

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

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Received and published: 9 April 2007

Comment 1) 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?

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Reply:

Page 1362, line 19: To clarify this point, the sentence is proposed “The samples were placed in acid-cleaned polystyrene Petri dishes with the cover removed and were artificially aged”

Page 1363, line 21: For clarification of the light sources, the following sentence is proposed. “Illumination of the samples was achieved using a carefully calibrated mix of fluorescent and incandescent light bulbs. The light output from the combination of these bulbs was similar to the solar spectrum, with some excess light in the near infrared region. The spectra from each type of bulb can be found in the supplemental material.”

Page 1362, line 21: To clarify this point, the following sentence is proposed. “Air conditioners supply the building with filtered air (95

Comment 2) 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.

Reply: Page 1372, begin line 11: We agree with the Reviewer that the deposition pattern/distribution of the particles could potentially affect the amount of radiation and air that the particles are exposed to. For further discussion on this point, the following passage is proposed. “Because the PM is collected in a narrow band, it is possible that some of the PM (especially the PM closest to the collection substrate) was not able to fully interact with the radiation or the atmosphere during the aging process. By knowing

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the total mass of the particles, assuming the average density of the particles to be 0.8 g ml⁻¹, and calculating the deposition area to be 30 mm², we can estimate the number of particle layers formed after sample collection. For this calculation, it was also assumed that the particles were packed distinct layers. For the >2.5 956;μm, 2.5-1.0 956;μm, and the 1.0-0.5 956;μm size fractions, we found that the PM forms an average of 1.0 ± 0.6 layers. The smallest size fraction (0.5-0.25 956;μm) which is collected by impaction forms an estimated 7.0 ± 1.8 layers. From this calculation, we can conclude that, for the three largest size fractions, the radiation and the air are likely interacting with all of the particles equally. While this may not be the case for the 0.5-0.25 size fraction, we do not observe the Fe(II) trends in this fraction to deviate significantly during any aging study compared to the 1.0-0.5 956;μm or the <0.25 956;μm fractions (See Figs. 8, 10, 11, and 12). Therefore, we will assume for this study that the atmosphere and radiation is interacting with all of the particles equally.”

Comment 3) 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?

Reply:

We agree with the Reviewer that biological activity may be an important process in the red-ox cycling of atmospheric iron. However, according to several studies (Peccia and Hernandez 2006; Wang et al. 2007) and references therein, bioaerosols are not ubiquitous to the coarse size fraction. Given the current knowledge on the subject, we do not feel that the iron red-ox changes in the coarse fraction are any more affected than the other size fractions.

Unexposed filters were used as controls and analyzed by XANES spectroscopy and

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the Ferrozine method at the various aging times. To show this point, the following sentence is proposed (Page 1366, line 8). “Unexposed filters submitted to the same aging procedure resulted in average soluble Fe(II) levels of 2.2 ng Fe(II) filter-1 (ranging from below the detection limit up to 4 ng Fe(II) filter-1), with no dependence on the aging time, suggesting that iron was not being deposited on the filter over the course of the aging.”

Comment 4) 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.

Reply: Total Fe(II) and Fe(III) were obtained by multiplying total iron data (from ICPMS) with XANES-determined oxidation state ratios; and as there is no independent method applicable to low-mass samples to directly measure total absolute concentrations of Fe(II) and Fe(III) in solids, a side-by-side comparison of the two methods cannot be performed. To clarify this point, the following additions and modifications are proposed:

Page 1365, line 10: In order to clarify the procedure used to determine the total Fe(II) and Fe(III), the following sentence was added following “ \checkmark Fe(II)/Fe(III) ratio.” “When XANES spectroscopy is used in conjunction with a method which can measure total iron (such as ICPMS), absolute mass of Fe(II) and Fe(III) can be estimated.

Page 1366, lines 20-23: To help avoid confusion, these sentences were changed to “The solid bars \checkmark were measure by both XANES spectroscopy (coupled with ICPMS measurements) and the Ferrozine method \checkmark ”

Page 1368, lines 1-2: “In Fig. 6, we show the \checkmark as measured by XANES spectroscopy and ICPMS.

Page 1368, lines 10-12: “Figure 7 presents the size-resolved total Fe(II) and Fe(III) content (derived from XANES and \checkmark ICPMS measurements) after aging \checkmark ”

Page 1372, lines 1-3: “In this study, we have developed a XANES spectroscopy method

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to determine the total Fe(II) and Fe(III) ratios in limited-mass atmospheric personal exposure samples. When applied in parallel with ICPMS, XANES spectroscopy can establish the average iron oxidation state in an aerosol sample.”

For a discussion of the potential for presence of Fe(0), please see Page 1372, line 19-25 in the original manuscript: While it is possible for there to be Fe(0) in the samples, however, it was not observed in the XANES spectra, indicating Fe(0) levels to be under 1

Comment 5) How realistic are long range transport simulations if there is no cloud processing? I 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.

Reply: Page 1373, line 21: We agree that cloud processing will play a large role in the red-ox transformations of atmospheric iron, therefore, we propose to add the following text. “Because of the low relative humidity condition used in this study, any changes in iron oxidation state will likely be the result of heterogeneous surface chemistry likely played a major role in the observed changes in iron oxidation state, and likely cannot be extended to those processes taking place in cloud and fog waters (Faust and Hoigne, 1990; Arakaki and Faust, 1998), which can have significant impacts in certain environments during atmospheric transport. However, it should be noted that even at the humidity levels used, the aerosols are not dry - a water layer is present in which aqueous phase chemistry can take place.”

Comment 6) 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?

Reply: To check for this effect, the plots were re-drafted using a lower cut-point of

50nm (instead of 20nm). For the zero point soluble iron (Fig. 9), we did not observe any changes in the overall soluble iron distribution. However, there were instances in the Waukesha data (Fig. 10, 1 and 6 day data points) where the <0.25 956;µm size-cut would be greater than the 0.50-0.25 956;µm mode. However, these effects are extremely small and we do not believe that they affect the overall interpretation of the data. Further, no substantive conclusions rely on the modal differentiation of the two smallest size-cuts.

Comment 7) 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?

Reply: We agree that a percent change would be helpful to the reader. Therefore, we propose that Fig. 8, 11, and 12 are re-drafted to show this. We feel that readers would still want to know the actual air concentrations, therefore the current versions of Fig. 8, 11, and 12 will be moved to the Supplementary Materials.

For clarification of the replicate samples, the following passage as added after the Reply to Comment 1c: "For each of these trials, total Fe(II) was determined by multiplying the fraction of Fe(II) by the total iron content (from ICPMS). For this sampling day, we found an average of 5.94 ± 0.84 ng m⁻³ (n=5), where the uncertainty is the standard deviation of all of the trials. This corresponds to a RSD of 14.2

Comment 8) Please state the level of the clean room facility.

Reply: In the first sentence of Section 2.2, the sentence is proposed to read "In a Class 50 (ISO Class 4.5) trace-metal clean room, the "

Comment 9) Please state the power of the microwave used for the digestion.

Reply: Page 1362, line 26-27: The following modification is proposed "Teflon filter digested using a low-volume microwave-assisted (maximum power = 1000W) acid digestion."

Comment 10) Please define PCIS at the first use of the term.

Reply: Page 1361, line 16: This sentence will be modified to read “For PM collection, four co-located SioutasŽ personal cascade impactor samplers (PCIS) (Misra et al., 2002Ž were used, each operated atŽ”

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

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