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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Application of synchrotron radiation for measurement of iron red-ox speciation in atmospherically processed aerosols" *by* B. J. Majestic et al.

Anonymous Referee #3

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The authors apply synchrotron radiation to the measurement of iron speciation in atmospheric aerosol particles. They furthermore perform aging studies to look at the impact of aerosol aging on iron speciation. The paper is an interesting and novel contribution to aerosol characterization and worth publishing in ACP. The analytical part is solid, as are the discussion of the ambient results. However, many questions and concerns surface in the 'aging of the aerosol' part of the paper. While I realize that this is a very challenging task to perform, there are a number of things which would need to be clarified and discussed.

- The experimental conditions for the aging experiments are lacking important details.

Were the samples exposed on the filter directly to radiation and some kind of atmosphere that was renewed over the course of the experiment? If so, was the chamber only used for exposing the filter or were other experiments performed at the same time? If the filters were kept in a receptacle (e.g. Petri dish) in a larger chamber with no air exchange to the outside, how would that impact the results in terms of radiation received and the realism of oxidant concentrations? In any case, what was the ambient atmosphere in which the samples were aged? Was it controlled or Wisconsin air, and was it renewed? What was the spectral output of the lamp used for the irradiation?

- Given the low relative humidity, is the logical assumption that all chemical aging would be through heterogeneous (gas/aerosol) reactions? Or will the reactivity be directly a function of available surface area, and hence will be impacted by the aerosol deposition on the filters? If the filters were heavily loaded, especially in this case where the deposits are on a narrow band, a large part of the aerosol may have no opportunity to interact with the atmosphere or radiation and thus would not be expected to show any kind of reactivity? These points would benefit from further discussion. Perhaps there is also a way to "normalize" the results by some kind of aerosol deposition density in order to make meaningful comparisons between size fractions.

- The authors observed the most substantial speciation changes in the aging of the coarse fraction. Alternatively the coarse fraction might contain biological material. Given that the Fe(II)/Fe(III) system is easily available to bacterial and microbial agents, is it possible that some of the variation is the result of bacterial activity in the larger size fractions? Was anything done to control for biological activity and/or determine contamination during aging?

- Does Fe(II) and Fe(III) always sum up perfectly to total Fe, or could there be some Fe(0) in the samples? If so was it apparent in XANES? The comparison of XANES results with other methods could and should be extended.

- How realistic are long range transport simulations if there is no cloud processing? I

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would suspect that cloud/haze/aerosol cycles would impact very strongly on iron speciation, since aqueous phase chemistry will be more active and solubility effects in these cloud/haze/aerosol cycles could enhance the fractionation.

- In the type of figures (log size distributions) used, the lower size-cut is critical in terms of the interpretation of how many modes are there. Is a lower size-cut of 20nm really reasonable for this sampler and for the observed particles? To what degree would shifting the lower size-cut to 40 or 50 change the interpretation on the number of modes?

- Figure 8 (also 11 and 12): Wouldn't a figure of percent change make more sense? What is represented by the error bars (analytical uncertainties)? Have there been any replicates performed on the ageing samples?

Further details:

- Please state the level of the clean room facility.

- Please state the power of the microwave used for the digestion.

- Please define PCIS at the first use of the term.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 1357, 2007.