

Response to reviews

We thank the two anonymous reviewers for their comments. Both referees state the applied setup is novel and that it provides certain advantages over traditional methods. Referee #1 indicates that there is potential for the method that goes beyond the claims made in the manuscript and suggests adding additional discussion of those points. Referee #2 comments on the novelty of the method and analysis and provides positive feedback on the technical approach and the modeling of the CCN behavior due to coatings. Then the referee follows up with the concern that the idea to derive coating thickness from mobility and volume equivalent black carbon diameters measured by the DMA and SP2 is incorrect, and asserts that this invalidates the conclusions of this study.

Referee #2 is correct to point out that: 1) the quantification of the coating thickness from DMA and SP2 data is uncertain due to particle shape (which we openly discussed in the draft manuscript), 2) that our description of the calculations section 4.1 was very implicit and needs to be improved, and 3) that methods that provide particle mass can improve quantification of the coating thickness. We strongly disagree with the referee, however, that the uncertainty in the coating thickness affects the conclusions of our study. Our objective was to describe the number fraction of particles that is CCN active at a certain supersaturation. This quantity is derived from the BC growth factor measurement alone and does not require quantification of the coating thickness from DMA and SP2. Thus the results of the paper stand even if no quantification of the coating amount from either DMA or SP2 measurements was possible. In the manuscript we use DMA/SP2 derived coating parameters only to demonstrate the conventional thinking regarding BC hygroscopicity, namely that particles that register as coated are also hygroscopic and particles that do not register as coated are not. It therefore is a check of consistency of the classical coating parameters, rather than an attempt to quantify them. This consistency check shows that despite the difficulties in relating coating thickness and changes in the morphology of fractal soot to hygroscopicity that there is a clear relationship between coating thickness and hygroscopicity of ambient particles, pointing the way for future studies to separate the aging processes of BC.

In the following, the original comments are in presented *italic font* and our responses are in regular roman font. Revisions are given in **bold font**.

Response to referee #1

Referee: The manuscript presents a comprehensive exercise on BC hygroscopicity and activation. The authors use state-of-the-art instrumentation to study water uptake and all relevant BC properties simultaneously, which is a great advantage over conventional monitoring techniques. The study extends from laboratory experiments with BC proxies to ambient measurements at an urban location. The approach the authors rely on is purely a modelling one, namely that BC is getting hygroscopic and becoming CCN in cloud formation. While this is clearly an important question and relevant for global aerosol climatology, the instrumentation used by the authors would allow more detailed answers, far beyond that required by the modellers.

Response: We agree with the reviewer that the presented method has potential to answer a suite of questions that touch on fundamental processes and will produce results that may be beyond what (global) modelers need. We chose to focus on one particular application here since we firmly believe that measurement and modeling are joint efforts in addressing important atmospheric science questions.

Revision: Additional discussion was added to the manuscript. Please see next comment for wording.

Referee: The simple view is that BC particles acquire some soluble coating which eventually makes them available as CCN at specific supersaturations as a result of the combined effects of increased size and higher water-soluble fraction. The coating likely consists of sulphate and perhaps some oxidized organic compounds (e.g. malonic acid) which deposit gradually on the solid BC core. The authors focus their discussion on the case of nucleation scavenging only. A more realistic scenario is that hydrophobic BC particles do not necessarily need to reach the fully developed hygroscopic state to be activated in clouds. It is enough for them to coagulate with hygroscopic particles or get effectively scavenged into existing cloud droplets (in-cloud scavenging) which then evaporate leaving a larger and more hygroscopic residue (in-cloud processing). It is a fundamental question how to include such complex processes into global models. On the other hand, it can be misleading to use an overly simplified approach to calculate BC distribution in the global troposphere.

Response: It is correct that we focus on nucleation scavenging only. The term “coating” that we use to describe particles that are not 100% composed of BC may have falsely given the impression that coatings can only arise due to deposition of secondary compounds on BC cores. This is incorrect as “coatings” can just as well arise from coagulation and cloud processing. In fact, the method we present cannot distinguish whether: a) the hygroscopic material arises from coagulation of a BC particle with a hygroscopic particle, b) it occurred via a deposition process, or c) it occurred via collision of a BC particle with a cloud drop via Brownian diffusion or inertial scavenging producing a cloud-processed hygroscopic BC particle. Thus the interpretation of our results depends on accurate knowledge on the history of the air mass.

Revisions: (1) We now clarify the terminology of coating in the introduction. (2) Additional discussion was added to the manuscript. Please see our response to the next comment for these additional changes made to the manuscript.

Changes made to the introduction:

Over time BC particles acquire hygroscopic material that lower the critical supersaturation (s) at which BC particles can undergo nucleation scavenging (Wyslouzil et al., 1994; Weingartner et al., 1997; Zhang et al., 2008). Hygroscopic material can be acquired by multiple processes, including condensation of secondary products such as sulfates and organics or coagulation with hygroscopic

particles or cloud drops. We will refer to internally mixed BC particles as “coated”, where it is understood that no specific process is implied.

Referee: The results of this study also confirm that there is no continuous transition in the hygroscopic behaviour of BC particles which could have been expected if there were only gas-phase coating processes. Instead, there are virtually two well-separated submodes: one with growth factor around 1.0, and another around 1.6. A BC particle can escape removal from the atmosphere only if it is sufficiently large to be effectively incorporated into cloud droplets (by in-cloud scavenging) (around 300 nm, see left curves on Fig. 3 f) and g)). Smaller particles (blue lines, same figure) which do get into cloud droplets acquire a soluble coating and in case they do not precipitate they become susceptible for subsequent wet scavenging processes. Therefore the aging of BC particles is not a straightforward chemical process in which a soluble coating is getting gradually deposited on particles, but rather a probability driven on-off process which determines which fraction of BC gets cloud-processed. In this respect, in-cloud scavenging efficiency of a given BC particle would probably be more relevant than its ability to form CCN at any specific supersaturation. The two processes have different requirements for BC properties. I would have expected the authors to elaborate on these mechanisms and to define an explicit ‘accumulation mode’ hydrophobic BC distribution that would effectively escape both in-cloud and nucleation scavenging and get transported into the global troposphere. From Figure 9, it turns out that the mean diameter of this fraction is around 0.2 micron, but no size distribution is provided. From the modelling perspective, it is therefore misleading to assume that all BC particles that are not efficient CCNs would not be scavenged from the atmosphere. In fact they will be if they are sufficiently small enough to be scavenged by already existing cloud droplets.

Response: The referee’s interpretation of the results is certainly a valid possibility. We are fully aware that the data presented here strictly apply to the nucleation scavenging mechanism and we do not wish to make any claims regarding to the relative importance of nucleation scavenging versus washout. Further, we cannot make claims regarding the mechanism by which the particles become mixed with hygroscopic material; we simply observe it to be so. We are therefore not confident that our limited measurements are sufficient to validate or disprove the referee’s hypothesis about the underlying process causing the observations. A mixture of fresh local sources and processed long-range transport can explain the data equally well and it is unclear that the sampled particles have ever been in contact with a cloud. We note however, that the presented method can be used to test the referee’s hypothesis in an experiment where BC hygroscopicity distributions before and after a rainstorm are examined. If it is a probability driven on-off process as posited, then hydrophobic BC should be removed. If it is dominated by nucleation scavenging, then hydrophobic BC should remain while hygroscopic BC is removed.

Revision: We incorporated the referee’s points into the text through the addition of a new subsection “Pathways to rBC coating and removal”:

Pathways to rBC coating and removal: Refractory BC particles may acquire coatings or otherwise become mixed with hygroscopic material and/or be scavenged through several different mechanisms. The most simple and that addressed most clearly in our current study is the nucleation scavenging pathway, in which a non-hygroscopic rBC particle becomes coated and CCN active at a specific supersaturation. Partially coated or non-coated rBC particles may also coagulate with hygroscopic particles or be scavenged by existing cloud droplets. If the cloud droplet evaporates the remaining hygroscopic residue would include the rBC particle.

The HTDMA-SP2 approach cannot distinguish between rBC particles that have acquired coatings through any of these mechanisms. The interpretation of the results requires some idea of the air mass history, such as whether it was likely to have been cloud processed prior to sampling. The

method would be useful in examining the importance of different scavenging methods in that it would be able to probe how hydrophobic and hygroscopic rBC particles are affected by a precipitation event at the measurement location or the presence of cloud at a higher elevation site. Our limited measurements in the current study are insufficient to make larger conclusions about the role of various scavenging and rBC mixing processes, but we believe additional measurements with similar systems in a range of location would be able to provide much more insight.

Response to referee report #2

Referee: This paper introduces a novel experimental technique to study the hygroscopicity of black carbon (BC) soot aerosol as a function of aging. The technique combines the hygroscopicity tandem differential mobility analyzer with the soot photometer as the particle detector to obtain detailed information of the mixing state of BC-containing particles that few other methods can provide. This study is not routine and presents several interesting ideas that make the manuscript interesting to read. Among those ideas are the technical approach itself and a way to separate the contributions from the particle size, coating thickness, and hygroscopicity to the particle CCN ability. The first half of the manuscript, including the Results section, reads nicely because it is well organized and clearly written.

Response: We thank the reviewer for these positive comments.

Referee: The Discussion section, however, raises a number of questions. First of all, the discussion on page 929 is very implicit. This reviewer had a hard time to understand what the authors tried to deliver. This section needs careful re-writing. A few simple formulae to support the written statements are required, such as the relationship between D_{bc} , D_{mob} , and the effective density. The coating thickness needs to be defined, i.e. whether it is based on volume equivalent, mass equivalent, or mobility diameters.

Response: We agree with the reviewer that Section 4.1 needed improvement. We completely reworked the section and now include the relevant equations. We have also attempted to simplify the terminology by introducing the mobility-derived coating thickness (CT_{mob}) and the optically-derived coating thickness (CT_{opt}), providing equations for both.

Revisions: (1) We reworked section 4.1. (2) We changed Figures 2 and 3 to express the coating in terms of CT_{mob} . The reworked section is:

Relationships with rBC mixing state: We examined the relationships between several estimates of rBC coating thickness and mixing state for hydrophobic and hygroscopic rBC particles. Ideally, coating thickness could be quantitatively related to rBC particle hygroscopicity, but uncertainties in the rBC effective density (ρ_e) (shape, porosity), optical properties, composition and density of coating and emissivity of rBC limit how quantitatively these relationships can be determined.

The relationship between rBC mass (m_{BC}), mobility diameter (D_{mob}) and effective density is given by

$$\rho_e = \frac{6 m_{BC}}{\pi D_{mob}^3} \quad (3)$$

The effective density depends on the morphology of the rBC particles and increases for more compact particles. We calculated a mobility-based coating thickness (CT_{mob})

$$CT_{mob} = \frac{1}{2} \left(D_{mob} - \sqrt[3]{\frac{6 m_{BC}}{\pi \rho_e}} \right), \quad (4)$$

where it is assumed that the effective density at low *gf* particles is the same for all *gf*. We estimated $\rho_e \approx 1\text{-}1.5 \text{ g cm}^{-3}$ for the laboratory standards and $\rho_e \approx 0.6 \text{ g cm}^{-3}$ for ambient samples at *gf* = 1 by assuming there was no coating associated with these rBC particles (setting $CT_{mob} = 0$) and solving Equation 4 for ρ_e . The lower ambient ρ_e suggested these particles were more fractal and less compact compared to the laboratory standards. Moteki and Kondo (2010) reported a similar discrepancy between laboratory generated rBC and ambient rBC measured in Tokyo and also measured a similar effective density ($\rho_e \approx 0.5 \text{ g cm}^{-3}$ for $D_{mob} = 200 \text{ nm}$) for the ambient rBC.

We calculated CT_{mob} at higher gf by assuming ρ_e was constant and show results for selected laboratory-generated and ambient gf scans in Figures 2 and 3. Note that if ρ_e was actually lower than the $\rho_e = 0.6 \text{ g cm}^{-3}$ obtained at $gf = 1$ for rBC particles measured at higher gf , Equation 4 would over-predict the true coating thickness and vice versa if ρ_e were higher. For example, we observed an increase in CT_{mob} of approximately 25 nm for $gf = 1.6$ for the scan shown in Figure 3g, which requires an $\rho_e \approx 0.25 \text{ g cm}^{-3}$ to obtain the same $D_{mob} = 193 \text{ nm}$ if no coating was present. We believe it more likely that the rBC cores for coated, hygroscopic particles collapsed to a more compact shape (Alexander et al., 2008; Zhang et al., 2008; Lewis et al., 2009; Pagels et al., 2009), resulting in a higher ρ_e and an underestimate of the true coating thickness by Equation 4. We did not expect ρ_e for the laboratory proxy rBC species we tested to change following mixing with other material because they were not fractal aggregates. The presence of coatings do not affect the determination of m_{BC} by the SP2 other than the possibility that the some coatings for small rBC cores may be too thick to completely evaporate in the laser beam (Slowik et al., 2007; Schwarz et al., 2008).

Referee: Second, having understood the text on page 929, I realized that the cornerstone idea that supports the rest of this study is unjustified.

Response: We disagree that coating quantification is a cornerstone idea. None of the subsequent analysis relies on the absolute thickness of the coating, but rather discusses: (1) observed number fraction of BC that is CCN active at 0.2% supersaturation in ambient measurements, (2) changes in this number that are related to changes in transport, and (3) suggests a framework for treating BC hygroscopicity. We believe that we were upfront about the uncertainties involved using mobility classified aerosol, although we agree that the discussion could have been much clearer.

Revision: See previous comment and response to subsequent comment.

Referee: Specifically, it is incorrect to derive the coating thickness from the difference between SP2-measured rBC diameters of non-hygroscopic and hygroscopic BC aerosol fractions because these two are largely unrelated. All they have in common is the mobility diameter according to which they were classified by the DMA. The hygroscopic BC fraction was not necessarily produced via coating the non-hygroscopic one. They are externally mixed BC aerosols of (possibly) different origin.

Response: The referee is correct that the BC are possibly of different origin and that the uncoated BC and coated BC are not necessarily linked through a coating process via condensation (see also response to reviewer #1). Our method merely describes the hygroscopic state of the BC (i.e. hygroscopic/non-hygroscopic). Process-level understanding requires an experiment that constrains the history of the air mass, e.g., a Lagrangian study.

Revision: Please see the changes to the text in response to the comments from Referee #1 where we discuss this point.

Referee: To derive the coating thickness, one would have to perform the volatility analysis of the HTDMA-classified aerosol, using a third DMA in combination with the CPC and SP2, to measure the difference between mobility diameters of fresh and heated particles of the same hygroscopic growth factor. Considering the fractal morphology of fresh and partially processed soot, an instrument capable

of non-destructive measurement of the particle mass (density), such as the aerosol particle mass analyzer or the couette centrifugal particle mass analyzer, is required instead of the third DMA to quantify the coating thickness (see for example, J. Pagels et al., Aerosol Sci. Tech. 43, 629, 2009; A. F. Khalizov et al., J. Geophys. Res. 114, D05208, doi:10.1029/2008JD010595, 2009).

Response: We reiterate that none of our conclusions rely on the measurement of coating thickness and thus we consider this a moot point. We did not set out to solve the problem of quantifying coatings on non-spherical particles in the atmosphere. We do, however, believe that our setup does provide a new constraint on coating thickness that it worth exploring in future studies. Specifically, the qualitative finding that particles that have an apparent coating (by our methods and those developed by other SP2 investigators) are also hygroscopic is encouraging.

It is well established that assumptions must be made in the analysis of particles that are absorbing and non-spherical. There are multiple methods to estimate coating thickness from our data that include coating thickness derived from mobility size, optical size, as well as from the measured κ provided the composition of the coating can be estimated. The setup proposed by the referee, who suggests the measurement of mass of the coated particle, provides yet another measurement of coating amounts. Single particle electron microscopy and single particle mass spectrometry can provide further constraints. Each of these methods will be susceptible to measurement error and analysis assumptions (particle shape, refractive, instrument resolution, assumptions/measurement of chemical composition, non-interference of coatings with BC mass measurements, phase state of the coating material, selectivity of chemical measurements. etc.). Carefully designed closure studies are required in order to obtain hard data on the reliability and quantification limits of each of these methods. These however, are not the subject of this manuscript.

We do point out, however, that three independent coating measures including two often used in the SP2 literature, i.e., mobility coating thickness, optical coating thickness, and number fraction of coated particles, increase as κ increases. Further, there is a good correlation between optically-derived and mobility-derived coating thickness that we now show in the manuscript. We therefore believe that our initial limited conclusion is justified.

Revisions: (1) We discuss the response to this comment in the text and (2) we removed Figure 6 that showed the relationship between coating thickness and κ for laboratory generated BC proxy particles, (3) we included the optically-derived coating thickness in a revised version of Figure 9.

We also used two additional estimates of rBC coating thickness and mixing state to compare high and low *gf* rBC particles and compared the results to CT_{mob} . We calculated the number fraction of thickly coated particles based on the distribution of delay times measured for rBC particles by the SP2. The optical coating thickness (CT_{opt}) was calculated using Equation 4 but replacing D_{mob} with the PSL-equivalent optical diameter determined from the SP2 light scattering measurement. Both of these estimates also increased with higher *gf* for both laboratory-generated and ambient samples. If the κ of the coating is known or assumed, then the *gf* themselves can be used to obtain an estimate of the coating thickness by solving Equation 2 for the volume fraction of the coating assuming a core-and-shell morphology and $\kappa = 0$ for rBC. Thus the HTDMA-SP2 system can provide three different estimates of coating thickness based on the relationships between m_{BC} and a) mobility (CT_{mob}), b) rBC optical size (CT_{opt}) and c) hygroscopicity (CT_{κ}). Each estimate has inherent uncertainties associated with particle shape and composition, but may be helpful in constraining predicted and measured rBC properties through closure approaches. The HTDMA-SP2 was combined with independent measures of coating mass, such as the DMA-aerosol particle mass analyzer technique used by Pagels et al. (2009) and Khalizov et al. (2009), to investigate the conditions for which the HTDMA-SP2 coating thickness estimates can be used with confidence.

The revised version of the figure is

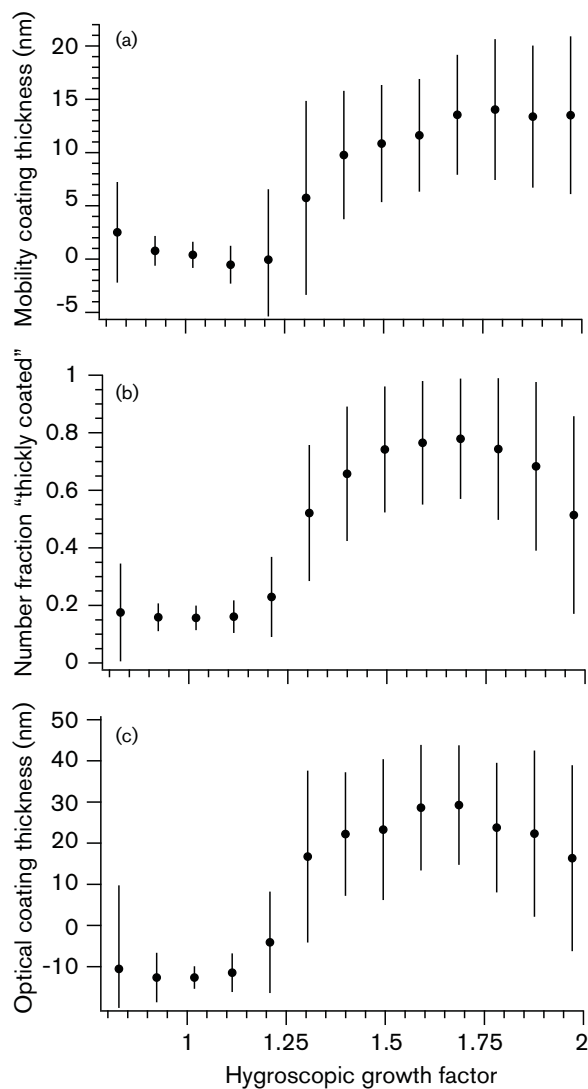


Figure: SP2-derived coating information for HTDMA-SP2 scans for ambient Manchester rBC between 11-16 August 2010. Shown are the mean and standard deviations binned by growth factor for mobility-derived coating thickness (a), number fraction of thickly coated rBC particles (b), and optically derived coating thickness (c).

Referee: I do not think that this manuscript in the present form is publishable and do not see an easy way of improving this manuscript to make it publishable without additional measurements. A number of other minor issues that need to be corrected are outlined below.

Response: We strongly disagree with the referee that a minor point of the paper, and one that is a common and implicit issue for most aerosol measurements, merits rejection of this manuscript. Our assumptions are clearly stated and uncertainties are included in the analysis. The main critique with respect to particle shape and uncertainty in derived coating thickness is not a cornerstone of the argument of the manuscript, but highlights further studies of research that would fully quantify the nature of the coating (e.g. the relationship of kappa vs. coating thickness). If the chemistry of the coating is known, the technique presented here could potentially be inverted to serve as additional constraint of the coating amount.

P. 923, L. 18: D_{BC} is introduced as “volume equivalent diameter” whereas in the rest of the manuscript it is referred to as “mass equivalent diameter”.

Response: We made the wording consistent

P. 924, L.7: What is the physical meaning of A in equation (1). Also, surface tension (σ) is referred to, but does not appear anywhere in the equations.

Response: Thanks for pointing this out. We unintentionally omitted σ and T from the equation defining A. Fixed.

P. 925, L.6: Not always critical supersaturation can be obtained from hygroscopicity measurements at subsaturated relative humidity (RH). For instance, as many organic acids do not deliquesce below about 99% RH, their kappa factor determined at 90% RH would be essentially zero.

Response: This is correct.

Revisions: We clarified our assumptions in two places of the manuscript

The relative number fraction of aged particles is then computed by integrating the growth factor distribution above the threshold value and dividing by the total rBC number concentration detected during the scan. This procedure rests on the assumption that growth factor-derived κ values can be reliably extrapolated to supersaturated conditions. If sparingly soluble compounds are present they will not contribute to the measured κ (Petters and Kreidenweis, 2008) and the fraction F_{aged} will be underestimated.

The calculation of F_{aged} from ambient data requires the assumption that κ from subsaturated measurements can be extrapolated to supersaturated conditions and that D_{mob} approximates the sphere equivalent diameter. Laboratory studies suggest that these assumptions are sufficient (Henning et al., 2010) but they should be scrutinized in future studies that also include a CCN instrument.

P.927, L.2-6: The way “non-hygroscopic mode” is used here makes this sentence somewhat confusing.

We rewrote this sentence.

Two ambient gf scans are shown in Figure 3f and 3g. These scans exhibited a non-hygroscopic mode centered at $gf = 1.0$ and a hygroscopic mode centered at $gf = \sim 1.5$. The population of particles that did not take up water as dominated by rBC with an $\sim 10\%$ contribution by number of non-rBC particles.

P. 928, L.7: Define abbreviation “a.g.l.” (above ground level?)

Yes, a.g.l. = above ground level. Done.

Figure 8: If number fractions shown in (a) and (b) summed together amount to 1, then either of them can be removed

Response: They do not sum to one, but address two different particle populations. One is the total rBC particles divided into hygroscopic and non-hygroscopic modes, the other non-hygroscopic mode divided into BC and non-BC. For example, consider a population of 10 particles, with 6 total hydrophobic particles and 4 total hygroscopic particles, with each mode containing 2 rBC particles. Figure 8a would show: $2 \text{ hygroscopic rBC} / 4 \text{ total rBC} = 0.5$ and Figure 8b would show: $2 \text{ hydrophobic rBC} / 6 \text{ total hydrophobic} = 0.33$.

Additional changes to the manuscript

We thank Professor Kim Prather for bringing to our attention a number of studies that have quantified the BC mixing state and were not included in the draft manuscript. We now include these studies in our overview of prior work. We also made a number of minor changes to the writing as indicated in the submission to the revised manuscript.

Added References:

Herich, H., Kammermann, L., Gysel, M., Weingartner, E., Baltensperger, U., Lohmann, U., Cziczo, D. J.: In situ determination of atmospheric aerosol composition as a function of hygroscopic growth, *Journal of Geophysical Research*, 113, D16213, doi:10.1029/2008JD009954, 2008.

Khalizov, A. F., Zhang, R., Zhang, D., Xue, H., Pagels, J., and McMurry, P. H.: Formation of highly hygroscopic soot aerosols upon internal mixing with sulfuric acid vapor, *Journal of Geophysical Research*, 114, D05208, doi:10.1029/2008JD010595, 2009.

Moffet, R. C., and Prather, K. A.: In-situ measurements of the mixing state and optical properties of soot with implications for radiative forcing estimates, *Proceedings of the National Academy of Sciences*, 106, 29, 11872-11877, 2009.

Moteki, N., Kondo, Y., Miyazaki, Y., Takegawa, N., Komazaki, Y., Kurata, G., Shirai, T., Blake, D. R., Miyakawa, T., and Koike, M.: Evolution of mixing state of black carbon particles: Aircraft measurements over the western Pacific in March 2004, *Geophysical Research Letters*, 34, L11803, doi:10.1029/2006GL028943, 2007.

Pagels, J., Khalizov, A. F., McMurry, P. H., and Zhang, R. Y.: Processing of soot by controlled sulphuric acid and water condensation-Mass and mobility relationships, *Aerosol Science and Technology*, 43, 7, 629-640, 2009.

Pratt, K. A., and Prather, K. A.: Aircraft measurements of vertical profiles of aerosol mixing states, *Journal of Geophysical Research*, 115, D11305, doi:10.1029/2009JD013150, 2010.

Zelenyuk, A., Imre, D., Han, J.-H., Oatis, S.: Simultaneous measurements of individual ambient particle size, composition, effective density, and hygroscopicity, *Analytical Chemistry*, 80, 1401-1407, 2008.