

Interactive comment on “Quantification of black carbon mixing state from traffic: implications for aerosol optical properties” by M. D. Willis et al.

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Received and published: 24 February 2016

Response to Anonymous Referee # 3

Specific comments

We thank Referee #3 for their comments on this manuscript, which have helped us to more clearly communicate some of the complexities in this work. One issue which was brought up by all reviewers is the need to incorporate more details and discussion from the Supplement into the main paper. As a result, sections 2, 3, 4 and 7 of the Supplement have been moved into the main text. Our responses to specific comments

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and the corresponding changes to the manuscript are detailed below.

1. Page 33557 Line 10: define “HOA” in the abstract.

Authors’ response: Done.

2. Page 33562, Line 5-7: Please be specific about “these calculations.”

Authors’ response: This sentence has been revised to “...that can impact the calculation of rBC mass fraction in rBC-containing particles.”

3. Page 33563 Line 19: define “HOA” as this is the first time this term appears in the main text. Also I suggest that the authors briefly mention the speciation of the organics in Section 2.1 (e.g., in page 33561, line 14).

Authors’ response: Hydrocarbon-like organic aerosol is now defined at the beginning of the results and discussion section in the revised manuscript. A sentence has been added to section 2.1 (page 33561, line 14) briefly describing the use of positive matrix factorisation to separate HOA, oxygenated organic aerosol (OOA), and biomass burning organic aerosol (BBOA), which is further described in the results and discussion.

4. Page 33564, Line 13: Are the BC particles in rBC-rich particles coated only with HOA-material? This statement sounded so but Figure 3 shows that there certainly are other types of coating materials such as nitrate and sulfate aerosols, which are often neglected in the discussion. For example, in Section 3.3, the effect of other (inorganic) coating materials on the modelled bulk particle hygroscopicity should also be discussed.

Authors’ response: We acknowledge that this is a potentially confusing point, and we have made an effort to clarify these details related to mixing state in the main paper. The important point is that rBC-rich and HOA-rich particle classes from both studies are

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identified as those related to fresh emissions, and their average mass spectra from the cluster analysis do not contain detectable inorganic species (i.e., sulfate and nitrate). The sulfate and nitrate visible in the size distributions in Figure 3 are associated with more aged particle classes, which are not the focus of this work. In addition, sulfate and nitrate are correlated with OOA and BBOA factors from positive matrix factorisation, meaning that these species are associated with more aged and transported aerosol observed at the sampling sites. Therefore, when particles are emitted into the box model we consider that they contain rBC and HOA in varying amounts. The particles are aged in the model and become mixed with inorganic species, influencing their hygroscopicity, but the different types of particles emitted into the model are aged in similar ways with respect to the condensation of inorganic species and therefore no differences in hygroscopicity are observed after 24 hours. The following sentence has been added to the main text of the paper in Section 3.2 to make this clearer:

“Positive matrix factorization (PMF) (Zhang et al., 2011; Ulbrich et al., 2009) indicates three major sources of rBC and organic aerosol in the roadside environment: transported biomass burning (BBOA), regional background (OOA), and traffic emissions comprised of two PMF factors (HOA-rich and rBC-rich factors, Figure 5c-f). Inorganic species evident in the bulk aerosol size distributions (Figure 3a and b) are largely associated with OOA and BBOA factors, while the traffic-related factors contain the majority of rBC and HOA.”

5. Page 33565, Line 11: It is stated that mf_{rBC} in HOA-rich factors is 0.16. I am a bit confused since in Page 33563 Line 26 the authors stated that the average mf_{rBC} in HOA-rich particles are 0.03 and 0.05 during the non-roadside and roadside studies. How are these numbers related?

Authors' response: The reviewer is correct that there is a difference in the mf_{rBC} between HOA-rich particle classes from single particle data, and the HOA-rich PMF factor derived from ensemble data. The likely cause of this discrepancy is related

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to the probability that we observe detectable rBC signals in a single particle. Since the sensitivity of the SP-AMS to rBC is relatively low (i.e., the sensitivity relative to ammonium nitrate is 0.2 ± 0.05) it is possible that on a per-particle basis we do not observe detectable rBC signal, or observe very few rBC ions per particle, and therefore may underestimate the mf_{rBC} . In the ensemble data, we are able to average signals for longer times, thus increasing our probability of observing detectable rBC signal and increasing mf_{rBC} . In support of this hypothesis, a substantial fraction of single particles in the HOA-rich class from the roadside study have mf_{rBC} near zero. But, since we detect some signal associated with these particles, we know that they must have contained some amount of rBC so that vaporization could occur. This bias in mf_{rBC} may also be due to incomplete evaporation of rBC-containing particles in the edges of the laser.

To clarify these differences and also to qualify our conclusion based on this potential measurement bias the following has been added to Section 3.2: “Differences in mf_{rBC} between single particle and ensemble measurements, especially for HOA-rich particles that contain a small amount of rBC, may be due to the probability of rBC detection in a single particle so that single particle mf_{rBC} may be underestimated relative to ensemble mf_{rBC} (Lee et al., 2015).”

6. Section 3.3: It would be good to compare the modelled particle absorption with the in situ PASS-3 measurement, which was very briefly mentioned in the method section and should be expanded, to assess the potential bias resulted from assuming a core/shell morphology using Mie calculation. Were there any scattering measurements during any or both of the studies? If so, it would be good to compare the modelled SSA with the measurement.

Authors' response: Firstly, regarding the lack of detail about the PASS measurements, a new section has been added to the Methods section as follows: “A photoacoustic soot spectrometer (PASS-3, Droplet Measurement Techniques, Boulder,

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CO) was used to measure aerosol absorption (b_{abs}) and scattering (b_{sca}) coefficients (Mm^{-1}) at 405 and 781 nm. A 532 nm laser is not installed in this particular unit. The PASS determines aerosol absorption (Mm^{-1}) in a cavity which acts as an acoustic resonator. The absorption of incoming radiation heats the particles, which in turn heat the surrounding air in the cavity (Arnott et al., 1999). The aerosol-laden air thus expands, resulting in a pressure disturbance. By modulating the laser power at the resonance frequency of the cavity, the pressure disturbance is amplified and the resulting acoustic wave is measured using a microphone. Light scattering at both wavelengths is concurrently measured using reciprocal nephelometry (Moosmüller et al., 2009; Flowers et al., 2010; Chan et al., 2011). Signals were not corrected for truncation; however, it should be noted that total particulate loading is relatively low at this site and saturation was not observed in scattering signals. The instrument was calibrated using a propane soot generator (miniCAST, 6203A, Jing); since a 532 nm laser was not present in this unit an NO_2 calibration was not possible. PASS measurements of the bulk single scattering albedo at 405 nm (selected due to superior signal-to-noise ratio for scattering relative to the 781 nm channel) are used here only to illustrate differences in optical properties in vehicle plumes with varying composition.” Secondly, regarding a direct comparison between measured and modelled absorption and scattering from the PASS, we do not believe that a direct comparison is viable, and may not be informative of biases introduced by the core-shell assumption, for the following three reasons. First, the modelled SSA is for 550 nm, while only measurements at 405 and 781 nm were available. Second, we measure the bulk SSA with the PASS, while we model the SSA of only a subset of the total aerosol population (i.e., those particles that contain rBC, measured by the SP-AMS). A sentence has been added to the main text of the paper to clarify this important difference. Thirdly, a direct comparison of the absorption with total rBC measured by the SP-AMS may not be quantitatively useful since we are aware that the SP-AMS has a lower size limit, owing to the aerodynamic lens, that means we underestimate rBC mass by missing smaller particles (i.e., those below ~ 80 nm in vacuum aerodynamic diameter). This is also

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evident from the sharp decrease in rBC signals at small size in the size-resolved mass spectra. However, it is important to note that total rBC from the SP-AMS is well correlated with b_{abs} from the PASS measurements (this is detailed in Healy et al. (2015)). As noted above, the PASS measurements of SSA are included only to illustrate that we observe differences in optical properties in vehicle plumes with varying composition.

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