Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-602-RC2, 2018

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Temporal variations of the hygroscopicity and mixing state of black carbon aerosols in a polluted megacity area" *by* Kangning Li et al.

Anonymous Referee #2

Received and published: 10 August 2018

Summary

The manuscript focuses on several weeks of measurements made by an HTDMA-SP2 operating in parallel with a single-particle aerosol mass spectrometer, and explores relationships between refractory black carbon (rBC) hygroscopicity, proxies for rBC "coatings" and single particle aerosol composition. Quantitative details regarding rBC aging and influences on rBC aging timescales in the literature remain rare, and the topic is important, so the subject of the manuscript is significant and well within the topic area of ACP, however the analysis is somewhat limited, and in some areas focused on observations that are less relevant to areas where current scientific understanding is low.

Printer-friendly version

Discussion paper

It was unfortunate the SPAMS could not be place downstream of the HTDMA in parallel with the SP2, as that would allow for some interesting direct comparisons between particles containing rBC (or EC) at different growth factors. This weakens the overall strength and novelty of the manuscript, because many of the results presented are inferred by similar patterns or relationships in diurnal data rather than direct comparison. Despite this overall weakness, the other results are still of value and I recommend they be published once the following comments have been addressed.

General Comments

There is very little discussion of timescales for BC aging, despite its importance and the potential opportunity for this study to provide some useful measurements to help constrain aging timescales. Including results for the fraction of BC (to total BC, not total aerosol) observed at higher GF, how it changes over time, and how it is correlated with the other chemical information would strengthen the paper. Further, the bulk of the analysis is centered on diurnal plots of different parameters rather than examining relationships between those parameters. I would be interested in seeing a plot showing the relationship between these parameters over the study (e.g., coating thickness of BC in the high GF modes versus different chemical indicators). In addition, seeing differences in the fractions present in the higher GF modes as a function of other indicators of chemical activity (nitrate production, SOC production, etc), would provide a more quantitative relationship that could potentially be extrapolated to other locations.

Not sure this is really “first report of links between temporal variations of the hygroscopic growth of BC particles and atmospheric aging processes in a polluted environment.”

In several places the manuscript asserts that fresh BC emissions would by hygroscopic. This may be true for those arising from traffic, but is less clear for other combustion sources, such as domestic fuel use. How prevalent is that in the Shanghai area? Some discussion of this possibility should be included.

The treatment of uncertainty and variability in the results is not sufficient. More details are needed regarding variability in the diurnal data (e.g., showing as a box-and-whisker plot instead of just the averages and an interpolated fit as is currently done for these figures). Further, I think a little more detail regarding the uncertainties for coating thickness measurements from the SP2 or SP2-DMA composition are needed, as is more information related to the inversion and resolution of the HTDMA set up. While this might be available in previous work some brief mention of this is needed in the main text.

Further, while previous work is described in the introduction, there is little comparison of the results from this study to similar measurements in other urban areas.

Recommend adoption of the term “refractory black carbon” when referring to material measured by the SP2.

Specific Comments

64-68: There are earlier references for these findings that should be referenced.

69-93: This section could be better organized by placing similar studies together and having the narrative flow more smoothly. I suggest beginning with the HTDMA-ATOFMS studies, including those by the authors, then transitioning to the HTDMA-SP2 studies and their findings. Missing from this literature review is earlier laboratory work examining BC hygroscopicity, as well as any relevant HTDMA only studies. While these are not able to discriminate between BC and non-BC containing particles, they are relevant to the manuscript’s topic and some discussion would be beneficial to the reader.

100-102: At least some of the studies mentioned here should be cited.

115: As written this sounds like the cited studies used an HTDMA-SP2 system, which is not accurate. Recommend modifying slightly to: Similar to systems that couple an HTDMA with another instrument, such as those used by Herich et al. (2008), Zelenyuk et al. (2008), and Wang et al. (2014), our system used an SP2 (DMT, Boulder, CO,

USA) downstream of an HTDMA to measure BC content as a function of hygroscopicity.

118: Suggest changing “monodisperse particles with a dry particle diameter” to “monodisperse dried particles”

120: From later descriptions in the text it sounds like the wet SMPS operated in a stepped mode rather than scanning continuous mode. Please clarify.

123-125: Please provide a little more detail on the SP2 measurement for the reader, such as the SP2 response range (e.g., it will not measure BC present in particles if the BC mass is less than about 0.3-0.5 fg) and how “mixing state” is being measured (light scattering, difference between the dry DMA mobility size and effective rBC diameter, etc). Also should be careful with language here. . .mixing state is not the right term. The SP2 measures BC mass in particles and in some situations approximates “coating thickness” for assumed geometry.

225: I’m not sure the authors mean to attribute the reduction in particle number to size-dependent growth. . .the reduction in number is just a function of the dry size distribution. Please clarify in the text.

228: Figure 3b shows the BC number fraction, not the number concentration, so is not a good way to support the claim of a single BC mode. What does the distribution of BC number concentration versus GF look like?

233: I’m surprised at this decision given the focus of the paper is on BC hygroscopicity, and BC present in particles with high GF represent the most hygroscopic fraction of the ambient BC. What fraction of the BC number concentration did these particles represent? Note that the number fraction relative to other hygroscopic particles is not particularly important from a BC aging perspective, which is the focus of the paper (versus an assessment of CCN concentrations where particle type).

247-253: This section is essentially a description of BC diurnal patterns in an urban environment, and should refer to earlier papers first describing this behavior from ob-

servations in the 1990s.

261-263: Careful with this statement. The reduction in the fraction of BC measured for a specific GF does not necessarily follow from fresh BC being below 200 nm. The larger BC measured at GF = 1.0 is presumably “fresh” as well, and in the absence of other particles the ratio would still be expected to be 1. Factors driving the BC number fractions at GF = 1.0 may be more related to the behavior of non-BC containing particles and their size dependence.

281-286: Take care not to treat D0 as the BC particle diameter, as the dry size reflects the size of the mixed particle, not just the BC. The amount of BC in the particle could still be small if it were mixed with other material, bringing its total size to D0 (and also increasing the hygroscopicity). So the increasing fraction of BC particles referred to in this section likely more reflects aging rather than a different source.

294: This section is too brief and ignores many subtleties in the data that are potentially interesting. I’m not sure that the derived coating thicknesses can make physical sense given the growth factors. For example, the GF = 1.0 results all show average coating thicknesses of at least 20-35 nm, suggesting a significant volume of non-BC material, which must also have a GF = 1.0. While this is certainly possible, it seems unlikely that particles with this much coating can have GF = 1.0. More likely is some type of shape effect, which would play a larger role for fresh, hydrophobic BC that are likely to be aggregates and non-spherical. In this case the mobility size to core diameter relationship is not simply that predicted for spheres and used to derive coating thickness.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-602, 2018.