

Interactive comment on “The 2005 Study of Organic Aerosols at Riverside (SOAR-1): instrumental intercomparisons and fine particle composition” by K. S. Docherty et al.

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Responses to comments of reviewer No. 2

General Comments

While the great majority of this information included in the study are valuable, the overall impact of the manuscript in its current form is inhibited by some shortcomings in its organization.

R2.1: My impression is that sections 4.1 and 4.2 are essentially preliminary material relative to the intent of this study. If similar analysis was included in the previous SOAR-

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1 papers these could be cited. If not, the site representativeness and meteorological analyses could be safely moved to the study overview (section 2).

Response: The information presented in sections 4.1 and 4.2 has not, to our knowledge, been presented in previous SOAR publications and its inclusion here is warranted to establish the consistency of PM_{2.5} concentrations in Riverside with those routinely experienced throughout the wider inland South Coast Air Basin and that meteorological, weather, and gas-phase pollutant concentrations during SOAR-1 were representative of those typically experienced in the region during the summer months.

Due to comments raised by both reviewers including the current comment, the Introduction and Overview sections of the paper have been reorganized. To this specific comment, the discussion regarding the site representativeness (previously Sec. 4.1) and meteorological analysis (previously Sec. 4.2) have been relocated to the overview section of the paper.

R2.2: The inclusion of the SOAR-2 met analysis does not add significant value to the paper, even as supplementary material, since SOAR-2 compositional data are not used in the paper.

Response: The SOAR-2 meteorological data has not been presented in any of the manuscripts arising from SOAR. Although SOAR-2 data is not specifically discussed in the current manuscript, the meteorological data has been included in the Supporting Information in order to document the data for future reference. From previous experience, this can prove very useful to future analyses and comparisons, as otherwise this type of supporting data can be hard to find.

R2.3: Sections 4.3 through 4.6 present the aerosol composition intercomparisons. There is enough analysis here to be a standalone section on the intercomparison theme, and this is recommended.

Response: We agree with the reviewer that these sections can be more effectively

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reorganized under a single heading “Aerosol Composition Intercomparisons” which will now be Sec. 4.3. Following this change, we will use the following organization:

4.3.1 Total PM_f intercomparisons 4.3.2 Intercomparisons of ToF-AMS measurements
4.3.3 Comparison of NR-PM₁ vs PM_{2.5} inorganics 4.3.4 OC Comparison between the HR-AMS and Sunset instruments

R2.4: There is also a need within this group of sections to more fully commit to a decision on whether material should be included in the main text or as a supplement. Figure S2 has a whole paragraph devoted to it in the main text, and figure S3 has a whole section devoted to it. If a figure merits a whole section in the manuscript, why would the figure itself be moved to the supplement? This is especially confusing because the results are clearly in line with the overall theme of the paper. If the authors feel strongly that the figure should be in the supplement, then perhaps the bulk of the accompanying text might also be moved there.

Response: Fig. S2 was included in the Supporting Information because the loss of semi-volatile material and particularly ammonium nitrate (NH₄NO₃) and semi-volatile organic material (SVOM) from the heated TEOM (TEOM50C) is well characterized in the literature. As a consequence, the substantially improved agreement between the TEOMFDMS and TEOM50C when the latter are supplemented with calculated NH₄NO₃ concentrations is not surprising. However, this result is worth discussing in the context of the larger comparison among the different TEOM and HR-AMS measurements in order to fully explain differences among those instruments and to further explore the contribution of SVOM during SOAR-1. For these reasons, we are disinclined to either move Fig. S2 to the main paper or the discussion of this figure to the Supporting Information. However, we have re-structured this first sentence of this discussion as follows in order to streamline the text which is at the heart of this reviewer's concern:

“A majority of SVM measured during SOAR-1 is NH₄NO₃. As shown in Fig. S10,

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the agreement between TEOM50C and TEOMFDMS measurements improves substantially during both P1 and P2 when TEOM50C measurements are supplemented with PM_{2.5} NH₄NO₃ concentrations (TEOM50C + NH₄NO₃). NH₄NO₃ concentrations were calculated using IC-nitrate measurements and assuming its full neutralization by NH₄, consistent with the HR-AMS ion balance as discussed below (Section 4.9). Linear regression of TEOM50C against TEOMFDMS during P1 and P2 (Fig. S10a) results in a slope of 0.61 and 0.42, respectively. The value of the slope obtained by linear regression of TEOM50C + NH₄NO₃ versus TEOMFDMS measurements (Fig. S10b) is higher during both periods. The increase in slope obtained during P2, however, is nearly double that during P1 indicating a much higher contribution of NH₃NO₄ during the latter sampling period. By extension, if we assume that the remaining difference between TEOMFDMS and TEOM50C + NH₄NO₃ is due to volatilization of SVOM, this comparison suggests that its contribution is relatively consistent at approximately 24% (+2%) of total PM_{2.5} mass during both P1 and P2, consistent with the findings of Grover et al. (2008) using measurements of Sunset2.”

Similarly, Fig. S3 was included in the Supporting Information because a similar comparison of HR-AMS and IC-nitrate measurements (Fig. S3A-S3B) was previously included in Farmer et al. (2010). For clarity, we have changed the discussion within the text as follows: “HR-AMS NR-PM₁ NO₃ and SO₄ concentrations are compared with corresponding PM_{2.5} IC-nitrate and IC-sulfate measurements, respectively, in Fig. S11. Similar comparisons of Cl and NH₄ are not possible because PM_{2.5} concentrations were not measured during SOAR-1. HR-AMS NO₃ is plotted against corresponding IC-nitrate measurements in Fig. S11a along with the results of linear regression. As this plot shows, NO₃ measurements from both instruments were very highly correlated. Both the standard and recovery slope obtained from linear regression are also very similar and near unity indicating that the measurements were highly consistent despite the different size cut between the two instruments, and suggests that only a small amount of NO₃ is contained in supermicron particles. Diurnal plots of both NR-PM₁ and PM_{2.5} NO₃ are shown in Fig. S11b. As expected, the diurnal profile using

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each technique exhibits similar broad, bi-modal maxima during the morning and early afternoon and minima during the late afternoon and early evening. HR-AMS NR-PM1 SO₄ is plotted against corresponding PM_{2.5} IC-sulfate measurements in Fig. S11c while diurnal profiles of each are provided in Fig. S11d. In contrast to the consistency and high correlation of NR-PM1 and PM_{2.5} NO₃ measurements, comparison of SO₄ measurements exhibit substantially higher scatter as evidenced by a low degree of correlation ($r^2=0.42$) between the measurements. Due to this scatter, results of linear regression differ widely depending on whether a fixed-zero intercept is used. In the absence of a fixed-zero intercept, a slope of 0.51 is obtained which increases to 0.82 when an intercept of zero is used. The recovery slope obtained in this case is likely more accurate considering both the amount of scatter associated between the two measurements and the fact that SO₄ concentrations rarely decreased below 2 $\mu\text{g m}^{-3}$ during SOAR-1, as well as the fact that the zero values of the HR-AMS was regularly checked with a HEPA filter. A substantial amount of the scatter between NR-PM1 and PM_{2.5} may be due to the different particle size fractions sampled by each instrument. It is worth noting, however, that compared a limited number of IC-sulfate measurements with PC-BOSS PM_{2.5} SO₄ and found a similar low degree of correlation (0.16-0.37). PC-BOSS SO₄ measurements were not available here and were not compared as a result. Diurnal profiles of NR-PM1 and PM_{2.5} SO₄ (Fig. S11d) do not exhibit prominent features, instead SO₄ concentrations in each case are relatively constant throughout the day indicating the continuous presence of SO₄ in the particle and its insensitivity to a widely range of ambient temperatures. The difference between hourly average SO₄ measurements indicate that PM_{2.5} SO₄ is ~20% higher than corresponding NR-PM1 measurements, indicating the presence of a supermicron SO₄ fraction.”

R2.5: Sections 4.8 through 4.10 synthesize the SOAR-1 fine PM composition measurements to produce an overall assessment of these properties. These sections directly relate to second theme of the paper and should be more explicitly lumped together.

Response: Again we agree with the reviewer’s suggestion to incorporate these sec-

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tions as subsections within a larger section titled “4.5 PM_f composition during SOAR-1” and have renumbered the sections in question as follows: 4.4.1 Average NR-PM1 + EC composition 4.4.2 Anion/cationic balance in NR-PM1 4.4.3 Average PM_{2.5} composition

R2.6: The placement of section 4.7 is a more challenging concern. EA analysis is still relatively novel, but it is obviously highly valuable and will soon be a standard component of the analysis for HR-AMS. Its potential is highlighted in the manuscript in that the results of the EA analysis are key to the value of two other analyses in the study (the OC intercomparison in section 4.5 and the ion balance analysis in section 4.9). The difficulty arises because, with respect to the two dominant themes of the overall manuscript, the EA analysis as a standalone section is somewhat of a distraction. It does not involve any instrument intercomparison directly, nor does it synthesize the overall composition in a way that will be useful to most readers. Several possibilities exist to fix this section might be rewritten to better merge it into the greater synthesis of aerosol composition. Or the section might be moved to an appendix or to the supplementary text.

Response: We disagree with the reviewer, and feel that the EA results do relate to the overall composition in a way that may be useful to readers. In addition, and as discussed in response to comments R1.5, R1.9, R1.15 and R1.78 from Reviewer 1, upon revision we have added more detail on the OA composition by including the results of PMF analysis, which include the elemental analysis of the OA components. For this reason we also believe that the EA results belong even more in the revised manuscript.

R2.7: Figures and tables were generally very good. The authors might consider adding some indication of the uncertainty associated with the diurnal pattern plots presented. Range values are sometimes given in the text, but it is difficult to assess the strength or consistency of these patterns when only the average is provided on the figures.

Response: We have used diurnal plots to illustrate the general daily trend of individual

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time series over the period of SOAR-1. In order to minimize the overall length of the manuscript and the number of included figures, several diurnal plots are routinely presented in the same panel. As a result, the addition of error bars to each point would make these figures cluttered and hard to interpret. While we fully agree with the reviewer that the best course of action would be to incorporate error bars to each of the diurnal patterns, we have decided to not include them in order to facilitate the ability of the reader to easily interpret these plots.

Specific Comments

R2.8: Line 455: The reference to “our group” should be changed unless the manuscript’s entire author list is included in the group.

Response: See response to R1.34.

R2.9: Line 459-461: This sentence has grammar and/or spelling errors that make its meaning unclear.

Response: The reviewer is referring to line numbers of the submitted PDF manuscript before typesetting by ACPD (corresponding to P6316 L3-7 in the ACPD manuscript). We had already corrected these errors in the ACPD proofs.

R2.10: Line 516: Should “Figure 1” in this sentence refer to Figure 2?

Response: We believe that the reviewer is referring specifically to P6318 L4 where “Fig. 1” is stated referring to the figure displaying the meteorological conditions present during SOAR-1. This is indeed an error and has been changed to “Fig. 2”.

R2.11: Lines 659-664: These sentences seem extraneous to this paper. Consider removing them.

Response: This text has already been revised in response to comment R1.61 from Reviewer 1, and we believe that the revised text does fit well within the context of this paper.

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R2.12: Lines 691-694: There seem to be several other possible reasons to explain the mismatch between the SO₄ measurements. How does one explain that NO₃ is found almost entirely on submicron particles, but that SO₄ is largely supermicron? The authors should defend their conclusion here in more detail. Could it not be an HR-AMS collection efficiency or data analysis issue?

Response: The comparison of PM_{2.5} and NR-PM₁ are complicated by the large amount of scatter in the data when one is compared against the other. This could, in part, be an influence of particle size and the fact that the HR-AMS and IC-sulfate instruments have different effective transmission size ranges. This possibility has been incorporated in the text in response to comments R1.62 from reviewer #1 and R2.4 from this reviewer). In addition, the agreement between two different PM_{2.5} SO₄ measurements (i.e., IC-sulfate and PC-BOSS (Grover et al., 2008)) was also characterized by a similarly low degree of correlation. To the extent the PM_{2.5} SO₄ measurements reflect actual concentrations and given the large uncertainty associated with the linear regression in this case, average PM_{2.5} SO₄ is ~20% higher than NR-PM₁ measurements which suggests the presence of supermicron SO₄. This effect is unlikely to be caused by variation in AMS collection efficiency (CE). As mentioned in the experimental section, a CE=0.5 was used for all species during data analysis, which is consistent with intercomparisons in a variety of urban locations as (e.g., Canagaratna et al., 2007 and references therein). An error in the analysis of the HR-AMS data is also an unlikely cause of the discrepancy. E.g. sulfate concentrations from HR-AMS and C-AMS instruments show good agreement as observed in Fig. 4F.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C9650/2011/acpd-11-C9650-2011-supplement.pdf>

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