

***Interactive comment on* “Chemical composition and sources of coastal marine aerosol particles during the 2008 VOCALS-REx campaign” by Y.-N. Lee et al.**

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This paper presents a comprehensive analysis of AMS and PILS-IC data obtained on the DOE G1 during VOCALS. The results are interpreted in the context of perceived wisdom on the driving factors of composition in the marine atmosphere and individual hypotheses of the mechanisms responsible for the various components are assessed. This kind of assessment is certainly relevant to the VOCALS campaign and wider atmospheric science, as aerosols in the marine atmosphere remain under-characterised, in spite of their recognised importance for the atmospheric radiative balance. While this paper is certainly comprehensive in its analysis, it does suffer from a certain lack of

focus in places and one is left to wonder whether certain observations are being over-analysed and some of the proposed explanations are not adequately supported. There is significant room for improvement, but I consider all of my concerns to be addressable, so I see no reason why I can't recommend that this is published in ACP subject to corrections. General comments: The data presented in this paper clearly suffers from serious quality issues in that the three measurements, the PILS, AMS and SMPS, fail to be reconciled, is in spite of the fact there are many examples in the literature of the three techniques agreeing. I can appreciate that the authors have probably worked long and hard to try to resolve these issues and various speculative reasons for the lack of agreement are offered (see specific comments). As far as I can tell, they have had to adopt the position of assuming the PILS to be the accurate measurement and scaling the other measurements to this. However, with none of the measurements being objectively validated by an external comparison, the decision to trust the PILS seems to be based on the authors having reasons to mistrust the other measurements. This being the case, they should explicitly state this early on in the measurement section, because the agreement between the measurements would be expected to be much better than what is reported. I can't help but feel that 26 figures is too many and some of them could easily be moved to supplementary material or removed entirely. I suggest the authors decide which figures are strictly necessary to support their conclusions. See also specific comments. If PMF analysis is being performed, it would be prudent to include more information about how the PMF analysis was performed in the form of supplementary material. Key details are the reasons for rejecting solutions with more factors and diagnostics pertaining to the quality of the solutions presented in terms of Q, residuals, rotational ambiguity and seed dependence. The authors make several inferences about loss mechanisms that are supported by some very weak assumptions (see specific comments). These should be toned down or removed entirely.

Reply: See below

I don't regard the conclusion that the MSA seen by the AMS as being anthropogenic

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as adequately supported. See specific comments for details.

Reply: Discussion deleted.

Specific comments:

Page 26048: Please provide a reference for the constant pressure inlet and provide details of any validation work performed looking at particle transmission vs size.

Reply: The constant pressure chamber upstream of the AMS inlet (the pinhole) was maintained using a continuously running small diaphragm pump pulling the sample air in the manifold through an automated actuated valve whose opening controlled by a PID controller with the process pressure compared to the set value. The particle transmission efficiency of the reduced inlet pressure was not directly characterized. However, we performed IE calibration of the AMS in the configuration in the field at end of flight missions in the conventional fashion using dry ammonium nitrate particles ($D_p = 300$ nm). Although the particle size dependent transmission efficiency was not experimentally determined, we assume that the change of transmission efficiency for particle size important in the AMS measurement, i.e., ~ 80 nm to 460 nm, remain unchanged from unity or decreased by a constant fraction across the size range).

Page 26048: Were denuders used to remove water-soluble gases upstream of the PILS? If so, this should be stated. If not, this should be also be stated because it is a potential source of artefacts.

Reply: Yes, 2 glass honeycomb denuders housed in a cartridge (Chemcomb model 3500, Thermo Scientific) were used (1 coated with sodium carbonate to remove acid gases, the other citric acid to remove base gases). (Language added to section 2.1.2 of the revised paper)

Page 26049: Given its importance later in the paper, there is insufficient detail on the isokinetic inlet presented, specifically regarding the reliability of the estimate of the 1.5 μ m upper cut size. How was this estimated? Has this been validated? If there are any

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additional references that can be cited, they would be welcome.

Reply: The cited technical report (Brechtel, 2002) contains all of the details regarding the design of the inlet and the tests that were performed to establish the aerosol transmission efficiency as a function of size. There is no publication regarding this inlet in the peer-reviewed literature.

Page 26051: More detail on the SMPS should be presented here, specifically whether the voltages were stepped or scanned, what data inversion method was used (if commercial software was used, this should be stated) and what model of CPC it was coupled to.

Reply: The voltage was scanned upward and downward in each of the 30 s scans that were averaged into a one-minute size distribution. The inversion software was based on that due to Collins et al. (Improved Inversion of Scanning DMA Data, Aerosol Sci. Technol. 36:1–9. 2002), the CPC used was a TSI model 3010. Since the principle and operation of the DMA used can be found in Wang et al. (2003), we did not provide a detailed description of this technique.

Page 26052: Variations in the CE cannot be responsible for the inconsistencies noted, as this would result in normalisation factors strictly between 1 and 2, which is inconsistent with the results shown in table 3. Neither could the upper size cut of the AMS or having SO₄ and NO₃ bound in sea salt particles be responsible, as these effects can only cause the AMS to measure less than the PILS. I would think that inaccuracies in the AMS calibrations are the most likely explanation, and I agree that insufficient warmup times could be responsible. In addition to reporting the IEs from the calibrations, it would be more informative to report the IE/AB ratio, as this is a better reflection of changes in fundamental instrument performance, as opposed to simple drifts in sensitivity that are captured as a function of time by the AB metric. If a relationship between IE/AB and the normalisation factor is found, then this would point strongly to inaccuracies in the calibrations. Were the calibrations performed before or after the

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flights? How long did the instrument typically have between the pumps powering on, the filament lighting and calibration? Was the RIE of sulphate calibrated?

Reply: We understand and agree with the reviewer's comments. With that said, we mentioned CE in the AMS and size cut difference between the two techniques as possible issues in the comparability in a general sense, perhaps being pedantic. Of course, they cannot account for the fact that the AMS measured higher SO₄ concentrations. We have added text to make this point clear. We recognize that the IE/AB ratio is a better metric for checking instrument performance. However, since the variability of IE was much greater than that of AB and we didn't detect a correlation between the normalization factor and the IE/AB ratio, we point out the variability in IE itself which was sufficiently large that the calibrations were suspect, as commented by the reviewer. The AMS was calibrated in the standard fashion using NH₄NO₃ on the ground at the end of flight mission, typically 7 hours after the instrument was powered on. RIE of SO₄ was not independently calibrated but based on the RIE of NH₄⁺.

Page 26056: I do not agree that the comparison between the measurements and SMPS should be presented in the discussion section, as this potentially highlights a data quality issue. This should be included with the AMS-PILS reconciliation subsection (3.2), especially seeing as the metrics are reported in the same table anyway.

Furthermore, given that the material densities of the particulate components are already known, why wasn't a time-dependent density calculated, allowing the AMS and PILS data to be converted to volume concentrations for a more direct comparison with the SMPS? I would also not be so quick to rule out the possibility that sea salt may be contributing to the smaller particles. While the correlations may appear good without any sea salt contributions, aircraft data tends to produce good correlations anyway, as many changes that affect concentration (e.g. changes in altitude and air mass) cause different components to exhibit covariance.

Reply: We have moved this section (old 4.1) into the Results section as the new 3.2.1

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per reviewer's suggestion. The reviewer is also correct that perhaps we could have converted mass to volume in order to make a direct comparison to the DMA volume. However, the comparison between mass concentrations and DMA volumes, which yields density as the slope, is also effective at revealing the discrepancy. We consider both approaches valid to reach the same point. Regarding SSA, despite the unresolved question of whether submicron size particles may be important, there is no doubt that SSA size distributions show a mode size greater than that of combustion particles. The attribution of the observed SSA to particles of $D_p > 440$ nm is also consistent with the correlation between SSA mass concentrations and the volume concentrations between 0.5 micron and 3.0 micron determined by the PCASP (which is deleted in the final version). The good correlation between mass and volume concentrations in Fig. 9a is based on data we collected exclusively in the MBL where the data does not range over a huge range of values. Thus, this is not a situation where the correlations are driven by outliers.

Page 26062: Rather than changes to the particle sizes, could this effect also be a manifestation of the size cut of the inlet changing with altitude? Given that the pressure, temperature (therefore air viscosity) and true air speed will all change with altitude, I would not consider a change in size cut to be unexpected.

Reply: This discussion has been deleted. However, we note that the inlet is designed to accommodate changes in true airspeed. Furthermore, the range of sampling altitudes for the data reported here is too small to induce significant inlet effects.

Page 26064, line 14: The statement that the oxidation of NO_x and SO₂ by OH occurs on similar timescales is at odds with established chemical kinetic data; for instance, the IUPAC values (http://www.iupackinetic.ch.cam.ac.uk/datasheets/summary/vol1_summary.xml) show an order of magnitude difference in their rate constants. The authors should state the rate constants they are using here and cite their sources. C9979

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Reply: The reviewer is correct. Text regarding oxidation of NO_x and SO₂ deleted. Discussion Paper Page 26064, line 27: I do not follow this logic at all; SO₄, as well as being produced by continental anthropogenic sources, is also produced by DMS oxidation, can be entrained from the FT and is a component of sea salt, so it is not surprising in the slightest that it is more ubiquitous in being above the LOD than NO₃. It is certainly not an observation that can be used to draw any conclusions regarding NO₃ losses.

Reply: The reviewer is right that SO₄ aerosols have additional sources, including DMS oxidation and transport from the FT (the sea water SO₄ is not detected by the AMS though). But, we argue that because NO₃⁻ (strictly from continental sources) is sequestered into SSA particles, which are typically larger in size than SO₄ aerosols, its disappearance can be due to the effective removal of larger size particles by drizzle. The shorter lifetime of NO_x pointed out by the reviewer suggests a near complete conversion of NO_x to HNO₃ at the sampling location. Because the SSA particles, in the size range being sampled, i.e., $< \sim 1.5 \mu\text{m}$, on which NO₃⁻ resides have a long life time against dry deposition, the fact that NO₃⁻ can disappear (to a near zero concentration) all together in some 1/3 of the samples strongly suggests a removal pathway. We see removal by precipitation as a plausible pathway.

Page 26068, line 24: SOA yields are known to be highly variable and the fundamental mechanisms are not fully understood. Furthermore, the relative emissions of precursors to CO will not necessarily be a constant either, so there is no reason to assume that the 60 $\mu\text{g}\text{-m}^{-3}\text{-ppm}^{-1}$ derived by Kleinman et al. for Mexico City would be applicable in this situation. As such, I do not see that the authors can draw any conclusions about removal mechanisms based on this data.

Reply: Kleinman et al. have found the proportionality between SOA and CO to be applicable to a megacity like Mexico City, as well as to mid-size cities such as Boston. This observation suggests that the major emission sources of urban areas are very similar, comprising that from transportation, power generation, petroleum based industry,

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cooking, etc., despite different emission control standards.

Page 26069, line 7: The authors state here that the NO₂ oxidation time is ~ 1 day at an [OH] of 5×10^{-7} cm⁻³. This is not only an unrealistically low [OH], but is inconsistent with what is stated previously on page 26064.

Reply: The reviewer is correct that we should have used 4×10^6 cm⁻³, consistent with earlier discussion. The characteristic lifetime of NO₂ is therefore much shorter, ~ 5 h.

Page 26069, line 11: The CO/NO_y ratio is also highly variable, depending not just on the age of vehicles, but also the relative prevalence of diesel and gasoline vehicles within the fleets, emission standards and also the presence of non-vehicular sources. There is nothing to say that the value derived for the US is applicable here, so again, I do not see that the conclusion regarding losses to be supportable.

Reply: Again, while the reviewer's point is correct, the CO/NO_y ratio is affected by many factors, statistically we consider this ratio a helpful guide, which ranges from 10 to 20. The median concentration of NO₃- using a median [CO] of 14 ppb is 0.14 to 0.7, significantly greater than the observed median of 0.08 ppb, suggesting NO₃- is rapidly removed after its formation.

Page 26075, line 17: If the authors used the default AMS fragmentation tables, the measured m/z 81 signal is assigned to inorganic sulphate. The organic signal at m/z 81 is predicted, based on the signals at m/z 67 and 95, so its absence from the MSA spectrum is expected.

Reply: Section 4.8 has been deleted

Page 26075, line 20: Given that the m/z 12 and 45 signals from MSA will make very small contributions to the overall variance (other organic species also generate fragments at these m/z), and positive values of f_{peak} were used, which will cause mass spectral peaks to be attracted to zero during fitting, their disappearance on one flight-Paper is most likely not indicative of anything physical. As such, I would not base any

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conclusions on this result.

Reply: Section 4.8 deleted

Page 26075, line 23: As well as the CE, Zorn et al. also showed the RIE of MSA to be highly variable and the fragmentation pattern very sensitive to the precise vaporiser temperature.

Reply: Section 4.8 deleted, but yes, the MSA spectrum we used as a reference was collected with a vaporizer temperature of 600 C, same as that used in this study.

Page 26075, line 24: The basis on which the authors 'assert' that the MSA is not from oceanic DMS appears purely to be its correlation with SO₄. This does not seem logical, because DMS oxidation also produces SO₄.

Reply: Section 4.8 deleted but- The MBL SO₄ aerosols observed in the VOCALS study region (east of 78 Lon) was dominated by continental anthropogenic sources based on air trajectories and combustion tracers such as CO, with a much smaller contribution from DMS as shown by many publications (e.g., Allen et al. 2011, and Yang et al., 2011). Since the longitudinal distribution of the MSA factor showed a good correlation with this continental derived SO₄, we surmise there is a good chance that this MSA is also continental.

Page 26076, line 4: If continental sources of MSA were significant, one would expect it to appear more AMS PMF datasets because the m/z 79 and 96 peaks are very uncommon peaks in reported mass spectra and allow for relatively low mass concentrations to be quantified. However, to this reviewer's knowledge, it has only ever been reported in marine airmasses.

Reply: Section 4.8 deleted but- Possible reasons that these fragments have not been "detected" in continental studies include (1) tendency to focus on subjects considered important only on land, and (2) the signals are small compared to that of other species and are overlooked. Field studies are needed to refine our understanding of known pro-

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cesses, but are also mechanisms for discovery of processes that have not previously been identified.

Page 26076, line 16: I would say that the presence of the methyl fragment is a very good basis for ruling out the possibility of HMSA. I would go so far as to say that if the authors want to propose HMSA as a candidate, they need to demonstrate that it can produce a mass spectrum similar to MSA.

Reply: Section 4.8 deleted but reviewer is correct

Figure 6: This figure is very hard to read, owing to the number of points overlaying each other. I suggest it be removed.

Reply: Figure 6 has been deleted

Figures 21-24: Many of these figures are surplus and can probably be moved to supplementary material. They should also have proper legends added.

Reply: Number of figures reduced from 26 to 16

Figures Technical corrections: General: The authors should state whether the mass concentrations reported are at standard or ambient air volumes.

Reply: Concentrations reported were ambient, not standard. Text added.

Page 26047, line 19: Correct 'BAAM' to 'FAAM'

Reply: Suggestion taken Discussion

Pages 26048-9: The methods used to determine LOD in the respective instruments should be stated.

Reply: Each instrument typically has a publication dedicated to its principal, operation, and calibration, and these details are in general not repeated in manuscripts like this. In the case of PILS, the LOD is taken as 3 times the standard deviation of the repeated (typically 3 to 5) values of the lowest concentration of the calibration standards.

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Page 26053: BC and AC are defined after they are first used further up the page. I would recommend that these definitions occur earlier in the paper, such as with the flight descriptions.

Reply: BC and AC are defined on page 26051 of the original manuscript

Page 26055, line 18; Page 26079, line 14: 'All but absent' is a peculiar choice of words, given that MSA was found in the AMS data (albeit at very low concentrations). I would recommend simply stating 'below the PILS detection limit'.

Reply: Changed to – 'was mostly below the detection limit of the PILS'

Page 26058: Please define 'equivalence ratio'

Reply: Changed to- 'equivalents ratio'

Page 26071, line 23: Replace 'till' with 'until'.

Reply: Done

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 26043, 2013.

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