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Atmospheric Chemistry and Physics Discussions
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Interactive comment on "Composition and oxidation state of sulfur in atmospheric particulate matter" *by* Amelia F. Longo et al.

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We thank this reviewer for their very helpful comments and suggestions.

Reviewer 2 sought further clarifications on the synchrotron-based methods used in this manuscript. Dwell time is used to refer to the time spent at each step in the S-NEXFS spectrum. In this case, because three spectra with a 1 s dwell time each were often necessary to get enough signal for a high quality spectrum, the effective dwell time was at least 3 s because a minimum of 3 s were spent at each energy step in the spectrum. With the 50 eV range and 0.33 eV step-size used in this study, measurements were taken at 150 energies per scan. For 150 energy steps with an effective dwell time of 3 s, the total time required to generate a S-NEXFS spectrum was approximately 7.5 minutes. We did oxidation tests on samples where we measured the same particle

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repeatedly, creating effective dwell times of more than 10 s. Even with this longer dwell time per energy step, we saw no noticeable shift in oxidation state or the relative abundance of the oxidation states.

The energy was calibrated using an elemental sulfur standard (S0) measured at beamline 2-ID-B. The whiteline energy of the elemental sulfur standard was aligned to 2472 eV (Cozzi et al., 2009). All subsequent data uses 2472 eV as the reference energy for S0 during the data alignment mentioned by both reviewers. Furthermore, for every measurement two spectra are collected: the specimen and an aluminum sulfate standard on the monitor stick. This approach means that all spectra are referenced to the aluminum sulfate standard and the initial calibration is not as crucial on this beamline.

Sulfur standards were ground using an agate mortar and pestle to the consistency of a fine talcum powder (approximately 10 microns). A cellulose acetate filter was gently dredged through a small quantity (less than 1 mg) of powder placed on a microscope slide. This procedure produced a thin and almost imperceptible coating on the filter in order to limit the thickness and thus self-absorption.

Reviewer 2 also wanted more detailed information to assist with the interpretation of the multi-energy maps presented in Figure S1. For the multi-energy maps, the units are raw counts from the detector. At this beamline, units such as mass per area are not provided. A more intense signal, that is the more counts present, indicates greater concentrations of sulfur in that region of the sample. The maps were generated at the whiteline energies of S0 and S+VI. The energies referenced in the methods are the actual settings used during experiment; in other words, these energies are not calibrated with the monitor stick. To identify the correct whiteline energies for the multi-energy mapping, a S-NEXFS spectrum was collected for the particle of interest immediately before mapping. The corresponding whiteline energies for S0 and S+VI were then taken directly off this spectrum. Individual maps were then collected at the whiteline energies determined for S0 and S+VI. Although it is possible that the energy drifted during mapping, the interval between the two measurements is short enough that this

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is not a problem. Due to the 6 ev difference in the whiteline energies of the S0 and S+VI oxidation states, we do not expect significant overlap between the two oxidation states in multi-energy mapping. Energy drift during mapping may reduce signal intensities of the S0 and S+VI oxidation states but the overall distribution patterns of the sulfur oxidation states in an individual particle should remain relatively unaffected.

Fitting was not done to determine the relative abundance of sulfur at each oxidation state for each pixel. Instead, more accurate data from individual particle spectroscopy was collected and presented in the paper and supplement. As the reviewer noted, individual particle spectroscopy was not collected for every sample in our collection. Individual particles were examined on samples other than those noted in Table S1; however, the particles did not generate useable spectra. Table S1 represents the number of spectra that were collected that could be used for further analysis.

Reviewer 2 also wanted clarification on the use of bulk emission source data. Emission sources were only characterized at the bulk level, and this poses a problem for data interpretation. We still use the emission source data for comparison with bulk ambient aerosol data and to a limited extent the individual particle data to glean any possible insights; however, we will further clarify that emission sources were collected in the bulk mode and any comparisons between the bulk emission source data and the ambient aerosol individual particle data are speculative.

In this manuscript, we postulate that organosulfates are not a major component of sulfate aerosol. We were able to account for the sulfate using our present database, which suggests that organosulfates likely do not account for a significant portion of the sulfate aerosol. We do, however, state that contributions near or below 10% could be below the detection limit of this method. Since this is approximately the level that organosulfates are hypothesized to occur, it makes sense that we are able to account for all sulfate present in the sample with our database, even if some small portion of organosulfate is present.

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A short sentence will be added to the Discussion about the possibility of secondary formation of sulfates. Using just these techniques, it is unclear what the role of secondary sulfates are in these ambient samples; however, secondary formation processes could certainly contribute to the S(+VI) pool.

Figures will be added to the supplement (see attachments) that show exemplars of both the linear combination fitting and Gaussian peak fitting that were used to determine the sulfate composition and relative abundance of each oxidation state, respectively.

We thank the reviewer for noting a few technical corrections as well. These and the above comments will be addressed in the revised manuscript, should the paper be accepted.

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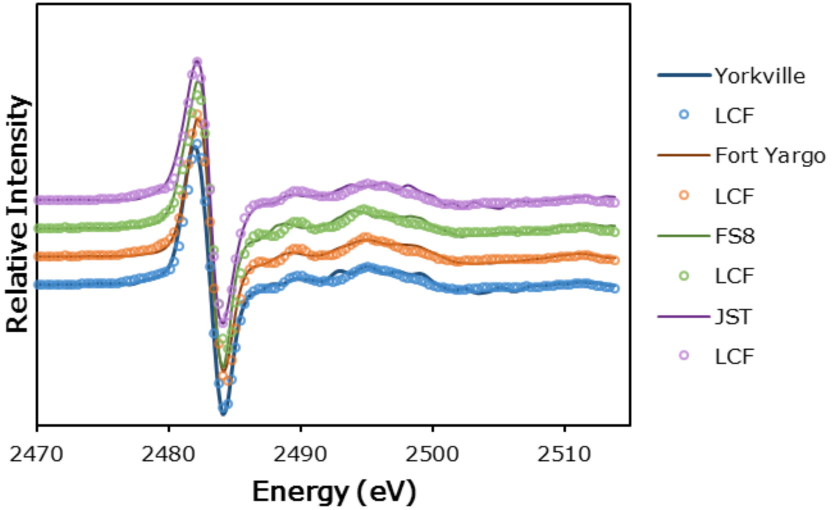

Figure S2: Linear combination fits of representative bulk samples. The first derivative was used to fit ambient aerosol samples (solid lines) with a database of sulfate standards. The resulting linear combination fits are shown with open circles.

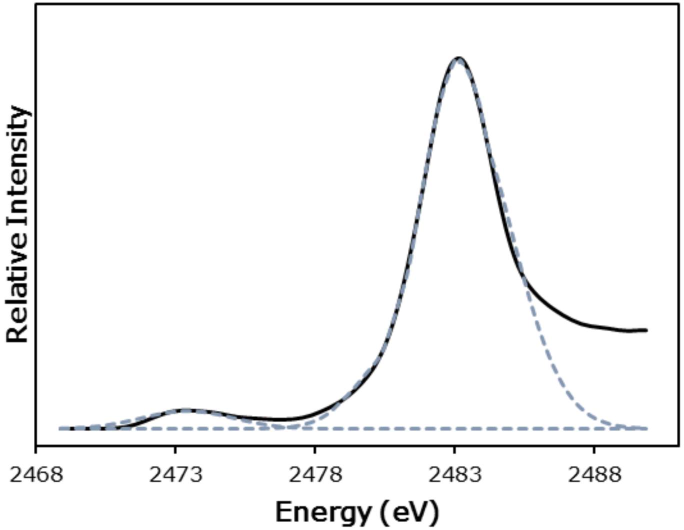

Figure S3: Gaussian peak fitting was used to determine the relative abundance of the S(0) and S(+VI) oxidation state in the aerosol samples. Athena's peak fitting protocol was used to fit Gaussian curves (dotted line) to the S-NEXFS spectrum (solid line) and to determine the area under the Gaussian curves.