Comments by referees are in blue.
Our replies are in black.
Changes to the manuscript are highlighted in red both here and in the revised manuscript.

Reply to referee #1

The manuscript investigated total Fe, dissolved Fe and Fe solubility for coarse (>1 μm) and fine (<1 μm) particles in four different seasons at Xi'an, China impacted by anthropogenic emissions and desert dust, combing with the relative humidity and aerosol pH. This work is very useful to realize the importance of RH and aerosol acidity in regulating Fe solubility in atmospheric particles. I would therefore consider the publication of this article once the authors have addressed the following comments.

Reply: We would like to thank Ref #1 for recommending our manuscript for final publication after minor revision. His/her comments, which have greatly helped us improve our manuscript, have been adequately addressed in the revised manuscript, as detailed below.

Major concerns:

I think in introduction there are wrong mentions. For example, the organic complexations in L. 74 are not analyzed in following results and discussions. The seasonal variation of Fe solubility, on another hand, has only been explored by a few previous studies as shown in the introduction. Again, you investigated seasonal variations of total Fe, dissolved Fe and Fe solubility in this article. So is it a repetitive work? Please go through the words logically.

Reply: In fact we discussed the correlation between Fe solubility and aerosol oxalate in the original manuscript (page 23-24). As a result, it is necessary to mention the effects of organic complexation on aerosol Fe solubility in the introduction.

As only a few studies examined seasonal variations of aerosol Fe solubility, our work which examines aerosol Fe solubility in Xi'an at different seasons is still novel, considering the importance of aerosol Fe solubility. In addition, compared to those previous studies, our work has further examined mechanisms which drive the observed seasonal variation. In the revised manuscript (page 5-6) we have added the following sentences to further explain what seasonal variation of aerosol Fe solubility can tell us: "For example, desert dust aerosol mainly occurs in spring at Xi'an where our present work was conducted, while anthropogenic emission become more important in winter (Cao and Cui, 2021); furthermore, higher temperature in summer causes more ammonium to partition in the gas phase and thus leads to higher aerosol acidity (Ding et al., 2019; Zhou et al., 2022)."

Combining with the Fig. 4, 8 and 9, as well as table A1, the aerosol Fe solubility in this field observation is lower than some previous studies based on field data on regions influenced by anthropogenic emission and pyrogenic iron source. Please give the reasons for the relative low Fe solubility in the article. If possible, the authors should cite more literatures and field data at sampling sites, summarizing in forms of table to show total Fe and Fe solubility in next revised manuscript.

Reply: As suggested by the referee, in the revised manuscript (page 21-22) we have included a new section (Section 4.1.2, and it two paragraphs) to compare our work with previous studies carried out in northern China.

It is true that our reported Fe solubility was much lower than those reported by some previous studied. As explained in Section 4.1.2 in the revised manuscript, it is because previous studies used sonication, larger filter pore size and/or stronger leaching solutions, leading to higher Fe solubility. For more details, please kindly refer to our revised manuscript (page 21-22).

Minor concerns:

49: "primary production" to "primary productions".

Reply: It has been corrected in the revised manuscript (page 4).

50: The authors need to clarify the chemical mechanisms as dissolved iron contributing to ROS formations in aerosols. It is not enough only listing the references. I think Fenton reaction is a good standpoint.

Reply: As suggested, in the revised manuscript (page 4) we have made the following change to clarify the mechanism for ROS formation: "…recognized as an important source of reactive oxygen species in aerosol particles via mechanisms such as the Fenton reaction…"

59: "a number of studies have been conducted in the last 2-3 decades." But authors only cite some references in recent years (2018 to 2021) and should replenish more studies in former years than 2010.

Reply: As suggested, in the revised manuscript we have cited a few important papers published before 2010.

66: "contribution" to "contributions".

Reply: It has been corrected in the revised manuscript (page 5).

74: Irrelevant statement in introduction. From view of this manuscript, the authors aim to study the effect of aerosol acidification on aerosol Fe solubility, rather than organic complexation, as yet it is not shown in entire paper. Please revise it.

Reply: In fact we discussed the correlation between Fe solubility and aerosol oxalate in the original manuscript (page 23-24). As a result, it is necessary to mention the effects of organic complexation on aerosol Fe solubility in the introduction.

112: "W41 filter used for aerosol sampling were acid-washed to reduce background levels." I am little confused by the acid-wash and you should explain the pretreatment. Or sampling cut-offs and sampler were acid-washed?

Reply: We applied acid-wash to our filters in order to reduce the background. As this was detailed in our previous work (Zhang et al., 2022), our current paper did not describe it in details. For better clarification, in the revised manuscript (page 7) we have changed the sentence to "W41 filters, which were used for aerosol sampling, were acid-washed to reduce background levels."

119, This sentence could be revised as "Each filter was equally halved."

Reply: As suggested, it has been corrected in the revised manuscript (page 7).

122, this again confusing. Why did the authors fill Teflon jar with 20 mL HNO3 after acid digestion? Whether the results were same if replacement with ultrapure waters?

Reply: After evaporation, we needed to dilute the residual in the Teflon jar to a given volume (20 mL in our work) for further ICP-MS analysis. We used 1% HNO_3 instead of ultrapure water because our standards used in ICP-MS analysis also contained 1% HNO_3; in addition, using HNO_3 (or other strong acids) will prevent re-precipitation of metals in the solutions.

Figure 3 and Figure 7: These plots missed the color legends labeling as the coarse or fine particles.

Reply: It is a good suggestion. As the two figures already contains many symbols, in the revised manuscript we have provided additional information in the figure captions: "Blue symbols represent fine particles and brown symbols represent coarse particles." Captions have also been updated for Figures in the supporting information.

369: Misspelling, please revise "Ass shown in Figure S11" to "As shown".

Reply: It has been corrected in the revised manuscript (page 26).

405: “Both Shi et al. (2020) and we suggested that high RH could promote Fe dissolution via acid processing.” Only relationship between RH and Fe fractional solubility is not persuasively in favour of it. If possible, the writer can add the soluble ion balance (I = 2[SO4] + [NO3]+ [Cl] − 2[Ca] − [NH4] − [Na] − 2[Mg] − [K]), a proxy of the acidification of the aerosol aqueous phase, in Fig. 8 to see if they correlate. When I >0, excess H+ is required in the associated aqueous phase to neutralize the excess anions.

Reply: The referee raised an interesting point. Indeed the relationship between RH and Fe solubility was not convincing enough, and this is exactly why we further discussed the dependence of Fe solubility on aerosol pH (calculated using ISORROPIA) in the next two paragraph (line 406-432 in the original manuscript). In response to this comment, in the revised manuscript we have deleted “via acid processing” as the effects of acid processing were specifically discussed in the next two paragraphs.

As it is widely believed that aerosol pH calculated using ISORROPIA, when compared to ion balance, can better represent aerosol acidity, in our work we have chosen to use aerosol pH instead of ion balance.

426: Did the lower aerosol pH exist in summer and autumn? Several studies have shown the formations of secondary inorganic aerosols during heavy haze episodes frequently in winter dominate the higher aerosol acidity in cities, so is conflicting with your findings? Can you give an interpretation for it?

Reply: Many studies (e.g., Tao and Murphy, 2019; Yang and Weber, 2022; Zhou et al., 2022) found lower aerosol pH in warm seasons (summer and autumn), as higher temperatures favors NH_3/NH_4^+ to partitioning into gas phase and thus leads to higher aerosol acidity (lower aerosol pH). Many studies discussed haze formation during winter when temperature variations are much smaller than those observed for different seasons; during haze formation aerosol sulfate and nitrate were usually increased a lot, leading to higher aerosol acidity. Therefore, lower aerosol pH in summer and autumn (compared to spring and winter) does not conflict with lower aerosol pH during haze events in winter (compared to non-haze periods); in fact, the two aerosol pH variations occurred at different timescales.

Furthermore, we have revised the last paragraph in the revised manuscript (page 31) to further discuss seasonal variation of aerosol acidity, and the referee is kindly referred to our revised manuscript for further information.

429: “the observed higher Fe solubility in summer and autumn” at L. 429 is completely contrary to the wordings at L. 443-444 as “dissolved Fe concentrations were lowest in spring and summer”. Please revise this.

Reply: The two statements are not contrary in fact, because Fe solubility is not equivalent to dissolved Fe, which also depend on total Fe. Although Fe solubility was high in summer, total Fe was lowest in summer; therefore, dissolved Fe was low in summer. Please refer to Figures 1 and 4 in our original manuscript for more information.

References:

Tao, Y. and Murphy, J. G.: The Mechanisms Responsible for the Interactions among Oxalate, pH, and Fe Dissolution in PM2.5, ACS Earth and Space Chem., 3, 2259-2265, 2019.

Yang, Y. and Weber, R. J.: Ultrafiltration to characterize PM2.5 water-soluble iron and its sources in an urban environment, Atmos. Environ., 286, 119246, 2022.

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