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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.

Anonymous Referee #2

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The manuscript "The 2005 Study of Organic Aerosols at Riverside (SOAR-1): instrumental intercomparisons and fine particle composition" by Docherty et al. reports data from a field campaign which took place in the South Coast Air Basin (SoCAB) in 2005. The results of the study are very interesting and important and, although many of the results have been presented before in other publications, the additional analysis justifies publication in ACP. However, there are shortcomings that should be addressed by the authors prior to final publication.

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.

There is also some discussion of the fine particle mass and its composition in the overview. The main manuscript, on the other hand, contains essentially no detailed discussion of the presented data elucidating the composition of the fine particle mass, although the title suggests otherwise. I would strongly suggest adding a section where the fine particle composition, possible changes, influences and sources are shown and discussed in detail. The authors mention that this will be part of an ongoing publication. They also cite a previous publication that had a similar topic (Docherty et al., 2008b in the manuscript). The same applies for the detailed discussion of the organic aerosol composition based on AMS measurements and using positive matrix factorization. According to the authors, this topic will also be presented in an upcoming manuscript. However, contradicting their own statement, this topic has apparently also already been presented in several publications (Docherty et al., 2008b, Eatough et al., 2008, Huffman et al., 2009; P6308L21-24 and P6308L28ff). 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).
The discussion should also include the air quality in the SoCAB. Since the SoCAB is known to be one of the regions strongest affected by anthropogenic pollution and urban settlement, it would be valuable and reasonable to include a short section on the 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 (for instance, from 20 or 30 years ago). This is reasonable given that the fine particle composition is one of the main topics (as reflected by the title).

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. This undermines the scientific value of this work.

Currently, the most severe problem of the manuscript is a lack of focus on the promised topic(s). The overview is far too long for a simple background but not detailed enough to constitute a complete, in-depth overview. The instrument comparison section lacks detailed descriptions of inlets, losses, and possible reasons for disagreements, often simply reporting results together with their correlation correlations. These correlations are useless without a thorough discussion. Also, 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.

I recommend that the authors focus on the topic they want to present and include a detailed and profound discussion of it.

Specific comments:

Abstract:
The abstract is generally not "intelligible to the general reader without reference to the text." The key findings of the article should be highlighted more clearly. According to ACP guidelines: "After a brief introduction of the topic, the summary presents the key points of the article and provides future directions where research could focus on in the near future."

The guidelines given by ACP also recommend that "non-standard abbreviations should not be included without explanations." While O/C and H/C might be common expressions, not only within the AMS community but also for chemists, N/C and S/C are expressions that are not yet frequently used. These expressions should be defined at their first use (i.e., oxygen-to-carbon ratio O/C etcetera). Abbreviations aside, it is not that clear why these ratios and their changes are important or when they increase by a factor of two and 30 respectively.

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.

P6305L1: "...despite the fact that OA contributes about half of PM_f mass on a global basis."

Should be "non refractory PM_f"

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 PM_f (de Gouw and Jimenez, 2009)."

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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.

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.

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

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.

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

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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."

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 "real-time" acquisition mode presented in (Kimmel et al., 2010)? Couldn't a similar or better time 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.

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.

P6308L26ff: "This latter analysis attributed over three-quarters of total PM_f to

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secondary processes. . . ”

Can this latter analysis be found somewhere? It doesn’t seem to be part of this study.

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.

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?

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.?

P6309L27ff: “Although a fraction of SOA is non water-soluble (Weber et al.,

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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?

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% ± 5%, then it is only slightly more than half of the total organic carbon fraction that is water soluble!

P6310L8: "For example, Reemtsma et al. observed …"
should be
"For example, Reemtsma et al. (2006) observed …".

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?

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?

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?

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?

P6311L13ff: “..indicating the presence of a residual OA fraction potentially having a lower volatility than $(NH_4)_2SO_4$.”

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?

P6312L3: Why is “*total*” formatted italic?

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

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

P6313L16ff: “The $TEOM_{50C}$ 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 50°C in the standard TEOM.

P6313L18ff: “However, this results in collateral loss of semi-volatile material (SVM) including ammonium nitrate (NH_4NO_3) and semi-volatile organic material (SVOM) (Eatough et al., 2003).”

Eatough et al. (2003) compared a TEOM (standard, 50°C) with the RAMS, their modified version of the TEOM which is similar to the $TEOM_{FDMS}$. 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.

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!

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 600°C) have been removed from both HR-AMS and C-AMS datasets, and only data are compared that were acquired during routine ambient sampling periods.”

P6315L20: Should be (Super, 2009); References, P6348L4-L5

P6316L1: “. . . developed by our group . . . ”

Who is “our group”? From the author list/affiliations, at least five groups participated in writing the current manuscript.

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.

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.

P6316L21: "Since the goal of this study ..."

Does "this study" refer to "this paper" or "SOAR-1"?

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 ..."

P6317L13-15: "Similar mass concentrations and the strong correlation observed here highlight the spatial consistency of PM_f mass in inland regions of the SoCAB and suggest that contribution of PM_f 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?

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

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 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).

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”.

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 PM_{10}, $PM_{2.5}$ or PM_1. 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 50°C. The $TEOM_{FDMS}$ is not supposed to be selective and should simply measure the whole mass fraction, in this case $PM_{2.5}$.

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

P6319L19-20: "Because of SVM volatilization, ToF-AMS measurements can either be greater (high SVM) or less than (low SVM) those of the $TEOM_{50C}$."

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 $TEOM_{50C}$"

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

P6319L26: "Although non-EC refractory material was not measured during SOAR-1..."

Obviously it was measured (for example by the TEOM), just not quantified separately.

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

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?

P6320L4ff: “Similarly, Chow et al. (1994) obtained an estimate of 1.6 µg 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?

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).

P6320L22: “AMS+EC and $TEOM_{FDMS}$ 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 $TEOM_{FDMS}$ 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 $\text{TEOM}_{\text{FDMS}}$ time series has a peak in the morning and for others the $\text{TEOM}_{\text{FDMS}}$ shows continuously higher mass concentrations. Could different air masses explain these differences, or are they traffic (and wind direction) related?

P6320L25: "24-h average TEOM_{50C} measurements (15.0 µg m^{-3}; -4.9-39.7 µg m^{-3}) are lower than those of . . . "

Should be "(15.0 µg m^{-3}; 4.9-39.7 µg m^{-3})", right? Or did you really measure negative concentrations of -5 µg 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 $\text{TEOM}_{\text{FDMS}}$ 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 µg m^{-3}; <LOD - 39.7 µg m^{-3})".

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.

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 $\text{TEOM}_{\text{FDMS}}$, 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.

P6321L4ff "As detailed in Table S2, $\text{TEOM}_{\text{FDMS}}$ and TEOM_{50C} 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?

P6321L8-L10 "The correlation between TEOM_{50C} and AMS+EC measurements ($r=0.46$) is significantly lower than that obtained from comparison of $\text{TEOM}_{\text{FDMS}}$ and AMS+EC measurements."

I suggest changing this to:

"The correlation between TEOM_{50C} and AMS+EC measurements ($r=0.46$) shown in Fig. 3E is significantly lower than that obtained from comparison of $\text{TEOM}_{\text{FDMS}}$ and AMS+EC measurements, most likely because of the loss of semi-volatile material within the TEOM_{50C}."

P6321L25: “24% (+2%)” should be “24% (±2%)”, right?

I think you should somehow clarify this passage. The main result, the contribution of semi-volatile organic mass to the $PM_{2.5}$ fraction is lost in the copious discussion about linear regressions and their slopes.

P6322L7ff: “HR-AMS and C-AMS measurements are plotted in Fig. 4. Total $NR\text{-}PM_1$ from both ToF-AMS instruments are shown in Fig. 4a along with $TEOM_{FDMS}$ $PM_{2.5}$ 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.

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

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.

P6323L18-L19: “In sharp contrast to the consistency and high correlation of ToF-AMS SO_4 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.

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 0.51with 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

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 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.

P6324L21ff: "Since there was always a significant OC background in Riverside during SOAR-1 which almost never went below 2.5 µgC 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!

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).

P6325L7ff: "HR-AMS and Sunset 2 OC are compared in Fig. 5c. In this case the … "

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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.

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."

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 and otherwise within ±25% of the HR-AMS OC, which is within the uncertainties of both measurements."

This might be true, but the trends are so different that they barely resemble each other! In my opinion this has to be mentioned and the differences and trends have to be discussed thoroughly.

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.

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!

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).

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.

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?

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?

P6330L7ff: “The majority of EC in the SoCAB during SOAR-1 should be due to diesel vehicles (~89%) based on the reported emissions factors of Kirchstetter et al. (1999) and CARB fuel usage data (California Air Resources Board, 2009).”

The emission factors from 1999 might be out of date, due to changes in fuel composition as well as changes in engine design. I suggest either using only newer sources or to discuss possible changes and consider also other sources. Again, a detailed discussion and a deeper consideration is missing.

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 as there is traffic?

P6330L15ff: “However, the relative contribution of OA increases in the afternoon, as OA contributes ~43% of PM_f mass . . . ”

“PM_f” should be “PM_1” or “NR-PM_1”. According to the $TEOM_{FDMS}$ diurnal profile the $PM_{2.5}$ mass is approximately 37 µg m^{-3}. Compared to less than 12 µg m^{-3} OA, this results in a contribution of less than 30%.

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).

P6331L6ff: “This is consistent with its non-volatile nature and also reflects the ubiquity of particulate SO_4 in inland regions of the SoCAB, consistent with a larger

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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?

P6332L3: "Due to high ammonia emissions upwind and concentrations in the area of Riverside, . . . "

Where or what are these ammonia emissions coming from exactly?

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.

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."

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.

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Fig. 9: The diurnal profile for ammonium is barely visible – please use a different (darker) color.

Fig. 9, 10, S3B: Why do NR-PM1 nitrate (measured with an AMS) and HR-AMS nitrate in all three plots not only have different diurnal patterns but also different mass concentrations (i.e., a maximum of 8 µg m^{-3} in Fig. 9, 13 µg m^{-3} in Fig. 10 and 9 µg m^{-3} in Fig. S3B)? The same is true for the diurnal profiles of NR-PM_1 sulfate in Fig. 9 and Fig. S3D, although the differences are much smaller.

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

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 µg m-3, and the number below %?

Also, the label below the figures should not read PM_1 and $PM_{2.5}$ - this is rather confusing. Before studying the caption it looks like the total mass of PM_1 (Fig. 12a) is larger than the total mass of $PM_{2.5}$ (Fig. 12b) (29.35 µg m-3 versus 28.55 µg m-3). I suggest switching the plots and labeling the second one “PM2.5 (based on PM1)” or something similar.

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.

Last comment: In my opinion, the use of abbreviations and acronyms within the manuscript is too excessive. I suggest using abbreviations and acronyms more

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sparingly. This will facilitate readability and comprehension of the manuscript for most readers. Also, please check all abbreviations and acronyms for inconsistencies.

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