

1 **Seasonal variation of aerosol iron solubility in coarse and fine particles at an inland**
2 **city in northwestern China**

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24

25 **Abstract**

26 This work investigated seasonal variation of aerosol iron (Fe) solubility for coarse ($>1\ \mu\text{m}$) and
27 fine ($<1\ \mu\text{m}$) particles at Xi'an, a megacity in northwestern China impacted by anthropogenic
28 emission and desert dust. Total Fe concentrations were lowest in summer and similar in other
29 seasons for coarse particles, while lowest in summer and highest in spring for fine particles;
30 for comparison, dissolved Fe concentrations were higher in autumn and winter than spring and
31 summer for coarse particles, while highest in winter and lowest in spring and summer for fine
32 particles. Desert dust aerosol was always the major source of total Fe for both coarse and fine
33 particles in all the four seasons, but it may not be the dominant source for dissolved Fe. Fe
34 solubility was lowest in spring for both coarse and fine particles, and highest in winter for
35 coarse particles and in autumn for fine particles. In general aerosol Fe solubility was found to
36 be higher in air masses originating from local and nearby regions than those arriving from
37 desert regions after long-distance transport. Compared to coarse particles, Fe solubility was
38 similar for fine particles in spring but significantly higher in the other three seasons, and at a
39 given aerosol pH range Fe solubility was always higher in fine particles. Aerosol Fe solubility
40 was well correlated with relative abundance of aerosol acidic species, implying aerosol Fe
41 solubility enhancement by acid processing; moreover, such correlations were better for coarse
42 particles than fine particles in all the four seasons. Fe solubility was found to increase with
43 relative humidity and acid acidity for both coarse and fine particles at Xi'an, underscoring the
44 importance of aerosol liquid water and aerosol acidity in regulating Fe solubility via chemical
45 processing.

46 **1 Introduction**

47 Deposition of aerosol particles is a major external source of dissolved iron (Fe) in many
48 open oceans (Boyd and Ellwood, 2010; Tagliabue et al., 2017), significantly affecting primary
49 productions in these regions (Moore et al., 2009; Tang et al., 2021) and thus the global carbon
50 cycle (Martin, 1990; Jickells et al., 2005). Dissolved Fe has also been recognized as an
51 important source of reactive oxygen species in aerosol particles via mechanisms such as the
52 Fenton reaction (Zhang et al., 2008; Fang et al., 2017; Wang et al., 2022) and thus may have
53 adverse impacts on human health (Kelly, 2003; Abbaspour et al., 2014). In addition, dissolved
54 Fe could catalyze aqueous oxidation of SO₂ (Martin and Good, 1991; Alexander et al., 2009;
55 Huang et al., 2014), leading to the formation of sulfate, a major secondary species in aerosol
56 particles. The various impacts of aerosol Fe are largely determined by its fractional solubility
57 (often abbreviated as solubility) which is the ratio of dissolved Fe to total Fe.

58 Due to the impacts of dissolved aerosol Fe on ocean biogeochemistry and human health,
59 a number of studies have been conducted in the last 2-3 decades (Chen and Siefert, 2004; Baker
60 and Jickells, 2006; Kumar et al., 2010; Sholkovitz et al., 2012; Mahowald et al., 2018;
61 Meskhidze et al., 2019; Zhu et al., 2020; Baker et al., 2021; Ito et al., 2021), leading to
62 significant advances in our knowledge of aerosol Fe solubility and sources of aerosol dissolved
63 Fe. For examples, many studies (Baker and Jickells, 2006; Sholkovitz et al., 2012) observed
64 the inverse relationship between Fe solubility and total aerosol Fe. It has been recently realized
65 that non-desert-dust sources, such as anthropogenic emissions and biomass burning, can be
66 important for dissolved aerosol Fe in many regions (Sholkovitz et al., 2009; Ito et al., 2019;

67 Hamilton et al., 2020; Liu et al., 2022), though their contributions to total aerosol Fe are usually
68 minor. Furthermore, atmospheric aging processes, such as acid processing and organic
69 complexation, may substantially enhance solubility of Fe in desert dust and coal fly ash (Paris
70 et al., 2011; Shi et al., 2012; Chen and Grassian, 2013; Li et al., 2017).

71 Despite significant progress, it remains difficult for modelling studies to reproduce the
72 wide range of Fe solubility observed for ambient aerosols (Mahowald et al., 2018; Meskhidze
73 et al., 2019). The relative contribution of non-desert-dust sources, versus desert dust, to
74 dissolved aerosol Fe is still rather uncertain (Myriokefalitakis et al., 2018; Ito et al., 2019). In
75 addition, the impacts of chemical processing (especially organic complexation) on aerosol Fe
76 solubility is yet to be quantified for ambient aerosols. Further field measurements are needed
77 to reduce the uncertainties in aerosol Fe solubility, in order to better understand the impacts of
78 aerosol Fe on marine biogeochemistry and human health.

79 Sources, compositions and physicochemical properties are very different for coarse (>1
80 μm) and fine ($<1 \mu\text{m}$) particles (Seinfeld and Pandis, 2016). Therefore, aerosol Fe solubility
81 may differ significantly and is regulated by different sources or processes for coarse and fine
82 particles, as found by previous work (Sakata et al., 2022; Zhang et al., 2022). In addition, both
83 sources and chemical processes of aerosol particles exhibit significant variability for different
84 seasons, consequently leading to seasonal variations in aerosol Fe solubility. For example,
85 desert dust aerosol mainly occurs in spring at Xi'an where our present work was conducted,
86 while anthropogenic emission become more important in winter (Cao and Cui, 2021);
87 furthermore, higher temperature in summer causes more ammonium to partition in the gas

88 phase and thus leads to higher aerosol acidity (Ding et al., 2019; Zhou et al., 2022). As a result,
89 examining seasonal variability of aerosol Fe solubility may provide clues for and insights into
90 factors which regulate Fe solubility. However, seasonal variation of Fe solubility has only been
91 explored by a few previous studies (Chen and Siefert, 2004; Tao and Murphy, 2019; Yang et
92 al., 2020; Yang and Weber, 2022). In the present work, we investigated seasonal variations of
93 total Fe, dissolved Fe and Fe solubility for fine and coarse particles at Xi'an, a megacity in
94 northwestern China severely affected by anthropogenic emission and desert dust (Cao and Cui,
95 2021).

96 **2 Methodology**

97 **2.1 Sample collection**

98 Aerosol sampling in Xi'an took place during 01-30 April 2021 (spring), 12 July to 14
99 August 2021 (summer), 07 October to 07 November 2021 (autumn) and 26 November to 31
100 December 2020 (winter). Xi'an has a population of ~13 million and is located in the middle of
101 the Guanzhong Plain which is surrounded by Qinling Mountains and Chinese Loess Plateau
102 (Figure S1), favoring accumulation of air pollutants and formation of severe air pollution (Cao
103 and Cui, 2021). In addition, Xi'an is adjacent to major deserts in China and thus frequently
104 affected by desert dust aerosol.

105 Sampling in winter took place at an urban site (34.23°N, 108.89°E) which is close to a
106 busy major road and located in residential and commercial areas (Cao et al., 2012), and was
107 carried out on a building roof (~10 m from the ground) in Institute of Earth Environment,
108 Chinese Academy of Sciences. Sampling in the other three seasons took place at another urban

109 site (34.37°N, 108.97°E) which is located in residential areas (Chen et al., 2021), and was
110 carried out on a building roof (~40 m from the ground) in Shaanxi University of Science and
111 Technology. Meteorological parameters (wind speed and direction, temperature, and relative
112 humidity) and PM_{2.5} and PM₁₀ mass concentrations were provided by nearby environmental
113 monitoring stations.

114 Coarse (>1 μm) and fine (<1 μm) aerosol particles were collected onto Whatman 41 (W41)
115 cellulose filters on a daily basis (from 08:00 am to 07:30 am next day) using a two-stage aerosol
116 sampler (TH-150C, Tianhong Co., Wuhan, China) with a flow rate of 100 L/min. W41 filters,
117 which were used for aerosol sampling, were acid-washed to reduce background levels. After
118 aerosol collection, filters were sealed individually in clean plastic Petri dishes and then stored
119 at -20 °C for further analysis. Our previous work (Zhang et al., 2022) described filter
120 pretreatment, aerosol sampling and filter storage in details. In the present work, 28, 32, 30 and
121 36 pairs of filter samples were collected in spring, summer, autumn and winter, respectively.

122 In our work, mass concentrations of various species in air, including PM_{2.5} and PM₁₀
123 concentrations, are reported under standard state conditions (at 0 °C and 1 atm) to remove the
124 effects of variations in temperature and atmospheric pressure.

125 **2.2 Sample processing and analysis**

126 Sample analysis was detailed in our previous work (Zhang et al., 2022; Li et al., 2023),
127 and as a result here we only provide key information in brief. Every filter was equally halved.
128 The first half filter, which was used to determine total Fe, was digested in a Teflon jar using
129 microwave digestion; after residual acids used in digestion were evaporated, the Teflon jar was

130 cooled to room temperature and then filled with 20 mL HNO₃ (1%). The solution was filtered
131 using a PTFE membrane syringe filter (pore size: 0.22 μm), and then analyzed using
132 inductively coupled plasma mass spectrometry (iCAP Q, Thermo Fisher Scientific, USA). In
133 total 14 elements were determined, including Fe, Al and Pb, and the recovery rates were found
134 to be 90-110% for Fe using certificated reference materials (GBW07454 and GSB07-3272-
135 2015).

136 The other half filter, which was used to determine dissolved Fe and soluble ions, was
137 immersed in 20 mL ultrapure water for 2 h during which an orbital shaker (300 r/min) was used
138 to stir the aqueous mixture. After that, the aqueous mixture was filtered using a PTFE
139 membrane syringe filter (pore size: 0.22 μm) and then divided further to two parts. The first
140 solution (~10 mL) was analyzed by ion chromatography to measure soluble anions and cations;
141 the second solution (10 mL) was acidified to contain 1% HNO₃ (using 147 μL 67% HNO₃) and
142 subsequently analyzed using inductively coupled plasma mass spectrometry.

143 **2.3 Aerosol acidity calculation**

144 The ISORROPIA-II model (Fountoukis and Nenes, 2007) was used in the “metastable +
145 forward” mode to calculate aerosol pH for coarse and fine particles, and input data included
146 concentrations of soluble anions (SO₄²⁻, NO₃⁻ and Cl⁻) and cations (NH₄⁺, Na⁺, K⁺, Ca²⁺ and
147 Mg²⁺), temperature and relative humidity (RH). The effects of NH₃(g) and HNO₃(g) were not
148 taken into account as their concentrations were not measured; this may cause some biases
149 (likely underestimation) in calculated aerosol pH (Guo et al., 2015; Hennigan et al., 2015; Pye
150 et al., 2020), but the overall trend of aerosol pH would not be significantly affected. The reverse

151 mode was not used in our work, as results calculated using the reverse mode are very sensitive
152 to uncertainties in concentrations of common aerosol ions (Hennigan et al., 2015). Coarse
153 particles are generally expected to be less acidic than fine particles, and it is not clear yet why
154 similar and even lower aerosol pH were observed for coarse particles (when compared to fine
155 particles) in spring and autumn at Xi'an (Figure S14). This may be caused by biases in aerosol
156 pH calculation, and lower aerosol pH values were also reported in previous work for coarser
157 particles carried out at northern Colorado, United States (Young et al., 2013). Concurrent
158 measurements of gaseous NH₃, HNO₃ and HCl would help reduce uncertainties in calculated
159 aerosol pH and have been implemented in our following studies since July 2022.

160 **2.4 Air mass back trajectory analysis**

161 The Hysplit-4 model (Draxier and Hess, 1998) was employed to calculate 48-h air mass
162 back trajectories, using meteorological data (horizontal resolution: 1°×1°; time resolution: 3 h)
163 from Global Data Assimilation System provided by National Centers for Environmental
164 Prediction. Back trajectories were determined with arrival height of 100 m above the ground
165 level and arrival time of 08:00, 14:00, 20:00 and 02:00 on the next day (Wang et al., 2020),
166 and every day four back trajectories were obtained. In total 120, 136, 128 and 144 back
167 trajectories were obtained in our work for spring, summer, autumn and winter, and all the back
168 trajectories were clustered using the cluster analysis method described elsewhere (Baker, 2010).

169 **3 Total and dissolved aerosol Fe**

170 **3.1 Meteorological conditions and aerosol concentrations**

171 The climate in Xi'an (and the Guangzhou Plain in general) is mainly regulated by the East
172 Asia monsoon. During our campaign, prevailing wind directions were west and southwest in
173 spring, northeast in summer, southwest and northeast in autumn, and west in winter (Figure
174 S2); furthermore, average wind speeds were >2 m/s in summer and autumn, and <2 m/s in
175 spring and winter. Median temperatures were 13.6, 27.0, 12.7 and 1.3 °C in spring, summer,
176 autumn and winter, and median RH were found to be 85%, 71%, 83% and 77% (Table S1).
177 Precipitation mainly took place in summer during our campaign in 2021, similar to previous
178 years (Cao and Cui, 2021).

179 Table S2 shows $PM_{2.5}$ and PM_{10} concentrations at Xi'an in four seasons. PM_{10}
180 concentrations were in the range of 15-243, 24-76, 22-151 and 41-212 $\mu\text{g}/\text{m}^3$ in spring, summer,
181 autumn and winter, and the average values were 93 ± 61 , 51 ± 16 , 70 ± 35 and 107 ± 39 $\mu\text{g}/\text{m}^3$,
182 suggesting highest levels in spring and winter and lowest levels in summer. $PM_{2.5}$ mass
183 concentrations were in the range of 11-62, 11-48, 13-97 and 13-156 $\mu\text{g}/\text{m}^3$, and the average
184 values were 35 ± 14 , 23 ± 8 , 40 ± 24 and 80 ± 32 $\mu\text{g}/\text{m}^3$, suggesting highest concentrations in winter
185 and lowest levels in summer.

186 $PM_{2.5}$ and PM_{10} concentrations were high in winter due to accumulation of anthropogenic
187 pollution, and the median $PM_{2.5}/PM_{10}$ ratio was 0.76. PM_{10} concentrations in spring were
188 significantly increased due to the impacts of desert dust aerosol, and the median $PM_{2.5}/PM_{10}$
189 ratio was only 0.44. Two major dust events occurred during our spring campaign (12-17 April
190 and 27-30 April). During the two dust events the average PM_{10} and $PM_{2.5}$ mass concentrations

191 were 151 ± 57 and 42 ± 12 $\mu\text{g}/\text{m}^3$, and $\text{PM}_{2.5}/\text{PM}_{10}$ ratios became even lower (0.20-0.31).

192 Furthermore, the median $\text{PM}_{2.5}/\text{PM}_{10}$ ratios were 0.44 in summer and 0.62 in autumn.

193 3.2 Total aerosol Fe

194 Figure 1a shows seasonal variation of total aerosol Fe in coarse and fine particles

195 measured by our work at Xi'an. Total aerosol Fe concentrations were in the range of 270-3095,

196 191-1992, 395-3492 and 269-3924 ng/m^3 for coarse particles in spring, summer, autumn and

197 winter, and the average values were 1504 ± 800 , 950 ± 524 , 1638 ± 830 and 1831 ± 866 ng/m^3

198 (Table A1); total aerosol Fe concentrations were in the range of 206-12144, 164-1591, 196-

199 2631 and 257-4268 ng/m^3 for fine particles in spring, summer, autumn and winter, and the

200 average values were 3717 ± 3387 , 721 ± 366 , 958 ± 516 and 2058 ± 1037 ng/m^3 . Average total Fe

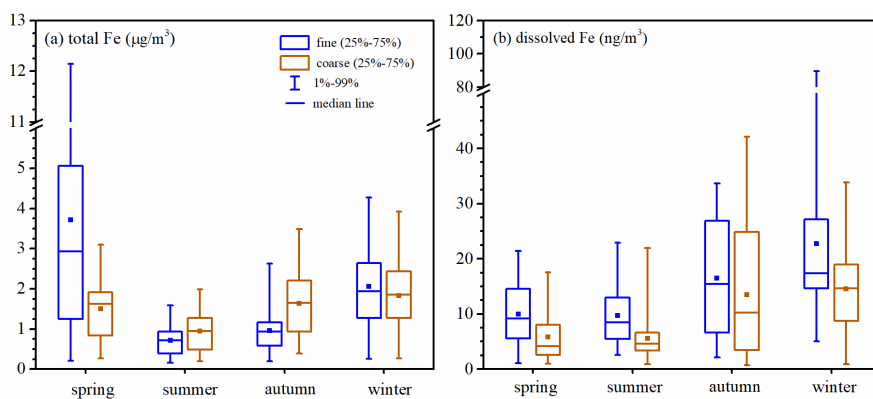
201 concentrations were measured to be 798 ± 466 and 801 ± 534 ng/m^3 for coarse and fine particles

202 in winter (November-December 2019) at Qingdao (Zhang et al., 2022), only 44% and 38% of

203 the average values (1831 ± 866 and 2058 ± 1037 ng/m^3) found in winter (November-December

204 2020) at Xi'an by the present work, mainly because during wintertime aerosol mass

205 concentrations were much higher at Xi'an than Qingdao.



206

207 **Figure 1.** Seasonal variations of (a) total Fe and (b) dissolved Fe for fine and coarse particles.

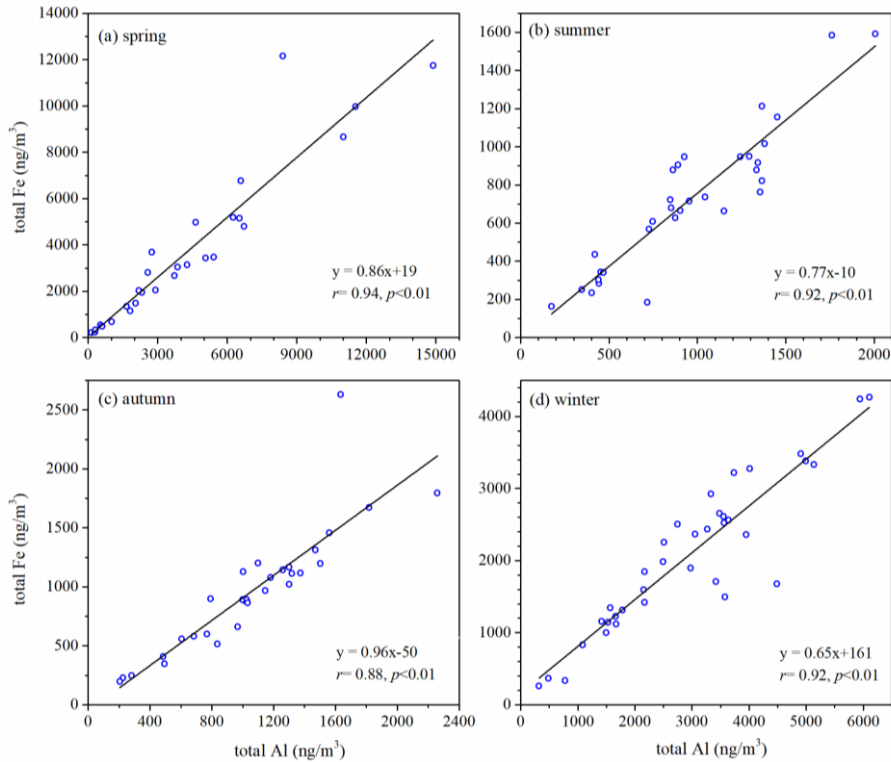
208

209 The average contribution of coarse particles to total Fe in TSP (total suspended particles)
210 were 29%, 57%, 63% and 47% in spring, summer, autumn and winter, being lowest in spring
211 when the influence of desert dust aerosol was largest. Statistical analysis (paired t-test)
212 suggested that compared to fine particles, total Fe in coarse particles was significantly lower in
213 spring ($p < 0.01$, $\alpha = 0.05$) while significantly higher in summer and autumn ($p < 0.01$, $\alpha = 0.05$); in
214 addition, there was no significant difference between coarse and fine particles in winter ($p = 0.13$,
215 $\alpha = 0.05$). The average contribution of coarse particles to total Al in TSP were 26%, 50%, 54%
216 and 40% in spring, summer, autumn and winter, also being lowest in spring. Furthermore,
217 during dust periods (12-17 and 27-30 April) the average contribution of coarse particles was
218 found to be 24% for total Fe and 23% for total Al in TSP, even slightly smaller than the average
219 values in spring. This is probably because for desert dust aerosol, Fe and Al were enriched in
220 fine particles while the major component in coarse particles was quartz (Journet et al., 2014);
221 nevertheless, further measurements are needed to better understand size distribution of trace
222 metals in desert dust aerosol.

223 Compared to other seasons, total Fe in fine and coarse particles were both lowest in
224 summer (Figure 1a), as aerosol mass concentrations were also lowest in summer (Section 3.1).
225 Similarly, previous measurements on Huaniao Island in the East China Sea (Yang et al., 2020)
226 and over the tropical and subtropical North Atlantic (Chen and Siefert, 2004) also found lowest
227 total aerosol Fe levels in summer. For the other three seasons (spring, autumn and winter), total
228 Fe in coarse particles were rather similar, while total Fe in fine particles were highest in spring

229 and lowest in autumn. Overall, compared to summer and autumn, total aerosol Fe were higher
230 in spring and winter when higher aerosol mass concentrations were also observed (Figure S3).

231 Total Fe was very well correlated with total Al ($0.87 < r < 0.96$, $p < 0.01$) for both coarse
232 (Figure S4) and fine particles (Figure 2) in all the four seasons, suggesting desert dust always
233 as the dominant source for total aerosol Fe at Xi'an, regardless of particle size range and
234 seasons. The median Fe/Al values, mass ratios of total Fe to total Al, were 0.975, 0.926, 1.269
235 and 0.940 in spring, summer, autumn and winter for coarse particles, and 0.735, 0.796, 0.870
236 and 0.744 for fine particles (Figure S5). Fe/Al were found to be 0.911 and 0.741 for PM₁₀ and
237 PM_{2.5} generated using surface soil samples collected over several major deserts in China
238 (Zhang et al., 2014). We found that Fe/Al measured for coarse and fine particles at Xi'an were
239 similar to these reported for desert dust (Zhang et al., 2014); coarse particles in autumn might
240 be one exception (Figure S5), showing slightly higher Fe/Al (median: 1.269) than desert dust.



241

242 **Figure 2.** Total Fe versus total Al for fine particles in different seasons: (a) spring; (b) summer;

243 (c) autumn; (d) winter.

244

245 3.3 Dissolved aerosol Fe

246 Figure 1b shows seasonal variation of dissolved aerosol Fe in coarse and fine particles at

247 Xi'an. Dissolved aerosol Fe concentrations were in the range of 1.0-17.5, 0.9-22.0, 0.7-42.2

248 and 0.9-33.8 ng/m³ for coarse particles in spring, summer, autumn and winter, and the average

249 values were 5.9±4.5, 5.6±4.0, 13.5±12.2 and 14.5±8.3 ng/m³; dissolved aerosol Fe

250 concentrations were in the range of 1.1-21.4, 2.6-22.9, 2.1-33.7 and 5.0-89.5 ng/m³ for fine

251 particles in spring, summer, autumn and winter, and the average values were 10.0±5.5, 9.7±5.6,

252 16.5±10.1 and 22.7±16.8 ng/m³. Average dissolved Fe concentrations were measured to be

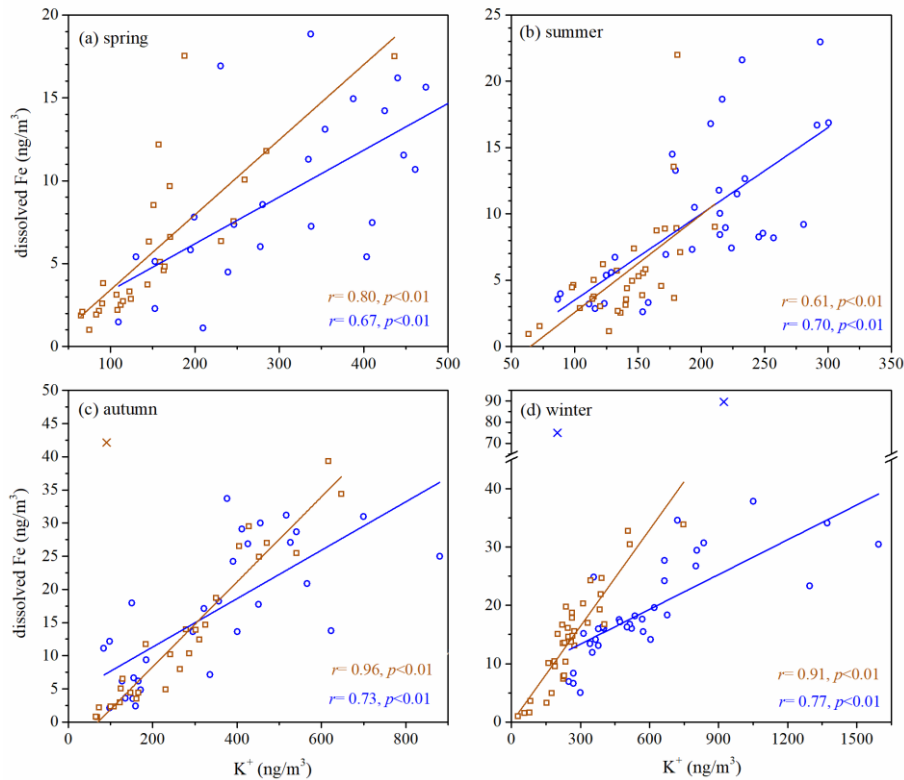
253 7.7±14.5 and 7.3±7.6 ng/m³ for coarse and fine particles in winter at Qingdao (Zhang et al.,

254 2022), only 53% and 32% of the average values (14.5 ± 8.3 and 22.7 ± 16.8 ng/m³) found in
255 winter at Xi'an by the present work, and one major reason is that total Fe concentrations were
256 significantly higher at Xi'an than Qingdao.

257 The average contribution of coarse particles to dissolved Fe in TSP were 37%, 36%, 45%
258 and 39% in spring, summer, autumn and winter. Compared to fine particles, dissolved Fe was
259 significantly lower in coarse particles for all the four seasons (paired t-test, $p < 0.01$, $\alpha = 0.05$) at
260 Xi'an, although total Fe in coarse particles were higher than or similar to fine particles (except
261 spring, as discussed in Section 3.2). This indicated that aerosol Fe solubility was lower in
262 coarse particle than fine particles, as further discussed in Section 4. Similar to our work, Sakata
263 et al. (2022) found that over the Pacific dissolved aerosol Fe concentrations in fine particles
264 (< 1.3 μm) were significantly higher than coarse particles (> 1.3 μm).

265 Compared to spring and summer, dissolved Fe concentrations were higher in autumn and
266 winter for coarse particles (Figure 1b); for fine particles, dissolved Fe concentrations were
267 highest in winter, followed by autumn, and lowest in spring and summer. Dissolved Fe
268 concentrations were low in summer, as total Fe concentrations were also low (Figure 1a). Total
269 Fe concentrations were high in spring (Figure 1a), but dissolved Fe concentrations were low;
270 this is because compared to other seasons, spring was most severely affected by desert dust
271 with low Fe solubility. Our previous study (Zhang et al., 2022) investigated aerosol Fe at
272 Qingdao in winter, and found that compared to clean days, dissolved Fe concentrations did not
273 change significantly during dust days although total Fe concentrations were remarkably
274 increased. Therefore, our previous (Zhang et al., 2022) and current studies imply that the

275 occurrence of desert dust aerosol may not necessarily lead to increase in dissolved Fe
276 concentrations in the air.



277
278 **Figure 3.** Dissolved Fe versus K^+ for fine and coarse particles in different seasons: (a) spring;
279 (b) summer; (c) autumn; (d) winter. Blue symbols represent fine particles and brown symbols
280 represent coarse particles. Cross symbols represent data points which are not included in
281 fittings.

282
283 As shown in Figure S6, overall the correlation between dissolved Fe and total Al was quite
284 weak at Xi'an, indicating that desert dust may not contribute dominantly to dissolved aerosol
285 Fe, although it was always the major source of total aerosol Fe (Section 3.2). We also examined
286 correlations between dissolved Fe and several other species (Table S3). Except for summer,

287 dissolved Fe was well correlated with secondary inorganic species (sulfate, nitrate and
288 ammonium) for coarse and fine particles, suggesting secondary formation (i.e. conversion of
289 insoluble Fe to dissolved Fe via chemical processing) as an important source of dissolved Fe.
290 Besides, Figure 3 shows that dissolved Fe was well correlated with K^+ (a tracer for biomass
291 burning) in coarse and fine particles at all the four seasons ($0.67 < r < 0.96$, $p < 0.01$), and this may
292 indicate biomass burning also as an important source for dissolved aerosol Fe.

293 Furthermore, good correlations with dissolved Fe were found in coarse particles for Pb,
294 Zn and As in three seasons (spring, autumn and winter), and in fine particles for Pb (spring,
295 autumn and winter), As (spring and autumn) and Zn (autumn). Aerosol Pb and Zn are mainly
296 emitted by vehicles and iron-steel industry (Chow et al., 2004; Cao and Cui, 2021), and the
297 major sources of aerosol As include coal combustion and metal smelting (Tian et al., 2010).
298 As a result, vehicle emission, coal combustion, iron-steel industry and metal smelting also
299 contributed to dissolved aerosol Fe at Xi'an.

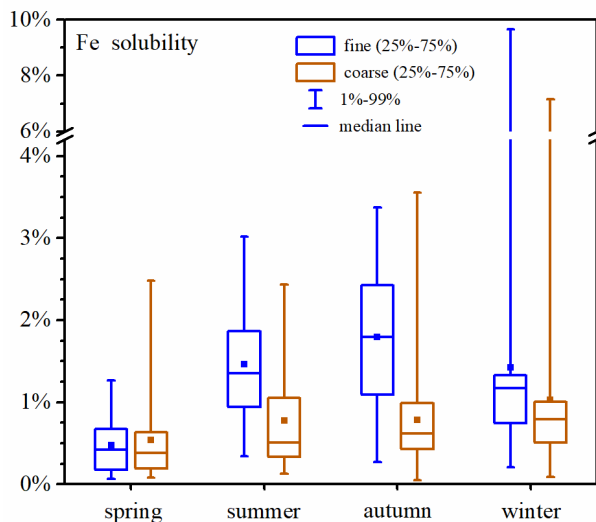
300 **4 Aerosol Fe solubility**

301 **4.1 Seasonal variation of Fe solubility**

302 **4.1.1 Seasonal variability**

303 Figure 4 and Table A1 display aerosol Fe solubility at Xi'an in different seasons. Fe
304 solubility was in the range of 0.08-2.48%, 0.13-2.44%, 0.05-3.55% and 0.09-7.16% for coarse
305 particles in spring, summer, autumn and winter, and the median values were 0.38%, 0.51%,
306 0.62% and 0.79%; for fine particles, Fe solubility was in the range of 0.06-1.26%, 0.34-3.02%,

307 0.27-3.37% and 0.21-9.65% in spring, summer, autumn and winter, and the median values
308 were 0.42%, 1.35%, 1.79% and 1.17%.



309

310 **Figure 4.** Seasonal variations of aerosol Fe solubility for fine and coarse particles at Xi'an.

311

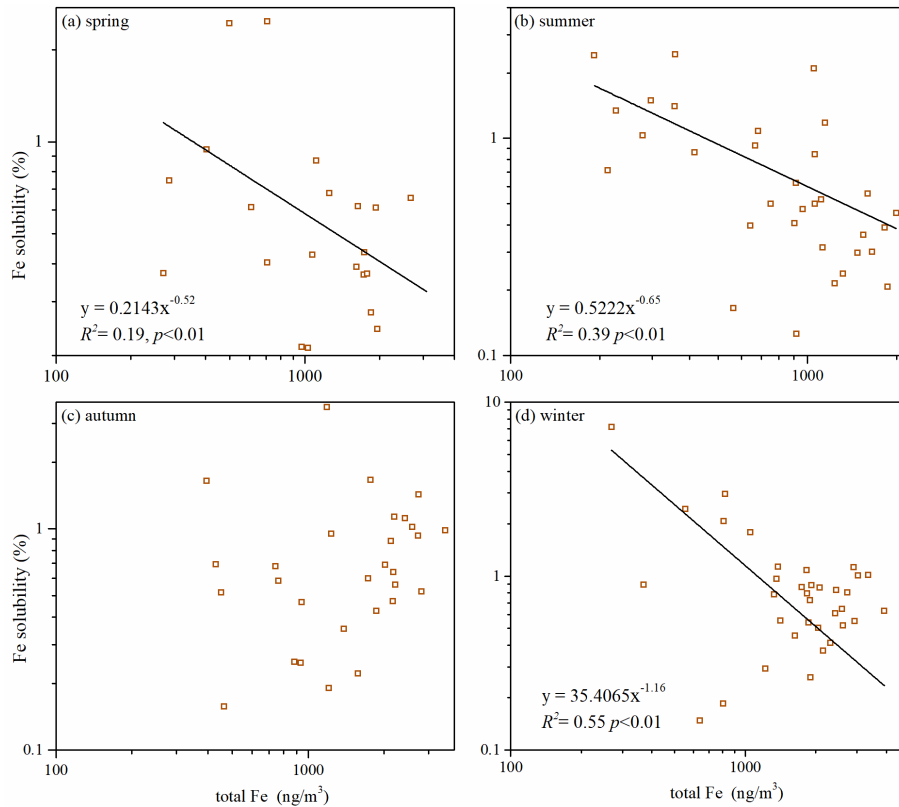
312 No significant difference in Fe solubility was found between coarse and fine particles at
313 Xi'an in spring (paired t -test, $p=0.17$, $\alpha=0.05$). In addition, the median values of Fe solubility
314 were both $<0.5\%$ for coarse and fine particles in spring, similar to desert dust (Schroth et al.,
315 2009; Shi et al., 2011b; Oakes et al., 2012b; Li et al., 2022), and this was because Xi'an was
316 frequently affected by desert dust aerosol in spring. In the other three seasons (summer, autumn
317 and winter), Fe solubility was significantly higher in fine particles than coarse particles (paired
318 t -test, $p<0.01$, $\alpha=0.05$); furthermore, in these three seasons the median Fe solubility was $>1\%$
319 for fine particles and $>0.5\%$ for coarse particles. For coarse particles, Fe solubility was highest
320 in winter and lowest in spring, while no significant difference was found between summer and
321 autumn (t -test, $p=0.95$, $\alpha=0.05$); for fine particles, Fe solubility can be described by the

322 following order: autumn > summer > winter > spring.

323 A number of field measurements (Hsu et al., 2005; Baker and Jickells, 2006; Sedwick et
324 al., 2007; Kumar et al., 2010; Sholkovitz et al., 2012; Winton et al., 2015; Shelley et al., 2018;
325 Yang et al., 2023) found inverse dependence of Fe solubility on total Fe (and Al). As shown in
326 Figures 5 and S7, Fe solubility was also observed in our work to decrease with total Fe for
327 coarse and fine particles in three seasons (spring, summer and winter), and such dependence
328 can be fitted using Eq. (1):

329
$$f_s(Fe) = a \times [Fe]_T^{-b} \quad (1)$$

330 where $f_s(Fe)$ is Fe solubility and $[Fe]_T$ is total Fe concentration, and b represents the sensitivity
331 of Fe solubility to relative change in total Fe concentration. As shown in Figures S8-S9, such
332 inverse dependence was also observed between Fe solubility and total Al in these three seasons.
333 Several mechanisms can qualitatively explain such inverse dependence, but a consensus has
334 not been reached yet (Mahowald et al., 2018; Meskhidze et al., 2019).



335

336 **Figure 5.** Fe solubility versus total Fe for coarse particles in different seasons: (a) spring; (b)

337 summer; (c) autumn; (d) winter.

338

339 However, no obvious relationship between Fe solubility and total Fe (or total Al) was
 340 found in autumn. Such inverse dependence was not found in some previous studies either (Paris
 341 et al., 2010; Oakes et al., 2012a), and was found for fine particles but not for coarse particles
 342 at Qingdao in the winter by our previous work (Zhang et al., 2022). Therefore, one may
 343 conclude that the inverse dependence of Fe solubility on total Fe (or total Al), though frequently
 344 observed, is not a universe rule. It is not clear yet why such inverse dependence was not
 345 observed in these studies.

346 A larger b value means that Fe solubility is more sensitive to relative change in total Fe
347 concentration. For our measurements conducted at Xi'an, b values were determined to be 0.30,
348 0.23 and 0.91 in spring, summer and winter for fine particles (Figure S7), and 0.52, 0.65 and
349 1.16 for coarse particles (Figure 5). One can see that the b values in winter were much larger
350 than those in spring and summer for both fine and coarse particles; furthermore, in each of the
351 three seasons (spring, summer and winter), the b value was larger for coarse particles than fine
352 particles.

353 **4.1.2 Comparison with previous work**

354 The median Fe solubility at Xi'an were 0.79% and 1.17% for coarse and fine particles in
355 winter, larger than those (0.34% and 0.66%, respectively) found in winter at Qingdao (Zhang
356 et al., 2022). One reason is that in winter Xi'an was frequently affected by haze pollution when
357 aerosol Fe solubility was significantly increased (Shi et al., 2020; Zhang et al., 2022; Zhu et
358 al., 2022); in addition, our winter sampling at Qingdao was severely affected by desert dust
359 aerosol (Zhang et al., 2022) with very low Fe solubility.

360 Several previous studies also investigated aerosol Fe solubility in northern China. Similar
361 to our current work, Chuang et al. (2005) reported low Fe solubility (<1%) for TSP during
362 spring at Dunhuang, a city in Northwest China. Average Fe solubility at Xi'an were reported
363 to be 10.4% for TSP (He et al., 2021) and $25.5 \pm 11.3\%$ for $PM_{2.5}$ (Lei et al., 2023), $5.0 \pm 3.8\%$,
364 $4.5 \pm 2.6\%$ and $2.7 \pm 1.5\%$ for $PM_{2.5}$ at three cities in North China (Zhu et al., 2020), and
365 $2.70 \pm 2.77\%$ for TSP at Qingdao (Shi et al., 2020). Compared to our work, some other studies
366 (Shi et al., 2020; Zhu et al., 2020; He et al., 2021; Lei et al., 2023) reported higher Fe solubility,

367 mainly because different leaching protocols were employed to extract dissolved Fe (Meskhidze
368 et al., 2019; Li et al., 2023): 1) sonication was used during extraction in three previous studies
369 (Shi et al., 2020; Zhu et al., 2020; He et al., 2021) but not in our work; 2) filter pore size Shi et
370 al. used (0.45 μm) was larger than that our work used (0.22 μm); 3) the leaching solution used
371 by Lei et al. (acetate buffer, pH=4.3) was more acidic than that we used (ultrapure water).

372 **4.1.3 Fe solubility during dust and haze events**

373 At Xi'an, dust events ($\text{PM}_{10} > 100 \mu\text{g}/\text{m}^3$ and $\text{PM}_{10}/\text{PM}_{2.5} > 3$) occurred in spring (12-17
374 and 27-30 April). During the two dust events average Fe solubility was $0.17 \pm 0.09\%$ and
375 $0.18 \pm 0.13\%$ for coarse and fine particles, similar to that reported for dust particles collected
376 from dust source regions (Shi et al., 2011b; Oakes et al., 2012b; Paris and Desboeufs, 2013; Li
377 et al., 2022); during non-dust periods in spring, average Fe solubility was found to be $0.75 \pm 0.66\%$
378 and $0.64 \pm 0.27\%$ for coarse and fine particles, higher than that observed for dust events. In fact,
379 much lower Fe solubility was also reported during dust events at Qingdao (Shi et al., 2020;
380 Zhang et al., 2022), Jeju Island (Chuang et al., 2005) and Hokkaido (Ooki et al., 2009), when
381 compared to non-dust periods.

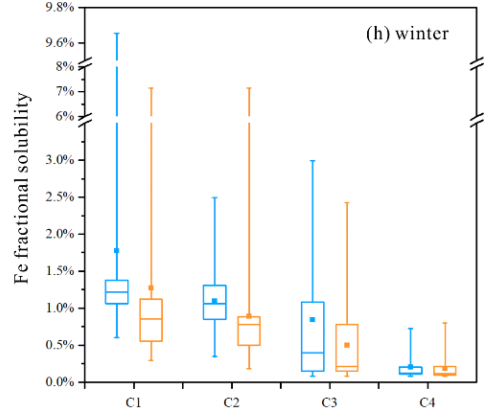
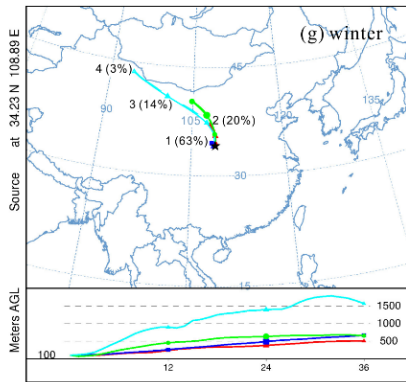
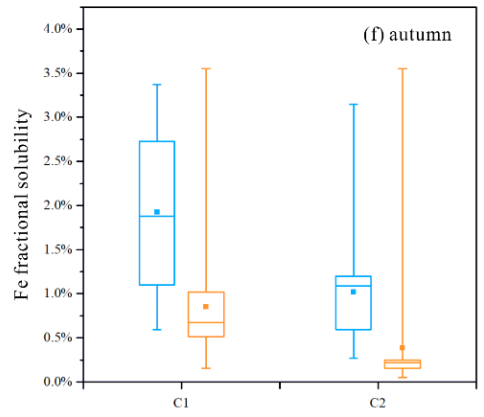
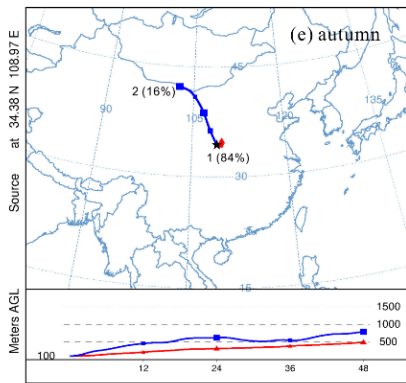
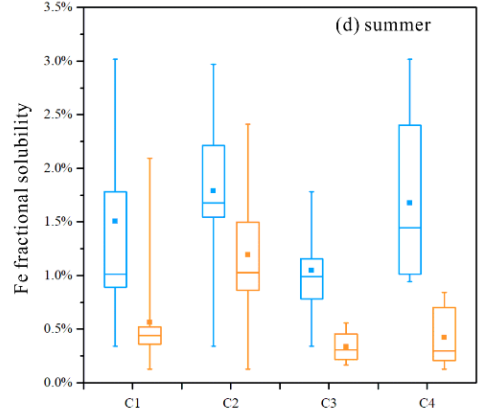
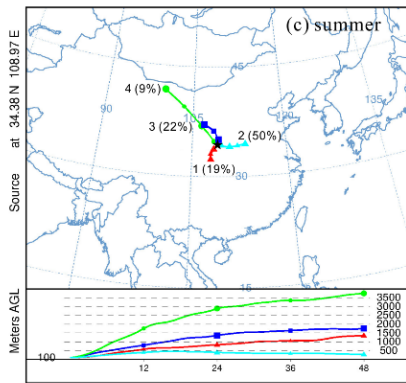
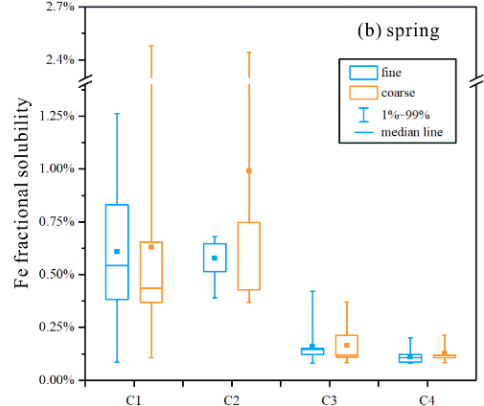
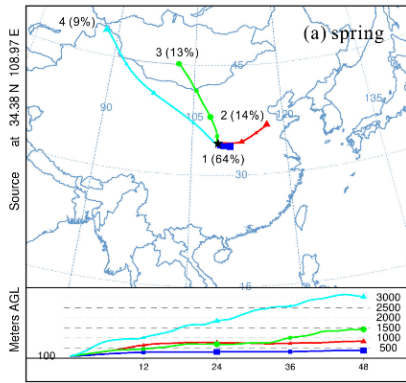
382 In this work we classified high-RH haze events as those with $\text{PM}_{2.5} > 80 \mu\text{g}/\text{m}^3$,
383 $\text{PM}_{2.5}/\text{PM}_{10} > 0.8$ and $\text{RH} > 80\%$. High-RH haze events at Xi'an only occurred in winter (26
384 November to 01 December, and 05-07 December). Average Fe solubility was measured to be
385 $2.03 \pm 2.07\%$ and $2.16 \pm 2.81\%$ for coarse and fine particles during high-RH haze events,
386 significantly higher than that observed for other days in winter ($0.69 \pm 0.46\%$ and $1.18 \pm 0.81\%$
387 on average, respectively). Some previous studies (Shi et al., 2020; Zhu et al., 2020; Zhang et

388 al., 2022; Zhu et al., 2022) also observed evaluated aerosol Fe solubility during haze periods,
389 attributed to increased contribution of anthropogenic Fe with high solubility and/or Fe
390 solubility enhancement via chemical processing.

391 **4.2 Influence of air mass sources on Fe solubility**

392 Back trajectories obtained for our campaign were clustered, and we further examined the
393 dependence of Fe solubility on air mass cluster types in different seasons. In spring (Figure 6a),
394 air mass cluster C1 originated locally and C2 originated from North China Plain with severe
395 air pollution, while C3 and C4 represented air mass arriving from desert regions in the north
396 and northwest after long-distance transport (compared to C1 and C2); as shown in Figure 6b,
397 Fe solubility in coarse and fine particles was significantly higher for C1 and C2, when
398 compared to C3 and C4.

399 In autumn (Figure 6e), air mass cluster C1 originated locally and C2 was transported from
400 desert regions in the north/northwest, and Fe solubility was much higher for C1 than C2 (Figure
401 6f). In winter (Figure 6g), air mass cluster C1 originated locally while C2, C3 and C4 originated
402 from desert regions in the north and northwest, and the transport distance increased from C2 to
403 C4; as shown in Figure 6h, Fe solubility followed the order $C1 > C2 > C3 > C4$, decreasing
404 with increase in transport distance. In contrast to other three seasons, no obvious dependence
405 of Fe solubility on air mass clusters was found in summer (Figure 6d).



407 **Figure 6.** The mean backward trajectory clusters obtained by HYSPLIT for (a) spring, (c)
408 summer, (e) autumn, and (g) winter; Fe solubility in fine and coarse particles for different air
409 mass clusters in (b) spring, (d) summer, (f) autumn, and (h) winter. C1-C4 represent different
410 air mass clusters.

411

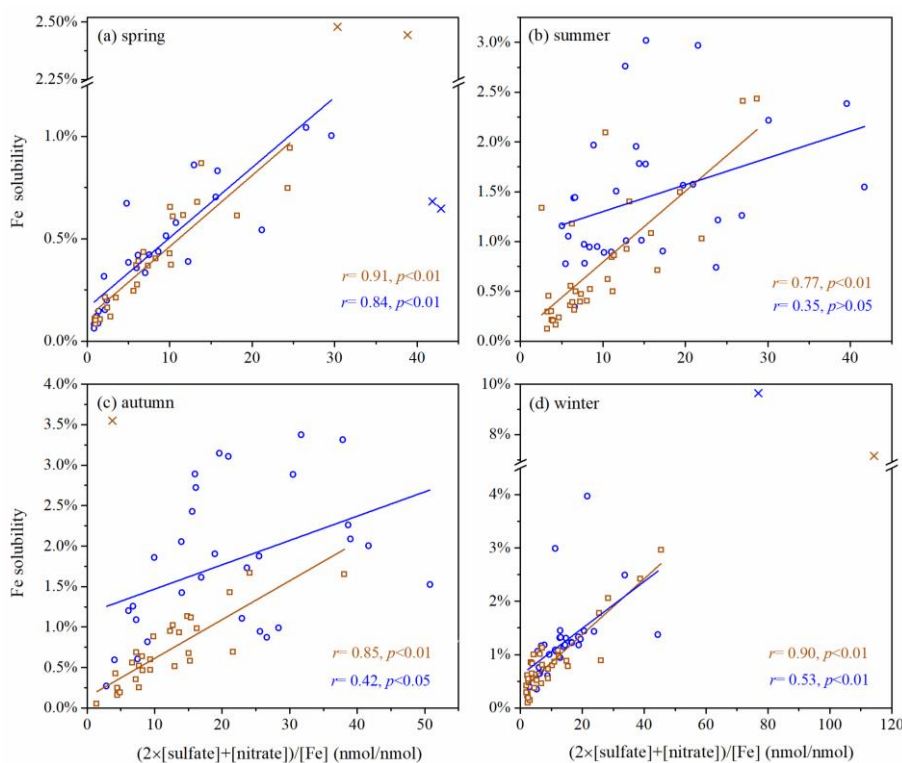
412 To summarize, our work found that in spring, autumn and winter, Fe solubility at Xi'an
413 was significantly higher when air masses originated from local and nearby regions, when
414 compared to those arriving from desert regions after long-distance transport. The reason is that
415 the contribution of anthropogenic emissions to aerosol Fe was elevated for air masses originating
416 from local and nearby sources (when compared to air masses originating from desert regions),
417 and anthropogenic aerosol Fe had higher solubility than desert dust (Schroth et al., 2009; Fu et
418 al., 2012; Oakes et al., 2012b). Similar to our work, over the Sargasso Sea aerosol Fe solubility
419 was much lower in Saharan air masses than North American air masses (Sedwick et al., 2007).

420 **4.3 Effects of chemical aging**

421 Laboratory studies (Shi et al., 2011a; Chen and Grassian, 2013; Wang et al., 2018)
422 suggested that chemical processing by acids, such as H₂SO₄ and HNO₃, could dissolve
423 insoluble Fe and thus enhance aerosol Fe solubility. Some field studies found that aerosol Fe
424 solubility was positively correlated with sulfate and/or nitrate (Shi et al., 2020; Zhu et al., 2020;
425 Liu et al., 2021; Zhang et al., 2022; Yang et al., 2023), indicating enhancement of Fe solubility
426 by atmospheric acid processing.

427 Figure 7 plots Fe solubility at Xi'an versus $(2 \times [\text{sulfate}] + [\text{nitrate}]) / [\text{Fe}]$ (in nmol/nmol,

428 referred to as relative abundance of aerosol acidic species), the molar ratio of two major acidic
 429 species to total Fe in aerosol particles. For coarse particles, aerosol Fe solubility was well
 430 correlated with relative abundance of aerosol acidic species in all the four seasons ($0.77 < r$
 431 < 0.91 , $p < 0.01$). For fine particles, good correlation was found in spring ($r = 0.84$, $p < 0.01$),
 432 moderate correlation was found in autumn and winter ($0.42 < r < 0.53$, $p < 0.01$), and no
 433 significant correlation was found in summer ($r = 0.35$, $p > 0.05$). In addition, as shown in Figures
 434 S10-S11, correlations of Fe solubility with $[\text{nitrate}]/[\text{Fe}]$ were better than (or very similar to)
 435 these with $[\text{sulfate}]/[\text{Fe}]$ for coarse particles in the four seasons, whereas no obvious trend was
 436 not observed for fine particles.



437
 438 **Figure 7.** Fe solubility versus $(2 \times [\text{sulfate}] + [\text{nitrate}]) / [\text{Fe}]$ for fine and coarse particles in
 439 different seasons: (a) spring; (b) summer; (c) autumn; (d) winter. Blue symbols represent fine

440 particles and brown symbols represent coarse particles. Cross symbols represent data points
441 which are not included in fittings.

442

443 Overall, correlations between Fe solubility and relative abundance of aerosol acidic
444 species were always better for coarse particles than fine particles (Figure 7), indicating that
445 acid processing may be more important in Fe solubility enhancement for coarse particles, when
446 compared to fine particles. A previous study (Zhang et al., 2022) also found that such
447 correlation was better in coarse particles than fine particles in winter at Qingdao, a coastal city
448 in northern China. Nevertheless, as discussed in Section 4.1, Fe solubility was higher in fine
449 particles than coarse particles. This may imply that primary emission of non-desert-dust Fe
450 (anthropogenic Fe) with higher solubility (Schroth et al., 2009; Oakes et al., 2012b) was more
451 important for Fe solubility enhancement in fine particles than coarse particles.

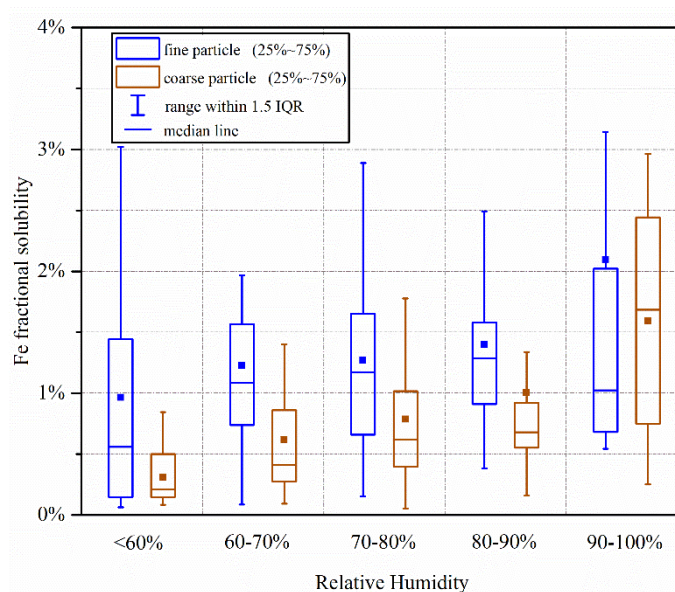
452 It was suggested by laboratory studies (Chen and Grassian, 2013; Paris and Desboeufs,
453 2013; Wang et al., 2017) that atmospheric organic ligands, such as oxalate, could increase
454 aerosol Fe solubility via ligand-promoted dissolution. As shown in Figure S12, our present
455 work found good correlation between Fe solubility with [oxalate]/[Fe] (in nmol/nmol) for
456 coarse particles ($0.70 < r < 0.88$, $p < 0.01$) and moderate correlation for fine particles ($0.40 < r < 0.67$,
457 $p < 0.01$) at Xi'an. Positive correlation between Fe solubility and oxalate was also observed
458 previously at Atlanta, USA (Yang and Weber, 2022), Toronto, Canada (Tao et al., 2022) and
459 Qingdao, China (Zhang et al., 2022).

460 We note that good correlation between Fe solubility and aerosol oxalate does not
461 necessarily mean Fe solubility enhancement by Fe-oxalate complexation. For example, it was
462 suggested that Fe could promote the formation of oxalate in aerosol particles (Tao and Murphy,
463 2019; Zhang et al., 2019), and thus good correlation between Fe solubility and oxalate could
464 also imply enhanced formation of oxalate by dissolved Fe. In addition, similar to sulfate and
465 nitrate, the major source of oxalate in the troposphere was secondary formation
466 (Myriokefalitakis et al., 2011; Kawamura and Bikkina, 2016), and in this aspect good
467 correlation between Fe solubility and relative abundance of oxalate could also indicate the
468 importance of secondary formation of dissolved aerosol Fe (i.e. dissolution of insoluble Fe to
469 dissolved Fe via aging processes).

470 **5 Discussion: roles of RH and aerosol acidity**

471 Figure 8 reveals the importance of RH in regulating aerosol Fe solubility. When RH was
472 increased from <60% to 60-70%, significant increase in Fe solubility was observed for both
473 coarse and fine particles. Sun et al. (2018) investigated hygroscopicity of aerosol particles
474 collected in North China, and found that most particles examined started to become deliquesced
475 when RH was increased to ~60%. The deliquescence RH reported for ambient aerosol particles
476 (Sun et al., 2018) coincided roughly with the RH threshold at which large increase in aerosol
477 Fe solubility was observed in our work. Previous studies (Shi et al., 2020; Zhu et al., 2020; Zhu
478 et al., 2022) also highlighted that RH and thus aerosol liquid water could substantially affect
479 Fe solubility. For examples, Zhu et al. (2020) measured Fe solubility at four cities in eastern

480 China in December 2017, and found that Fe solubility at >50% RH was significantly larger
481 than that at <50% RH.



482
483 **Figure 8.** Fe solubility in different RH (relative humidity) ranges for fine and coarse particles.
484 (RH<60%: 18 days; 60%<RH<70%: 23 days; 70%<RH<80%: 48 days; 80%<RH<90%: 28
485 days; RH>90%: 10 days).

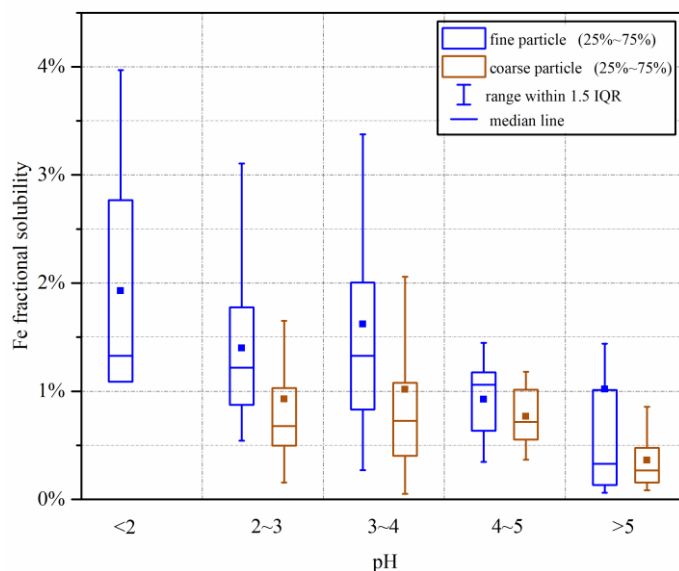
486
487 In addition, as shown in Figure 8, when RH was increased from 80-90% to >90%, median
488 Fe solubility was remarkably increased from 0.67% to 1.68% for coarse particles. Similar to
489 our work, Shi et al. (2020) also found that aerosol Fe solubility at Qingdao was significantly
490 increased under foggy weather when compared to other weather conditions. Therefore, both
491 Shi et al. (2020) and our present work suggested that high RH could promote Fe dissolution.

492 We further examined the impact of aerosol acidity on Fe solubility, and the results are
493 displayed in Figure 9. For coarse particles, increase in pH did not lead to apparent change in
494 Fe solubility as long as aerosol pH was <5; however, Fe solubility was greatly decreased when

495 aerosol pH was increased to >5 . For fine particles, Fe solubility in general decreased with
496 increasing aerosol pH (from <2 to >5). Previous work carried out at six Canadian sites (Tao
497 and Murphy, 2019) and Atlanta, USA (Wong et al., 2020; Yang and Weber, 2022) also reported
498 higher Fe solubility at lower aerosol pH. Similar to our previous work at Qingdao in the winter
499 (Zhang et al., 2022), our current study found that for coarse and fine particles at Xi'an, aerosol
500 pH was mostly <4 when Fe solubility exceeded 1% (Figure S13). It should be pointed out that
501 for some samples collected at Xi'an, Fe solubility could still be very low ($<1\%$) even when
502 aerosol pH was low and RH was high (Figure S13). In total 34 samples for coarse particles (9
503 in spring, 8 in summer, 12 in autumn and 5 in winter) and 18 samples for fine particles (7 in
504 spring, 6 in summer, 4 in autumn and 1 in winter) fulfilled the above conditions ($\text{pH}<4$,
505 $\text{RH}>80\%$, and Fe solubility $<1\%$). Fe mineralogy may possibly explain the observed low Fe
506 solubility despite high RH and aerosol acidity, and concurrent measurements of Fe mineralogy
507 could provide further clues.

508 In addition, as shown in Figure 9, at a given pH range Fe solubility was always higher in
509 fine particles than coarse particles. If we assume at the same pH range Fe solubility
510 enhancement by acid processing was similar for fine and coarse particles, the results displayed
511 in Figure 9 may imply that anthropogenic and pyrogenic Fe played a more important role in Fe
512 solubility enhancement in fine particles at Xi'an, when compared to coarse particles. Mcdaniel
513 et al. (2019) found that soluble Fe concentration was strongly correlated with aerosol surface
514 area for size-resolved aerosol samples collected from several different regions, and suggested
515 surface area as the main factor which affected Fe solubility; they further suggested that this

516 was because Fe solubility enhancement by acid processing could be more effective for aerosol
517 particles with larger surface area and thus smaller particle size.



518
519 **Figure 9.** Fe solubility in different pH ranges for fine and coarse particles at Xi'an.

520
521 Our work found that at Xi'an aerosol pH values for both coarse and fine particles were
522 lower (t -test, $p < 0.01$, $\alpha = 0.05$) in summer and autumn than spring and winter (Table S4 and
523 Figure S14). Compared to summer and autumn, lower temperature in winter favored
524 partitioning of ammonium in aerosol particles and thus led to higher aerosol pH. Average
525 temperatures were similar in spring and autumn at Xi'an (Table S1), but aerosol pH was higher
526 in spring than autumn (Table S4). Higher aerosol pH in spring at Xi'an, when compared to
527 autumn, was caused by increase of non-volatile cations in spring due to the influence of desert
528 dust aerosol; in fact, we found that the abundance of Ca^{2+} (relative to sulfate) was much higher
529 in spring for both fine and coarse particles. Meanwhile, Fe solubility was higher in summer
530 (median: 1.35%) and autumn (median: 1.79%) than spring (median: 0.42%) and winter (median:

531 1.17%) for fine particles, and was also higher in summer (median: 0.51%) and autumn (median:
532 0.62%) than spring (median: 0.38%) for coarse particles. As a result, lower aerosol pH (thus
533 higher aerosol acidity) in summer and autumn may at least partly explain the observed higher
534 Fe solubility in these two seasons. Our results were corroborated by a previous study (Yang
535 and Weber, 2022) which found that compared to the cold season, higher Fe solubility was
536 found at Atlanta (Georgia, USA) in the warm season when aerosol pH was lower.

537 **6 Summary and conclusion**

538 Our work investigated total Fe, dissolved Fe and Fe solubility for coarse ($>1\ \mu\text{m}$) and fine
539 ($<1\ \mu\text{m}$) particles in four different seasons at Xi'an, a megacity in northwestern China impacted
540 by anthropogenic emissions and desert dust. Total Fe concentrations in coarse particles were
541 lowest in summer and similar in the other three seasons, while for fine particles total Fe
542 concentrations were lowest in summer and highest in spring. Good correlations were found
543 between total Fe and total Al for both coarse and fine particles in all the four seasons,
544 suggesting desert dust aerosol as the major source of total Fe regardless of particle size (below
545 or above $1\ \mu\text{m}$) and season.

546 Dissolved Fe concentrations were higher in autumn and winter than spring and summer
547 for coarse particles; for fine particles, dissolved Fe concentrations were highest in winter,
548 followed by autumn, and lowest in spring and summer. Compared to other seasons, although
549 total Fe concentrations were evaluated in spring due to the impacts of desert dust, increase in
550 dissolved Fe levels was not observed. This may imply that the occurrence of desert dust aerosol
551 may not necessarily lead to increase in dissolved Fe concentrations, as also revealed in our

552 previous study (Zhang et al., 2022) carried out at a coastal city in northern China. Dissolved
553 Fe was significantly lower for coarse particles (compared to fine particles) in all the four
554 seasons, although total Fe in coarse particles were higher than or similar to fine particles in
555 three seasons (but not spring), implying higher Fe solubility in fine particles. Overall the
556 correlation between dissolved Fe and total Al was rather weak, suggesting that desert dust may
557 not contribute dominantly to dissolved Fe at Xi'an, although it was always the major source of
558 total Fe.

559 Highest Fe solubility was observed in winter for coarse particles and in autumn for fine
560 particles; meanwhile, lowest Fe solubility was observed in spring for both coarse and fine
561 particles, with median Fe solubility both below 0.5%. Compared to coarse particles, Fe
562 solubility was similar for fine particles in spring but significantly higher in the other three
563 seasons. Inverse dependence of Fe solubility on total Fe concentration was observed for coarse
564 and fine particles in spring, summer and winter, while there was no such dependence for either
565 fine or coarse particles in autumn. Furthermore, aerosol Fe solubility was higher in air masses
566 originating from local and nearby regions than those arriving from desert regions after long-
567 distance transport in three seasons (spring, autumn and winter), while no apparent dependence
568 of Fe solubility on air mass origins was found in summer.

569 Our work found better correlation between Fe solubility and relative abundance of aerosol
570 acidic species for coarse particles than fine particles in all the four seasons, probably suggesting
571 that acid processing was more important for Fe solubility enhancement in coarse particles. This
572 may further mean that non-desert-dust Fe (e.g., anthropogenic and biomass burning Fe) was

573 more important for Fe solubility enhancement in fine particles, since Fe solubility was higher
574 in fine particles than coarse particles. We also found that overall Fe solubility increased with
575 RH and acid acidity for coarse and fine particles, underscoring the importance of aerosol liquid
576 water and aerosol acidity in enhancing Fe solubility via acid processing. Our work further
577 found that at a given pH range aerosol Fe solubility was always higher in fine particles than
578 coarse particles.

579

580

581 **Appendices**

582 **Table A1.** Overview of total Fe (in ng/m³), dissolved Fe (in ng/m³) and Fe solubility (in %) for
 583 fine and coarse particles in different seasons at Xi'an.

	fine particles			coarse particles		
Spring	range	median	average	range	median	average
total Fe	206-12144	2925	3717±3387	270-3095	1626	1504±800
dissolved Fe	1.1-21.4	9.2	10.0±5.5	1.0-17.5	4.2	5.9±4.5
Fe solubility	0.06-1.26	0.42	0.48±0.32	0.08-2.48	0.38	0.54±0.59
Summer	range	median	average	range	median	average
total Fe	164-1591	719	721±366	191-1992	942	950±524
dissolved Fe	2.6-22.9	8.5	9.7±5.6	0.9-22.0	4.6	5.6±4.0
Fe solubility	0.34-3.02	1.35	1.46±0.67	0.13-2.44	0.51	0.78±0.63
Autumn	range	median	average	range	median	average
total Fe	196-2631	934	958±516	395-3492	1651	1638±830
dissolved Fe	2.1-33.7	15.4	16.5±10.1	0.7-42.2	10.3	13.5±12.2
Fe solubility	0.27-3.37	1.79	1.80±0.88	0.05-3.55	0.62	0.79±0.67
Winter	range	median	average	range	median	average
total Fe	257-4268	1942	2058±1037	269-3924	1850	1831±866
dissolved Fe	5.0-89.5	17.4	22.7±16.8	0.9-33.8	14.7	14.5±8.3
Fe solubility	0.21-9.65	1.17	1.43±1.58	0.09-7.16	0.79	1.03±1.22

584

585 **Data availability.**

586 Data are available upon request (Mingjin Tang: mingjintang@gig.ac.cn).

587 **Competing interests.**

588 The authors declare that they have no conflict of interest.

589 **Author contribution.**

590 **Huanhuan Zhang:** investigation, formal analysis, writing-original draft, writing-review &
591 editing; **Rui Li:** investigation, writing-original draft; **Chengpeng Huang:** investigation;
592 **Xiaofei Li:** investigation; **Shuwei Dong:** investigation; **Fu Wang:** investigation; **Tingting Li:**
593 investigation; **Yizhu Chen:** investigation; **Guohua Zhang:** resource, writing-review & editing;
594 **Yan Ren:** resource; **Qingcai Chen:** resource; **Ru-jin Huang:** resource; **Siyu Chen:** writing-
595 review & editing; **Xinming Wang:** resource; **Mingjin Tang:** conceptualization, formal
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605

606

607 **References**

- 608 Abbaspour, N., Hurrell, R., and Kelishadi, R.: Review on iron and its importance for
609 human health, *J. Res. Med. Sci.*, 19, 164-174, 2014.
- 610 Alexander, B., Park, R. J., Jacob, D. J., and Gong, S. L.: Transition metal-catalyzed
611 oxidation of atmospheric sulfur: Global implications for the sulfur budget, *J. Geophys. Res.-*
612 *Atmos.*, 114, D02309, doi: 02310.01029/02008jd010486, 2009.
- 613 Baker, A. R. and Jickells, T. D.: Mineral particle size as a control on aerosol iron solubility,
614 *Geophys. Res. Lett.*, 33, L17608, doi: 17610.11029/12006GL026557, 2006.
- 615 Baker, A. R., Kanakidou, M., Nenes, A., Myriokefalitakis, S., Croot, P. L., Duce, R. A.,
616 Gao, Y., Guieu, C., Ito, A., Jickells, T. D., Mahowald, N. M., Middag, R., Perron, M. M. G.,
617 Sarin, M. M., Shelley, R., and Turner, D. R.: Changing atmospheric acidity as a modulator of
618 nutrient deposition and ocean biogeochemistry, *Science Advances*, 7, eabd8800,
619 10.1126/sciadv.abd8800, 2021.
- 620 Baker, J.: A cluster analysis of long range air transport pathways and associated pollutant
621 concentrations within the UK, *Atmos. Environ.*, 44, 563-571, 2010.
- 622 Boyd, P. W. and Ellwood, M. J.: The biogeochemical cycle of iron in the ocean, *Nature*
623 *Geosci.*, 3, 675-682, 2010.
- 624 Cao, J. J. and Cui, L.: Current Status, Characteristics and Causes of Particulate Air
625 Pollution in the Fenwei Plain, China: A Review, *J. Geophys. Res.-Atmos*, 126,
626 e2020JD034472, doi: 034410.031029/032020JD034472, 2021.
- 627 Cao, J. J., Wang, Q. Y., Chow, J. C., Watson, J. G., Tie, X. X., Shen, Z. X., Wang, P., and
628 An, Z. S.: Impacts of aerosol compositions on visibility impairment in Xi'an, China, *Atmos.*
629 *Environ.*, 59, 559-566, 2012.
- 630 Chen, H. H. and Grassian, V. H.: Iron Dissolution of Dust Source Materials during
631 Simulated Acidic Processing: The Effect of Sulfuric, Acetic, and Oxalic Acids, *Environ. Sci.*
632 *Tech.*, 47, 10312-10321, 2013.
- 633 Chen, Q. C., Hua, X. Y., Li, J. W., Chang, T., and Wang, Y. Q.: Diurnal evolutions and
634 sources of water-soluble chromophoric aerosols over Xi'an during haze event, in Northwest
635 China, *Sci. Total Environ.*, 786, 147412, 10.1016/j.scitotenv.2021.147412, 2021.
- 636 Chen, Y. and Siefert, R. L.: Seasonal and spatial distributions and dry deposition fluxes
637 of atmospheric total and labile iron over the tropical and subtropical North Atlantic Ocean, *J.*
638 *Geophys. Res.-Atmos*, 109, D09305, doi: 09310.01029/02003JD003958, 2004.
- 639 Chow, J. C., Watson, J. G., Kuhns, H., Etyemezian, V., Lowenthal, D. H., Crow, D., Kohl,
640 S. D., Engelbrecht, J. P., and Green, M. C.: Source profiles for industrial, mobile, and area
641 sources in the Big Bend Regional Aerosol Visibility and Observational study, *Chemosphere*,
642 54, 185-208, 2004.
- 643 Chuang, P. Y., Duvall, R. M., Shafer, M. M., and Schauer, J. J.: The origin of water soluble
644 particulate iron in the Asian atmospheric outflow, *Geophys. Res. Lett.*, 32, L07813, doi:
645 07810.01029/02004GL021946, 2005.

646 Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving
647 factors in Beijing, *Atmos. Chem. Phys.*, 19, 7939-7954, 2019.

648 Draxier, R. R. and Hess, G. D.: An overview of the HYSPLIT_4 modelling system for
649 trajectories, dispersion and deposition, *Aust. Meteorol. Mag.*, 47, 295-308, 1998.

650 Fang, T., Guo, H. Y., Zeng, L. H., Verma, V., Nenes, A., and Weber, R. J.: Highly Acidic
651 Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and
652 Aerosol Toxicity, *Environ. Sci. Technol.*, 51, 2611-2620, 2017.

653 Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient
654 thermodynamic equilibrium model for K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosols,
655 *Atmos. Chem. Phys.*, 7, 4639-4659, 2007.

656 Fu, H. B., Lin, J., Shang, G. F., Dong, W. B., Grassian, V. H., Carmichael, G. R., Li, Y.,
657 and Chen, J. M.: Solubility of Iron from Combustion Source Particles in Acidic Media Linked
658 to Iron Speciation, *Environ. Sci. Technol.*, 46, 11119-11127, 2012.

659 Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr, J. R., Carlton, A.
660 G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and
661 pH in the southeastern United States, *Atmos. Chem. Phys.*, 15, 5211-5228, 2015.

662 Hamilton, D. S., Scanza, R. A., Rathod, S. D., Bond, T. C., Kok, J. F., Li, L., Matsui, H.,
663 and Mahowald, N. M.: Recent (1980 to 2015) Trends and Variability in Daily-to-Interannual
664 Soluble Iron Deposition from Dust, Fire, and Anthropogenic Sources, *Geophys. Res. Lett.*, 47,
665 e2020GL089688, 2020.

666 He, X., Liu, P., Zhao, W., Xu, H., Zhang, R., and Shen, Z.: Size distribution of water-
667 soluble metals in atmospheric particles in Xi'an, China: Seasonal variations, bioavailability,
668 and health risk assessment, *Atmospheric Pollution Research*, 12, 101090,
669 <https://doi.org/10.1016/j.apr.2021.101090>, 2021.

670 Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical
671 evaluation of proxy methods used to estimate the acidity of atmospheric particles, *Atmos.*
672 *Chem. Phys.*, 15, 2775-2790, 2015.

673 Hsu, S.-C., Lin, F.-J., and Jeng, W.-L.: Seawater solubility of natural and anthropogenic
674 metals within ambient aerosols collected from Taiwan coastal sites, *Atmos. Environ.*, 39, 3989-
675 4001, 2005.

676 Huang, X., Song, Y., Zhao, C., Li, M., Zhu, T., Zhang, Q., and Zhang, X.: Pathways of
677 sulfate enhancement by natural and anthropogenic mineral aerosols in China, *J. Geophys. Res.-*
678 *Atmos.*, 119, 14165-14179, 2014.

679 Ito, A., Ye, Y., Baldo, C., and Shi, Z. B.: Ocean fertilization by pyrogenic aerosol iron,
680 *NPJ Clim. Atmos. Sci.*, 4, 30, doi: 10.1038/s41612-41021-00185-41618, 2021.

681 Ito, A., Myriokefalitakis, S., Kanakidou, M., Mahowald, N. M., Scanza, R. A., Hamilton,
682 D. S., Baker, A. R., Jickells, T., Sarin, M., Bikkina, S., Gao, Y., Shelley, R. U., Buck, C. S.,
683 Landing, W. M., Bowie, A. R., Perron, M. M. G., Guieu, C., Meskhidze, N., Johnson, M. S.,
684 Feng, Y., Kok, J. F., Nenes, A., and Duce, R. A.: Pyrogenic iron: The missing link to high iron
685 solubility in aerosols, *Science Adv.*, 5, eaau7671, doi: 7610.1126/sciadv.aau7671, 2019.

686 Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., Cao,
687 J. J., Boyd, P. W., Duce, R. A., Hunter, K. A., Kawahata, H., Kubilay, N., laRoche, J., Liss, P.
688 S., Mahowald, N., Prospero, J. M., Ridgwell, A. J., Tegen, I., and Torres, R.: Global Iron
689 Connections between Desert Dust, Ocean Biogeochemistry, and Climate, *Science*, 308, 67-71,
690 2005.

691 Journet, E., Balkanski, Y., and Harrison, S. P.: A New Data Set of Soil Mineralogy for
692 Dust-cycle Modeling, *Atmos. Chem. Phys.*, 14, 3801-3816, 2014.

693 Kawamura, K. and Bikkina, S.: A review of dicarboxylic acids and related compounds in
694 atmospheric aerosols: Molecular distributions, sources and transformation, *Atmos. Res.*, 170,
695 140-160, 2016.

696 Kelly, F. J.: Oxidative stress: Its role in air pollution and adverse health effects,
697 *Occupational and Environmental Medicine*, 60, 612-616, 2003.

698 Kumar, A., Sarin, M. M., and Srinivas, B.: Aerosol iron solubility over Bay of Bengal:
699 Role of anthropogenic sources and chemical processing, *Mar. Chem.*, 121, 167-175, 2010.

700 Lei, Y., Li, D., Lu, D., Zhang, T., Sun, J., Wang, X., Xu, H., and Shen, Z.: Insights into
701 the roles of aerosol soluble iron in secondary aerosol formation, *Atmos. Environ.*, 294, 119507,
702 <https://doi.org/10.1016/j.atmosenv.2022.119507>, 2023.

703 Li, R., Zhang, H. H., Wang, F., He, Y. T., Huang, C. P., Luo, L., Dong, S. W., Jia, X. H.,
704 and Tang, M. J.: Mass fractions, solubility, speciation and isotopic compositions of iron in coal
705 and municipal waste fly ash, *Sci. Total Environ.*, 838, 155974, 2022.

706 Li, R., Dong, S. W., Huang, C. P., Yu, F., Wang, F., Li, X. F., Zhang, H. H., Ren, Y., Guo,
707 M. X., Chen, Q. C., Ge, B. Z., and Tang, M. J.: Evaluating the effects of contact time and
708 leaching solution on measured solubilities of aerosol trace metals, *Appl. Geochem.*, 148,
709 105551, 2023.

710 Li, W. J., Xu, L., Liu, X. H., Zhang, J. C., Lin, Y. T., Yao, X. H., Gao, H. W., Zhang, D.
711 Z., Chen, J. M., Wang, W. X., Harrison, R. M., Zhang, X. Y., Shao, L. Y., Fu, P. Q., Nenes,
712 A., and Shi, Z. B.: Air pollution–aerosol interactions produce more bioavailable iron for ocean
713 ecosystems, *Science Adv.*, 3, e1601749, 2017.

714 Liu, L., Lin, Q., Liang, Z., Du, R., Zhang, G., Zhu, Y., Qi, B., Zhou, S., and Li, W.:
715 Variations in concentration and solubility of iron in atmospheric fine particles during the
716 COVID-19 pandemic: An example from China, *Gondwana Research*, 97, 138-144, 2021.

717 Liu, M. X., Matsui, H., Hamilton, D. S., Lamb, K. D., Rathod, S. D., Schwarz, J. P., and
718 Mahowald, N. M.: The underappreciated role of anthropogenic sources in atmospheric soluble
719 iron flux to the Southern Ocean, *Npj Climate and Atmospheric Science*, 5, 28, 10.1038/s41612-
720 022-00250-w, 2022.

721 Mahowald, N. M., Hamilton, D. S., Mackey, K. R. M., Moore, J. K., Baker, A. R., Scanza,
722 R. A., and Zhang, Y.: Aerosol trace metal leaching and impacts on marine microorganisms,
723 *Nature Comm.*, 9, 2614, 2018.

724 Martin, J. H.: Glacial-interglacial CO₂ change: the iron hypothesis, *Paleoceanography*, 5,
725 1-13, 1990.

726 Martin, L. R. and Good, T. W.: Catalyzed oxidation of sulfur dioxide in solution: The
727 iron-manganese synergism, *Atmos. Environ.*, 25A, 2395-2399, 1991.

728 McDaniel, M. F. M., Ingall, E. D., Morton, P. L., Castorina, E., Weber, R. J., Shelley, R.
729 U., Landing, W. M., Longo, A. F., Feng, Y., and Lai, B.: Relationship between Atmospheric
730 Aerosol Mineral Surface Area and Iron Solubility, *ACS Earth and Space Chem.*, 3, 2443-2451,
731 2019.

732 Meskhidze, N., Volker, C., Al-Abadleh, H. A., Barbeau, K., Bressac, M., Buck, C., Bundy,
733 R. M., Croot, P., Feng, Y., Ito, A., Johansen, A. M., Landing, W. M., Mao, J. Q.,
734 Myriokefalitakis, S., Ohnemus, D., Pasquier, B., and Ye, Y.: Perspective on identifying and
735 characterizing the processes controlling iron speciation and residence time at the atmosphere-
736 ocean interface, *Mar. Chem.*, 217, 103704, 2019.

737 Moore, C. M., Mills, M. M., Achterberg, E. P., Geider, R. J., LaRoche, J., Lucas, M. I.,
738 McDonagh, E. L., Pan, X., Poulton, A. J., Rijkenberg, M. J. A., Suggett, D. J., Ussher, S. J.,
739 and Woodward, E. M. S.: Large-scale distribution of Atlantic nitrogen fixation controlled by
740 iron availability, *Nature Geosci.*, 2, 867-871, 2009.

741 Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura,
742 K., Segers, A., and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-
743 D modeling study, *Atmos. Chem. Phys.*, 11, 5761-5782, 2011.

744 Myriokefalitakis, S., Ito, A., Kanakidou, M., Nenes, A., Krol, M. C., Mahowald, N. M.,
745 Scanza, R. A., Hamilton, D. S., Johnson, M. S., Meskhidze, N., Kok, J. F., Guieu, C., Baker,
746 A. R., Jickells, T. D., Sarin, M. M., Bikkina, S., Shelley, R., Bowie, A., Perron, M. M. G., and
747 Duce, R. A.: Reviews and syntheses: the GESAMP atmospheric iron deposition model
748 intercomparison study, *Biogeosciences*, 15, 6659-6684, 2018.

749 Oakes, M., Weber, R. J., Lai, B., Russell, A., and Ingall, E. D.: Characterization of iron
750 speciation in urban and rural single particles using XANES spectroscopy and micro X-ray
751 fluorescence measurements: investigating the relationship between speciation and fractional
752 iron solubility, *Atmos. Chem. Phys.*, 12, 745-756, 2012a.

753 Oakes, M., Ingall, E. D., Lai, B., Shafer, M. M., Hays, M. D., Liu, Z. G., Russell, A. G.,
754 and Weber, R. J.: Iron Solubility Related to Particle Sulfur Content in Source Emission and
755 Ambient Fine Particles, *Environ. Sci. Technol.*, 46, 6637-6644, 2012b.

756 Ooki, A., Nishioka, J., Ono, T., and Noriki, S.: Size dependence of iron solubility of Asian
757 mineral dust particles, *J. Geophys. Res.-Atmos.*, 114, D03202, doi:
758 10.1029/2008JD010804, 2009.

759 Paris, R. and Desboeufs, K. V.: Effect of atmospheric organic complexation on iron-
760 bearing dust solubility, *Atmos. Chem. Phys.*, 13, 4895-4905, 2013.

761 Paris, R., Desboeufs, K. V., and Journet, E.: Variability of dust iron solubility in
762 atmospheric waters: Investigation of the role of oxalate organic complexation, *Atmos. Environ.*,
763 45, 6510-6517, 2011.

764 Paris, R., Desboeufs, K. V., Formenti, P., Nava, S., and Chou, C.: Chemical
765 characterisation of iron in dust and biomass burning aerosols during AMMA-SOP0/DABEX:
766 implication for iron solubility, *Atmos. Chem. Phys.*, 10, 4273-4282, 2010.

767 Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett Jr,
768 J. L., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I. T.,
769 McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J. T., Wang, T., Weber,
770 R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles and clouds,
771 *Atmos. Chem. Phys.*, 20, 4809-4888, 2020.

772 Sakata, K., Kurisu, M., Takeichi, Y., Sakaguchi, A., Tanimoto, H., Tamenori, Y., Matsuki,
773 A., and Takahashi, Y.: Iron (Fe) speciation in size-fractionated aerosol particles in the Pacific
774 Ocean: The role of organic complexation of Fe with humic-like substances in controlling Fe
775 solubility, *Atmos. Chem. Phys.*, 22, 9461-9482, 2022.

776 Schroth, A. W., Crusius, J., Sholkovitz, E. R., and Bostick, B. C.: Iron solubility driven
777 by speciation in dust sources to the ocean, *Nature Geosci.*, 2, 337-340, 2009.

778 Sedwick, P. N., Sholkovitz, E. R., and Church, T. M.: Impact of anthropogenic
779 combustion emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso
780 Sea, *Geochim. Geophys. Geosyst.*, Q10Q06, DOI: 10.1029/2007GC001586, 2007.

781 Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution
782 to Climate Change* (Third edition), Wiley Interscience, New York 2016.

783 Shelley, R. U., Landing, W. M., Ussher, S. J., Planquette, H., and Sarthou, G.: Regional
784 trends in the fractional solubility of Fe and other metals from North Atlantic aerosols
785 (GEOTRACES cruises GA01 and GA03) following a two-stage leach, *Biogeosciences*, 15,
786 2271-2288, 2018.

787 Shi, J. H., Guan, Y., Ito, A., Gao, H. W., Yao, X. H., Baker, A. R., and Zhang, D. Z.: High
788 Production of Soluble Iron Promoted by Aerosol Acidification in Fog, *Geophys. Res. Lett.*, 47,
789 e2019GL086124, 10.1029/2019gl086124, 2020.

790 Shi, Z., Bonneville, S., Krom, M. D., Carslaw, K. S., Jickells, T. D., Baker, A. R., and
791 Benning, L. G.: Iron dissolution kinetics of mineral dust at low pH during simulated
792 atmospheric processing, *Atmos. Chem. Phys.*, 11, 995-1007, 2011a.

793 Shi, Z. B., Krom, M. D., Jickells, T. D., Bonneville, S., Carslaw, K. S., Mihalopoulos, N.,
794 Baker, A. R., and Benning, L. G.: Impacts on iron solubility in the mineral dust by processes
795 in the source region and the atmosphere: A review, *Aeolian Res.*, 5, 21-42, 2012.

796 Shi, Z. B., Woodhouse, M. T., Carslaw, K. S., Krom, M. D., Mann, G. W., Baker, A. R.,
797 Savov, I., Fones, G. R., Brooks, B., Drake, N., Jickells, T. D., and Benning, L. G.: Minor effect
798 of physical size sorting on iron solubility of transported mineral dust, *Atmos. Chem. Phys.*, 11,
799 8459-8469, 2011b.

800 Sholkovitz, E. R., Sedwick, P. N., and Church, T. M.: Influence of anthropogenic
801 combustion emissions on the deposition of soluble aerosol iron to the ocean: Empirical
802 estimates for island sites in the North Atlantic, *Geochim. Cosmochim. Acta*, 73, 3981-4003,
803 2009.

804 Sholkovitz, E. R., Sedwick, P. N., Church, T. M., Baker, A. R., and Powell, C. F.:
805 Fractional solubility of aerosol iron: Synthesis of a global-scale data set, *Geochim. Cosmochim.
806 Acta*, 89, 173-189, 2012.

807 Sun, J. X., Liu, L., Xu, L., Wang, Y. Y., Wu, Z. J., Hu, M., Shi, Z. B., Li, Y. J., Zhang, X.
808 Y., Chen, J. M., and Li, W. J.: Key Role of Nitrate in Phase Transitions of Urban Particles:
809 Implications of Important Reactive Surfaces for Secondary Aerosol Formation, *J. Geophys.*
810 *Res.-Atmos.*, 123, 1234-1243, 2018.

811 Tagliabue, A., Bowie, A. R., Boyd, P. W., Buck, K. N., Johnson, K. S., and Saito, M. A.:
812 The integral role of iron in ocean biogeochemistry, *Nature*, 543, 51-59, 2017.

813 Tang, W., Llorc, J., Weis, J., Perron, M. M. G., Basart, S., Li, Z., Sathyendranath, S.,
814 Jackson, T., Sanz Rodriguez, E., Proemse, B. C., Bowie, A. R., Schallenberg, C., Strutton, P.
815 G., Matear, R., and Cassar, N.: Widespread phytoplankton blooms triggered by 2019–2020
816 Australian wildfires, *Nature*, 597, 370-375, 2021.

817 Tao, Y. and Murphy, J. G.: The Mechanisms Responsible for the Interactions among
818 Oxalate, pH, and Fe Dissolution in PM_{2.5}, *ACS Earth and Space Chem.*, 3, 2259-2265, 2019.

819 Tao, Y., Moravek, A., Furlani, T. C., Power, C. E., VandenBoer, T. C., Chang, R. Y. W.,
820 Wiacek, A., and Young, C. J.: Acidity of Size-Resolved Sea-Salt Aerosol in a Coastal Urban
821 Area: Comparison of Existing and New Approaches, *ACS Earth and Space Chemistry*, 6, 1239-
822 1249, 2022.

823 Tian, H. Z., Wang, Y., Xue, Z. G., Cheng, K., Qu, Y. P., Chai, F. H., and Hao, J. M.:
824 Trend and characteristics of atmospheric emissions of Hg, As, and Se from coal combustion in
825 China, 1980–2007, *Atmos. Chem. Phys.*, 10, 11905-11919, 10.5194/acp-10-11905-2010, 2010.

826 Wang, Y., Salana, S., Yu, H., Puthussery, J. V., and Verma, V.: On the Relative
827 Contribution of Iron and Organic Compounds, and Their Interaction in Cellular Oxidative
828 Potential of Ambient PM_{2.5}, *Environmental Science & Technology Letters*, 9, 680-686, 2022.

829 Wang, Y. Q., Wang, M. M., Li, S. P., Sun, H. Y., Mu, Z., Zhang, L. X., Li, Y. G., and
830 Chen, Q. C.: Study on the oxidation potential of the water-soluble components of ambient
831 PM_{2.5} over Xi'an, China: Pollution levels, source apportionment and transport pathways,
832 *Environ. Int.*, 136, 105515, 10.1016/j.envint.2020.105515, 2020.

833 Wang, Z., Fu, H., Zhang, L., Song, W., and Chen, J.: Ligand-Promoted Photoreductive
834 Dissolution of Goethite by Atmospheric Low-Molecular Dicarboxylates, *J. Phys. Chem. A*,
835 121, 1647-1656, 2017.

836 Wang, Z., Li, R., Cui, L., Fu, H., Lin, J., and Chen, J.: Characterization and acid-
837 mobilization study for typical iron-bearing clay mineral, *J. Environ. Sci.*, 71, 222-232, 2018.

838 Winton, V. H. L., Bowie, A. R., Edwards, R., Keywood, M., Townsend, A. T., van der
839 Merwe, P., and Bollhofer, A.: Fractional iron solubility of atmospheric iron inputs to the
840 Southern Ocean, *Marine Chemistry*, 177, 20-32, 2015.

841 Wong, J. P. S., Yang, Y., Fang, T., Mulholland, J. A., Russell, A. G., Ebel, S., Nenes, A.,
842 and Weber, R. J.: Fine Particle Iron in Soils and Road Dust Is Modulated by Coal-Fired Power
843 Plant Sulfur, *Environ. Sci. Technol.*, 54, 7088-7096, 2020.

844 Yang, J., Ma, L., He, X., Au, W. C., Miao, Y., Wang, W. X., and Nah, T.: Measurement
845 report: Abundance and fractional solubilities of aerosol metals in urban Hong Kong – insights
846 into factors that control aerosol metal dissolution in an urban site in South China, *Atmos. Chem.*
847 *Phys.*, 23, 1403-1419, 2023.

848 Yang, T., Chen, Y., Zhou, S., Li, H., Wang, F., and Zhu, Y.: Solubilities and deposition
849 fluxes of atmospheric Fe and Cu over the Northwest Pacific and its marginal seas, *Atmos.*
850 *Environ.*, 239, 117763, 2020.

851 Yang, Y. and Weber, R. J.: Ultrafiltration to characterize PM_{2.5} water-soluble iron and
852 its sources in an urban environment, *Atmos. Environ.*, 286, 119246, 2022.

853 Young, A. H., Keene, W. C., Pszenny, A. A. P., Sander, R., Thornton, J. A., Riedel, T. P.,
854 and Maben, J. R.: Phase partitioning of soluble trace gases with size-resolved aerosols in near-
855 surface continental air over northern Colorado, USA, during winter, *J. Geophys. Res.-Atmos.*,
856 118, 9414-9427, 2013.

857 Zhang, G. H., Lin, Q. H., Peng, L., Yang, Y. X., Jiang, F., Liu, F. X., Song, W., Chen, D.
858 H., Cai, Z., Bi, X. H., Miller, M., Tang, M. J., Huang, W. L., Wang, X. M., Peng, P. A., and
859 Sheng, G. Y.: Oxalate Formation Enhanced by Fe-Containing Particles and Environmental
860 Implications, *Environ. Sci. Technol.*, 53, 1269-1277, 2019.

861 Zhang, H. H., Li, R., Dong, S. W., Wang, F., Zhu, Y. J., Meng, H., Huang, C. P., Ren, Y.,
862 Wang, X. F., Hu, X. D., Li, T. T., Peng, C., Zhang, G. H., Xue, L. K., Wang, X. M., and Tang,
863 M. J.: Abundance and Fractional Solubility of Aerosol Iron During Winter at a Coastal City in
864 Northern China: Similarities and Contrasts Between Fine and Coarse Particles, *J. Geophys.*
865 *Res.-Atmos.*, 127, e2021JD036070, 2022.

866 Zhang, R., Cao, J. J., Tang, Y. R., Arimoto, R., Shen, Z. X., Wu, F., Han, Y. M., Wang,
867 G. H., Zhang, J. Q., and Li, G. H.: Elemental profiles and signatures of fugitive dusts from
868 Chinese deserts, *Sci. Total Environ.*, 472, 1121-1129, 2014.

869 Zhang, Y. X., Schauer, J. J., Shafer, M. M., Hannigan, M. P., and Dutton, S. J.: Source
870 apportionment of in vitro reactive oxygen species bioassay activity from atmospheric
871 particulate matter, *Environ. Sci. Technol.*, 42, 7502-7509, 2008.

872 Zhou, M., Zheng, G., Wang, H., Qiao, L., Zhu, S., Huang, D., An, J., Lou, S., Tao, S.,
873 Wang, Q., Yan, R., Ma, Y., Chen, C., Cheng, Y., Su, H., and Huang, C.: Long-term trends and
874 drivers of aerosol pH in eastern China, *Atmos. Chem. Phys.*, 22, 13833-13844, 2022.

875 Zhu, Y., Li, W., Wang, Y., Zhang, J., Liu, L., Xu, L., Xu, J., Shi, J., Shao, L., Fu, P.,
876 Zhang, D., and Shi, Z.: Sources and processes of iron aerosols in a megacity in Eastern China,
877 *Atmos. Chem. Phys.*, 22, 2191-2202, 2022.

878 Zhu, Y. H., Li, W. J., Lin, Q. H., Yuan, Q., Liu, L., Zhang, J., Zhang, Y. X., Shao, L. Y.,
879 Niu, H. Y., Yang, S. S., and Shi, Z. B.: Iron solubility in fine particles associated with secondary
880 acidic aerosols in east China, *Environ. Pollut.*, 264, 114769, 2020.

881