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## Comment on acp-2022-725

Anonymous Referee #3

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Referee comment on "Seasonal variation of aerosol iron solubility in coarse and fine particles at an inland city in northwestern China" by Huanhuan Zhang et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-725-RC3>, 2022

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### General comments

The study reports seasonal variation of total and dissolved Fe concentrations and fractional solubility in coarse and fine particles collected in Xi'an. More than 120 samples collected over a year are a valuable data set on Fe solubility in East Asia, which can contribute to a better understanding of the factors controlling Fe solubility. However, these valuable data sets were not fully utilized in the paper, as the discussion in this paper is mainly about averages (or medians) for concentrations and Fe solubility. There was no discussion of total and dissolved Fe or its solubility during the two Asian dust events, which have the potential to be important Fe supply events to the ocean surface. Furthermore, Fe solubility in some of the winter samples exceeded 5%, and the reasons for their high solubility should be mentioned. It would be desirable to discuss the daily variation of Fe concentration and Fe solubility in each season to solve these problems.

The importance of anthropogenic Fe on enhancement of Fe solubility in fine aerosol particles were reported by this study. However, the discussions on the emission sources of anthropogenic Fe and its tracer elements are a little bit broad. For instance, the dominant source of anthropogenic Fe in coarse and fine aerosol particles was biomass burning due to a good correlation between dissolved Fe and  $K^+$  concentrations. It is suspicious that  $K^+$  in coarse particles is from biomass burning because aerosols from high-temperature combustion, including biomass burning, are abundant in fine aerosol particles. As the authors said in the introduction, emission sources and physicochemical properties are different between coarse and fine aerosol particles. Therefore, discussions on the emission source of anthropogenic Fe and its tracer elements in each size fraction is required. I think that Table S3 is supported to evaluate the emission source of anthropogenic Fe.

The relationship between aerosol pH and iron solubility is the most important topic in this paper. Aerosol pH in coarse aerosol particles is usually 1 to 4 units higher than that in fine aerosol particles because non-volatile cation (e.g., Na, K, Mg, and Ca) is mainly present in coarse aerosol particles. However, the median aerosol pH in coarse aerosol particles was

almost the same or lower than those in fine aerosol particles. If the low pH of the coarse particles is due to a bias in the thermodynamic calculations, it may overestimate the importance of acidic processes in the coarse particles. Please explain the reason for lower pH in coarse aerosol particles than in fine aerosol particles.

I am also concerned that the Fe solubility reported by this study was much lower than those in aerosol particles collected in China by previous studies. High Fe solubility (>10%) has been observed in aerosol particles collected in China, including Xi'an, but such high Fe solubilities were not found in this study. It is necessary to explain why Fe solubility differs significantly from previous studies, even though the aerosols were collected in the same city. Since there are several concerns, I cannot recommend the publication of this study in ACP in its current state. However, this manuscript would represent a valuable contribution to the field of aerosol research after major revisions because there are few studies on seasonal variation of Fe solubility and its controlling factors.

### **Specific comments**

L81–83: Please provide specific examples of how seasonal variations of emission sources and chemical processes of Fe affect its solubility.

L95: Many readers are not familiar with Xi'an and its surrounding topography. Please provide a map showing the sampling site and the surrounding area.

L121: Please clarify acid compositions.

L124–126: How were recoveries of target elements determined? If you measure certificated reference material, please specify it.

L135–136: If gas species is not employed as an input parameter, the reverse mode would be the appropriate calculation method.

L161–163: I guess that the standard deviation of aerosol mass concentration in spring is too small for the concentration range of PM<sub>10</sub>. Please confirm it.

L182–186: Why were the Fe concentrations of aerosol particles collected in Xi'an higher than those collected in Qingdao? Is Qingdao classified as an industrial, residential, or background area?

L:185: There is a garbled text between  $1831 \pm 866$  and  $2058 \pm 1037$  ng/m<sup>3</sup>. The same garbled text was found in line 229.

L190–195: Iron in mineral dust is mainly present in coarse aerosol particles. Indeed, the contribution of aerosol mass concentration of coarse aerosol particles in spring and Asian dust events was larger than in other seasons due to the low PM<sub>2.5</sub>/PM<sub>10</sub> ratio. However, the contribution of Fe in coarse aerosol particles to total Fe in TSP was lower than in other seasons. This result is inconsistent with a mass ratio of PM<sub>5</sub>/PM<sub>10</sub>. Please explain the reason for the lowest contribution of Fe in coarse aerosol particles to that in spring samples. In addition, nss-Ca, Al, and Ti are good tracers of Asian dust. Are these elements in the aerosol collected in the spring also present mainly in the fine particles?

L199: Aerosol particles collected in North America and the Atlantic Ocean are unlikely appropriate comparison targets of Fe solubility in aerosol particles collected in China. I would suggest a comparison with dissolved iron in aerosols collected in Xi'an (e.g., He et al., 2021: <https://doi.org/10.1016/j.apr.2021.101090>, Lei et al., 2023: <https://doi.org/10.1016/j.atmosenv.2022.119507>).

L208: In general, [Fe]/[Al] means molar concentration ratio rather than mass concentration ratio. Please removed the bracket.

L258–261: Coal combustion is also a dominant source of K<sup>+</sup> in fine aerosol particles. Indeed, dissolved Fe concentration correlated with Pb as a tracer element of coal combustions. In addition, fuel oil (e.g., heavy oil, gasoline, and diesel) combustions emit dissolved Fe. Furthermore, the steel industry is the dominant source of anthropogenic Fe-oxides. A more detailed discussion of the emission sources of dissolved Fe in aerosol particles is needed.

L262–265: Please discuss in detail regarding emission sources of Pb and dissolved Fe in coarse and fine aerosol particles. Lead in fine aerosol particles is derived from high-temperature combustions (e.g., coal combustions and municipal solid waste incineration). In contrast, Pb in coarse aerosol particles is derived from the resuspension of road dust (e.g., the pigment of road paint). Therefore, emission sources of dissolved Fe are likely different between coarse and fine aerosol particles.

L305–306: Please explain why the inverse relationship between Fe solubility and total Fe in autumn samples could not be observed. In addition, it seems that the constant of a and the power of b in equation 1 has seasonal dependence. Please discuss the reason for the seasonal variation of the fitting equation.

L347–349: Why not evaluate the relationship of Fe solubility with nitrate and sulfate separately? Identifying the acid species that increase iron solubility is one of the important

topics.

L369: Ass rephrased by as.

L414–416: Please explain why Fe solubility was low (<1%) in some aerosol particles despite low pH and high RH. Also, were the aerosol samples with lower Fe solubility at low pH and high RH found in a particular season or in any season?

L416–419: Specific surface area is one of the factors controlling fractional Fe solubility in aerosol particles (Baker and Jickells, 2006; McDaniel et al., 2019). The specific surface area of fine aerosol particles is usually higher than that of coarse aerosol particles, indicating that fine aerosol particles are more reactive than coarse aerosol particles. Therefore, the fact that the Fe solubility of fine aerosol particles is higher than that of coarse aerosol particles does not guarantee that the contribution of anthropogenic Fe to Fe solubility is greater.

L425–429: Indeed, aerosol pH in spring was higher than those in autumn, but median temperature and RH were almost the same between spring and autumn. Therefore, temperature and RH are not the reason for the higher pH of spring than autumn. One possible reason for high aerosol pH in spring is the large abundance of CaCO<sub>3</sub> in Asian dust that acts as buffer species. Please discuss the seasonal variability of aerosol pH with accurate descriptions of the relationship of aerosol pH with temperature, RH, non-volatile cation concentration, etc.

L427: Please rephrase Table S5 by Table S4.

Figure 1: Does the solid line represent the median and the closed square the mean? Please provide legends for the median and average (as well as other box plots).

Figure 3: Several plots in panels (c) and (d) are shown with cross symbol. What does the cross symbol represent? Cross symbols can be found in Figures 7, S6 and S11.

Table S3. More detailed discussion on correlation of dissolved Fe concentration with trace elements are required to estimate anthropogenic Fe source. Are correlation coefficients higher than 0.5 listed in bold? If so, please specify that. Also, please bold the correlation coefficient for Pb in fine grains collected in winter.

Figure S7. This figure is not cited in the main text.

