

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.

K. S. Docherty et al.

docherty.kenneth@epa.gov

Received and published: 1 October 2011

Responses to comments of anonymous reviewer No. 1

General Comments

R1.1: In my opinion, the use of abbreviations and acronyms within the manuscript is too excessive. I suggest using abbreviations and acronyms more sparingly. This will facilitate readability and comprehension of the manuscript for most readers. Also, please check all abbreviations and acronyms for inconsistencies.

Response: We have made every effort to minimize the number of abbreviations and

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acronyms contained in the text, but the use of a certain number of them is unavoidable. To facilitate readability, we have added a list of abbreviations and acronyms to the Supporting Information section of the paper.

R1.2: The overview part is too long and detailed. Instruments and experimental details from the campaign are described without the data ever being presented. These parts should be removed because they don't contribute scientifically to the manuscript. The overview is far too long for a simple background but not detailed enough to constitute a complete, in-depth overview.

Response: Based on comments received from both reviewers, Sec. 2 (Overview of SOAR) has been substantially changed and now contains only information contained in former Sec. 4.1 (site representativeness) and Sec. 4.2 (meteorology and gas-phase concentrations). The discussion previously contained in Sec. 2 has been substantially shortened and moved to the Introduction.

R1.3: Large portions of this paper simply report measured results and statistics of linear fits and their correlation coefficients with no underlying discussion of what these results mean in a broader context. The instrument comparison section lacks detailed descriptions of inlets, losses, and possible reasons for disagreements, often simply reporting results together with their correlation correlations.

Response: This general comment is restated by many of the reviewer's specific comments below, each of which has been addressed individually.

R1.4: I would strongly suggest adding a section where the fine particle composition, possible changes, influences and sources are shown and discussed in detail. The discussion should also include the air quality in the SoCAB (history and changes in air quality and their impact on the fine particle composition and a comparison of these results with historic values from within the SoCAB)

Response: In response to later comments from this reviewer, we have added material

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to the manuscript discussing the composition of the organic aerosol fraction in more detail. We have also added a brief comparison of the PM_f levels observed here with those from previous studies. A substantial discussion on the suggested topics could easily be one (or several) additional manuscripts, and given the length of our manuscript, we believe that to be outside the scope of the present work.

R1.5: The most severe problem of the manuscript is a lack of focus on the promised topic(s). The viewpoint of this article is often very narrow and mostly from the perspective of AMS data, disregarding the limited capabilities of the AMS and the fractions of the aerosol that cannot be measured with it (aside from EC). The same applies to the discussion of the fine particle composition. This is only discussed as far as it seems suitable and fails to deeply present or discuss organic aerosol which is an essential part of the fine particle composition. Why has this work been split into so many different publications? The composition of the organic aerosol is an essential part of any discussion of the fine particle mass composition and these topics should not be separated from another, especially with regard to the focus of the campaign (Study of Organic Aerosols at Riverside, SOAR). I recommend that the authors focus on the topic they want to present and include a detailed and profound discussion of it. The key findings of the article should be highlighted more clearly.

Response: We strongly disagree with this reviewer's comment that the manuscript lacks focus on the promised topics. Of the 27+ manuscripts that have been published as a result of the SOAR study (see <http://cires.colorado.edu/jimenez-group/Field/Riverside05/Papers>), none has presented an overview of the composition of fine particulate matter observed at the time. We have done so in the current manuscript. Additionally, as stated in the text, SOAR-1 represents one of the most extensive studies of organic aerosol to date and saw the deployment of many then novel instruments in the field for the first time. Many of these instruments are starting to be more widely used in atmospheric research and monitoring efforts and it is, therefore, relevant to make comparisons among the various measurements during SOAR-1 due

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to their collocation at the time.

We had not included a discussion of the positive matrix factorization (PMF) results for organic aerosols in order to restrain the length of the manuscript, and we were planning to submit a separate paper on that topic. However, given the comments from both reviewers, we had decided to add the key results on the PMF analysis of organic aerosols to this paper, while the (very interesting and unique) technical details of the PMF solutions have been documented in the revised supplementary information section. Thus, no separate manuscript on those topics will be submitted later.

Specific Comments

R1.6: - P6304L26: "Due to the small number of species involved and relatively simple chemistry, the inorganic fraction of ambient aerosols is reasonably well characterized." This statement is overly speculative and seems to be based solely on the data for the non-refractory inorganic fraction of the submicron aerosol that can be measured with the Aerodyne AMS. Looking at global aerosol composition, sea salt and mineral dust are important contributors depending on the definition of PM_f. The composition of the latter is highly variable and depends on the source. Furthermore, for insoluble inorganics like mineral dust and metals, the concentrations are often unknown due to a lack of suitable instrumentation.

Response: We have changed the text to:

"Although the contributions of insoluble inorganic species such as mineral dust and metals are uncertain due primarily to instrumental limitations, the bulk of inorganics resulting from secondary atmospheric processes, including ammonium nitrate and ammonium sulfate, are reasonably well characterized due to the small number of species involved and the relatively simple chemistry of those species."

R1.7: - P6305L1: ". . . despite the fact that OA contributes about half of PM_f mass on a global basis." Should be "non refractory PM_f "

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Response: We have changed the sentence to:

“The composition of OA in PMf remains poorly characterized despite the fact that it contributes a substantial fraction of the PMf mass globally (Zhang et al., 2007).”

R1.8: - P6305L6: “The distinction between POA and SOA and the apportionment of each to various sources has profound implications for regulatory and control strategies that seek to mitigate the negative consequences of PMf (de Gouw and Jimenez, 2009).” This statement is a bit mysterious – what are these implications, and why are they mentioned? If they are not interesting enough or do not contribute to the cause of the paper, this statement is unnecessary.

Response: To clarify, we have changed this sentence to:

“The distinction between POA and SOA, can provide greater insight to regulatory and control strategies that seek to reduce emissions from various sources and thereby mitigate the negative consequences of PMf (de Gouw and Jimenez, 2009).”

R1.9:- P6305L26-27: “Factor analysis of AMS OA spectra has allowed for the quantification of several characteristic OA components” Not really components, but fragments and patterns typical for distinct types of sources! The nature of individual organic compounds cannot be determined by the Aerodyne AMS.

Response: There seems to be a confusion here between the terms “components” which is used here and in many other publications as a synonym of factors (e.g. as in principal component analysis), and “compounds,” meaning individual molecular species. We believe that this is already clear in the literature, in the references provided, and also with the new section being added to our manuscript upon revision on the PMF analysis of the OA from SOAR-1.

R1.10: - P6305L29: “. . . most of which are consistent at many locations throughout the world” (Ng. et al 2010) show that the “characteristic OA components” can vary strongly depending on location and season and should rather be described in terms of

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the ratio of the main fragments formed (f43 vs. f44) than by the actual spectrum.

Response: The components found by factor analysis of AMS spectra at different locations (HOA, SV-OOA, LV-OOA, BBOA. . .) are indeed consistent between different locations, even though the detailed spectra are not identical at the different locations. Note that Ng et al. (EST, 2011) have published a compilation of spectra of AMS OA components at different locations, and illustrated both their general consistency, and the variability within each class. To clarify, we have changed this sentence to:

“...most of which are generally consistent at many locations throughout the world (Zhang et al., 2007; Jimenez et al., 2009; Ng et al., 2010; Ng et al., 2011).”

R1.11: P6306L7: “. . . by tall mountains ranging in height from 1 to < 3 km” should be “. . . by mountains ranging in height between 1000 m and 2900 m” The height should be expressed in meters rather than kilometers.

Response: We have changed this sentence to:

“...by mountains ranging in height between 1000 m and 2900 m...”

R1.12: - P6306L8-10: “. . . during the summer the region is characterized by a persistent on-shore (westerly) air flow at the surface” From Fig. 2, C1 and C2 there seems to be a sea breeze circulation (i.e., strong winds from the ocean during daytime, with a much weaker land breeze during nighttime, as one would expect) and not a persistent on-shore air flow. I recommend changing the sentence to: “Additionally, during the summer the region has a pronounced sea breeze circulation (westerly) that transports air masses inland from the coast and which is characterized by strong temperature inversions that limit vertical dilution of pollutants.”

Response: we have changed the sentence as suggested.

R1.13: - P6308L9-10: “. . . as well as a high time resolution (Kimmel et al., 2010).” The term “high time resolution” is misleading. Are you talking about the “realtime” acquisition mode presented in (Kimmel et al., 2010)? Couldn't a similar or better time

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resolution also be achieved using the C-AMS, especially since the ToF-extraction frequency is generally higher due to the shorter ion flight path and geometry? Therefore it is not a benefit exclusive to the HR-AMS. Also, since the real-time mode was not used during SOAR, I think DeCarlo et al. (2006) would be the more appropriate citation.

Response: we have changed this citation to DeCarlo et al. (2006) as suggested.

R1.13: - P6308L18-21: "Following the study, various source apportionment methods were applied to SOAR-1 measurements in a number of independent analyses the results of which contrasted sharply with earlier studies in that each consistently indicated that the vast majority of OA mass during SOAR-1 was secondary in nature." Could the changes in air quality in the SoCAB be a result of the Clean Air Act regulation over the last three decades? The resulting move towards cleaner and more efficient combustion in factories and engines might also be responsible for the disagreement with previous studies. A discussion of this would improve the scientific value of the paper.

Response: The causes of the discrepancy between historical source apportionment efforts and those of data from SOAR-1 are complex, difficult to identify conclusively, and beyond the scope of this paper. However, potential causes have been discussed previously in Docherty et al. (2008) which dealt specifically with source apportionment of SOAR-1 OA using a number of different methodologies. However, we note that several of the studies we compared with in Docherty et al. (2008) used data from a carried out one (and not 3) decades before SOAR-1.

R1.14:- P6308L26ff: "This latter analysis attributed over three-quarters of total PMf to secondary processes. . ." Can this latter analysis be found somewhere? It doesn't seem to be part of this study.

Response: To clarify, the sentence has been changed to:

"The analysis of Eatough et al., (2008) which incorporated HR-AMS and A-ATOFMS data attributed over three-quarters of total PMf to secondary processes..."

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R1.15: - P6308L29: (Docherty et al., 2010) should be at least (Docherty et al., 2011), or even (Docherty et al., in preparation). Otherwise it might be difficult to find for the reader of the final publication.

Response: As discussed in response to comment R1.5 above, we have decided to include the key results of PMF analysis of organic aerosols in this manuscript, and thus the paper being referred to in this comment will no longer be submitted. Therefore we have removed that citation from the text.

R1.16: - P6309L3ff: "Williams et al. (2010a) also applied PMF to hourly TAG measurements obtained during SOAR." and "The most comprehensive source apportionment analysis was performed by Docherty et al. (2008b) . . ." and "The five different methods consistently indicated . . ." Why isn't a comparison between these different methods and results part of this publication, especially if these results have been published before separately? I would think this to be an important part of the characterization of the "fine particle composition". Also, how do these components compare to each other from one method to another?

Response: Of the five different methods employed by Docherty et al., 2008b, only the PMF analysis of HR-AMS data resulted in the identification of individual OA components. The remainder provided only an apportionment between POA and SOA. Although comparing the results of apportionment from PMF analysis of HR-AMS and TAG data is certainly of interest, incorporating that discussion in the current manuscript would unreasonably increase its length and would undermine its current content.

R1.17: - P6309L24-26: "Although this fraction was expected to be secondary in nature based on its chemical characteristics, it suggests the presence of yet unknown sources and mechanisms of SOA formation in the SoCAB." Why was it expected to be of secondary origin if it could not be attributed to either? Also, what were the "chemical characteristics" that classified it as "secondary", e.g., which markers etc.?

Response: This comment refers to the part of the paper (now in the introduction) where

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we summarize previously published papers from SOAR-1. The analysis of Stone et al. (2009b) employed chemical mass balance of measured organic molecular marker concentrations during SOAR-1 to apportion the contribution of primary organic aerosol (POA), biomass burning, vegetative detritus, and secondary organic aerosol (SOA) to total organic aerosol. Using CMB, Stone et al., 2009b estimated that primary sources contributed 21 +/- 3

“Although this fraction was expected to be secondary in nature based on both the agreement of the POA apportionment with those of multiple other methods (Docherty et al., 2008; Williams et al., 2010) and its chemical characteristics, it suggests the presence of additional sources and mechanisms of SOA formation in the SoCAB beyond those considered in the Stone et al. (2009b) study, namely aromatic and biogenic precursors”

R1.18: - P6309L27ff: “Although a fraction of SOA is non water-soluble (Weber et al., 2007), SOA generally dominates WSOC in the absence of biomass burning events, as was the case during SOAR-1 (Docherty et al., 2008b), due to its higher degree of oxidation and increased polarity.” Please reword this sentence – the way it is written it is not clear. I guess what you want to say is that secondary organic aerosol in the absence of biomass burning events is mostly dominated by WSOC because of the higher degree of oxidation of the secondary material which also leads to an increased polarization of the organic compounds and therefore to a higher solubility in water – and that this was also the case during SOAR-1, right?

R1.19: - P6310L3: “. . . that the majority (0.56+0.05) of total OC sampled during SOAR-1 . . . ” (0.56 + 0.05) of what? Please use some units or percent. And, I believe this has to be “0.56 ± 0.05” of whatever. How can it be the total OC if the PILS measures only WSOC? Or was this compared to another measurement? And, if this is 56

R1.20: - P6310L8: “For example, Reemtsma et al. observed . . . ” should be “For

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example, Reemtsma et al. (2006) observed . . . ”.

Response: The specific text at issue in R1.18-R1.19 has been removed and the text of R1.20 has been modified as suggested by the reviewer.

R1.21: - P6310L21: How was the contribution of HULIS to total measured (organic?) carbon calculated? Based on the LC-MS/MS measurements? How quantitative is this method?

Response: This text has now been moved to the introduction of our paper, in response to several comments from this reviewer. As it is normally done in such cases, readers can find further details of the cited works in those references.

R1.22: - P6310L24: “. . . they (oligomers) have not been widely identified in ambient aerosols.” Is this because nobody looked for them, because they do not exist in ambient aerosols, or because it is hard to identify them?

Response: This sentence has been clarified as follows:

“Although oligomers have been frequently identified from OA formed in chamber reactions (Kalberer et al., 2004; Tolocka et al., 2004; Gao et al., 2004), they have not been widely identified in ambient aerosols due to their tendency to thermally decompose back to the constituent monomers when subjected to traditional analytical techniques such as GC/MS (Tolocka et al., 2004).”

R1.23: - P6311L5-6: “Oligomeric spectra were not directly observed by the TD-AMS.” Is this a special instrument or simply the HR-AMS interfaced with the TD which will be mentioned later in section 3.3? How would you “identify” an “oligomeric spectrum”? What marker or fragment is generated by an instrument using electron impact ionization?

Response: The reviewer correctly points out that the abbreviation “TD-AMS” has not been defined prior to its use here. As this is the only instance where this abbreviation is used throughout the text, the abbreviation has been removed and replaced with “HR-

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AMS” which is the consistent abbreviation referring to the Aerodyne high resolution aerosol mass spectrometer used throughout the text.

Oligomers in the AMS can produce similar spectra as in other instruments, albeit at much reduced relative intensity due to the higher degree of fragmentation. See for example the spectra of oligomers in isoprene SOA in Figures 6 and 8 of Kroll et al. (EST, 2006). Such spectra were not observed during the SOAR study.

R1.24: - P6311L6ff: “However, the measurements of Huffman et al. (2009) are consistent with their possible presence in aerosol sampled during SOAR-1.” In which regard are they consistent with the presence of oligomers? Would the measurements also be consistent with the “non-presence” of oligomeric species? Again, would it be possible to see oligomers with an instrument using the high fragmentation that comes along with the electron impact ionization?

Response: As discussed in the previous response and exemplified by the Kroll et al. (2006) study, it is indeed possible to identify the presence of oligomers with the AMS, at least in some cases. To clarify, this sentence has been changed to read:

“However, in analyzing thermally-denuded HR-AMS data, Huffman et al. (2009) observed an OA fraction with very low volatility. Although TD measurements have consistently indicated that NR-PM1 sulfate (mostly as ammonium sulfate) has a lower average volatility than bulk OA, a small fraction of OA dominated the residual mass at the highest TD temperatures in both Riverside and Mexico City, consistent with the potential presence of oligomers in aerosol in these locations that may be formed or enhanced due to TD heating.”

R1.25: - P6311L13ff: “..indicating the presence of a residual OA fraction potentially having a lower volatility than (NH4)2SO4.” What kind of organic compound would that be? Is it possible that part of the original organic fraction simply melts inside the thermodenuder to form longer chain organic molecules and oligomers like sugar in a hot pan?

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Response: See response to comment R1.24. As to whether this fraction could be formed as a result of TD heating was addressed by the final sentence in this paragraph which reads

“...the residual mass at the highest TD temperatures in both Riverside and Mexico City, consistent with the potential presence of oligomers in aerosol in these locations that may be formed or enhanced due to TD heating.”.

R1.26: - P6312L3: Why is “total” formatted italic?

Response: “total” has been italicized in this case to highlight that the only comparison of the various carbon measurements conducted during SOAR-1 has been that of Grover et al. (2008) which compared a limited number of total carbon (sum of EC and OC) measurements. Detailed comparisons of OC and OA measurements during SOAR-1 have not been previously presented.

R1.27: - P6313L5: “ 700 ft. elevation” should be “ 210 m elevation”

Response: This sentence has been modified as suggested by the reviewer.

R1.28: - P6313L6: “(PST, i.e.: local time -1 h.)” should be “(PST, i.e., local time -1 h.)”

Response: This sentence has been modified as suggested by the reviewer.

R1.29: - P6313L16ff: “The TEOM50C filter is operated at an elevated temperature to remove particle-bound water and water adsorbed to the filter which can cause high measurement noise.” It is actually the inlet and the instrument/filter that is heated to 50C in the standard TEOM.

Response: This sentence was modified as follows:

“The TEOM50C inlet and instrument filter is heated to 50oC to remove particle-bound water and water absorbed to the filter which can cause high measurement noise.”

R1.30: - P6313L18ff: “However, this results in collateral loss of semi-volatile mate-

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rial (SVM) including ammonium nitrate (NH₄NO₃) and semi-volatile organic material (SVOM) (Eatough et al., 2003).” Eatough et al. (2003) compared a TEOM (standard, 50C) with the RAMS, their modified version of the TEOM which is similar to the TEOMFDMS. However, the loss of volatile compounds in the TEOM inlet was known before, that is why the FDMS module was invented. Patashnik et al. (2001) actually compared the original TEOM with the FDMS TEOM. I recommend strongly citing their paper instead of, or at least together with, Eatough et al., 2003.

Response: The Patashnik et al. (2001) reference has been added at this point. We prefer to also retain the Eatough et al. (2003) as the documentation of similar results by two separate groups using slightly different techniques adds to our confidence on the conclusions.

R1.31:- P6313L24ff: “PM_{2.5} inorganic nitrate (IC-nitrate) and sulfate (IC-sulfate) concentrations were also measured hourly by ion chromatography (Grover et al., 2008)” How? Were they sampled on a filter, or on a denuder, or... You explain the AMS sampling in detail, even parameters that are not important for this publication but leave it to the readers to find out about the other measurements. However, part of an “instrumental comparison” is to compare all used instruments and methods in an equally detailed and thorough way!

Response: The sentence in question has been modified as follows:

“PM_{2.5} inorganic nitrate (IC-nitrate) and sulfate (IC-sulfate) concentrations were also measured hourly by Dionex (Thermo Fisher Scientific, Waltham, MA, USA) GP-IC ion chromatography system (Grover et al., 2008). This system samples ambient aerosol through a parallel plate wet denuder using 0.5mM hydrogen peroxide as a scrubber liquid to remove soluble inorganic gases while water is condensed on remaining particles. Water is passed through a 0.5 mm filter prior to analysis to remove insoluble particles. The solution on the downstream side of the filter is aspirated by a peristaltic pump and sent to a Dionex TAC-ULP1 preconcentration column of an ion chromatograph for

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anion analysis.”

R1.32:- P6315L3ff: “Unique to SOAR-1 is the fact that both of these instruments were operated using specialized sampling protocols including an in-line heated thermal denuder (TD) (Huffman et al., 2008) and vaporizer temperature cycling . . . ” until P6315L18: “ . . . have been removed from both HR-AMS and C-AMS datasets to compare data that were acquired only during routine ambient sampling periods.” Since data measured in these modes is not part of the current publication, neither the times nor the detailed explanations about the operation are needed; therefore, I recommend replacing this paragraph with: “Unique to SOAR-1 is the fact that both of these instruments were operated using specialized sampling protocols including an in-line heated thermal denuder (Huffman et al., 2008) and vaporizer temperature cycling (Docherty et al., 2008a). For the current analyses, data collected during these non-standard sampling intervals (i.e., thermodenuder or with vaporizer temperature below 600C) have been removed from both HR-AMS and C-AMS datasets, and only data are compared that were acquired during routine ambient sampling periods.”

Response: This paragraph has been modified as suggested by the reviewer.

R1.33:- P6315L20: Should be (Sueper, 2009); References, P6348L4-L5

Response: “(Sueper, 2008)” has been changed to (Sueper, 2009) as suggested by the reviewer.

R1.34:- P6316L1: “. . . developed by our group . . . ” Who is “our group”? From the author list/affiliations, at least five groups participated in writing the current manuscript.

Response: The group is that of the first and corresponding authors. The sentence in question has been modified as follows:

“High resolution (HR) spectra from the HR-AMS were analyzed using a custom data analysis module (Pika) developed by the Jimenez group (DeCarlo et al., 2006) in Igor Pro.”

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R1.35:- P6316L1ff: “Elemental analysis (EA) of HR OA spectra was conducted . . . ” How did you obtain high resolution organic aerosol spectra? Was there a separation between organic and inorganic compounds prior to the analysis? Was this a special instrument (I assume AMS) that measured only organic aerosols? Or did you simply analyze high resolution spectra from a conventional Aerodyne AMS only using the organic fragments? In the last case, I suggest changing this to “Elemental analysis (EA) of high resolution AMS spectra was conducted . . . ” since the mass spectra are in no way limited to organic fragments.

Response: The Pika data analysis package of HR-AMS spectra allows the quantification and assignment of elemental composition to each ion present in the high resolution spectrum. As described in the Aiken et al. (2008) paper that is cited at the end of this sentence, the HR-AMS elemental analysis software package uses these assignments to determine the elemental composition of the bulk OA, by using only those ions that contain a carbon atom (with a correction to account for HxO+ ions resulting from OA). The elemental analysis procedure and the associated calculations are discussed in great detail in Aiken et al. (2008), and also in Aiken et al. (2007), which has been added to the citation at the end of this sentence.

R1.36:- P6316L15ff: “The sampling site was located near potential local emission sources . . . ” Since this is supposed to present an overview over the SOAR-1 campaign, a map of the SoCAB and the different sampling locations would be really helpful to the reader.

Response: We have added maps with the topography and the CO emissions in the SoCAB basin to the supplementary information of our paper, and referenced them at this point in the manuscript.

R1.37:- P6316L21: “Since the goal of this study . . . ” Does “this study” refer to “this paper” or “SOAR-1”?

Response: “This study” has been changed to “SOAR-1”.

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R1.38:- P6316L23: “. . . in order to evaluate to what extent, these local sources contributed . . . ” Should be: “. . . in order to evaluate to what extent these local sources contributed . . . ”

Response: The comma in the sentence in question has been removed as suggested by the reviewer.

R1.39:- P6317L13-15: “Similar mass concentrations and the strong correlation observed here highlight the spatial consistency of PMf mass in inland regions of the SoCAB and suggest that contribution of PMf mass from very local sources is minor.” If the wind was predominantly westerly (as indicated) and there are no dominant local sources, what are the sources in the SoCAB? Marine? Or does “local” mean that there has to be a factory right next to the measurement station?

Response: The emphasis here and indeed the purpose behind comparing on- and off-site measured PMf mass concentrations was to evaluate those sources immediately local to the sampling site such as the upwind freeway, the water cooling towers, and the agricultural greenhouses. Obviously there are large PMf sources in the entire SoCAB basin. To clarify the sentence in question has been changed to:

“Similar mass concentrations and the strong correlation observed here highlight the spatial consistency of PMf mass in inland regions of the SoCAB and suggest that contribution of PMf mass from sources within a few miles of the sampling site is a minor fraction of the measured concentrations.”

R1.40:- P6317L18: What are “low-mass” particles? I suggest using “small particles” or “particles with diameters smaller than nm” instead.

Response: “low-mass particles” has been changed to “ultrafine particles”.

R1.41:- P6318L6ff: “Wind speed and direction were highly repetitive displaying little day-to-day variation. Wind speed was low (0.2 ms⁻¹) and its direction variable during the late evening and overnight periods. On average, air masses arrived to the site from

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the south during the night, while maximum wind speeds (2 ms^{-1}) were associated with westerly winds during the warmest part of the day.” This is called sea breeze circulation and is a well-known daytime climatology in coastal areas, especially in the summer. The corresponding night time climatology is called land breeze circulation, but is generally much less pronounced than the sea breeze (like in your case).

Response: The passage in question has been changed to:

“Inland regions of the SoCAB including Riverside were characterized by a prominent sea breeze circulation during SOAR-1. Nighttime wind speeds were low (0.2 m s^{-1}) with variable, generally southerly, direction while maximum speed (2 m s^{-1}) westerly winds were experienced during the warmest part of the day.”

R1.42:- P6318L21ff: “Although the SoCAB is often severely impacted by wildfires that can significantly increase particle concentrations . . . ” I don’t really understand what this has to do with the title of this section which is “Meteorology and gas phase pollutants”, and not “Meteorology, gas phase pollutants and impact from wildfires on the particle composition during SOAR-1”.

Response: The title of section 4.2 has been changed to “Meteorology, gas-phase pollutant concentrations, and lack of biomass burning events during SOAR-1”.

R1.43:- P6319L4-6: “The TEOM and ToF-AMS differ both in size cut and the measurement of refractory and semi-volatile material (SVM). Both TEOM instruments measure PM_{2.5} and refractory material.” The size fraction measured by a TEOM depends mostly on the inlet used, i.e., it can be PM₁₀, PM_{2.5} or PM₁. Also, a TEOM does not measure “PM_{2.5} and refractory material” but simply the total PM_{2.5} mass if used with a PM_{2.5} sampling inlet. An AMS measures only non-refractory species, while a standard TEOM measures everything except semi-volatile species that evaporate below 50C. The TEOMFDMS is not supposed to be selective and should simply measure the whole mass fraction, in this case PM_{2.5}.

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Response: The sentence in question has been changed to:

“As discussed above, the TEOMs and ToF-AMS differ both in effective size cut and the measurement of refractory material and SVM. Both TEOM instruments sampled through a PM_{2.5} cyclone (Grover et al., 2008) and their reported concentrations include any refractory material contained within this size fraction.”

R1.44:- P6319L12: Again, I would cite (Patashnick et al., 2001) instead of (Eatough et al., 2003).

Response: We have added a citation to Patashnick et al. (2001), but also kept the citation of Eatough et al., (2003), for the reason explained in response to comment R1.30 above.

R1.45:- P6319L19-20: “Because of SVM volatilization, ToF-AMS measurements can either be greater (high SVM) or less than (low SVM) those of the TEOM50C.” Because this sentence is difficult to understand, I suggest changing it: “Depending on the actual composition and volatility of the semi-volatile material TOF-AMS measurements can either be larger (high volatility of SVM) or smaller (low volatility of SVM) than those obtained by the TEOM50C”

Response: This sentence has been changed to that suggested by the reviewer.

R1.46:- P6319L24: What was the inlet cut-off of the Sunset 1 and Sunset 2 EC/OC monitor?

Response: Both Sunset1 and Sunset2 sampled through individual PM_{2.5} cyclones. Based on the reviewer’s comment regarding more completely presenting information regarding those instruments providing the measurements which served as the basis of the comparisons contained in the manuscript, the size cut of each Sunset instrument has been specified in the Experimental section.

R1.47:- P6319L26: “Although non-EC refractory material was not measured during SOAR-1. . . ” Obviously it was measured (for example by the TEOM), just not quanti-

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fied separately.

Response: The reviewer is technically correct and the sentence has been changed to “Although non-EC refractory material was not separately quantified during SOAR-1. . .”

R1.48:- P6319L27: Is this the previously mentioned A-ATOFMS or a different instrument?

Response: Two different ATOFMS instruments were deployed during SOAR-1: a standard ATOFMS and a then-new aircraft-ATOFMS (A-ATOFMS). The estimate of aged sea salt and dust was obtained from the standard ATOFMS instrument, as detailed in the Qin et al. reference cited at this point.

R1.49:- P6319L28: “The concentration of refractory material estimated using ATOFMS measurements” Does this estimate include or exclude EC contributions? How could concentrations be calculated/estimated based on ATOFMS measurements, which are not quantitative? What are the uncertainties of these estimates?

Response: The use of “refractory material” in this case was an error as this sentence refers specifically to non-EC refractory material, the composition of which was described in the previous sentence. Accordingly, “refractory material” in this sentence has been changed to “non-EC refractory material”.

R1.50:- P6320L4ff: “Similarly, Chow et al. (1994) obtained an estimate of $1.6 \mu\text{g m}^{-3}$ in Rubidoux. This latter estimate did not consider contributions from metals or sea salt and is, therefore, likely be a lower bound estimate of non-EC refractory material.” What method was used for these measurements? If sea salt and metals (which are an integral part of dust) were excluded, what was the chemical composition of the remaining fraction?

Response: This text has been changed to:

“Similarly, Chow et al. (2004) used measured concentrations of aluminum, silicon,

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calcium, and iron to obtain an estimate of $1.6 \mu\text{g m}^{-3}$ for crustal material in Rubidoux during the summer. This latter estimate did not consider contributions from sea salt and is, therefore, likely be a lower bound estimate of non-EC refractory material.”

R1.51:- P6320L17ff: “Daily minimum concentrations” A reference to the diurnal plot (Fig. 3c) in the text would be nice. Also, a short explanation or discussion of this topic might be a good idea (i.e., daytime/nighttime NO_x chemistry).

Response: A reference to Fig. 3c has been included in this discussion as follows:

“Diurnal profiles of each measurement (shown in Fig. 2c) are also similar with prominent maxima at 0800, concurrent with morning rush-hour traffic, and a second smaller maximum in the early afternoon.”

R1.52:- P6320L22: “AMS+EC and TEOMFDMS are highly correlated” I’m not sure that $r^2=0.77$ qualifies as “highly correlated”. Fig. 3E is not discussed at all, although it shows (not surprisingly) that AMS+EC and TEOM are only marginally correlated, if at all. I actually find the differences between the TEOMFDMS and the AMS instruments very interesting. I think the authors should have investigated these differences more deeply. In my opinion an elaborate discussion of this is necessary, especially in an instrumental comparison paper. For example, why do the measurements agree for some periods while for some other times the TEOMFDMS time series has a peak in the morning and for others the TEOMFDMS shows continuously higher mass concentrations. Could different air masses explain these differences, or are they traffic (and wind direction) related?

Response: To the reviewer’s first point, the use of “highly correlated” with an $r^2 = 0.77$ is perhaps overstating the case and has been changed to “well correlated”. To the second point that Figure 3E is not discussed at all, the following sentences have been added at the end of this paragraph:

“A similar plot of HR-AMS+EC versus TEOM50C is shown in Fig. 2e. The slope in

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this case is near or higher than unity depending on the choice of intercept. However, these results are likely influenced by the much lower correlation ($r^2=0.46$) between the measurements caused by the loss of SVM from the TEOM50C.”

Finally, as stated in the text, differences between measured AMS+EC and TEOMFDMS concentrations could be due to the different particle size fractions sampled by each instrument (i.e., PM1 or PM2.5) or the presence of non-EC refractory material within the PM1 size fraction. Any investigation into these differences is difficult in the absence of directly-measured time series for these components and would at best be speculative.

R1.53:- P6320L25: “24-h average TEOM50C measurements ($15.0 \mu\text{g m}^{-3}$; -4.9 - $39.7 \mu\text{g m}^{-3}$) are lower than those of . . . ” Should be “($15.0 \mu\text{g m}^{-3}$; 4.9 - $39.7 \mu\text{g m}^{-3}$)”, right? Or did you really measure negative concentrations of $-5 \mu\text{g m}^{-3}$ with the standard TEOM? If so, then these values should be removed from consideration since they are most likely instrumental artifacts. Such strong negative measurements from a TEOM are often a sign for a measurement bias after filter change or water in the system. And again, it is not surprising that TEOM measurements are much lower than TEOMFDMS measurements, that’s why the FDMS module was developed (Patashnick et al., 2001). If the latter is the case, then the above statement should be changed to “($15.0 \mu\text{g m}^{-3}$; $<\text{LOD} - 39.7 \mu\text{g m}^{-3}$)”.

Response: A single negative value (-4.9) was present for the TEOM50C. Following the reviewer’s suggestion, this value was removed and the new average and range (15.1 ; 2.0 - $39.7 \mu\text{g m}^{-3}$) has been used.

R1.54:- P6321L1-L2: “The contribution of SVM, however, appears to vary both throughout the day as well as over extended periods during SOAR-1.” Again, it would be nice to see a scientific discussion of these changes somewhere in the manuscript.

Response: for clarity we have rephrased this text to:

“Interestingly, the contribution of SVM varies during SOAR-1 throughout the day as well

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as over extended periods.”

The interpretation of these changes in time, to the extent that it can be directly investigated using the available data, was already discussed in the next paragraph and Figure S2 of the manuscript. The text in question has been clarified in response to comment R1.58 below.

R1.55:- P6321L2-L4: “On a daily basis, the diurnal profile of TEOM measurements displays many of the same features as the other measurements including maximum concentrations during the morning.” In my opinion it is not the similarities but the differences that are noteworthy because within them information about the SVM can be found that would not be accessible without the two measurements! If this is not used, I actually don’t see any reason to compare a standard TEOM with a TEOMFDMS, especially when using the same inlet cut-off. That the TEOM evaporates the SMV due to the heated inlet has been known for more than a decade and is in no way surprising and in my opinion not a noteworthy feature.

Response: Again, these differences were already discussed in the next paragraph and Figure S2 of the manuscript. The text in question has been clarified in response to comment R1.58 below. While the losses of SVM by the TEOM50C were known already, to our knowledge they had not been compared to fast chemically-resolved measurements as it is done in this paper. Thus we believe there is value in retaining the discussion of the TEOM50C data within this manuscript.

R1.56:- P6321L4ff “As detailed in Table S2, TEOMFDMS and TEOM50C measurements are more similar during the first half of SOAR-1 (P1: 7/18–8/1) whereas these measurements exhibit a larger deviation during the latter half (P2: 8/2–8/14) thereby suggesting a larger contribution of SVM, or a variation in instrument performance.” If it is because of instrument performance (which would actually call into question the whole comparison), what could be the reasons for this difference? Besides, why were these time intervals chosen and not the ones presented in Fig. 3A and 3B?

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Response: Again, these differences were already discussed in the next paragraph and Figure S2 of the manuscript. The text in question has been clarified to read:

“Moreover, as detailed in Table S2, the contribution of SVM is substantially higher during P2 (8/2-8/14) as indicated by the larger difference between TEOMFDMS and TEOM50C measurements. This general trend can also be observed in TS shown in Fig. 2a and 2b.”

R1.57:- P6321L8-L10 “The correlation between TEOM50C and AMS+EC measurements ($r=0.46$) is significantly lower than that obtained from comparison of TEOMFDMS and AMS+EC measurements.” I suggest changing this to: “The correlation between TEOM50C and AMS+EC measurements ($r=0.46$) shown in Fig. 3E is significantly lower than that obtained from comparison of TEOMFDMS and AMS+EC measurements, most likely because of the loss of semi-volatile material within the TEOM50C.”

Response: This sentence was clarified as recommend by the reviewer:

“A similar plot of HR-AMS+EC versus TEOM50C is shown in Fig. 2e. The slope in this case is near or higher than unity depending on the choice of intercept. However, these results are likely influenced by the much lower correlation ($r^2=0.46$)”

R1.58:- P6321L25: “24

Response: To the reviewer’s first comment, “24

Additionally, in order to lend clarity to the paragraph that is the subject of both this reviewer’s comment and those of Reviewer 2, this passage has been changed to read: “A majority of SVM measured during SOAR-1 is NH_4NO_3 . As shown in Fig. S10, the agreement between TEOM50C and TEOMFDMS measurements improves substantially during both P1 and P2 when TEOM50C measurements are supplemented with $\text{PM}_{2.5}$ NH_4NO_3 concentrations (TEOM50C + NH_4NO_3). NH_4NO_3 concentrations were calculated using IC-nitrate measurements and assuming its full neutralization by

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NH_4 , 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 + NH_4NO_3 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 NH_3NO_4 during the latter sampling period. By extension, if we assume that the remaining difference between TEOMFDMS and TEOM50C + NH_4NO_3 is due to volatilization of SVOM, this comparison suggests that its contribution is relatively consistent at approximately 24

R1.59:- P6322L7ff: “HR-AMS and C-AMS measurements are plotted in Fig. 4. Total NR-PM_{10} from both ToF-AMS instruments are shown in Fig. 4a along with TEOMFDMS $\text{PM}_{2.5}$ for comparison.” It is actually quite confusing, that the same measurement is once called AMS+EC (Fig. 3) and later HR-AMS+EC (Fig. 8). It is even more confusing that the symbols used in Fig. 3 for AMS+EC are the same symbols that are used in Fig. 4 for HR-AMS and in Fig. 8 for HR-AMS total (without the EC). Because of the size of the symbols and the small contribution of EC, the reader could get the impression that this is actually the same time series.

Response: To clarify, this sentence has been changed to read:

“HR-AMS total is also plotted against C-AMS total in Fig. 3b while speciated HR-AMS measurements are plotted against those of the C-AMS in Fig. 3c-3g along with the results of linear regression in each case.”

Additionally, the symbols representing HR-AMS and C-AMS total NR-PM_{10} have been changed in Fig. 3a as suggested by the reviewer.

R1.60:- P6322L14-15: “. . . the zero of both ToF-AMS instruments was checked regularly by sampling through a HEPA filter.” This part of the sentence does not make sense – what is the “zero” of an instrument? And how could one measure the “zero” of an instrument, especially an AMS, by using a HEPA capsule? All you can measure this

C9635

way is the gas phase and instrument background, which depends on the instrumental conditions and parameters. Please reword the second part of this sentence.

Response: We disagree with the reviewer on this point, although the wording can be made clearer. It is a standard practice to check the zero of many instruments, including the AMS, by sampling air in which the analyte of interest has been removed. E.g. this is routinely done for gas-phase analyzers such as for CO or ozone. In the case of the AMS, when a HEPA filter is put in the sampling line before the AMS, all particles are removed, and the AMS still reports a concentration. If the instrument and the fragmentation table used in the data analysis have been adjusted properly, this measurement is just noise around an average of 0 ug m⁻³. This is what we are describing in this sentence, which we perceive to be an every day operation in the AMS community and thus one that does not require a detailed explanation in our paper.

For clarity, this sentence has been changed to read:

“...an intercept of zero was confirmed for both ToF-AMSs by sampling ambient air through a HEPA filter and measuring the resulting signal of particle-free air.”

R1.61:- P6322L22-25: “. . . slightly better than those obtained from the comparisons of Salcedo et al. (2005) and Hings et al. (2007) despite the fact that these previous studies compared 30 min average measurements while five minute averages were compared here.” I think this comment should be removed since it is misleading the way it is written. As you state yourself, Salcedo et al. compared measurements of instruments separated from one another and using different inlets. Hings et al. compared two instruments with different detectors - a quadrupole mass spectrometer and a Time-Of-Flight instrument. Therefore, it is not surprising that these measurements did not match each other as well as the measurements of two ToF-instruments, regardless of their different sampling intervals. If the authors really want to compare their results with previous AMS comparisons, they should also explain these instrumental details more clearly.

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Response: We disagree that the text is misleading as written. The distance between the inlets in the Salcedo et al. case (which is a publication of the Jimenez group) was minor and very unlikely to have caused differences in the sampled concentrations. E.g. when we have tried to measure vertical gradients by using an instrument and several inlets at different heights, it has turned out to be an extremely difficult proposition, due to the very weak gradients caused by the very slow dry deposition of submicron aerosols. However, to more clearly convey the points of the text in P6322 L21-20 and P6223 L1-2, we have reworded it to:

“Results obtained here are similar to or, in some cases, slightly better than those obtained from the comparisons of Salcedo et al. (2005) and Hings et al. (2007) despite the fact that these previous studies compared 30 min average measurements while five minute averages were compared here. Possible causes of variability within instruments in previous studies include the use of different inlets in the case of Salcedo et al. (2005) and the use of a Q-AMS and a C-AMS by Hings et al. (2007).”

R1.62:- P6323L18-L19: “In sharp contrast to the consistency and high correlation of ToF-AMS SO₄ measurements . . . ” I don't think the comparison is fair – you're comparing measurements from two similar instruments with similar size ranges connected to the same inlet to measurements obtained by a different technique and having a different size range.

Response: see response to R1.63.

R1.63:- P6323L21-L23: “Due to the amount of scatter, the choice of intercept has a large influence on regression results. For example, standard linear regression provides a slope of 0.51 with an intercept value of 1.44 while the recovery slope is 0.82.” This is a very theoretical discussion about statistics. However, when looking at Fig. S3E it seems questionable whether this plot simply shows scatter or different fractions (e.g., different size ranges), and furthermore if a linear regression is useful in this case. Section 4.6.; also

C9637

Response: This comment and R1.62 are being addressed together here. The reviewer's points are well taken. The HR-AMS and IC-sulfate do indeed differ in the effective size range of particle sampling, which may lead to some of the scatter in Fig. S3E. However, the low degree of correlation among SO₄ was also additionally observed between PC-BOSS and IC sulfate measurements (Grover et al., 2008). As a result, we are inclined to keep the majority of the original text with some modifications as specified below. The passage in question now reads:

“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 Grover et al. (2008) 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.”

R1.64:- P6324L19: “. . . still exist such as different sampling lines, etc.” It would be helpful to at least briefly discuss the inlet systems of the two EC/OC analyzers, especially in sight of the partial agreement between the HR-AMS OC and the Sunset

C9638

1 OC and the disagreement with the Sunset 2 OC. This becomes even more urgent when suggesting that instrumental biases and problems might be responsible. In fact, since instrumental comparison is a topic of this manuscript, a detailed discussion about the inlets used as well as inlet- and line losses for all instruments is essential.

Response: The following additional information regarding the different inlet systems for the EC/OC analyzers (e.g., regarding flowrate, size fractionation, denuder usage) has been provided in the experimental section.

“Briefly, for Sunset1 sample collection was accomplished at a flow rate of 24.0 L min⁻¹ through an inlet equipped with a sharp-cut PM_{2.5} cyclone and a carbon impregnated parallel plate denuder designed to remove gas-phase organic compounds upstream of the collection filter. For Sunset2, aerosol was sampled at 8 L min⁻¹ through a PM_{2.5} sharp-cut cyclone and a similar parallel plate charcoal impregnated filter denuder both of which were supplied by the manufacturer.”

R1.65:- P6324L21ff: “Since there was always a significant OC background in Riverside during SOAR-1 which almost never went below 2.5 $\mu\text{gC m}^{-3}$, the results of regressions calculated with both a free and fixed-zero intercept are shown.” The whole sentence and especially the justification for performing both fixed zero and floating intercept does not make sense. If there is a significant background then this background should be seen by both instruments, assuming filter measurements have been removed. Using a fixed-zero and a free intercept can tell about a BIAS or instrumental issues/backgrounds, but should not be affected or influenced by an ambient background! This can actually be seen by the very small intercept and the very similar slope of the regression!

Response: We agree with the reviewer in this case and have removed the results of linear regression with a floating intercept. Additionally, the text in question was changed to read:

“HR-AMS OC is plotted against Sunset1 measurements in Fig. 4a along with the re-

C9639

sults of linear regression calculated using a fixed-intercept of zero which results in a slope of 1.08 and moderate correlation ($r^2=0.53$)."

R1.66:- P6325L3: ". . . the inability of the PILS-OC to measure large insoluble particles." I think this statement needs a citation. The PILS-OC, its operation, abilities and instrumental problems are not that widely known. I suggest (Peltier et al., 2007).

Response: Peltier et al. (2007) was added as a reference as suggested by the reviewer.

R1.67: - P6325L7ff: "HR-AMS and Sunset 2 OC are compared in Fig. 5c. In this case the" Again, I don't think a linear regression is appropriate for a scatter cloud.

The $r^2=0.36$ of the zero-intercept tells you that there seems to be no real correlation. P6325L17: "The linear regression results are relatively insensitive to the choice of intercept". They are the same to within the errors of the fits.

Response: As discussed in response to comment R1.66, we have removed the regressions with a non-zero intercept, since they do not add information given the nature of our datasets, and they seem to create significant clutter and confusion.

We note that the Pearson correlation coefficient does not depend on the type of regression made, as it is the result of a calculation separate from the regression ones.

R1.68:- P6325L26-27: "EC, OC, and TC measured by Sunset 1 are plotted against corresponding Sunset 2 measurements in Fig. S4. Among these measurements, EC is the most highly correlated with $r^2 = 0.77$. Even in this case, however, both instruments are not equivalent as demonstrated by the consistent slope of 0.63–0.64 using linear regression in the presence and absence of a fixed-zero intercept." This part is difficult to understand. I suggest changing to: "EC, OC, and TC measured by Sunset 1 are plotted against corresponding Sunset 2 measurements in Fig. S4. Among these measurements, EC shows the highest correlation with $r^2 = 0.77$. The consistent slope of best fit lines (whether using a fixed zero intercept or not) of 0.63-0.64 shows a systematic difference between the two measurement techniques."

C9640

Response: This sentence was modified along the lines suggested by the reviewer. The revised text reads:

"Comparison of EC, OC, and TC measured by both Sunset instruments (ref. Fig. S12) reveals a substantially lower degree of correlation in each case than that observed between corresponding ToF-AMS NR-PM1 OA measurements. EC (Fig S5a) is the most highly correlated of the Sunset measurements with an $r^2=0.77$. The consistent slope of best fit lines (whether using a fixed intercept or not) of 0.63-0.64 shows a systematic difference between the two EC measurements."

R1.69:- P6326L20ff: "It should be noted however, that even during these times, the difference between HR-AMS and the Sunset OC measurements are mostly within ± 15

Response: We disagree with the reviewer's assessment that the diurnal profiles barely resemble each other while acknowledging that some additional discussion on this point is warranted. The passage in question was changed to read:

"Overall, the average discrepancy between HR-AMS and Sunset1 OC is 10

R1.70:- P6326L26ff: "In summary, the differences between the base Sunset and Sunset +SVOC measurements are as large as those observed between the HR-AMS and either base measurement." Table S3 actually gives the impression that the differences between (Sunset 2 +SVOC) and the Sunset base measurements are always higher than the differences between HR-AMS and the Sunset base measurements, especially between HR-AMS and Sunset 1.

Response: The sentence in question was revised to read: "Table S3 provides a summary of statistical comparisons between all OC measurements including the difference between HR-AMS and Sunset OC measurements. As this table shows, not only is the correlation between corresponding Sunset OC measurements equivalent to or lower than the correlation between HR-AMS and Sunset OC measurements, but the differences between either base Sunset or Sunset2+SVOC concentrations are also as large

C9641

or larger than those observed between HR-AMS and Sunset measurements. Diurnal profiles of both HR-AMS and the various Sunset OC concentrations (Fig. S13a) and the absolute difference between the HR-AMS and each Sunset measurement (Fig. S13b), highlight similarities and differences among each OC measurement.”

R1.71:- P6327L20ff: “Diurnal profiles of OM/OC and O/C ratios are broadly anti-correlated with H/C.” This is just a consequence of chemistry, fragmentation and the way atomic O/C, H/C and OM/OC ratios are calculated, and should always be similar. A shift towards more hydrogenated (and more volatile and therefore less abundant in the particle phase) compounds will cause the H/C ratio to go up and the OM/OC ratio to go down. If such a trivial statement is made it should at least be explained and not be presented as an amazing result, which it is not!

Response: We disagree with the reviewer on this point. This result is expected, once it is established (as it is done in this study) that other heteroatoms such as N and S are only minor contributors to the organic aerosol mass. If either N or S were major contributors to OM (as some published studies have argued for other locations), then these diurnal profiles could show different trends than the ones apparent here. In order to reflect this, the sentence was changed to read:

“Diurnal profiles of OM/OC and O/C ratios are broadly anti-correlated with H/C, as expected due to the low contributions of N and S to OM in this study (see below).”

R1.71:- P6328L16-17: “The intercept is substantially lower than observed in Mexico City, but its value is poorly constrained as no measurements were observed at very low average O/C due to the continuous dominance of SOA during SOAR-1.” Does this imply that organic aerosol dominated by HOA, which should result in a high H/C and a low O/C ratio, is not secondary? Maybe it would be better to speak about SOA dominated by oxidized organic aerosol (OOA).

Response: We are confused by the reviewer’s comment. It is well-established that HOA is dominated by POA in urban areas, and is not of secondary origin (see e.g.

C9642

Zhang et al., EST 2005; Zhang et al., ACP 2005; Lanz et al., ACP 2007; Ulbrich et al., ACP 2009; Ng et al., EST 2011, and references therein). No change has been made to the text at this location.

R1.72:- P6328L29ff: “Similarly S from species such as sulfonic acids will be captured by our analysis, but S arising from organosulfates (OS) is lumped with “sulfate” and is not separately quantified in standard AMS field analysis (Farmer et al., 2010).” How? Didn’t Farmer et al. (2010) show that these species will produce ions similar to those found from organosulfates? Furthermore, according to (Farmer et al, 2010), the only ion suitable for estimating an upper limit for organosulfates is produced by organosulfates as well as by sulfonic acids.

Response: Farmer et al. (2010) investigated ions produced from the fragmentation of laboratory organonitrate (ON) and organosulfate (OS) standards and the ability to distinguish these compounds from inorganic sources of nitrate (predominantly NH_4NO_3) and sulfate (predominantly $(\text{NH}_4)_2\text{SO}_4$). In each case, the nitrogen and sulfur containing fragments present in ON and OS spectra were the same as those characteristically found in the inorganic spectra. With regard to OS, the sample analyzed in that work created a single ion (CH_2SO_3^+) that was not present in the $(\text{NH}_4)_2\text{SO}_4$ spectrum but the intensity of this ion was very low compared to those of the “nominally inorganic” ions, and its mass defect was not sufficiently large enough to separate from a prominent organic fragment in ambient mass spectra. It was, therefore, an insufficient marker to directly enable quantification of OS in ambient air. These details are already clearly explained in the reference provided (Farmer et al., 2010). However, mass spectra of ambient samples and particularly those from SOAR-1 clearly show CH_3SO_2^+ signals, the mass defect of which provides sufficient separation from prominent organic fragments to be isolated. In the case of SOAR-1, this fragment was likely to have been partly or even wholly due to the presence of MSA.

R1.73:- P6329L6: “S/C was calculated using a calibration factor of 1.0. . .” What kind of calibration factor is that and where does it come from?

C9643

Response: With regard to HR-AMS elemental analysis, calibration factors were determined from the studies of Aiken et al. (2007, 2008) and are based on a regression of the actual atomic ratios of multiple standards to the measured values using the HR-AMS. The need for calibration factors arises due to the possibility of biases in the measured (or raw) spectrum due to the influence of unimolecular decomposition reactions, in which a fragment with an electronegative atom such as oxygen may have a larger tendency to become the neutral fragment rather than the resulting cation. Those calibration factors are of the order of 1. The calibration factor of S/C has not been determined in the laboratory to our knowledge, and as a result a calibration factor of one was used. We believe that this topic was already appropriately described in the manuscript, with further details available in the reference provided in the text (Aiken et al., 2007).

R1.74:- P6329L27ff: "In summary, these estimates suggest that neglecting ON and OS in the standard EA method results in minor difference in H/C, substantial increases in O/C and N/C, . . ." What are the uncertainties of these calculations?

Response: The uncertainties would be of the order of a fraction of the corrections, which are given numerically in P6329.

R1.75:- P6330L7ff: "The majority of EC in the SoCAB during SOAR-1 should be due to diesel vehicles (89

Response: We have repeated these calculations using updated data, but we still obtained the same result. We have updated this text with new references to read:

"The majority of EC in the SoCAB during SOAR-1 should be due to diesel vehicles (89

R1.76:- P6330L12: "EC concentrations decline after 0800. EC displays minimum concentrations in the mid afternoon while OA increases again during the mid afternoon to another maximum at 1300." Why is that? Are trucks (diesel vehicles) only driving in the morning? If they are the major source for EC, shouldn't EC values be high as long

C9644

as there is traffic?

Response: The decrease in EC concentrations is likely dominated by increased dilution due to both an increase in the height of the boundary layer due to heating at the surface and increased wind speed. The sentence was changed to reflect this and now reads:

"EC concentrations decline after 0800 mostly due to increased dilution due to breakdown of the nocturnal boundary layer at this time causing rapid downward mixing of cleaner air from aloft (Snyder et al., 2008)."

R1.77:- P6330L15ff: "However, the relative contribution of OA increases in the afternoon, as OA contributes 43

Response: The text in question has been changed to read:

"While absolute OA concentrations in the morning (avg. of 11.9 $\mu\text{g m}^{-3}$) and mid afternoon (11.4 $\mu\text{g m}^{-3}$) are similar, the relative contribution of OA to HR-AMS+EC increases from 43

R1.78:- P6330L21ff: "Source apportionment of OA during SOAR-1 is beyond the scope of the current manuscript and so is not discussed here but is the subject of an upcoming manuscript (Docherty et al., 2010)." Why? Isn't that essential for understanding the fine particle composition? Again, the authors need to focus the manuscript. If it is just an instrumental comparison, then the title as well as the instrumental comparison and discussion should reflect that accordingly. If the composition of the fine particle mass is also a topic of this manuscript (as reflected by the current title), then it should be discussed in detail and elaborately, especially since this has already at least partially been published in (Docherty et al.: Apportionment of Primary and Secondary Organic Aerosols in Southern California during the 2005 Study of Organic Aerosols in Riverside (SOAR-1), 2008.

Response: As stated in response to comment R1.5 above, we have included the results of PMF analysis of the organic aerosol spectra to the revised manuscript.

C9645

R1.79:- P6331L6ff: "This is consistent with its non-volatile nature and also reflects the ubiquity of particulate SO₄ in inland regions of the SoCAB, consistent with a larger fraction from non-local production through regional secondary processes." If you had westerly winds during daytime with average wind speeds between 5 km/h and 10 km/h, where are the sources, if not within the SoCAB? Is it all of marine origin?

Response: Information regarding the sulfate sources in the SoCAB was already contained within the Introduction of the ACPD manuscript (P6306 L25-27 and P6307 L1-6). The relative importance of different sources of sulfate in the SoCAB are actually unclear and are the subject of ongoing research by several groups (not including ours), and we already cite several recent papers such as Vutukuru and Dabdub (2008) and Huang et al. (2010) within that text in the introduction. We are aware of at least two other papers in preparation on this topic.

R1.80:- P6332L3: "Due to high ammonia emissions upwind and concentrations in the area of Riverside, . . ." Where or what are these ammonia emissions coming from exactly?

Response: Sources of ammonia in the immediate vicinity of Riverside were already discussed on P6306 L18-25 of the ACPD manuscript. Nevertheless, the passage in question has been modified as follows to include a discussion of the sources of ammonium immediately upwind of Riverside.

"Ammonia (NH₄) is the principal anion in ambient aerosols, particularly in the SoCAB due to high emissions from a variety of sources. NH₄ emissions in the basin originate from livestock and soils as well as from mobile, industrial, and domestic sources with livestock contributing approximately one-third of total NH₄ emissions (Chitjian and Koizumi, 2000). The Chino/Ontario area is directly upwind of Riverside under prevailing wind conditions and is one of the most dense dairy cow populations in the United States having approximately 300 dairies with over 250,000 cows. Although a number of dairy operations have been relocated out of the basin in recent years, 314 operations

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remained as of 2002 with the vast majority (87

R1.81:- P6333L16ff: "OS and ON have the largest impact on the HR-AMS ion balance with the regression slope increasing from 0.86 to 0.94 when the estimates of OS and ON are used in the charge balance calculation." I think this is a very important result and should be emphasized more. This allows calculation, or at least estimation of contribution from ON and OS, which are quantities currently of great interest to the community in general.

Response: We agree with the reviewer that this is an important result, and in fact it was already summarized in the last sentence of the abstract and the last sentence of the conclusions, which constitute sufficient emphasis in our opinion. We caution, however, that this fraction may be very different at other locations due to different proportions of inorganic anions/cations, ON, OS, and amines. Given that the latter 3 constituents are poorly understood and quantified by the community at present, we would not want to give the impression that the amounts at other locations may be similar to the estimates from this study.

R1.82:- P6336L6-7: ". . . while amines made a very minor impact." Since you didn't really measure or quantify amines, I suggest changing this to: ". . . while potential contribution from amines was very minor."

Response: We did measure an OA component that likely contains amine groups, and this is discussed in P6333 L11-15 of the ACPD manuscript.

R1.83:- Fig. 3 and 4: Although it is hard to tell it looks like the time series for the AMS+EC in Fig. 3 is the same time series labeled HR-AMS in Fig. 4. I would suggest the authors check the plots and potentially change the symbols.

Response: The time series are indeed different and the symbols were changed to represent this difference as also suggested by this reviewer in comment R1.59.

R1.84:- Fig. 9: The diurnal profile for ammonium is barely visible – please use a

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different (darker) color.

Response: The color of the ammonium diurnal profile has been changed as requested.

R1.85:- Fig. 9, 10, S3B: Why do NR-PM1 nitrate (measured with an AMS) and HRAMS nitrate in all three plots not only have different diurnal patterns but also different mass concentrations (i.e., a maximum of $8 \mu\text{g m}^{-3}$ in Fig. 9, $13 \mu\text{g m}^{-3}$ in Fig. 10 and $9 \mu\text{g m}^{-3}$ in Fig. S3B)? The same is true for the diurnal profiles of NR-PM1 sulfate in Fig. 9 and Fig. S3D, although the differences are much smaller.

Response: The diurnal profile of NO_3 shown in Fig. 10 actually represented average hourly concentrations during only P2, during which time NO_3 concentrations were substantially higher as discussed in the text and has been replaced with the profile obtained using NO_3 concentrations throughout the duration of SOAR-1. The profiles in Fig. 9 and S3B were only slightly different. The same is true of SO_4 profiles Fig. 9 and S3D.

R1.86:- Fig. 10 and 12: The quality of these figures is poor – please replace these with figures with a higher resolution.

Response: These plots have been replaced with higher resolution images.

R1.87:- Fig. 12: The diagrams in Fig. 12 are a bit difficult to understand, and I believe there are some mistakes, either in the calculations or more likely in the presentation. First of all, the units are missing - I assume, the top number is $\mu\text{g m}^{-3}$, and the number below

Response: To clarify, units have been added to the numbers presented in this figure and an error in calculating the $\text{NRPM}_{2.5-1}$ concentration has been corrected. Finally, as suggested by the reviewer, the order and labels of the pie charts has been changed as follows:

the order of the pie charts has been reversed with the $\text{PM}_{2.5}$ composition based on several different instruments shown on the left (Figure 12A), while the composition

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based on HR-AMS measurements has been shown on the right (Figure 12B). This change has been reflected in the text as well, and; the title of the composition based on HR-AMS measurements has been changed to “ $\text{PM}_{2.5}$ (based on PM_1)” again as suggested by the reviewer.

R1.88:- Table S1: While everywhere else in the publication it is HR-AMS and C-AMS, in this table the instruments are referred to as HR-ToF-AMS and C-ToF-AMS. Be consistent.

Response: “HR-ToF-AMS” and “C-ToF-AMS” in Table S1 has been changed to “HR-AMS” and “C-AMS”, respectively, in order to be consistent with abbreviations introduced in the text.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C9612/2011/acpd-11-C9612-2011-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 6301, 2011.