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Interactive comment on "The Pasadena Aerosol Characterization Observatory (PACO): chemical and physical analysis of the Western Los Angeles Basin aerosol" *by* S. P. Hersey et al.

S. P. Hersey et al.

shersey@caltech.edu

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The presence of amines was speculated based on ion balance analysis that indicates an excess of particulate NH4+ in aerosols during the hot, dry regime III condition. However, another possible reason for the seemingly surplus of NH4+ is the incomplete counting of anions. Organic acids are not quantiïňAed separately by the AMS and therefore not included in the anion budget. But it is possible that NH4+ is associated with organic anions. Were the PILS samples analyzed for small organic acids? It will be interesting to see if there are indications of enhanced organic anion concentrations during periods with excess NH4+. Besides, even if sulfate and nitrate indeed dominate

the anion budget for this study, I am not convinced that the observation of excess NH4+ needs to be attributed to the presence of amines. Most amines are bases with a positively charged nitrogen center. Amine tends to behave similarly to ammonia and its protonated form requires an anion to balance the charge. Given that aminium salts are likely nonrefractory, AMS will be able to detect their anions. It will be useful to check if the RIE of NH4+ changed during this study. This can be done using the NH4NO3 data if more than one IE calibrations were performed during this study.

This is an excellent point about organic-acid-associated NH4+ influencing the ammonium balance. Unfortunately we were unable to quantify small organic acids with the PILS-IC, and the C-ToF-AMS did not detect any aminium salts. We were unable to check the RIE of NH4+, but we agree that the presence of organic acids may be an alternate explanation for the observed trend in ammonium ratio. We have revised the text after line 9 on page 5884 of the original manuscript:

One explanation for these trends is that ammonium may be chiefly inorganic during the moister, marine-layer-influenced regimes I and II, serving primarily to neutralize SO42- and NO3-, while there may be an influence from organic amines in the absence of marine layer influence during regime III. While particulate amines have been observed in the particle phase (Ge et al. (2010)), it is unclear why they would appear to be more prevalent in regime III, as amines are typically associated with cooler, moister environments (Rhebein et al. (2011)). Another explanation is that the "excess" NH4+ may be associated with organic anions. An enhancement in acidic organic species, which would not be unexpected in a hot, dry, photochemically active regime, may lead to a corresponding enhancement in neutralizing NH4+. Since the AMS does not specifically quantify organic anions, such an enhancement in both organic acids and associated NH4+ would lead to an increased ammonium ratio.

The behaviors of the SV-OOA factor are quite interesting. It correlates well with DMA particle number concentration and O3 but not so with nitrate and chloride. Instead, LVOOA correlates better with nitrate and chloride than SV-OOA does. Since the nam-

ing of SV-OOA and LV-OOA suggest their volatilities, it will be helpful that the authors discuss this inconsistency.

Discussion added on p. 5889, after line 8 of the original manuscript (at the end of the SV-OOA paragraph in Section 3.3):

Traditional PMF analysis correlates LV-OOA with sulfate, since SO4(2-) is essentially nonvolatile, and SV-OOA with nitrate since NO3- is more volatile. These correlations are not necessarily based on mechanistic chemistry, but rather a similarity in volatilities. So there is no reason, on a fundamental chemical basis, that NO3- should correlate better with SV-OOA than with LV-OOA. That is, the routes by which semivolatile organics and NO3- reach the particle phase are distinctly different chemically. In the Los Angeles aerosol, these distinct pathways result in a relatively poor correlation between SV-OOA and NO3-. A better correlation between inorganics and LV-OOA suggests that the pathways by which they reach the aerosol phase are more similar than for SV-OOA in transported Los Angeles aerosol.

In addition, it is said in page 5889 (line 7-8) that SV-OOA is considered to be mainly SOA with 1-2 hr of age. It is however unclear how the 1-2 hr determined.

The age is estimated based on the transport time from source-rich areas near downtown to the sampling site in Pasadena. This is clarified in the text.

Another major comment I have is regarding the PMF analysis. Given the length of the study, three distinct meteorological regimes were encountered and organic aerosol compositions appear to be siĝniïňĄcantly different among these regimes. It is therefore a question whether it is appropriate to perform PMF on the whole data set. Above all, an underlying assumption of bilinear modeling is that the OA factors have constant mass spectra during the speciïňĄed time period. This assumption should hold even less true for a situation when OA compositions are obviously different among periods. It might be worthwhile to perform PMF analysis to segregated time periods classiïňĄed according to the three regimes and make discussions accordingly.

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Excellent point. We considered this issue in depth, and performed a PMF analysis on each regime individually to determine the sensitivity of our solution to the assumption that the OA factors have constant mass spectra. Results from the PMF analysis of individual regimes resolved nearly identical factors to those resolved by PMF analysis on the entire dataset. In regime I, HOA and LV-OOA factors dominated the OA, while in regimes II and III it was the SV- and LV-OOA factors that dominated OA. In all cases (HOA, SV-OOA, and LV-OOA), the factors resolved by PMF on separate regimes displayed a high degree of correlation (Pearson's R generally on the order of 0.94-0.99 for LV-OOA, SV-OOA, and HOA) with those resolved in the bulk analysis. Only the HOA factor from regime II had a Pearson's R correlation lower than 0.94, compared with the bulk solution (Pr = 0.76), and this poorer correlation is likely due in part to the fact that HOA contributed the lowest fraction of OA of the entire PACO study during regime II. This is noted on p. 5886, line 18 of the original manuscript.

Detailed comments: It is said that sulfate observed in this study was primarily the result of marine sources. It is curious whether it was mainly from biogenic (e.g., DMS) or from anthropogenic (e.g., SO2 from ship emissions) precursors.

The original manuscript was not clear. P. 5871, lines 4-5 have been changed to reflect the influence of anthropogenic marine sulfate on Los Angeles Aerosol, and a reference to Ault et al. (2010) is added:

Primary marine and secondary sulfate aerosol are expected to contribute a relatively uniform loading of sulfate across the Los Angeles Basin (Watson et al. 1994). Marine sulfate is expected to be contributed by natural primary processes (biological, sea spray, bubble bursting), with anthropogenic shipping-related emissions contributing a varied and often significant loading of sulfate (Ault et al. 2010).

P5869, lines 15-16, are the k values corresponding to the organic fraction only or to the bulk aerosol?

The k values here refer to the bulk aerosol. But we have addressed the omission of

organic kappa estimations by adding a brief section explaining the derivation of organic kappa and presenting results from this analysis. Organic kappa values are reported in the abstract and conclusions, as well as in section 3.5. The discussion appears after p. 5895, line 19 of the original manuscript (equation numbers will be different in the manuscript):

In order to further investigate the hygroscopicity of organics, κ calculations were combined with AMS data giving mass fractions of individual aerosol species in order to estimate a κ value for organics, κ_{org}. If the overall hygroscopicity parameter, κ is given by:

$$\kappa = \sum_{i=1}^{n} \kappa_i \cdot \chi_i, \tag{1}$$

where n is the number of chemical constituents, i, with mole fraction χ_i and hygroscopicity parameter κ_i, then the organic hygroscopicity parameter, κ_{org} can be estimated by:

$$\kappa_{org} = \frac{\kappa - \displaystyle\sum_{i=1}^{n_{inorg}} \kappa_i \cdot \chi_i}{\chi_{org}}, \tag{2}$$

where n_{inorg} is the number of inorganic constituents, i, with hygroscopicity parameter κ_i and mole fraction χ_i, and χ_{org} is the mole fraction of organics in the aerosol. Previous publications have assumed κ_{org} of 0.1 for "hygroscopic" organics, and 0 for "nonhygroscopic" organics (Dusek et al., 2010; Wang et al., 2010; Wex et al., 2010). Assuming κ_i for inorganics to be 0.6 and κ_i for sea salt to be 1.3 (Wex et al., 2010), Eq. 2 gives κ_{org} of 0.16 for urban background aerosol transported to the PACO sampling site. Assuming κ_i for inorganics to be 0.7 (Dusek et al., 2010) gives κ_{org} of 0.12. Taking a median κ_{org} of 0.14, it is clear that the organics measured during PACO are

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significantly more hygroscopic than those previously measured in urban areas. This is not unexpected, given the consistently high O:C ratios of organics and the dominance of SV-OOA and LV-OOA during all three regimes of PACO. Further, the PACO sampling site is relatively free from the influence of local sources of primary aerosol, which would have the effect of reducing κ_{org}. Given that organics dominate aerosol in most urban areas, it is potentially significant to find that organics in an important urban center such as Los Angeles would have a value of κ_{org} appreciably higher than previously calculated for urban aerosol.

P5888, line 19-20 in discussion of diurnal trends, it will be useful to show the diurnal plots either in the main text or as supplementary.

We will note this to the publisher.

page 5896, Line 20, O/C ratio is higher by how much during Regime II?

O:C ratios are 15-25% higher in regime II. This is now explicitly noted in the text.

page 5896, Line 22-24, it states "Afternoons during regime II and III are characterized by the appearance of a ïňĄne organic mode, suggesting that SOA may be responsible for growth of ïňĄne particles." Didn't secondary inorganic species contribute to particle growth too?

This is rephrased to say: "Afternoons during regime II and III are characterized by the appearance of a fine organic mode, suggesting that SOA contributes significantly to growth of fine particles."

Page 5898, line 24, it is concluded that the observed less inhibition of aerosol hygroscopicity by organics in LA was potentially owing to less surface-active behavior. Was surface tension measured during this study or are there other measurement data to support this assumption?

Unfortunately there are no data available for surface tension. The text currently reads: It appears that organics in Los Angeles inhibit hygroscopicity less than those mea-

sured in Central Mexico and oïňĂ the N. American West Coast, potentially owing to less surface-active behavior or an organic fraction comprised of more water soluble species." We feel that it is appropriate to offer these as potential explanations for the trends observed.

Two green colors for LV- and SV-OOA in Fig 1 cannot be clearly distinguished.

The colors have been adjusted to provide more contrast.

The axis labels for several ïňĄgures are too small to read in print out version, particularly those for the bar graph in Fig. 6 and Fig. A6, A7.

These figures have been modified to print more clearly.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 5867, 2011.

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