1 | 0.0 ± 0.1 | 12.8 ± 6.1 | 37.6 ± 16.8 |
| | Summer-2015 | 0.0 ± 0.0 | 0.4 ± 0.3 | 5.5 ± 3.2 | 0.4 ± 0.3 | 0.2 ± 0.2 | 0.5 ± 0.5 | 0.0 ± 0.0 | 0.4 ± 0.5 | 0.1 ± 0.1 | 5.7 ± 5.8 | 0.0 ± 0.1 | 11.9 ± 6.2 | 25.2 ± 15.7 |
| | Autumn-2015 | 0.0 ± 0.0 | 0.4 ± 0.3 | 7.3 ± 3.3 | 0.9 ± 0.4 | 0.1 ± 0.0 | 0.4 ± 0.2 | 0.0 ± 0.0 | 0.9 ± 0.6 | 0.1 ± 0.1 | 12.3 ± 8.9 | 0.2 ± 0.3 | 12.7 ± 6.0 | 35.2 ± 18.0 |
| | Annual average | 0.0 ± 0.0 | 0.5 ± 0.3 | 9.1 ± 5.7 | 0.9 ± 0.7 | 0.2 ± 0.2 | 0.6 ± 0.4 | 0.1 ± 0.1 | 1.7 ± 1.9 | 0.1 ± 0.2 | 14.2 ± 11.3 | 0.1 ± 0.2 | 13.8 ± 7.6 | 41.3 ± 25.5 |

903 **Table 4**

904 Seasonal principal component analysis results for water-soluble inorganic ions in PM_{2.5} of northern Zhejiang
 905 Province

| Season | 2014-Winter | | | 2015-Spring | | 2015-Summer | | 2015-Autumn | | |
|-------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| | Component | | | Component | | Component | | Component | | |
| | 1 | 2 | 3 | 1 | 2 | 1 | 2 | 1 | 2 | 3 |
| Na ⁺ | 0.555 | 0.582 | | 0.687 | 0.337 | 0.342 | 0.642 | 0.413 | 0.571 | 0.490 |
| NH ₄ ⁺ | 0.931 | | | 0.806 | - | 0.835 | - | 0.957 | | |
| K ⁺ | 0.868 | | | 0.675 | | 0.820 | | 0.942 | | |
| Mg ²⁺ | | 0.377 | 0.744 | 0.438 | 0.505 | | 0.554 | | 0.695 | -0.348 |
| Ca ²⁺ | | 0.730 | | | 0.815 | 0.484 | 0.673 | 0.311 | 0.505 | -0.623 |
| Cl ⁻ | 0.558 | 0.507 | | 0.465 | 0.534 | 0.564 | 0.359 | 0.442 | 0.538 | 0.450 |
| NO ₂ ⁻ | | - | 0.725 | | | | | | | 0.533 |
| NO ₃ ⁻ | 0.891 | | | 0.910 | | 0.846 | | 0.949 | | |
| SO ₄ ²⁻ | 0.882 | | | 0.729 | | 0.840 | - | 0.848 | | |
| Initial eigenvalue | 3.856 | 1.539 | 1.168 | 3.383 | 1.670 | 3.473 | 1.799 | 4.002 | 1.456 | 1.295 |
| % of Variance explained | 42.84 | 17.09 | 12.98 | 37.59 | 18.55 | 38.58 | 19.98 | 44.46 | 16.17 | 14.38 |
| % of Cumulative variance | 8 | 8 | 3 | 0 | 3 | 8 | 4 | 3 | 5 | 7 |
| | 42.84 | 59.94 | 72.92 | 37.59 | 56.14 | 38.58 | 58.57 | 44.46 | 60.63 | 75.02 |
| | 8 | 6 | 9 | 0 | 3 | 8 | 1 | 3 | 7 | 4 |

906 *Blanks in table are value < 0.3*