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

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Abstract

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

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1 Introduction

Deposition of aerosol particles is a major external source of dissolved iron (Fe) in many open oceans (Boyd and Ellwood, 2010; Tagliabue et al., 2017), significantly affecting primary production in these regions (Moore et al., 2009; Tang et al., 2021) and thus the global carbon cycle (Martin, 1990; Jickells et al., 2005). Dissolved Fe has also been recognized as an important source of reactive oxygen species in aerosol particles (Zhang et al., 2008; Fang et al., 2017; Wang et al., 2022) and thus may have adverse impacts on human health (Kelly, 2003; Abbaspour et al., 2014). In addition, dissolved Fe could catalyze aqueous oxidation of SO_2 (Martin and Good, 1991; Alexander et al., 2009; Huang et al., 2014), leading to the formation of sulfate, a major secondary species in aerosol particles. The various impacts of aerosol Fe are largely determined by its fractional solubility (often abbreviated as solubility) which is the ratio of dissolved Fe to total Fe.

Due to the impacts of dissolved aerosol Fe on ocean biogeochemistry and human health, a number of studies have been conducted in the last 2-3 decades (Mahowald et al., 2018; Meskhidze et al., 2019; Baker et al., 2021; Ito et al., 2021), leading to significant advances in our knowledge of aerosol Fe solubility and sources of aerosol dissolved Fe. For examples, many studies (Baker and Jickells, 2006; Sholkovitz et al., 2012) observed the inverse relationship between Fe solubility and total aerosol Fe. It has been recently realized that non-desert-dust sources, such as anthropogenic emissions and biomass burning, can be an important source of dissolved aerosol Fe in many regions (Sholkovitz et al., 2009; Ito et al., 2019; Hamilton et al., 2020; Liu et al., 2022), though their contribution to total aerosol Fe is usually

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minor. Furthermore, atmospheric aging processes, such as acid processing and organic complexation, may substantially enhance solubility of Fe in desert dust and coal fly ash (Paris et al., 2011; Shi et al., 2012; Chen and Grassian, 2013; Li et al., 2017).

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

Sources, compositions and physicochemical properties are very different for coarse (>1 μm) and fine (<1 μm) particles (Seinfeld and Pandis, 2016). Therefore, aerosol Fe solubility may differ significantly and is regulated by different sources or processes for coarse and fine particles, as found by previous work (Sakata et al., 2022; Zhang et al., 2022). In addition, both sources and chemical processes of aerosol particles exhibit significant variability for different seasons, consequently leading to seasonal variations in aerosol Fe solubility. As a result, examining seasonal variability of aerosol Fe solubility may provide clues for and insights into factors which regulate Fe solubility. However, seasonal variation of Fe solubility has only been explored by a few previous studies (Chen and Siefert, 2004; Tao and Murphy, 2019; Yang et al., 2020; Yang and Weber, 2022). In the present work, we investigated seasonal variations of

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total Fe, dissolved Fe and Fe solubility for fine and coarse particles at Xi'an, a megacity in northwestern China severely affected by anthropogenic emission and desert dust (Cao and Cui, 2021).

2 Methodology

2.1 Sample collection

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

Sampling in winter took place at an urban site (34.23°N, 108.89°E) which is close to a busy major road and located in residential and commercial areas (Cao et al., 2012), and was carried out on a building roof (~10 m from the ground) in Institute of Earth Environment, Chinese Academy of Sciences. Sampling in the other three seasons took place at another urban site (34.37°N, 108.97°E) which is located in residential areas (Chen et al., 2021), and was carried out on a building roof (~40 m from the ground) in Shaanxi University of Science and Technology. Meteorological parameters (wind speed and direction, temperature, and relative humidity) and $PM_{2.5}$ and PM_{10} mass concentrations were provided by nearby environmental monitoring stations.

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

2.2 Sample processing and analysis

Sample analysis was detailed in our previous work (Zhang et al., 2022), and as a result here we only provide key information in brief. Every filter was equally cut into two halves. The first half filter, which was used to determine total Fe, was digested in a Teflon jar using microwave digestion; after residual acids used in digestion were evaporated, the Teflon jar was cooled to room temperature and then filled with 20 mL HNO_3 (1%). The solution was filtered using a PTFE membrane syringe filter (pore size: 0.22 μm), and then analyzed using inductively coupled plasma mass spectrometry (Thermo Fisher Scientific, USA). In total 14 elements were determined, including Fe, Al and Pb, and the recovery rates were found to be 90-110% for Fe.

The other half filter, which was used to determine dissolved Fe and soluble ions, was immersed in 20 mL ultrapure water for 2 h during which an orbital shaker (300 r/min) was used to stir the aqueous mixture. After that, the aqueous mixture was filtered using a PTFE

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membrane syringe filter (pore size: 0.22 μm) and then divided further to two parts. The first solution (~10 mL) was analyzed by ion chromatography to measure soluble anions and cations; the second solution (10 mL) was acidified to contain 1% HNO_3 (using 147 μL 67% HNO_3) and subsequently analyzed using inductively coupled plasma mass spectrometry.

2.3 Aerosol acidity calculation

The ISORROPIA-II model (Fountoukis and Nenes, 2007) was used in the "metastable + forward" mode to calculate aerosol pH for coarse and fine particles, and input data included concentrations of soluble anions (SO_4^{2-}, NO_3^- and Cl^-) and cations (NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}), temperature and relative humidity (RH). The effects of NH_3(g) and HNO_3(g) were not taken into account as their concentrations were not measured, and this may cause some biases (likely underestimation) in calculated aerosol pH (Guo et al., 2015; Hennigan et al., 2015; Pye et al., 2020).

2.4 Air mass back trajectory analysis

The Hysplit-4 model (Draxier and Hess, 1998) was employed to calculate 48-h air mass back trajectories, using meteorological data (horizontal resolution: 1°×1°; time resolution: 6 h) from Global Data Assimilation System provided by National Centers for Environmental Prediction. Back trajectories were determined with arrival height of 100 m above the ground level and arrival time of 08:00 every day (Wang et al., 2020). In total 120, 136, 128 and 144 back trajectories were obtained in our work for spring, summer, autumn and winter, and all the back trajectories were clustered using the cluster analysis method described elsewhere (Baker, 2010).

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3 Total and dissolved aerosol Fe

3.1 Meteorological conditions

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

Table S2 shows $PM_{2.5}$ and PM_{10} concentrations at Xi'an in four seasons. PM_{10} concentrations were in the range of 15-243, 24-76, 22-151 and 41-212 μg/m^3 in spring, summer, autumn and winter, and the average values were 93±6, 51±16, 70±35 and 107±39 μg/m^3, suggesting highest levels in spring and winter and lowest levels in summer. $PM_{2.5}$ mass concentrations were in the range of 11-62, 11-48, 13-97 and 13-156 μg/m^3, and the average values were 35±14, 23±8, 40±24 and 80±32 μg/m^3, suggesting highest concentrations in winter and lowest levels in summer.

$PM_{2.5}$ and PM_{10} concentrations were high in winter due to accumulation of anthropogenic pollution, and the median $PM_{2.5}/PM_{10}$ ratio was 0.76. PM_{10} concentrations in spring were significantly increased due to the impacts of desert dust aerosol, and the median $PM_{2.5}/PM_{10}$ ratio was only 0.44. Two major dust events occurred during our spring campaign (12-17 April

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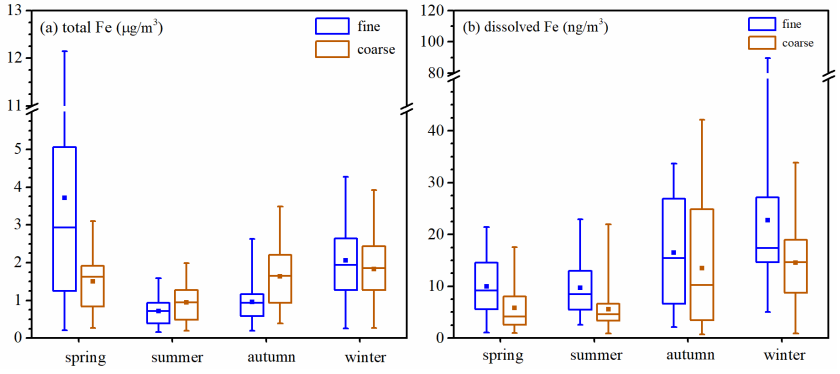
and 27-30 April). During the two dust events the average PM_{10} and $PM_{2.5}$ mass concentrations were 151±57 and 42±12 μg/m^3, and $PM_{2.5}/PM_{10}$ ratios became even lower (0.20-0.31). Furthermore, the median $PM_{2.5}/PM_{10}$ ratios were 0.44 in summer and 0.62 in autumn.

3.2 Total aerosol Fe

Figure 1a shows seasonal variation of total aerosol Fe in coarse and fine particles measured by our work at Xi'an. Total aerosol Fe concentrations were in the range of 270-3095, 191-1992, 395-3492 and 269-3924 ng/m^3 for coarse particles in spring, summer, autumn and winter, and the average values were 1504±800, 950±524, 1638±830 and 1831±866 ng/m^3 (Table A1); total aerosol Fe concentrations were in the range of 206-12144, 164-1591, 196-2631 and 257-4268 ng/m^3 for fine particles in spring, summer, autumn and winter, and the average values were 3717±3387, 721±366, 958±516 and 2058±1037 ng/m^3. Average total Fe concentrations were measured to be 798±466 and 801±534 ng/m^3 for coarse and fine particles in winter (November-December 2019) at Qingdao (Zhang et al., 2022), only 44% and 38% of the average values (1831±866 和 2058±1037 ng/m^3) found in winter (November-December 2020) at Xi'an by the present work.



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

189

190 The average contribution of coarse particles to total Fe in TSP (total suspended particles)
191 were 29%, 57%, 63% and 47% in spring, summer, autumn and winter. Statistical analysis
192 (paired t-test) suggested that compared to fine particles, total Fe in coarse particles was
193 significantly lower in spring ($p<0.01$, $\alpha=0.05$) while significantly higher in summer and autumn
194 ($p<0.01$, $\alpha=0.05$); in addition, there was no significant difference between coarse and fine
195 particles in winter ($p=0.13$, $\alpha=0.05$).

196 Compared to other seasons, total Fe in fine and coarse particles were both lowest in
197 summer (Figure 1a), as aerosol mass concentrations were also lowest in summer (Section 3.1).
198 Similarly, previous measurements on Huaniao Island in the East China Sea (Yang et al., 2020)
199 and over the tropical and subtropical North Atlantic (Chen and Siefert, 2004) also found lowest
200 total aerosol Fe levels in summer. For the other three seasons (spring, autumn and winter), total
201 Fe in coarse particles were rather similar, while total Fe in fine particles were highest in spring
202 and lowest in autumn. Overall, compared to summer and autumn, total aerosol Fe were higher
203 in spring and winter, as the two seasons were severely affected by desert dust and
204 anthropogenic emissions, respectively.

205 Total Fe was very well correlated with total Al ($0.87<r<0.96$, $p<0.01$) for both coarse
206 (Figure S3) and fine particles (Figure 2) in all the four seasons, suggesting desert dust always
207 as the dominant source of total aerosol Fe at Xi'an, regardless of particle size range and seasons.
208 The median [Fe]/[Al] values, mass ratios of total Fe to total Al, were 0.975, 0.926, 1.269 and

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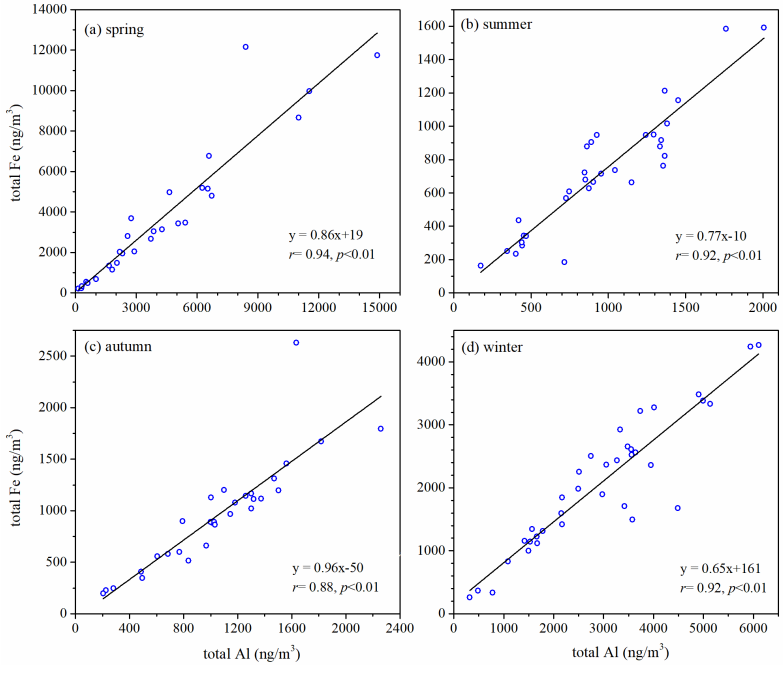
209 0.940 in spring, summer, autumn and winter for coarse particles, and 0.735, 0.796, 0.870 and
210 0.744 for fine particles (Figure S4). [Fe]/[Al] were found to be 0.911 and 0.741 for PM_{10} and
211 $PM_{2.5}$ generated using surface soil samples collected over several major deserts in China
212 (Zhang et al., 2014). We found that [Fe]/[Al] measured for coarse and fine particles at Xi'an
213 were similar to these reported for desert deust (Zhang et al., 2014); coarse particles in autumn
214 might be one exception (Figure S4), showing slightly higher [Fe]/[Al] (median: 1.269) than
215 desert dust.



216

217 **Figure 2.** Total Fe versus total Al for fine particles in different seasons: (a) spring; (b) summer;
218 (c) autumn; (d) winter.

219

220 **3.3 Dissolved aerosol Fe**

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Figure 1b shows seasonal variation of dissolved aerosol Fe in coarse and fine particles at Xi'an. Dissolved aerosol Fe concentrations were in the range of 1.0-17.5, 0.9-22.0, 0.7-42.2 and 0.9-33.8 ng/m^3 for coarse particles in spring, summer, autumn and winter, and the average values were 5.9±4.5, 5.6±4.0, 13.5±12.2 and 14.5±8.3 ng/m^3; dissolved aerosol Fe concentrations were in the range of 1.1-21.4, 2.6-22.9, 2.1-33.7 and 5.0-89.5 ng/m^3 for fine particles in spring, summer, autumn and winter, and the average values were 10.0±5.5, 9.7±5.6, 16.5±10.1 and 22.7±16.8 ng/m^3. Average dissolved Fe concentrations were measured to be 7.7±14.5 and 7.3±7.6 ng/m^3 for coarse and fine particles in winter at Qingdao (Zhang et al., 2022), only 53% and 32% of the average values (14.5±8.3 和 22.7±16.8 ng/m^3) found in winter at Xi'an by the present work.

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

Compared to spring and summer, dissolved Fe concentrations were higher in autumn and winter for coarse particles (Figure 1b); for fine particles, dissolved Fe concentrations were highest in winter, followed by autumn, and lowest in spring and summer. Dissolved Fe

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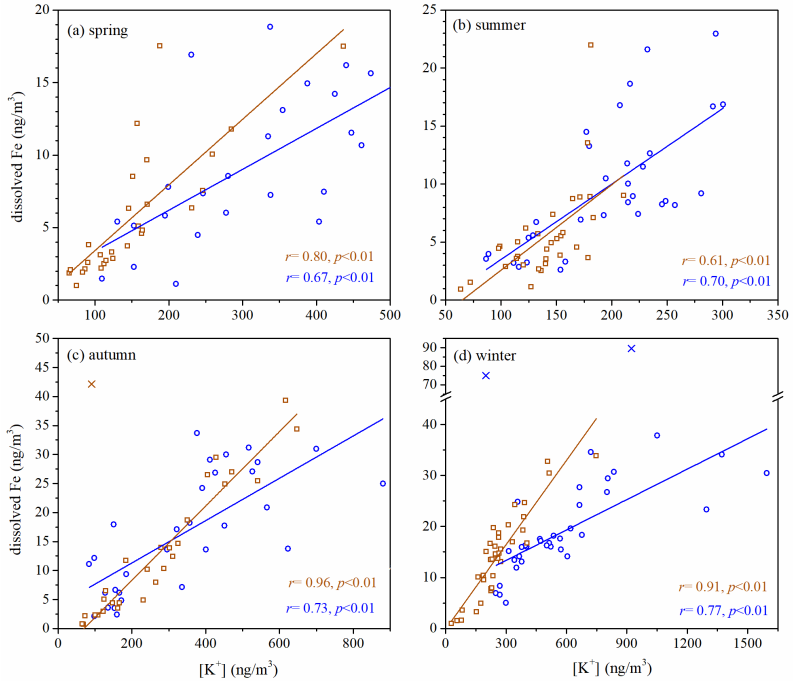
242 concentrations were low in summer, as total Fe concentrations were also low (Figure 1a). Total
243 Fe concentrations were high in spring (Figure 1a), but dissolved Fe concentrations were low;
244 this is because compared to other seasons, spring was most severely affected by desert dust
245 with low Fe solubility. Our previous study (Zhang et al., 2022) investigated aerosol Fe at
246 Qingdao in winter, and found that compared to clean days, dissolved Fe concentrations did not
247 change significantly during dust days though total Fe concentrations were remarkably
248 increased. Therefore, our previous (Zhang et al., 2022) and current work imply that the
249 occurrence of desert dust aerosol may not necessarily lead to increase in dissolved Fe
250 concentrations in the air.



251

252 **Figure 3.** Dissolved Fe versus [K^+] for fine and coarse particles in different seasons: (a) spring;
253 (b) summer; (c) autumn; (d) winter.

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As shown in Figure S5, overall the correlation between dissolved Fe and total Al was quite weak at Xi'an, indicating that desert dust may not contribute dominantly to dissolved aerosol Fe, although it was always the major source of total aerosol Fe (Section 3.2). We also examined correlations between dissolved Fe and several other species (Table S3). Figure 3 shows that dissolved Fe was well correlated with K^+ (a tracer for biomass burning) in coarse and fine particles at all the four seasons ($0.67<r<0.96$, $p<0.01$), and such correlation was better in autumn and winter than spring and summer. This may indicate biomass burning as an important source for dissolved aerosol Fe at Xi'an, especially in autumn and winter. Good correlation ($0.64<r<0.88$, $p<0.01$) was also found between dissolved Fe and total Pb for coarse and fine particles except summer (Figure S6), indicating that anthropogenic emission was an important source of dissolved aerosol Fe in spring, autumn and winter. The contribution of anthropogenic emission to dissolved aerosol Fe was small in summer, partly because effective emission reduction measures were implemented during July-September 2021 at Xi'an and surrounded regions, leading to large reduction in anthropogenic emissions.

4 Aerosol Fe solubility

4.1 Seasonal variation of Fe solubility

Figure 4 and Table A1 display aerosol Fe solubility at Xi'an in different seasons. Fe 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 particles in spring, summer, autumn and winter, and the median values were 0.38%, 0.51%, 0.62% and 0.79%; for fine particles, Fe solubility was in the range of 0.06-1.26%, 0.34-3.02%,

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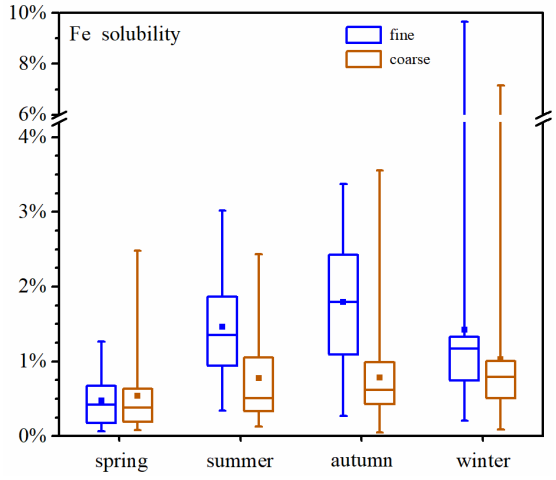
275 0.27-3.37% and 0.21-9.65% in spring, summer, autumn and winter, and the median values
276 were 0.42%, 1.35%, 1.79% and 1.17%.



277

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

279

280 No significant difference in Fe solubility was found between coarse and fine particles at
281 Xi'an in spring (paired *t*-test, p=0.17, α=0.05). In addition, the median values of Fe solubility
282 were both <0.5% for coarse and fine particles in spring, similar to desert dust (Schroth et al.,
283 2009; Shi et al., 2011b; Oakes et al., 2012b; Li et al., 2022), and this was because Xi'an was
284 frequently affected by desert dust aerosol in spring. In the other three seasons (summer, autumn
285 and winter), Fe solubility was significantly higher in fine particles than coarse particles (paired
286 *t*-test, p<0.01, α=0.05); furthermore, in these three seasons the median Fe solubility was >1%
287 for fine particles and >0.5% for coarse particles. For coarse particles, Fe solubility was highest
288 in winter and lowest in spring, while no significant difference was found between summer and
289 autumn (t-test, p=0.95, α=0.05); for fine particles, Fe solubility can be described by the

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following order: autumn > summer > winter > spring.

A number of field measurements (Hsu et al., 2005; Baker and Jickells, 2006; Sedwick et al., 2007; Kumar et al., 2010; Sholkovitz et al., 2012; Winton et al., 2015; Shelley et al., 2018; Yang et al., 2022) found inverse dependence of Fe solubility on total Fe (and Al). As shown in Figures 5 and S8, Fe solubility was also observed in our work to decrease with total Fe for coarse and fine particles in three seasons (spring, summer and winter), and such dependence can be fitted using Eq. (1):

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

where f_s(Fe) is Fe solubility and $[Fe]_T$ is total Fe concentration. As shown in Figures S9-S10, such inverse dependence was also observed between Fe solubility and total Al in these three seasons.

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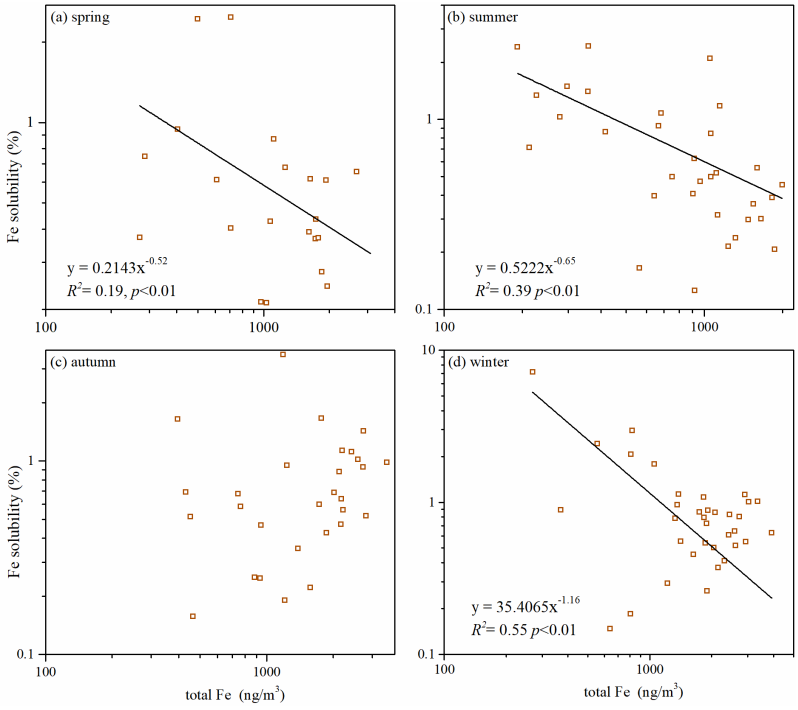

Figure 5. Fe solubility versus total Fe for coarse particles in different seasons: (a) spring; (b) summer; (c) autumn; (d) winter.

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

4.2 Influence of air mass sources on Fe solubility

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

319 In autumn (Figure 6e), air mass cluster C1 originated locally and C2 was transported from
320 desert regions in the north/northwest, and Fe solubility was much higher for C1 than C2 (Figure
321 6f). In winter (Figure 6g), air mass cluster C1 originated locally while C2, C3 and C4 originated
322 from desert regions in the north and northwest, and the transport distance increased from C2 to
323 C4; as shown in Figure 6h, Fe solubility followed the order C1 > C2 > C3 > C4, decreasing
324 with increase in transport distance. In contrast to other three seasons, no obvious dependence
325 of Fe solubility on air mass clusters was found in summer (Figure 6d).

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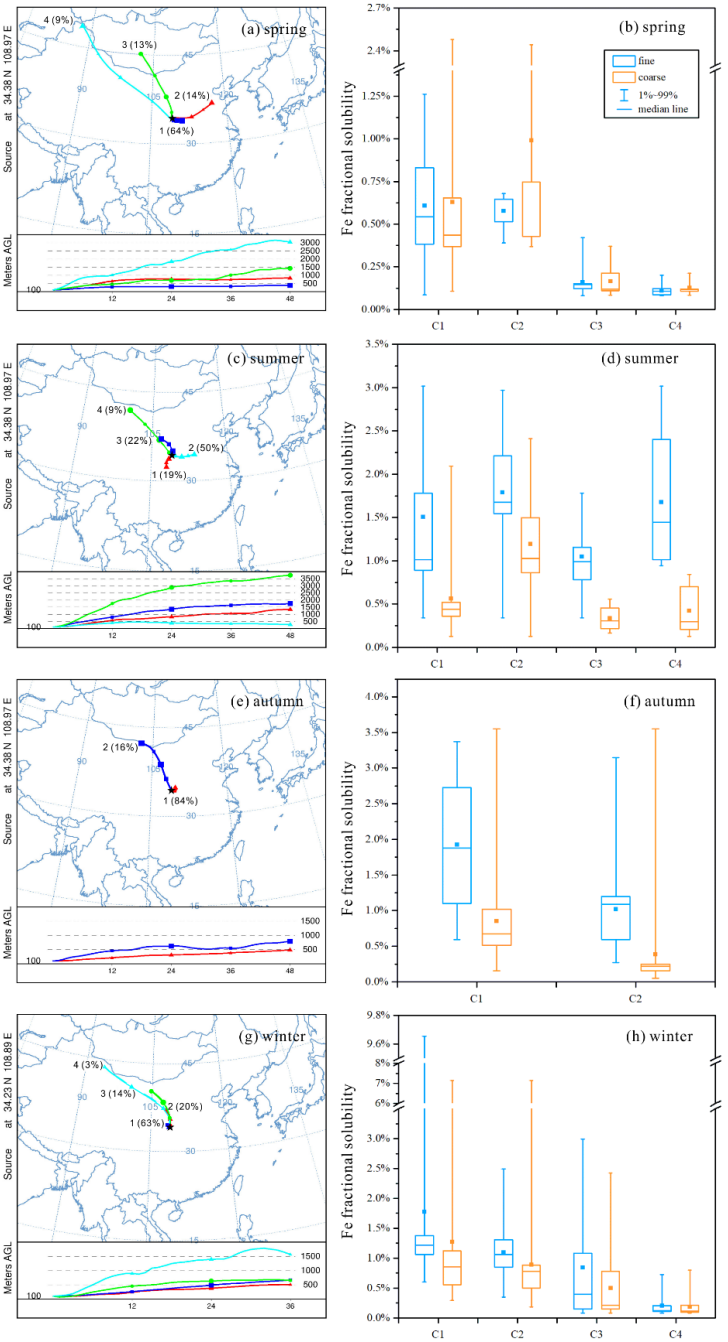

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Figure 6. The mean backward trajectory clusters obtained by HYSPLIT for (a) spring, (c) summer, (e) autumn, and (g) winter; Fe solubility in fine and coarse particles from different air mass clusters in (b) spring, (d) summer, (f) autumn, and (h) winter.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

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

4.3 Effects of chemical aging

Laboratory studies (Shi et al., 2011a; Chen and Grassian, 2013; Wang et al., 2018) suggested that chemical processing by acids, such as H_2SO_4 and HNO_3, could dissolve insoluble Fe and thus enhance aerosol Fe solubility. Some field studies found that aerosol Fe solubility was positively correlated with sulfate and/or nitrate (Shi et al., 2020; Zhu et al., 2020; Liu et al., 2021; Yang et al., 2022; Zhang et al., 2022), indicating enhancement of Fe solubility by atmospheric acid processing.

Figure 7 plots Fe solubility at Xi'an versus (2×[sulfate]+[nitrate])/[Fe] (in nmol/nmol,

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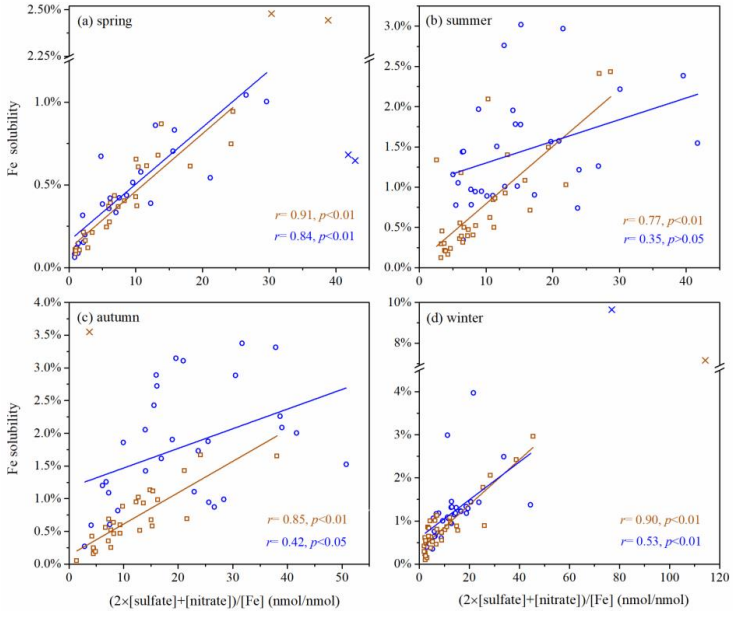
348 referred to as relative abundance of aerosol acidic species), the molar ratio of two major acidic
349 species to total Fe in aerosol particles. For coarse particles, aerosol Fe solubility was well
350 correlated with relative abundance of aerosol acidic species in all the four seasons (0.77 <*r*
351 <0.91, p<0.01). For fine particles, good correlation was found in spring (*r*=0.84, p<0.01),
352 moderate correlation was found in autumn and winter (0.42<*r*<0.53, p<0.01), and no
353 significant correlation was found in summer (*r*=0.35, p>0.05).



354

355 **Figure 7.** Fe solubility versus (2×[sulfate]+[nitrate])/[Fe] for fine and coarse particles in
356 different seasons: (a) spring; (b)summer; (c)autumn; (d)winter.

357

358 Overall, correlations between Fe solubility and relative abundance of aerosol acidic
359 species were always better for coarse particles than fine particles (Figure 7), indicating that
360 acid processing may be more important in Fe solubility enhancement for coarse particles, when

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compared to fine particles. A previous study (Zhang et al., 2022) also found that such correlation was better in coarse particles than fine particles in winter at Qingdao, a coastal city in northern China. Nevertheless, as discussed in Section 4.1, Fe solubility was higher in fine particles than coarse particles. This may imply that primary emission of non-desert-dust Fe (anthropogenic Fe) with higher solubility (Schroth et al., 2009; Oakes et al., 2012b) was more important for Fe solubility enhancement in fine particles than coarse particles.

It was suggested by laboratory studies (Chen and Grassian, 2013; Paris and Desboeufs, 2013; Wang et al., 2017) that atmospheric organic ligands, such as oxalate, could increase aerosol Fe solubility via ligand-promoted dissolution. Ass shown in Figure S11, our present work found that good correlation between Fe solubility with [oxalate]/[Fe] (in nmol/nmol) was found for coarse particles ($0.70<r<0.88$, $p<0.01$) and moderate correlation was found for fine particles ($0.40<r<0.67$, $p<0.01$) at Xi'an. Positive correlation between Fe solubility and oxalate was also observed previously at Atlanta, USA (Yang and Weber, 2022), Toronto, Canada (Tao et al., 2022) and Qingdao, China (Zhang et al., 2022).

We note that good correlation between Fe solubility and aerosol oxalate does not necessarily mean Fe solubility enhancement by Fe-oxalate complexation. For example, it was suggested that Fe could promote the formation of oxalate in aerosol particles (Tao and Murphy, 2019; Zhang et al., 2019), and thus good correlation between Fe solubility and oxalate could also imply enhanced formation of oxalate by dissolved Fe. In addition, similar to sulfate and nitrate, the major source of oxalate in the troposphere was secondary formation (Myriokefalitakis et al., 2011; Kawamura and Bikkina, 2016), and in this aspect good

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correlation between Fe solubility and relative abundance of oxalate could also indicate the importance of secondary formation of dissolved aerosol Fe.

5 Discussion: roles of RH and aerosol acidity

Figure 8 reveals the importance of RH in regulating aerosol Fe solubility. When RH was increased from <60% to 60-70%, significant increase in Fe solubility was observed for both coarse and fine particles. Sun et al. (2018) investigated hygroscopicity of aerosol particles collected in North China, and found that most particles examined started to become deliquesced when RH was increased to ~60%. The deliquescence RH reported for ambient aerosol particles (Sun et al., 2018) coincided roughly with the RH threshold at which large increase in aerosol Fe solubility was observed in our work. Previous studies (Shi et al., 2020; Zhu et al., 2020; Zhu et al., 2022) also highlighted that RH and thus aerosol liquid water could substantially affect Fe solubility. For examples, Zhu et al. (2020) measured Fe solubility at four cities in eastern China in December 2017, and found that Fe solubility at >50% RH was significantly larger than that at <50% RH.

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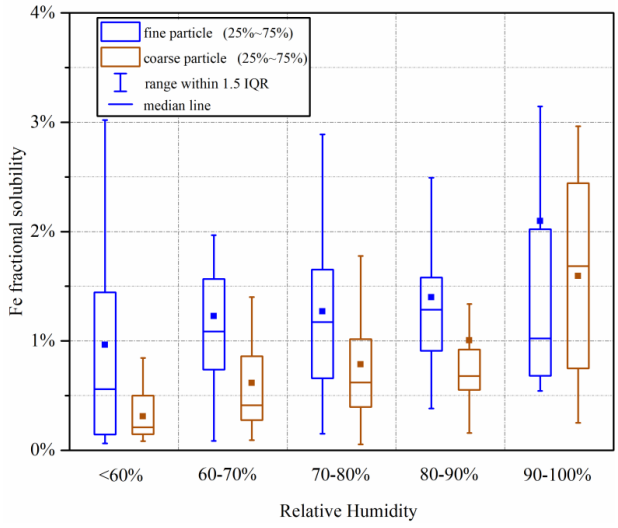

396

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

400

401 In addition, as shown in Figure 8, when RH was increased from 80-90% to >90%, median
402 Fe solubility was remarkably increased from 0.67% to 1.68% for coarse particles. Similar to
403 our work, Shi et al. (2020) also found that aerosol Fe solubility at Qingdao was significantly
404 increased under foggy weather when compared to other weather conditions. Both Shi et al.
405 (2020) and we suggested that high RH could promote Fe dissolution via acid processing.

406 We further examined the impact of aerosol acidity on Fe solubility, and the results are
407 displayed in Figure 9. For coarse particles, increase in pH did not lead to apparent change in
408 Fe solubility as long as aerosol pH was <5; however, Fe solubility was greatly decreased when
409 aerosol pH was increased to >5. For fine particles, Fe solubility continuously decreased with

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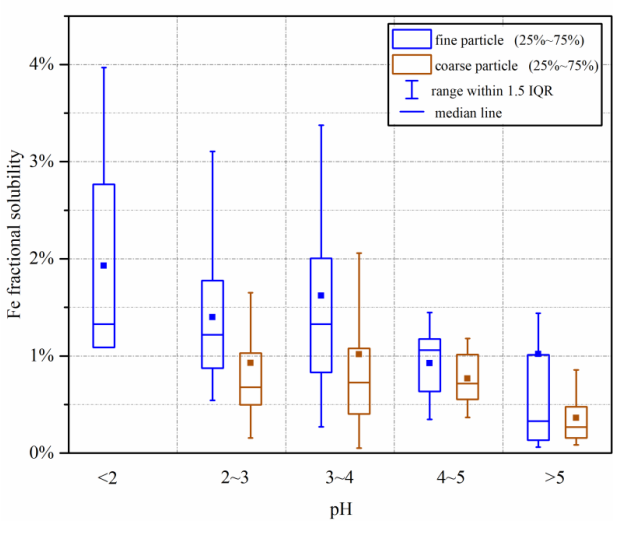
410 increasing aerosol pH (from <2 to >5). Previous work carried out at six Canadian sites (Tao
411 and Murphy, 2019) and Atlanta (Georgia, USA) (Wong et al., 2020; Yang and Weber, 2022)
412 also reported higher Fe solubility at lower aerosol pH. Similar to our previous work at Qingdao
413 in the winter (Zhang et al., 2022), our current study found that for coarse and fine particles at
414 Xi'an, aerosol pH was mostly <4 when Fe solubility exceeded 1% (Figure S12). It should be
415 pointed out that for some samples collected at Xi'an, Fe solubility could still be very low (<1%)
416 even when aerosol pH was low and RH was high (Figure S12). In addition, as shown in Figure 9,
417 at a given pH range Fe solubility was always higher in fine particles than coarse particles; this
418 may again imply that anthropogenic and pyrogenic Fe played a more important role in Fe
419 solubility enhancement in fine particles at Xi'an, when compared to coarse particles.



420

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

422

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At Xi'an, Fe solubility was higher in summer (median: 1.35%) and autumn (median: 1.79) than spring (median: 0.42) and winter (1.17%) for fine particles, and was also higher in summer (median: 0.51%) and autumn (0.62%) than spring (median: 0.79%). Meanwhile, our work found that aerosol pH values for both coarse and fine particles were lower (*t*-test, $p<0.01$, $\alpha=0.05$) in summer and autumn than spring and winter (Table S5 and Figure S13). As a result, lower aerosol pH (thus higher aerosol acidity) in summer and autumn may at least partly explain the observed higher Fe solubility in these two seasons. Our results were corroborated by a previous study (Yang and Weber, 2022) which found that compared to the cold season, higher Fe solubility was found at Atlanta (Georgia, USA) in the warm season when aerosol pH was lower.

6 Summary and conclusion

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

Dissolved Fe concentrations were higher in autumn and winter than spring and summer for coarse particles; for fine particles, dissolved Fe concentrations were highest in winter,

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444 followed by autumn, and lowest in spring and summer. Compared to other seasons, although
445 total Fe concentrations were evaluated in spring due to the impacts of desert dust, increase in
446 dissolved Fe levels was not observed. This may imply that the occurrence of desert dust aerosol
447 may not necessarily lead to increase in dissolved Fe concentrations, as also revealed in our
448 previous study (Zhang et al., 2022) carried out at a coastal city in northern China. Dissolved
449 Fe was significantly lower for coarse particles (compared to fine particles) in all the four
450 seasons, although total Fe in coarse particles were higher than or similar to fine particles in
451 three seasons (but not spring), implying higher Fe solubility in fine particles. Overall the
452 correlation between dissolved Fe and total Al was rather weak, suggesting that desert dust may
453 not contribute dominantly to dissolved Fe at Xi'an, although it was always the major source of
454 total Fe.

455 Highest Fe solubility was observed in winter for coarse particles and in autumn for fine
456 particles; meanwhile, lowest Fe solubility was observed in spring for both coarse and fine
457 particles, with median Fe solubility both below 0.5%. Compared to coarse particles, Fe
458 solubility was similar for fine particles in spring but significantly higher in the other three
459 seasons. Inverse dependence of Fe solubility on total Fe concentration, was observed for coarse
460 and fine particles in spring, summer and winter, while there was no such dependence for either
461 fine or coarse particles in autumn. Furthermore, aerosol Fe solubility was higher in air masses
462 originating from local and nearby regions than those arriving from desert regions after long-
463 distance transport in three seasons (spring, autumn and winter), while no apparent dependence
464 of Fe solubility on air mass origins was found in summer.

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Our work found better correlation between Fe solubility and relative abundance of aerosol acidic species for coarse particles than fine particles in all the four seasons, probably suggesting that acid processing was more important for Fe solubility enhancement in coarse particles. This may further mean that non-desert-dust Fe (e.g., anthropogenic and biomass burning Fe) was more important for Fe solubility enhancement in fine particles, since Fe solubility was higher in fine particles than coarse particles. We also found that overall Fe solubility increased with RH and acid acidity for coarse and fine particles, underscoring the importance of aerosol liquid water and aerosol acidity in enhancing Fe solubility via acid processing. Our work further found that at a given pH range aerosol Fe solubility was always higher in fine particles than coarse particles.

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Appendices

Table A1. Overview of total Fe (in ng/m^3), dissolved Fe (in ng/m^3) and Fe solubility (in %) for 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

Data availability.

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

Competing interests.

The authors declare that they have no conflict of interest.

Author contribution.

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

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