

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<sub>2.5</sub> concentration was  $66.2 \pm 37.7 \mu\text{g m}^{-3}$  and urban sites  
33 were observed with more severe PM<sub>2.5</sub> 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  $\text{SO}_4^{2-}$  ( $10.3 \mu\text{g m}^{-3}$ ),  
35  $\text{NO}_3^-$  ( $8.9 \mu\text{g m}^{-3}$ ),  $\text{NH}_4^+$  ( $6.6 \mu\text{g m}^{-3}$ ),  $\text{Cl}^-$  ( $1.3 \mu\text{g m}^{-3}$ ) and  $\text{K}^+$  ( $0.7 \mu\text{g m}^{-3}$ ).  $\text{NH}_4^+$  was highly  
36 correlated with  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ( $r$ : 0.8~1.0) throughout the sampling period at 4 sites and the  
37 annual averaged molar ratio of  $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$  of 4 sites were all above 3.3, indicating  $\text{NH}_4^+$   
38 existed predominantly as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$  and  $\text{NH}_4\text{NO}_3$  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  $\text{SO}_2 - \text{SO}_4^{2-}$  and  $\text{NO}_2 - \text{NO}_3^-$   
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<sub>2.5</sub>, 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  $\text{SO}_2$  and  $\text{NO}_2$   
57 emitted mostly from coal-fired power plants and vehicles can be oxidized and converted to  $\text{SO}_4^{2-}$   
58 and  $\text{NO}_3^-$  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  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ , and  $\text{NH}_4\text{NO}_3$  through the neutralization reactions with  
61  $\text{NH}_4^+$ , which is originated from gas-phase  $\text{NH}_3$ . 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 (NZIP), 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 NZP, 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 NZP, 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<sub>2.5</sub> 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<sub>2.5</sub> samplers (Model: TH-150CIII, Tianhong  
134 Instrument CO., Ltd. Wuhan, China), operating at a flow rate of 80 L min<sup>-1</sup> and PM<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> mass on 90mm quartz fiber filters were measured by an ultra-  
142 microbalance (Model: SE2-F, Sartorius, precision 0.1  $\mu\text{g}$ ). After that, filters were wrapped in  
143 prebaked aluminum foil and stored in refrigerator under  $-20^{\circ}\text{C}$  until analysis.

144 Meteorological data (wind speed, precipitation, temperature and relative humidity) and  
145 concentrations of gaseous pollutants ( $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{O}_3$ ) 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  $4^{\circ}\text{C}$  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<sub>2.5</sub> 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 ( $\text{m s}^{-1}$ ), 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  $26.7^{\circ}\text{C}$  during summer and the lowest was  $6.3^{\circ}\text{C}$  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<sub>2.5</sub> concentration in this region (calculated as the average of PM<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> concentration (47 μg m<sup>-3</sup>)  
209 measured in Shanghai (Wang et al., 2016c), but comparable with the annual PM<sub>2.5</sub> occurrence  
210 levels in Hangzhou (64 ± 47 μg m<sup>-3</sup>) and Nanjing (75 ± 50 μg m<sup>-3</sup>) (Wang et al., 2014). The  
211 annual average concentration of PM<sub>2.5</sub> at four sites ranked as: UNNC (51.2 ± 29.1 μg m<sup>-3</sup>) <  
212 LRABS (66.3 ± 36.6 μg m<sup>-3</sup>) < NMB (70.4 ± 40.6 μg m<sup>-3</sup>) < HMB (80.0 ± 39.6 μg m<sup>-3</sup>). Clearly,  
213 the annual average PM<sub>2.5</sub> 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<sub>2.5</sub>  
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<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> 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<sub>2.5</sub> 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 <sup>3</sup>, 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,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  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  $30^\circ\text{C}$  (Deng et al.,

298 2015). The seasonal variation of nitrate concentration could also be attributed to the seasonality  
299 of NO<sub>x</sub> emission (Li and Han, 2016). It is known that both HCl and SO<sub>2</sub> 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 NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, the concentration of K<sup>+</sup> was the highest among the rest  
309 ions. The highest concentration of K<sup>+</sup> 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<sup>+</sup> during winter (1.0 μg m<sup>-3</sup>) and spring (0.9 μg m<sup>-3</sup>) 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:

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

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

Where,  $F^-$ ,  $Cl^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $Li^+$ ,  $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  refer to their mass concentrations ( $\mu g m^{-3}$ ). Through calculations by the above equations, the anion and cation concentrations ( $\mu g m^{-3}$ ) were converted into their corresponding micro-equivalents ( $\mu mol m^{-3}$ ) and the relationships between AE and CE in four seasons of the sampling sites are plotted in Fig. 3.

As shown in Fig. 3, good correlations and very small intercepts between AE and CE were found in 4 seasons; therefore, the anion/cation equivalent ratios (AE/CE) were defined as the slopes of linear regressions in this study. At 4 sites, the correlation coefficients of AE and CE were in the range of 0.77~0.99, similar to the results in another study of YRD (0.72~0.94) (Wang et al., 2015a). At UNNC and HMB, the AE/CE ratios in four seasons were mostly above 1.0, except the ratio close to 1 in the summer of UNNC. These results indicated a deficiency in cations of  $PM_{2.5}$  samples in UNNC and HMB, anions were not fully neutralized and caused acidic nature of fine particles at these two sites. When using the equivalent ratio of  $[NH_4^+]/[NO_3^-+SO_4^{2-}]$  to evaluate the aerosol acidity (Wang et al., 2016a), the ratio at HMB was 0.99, indicating a good neutralization relationship between the major secondary species at this site during the sampling period. At UNNC, the annual averaged equivalent ratio of  $[NH_4^+]/[NO_3^-+SO_4^{2-}]$  was only 0.89, while the annual averaged equivalent ratio of  $[NH_4^++Ca^{2+}]/[NO_3^-+SO_4^{2-}]$  of UNNC could be up to 0.98, suggesting  $Ca^{2+}$  might be another main cation affecting the neutralization of  $NO_3^-$  and  $SO_4^{2-}$ . This could be explained by the fact that a number of construction sites existed around UNNC during this sampling campaign, which might be the dominant sources of  $Ca^{2+}$  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  $\text{NO}_3^-$  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  $\text{NH}_4^+$  was over-sufficient to neutralize  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The excess of  $\text{NH}_4^+$  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  $\text{NH}_3$  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  $\text{NH}_4^+$  at urban site NMB ( $6.6 \mu\text{g m}^{-3}$ ) than suburban site UNNC ( $3.9 \mu\text{g}$   
365  $\text{m}^{-3}$ ) 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-Ca<sup>2+</sup>, Mg<sup>2+</sup>, nss-K<sup>+</sup> and NH<sub>4</sub><sup>+</sup>) were individually  
369 estimated by applying the Neutralization Factors (NFs). SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were considered as the  
370 dominant acidifying anions. Na<sup>+</sup> and Cl<sup>-</sup> 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<sup>+</sup> and Cl<sup>-</sup> (r<sup>2</sup> < 0.5) were  
373 found at all four sites, suggesting possible different origins of Cl<sup>-</sup>. Moreover, the Na<sup>+</sup>/ Cl<sup>-</sup>  
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<sup>-</sup> 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<sup>+</sup>/ Cl<sup>-</sup> equivalent ratio (0.91) and lowest Cl<sup>-</sup>/ PM<sub>2.5</sub> 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<sup>-</sup> in neutralization could not be neglected in this study. As Na<sup>+</sup> 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<sup>-</sup>] can be calculated by subtracting [Na<sup>+</sup>] from [Cl<sup>-</sup>] 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  $\text{nss-SO}_4^{2-}$ ,  $\text{nss-K}^+$  and  $\text{nss-Ca}^{2+}$  were  
389 estimated in section 3.4.1.

390 Fig. 4 depicts the NFs of  $\text{nss-Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{nss-K}^+$  and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  at 4 sites of northern  
391 Zhejiang Province. As expected,  $\text{NH}_4^+$  was the predominant neutralizing cation with the highest  
392 NF, and the average annual NF of  $\text{NH}_4^+$  at 4 sites were LRABS (1.12) > NMB (1.08) > HMB  
393 (0.95) > UNNC (0.83). The annual NF of  $\text{NH}_4^+$  in LRABS and NMB were above 1, indicating  
394 the excess of  $\text{NH}_4^+$  after neutralizing  $\text{nss-SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , 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  $\text{nss-Ca}^{2+}$ ,  $\text{nss-K}^+$  and  $\text{Mg}^{2+}$  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:  $\text{NH}_4^+$  >  $\text{nss-Ca}^{2+}$  >  $\text{nss-K}^+$  >  
399  $\text{Mg}^{2+}$ .  $\text{nss-Ca}^{2+}$  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  $\text{nss-K}^+$  was the second highest after  $\text{NH}_4^+$ , 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  $\text{nss-K}^+$  to the local atmosphere. In HMB, NFs of  $\text{nss-}$   
404  $\text{K}^+$  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  $\text{K}^+$  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.  $\text{Na}^+$  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  $\text{Na}^+_i$  represent the ion and  $\text{Na}^+$  concentration in aerosol samples respectively.  
419  $(\text{X/Na}^+)_{\text{sea}}$  is ratio of ion and  $\text{Na}^+$  in seawater. The  $(\text{X/Na}^+)_{\text{sea}}$  ratios for  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{SO}_4^{2-}$  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- $\text{SO}_4^{2-}$ , nss- $\text{K}^+$ , nss- $\text{Ca}^{2+}$  and the respective nss- $\text{SO}_4^{2-}$   
423 / $\text{SO}_4^{2-}$ , nss- $\text{K}^+/\text{K}^+$  and nss- $\text{Ca}^{2+}/\text{Ca}^{2+}$  ratios. High ratios ( $\geq 0.86$ ) of nss- $\text{SO}_4^{2-}/\text{SO}_4^{2-}$ , nss- $\text{K}^+/\text{K}^+$   
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- $\text{K}^+$  has been revealed as a tracer of biomass burning (Chow et al., 2004), the nss- $\text{K}^+$   
433 concentration in winter were more than twice that in summer and the highest nss- $\text{K}^+/\text{K}^+$  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  $\text{NH}_4\text{NO}_3$ . Higher correlations between  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  than  $\text{NH}_4^+$  and  $\text{NO}_3^-$  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,  $\text{NO}_2^-$  was  
462 found to correlate highly with  $\text{Mg}^{2+}$  ( $r = 0.80$ ) and  $\text{Ca}^{2+}$  ( $r = 0.88$ ) in UNNC (Table S1), implying  
463 the major existence of  $\text{NO}_2^-$  was  $\text{Mg}(\text{NO}_2)_2$  and  $\text{Ca}(\text{NO}_2)_2$ . Since it has been reported that  $\text{NO}_2^-$   
464 can be formed through heterogeneous conversion of  $\text{NO}_2$  on wet particle surface (Wang et al.,  
465 2015b), good correlations between  $\text{NO}_2^-$  and  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  could possibly be due to the efficient  
466 conversion from  $\text{NO}_2$  to  $\text{NO}_2^-$  on these mineral particles.  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  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,  $\text{K}^+$  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  $\text{NH}_3$  from land clearing activity (Whitburn et al., 2015), good  
476 correlations between  $\text{K}^+$  and  $\text{NH}_4^+$  ( $r=0.80$ , Table S13) also supported the above statement on  
477 contribution of biomass burning to high aerosol concentrations at Hangzhou.

478 In spring at UNNC,  $\text{K}^+$  and  $\text{NH}_4^+$  ( $r = 0.82$ ),  $\text{Cl}^-$  and  $\text{NO}_2^-$  ( $r = 0.87$ ) 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  $\text{Na}^+$  and  $\text{Cl}^-$  correlated very well ( $r$   
481 = 0.88), the equivalent ratio of  $\text{Na}^+/\text{Cl}^-$  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  $\text{NO}_x$  is also  
484 emitted from biomass burning (Chen et al., 2016), good correlations ( $r = 0.83$  and  $0.87$ ,  
485 respectively, Table S10) between  $\text{K}^+$  and  $\text{NO}_3^-$  may imply their common source of biomass  
486 burning at NMB and Lin'an. In Hangzhou (Table S14),  $\text{Mg}^{2+}$  correlated with  $\text{Ca}^{2+}$  ( $r = 0.85$ ) and  
487  $\text{NO}_2^-$  ( $r = 0.81$ ), which might be due to the efficient heterogeneous conversion of  $\text{NO}_2$  to  $\text{NO}_2^-$   
488 on mineral surface as explained, which is also supported by the highest concentration of  $\text{Ca}^{2+}$  in  
489 spring of HMB. High correlation between  $\text{Cl}^-$  and  $\text{NO}_3^-$  ( $r = 0.84$ ) 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,  $\text{K}^+$  correlated very  
493 well with  $\text{Cl}^-$  ( $r = 0.90$ ) and  $\text{SO}_4^{2-}$  ( $r = 0.88$ ), and  $\text{Cl}^-$  also correlated well with  $\text{NO}_3^-$  ( $r = 0.83$ ) and  
494  $\text{SO}_4^{2-}$  ( $r = 0.80$ ), 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,  $\text{K}^+$  is found to correlate very well with  $\text{PM}_{2.5}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  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  $\text{Na}^+$  and  $\text{Cl}^-$  ( $r = 0.80$ ),  $\text{Ca}^{2+}$  and  $\text{NO}_2^-$  ( $0.88$ ) were observed in HMB (Table S16).  $\text{Na}^+$  is also  
501 found to correlate well with  $\text{NO}_2^-$  ( $r = 0.87$ ) at UNNC (Table S4), and  $\text{K}^+$  is found to correlate  
502 with both primary  $\text{Ca}^{2+}$  ( $r = 0.80$ ) and secondary  $\text{SO}_4^{2-}$  ( $r = 0.87$ ) 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  $\text{SO}_2$  and  $\text{NO}_2$   
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  $\text{N}_2\text{O}_5$  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  $\text{SO}_2$  and  $\text{NO}_2$ , and more secondary aerosols  
519 would be produced. The seasonal averaged  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{O}_3$  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  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  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  $\text{SO}_2$  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  $\text{SO}_2$  to sulfate. As the homogeneous reaction of  $\text{SO}_2$  and

526 OH• radical is a strong function of solar irradiation and ambient temperature (Meng et al., 2016),  
527 homogeneous transition of SO<sub>2</sub> – SO<sub>4</sub><sup>2-</sup> may have contributed to the highest SOR in hot summer.  
528 High presence of O<sub>3</sub> in summer may have also helped the oxidation of SO<sub>2</sub> (Meng et al., 2016).  
529 Additionally, more efficient heterogeneous aqueous reaction of SO<sub>2</sub> and NO<sub>2</sub> 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 SO<sub>2</sub> concentration were observed  
532 simultaneously during the summer at all sites in NZP, very possibly due to 1) strong oxidation  
533 of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup>; 2) the highest precipitation rate favorable for the efficient scavenging of SO<sub>2</sub>  
534 and 3) high PBL height during the summer beneficial to dispersion of SO<sub>2</sub>. 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 SO<sub>2</sub> 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 SO<sub>2</sub> – SO<sub>4</sub><sup>2-</sup> (Hua et al., 2008; Liu et al., 2016); 3) lowest RH reduced  
541 the possibility of heterogeneous aqueous reaction of SO<sub>2</sub> – SO<sub>4</sub><sup>2-</sup>, 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 NO<sub>2</sub> to

549 particulate  $\text{NO}_3^-$  (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  $\text{NO}_2$  to  
551  $\text{NO}_3^-$  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  $\text{SO}_2$  and  $\text{NO}_2$  to generate sulfate and gas-phase HONO, while less  $\text{NO}_2$   
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  $\text{NO}_3^-$  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 ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) in NZP were selected for PCA  
569 analysis.  $\text{Li}^+$ ,  $\text{F}^-$  and  $\text{PO}_4^{3-}$  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  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , 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  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ , 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  $\text{Mg}^{2+}$  and  $\text{NO}_2^-$ . Since  $\text{NO}_2$  on wet crustal particle surface can form  $\text{NO}_2^-$  through  
578 heterogeneous reaction (Wang et al., 2015b) and crustal originated  $\text{Mg}^{2+}$  ( $r = 0.80$ ) and  $\text{Ca}^{2+}$  ( $r =$   
579  $0.88$ ) were also found correlated well with  $\text{NO}_2^-$  during winter at UNNC, therefore,  $\text{Mg}^{2+}$  and  
580  $\text{NO}_2^-$  loaded factor 3 could be the result of heterogeneous conversion of  $\text{NO}_2$ .

581 In spring, 2 factors were obtained from PCA model. Factor 1, explaining 37.6% of variables,  
582 is loaded with  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , indicating likely sources from sea salts, biomass  
583 burning and secondary aerosols. Factor 2 explains 18.6% of the variables, is affected by  $\text{Mg}^{2+}$ ,  
584  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ , 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  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , suggesting  
588 contributions from industrial emissions, biomass burning and coal burning. Factor 2 explains  
589 20.0% of the variance with loading of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , 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  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  with obvious loading  
596 above 0.8, and  $\text{K}^+$  is found to correlate very well with  $\text{PM}_{2.5}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  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  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ , indicating  
599 sources like sea salt, dust particles and coal burning. Only  $\text{NO}_2^-$  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  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$  and  $\text{K}^+$ .  
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,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$   
612 were mostly neutralized by  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ . 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  $\text{NH}_3$ . Among all cations,  $\text{NH}_4^+$  was the predominant neutralizing ion

616 with the highest neutralization factor (NF); while the NFs of  $\text{nss-Ca}^{2+}$ ,  $\text{nss-K}^+$  and  $\text{Mg}^{2+}$  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  $\text{NH}_4^+$  with  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ( $r$ :  
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  $\text{NH}_4^+$  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**

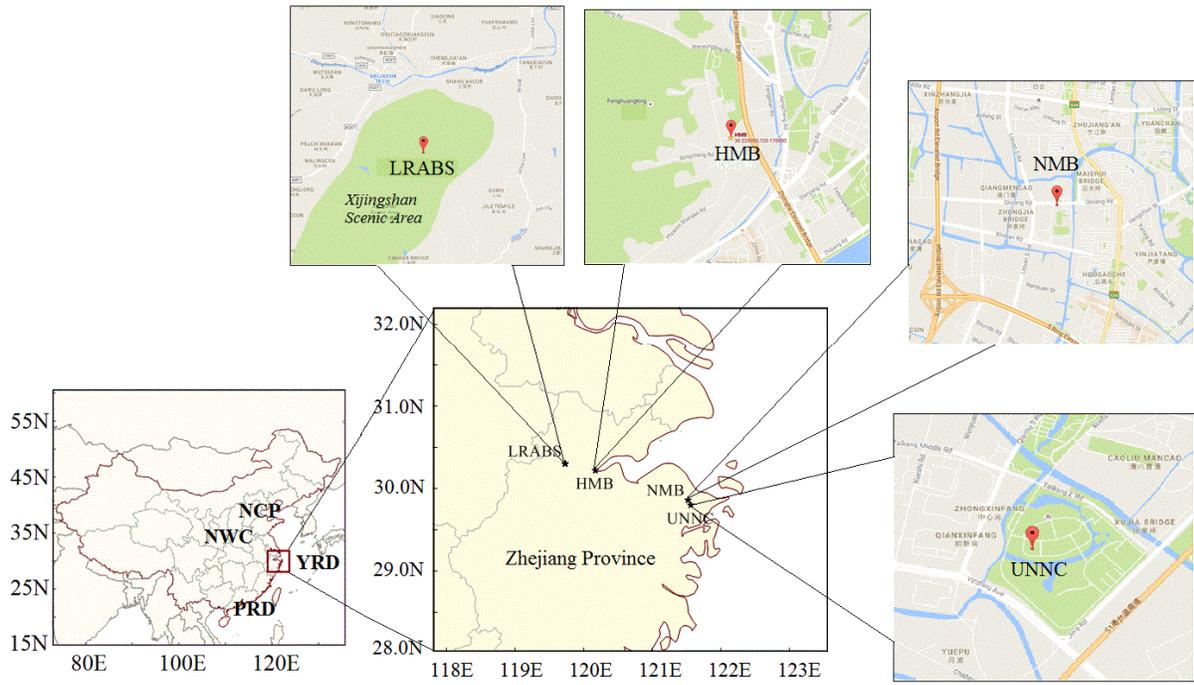
858 **Fig. 1** Locations of sampling sites in NZP, China (NCP: North China Plain; NWC: Northwest  
859 China; PRD: Pearl River Delta; YRD: Yangtze River Delta)

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  $\text{nss-Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{nss-K}^{+}$  and  $\text{NH}_4^{+}$  in  $\text{PM}_{2.5}$  at 4 sites of NZP

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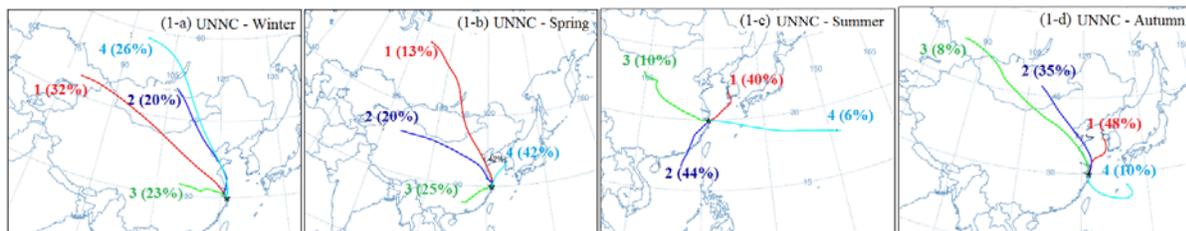


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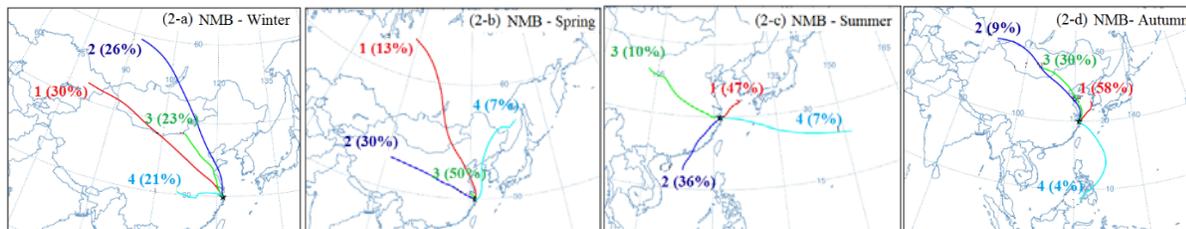
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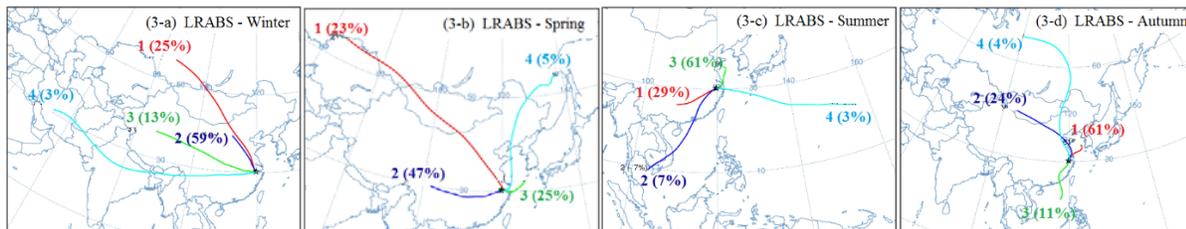
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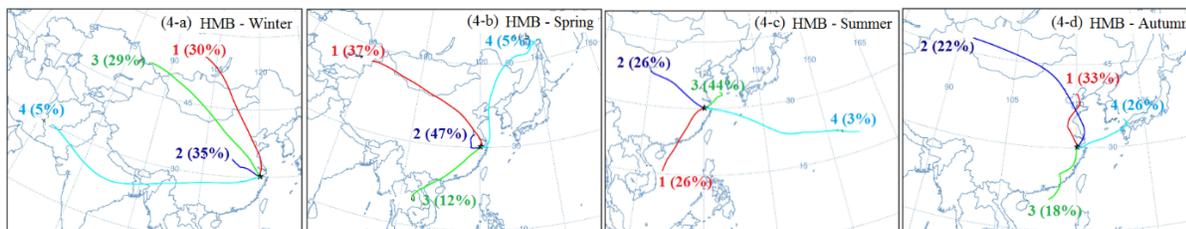
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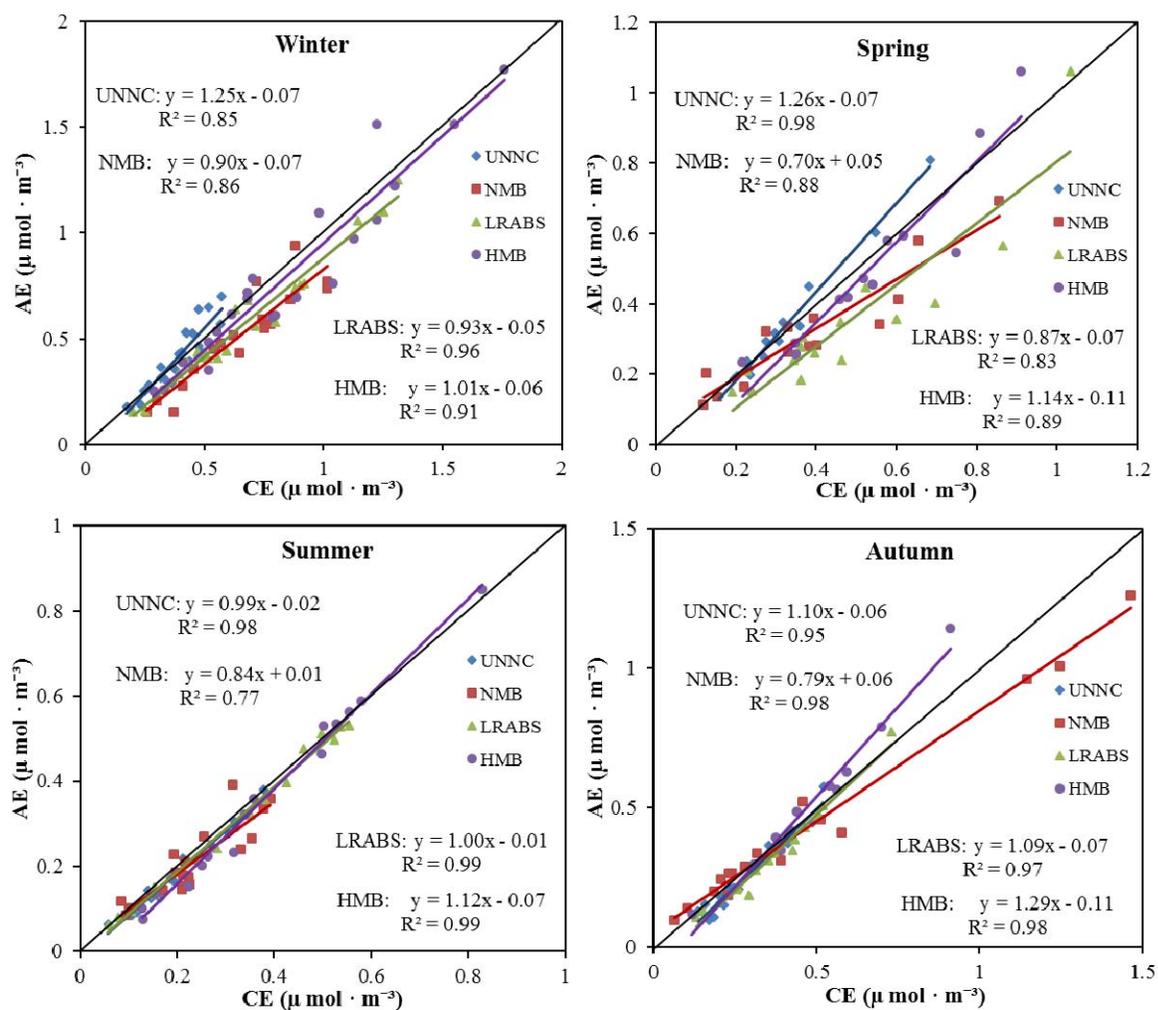


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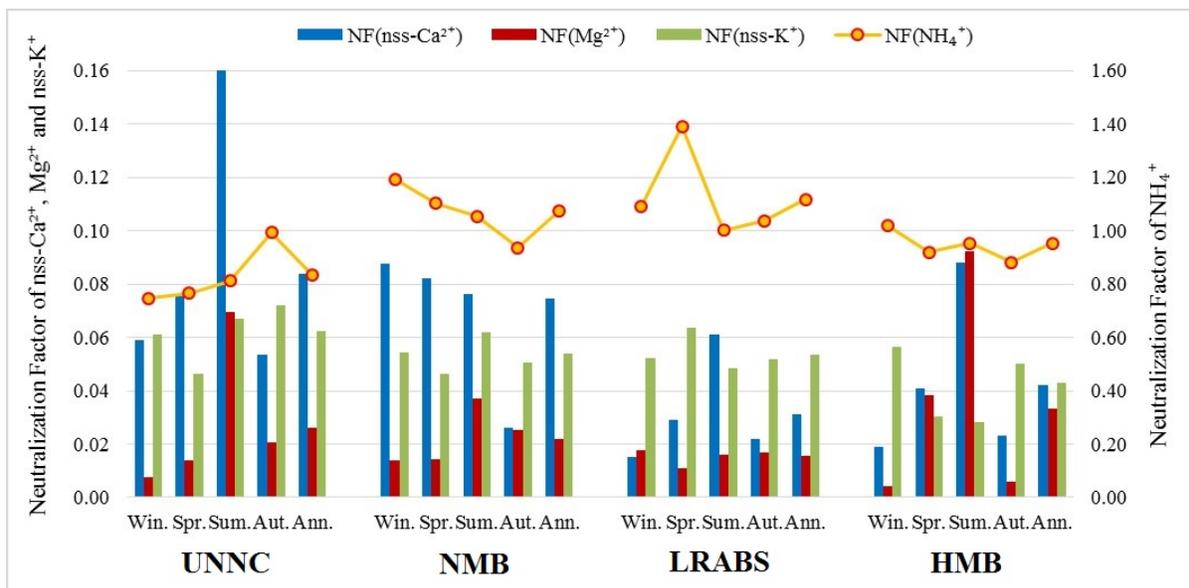
Fig. 2. Clusters of air mass backward trajectories during each season in sampling sites of NZP



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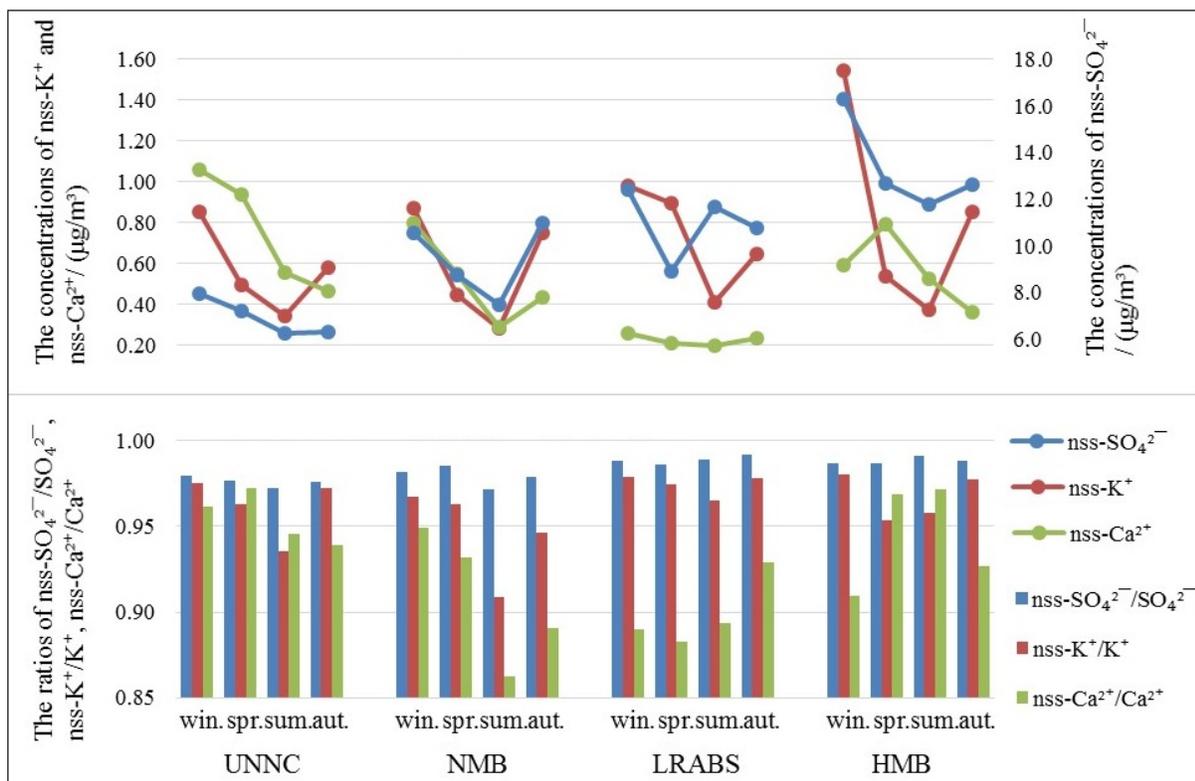
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**Fig. 3.** Plot of anion equivalents (AE) vs cation equivalents (CE) in four seasons of NZP



**Fig. 4.** The neutralization factors of nss-Ca<sup>2+</sup>, Mg<sup>2+</sup>, nss-K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub> at 4 sites of NZP

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891 2014-2015 sampling campaign

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894 **Table 1**895 Seasonal averaged PM<sub>2.5</sub> concentrations and meteorological data at four sampling sites during the 2014-2015  
896 sampling campaign

		PM <sub>2.5</sub> concentrations ( $\mu\text{g m}^{-3}$ )	Wind Speed ( $\text{m s}^{-1}$ )	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<sub>2.5</sub>, WSII, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> 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 (µg m <sup>-3</sup> )					References
		PM <sub>2.5</sub>	Total WSII (Total WSII/ PM <sub>2.5</sub> )	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	
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 <sup>+</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	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<sub>2.5</sub> 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 <sup>+</sup>	<b>0.555</b>	<b>0.582</b>		<b>0.687</b>	0.337	0.342	<b>0.642</b>	0.413	<b>0.571</b>	0.490
NH <sub>4</sub> <sup>+</sup>	<b>0.931</b>			<b>0.806</b>	-	<b>0.835</b>	-	<b>0.957</b>		
K <sup>+</sup>	<b>0.868</b>			<b>0.675</b>		<b>0.820</b>		<b>0.942</b>		
Mg <sup>2+</sup>		0.377	<b>0.744</b>	0.438	<b>0.505</b>		<b>0.554</b>		<b>0.695</b>	-0.348
Ca <sup>2+</sup>		<b>0.730</b>			<b>0.815</b>	0.484	<b>0.673</b>	0.311	<b>0.505</b>	-0.623
Cl <sup>-</sup>	<b>0.558</b>	<b>0.507</b>		0.465	<b>0.534</b>	<b>0.564</b>	0.359	0.442	<b>0.538</b>	0.450
NO <sub>2</sub> <sup>-</sup>		-	<b>0.725</b>							<b>0.533</b>
NO <sub>3</sub> <sup>-</sup>	<b>0.891</b>			<b>0.910</b>		<b>0.846</b>		<b>0.949</b>		
SO <sub>4</sub> <sup>2-</sup>	<b>0.882</b>			<b>0.729</b>		<b>0.840</b>	-	<b>0.848</b>		
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*