High spatial resolution mapping and source-apportionment of aerosol composition in Oakland, California using mobile aerosol mass spectrometery

Responses by Shah et al. to referee comments

Referee comments are in regular font. Author responses are in red. Text quoted from the manuscript is *italicized*.

Referee #1

This manuscript shows high-resolution spatial patterns of PM composition and amount measured by an AMS on a truck in Oakland. Overall, I found the paper to be well within the scope of ACP, the analysis was well done, and the paper was well written. I have several comments that I'd like addressed before publication in ACP.

We thank the referee for their constructive feedback.

General comment (because it shows up in a few places):
Bottom $\frac{1}{3}$ of P18, but also the abstract and point #3 on P23: To me, the simplest explanation as to why SV-OOA is higher in downtown is that its the location thats farthest downwind (wind typically heading from west to east in Figure S16). The mid-day gradient in SV-OOA appears to be steadily increasing from west to east in Figure 9, rather than a step change to higher values when entering downtown. The air starts picking up SOA precursors when it first hits land (either on the west or east sides of the bay) and SOA forms as the air moves across Oakland. Certainly more precursors are being added in Downtown, which helps, but the air as simply had more time to make SOA from the precursors (or oxidize the HOA and COA) by the time the air reaches downtown. The proposed hypotheses in the manuscript that deal with enhanced photochemical activity seem like less straightforward explanations. Downtown might be in a high-NOx regime, which would lower OH (acting against the proposed HONO source). Unless I'm missing something, I dont know why the simple amount of time spent over land hypothesis isnt prominent in the paper.

The referee raises a very good point in this paragraph: SV-OOA is steadily increasing with inland distance. This indeed suggests the simple time-over-land explanation for the observed SV-OOA trends in Figure 9 (Figure 8 in revised manuscript). We have added this discussion to the manuscript:

The increasing concentrations of SV-OOA with increasing inland distance (Figure 8) can be explained by the predominant Westerly winds (Figure S17). At the typical wind speed of $\sim$ 15 kmph, downtown is 10-15 min downwind from the Port. The additional processing of OA in this time can result in higher SV-OOA in downtown.

However, this is not sufficient to explain the observed diurnal change in the spatial pattern of SV-OOA. The spatial gradient of SV-OOA is the largest in the morning (Figure 7 in revised manuscript), which is when primary emissions are also higher in downtown. This suggests that enhanced photochemistry could also be playing a role.

The referee mentions that downtown being in a high-NO_x regime should lower the OH. This should be the case if the OH production rate is constant throughout the whole Oakland domain. However, if there is an additional OH source that helps to drive chemistry downtown (e.g., HONO emissions), then [OH] could be higher in that microenvironment. We did not measure VOC or NO_x, so we cannot directly address the question of LO-OOA

production rates. However, as we discuss in the manuscript, the observation of elevated LO-OOA and sulfate downtown suggests faster photochemistry there. We offer HONO emissions from cars as one possible explanation. Herndon et al. (2008) previously showed that OOA formation scales with odd oxygen (NO_2 + O_3), and odd oxygen has been shown to be elevated in street canyons (Villena et al., 2011); this would be consistent with the additional LO-OOA we observe downtown.

Specific comments:

Abstract: The final sentence is subjective and unnecessary, in my opinion. The paper shows many things that would seem to be unique to Oakland (in addition to things that are likely common with other urban locations).

We removed this sentence.

P2 L14-15: The length and time scales dont seem to match. Winds would need to be very stagnant ($\ll$ 1 km/hr) in order for "hundreds of meters" to correspond to "hours".

We reworded this sentence. It now reads: *This rapid mixing occurs over tens to hundreds of meters downwind of the source (Canagaratna et al., 2010; Saha et al., 2018).*

P3 L7: need a comma after "legislations"

We added a comma there.

P3 L10: I had to look up what "drayage" meant, and I suspect others might not know as well. Since the word is used quite a bit in the paper, it may be worth giving a very brief explanation here.

We added a definition of drayage trucks the first time the term is used. It now reads: *Several prior studies have focused on air quality in Oakland because of the influence of ships and associated drayage trucks (trucks that transport cargo between the port and warehouses) driving through the residential district.*

P6 L25-30: I know, generally, what bootstrapping statistical methods are, and I've used some. However, there was not enough info in this paragraph to really understand what was done (I could not repeat the analysis based on this description).

We added a description of the math. It now reads:

Bootstrap resampling: In order to compare observations of OA and its factors across areas influenced by different emissions (Port, West Oakland and downtown), we first determined the precision of these measurements by resampling the pool of data occurring in these areas. The strength (i.e., number of elements) of a bootstrapped dataset was the same as the strength of the dataset collected in that area. For instance: $\boldsymbol{M} = \{m_1, m_2, ...m_n\}$ *was the original set of n measurements performed in an area (e.g., Port). From all n measurements in* $\boldsymbol{M}$*, a measurement was randomly drawn to populate a synthetic set* $\boldsymbol{M'_1}$*. Each random draw was from the original set* $\boldsymbol{M}$ *with replacement i.e., independent of previous draws. The synthetic set* $\boldsymbol{M'}$ *was populated until its strength was n (same as of the original set* $\boldsymbol{M}$*). Generating such synthetic sets* 10^4 *times resulted in a bootstrapped pool* $\boldsymbol{M_B}$=$\{\boldsymbol{M'_1}, \boldsymbol{M'_2}, ...\boldsymbol{M'_{10^4}}\}$*. From this, a bootstrap statistic set,* $\boldsymbol{S} = \{\tilde{s}_1, \tilde{s}_2, ...\tilde{s}_{10^4}\}$*, was created where* $\tilde{s}_i$ *was the median of the synthetic set* $\boldsymbol{M_i}$*. Finally, the difference between* 5^{th} *and* 95^{th} *percentile of all elements of* $\boldsymbol{S}$ *was used as a dispersion statistic of the median. This results in a bootstrapped median and its 95% confidence interval for the area whose data were chosen to be the original dataset* $\boldsymbol{M}$*. We thus use the 95% confidence interval of the median as the precision of our measurements. Spatial differences larger than this precision are then deemed statistically significant. We are not*

aware of any prior studies that report precision of OA factors.

Referee #2

General comments:
This paper presents a detailed study on aerosol composition, focusing on the organic components, in Oakland, California. A mobile laboratory carrying an aerosol mass spectrometer (HR-ToF-AMS) was used to map the city roads in about 160 hours of measurements, resulting in a highly spatial resolved data set. The organic aerosol was separated using PMF into HOA, COA, and SV-OOA. While the manuscript is technically very sound and presents the AMS data analysis in great detail, it falls short in the interpretation of the results. To my opinion, more could have been done (or has to be done) in this direction, before publication in ACP can be recommended. My detailed comments are listed in the following.

We thank the referee for their constructive feedback.

Major comments

1. As written above, the interpretation of the results is not satisfying. That a large city like Oakland has a strong HOA influence would have been expected. The authors emphasize that Oakland has one of the largest shipping ports in the US. Thus, I would have expected to see as a result a separation of the HOA influence between ship exhausts, port-related traffic (trucks) and individual car traffic. I do not find any of this in the results or conclusions sections, only a little of such an analysis in section 3.2. The title suggests that not only the spatial distribution but also the sources of aerosol particles are investigated. It would have been interesting to learn about the reduction potential for the PM burden in a city like Oakland, e.g. whether reduction of ship emissions, truck or car traffic have a higher impact on PM loads.

   We have made substantial changes to the section discussing BC measurements (Section 3.2 in ACPD version, section 3.4 in revised version with modified title). In addition to the OA/BC map that was in the ACPD version, we have added HOA/CO and BC/CO ratio maps to further bring out the influence of truck emissions at the Port. We also performed PMF separately on Port-only and downtown-only OA datasets and compared the two Port-HOA and downtown-HOA chemical mass spectra. However, unsurprisingly, the two factors look nearly identical, which underscores how challenging it is to determine HOA fraction from trucks v. cars. Regarding ship emissions: Tao et al. (2013) used particulate vanadium as a marker of ship emissions and found a median concentration of $\sim$ 1 ng m^{-3} in West Oakland. We attempted to extract a vanadium signal in the AMS data (m/z 50.94), but the signal values were below the instrument detection limit (3 ng m^{-3}).

   Lastly, the term "sources" in our title simply refers to the chemical nature of OA and its apportionment to distinct emission/formation types e.g., traffic, cooking, etc. using PMF. We changed the title of our manuscript to clarify this.

2. The data analysis is restricted to AMS and black carbon data. But, as was written in section 2.2, also CO, CO2 and particle number concentration was measured. Apparently neither CO2 nor particle number were used here in the analysis. No correlation between CO and HOA is presented. I think that the addition of these parameters (e.g. ratios OA/CO, correlations between BC and CO, HOA and CO, HOA and particle number. . .) would be a benefit for the analysis.
We agree with the referee that we can make more from our measurements to distinguish emissions from cars and trucks e.g., by looking at relation between HOA and BC, HOA and CO, etc. We added a section addressing this truck/car comparison, as described in our response to the previous major comment.

Minor comments:

Page 2 line 24-25: Also in Paris (MEGAPOLI) COA was identified to be of high importance (Crippa et al., 2013b; Freutel et al., 2013)

We added this citation at this point in the text.

Page 7, Figure 2: The figure suffers from too much information. I suggest adding an extra figure in the Supplement with the number of unique samples and have in this figure only filled symbols color coded for OA.

Good suggestion. We followed it.

Page 8, lines 8.9: "Ambient measurements typically exhibit a positively-skewed distribution under the influence of local emission events." Really? Are three papers enough to say "typically"? And why is that so?

In ambient measurements, local emission events (e.g., driving by an open barbecue site while mobile sampling) and short-lived events (e.g., nucleation event measured by stationary monitor) will cause significantly high, narrow peaks in the time series of primary species (e.g., CO, NO_x, particle number). The median is insensitive to these, but the mean can be very sensitive depending on number of data being averaged. Hence, mean > median and the distributions exhibit a positive skew. This behavior of pollutant probability distribution functions has been explained in Seinfeld and Pandis (2006). We cited the three papers because all of them performed mobile sampling in urban areas, and all of them attributed positive skews to local emissions. However, there are other examples, a mixture of stationary and mobile sampling studies, all of which report positively skewed distributions of primary species: Hoek et al. (2002); Apte et al. (2011); Von Der Weiden-Reinmüller et al. (2014); Tan et al. (2014, 2016); Zimmerman et al. (2018). We added the Seinfeld and Pandis textbook citation to our manuscript.

Page 10, lines 11-15: It was suggested by Sally Ngs group (e.g., Xu et al. (2015)) to replace "LV-OOA" and "SV-OOA" by "More-oxidized and less-oxidized oxygenated organic aerosol (MO-OOA and LO-OOA)". You may consider using LO-OOA instead of SV-OOA.

We replaced our factor terminology to LO- and MO-OOA.

Page 12: lines 0-5: Oceanic air masses: There is literature on marine OOA factors (e.g., Ovadnevaite et al., 2011; Schmale et al., 2013). There is some potential in this marine influence on aerosol properties. You could make more of it.

Schmale et al. (2013) reported a "MSA-OA (methanesulfonic acid OA)" factor. As the referee correctly pointed out, marine influence on aerosol properties can be impor-

tant. By correlating particulate sulfate with this MSA mass contribution, Schmale et al. (2013) indeed show that marine influence on aerosol properties can be important (Figure 1A). However, we do not observe this marine influence in our data. Multiple lines of evidence point to this assessment: a) the correlation between particulate sulfate and MSA in Oakland (our data; Figure 1B) is $R^2 = 0.12$, while that of Schmale et al. (2013) is $R^2 = 0.72$, b) the ratio of MSA/sulfate in Oakland is only ~ 0.01, while that reported by Schmale et al. (2013) is ~ 0.25, c) the relative contribution of this MSA factor to the total OA in Oakland is less than 1% while that reported by Schmale et al. (2013) is 25%. That Oakland is an urban area and the measurement location of Schmale et al. (2013) was a remote island in the Antarctic explains these differences between the two datasets. Similarly, the work of Ovadnevaite et al. (2011) reported measurements in a remote location in Mace Head, Ireland which had a significant influence from marine OA with minor urban sources.

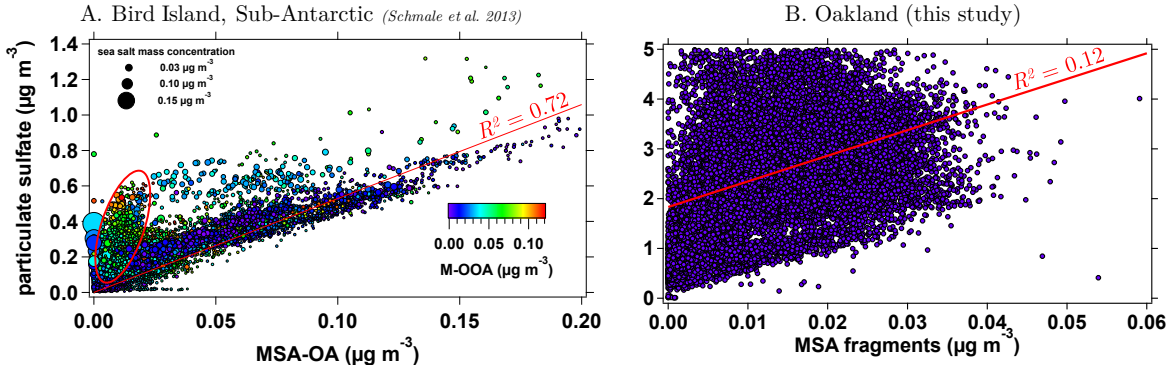

Figure 1: Correlation between particulate sulfate and methanesulfonic acid (MSA) OA reported in A) remote location of Bird Island research station in the sub-Antarctic region by Schmale et al. (2013) and B) Oakland (this study). Note: the axes on the two subplots are scaled differently. In the linear fit in the left subplot, Schmale et al. (2013) excluded data with M-OOA > 0.01 μgm^{-3} (e.g., data cluster in the ellipse), where M-OOA was a highly oxygenated PMF factor (O/C > 1), attributed to background wind trajectories.

Contrasting to these two studies in remote locations, Crippa et al. (2013a) and Mohr et al. (2015) performed measurements in urban areas and their PMF results showed urban OA factors (HOA, COA, SV-OOA). Similar to our results from Oakland, Mohr et al. (2015) revealed no marine OA influence in Barcelona, despite it being a coastal location and receiving sea breezes. On the other hand, Crippa et al. (2013a) reported a marine factor in Paris. Paris receives influence from different directions (urban as well as clean marine wind masses). Due to these very different static contributions to the total OA, the PMF analysis of Crippa et al. (2013a) was able to identify a distinct marine factor. However, in the case of Oakland, we are unable to mathematically show a distinct marine factor presence because the wind directions remain relatively stable. As a result, rather than identify a distinct marine factor, PMF performs what is likely an artificial splitting, as explained in our discussion on *"Quality of PMF solution"*.

We added the above figure and discussion to the supporting information.

Summary and conclusions: As already mentioned above, this section is very short. I think a statement on the relative influence of ships at the port, trucks at the port, and individual car traffic on the aerosol burden in the city would have been the desired output

of this study.

We have added some text addressing this gap.

Technical

Page 6, line 22: Link to appendix is missing

We added this link.

Page 12, line 34: Oberdörster

We corrected this error.

Additional changes made by authors

- All occurrences of μgm^{-3} were changed to μg m^{-3}.
- A few weeks after our submission to ACPD, the study of Preble et al. (2018) was published, reporting the exhaustion of diesel particulate filters and its influence on BC emissions at the Port of Oakland. This being very relevant to the conclusions drawn by us in this study, we have added a few sentences citing Preble et al. (2018) and highlighting the connection to our study (Sections 3.4 and 4 in revised version).

References

Apte, J. S., Kirchstetter, T. W., Reich, A. H., Deshpande, S. J., Kaushik, G., Chel, A., Marshall, J. D. and Nazaroff, W. W. (2011), 'Concentrations of fine, ultrafine, and black carbon particles in auto-rickshaws in New Delhi, India', *Atmospheric Environment* **45**(26), 4470–4480.

Canagaratna, M. R., Onasch, T. B., Wood, E. C., Herndon, S. C., Jayne, J. T., Cross, E. S., Miake-Lye, R. C., Kolb, C. E. and Worsnop, D. R. (2010), 'Evolution of vehicle exhaust particles in the atmosphere', *Journal of the Air and Waste Management Association* **60**(10), 1192–1203.

Crippa, M., Decarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J. B., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J. L., Prévôt, A. S. and Baltensperger, U. (2013b), 'Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris', *Atmospheric Chemistry and Physics* **13**(2), 961–981.

Crippa, M., El Haddad, I., Slowik, J. G., Decarlo, P. F., Mohr, C., Heringa, M. F., Chirico, R., Marchand, N., Sciare, J., Baltensperger, U. and Prévôt, A. S. (2013a), 'Identification of marine and continental aerosol sources in Paris using high resolution aerosol mass spectrometry', *Journal of Geophysical Research Atmospheres* **118**(4), 1950–1963.

Freutel, F., Schneider, J., Drewnick, F., Von Der Weiden-Reinmüller, S. L., Crippa, M., Prévôt, A. S., Baltensperger, U., Poulain, L., Wiedensohler, A., Sciare, J., Sarda-Estève, R., Burkhart, J. F., Eckhardt, S., Stohl, A., Gros, V., Colomb, A., Michoud, V., Doussin, J. F., Borbon, A., Haeffelin, M., Morille, Y., Beekmann, M. and Borrmann, S. (2013), 'Aerosol particle measurements at three stationary sites in the megacity of Paris during summer 2009: Meteorology and air mass origin dominate aerosol particle composition and size distribution', *Atmospheric Chemistry and Physics* **13**(2), 933–959.

Herndon, S. C., Onasch, T. B., Wood, E. C., Kroll, J. H., Canagaratna, M. R., Jayne, J. T., Zavala, M. A., Knighton, W. B., Mazzoleni, C., Dubey, M. K., Ulbrich, I. M., Jimenez, J. L., Seila, R., de Gouw, J. A., de Foy, B., Fast, J., Molina, L. T., Kolb, C. E. and Worsnop, D. R. (2008), 'Correlation of secondary organic aerosol with odd oxygen in Mexico City', *Geophysical Research Letters* **35**(15), 1–6.

Hoek, G., Meliefste, K., Cyrys, J., Lewné, M., Bellander, T., Brauer, M., Fischer, P., Gehring, U., Heinrich, J., Van Vliet, P. and Brunekreef, B. (2002), 'Spatial variability of fine particle concentrations in three European areas', *Atmospheric Environment* **36**(25), 4077–4088.

Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Richter, R., Crippa, M., Querol, X., Baltensperger, U. and Prevot, A. S. H. (2015), 'Spatial Variation of Aerosol Chemical Composition and Organic Components Identified by Positive Matrix Factorization in the Barcelona Region', *Environmental Science and Technology* **49**(17), 10421–10430. **URL:** *http://dx.doi.org/10.1021/acs.est.5b02149*

Ovadnevaite, J., O'Dowd, C., Dall'Osto, M., Ceburnis, D., Worsnop, D. R. and Berresheim, H. (2011), 'Detecting high contributions of primary organic matter to marine aerosol: A case study', *Geophysical Research Letters* **38**(2), 2–6.

Preble, C. V., Cados, T. E., Harley, R. A. and Kirchstetter, T. W. (2018), 'In-use performance and durability of particle filters on heavy-duty diesel trucks', *Environmental Science & Technology* **0**(0), null. PMID: 30153019.
URL: *https://doi.org/10.1021/acs.est.8b02977*

Saha, P. K., Khlystov, A., Snyder, M. G. and Grieshop, A. P. (2018), 'Characterization of air pollutant concentrations, fleet emission factors, and dispersion near a North Carolina interstate freeway across two seasons', *Atmospheric Environment* **177**(April 2017), 143–153.
URL: *https://doi.org/10.1016/j.atmosenv.2018.01.019*

Schmale, J., Schneider, J., Nemitz, E., Tang, Y. S., Dragosits, U., Blackall, T. D., Trathan, P. N., Phillips, G. J., Sutton, M. and Braban, C. F. (2013), 'Sub-Antarctic marine aerosol: Dominant contributions from biogenic sources', *Atmospheric Chemistry and Physics* **13**(17), 8669–8694.

Seinfeld, J. and Pandis, S. N. (2006), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2 edn, John Wiley and Sons, Inc., New York, chapter 21, Section 26.2.

Tan, Y., Dallmann, T. R., Robinson, A. L. and Presto, A. A. (2016), 'Application of plume analysis to build land use regression models from mobile sampling to improve model transferability', *Atmospheric Environment* **134**, 51–60.
URL: *http://dx.doi.org/10.1016/j.atmosenv.2016.03.032*

Tan, Y., Lipsky, E. M., Saleh, R., Robinson, A. L. and Presto, A. A. (2014), 'Characterizing the Spatial Variation of Air Pollutants and the Contributions of High Emitting Vehicles in Pittsburgh, PA.', *Environmental science & technology* .
URL: *http://dx.doi.org/10.1021/es5034074*

Tao, L., Fairley, D., Kleeman, M. J. and Harley, R. A. (2013), 'Effects of switching to lower sulfur marine fuel oil on air quality in the San Francisco Bay area', *Environmental Science and Technology* **47**(18), 10171–10178.
URL: *http://dx.doi.org/10.1021/es401049x*

Villena, G., Kleffmann, J., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M. A., Croxatto, G. and Rappenglück, B. (2011), 'Vertical gradients of HONO, NOx and O3 in Santiago de Chile', *Atmospheric Environment* **45**(23), 3867–3873.
URL: *http://dx.doi.org/10.1016/j.atmosenv.2011.01.073*

Von Der Weiden-Reinmüller, S. L., Drewnick, F., Zhang, Q. J., Freutel, F., Beekmann, M. and Borrmann, S. (2014), 'Megacity emission plume characteristics in summer and winter investigated by mobile aerosol and trace gas measurements: The Paris metropolitan area', *Atmospheric Chemistry and Physics* **14**(23), 12931–12950.

Xu, L., Suresh, S., Guo, H., Weber, R. J. and Ng, N. L. (2015), 'Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry:

Spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates', *Atmospheric Chemistry and Physics* **15**(13), 7307–7336.

Zimmerman, N., Li, H. Z., Ellis, A. A., Hauryliuk, A., Robinson, E. S., Gu, P., Shah, R. U., Ye, Q., Snell, L., R., S., Robinson, A. L., Apte, J. S. and Presto, A. A. (2018), 'Integrating spatiotemporal variability and modifiable factors into air pollution estimates: The center for air, climate, and energy solutions air quality observatory', *Atmospheric Environment* **Submitted**.