**Atmospheric
Chemistry
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Discussions**

Interactive
Comment

Interactive comment on "

Characterization of iron speciation in single particles using XANES spectroscopy and micro X-ray fluorescence measurements: insight into factors controlling iron solubility" *by* M. Oakes et al.

Anonymous Referee #2

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Review of "Characterization of iron speciation in single particles using XANES spectroscopy and micro X-ray fluorescence measurements: insight into factors controlling iron solubility"

The authors examine the composition (oxidation state and minerology) and solubility of

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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 minerology (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 minerology 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 minerology 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:

— 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).

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

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

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 um^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.

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

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

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expected trend.

Previous hypotheses have suggested size and composition (oxidation state and minerology) 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 minerology is important. Despite the fact that the authors actually provide some information on the inferred minerology (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 minerology). Therefore, the title of the manuscript is not exactly appropriate as the findings do not necessarily extend previous "insights" reported in the literature.

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 ug/cmˆ2 and Soluble Fe in ug/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).

— 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?

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

p. 22787 - "its" solubility

— 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 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 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.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 22771, 2011.