

Reviewer 2 comments:

The authors examine the composition (oxidation state and mineralogy) and solubility of Fe aerosols using XANES (single-particle) and ferrozine method (bulk) for several filters. The measurement (especially the concurrent elemental maps) and some aspects of the interpretation are valuable and should therefore be published in some form, but only after substantial restructuring of the manuscript. The title and main points are perhaps too overgeneralized, given the small number of samples analyzed and insufficient "dynamic range" in observed mineralogy (the former is a limitation of beamtime allocation and the time for XANES analysis). The main contribution of the authors is the observation and inference of mineralogy in ambient particle samples, and their apparent insolubility. There is some disconnect between the small number of particles for which Fe concentrations are measured and the solubility analysis which is a bulk sample analysis, which the authors try to bridge by introducing a method of scaling. Unfortunately, for the small sample size (of windows/images) and the variations among them, the scaling does not provide insightful results. The authors would best serve the community if they focus on the mineralogy of Fe aerosols and discuss their XANES measurement interpretation in this context, and report solubility of the bulk aerosol measured for these samples but not necessarily imply that the content or composition obtained from their small number of Fe aerosols analyzed are representative of the bulk, or that the uncertainty in the scaling is small enough to serve as a predictor of bulk solubility in this analysis.

I am generally in agreement with the assessment and points made by first reviewer. In addition, I would like to add the following comments and suggestions for revisions:

*The authors would like to thank the reviewer for his/her constructive comments and suggestions. In response to the reviewer's comments, we have modified the manuscript, discussing the uncertainty in the scaling approach in detail (single particle speciation and bulk solubility analysis comparisons, refer to Page 13-14, Line 274-282; text within Section 3.5), and have attempted to better qualify our conclusions. Issues relating to limited sample size are also discussed in our responses to Reviewer #1. A detailed point-by-point response to general comments is presented below.*

— General comments —

The extraction procedure uses only deionized water. Generally, a solvent with lower surface tension (often methanol) should be added prior to the water to fully extract the water-soluble fraction of particles into an aqueous solution - could not the authors be missing a variable fraction of Fe in some samples through incomplete extraction? Also, the smallest size captured by a nominally 0.45 micrometer pore-size PTFE filter should be less than 0.45 micrometers (for reasons of diffusion, interception, and so on).

*Generally, adding methanol to lower surface tension and improve extraction of water-soluble components from hydrophilic filters was common in the past, but is not as frequently used in current studies. Extensive comparisons between online and offline (filter-based) measurements of water-soluble inorganic PM<sub>2.5</sub> species, including soluble iron (Rastogi et. al., 2008), generally show good agreement when a pure water filter extraction is used without the addition of a solvent. Thus, we do not expect to miss a significant fraction of the water-soluble component of iron with the extraction method used in this study.*

*In this study, we followed the protocol for soluble iron PM<sub>2.5</sub> extraction on PTFE and Teflon filters published by Majestic et. al. (2006). Several other studies involving soluble iron PM<sub>2.5</sub> extraction on PTFE have conducted similar versions of this protocol, which also forgo the addition of a solvent prior to water extraction (Shafer et. al., 2010; Buck et. al., 2010). However, given that previous filter-based soluble iron studies have added a solvent (Chen and Siefert, 2003), it would be useful to quantify this effect on soluble iron PM<sub>2.5</sub> filter extraction in another study.*

*Regarding the collection of particles smaller than the filter pore size of 0.45µm, this is true, filtering of air of particles by pore filters collect particles over a broad size range down to nm-sizes.*

*Majestic, B. J., Schauer J. J., and Shafer, M. M. Development of wet chemical method for the speciation of iron in atmospheric aerosols, Env. Sci. & Technol. 40, 2346-2351, 2006.*

*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.*

*Buck, C.S., Landing, W. M., Resing, J. A.: Particle size and aerosol iron solubility: a high-resolution analysis, Mar. Chem. 120, 14-24, 2010.*

*Chen, Y., Sierfer, R. L., Determination of various types of labile atmospheric iron over remote oceans, J. Geophys. Res. 108, 4774, doi:10.1029/2003JD003515, 2003.*

Regarding the XANES measurements, interferences from PTFE is common in spectroscopic studies - this is not an issue here?

*Though PTFE may cause interferences in other spectroscopic studies, it was neither an issue in this study (as seen in figure 1 by minimal background interference) nor in a previous study (Werner et. al., 2006) that performed micro-XANES analysis on Cr PM<sub>2.5</sub> deposited on similar filter media (25mm Zeflour or Teflon filters).*

*Text was modified in Page 10, 186-187 to clarify this point.*

*Werner, M.L., Nico, P. S., Marcus, M. A. Anastasio, C.: Use of micro-XANES to speciate chromium in airborne fine particles in the sacramento valley. Environ. Sci. Technol. 41, 4919-4924, 2007*

Quantitative calibration and analysis of XANES/NEXAFS spectra are rather rare in the literature; more detail regarding the preparation, range, and final calibration curves should be included in the supplemental section. How accurate can this calibration be when applied over a 400nm spot size?

*The authors have provided more detail to the text in the Methods section (Section 2.3, Page 11, Line 209-212 and Page 12, Line 230-231) and have added figure S1 and table S1 to Supplemental Information to support this text. Given that all XANES analyses for standard and ambient samples were performed using a 400 nm spot size X-ray beam, the calibrations can be easily applied to the ambient samples.*

The authors have addressed the potential freezing artifact thoroughly, but could not the denuding evaporate acids/ammonia from the condensed phase and subsequently change the precipitated solid?

*While the reviewer highlights an interesting point, many studies measuring offline and online PM<sub>2.5</sub> show that the most important components controlling particle pH in the southeastern US are sulfate and ammonium, which are not volatile. Nitrate, which is semi-volatile, typically is at least an order of magnitude lower concentration than sulfate in the southeast in summer. Given these trends, we do not expect that iron in our samples will be susceptible to significant artifacts by denuding our samples.*

Invoking an assumption of homogeneous deposition and using a small section of the filter to approximate loading on the filter (as is done in XRF) is not necessarily invalid in principle. However, the fact that the total Fe concentrations lie within range of "typical" Fe concentrations in Atlanta is too relaxed to be a good metric for quality evaluation. For example, the +/- values (are standard deviations or standard errors?) indicate that with this much variation among the different 40x40  $\mu\text{m}^2$  maps from the same filter. Therefore, it is not possible to differentiate a value of total Fe on one filter from another; conclusions based on variations, correlations, and comparisons based on this value (also when used for normalization) is not valid and therefore this part of the analysis and presentation must be revised.

*The authors agree that a moderate degree of uncertainty is associated with total iron measured by micro-XRF techniques (~20-55%), which ultimately impacts fractional iron solubility used to interpret the data in this manuscript. Furthermore, we agree that micro-XRF total iron measurements cannot be sufficiently validated by a simple comparison to typical Atlanta Fe concentrations. To address these concerns, we have modified table 2, figure 6, and text in Section 2.4 (Page 14, Line 274-282) and Section 3.5 (Page 21-22, Line 441-448) to demonstrate the error associated with these measurements. Even though fractional iron solubility has moderate error (23-55% error), it does not appear to significantly affect observed trends, and thus the findings*

*in this study (refer table 2 and figure 6). Therefore, we believe it is very reasonable to draw conclusions based on these measurements within the limits of uncertainty.*

What is the size distribution of particles analyzed? Would the authors expect that this is representative of the Fe particle size distribution?

*Fine particles were analyzed in this study (0.4  $\mu\text{m}$  (spot size of X-ray beam) and 2.5  $\mu\text{m}$  (cyclone upstream of filter cut size)). However, no detailed size distribution data were collected. Given that our speciation results compare well with results from other studies focusing on fine iron particles (Majestic et. al., 2007; Takahama et. al., 2008), we expect that our samples represent this size distribution reasonably well.*

*Text was added to the Results and Discussion Section 3.5 (Page 24, Line 504-513) to discuss the size distribution analyzed.*

*Majestic, B.J., Schauer, J.J. and Shafer, M.M.: Application of synchrotron radiation for measurement of iron red-ox speciation in atmospherically processed aerosols. Atmos. Chem. Phys. 7, 2475-2487, 2007.*

*Takahama, S., Gilardoni, S. and Russell, L.M.: Single-particle oxidation state and morphology of atmospheric iron. J. Geophys. Res.-Atmos. 113, doi:10.1029/2009JD009810, 2008.*

Section 3.4 – Statements regarding geographical and seasonal trends should not be made from comparisons of single filter samples representing each category; even rural vs. urban comparisons may be a bit of a stretch. It is probably best to just report that specific samples were collected at a particular type of location and season, but not to imply that differences observed are in any way representative or indicative of a trend, though it may be acceptable to (cautiously) state that observations follow a reported or expected trend.

*The reviewer suggests a valid point. The authors modified the title (Iron Mineralogy at Different Sites) and text in Section 3.4 to address the reviewer's concern. The revised text focuses on reporting differences in iron phases observed in different samples rather than inferring seasonal or spatial trends.*

Previous hypotheses have suggested size and composition (oxidation state and mineralogy) as important variables to consider in Fe solubility, though there is often a confounding effect that these two characteristics are often coupled across various source emissions. In this study, the authors reemphasize that not only the oxidation state but also the mineralogy is important. Despite the fact that the authors actually provide some information on the inferred mineralogy (in contrast to many previous studies which the authors have cited), they were not able to report a direct observation of co-occurrence or variation in solubility based on this factor (because of insufficient variation in mineralogy). Therefore, the title of the manuscript is not exactly appropriate as the findings do not necessarily extend previous "insights"

reported in the literature.

*We have revised the title taking the reviewer's concerns into account.*

Given the potential errors in the Total Fe estimate as stated above, the lack of correlation between Fe(II)/Total Fe and Soluble Fe/Total Fe (or Fe(II) in  $\mu\text{g}/\text{cm}^2$  and Soluble Fe in  $\mu\text{g}/\text{filter}$ ) does not necessarily imply anything other than lack of statistical power, and not a definitive finding that other factors must be responsible for the variations in solubility (not to say that more research is not necessary).

*We agree that conclusions based on these two parameters (Fe(II) content and fractional iron solubility) are uncertain. We have modified text in the manuscript, (e.g. text added to Section 3.5, Page 22, Line 455-462) table 2, and figure 6 to thoroughly address the uncertainty associated with these two parameters. Furthermore, we have qualified the conclusions based on these parameters, with consideration of the reviewer's comments.*

— Specific comments —

p. 22786 - "Given the limited single particle analysis" - which limitation, specifically? Detection limit of the analytical method, or the small number of samples?

*Text was modified on Page 23, Line 489.*

p. 22784 - "was observed in urban areas" should be "was observed in samples collected in urban areas", and so on.

*Text was modified on Page 20, Line 412.*

p. 22787 - "its" solubility

*Text was modified Page 26, Line 545.*

— Figures —

Figure 2 - Number of "Data Points" should be Number of Particles? Also, given the small number of particles/data points, it may make more sense to present individual points rather than a box-and-whisker plots.

*Figure 2 was modified, but maintained as a box and whisker plot.*

Figure 4 - The two panels seems redundant and would be much more clear if a single panel is used and the two types of reference spectra are differentiated with separate colors.

*Figure 4 was condensed into one panel with consideration of the reviewer's suggestions.*

Figure 5 - Is it necessary to have two figures showing the same data points? Symbols can be used to represent location type and colors can be used to represent Si content in the same figure. The authors may also consider the use of a ternary plot. Also, in this case it would be more appropriate to report/show original units, rather than the "scaled up" units, even if an appropriate scaling method was devised.

*Figure 5 was condensed into 1 figure as the reviewer suggested. Though a ternary plot can be used to present this data, the authors think that a scatter plot presentation is more effective.*