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Atmospheric Chemistry and Physics
Discussions

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

Anonymous Referee #2

Received and published: 13 December 2013

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 the 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.

I don't regard the conclusion that the MSA seen by the AMS as being anthropogenic as adequately supported. See specific comments for details.

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.

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.

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 μm upper cut size. How was this estimated? Has this been validated? If there are any additional references that can be cited, they would be welcome.

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.

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

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 airmass) cause different components to exhibit covariance.

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.

Page 26064, line 14: The statement that the oxidation of NOx and SO2 by OH occurs on similar timescales is at odds with established chemical kinetic data; for instance, the IUPAC values (http://www.iupac-kinetic.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.

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.

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 μgm-3ppm-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.

Page 26069, line 7: The authors state here that the NO2 oxidation time is $\sim$1 day at an [OH] of 5e-7 cm-3. This is not only an unrealistically low [OH], but is inconsistent with what is stated previously on page 26064.

Page 26069, line 11: The CO/NOy 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.

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.

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 fpeak were used, which will cause mass spectral peaks to be attracted to zero during fitting, their disappearance on one flight

is most likely not indicative of anything physical. As such, I would not base any conclusions on this result.

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.

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.

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.

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.

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

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

Technical corrections:

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

Page 26047, line 19: Correct ‘BAAM’ to ‘FAAM’

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

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.

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’.

Page 26058: Please define ‘equivalence ratio’

Page 26071, line 23: Replace ‘till’ with ‘until’.

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