

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 #2

This study by Zhang et al., investigated the seasonal variation of aerosol Fe solubility for coarse and fine particles at Xi'an. Overall, the manuscript is well organized and the results are clearly presented with comprehensive discussion. The topic of this study is of great interest in the community. The results of this study are interesting and important for the understanding the role of Fe in atmosphere, especially for the biogeochemical cycle of Fe. I am very pleased to recommend this manuscript for publication after a minor revision. My comments are shown as below.

Reply: We would like to thank Ref #2 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.

Line 140: Gaseous compounds were not considered when calculating aerosol acidity. Clarify if this will affect the trend of aerosol acidity. This is important for the discussion on aerosol acidity. Generally, omission of gaseous compounds will lead systematically underestimation of pH (over estimation of acidity). I believe that the trend of aerosol acidity would not be affected significantly; therefore, the discussion on aerosol acidity is still valid. But a clarification is needed here.

Reply: It is true that our calculation may underestimate aerosol pH (as we stated in our original manuscript), and as the referee pointed out, the general trend would not be significantly affected. In the revised manuscript (page 8), we have added one sentence to clarify it: "...this may cause some biases (likely underestimation) in calculated aerosol pH (Guo et al., 2015; Hennigan et al., 2015; Pye et al., 2020), but the overall trend of aerosol pH would not be significantly affected."

Line 146: If the arrival time is 8 am of each day, the number of trajectories should be same as the samples. But the number of trajectories is much more than that of samples. Please verify the accuracy of the description.

Reply: In fact we have four back trajectories for each day. In the revised manuscript (page 9) we have revised this sentence to provide accurate description: "Back trajectories were determined with arrival height of 100 m above the ground level and arrival time of 08:00, 14:00, 20:00 and 02:00 on the next day (Wang et al., 2020), and every day four back trajectories were obtained."

It is stated that "...suggesting desert dust always as the dominant source of total aerosol Fe at Xi'an, regardless of particle size range and seasons." (Line 206-207). But in line 202-204, the authors also mentioned anthropogenic emissions as an important factor. The authors need to clarify how they are consistent.

Reply: The statement in our original manuscript (line 202-204) was not accurate and appeared to be inconsistent with the statement in line 206-207. In the revised manuscript (page 13), it has been changed to "Overall, compared to summer and autumn, total aerosol Fe were higher in spring and winter when higher aerosol mass concentrations were also observed (Figure S3)."

Line 229-230: Authors indicated that dissolved Fe concentration in winter for Xi'an is higher than that for Qingdao. It may be resulted from the differences of total Fe concentrations in the two cities. Authors can add one sentence here to make an explanation.

Reply: The referee is right. As discussed in the original manuscript (Section 3.2), total Fe concentrations were much higher in Xi'an than Qingdao for both coarse and fine particles. In response to this comment, in the revised manuscript (page 15) we have added one sentence to

explain why dissolved Fe concentration in winter for Xi'an is higher than that for Qingdao: "... and one major reason is that total Fe concentrations were significantly higher at Xi'an than Qingdao"

Line 255-268: When investigating the source of soluble Fe, the authors talked about the correlation of soluble Fe with elements like K⁺, Pb and Al, which is valid. However, the authors started the discussion from K⁺ without any justifications. The correlation with all elements has been actually listed in Table S3. I suggest the authors to have an overall description of the correlation with all elements before mentioned K⁺ (with the highest correlation).

Line 261-262: Any literature to support that biomass burning emission is important for autumn and winter in Xi'an?

Line 264: "anthropogenic emission" is a vague description. Please specify it or list some possible anthropogenic sources.

Reply: The three comments list above are all related to sources of dissolved aerosol Fe, and thus are replied here together.

As suggested by ref#2, in the revised manuscript (page 16-17) we have discussed correlations between dissolved Fe and several aerosol species (including but not limited to K⁺) to further use the information provided in Table S3. After revision, we have gained further insights into important sources for dissolved aerosol Fe, including secondary formation, biomass burning, as well as vehicle emission, coal combustion, steel industry and metal smelting. Please refer to the last two paragraphs (page 16-17) in Section 3.3 for more details.

Section 4.1: Authors may need to compare the Fe solubilities in winter between Qingdao and Xi'an, as the comparisons for total and dissolved Fe between these two cities.

Reply: It is a good point. In Section 4.1.2 of the revised manuscript (page 21-22), we have compared wintertime results between Qingdao and Xi'an, and briefly discussed the possible reasons for the difference.

Line 308-310: This sentence does not provide sufficient information. To my understanding, the reverse relationship actually reflects the different source (or affecting factor) of total Fe and water-soluble Fe. The authors can try to explain the mechanism or just state that the mechanism needs to be further investigated.

Reply: In fact several mechanisms could possibly explain such inverse relationship, as discussed in a few review papers (Mahowald et al., 2018; Meskhidze et al., 2019). It may not be necessary in our manuscript to repeat these explanations. Instead, in the revised manuscript (page 19) we have added two references from which interested authors can find more information: "Several mechanisms can qualitatively explain such inverse dependence, but a consensus has not been reached yet (Mahowald et al., 2018; Meskhidze et al., 2019)."

Line 383: I am not sure if the description of "Secondary formation of dissolved aerosol Fe" is accurate. I understand that secondary process may promote the dissolve of Fe but this description may be misleading.

Reply: In our work we use primary sources to represent dissolved Fe associated with un-processed mineral dust and anthropogenic particles, and secondary source to represent dissolved Fe which is formed via dissolution of insoluble Fe by chemical aging. To increase clarity, in the revised manuscript (page 28) we have made the following modification: "...indicate the importance of secondary formation of dissolved aerosol Fe (i.e. dissolution of insoluble Fe to dissolved Fe via aging processes)."

Line 409-410: Authors stated that Fe solubility continuously decreased with increasing aerosol pH (from <2 to >5) for fine particles, this trend is generally right. But if we see Figure 9,

Fe solubility slightly increased with pH from <3 to >3 for fine particles, so please make your description be more conservative.

Reply: The referee is right. The word “continuously” is not accurate. In order to make our statement more accurate, in the revised manuscript (page 30) we have changed this sentence to “For fine particles, Fe solubility in general decreased with increasing aerosol pH (from <2 to >5)”.

Authors indicated that desert dust was not the main source of dissolved Fe, and chemical aging showed a small impact on Fe solubility for fine particles. It may imply that anthropogenic emission is the dominant source of dissolved Fe in fine particles. Authors can add some sentences in section 6 to illustrate it and make your conclusions be more specific.

Reply: We would like to thank ref #2 for his/her kind suggestion. We have thought about making this conclusion more specific and stronger. However, as we do not have direct or quantitative results, we would like to be conservative at this point and thus no change has been made.

Some other minor issues as listed below:

1) The title of section 3.1 may be more suitable with “Meteorological conditions and particulate matter concentrations” since particulate matter concentrations are also discussed in this section.

Reply: As suggested, the title has been changed to “Meteorological conditions and aerosol concentrations” in the revised manuscript (page 9).

2) Line 109: Please delete the second word of “and” in “Coarse (>1 μm) and fine (<1 μm) and aerosol particles”.

Reply: The redundant “and” has been deleted in the revised manuscript.

3) Line 110: Specify the time is am or pm.

Reply: The time has been specified in the revised manuscript (page 7): “...from 08:00 am to 07:30 am next day...”

4) Line 124: Specify the model of the ICP-MS and the MDL.

Reply: In the revised manuscript (page 8) more information has been provided for the ICP-MS we used: “...using inductively coupled plasma mass spectrometry (iCAP Q, Thermo Fisher Scientific, USA).”

5) Line 144: Verify the time resolution is 3 or 6 hours.

Reply: The time resolution is actually 3 h, and in the revised manuscript (page 9) we have corrected it.

6) Line 185 and line 229: Please replace the Chinese character in parentheses with “and”.

Reply: These two errors have been corrected in the revised manuscript (page 11 and page 15).

7) Line 213: Correct the typo “deust”.

Reply: This typo has been corrected in the revised manuscript (page 13).

8) Line 356: Space should be added between the parentheses and word.

Reply: The suggested corrections have been implemented in the revised manuscript.

9) Line 405: Change “we” to “the current study”.

Reply: As suggested, in the revised manuscript (page 29) this sentence has been changed to: “Therefore, both Shi et al. (2020) and our present work suggested that...”

10) Line 425: The values of Fe solubility for coarse particles in parentheses were wrong. Please follow Table A1 and revise them.

Reply: We have carefully checked all the numbers in parentheses in this paragraph, and made necessary corrections in the revised manuscript (page 31).