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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Downwind evolution of the volatility and mixing state of near-road aerosols near a US interstate highway" *by* Provat Kumar Saha et al.

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Anonymous Referee #1 In this study, the authors report composition, volatility and mixing state of traffic-related aerosols measured near a highway, 10 m to 220 m from the road edge. Measurements were conducted under varied environmental conditions including winter and summer campaigns. The investigation is important because vehicle emissions undergo a rapid transformation in ambient air which influences the key properties of combustion emissions with respect to their health and environmental effects. The data provided by this work is valuable and data-analysis is ambitious. Especially, this manuscript offers a high-quality data about the volatility distribution of traffic emis-

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sions. The topic is fitting well in the scope of ACP. Revised manuscript is suitable for publication in ACP after following comments are addressed:

We thank the reviewer for the encouraging comments.

The last paragraph of chapter 3.4 (tracer m/z based factor analysis) should be shortened. Perhaps, this paragraph could be moved to the supplement. Did you use estimation HOA = 13.4 $\times$ (C57 - 0.1 $\times$ C44) (Ng et al., 2011)? I would recommend using PMF (Ulbrich et al., 2009) instead of tracer-based factor analysis, if possible.

Following the reviewer's suggestion, we revisited the last paragraph of section 3.4. The details on tracer m/z based analysis and the corresponding discussion are moved to the supplement (see Sec. S5: Tracer m/z based factor analysis of ACSM dataset) and this analysis is now only briefly mentioned in the main text. As the reviewer inferred, tracer m/z based OA components are estimated following Ng et al. (2011) as: hydrocarbon-like OA (HOA $\sim$ 13.4 $\times$ (C57 $-$ 0.1 $\times$ C44)) and oxygenated OA (OOA $\sim$ 6.6 $\times$ C44), where C57 and C44 are the equivalent mass concentration of tracer ion m/z 57 and 44, respectively. Previous evaluation of this method has shown that it can reproduce the HOA and OOA concentrations to within $\sim$30% of the results from detailed PMF analysis (Ng. et al. 2011). A detailed PMF analysis of this data set would require an extensive new analysis and thus we considering it beyond the scope of this manuscript. Further, since the estimated traffic-OA (HOA factor) contribution was found to be $\sim$5-10x lower than that derived based on background-subtracted roadside concentrations measured by SMPS, we do not expect that a detailed PMF analysis will close this gap. We have discussed several factors that likely contribute to this discrepancy.

Revision: Please see revised SI, Sec. S5: Tracer m/z based factor analysis of ACSM data set.

Figure 8: Figure 8 is quite hard to read and should be improved e.g. by adding summer and winter volatility distributions (Table 1) to Fig. 8b for comparison and clarify figure

caption. If bins 2-6 (Table 1) are not applied in this work, please, consider removing these bins from Table 1 (or add marking for these).

We thank the reviewer for paying special attention to Fig. 8, and we agree that some clarification is needed. One thing requiring clarification is that the purpose of the analysis in Fig. 8 is not to show the volatility distributions from summer and winter. We show simplified versions of the volatility distributions from summer and winter at different distances from the highway in Fig. 7 and the full distributions are listed in table 1. The purpose of the analysis resulting in Fig. 8 was to examine how well a laboratory-measured volatility distribution of traffic POA (May et al., 2013) can explain the observed partitioning of vehicle emissions in a complex near-road environment. In this analysis, we hypothesized that the volatility distribution of road-side OA results from a superposition/weighted average of the volatility distributions of traffic-contributed OA and background OA. We compare our measured road-side volatility distribution (at 10 m) with a reconstructed distribution using the volatility distribution from laboratory vehicle measurements described in May et al. (2013) and the 'background' distribution measured at our furthest-from-road location (220 m). In the revised manuscript, we tried to clarify the discussion of Fig. 8 by changing the figure caption and legend, adding markers to the figure, improving the text description and adding a new supporting section in SI (sec. S4) that describes the analysis approach step-by-step.

Revision: Please see (i) revised Fig. 8, (ii) revised text in Sec. 3.4 and (iii) new addition of Sec. S4 in SI

Fig S3: Size distributions of nucleation mode particles look odd. Please, check SMPS data carefully, especially particles smaller than 10 nm

We thank the reviewer for taking a close look at this Figure and pointing out this issue. Fig.S3 showed example data from a typical transect measurement to demonstrate the relative change in particle number distributions at different distances from the highway. Data were collected using an SMPS system with a TSI 3010 CPC, which has a de-

tection limit (lower size cut) of 10 nm. Therefore, counting for particles smaller than 10 nm was distorted and should have been excluded from the original figure. In revision, we show a similar example data set from another transect run with data below 10 nm excluded. We mainly made this change to include an example that more clearly demonstrates, in a relative sense, the strong spatial gradient of PN size distribution above 10 nm.

Revision: Please see revised Figure S3

- Fig S7: AN and AS mass concentrations (calculation) based on a statement that aerosols are neutral. Please, add acidity plot (NH4 measured vs. NH4 calculated) to prove that assumption (Supplement) or use model such as Aerosol Inorganic Model II (AIM-II) (Clegg et al., 1998) for acidity calculation. An effective density calculation (Kuwata et al., 2012) of OA is limited to particle components having negligible quantities of additional elements. How traffic emissions components such as black carbon and NO3 effect on density calculations?

An acidity plot (of measured vs. predicted NH4) has been added as Fig. S7, panel (b). The NH4 predicted is estimated as: NH4 predicted = 2*(18/98)*SO4 + (18/63)*NO3 + (18/35)*Cl, where the fractional amounts correspond to the molecular weights of the relevant species. An ammonium balance can provide insights into the validity of assumption of neutral aerosol. Since the acidity plot (of measured vs. predicted NH4) has an average slope closer to $\sim$1 (1.1$\pm$0.03), indicating an ammonium balance. Therefore, assumption of neutral aerosols at the measurement location was reasonable.

We agree that it is important to note the limitations associated with the application of the Kuwata et al. (2012) parameterization for OA density, which was developed based on laboratory data with negligible BC or nitrogen content. However, we are unable to comment on the extent to which this deviation will affect the density calculated in this way. We do note that Kuwata et al. applied their parameterization to data from the AMAZE campaign, which had an average OA fraction of 0.8 (versus 0.74 for our data), and

found that the results agreed well with their measured density. Therefore, and given that we found the overall OA mass at this site to be dominated by relatively oxidized (OOA-like) spectra, we suspect that this parameterization does a reasonably good job describing our OA density. Therefore, we do not expect that the use of the Kuwata et al. (2012) parameterization, which assumes particle components having negligible quantities of additional elements, would introduce any dramatic bias. As noted elsewhere, we calculated the overall effective density of PM by weighting fractional contribution of major PM species (OA, BC, AN, and AS) with their respective densities; effective density of submicron PM = dens of OA $\times$fOA + dens of BC $\times$fBC + dens of AN $\times$fAN + dens of AS $\times$fAS. The campaign average fractional contributions are OA $\sim$74%, AS $\sim$13%, AN $\sim$7%, and BC $\sim$6%. The density of OA is calculated using the Kuwata et al. (2012) parameterization, which depends on the molecular composition of OA (O:C, H:C). OA was the dominant component of measured PM ($\sim$ 75%) and overall contribution of traffic emitted inorganic components ($\sim$ BC) was relatively small (BC$\sim$ 6%). Finally, since our mass comparison based on application of this density to SMPS-measured volume and ACSM+BC mass showed good agreement (Fig. S7a), this indicates our overall estimated effective density, on which OA density has the largest influence, is well constrained.

Revision: Please see revised Figure S7 and text in the caption.

References

Kuwata, M., Zorn, S. R. and Martin, S. T.: Using Elemental Ratios to Predict the Density of Organic Material Composed of Carbon, Hydrogen, and Oxygen, Environ. Sci. Technol., 46(2), 787–794, doi:10.1021/es202525q, 2012. May, A. A., Presto, A. A., Hennigan, C. J., Nguyen, N. T., Gordon, T. D. and Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: (1) Gasoline vehicle exhaust, Atmos. Environ., 77, 128–139, doi:10.1016/j.atmosenv.2013.04.060, 2013. Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M. and Worsnop, D. R.: Real-Time Methods for Estimating Organic Component Mass Concentrations from Aerosol Mass

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