

Responses to the reviewer comments on

“Sources and processes of iron aerosols in a megacity of Eastern China” by Zhu et al.

The authors would like to thank both reviewers for their constructive and good suggestions to improve our manuscript. We have carefully considered all the review comments and revised the manuscript. Below, we provide responses to the comments in **blue**, with changes made in the manuscript highlighted in **red**.

Response to Reviewer 2:

This paper deals with the Fe aerosol particles reactivity in an urban environment, according to variable weather conditions. I would like to commend the authors for their work: it is a very relevant study, dealing with an essential issue in Fe atmospheric chemistry for four main reasons: Soluble Fe plays an important role in many environmental processes, including in ocean biogeochemistry and thereby the global carbon cycle; Fe-bearing particles may have adverse health effects; Anthropogenic Fe particles have been the subject of increased interest in recent years due to their significant solubility; Very few atmospheric Fe solubilities inferred from urban field studies have been reported in the literature. I cannot however recommend the publication of this study in a high ranked journal as Atmospheric Chemistry and Physics in its present form. Please find below some suggestions, as an attempt to improve the manuscript before resubmission.

Response: We appreciate the reviewer for the helpful comments and suggestions. Below we address the comments and have revised the manuscript accordingly. For clarity, the reviewer’s comments are listed below in *black italics*, while our responses and changes in manuscript are shown in **blue** and **red**, respectively.

1. Section 3.1 (Pollution Levels): This section only gives an overview of the air pollution in the study area, without the results being directly related to the rest of the study, i.e. the evolution of the solubility of particulate iron as a function of the ambient meteorological conditions. I therefore suggest that the authors place the

detailed discussion of the results of this section in the "Supplementary Information" section and keep only a summary in the main body of the text.

Response: We have moved descriptions about SO₂, NO₂, inorganic ions and elements to the Supplemental Information, and the changed Section 3.1 are as follows:

The average PM_{2.5} concentration was the highest at $98.3 \pm 20.6 \mu\text{g m}^{-3}$ in haze days, followed by $59.3 \pm 11.1 \mu\text{g m}^{-3}$ in dust days, $57.5 \pm 26.9 \mu\text{g m}^{-3}$ in fog days, $33.6 \pm 14.5 \mu\text{g m}^{-3}$ in clear days, and $31.4 \pm 8.1 \mu\text{g m}^{-3}$ in rain days (Fig. S2). About 100%, 29%, and 8% of PM_{2.5} concentrations in haze, fog, and dust days were higher than the Grade II national PM_{2.5} standard of $75 \mu\text{g m}^{-3}$ (24 h average standard, GB 3095-2012, China), respectively. However, all of PM_{2.5} concentrations in clear and rain days were lower than the PM_{2.5} Grade II standard. PM_{2.5} concentrations differed significantly according to weather conditions ($p < 0.01$, independent sample T test, Table S4).

The concentrations of SO₂, NO₂, all detected inorganic ions and elements also differed significantly according to weather conditions (Table S4). The concentration order of SO₂ or NO₂ in different weather conditions was haze > fog > dust > clear > rain days (Fig. S2). However, the concentration orders of all detected inorganic ions and elements were fog > haze > dust > rain > clear days and dust > clear > fog > haze > rain days, respectively. Detailed descriptions of SO₂, NO₂, all detected inorganic ions and elements were given in Supplemental Information.

(Page 7, Line 184-195)

2. Section 3.2 (Fe content and solubility): *At the end of this section the authors compare their results (PM_{2.5}) with those of Shi et al. (2020) for TSP and state that it is not surprising that the solubilities reported in the present study are consistently higher than those reported by Shi et al. This statement seems premature to me because, to my knowledge, Shi et al. do not provide any indication of what the coarse fraction of the aerosol (> 2.5 microns) in their samples represents. In my opinion, the end of section 3.2 should be deleted as it does not add anything to the authors' statements.*

Response: We agree. We deleted the comparison with Shi et al. (2020).

3. Section 4. Summary and atmospheric implications: *It is surprising that the authors*

can state that the majority of the iron particles observed in TEM-EDS contain, in addition to sulfates, nitrate ions, because nitrogen is extremely difficult to detect in individual analysis by this technique, unless a cryogenic system is available. Moreover, no nitrogen signal is visible on the spectra of Figure 4. What is the basis for the authors' assertion that iron is associated with nitrates in the collected aerosol?

Response: It is true that N peak is very low or hard to be seen in Figure 4. Our previous individual particle analyses, including cryogenic TEM, have clearly shown that individual particles in urban air more or less contain sulfate, nitrate and secondary organic matter (Li et al., 2016). This has been confirmed in single particle mass spectrometry studies (Whiteaker et al., 2002). We have added corresponding sentences in the manuscript as follows:

It should be noted that individual secondary sulfate particle in urban air normally contain nitrate, which has been confirmed in single particle mass spectrometry studies (Whiteaker et al., 2002; Li et al., 2016).

(Page 12, Line 361-363)

References:

Li, W., Sun, J., Xu, L., Shi, Z., Riemer, N., Sun, Y., Fu, P., Zhang, J., Lin, Y., and Wang, X.: A conceptual framework for mixing structures in individual aerosol particles, *J. Geophys. Res. Atmos.*, 121, 13784-13798, <https://doi.org/10.1002/2016JD025252>, 2016.

Whiteaker, J. R., Suess, D. T., and Prather, K. A.: Effects of Meteorological Conditions on Aerosol Composition and Mixing State in Bakersfield, CA, *Environ. Sci. Technol.*, 36, 2345-2353, <https://doi.org/10.1021/es011381z>, 2002.

4. Section 2.2: Sample collection: When collecting aerosol samples during rain or fog days, there is a risk that the surface of the filter will be washed away and that leaching of the particles will occur. Thus the soluble fraction of the aerosol will be carried into the air pumping system. What precautions do the authors take to avoid this leaching?

Response: Particulate matter (PM) samplers are designed to be water proof, so no water will get into the samplers to wet the filters even under heavy rain and storm.

Moreover, we collected PM samples with a PM_{2.5} sampling head, rather than a total suspended particulate (TSP) inlet. A majority of cloud and fog droplets are larger than 2.5 μm, so they are not collected into our samplers. It is possible that some tiny fog / cloud droplets have been collected, but the large surface area and small mass of particles mean that such fog or cloud droplets will not cause the “leaching” as mentioned by the reviewer. This is further confirmed in the visual inspection of the filters after sampling. Therefore, we are highly confident that the “leaching” effect does not exist in our samples.

5. Section 3.3.2: Atmospheric acidification processing, lines 293-294: The authors state that the fact that a significant proportion of dissolved iron is associated with secondary sources is evidence of the important contribution of atmospheric processing to soluble iron production. I am absolutely convinced of the importance of atmospheric processes in the production of soluble iron. However, examination of Figure 3 indicates that industrial type 2 sources contribute equally to soluble iron production regardless of weather conditions (38.9 to 42.6%, except for dusty days). This demonstrates to me that the chemical composition of particulate matter emitted by industry is as important as atmospheric processes in the production of soluble iron. I would therefore suggest that the authors be careful when they insist on the influence of atmospheric processes in the production of soluble iron.

Response: We appreciate your comments. We checked and re-calculated PMF results, and found that industrial emissions were still the largest contributor to dissolved Fe. The revised Figure 3 is as follows:

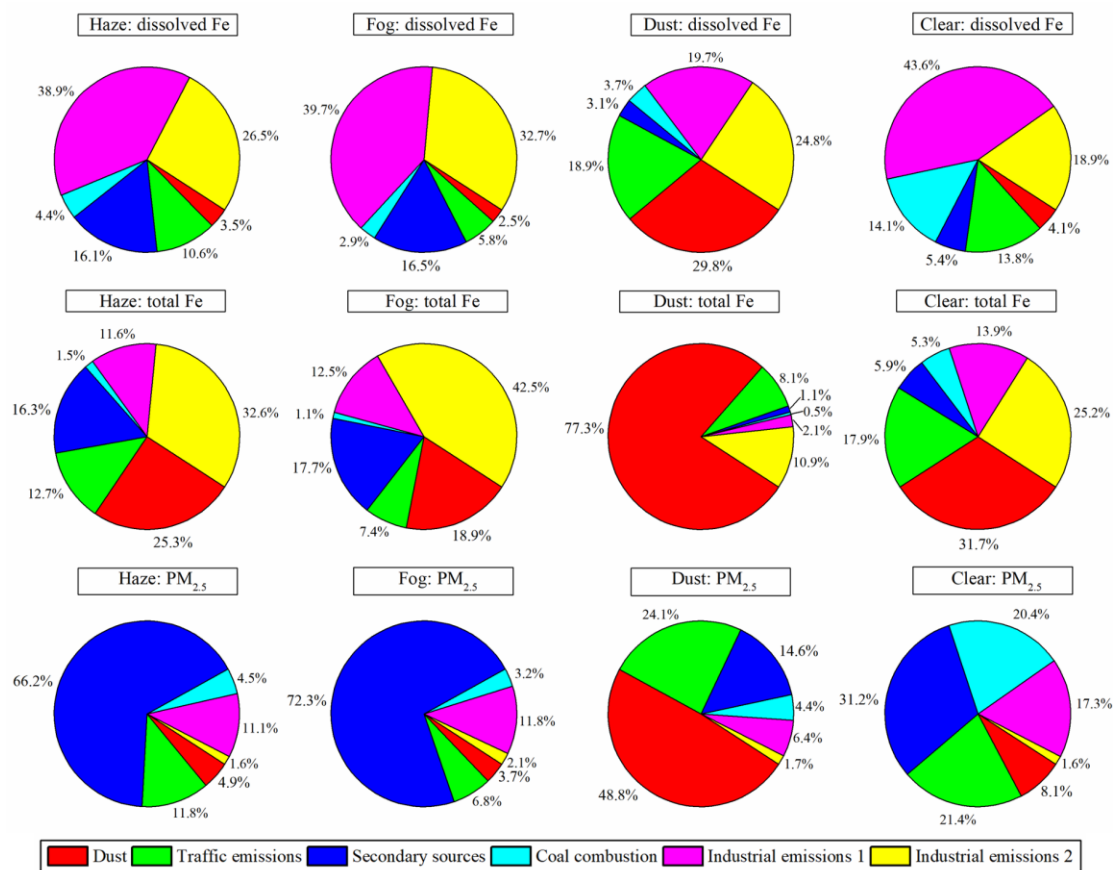


Figure 3. Contributions of identified sources to dissolved Fe, total Fe, and PM_{2.5} in haze, fog, dust, and clear days by PMF model.

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We added discussions about the large contributions of industrial emissions 1 & 2 and the relatively low contributions of secondary sources to dissolved Fe in the manuscript as follows:

Figure 3 also shows that although industrial emissions (factor 5&6 or industrial emissions 1 + industrial emissions 2) contributed less than 20% to PM_{2.5} in haze, fog, dust, and clear days, they were the largest contributor to dissolved Fe in haze (65.4%), fog (72.4%), dust (44.5%), and clear (62.5%) days, and they also were the largest contributor to total Fe in haze (44.2%), fog (55.0%), and clear (39.1%) days except dust days. Industrial emissions 1 (factor 5) contributed similarly to dissolved Fe regardless of weather conditions (38.9% to 43.6%, except for dusty days), while it only contributed 11.6% to 13.9% to total Fe (except dusty days). Heavy oil

combustion related aerosols have the highest Fe solubility (up to 78%) from all major Fe aerosol sources (Schroth et al., 2009; Ito et al., 2021). This may explain the much larger contribution of industrial emissions 1 to dissolved Fe than total Fe. As far as we know, there is no published data on Fe solubility in particulate matter from metal industrial emissions. Considering the dominance of iron and steel plants in total Fe emissions (Rathod et al., 2020) and the low Fe solubility in smelter ash from a steel plant (Li et al., 2017), it is difficult to understand why industrial emissions 2 (factor 6) contributes so much to dissolved Fe. Furthermore, PMF results indicated that secondary sources were the largest contributor to PM_{2.5} in haze (66.2%), fog (72.3%), and clear (31.2%) days except dust days. However, the contribution of secondary sources to dissolved Fe was relatively low: 16.1% in haze days, 16.5% in fog days, 3.1% in dust days, and 5.4% in clear days.

The likely reason for the high contribution of industrial emissions 2 and the relatively low contribution of secondary sources to dissolved Fe is that PMF is unable to completely separate secondary sources of dissolved Fe (i.e., dissolved from insoluble Fe due to atmospheric processing) from primary sources. This means that some of dissolved Fe due to atmospheric processing may still be assigned to its primary factors if there is a strong co-variation between dissolved Fe and primary tracers. This suggests that the contribution of secondary sources to dissolved Fe is likely higher than that indicated by the PMF. It should also be noted that industrial emissions are outside the city and thus particles from these sources undergo long-range transport before reaching the sampling site. This provides more time for chemical processing in the atmosphere, leading to Fe solubilisation.

(Page 11, Line 325-347)