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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Size-resolved observations of refractory black carbon particles in cloud droplets at a marine boundary layer site" *by* J. C. Schroder et al.

Anonymous Referee #2

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Review of Size resolved observations of refractory BC particles in cloud droplets at a marine boundary layer site, by J. C. Schroder et al., for ACPD 2014

The manuscript presents total and cloud-residual aerosol measurements from two cloud events. There is a strong focus on BC aerosol, with interpretation of the ratio of total to cloud-droplet residual concentrations for activated fraction, and of "coating thickness" on BC for consistency with kappa-Koehler theory for CCN activation. This is an interesting "pool to play in", and the observations are interesting; however, more discussion and analysis need to be included to present and support hypotheses about the implications and science to be gleaned from the two case studies included. Two

specific areas that need more attention are the SP2 analysis, and inclusion of some discussion about the implicit assumption that BC is involved in the particles that activate as CCN before a droplet forms.

For the SP2 analysis, my concern is focused on two points. First, the detection efficiency of the SP2 is strongly dependent on laser intensity, the mass of BC in the particles, and, for small BC, the amount of non-BC material internally mixed with BC (Laborde et al., AMT 2012, Atmos. Meas. Tech., 5, 3077–3097, 2012 www.atmos-meas-tech.net/5/3077/2012/doi:10.5194/amt-5-3077-2012). This may be influencing the sharp reduction in apparent BC activated fraction at small sizes (Figure 6). The authors should include more information about SP2 laser power, and the level of agreement observed between the SP2s in cloud-free sampling. Note that cloud processed BC will naturally have thicker coatings than unactivated BC independent of the mechanism by which rBC became associated with the cloud droplets. This potential bias could affect the conclusion about the size distribution of rBC in the cloud residuals compared to total rBC. (On another note, the influence of fresh rBC that likely is not thickly coated from the recent city overpass should also be explicitly considered)

Secondly, not enough information is given about the potential biases associated with coating thickness determinations for the rBC-containing residual particles; I am concerned that the statement about increasing coating thickness with decreasing rBC core diameter could merely be due to an artifact (although it is expected a priori from our understanding of CCN), and encourage the authors to consider possible bias in their interpretation. At the heart of this issue the point that the SP2 is typically unable to optically optically size all rBC below an optical size roughly equivalent to that of a 220 nm PSL particle, which I think is roughly equivalent to the optical size of a bare rBC particle of volume equivalent diameter ~160nm. If one only sizes rBC-containing particles with at least this optical size, one will never capture the contribution to coating thickness of small bare or thinly coated rBC masses, but will only size small rBC masses with sufficient internally mixed material to reach this optical size threshold. I suggest that the authors carefully look at and present the statistics of LEO success in different rBC mass ranges to explore this (i.e. in your nomenclature, how what fraction of failed LEO fits is attributed to lack of elastic scattering signal at the 5% of peak laser power point, and how does this fraction change with rBC core mass?). I think that you need more analysis to evaluate whether the biases incurred from 50% LEO failure is affecting your interpretation of coating thickness trends. Finally, I don't understand how your failure "b" of scattering at time zero (i.e at the center of the laser beam?) is relevant to the LEO fit. These issues affect figures 6 and 7.

The needs more discussion of the microphysical route that rBC takes to get incorporated into the cloud droplets. What is the working hypothesis about the interaction? Do you believe that BC are internally mixed with other materials in CCN before activation? What is the coagulation rate for the freshly emitted rBC from the city with existing cloud drops? What do these measurements potentially teach us about BC interactions with cloud droplets? How do these results bear on the different approaches to modeling included in the introduction? What is learned from having observed two clouds? The statement that "rBC contributes to CCN" suggests (to me) an active role, what evidence supports this?

Specific comments:

Introduction: please clarify the sentence including "we measured BC as a function of size. . .compared to BC as a function of size."

Section 2.4:

Aquadag causes a higher SP2 response per unit mass than ambient rBC. For aquadag calibrations, it is recommended that the Aquadag signal used in the calibration be downward scaled by 0.75 for a better calibration (see Baumgardner et al.: Atmos. Meas. Tech., 5, 1869-1887, 2012 www.atmos-meas-tech.net/5/1869/2012/ doi:10.5194/amt-5-1869-2012). It does not appear that this was done here.

Section 2.5:

Please explicitly note that the coating thickness has not been validated experimentally, and merely provides consistency between observed optical scattering and mie theory. Of course having noted this, I'll suggest that you extrapolate even further, to coating volume, which is the more relevant quantity for kappa-Koehler.

Non-rBC particles passing through the SP2 can be used to constrain peak position and full width half maximum at times concurrent with the BC observations. These parameters can drift, so I suggest that you check variability in this way, and update the parameters on a reasonable time scale if necessary.

Note that for the SP2 measurement at 1064 nm, there are better estimates for the index of refraction of rBC – see: Method to measure refractive indices of small nonspherical particles: Application to black carbon particle by Nobuhiro Moteki, Yutaka Kondo, Shinichi Nakamura, 2010, in JAS. It is necessary to include the density of the rBC assumed in converting SP2 mass to mie-diameter.

Section 2.6: SMPS and SEMS agree to 4% in what? Total count? Count at each size?

Section 3.2:

$\pm$5 sigma does not give the reader much information. Can you present in a more useful was as, e.g. stability in CVI-D50, or % flow?

Figure 3 does not do a good job in showing the narrated relationship between droplet number and LWC. Perhaps a scatter plot would get this point across more clearly and strongly.

Section 3.3.2:

Please comment on the likelihood of droplet condensation on affecting bulk residual size distributions; it is not clear that the CCN that activated have not been affected in the cloud.

It is not clear if the residual rBC size distributions have been biased by low laser power/size dependent SP2 detection efficiency. The Detection Efficiency of the Single Particle Soot Photometer, doi:10.1080/02786826.2010.481298 by J. P. Schwarzab, J. R. Spackmanab, R. S. Gaoa, A. E. Perringab, E. Crossc, T. B. Onaschc, A. Ahernd, W. Wrobeld, P. Davidovitsd, J. Olferte, M. K. Dubeyf, C. Mazzolenig & D. W. Faheyab AS&T 2010 discusses these issues. If there is concern about this biasing rBC results, an easy fix is to remove the smallest rBC cores (e.g. below 100 nm or so?) from the analysis.

Section 3.5:

These results should be examined for possible bias as discussed above.

Section 3.6:

As the rBC-containing particle size distribution in the ambient is different than that of bulk aerosol, it is not clear to me what Figure 7 is meant to show in terms of the comparison of rBC and bulk aerosol.

Section 3.7:

"rBC cores have thick coatings which lead to overall particle diameters > 100 nm".. This assumes that rBC was present before activation. Please add discuss/support.

The relevant parameters for kappa-Koehler are the volume and kappa of non-BC material. Figure 9 essentially hides the fact that this is independent of BC content. I suggest explicitly discussing this, and attempting to show this in the context of both Figures 7 & 9, by plotting the horizontal axis as a diameter of non-BC materials (i.e. the diameter of only relevant materials for kappa-Koehler theory).

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 11447, 2014.