

More particular comments include:

In general, this is an interesting paper and is well written and well organized. The data presented in this paper are extremely difficult to obtain and are useful to understand the Fe speciation and mineralogy of particles in the atmospheric aerosol particles.

There are some problems in the manuscript, which need to be clarified. Particularly, the results are based on single samples in particular season and at particular site but the authors have tried to discuss the spatial and seasonal trends. This is questionable because there is no evidence that such as a single sample could be representative of the whole season or a single site. Also, the uncertainties associated with the limited number of particles analyzed should be addressed in the paper (see more detailed comments below).

The authors thank the reviewer for his/her constructive comments. One particular issue raised by the reviewer is inferring spatial and seasonal trends with a limited number of samples. The authors agree that no strong conclusions can be drawn about spatial and seasonal variability in this study and have addressed this concern by modifying text in section 3.4. A more detailed response by the authors is shown in comment 20.

In addition, the uncertainties associated with the limited sample size are addressed in the manuscript. The authors have added text and error bars in figure 6 and table 2 that demonstrate the uncertainty associated with single particle analysis. The authors have attempted to better qualify the conclusions throughout the manuscript based on these uncertainties. More detailed responses to this issue can be seen in comments 14, 20, 31, and 32.

More particular comments include:

1) Abstract: solubility needs to be defined. It is not clear in the abstract and the paper that where the authors want to mention solubility (in a geochemical sense, which is a thermodynamic parameter) or where fractional solubility. For example, in line 19, what does this solubility refer to? They need to be consistent throughout the paper and the abstract and should be defined the first time it appears.

The reviewer brings up an important issue in the paper. Solubility refers to fractional iron solubility, which is the fraction of total iron aerosol that is water-soluble (e.g. soluble iron/total iron). Text was modified in the abstract and throughout the manuscript to clarify fractional iron solubility.

2. Page 22772, Line 12: What “elemental analyses” with what methodology?

In this study, elemental analysis refers to single particle elemental data (Al to Fe) collected by micro X-ray fluorescence measurements. Various molar ratios (e.g. Fe/Al

and Si/Al) of the elemental data were used to provide insight into iron speciation. Text was added to the abstract (Page 2, Line 30-31) to clarify this point.

3. Abstract, last sentence: Is this the key point of this paper? If it is, it needs to be strengthened in the paper. A direct comparison of the abundance (should be number abundance by the way) of Al-Fe oxides and Fe-aluminosilicates was only mentioned briefly at the end of a paragraph in 22785. Figure 6 and table 2 showed some data about the Fe(II)/total Fe but not the number abundance. Also, a large part of paper is discussing about Fe(II)/total Fe (for example, Fig. 2) rather than focusing on the key point (i.e., the last sentence). It is suggested that a figure or a table is added to the paper (or add further data on particle abundance in table 2) for a more direct comparison of the Fe-particle abundance with fractional Fe solubility.

While the reviewer highlights an important point, the mineralogy of several particles was difficult to determine as mentioned by the reviewer in comment 29 and as shown in figure 5 in the manuscript (particles with low Fe, Al, and Si molar concentrations). Therefore, quantifying the abundance of iron phases at different sites was uncertain to some extent. However, in this study, we were able to establish a difference between the mineralogy observed at Fire Station 8 (Al-substituted Fe-oxides) and Fort Yargo summer (processed Fe-aluminosilicates) samples based on elemental analyses (Fe, Si, and Al molar ratios) and XANES spectra. Since the mineralogy observed here did not follow any trends with fractional iron solubility, the authors concluded that fractional iron solubility depended on factors other than iron mineralogy.

Text has been added throughout the results and discussion section (Page 18, Line 357-58 and Page 20, Line 402-405) to address the reviewer's comments.

4. Page 22773, Line 14-16: There is probably some misunderstanding here. It does not seem to be right to say that “there are ample evidence. . .”. Meskhidze et al. (2005) is a modelling study not a laboratory or field study. Shi et al. (2009) is a laboratory and field study but they did not suggest that in-cloud processing has a positive relationship with fractional Fe solubility. They found Fe nanoparticles in the natural clouds, which indirectly suggested that dust had been acid processed before being deposited in the rain.

5. Page 22773, line 17: Baker and Jickells (2006) did not observe an inverse relation between size and fractional solubility. What they have showed is that fractional Fe solubility increases with decreasing dust mass concentration (which is likely accompanied by decreasing average sizes).

In comments 4 and 5, the reviewer highlights a few misrepresentations of previous studies (Meskhidze et. al. (2005), Shi et. al., (2009), and Baker and Jickells (2006)). The authors added text to the introduction (Page 4, Line 62-64 and Page 5, Line 67-76) to clarify this point.

6. Page 22774: line 5: “association to” should be “association with”?

Text was changed on Page 6, Line 97.

7. Use either “iron” or “Fe” throughout the paper. Do not mix them.

The authors have changed text throughout the manuscript to maintain consistency in nomenclature.

8. Page 22775, line 1: “Fe particles” should be “Fe-containing” particles. It is very unlikely that a natural particle is composed of Fe only.

The reviewer makes a valid point. Fe-containing particles instead of Fe particles was used throughout the manuscript.

9. Page 22777, line 5: Define “NBS”

Text was changed in Section 2.2 to define NBS.

10. Figure 4: were the spectra of standard minerals taken under the same condition and same time of the XANES analyses of natural aerosol samples? Are they similar or the same to the spectra in literature?

The XANES spectra of standard minerals were collected on the same beamline (2-ID-D) under similar conditions as the ambient samples. The spectra of iron minerals in this study compared reasonably well to archived XANES and EXAFS spectra published by Marcus et. al. (2008). The only observed difference between our spectra and archived spectra was the pre-edge centroid position, which is dependent upon beamline calibration and XANES sampling conditions. However, the shift in pre-edge centroid position for Fe(II) and Fe(III) minerals observed in this study compares well to the shift observed in other studies which have extensively explored iron minerals using XANES and EXAFS.

Text was added to the manuscript in the Section 2.3 (Page 11, Line 211-216) to address the reviewer's point

Marcus, M.A., Westphal, A.J. and Fakra, S.C.: Classification of Fe-bearing species from k-edge xanes data using two parameter correlation plots. Journal of Synchrotron Radiation. 15, 463-468, 2008.

11. Page 22778, line 15: “Fe solubility of the filter samples” cannot be measured by ferrozine. The ferrozine method could only give the soluble Fe concentration, but not the Fe solubility of a sample.

Text was modified in Section 2.4 (Page 12, Line 233) to correct this inaccuracy.

12. Page 22778, section 2.4: what is the detection limit of the method for soluble Fe?

What is the accuracy? What is the lowest soluble Fe concentration in the aerosol sample leach?

The method limit of detection (LOD) and lowest soluble iron concentration in the sample leach are well below typical ambient soluble iron concentrations observed in urban areas (~0.11 ng m⁻³ (LOD) and < 1 ng m⁻³ for average soluble iron in sample leach). Text was added to Section 2.4 to provide more detail on the soluble iron analysis.

13. Page 22779, line 12, end of paragraph: here it is necessary to mention how the fractional Fe solubility is calculated and how the total Fe is measured.

Text was moved from the Results and Discussion section to the Methods section (Section 2.4) to describe the approach used to measure total iron concentration and its corresponding uncertainties.

14. Page 22779-22780 and table 2: here the authors showed the total Fe was measured by microscopic X-ray fluorescence. The total Fe data were then compared with literature data. This is a very awkward way of validating the data because it does not provide evidence of the accuracy of the measurements. For example, total Fe ranges by more than an order of magnitude in the Southeastern US, so your total in a particular sample falls in this range does not mean your data are accurate. Obviously, the best option was to analyze total Fe using XRF or ICP-MS/ICP-AES. However, it seems that such analyses had not been done on the filter. If the samples are still available, the best way is to analyze them directly. Otherwise, the uncertainty should be addressed.

The authors have mentioned in line 16 of page 22779 that scans were made for 1- 4 maps per filter. This gave some indications of the variability or uncertainty of the total Fe measurement, which is shown in Table 2. Since a large part of the paper is dependent on the results in the fractional Fe solubility, it is necessary that such uncertainty is mentioned clearly in the paper and the calculated ranges (or at least standard deviation) of fractional Fe solubility should be plotted in Figure 6 as well.

We agree that ICP-MS and ICP-AES are more appropriate (e.g. more robust, less uncertain) than micro XRF techniques for quantifying total iron in aerosols. Though it would be nice to have both micro XRF and ICP-MS/ICP-AES total iron measurements to reduce uncertainty and compare techniques, this data is simply not available. However, for the purpose of our study, the uncertainty associated with total iron measurements (determined from micro XRF) does not appear to affect the trends observed in fractional iron solubility (as seen in table 2 and figure 6), thus, the findings in this manuscript. Therefore, this technique is sufficient for this study.

In order to accurately represent the uncertainty in total iron measurements and fractional iron solubility, text was added to the Section 2.4 and Section 3.5.

15. Page 22780, line 4-5: this is a methodology and should have been mentioned in Section 2. See comment 13.

Refer to the author's response in comment 13.

16. Page 22782, line 5: What does “reduced particles” mean? Please clarify.

Reduced (Fe(II)) and oxidized (Fe(III)) Fe-containing particles were identified on these samples based on the pre-edge centroid position of XANES spectra. Here, “reduced particles” refers to iron-containing particles with pre-edge centroid positions in the Fe(II) standard range (as shown in figure S2). Text was added to Section 3.2 (Page 17, Line 330-331) to clarify this point.

17. Figure 4: can the authors give some explanations why there are substantially amount Fe(II) in the so-called Fe oxides particles in this study?

Text was added to Section 3.2 (Page 17, Line 346-48) to explain the presence in Fe(II) in Fe-oxide like particles.

18. Page 22783, line 11-12: What “enhanced levels of silicon and aluminium” mean? It is necessary to give some values. Otherwise, readers would not know how you have classified these particles into different groups.

Text was modified in Section 3.3 (Page 18, 373-374) to define “enhanced levels of silicon and aluminum”.

19. Page 22783, line 17-19: Where are the examples of the spectra? Please refer to a figure in the paper. If the authors are referring to Fig. 4b, then the reviewer is unable to find any similarities of the iron-containing aluminosilicates (natural aerosol particle) and standard Fe oxides (maybe this is because I am not an expert of XANES analyses?). If this is true, then the discussion on the Fe oxides as the surface oxidation products of aluminosilicate is not justified.

The authors acknowledge that this text may lead to confusion. In this study, two different trends were identified in iron-containing particles based on elemental analyses (e.g. molar ratios), suggesting the presence of two iron phases. The second phase described in the manuscript was characterized by particles (26 out of 221) with a Si/Al molar ratio of 1.4, which is commonly observed in iron-containing aluminosilicate minerals. While the Si/Al molar ratio indicated that these particles were iron-containing aluminosilicates, the majority of XANES spectra (24 out of 26) resembled a typical iron oxide mineral, as shown by Sample 1 in figure 4. Therefore, these particles were identified as processed Fe-aluminosilicates.

Text was changed in Section 3.3 (Page 19, Line 378-384) to clarify this point.

20. Section 3.4: The data in this paper cannot provide enough evidence to discuss about the spatial and seasonal trends. The reviewer is not even sure the authors could conclude that “whether there are significant variations in the Fe speciation in the aerosols collected during different time and at different sites”. See major concerns above.

The reviewer’s suggestions are correct. The sample size is not large enough to draw strong conclusions on spatial and seasonal variations in iron phases. However, the purpose of this section is to show that variations in iron phases exist at different urban and rural sites. These variations in iron phases (Al-substituted Fe-oxides vs. Fe-aluminosilicates) allow us to investigate the relationship between fractional iron solubility and mineralogy in this study.

Section 3.4 was renamed to Iron Mineralogy at Different Sites, and text was modified in this section to reflect the reviewer’s concerns.

21. Page 22784, line 7: Is “78

Text was modified on Page 20, Line 401.

22. Page 22784, line 16: why Fe solubility ranges 4.3 to 5.8 ng/m³? It should not have a unit.

Text was modified on Page 20, Line 413.

23. Page 22784, line 22-25: How could 1-6

The authors could not find the error the reviewer highlights.

24. Page 22784, line 12: “data were collected. . .”? This sentence needs re-written.

The sentence was re-written on Page 20, Line 409.

25. Section 3.6: This section is less convincing and not immediately relevant to the results of this paper. The reviewer, if was the author, would simply remove this section.

While the reviewer provides an interesting suggestion, we think the content of this section is relevant to the aerosol research community interested in human health effects. Since many recent studies have linked redox active metals in urban aerosols to human health (by ROS formation) and have identified iron as a significant contributor to ROS formation (Shafer et. al., 2010; Zhang et. al. 2008), we argue that a brief discussion on how our unique iron data may relate to human health is relevant. Therefore, we have left this section in the revised draft.

Shafer, M.M., Perkins, D.A., Antkiewicz, D.S., Stone, E.A., Quiraishi, T.A. and Schauer, J.J.: Reactive oxygen species activity and chemical speciation of size-fractionated atmospheric particulate matter from lahore, pakistan: An important role for transition metals. Journal of Environmental Monitoring. 12, 704-415, 2010.

Zhang, Y., Schauer, J., Shafer, M.M., Hannigan, M.P. and Dutton, S.J.: Source apportionment of in vitro reactive oxygen species bioassay activity from atmospheric particulate matter. Environ. Sci. Technol. 42, 7502-7509, 2008.

26. Page 22788, line 1: "size" is not mentioned in the main text. It is important to know the size and the mineralogy and therefore such information should be presented and discussed in the main text.

The reviewer highlights a valid point that is of interest to the iron aerosol community. However, given the limited size range (between 0.4 – 2.5 μm) and instrument limitations (difficult to detect minor differences in sizes) in this study, particle size could not be accurately determined. Therefore, the impact of particle size on fractional iron solubility could not be evaluated. Text has been added to the Section 3.5 (Page 24, Line 507-513) to clarify this point.

27. Figure 3: it would be better if the positions of the Fe(II) and Fe(III) are shown in the figure.

Modifications were made to figure 3 to show Fe(II) and Fe(III) positions for XANES spectra.

28. Figure 4: The two figures should be combined to make one figure. Most of the spectra are exactly the same and it is not necessary to use two figures. In the caption, what "horizontal lines" are referred to? Should they be "vertical lines" in the figure? Why there is significant shift to the left for Fe(II) oxalate and Fe(II) sulphate? Are these spectra similar to those in literature?

Figure 4a and 4b were combined into one figure, and the figure caption was modified to reflect vertical instead of horizontal lines (see modified figure 4).

The energy shift in K-edge position for Fe(II) minerals (e.g. Fe(II) oxalate and Fe(II) sulfate) is expected (as seen in figure 4). As noted in the text (Page 15, Line 284-85), the energy of the pre-edge centroid position shifts anywhere from 1.4 to 3 eV for a change of one valence electron (e.g. Fe(II) to Fe(III)). Similar energy shifts in the K-edge position are also expected; however, these shifts are much greater than that observed in the pre-edge centroid region. For instance, Prietzel et. al (2007) showed the difference in K-edge position among common Fe(II) and Fe(III) minerals can be as large as 10eV. Therefore, XANES spectra Fe(II) oxalate and Fe(II) sulfate standards correspond well to previous studies.

Prietzl, J., Thieme, J., Eusterhues, K. and Eichert, D.: Iron speciation in soils and soil aggregates by synchrotron-based x-ray microspectroscopy (xanes, mu-xanes). European Journal of Soil Science. 58, 1027-1041, 2007.

29. Figure 5: how the two datasets are separated? At the left bottom corner, there are lots of data points, which could be either classified to group 1 or 2. What standards have been used to classify them?

As mentioned in Section 3.3, elemental molar ratios, specifically Fe/Al and Si/Al, and XANES spectra were used to classify the two groups. However, the authors agree that particles with low Fe, Si, and Al concentrations were difficult to classify based solely on this criteria.

Text has been added throughout results and discussion section (Page 18, Line 357-358 and Page 20, Line 402-403) to address the reviewer's comments.

30. Figure 6: it would have been much easier to read and interpret if the data are plotted as scatter plot. However, if the standard deviation is also to be plotted, it might still be better to use the original style. Therefore, it is up to the authors to decide what would be the best way to present the data.

Standard deviation bars are now included in figure 6.

31. Table 2: the number of particles analyzed for each filter should also be listed in the table. Fig. 2 showed that there are large variations in Fe(II)/total Fe in the individual particles and the number of particles analyzed was very small. The standard deviation and range of Total Fe(II)/Total Fe for each sample should also be listed in the table. The number of particles analyzed is worryingly small, which would have made the direct comparison of the Fe(II)/total Fe with the also to some extent uncertain fractional Fe solubility less useful.

The authors agree that this scaling technique leads to large uncertainties. The authors have noted this uncertainty in the manuscript, (e.g. text added to Section 3.5 Page 22, Line 455-462) table 2, and figure 6. Furthermore, the authors have attempted to better qualify conclusions based on these parameters, taking into account the reviewer's comments on uncertainty.

32. Can Total Fe(II)/Total Fe be calculated from the XANES spectra of an area rather than individual particles, like that in Majestic et al. (2007, ACP)? If it can, it will give much more credible data on total Fe(II)/total Fe than what were presented in this table (the average total Fe(II)/total Fe from limited number of particles analyzed). Again, the comparison between number abundance of iron minerals (Al-substituted Fe oxides and Fe-aluminosilicate) and the fractional Fe solubility seems to be the key result the authors wanted to mention and therefore the data should be presented more clearly.

While the reviewer highlights an interesting point, such data (similar to Majestic et. al., 2007) are not available. As noted by reviewer 2, there are limitations to XANES experiments, such as time allocated for analysis at the synchrotron facility (~3-4 days). Although bulk analysis of iron speciation on an aerosol filter sample is possible to some extent (typical sample area ~0.4 X 1 mm²), we were unable to do this analysis within our limited experimental time frame. However, it would be interesting to evaluate how well single particle data represent bulk sample properties. Based on our findings, there are clearly large variations in single particle iron speciation (Fe(II) content and mineralogy). An extensive study comparing single particle and bulk iron speciation data from XANES analysis would be interesting when we have more time allocated for XANES experiments.

To clarify the uncertainty between single particle and bulk measurements, text has been added to Section 3.5 (Page 25, 516-525).