

## Author reply to the short comment by E. Lewis and A. J. S. Sedlacek:

We thank Ernie Lewis and Arthur Sedlacek for their detailed examination of our data set and for their suggestions. Their comments are repeated in plain black font, author replies are provided in plain blue font and modified/additional excerpts of the manuscript are provided in quoted *italic blue font*.

As black carbon (BC) particles are typically not spherical but rather composed of aggregates of smaller spherules, determination of the mass  $m$  of such a particle from its mobility diameter  $D_{\text{mob}}$  is not straightforward. The authors parameterize the relation between  $m$  and  $D_{\text{mob}}$  in terms of the effective density  $\rho_{\text{eff}}$ , which is the density calculated under the assumption that the particle is spherical with diameter equal to the mobility diameter. Further, they present relations between this effective density and mobility diameter for Aquadag particles with  $D_{\text{mob}}$  between 60 and 710 nm and for Fullerene particles with  $D_{\text{mob}}$  between 65 and 900 nm, which they display (along with their measurements) on a log-log plot. The relation for Aquadag is an 8th order polynomial and that for Fullerene a 9th order polynomial, with coefficients presented in Table 1, together with a warning not to round to coefficients to fewer significant digits (most are given to six significant digits). However, despite the appearance of high accuracy, the estimated accuracy of the measurements is only  $\pm 10\%$ . In light of such a large uncertainty it would seem that such a function form for the fits is a bit excessive, and that the data could be represented nearly as well with a simpler fit.

We had some discussions among ourselves about the required number of polynomial coefficients and the number of significant digits to be provided. As a consequence the first author of this manuscript made the tedious effort, already for the AMTD version of this manuscript, to determine the minimum number of coefficients and number of significant digits, required to assure 1% relative precision of the polynomial fit across the whole diameter range, separately for every single polynomial coefficient provided in Table 1. It has to be emphasized that more than  $n$  significant digits in the polynomial coefficients may be required to achieve  $n$  significant digits in the corresponding value of the polynomial! Reducing the number of significant digits by one in all coefficients, i.e. increasing the tolerance to 10% precision wouldn't make much sense as we don't want to add an extra 10% uncertainty on top of the experimental uncertainty. In summary, reducing the number of digits in the polynomial coefficients is a no-go, as emphasized in the caption of Table 1.

Indeed, if the effective density for Aquadag and Fullerene is graphed against the mobility diameter on a linear-linear plot, as shown in Figure 1, an underlying linear relationship is seen to represent the data exceedingly well over the vast majority of the range of mobility diameters. The relations  $\rho_{\text{eff}} = 820 - 0.64D_{\text{mob}}$  for Aquadag and  $\rho_{\text{eff}} = 770 - 0.53D_{\text{mob}}$  for Fullerene can be clearly seen to be quite accurate over most of the range of accumulation mode mobility diameters studied, agreeing to within 5% for mobility diameters greater than 100 nm for Aquadag and 150 nm for Fullerene, and to within approximately 1% for mobility diameters greater than 115 nm for Aquadag and 185 nm for Fullerene. For the sake of completeness, and to facilitate calculation of the effective density for lower sizes, the fits  $\rho_{\text{eff}} = 1490 - 10.9D_{\text{mob}} + 0.039D_{\text{mob}}^2$  for Aquadag and  $\rho_{\text{eff}} = 1640 - 10.8D_{\text{mob}} + 0.031D_{\text{mob}}^2$  for Fullerene (shown in Figure 1 by dashed lines) match those presented by the authors to within 1% for  $D_{\text{mob}}$  in the ranges 60-140 nm for Aquadag and 65-165 nm for Fullerene.

We had some discussion among ourselves about the most suitable form of parametrisation to be used for the effective density and mass as a function of mobility diameter before submitting the manuscript to AMTD. Briefly, mainly two conditions have to be fulfilled by any acceptable fit:

1. The fit should represent the experimental data within their own spread and experimental uncertainty across the whole parameter space.

- II. The fitted mass-mobility diameter relationship AND its first derivative MUST be continuous. (Otherwise one will end up with discontinuities in the measured mass size distribution of the investigated calibration material, if one applies this mass-mobility diameter relationship to convert the SP2's mass measurement to diameter values. This step is very useful to cross-check the fitted calibration curve against the calibration data set. A continuous derivative will also assure a smooth size dependence of the fractal dimension as a function of mobility diameter.)

Besides it is of course desirable to keep the parametrisation as simple as possible. The alternative fit approach suggested in this comment (fulfills condition I) but condition II) is not fulfilled at the point where the linear and quadratic parts of the fit are stitched together. This could be solved by fitting a continuous two segment spline with continuous derivative and the additional constraints that the lower and upper spline segments are second and first order polynomials, respectively. The first author actually started off with using multi-segment polynomial splines to parametrise the experimental data. However, in the end we came to the conclusion that a single higher order polynomial valid for the whole range of mobility diameters covered by the experiment is at least as simple to explain to the readership, to present in a table and to implement in the data analysis code, compared to providing and implementing a multi-segment spline stitched together from multiple lower order polynomials. Therefore we keep the parametrisation as is. Any user of the experimental data reported here (provided as supplementary information) can of course fit and use its own parametrisations as long as they represent the data well.

The departure of  $\rho_{\text{eff}}$  from the linear trend at small mobility diameters reflects the fact that as the size of the aggregate decreases the effective density must approach that of the primary particles (i.e., individual spherules) that make up the aggregate (in the limit of the 'aggregate' consisting of a single primary particle the effective density would equal that of the primary particle itself). To illustrate this point, consider a Fullerene particle comprised of primary particles of diameter 50 nm and density 1200 kg m<sup>-3</sup> (the values stated in the paper). A particle with  $D_{\text{mob}} = 100$  nm would consist of approximately 5 primary particles, and one with  $D_{\text{mob}} = 70$  nm (the leftmost data point on Figure 4 of the paper) of only 2.4 primary particles. If it were assumed instead that the individual spherules had diameter 60 nm, the number of primary particles would be 3 and 1.4, respectively. An aggregate consisting of so few primary particles cannot attain the "wispieness" or fractal nature that larger aggregates can, and thus it is not surprising that the density deviates from the linear relationship exhibited by these larger aggregates. Additionally, it should be noted that discrete values of the mobility diameters should occur at small sizes, reflecting the small number of configurations possible for few primary particles.

Aquadag particles are aggregates of irregular flakes of graphite (Moteki et al., 2009) and fullerene soot particles are aggregates of spherical primary particles with ~50 nm diameter (Moteki et al., 2009). Either material has kind of a fractal-like structure, which explains the sharp increase of effective density at small mobility diameters, as detailed in this comment. However, occurrence of discrete values of mobility diameters and effective density values are not expected, as the building blocks of these aggregates vary in size and to some extent in shape, and they tend, at least in the case of fullerene soot, to conglomerate with each other (Moteki et al., 2009).

We added the following statement to discussion of the results for Aquadag:

*"Decreasing effective density with decreasing mobility diameter is consistent with aggregates of small irregular flakes of graphite (see Moteki et al., 2009, for a detailed characterisation of the structure of Aquadag)."*

And the discussion of the results for fullerene soot reads now:

*"The effective density of fullerene soot decreases from ~1000 kg/m<sup>3</sup> at  $D_{\text{mob}}=80$  nm to <400 kg/m<sup>3</sup> at  $D_{\text{mob}}>700$  nm. This is much lower than the bulk density of fullerene soot of ~1720 kg/m<sup>3</sup> (Kondo et al., 2011), and consistent with a fractal-like agglomerate of small primary spheres (see Moteki et al., 2009, for a detailed characterisation of the structure of fullerene soot)."*

Finally, we would also like to point out that the Gysel dataset offers the opportunity to examine the fractal dimension, defined as  $D_f = \partial \ln(m) / \partial \ln(D_{mob})$ , for these two substances. Using the expression for mass in terms of effective density given above, this expression is equivalent to  $D_f = 3 + (D_{mob} / \rho_{eff}) (\partial \rho_{eff} / \partial D_{mob})$ . The values of  $D_f$  calculated using the linear relations presented above are shown in Figure 2 as a function of mobility diameter. As per expectations, the fractal dimension approaches 3 at the smaller aggregate sizes, reflecting the limited clustering that can occur with few spherules, and decreases as the number of primary particles that make up the aggregate increases, reflecting the increased wispieness of these larger aggregates. (There is some anomalous behavior of the fractal dimension at mobility diameters below that at which the data deviate from the linear fit, possibly due to the few number of primary particles resulting in  $D_{mob}$  not being a continuous function, as required for the derivative in the definition of fractal dimension, but rather a discrete quantity.) It is hoped that this brief “back-of-the-envelope” analysis will inspire the authors to examine additional lines of inquiry. For example, why is the effective density approximately linear in mobility diameter, and what is the criterion, in terms of mobility diameter or number of primary particles, above which this linear relation holds?

We agree that the fractal dimension increases, as expected, with decreasing particle diameter down to  $D_{mob} \sim 200$  nm, and that some anomalous behavior of the fractal dimension occurs at mobility diameters below that. The data set available in this study does not allow making conclusive statements on the reasons for the observed size dependence of the fractal dimension. Therefore we decided not to include such a discussion, which would be speculative for the most part, in the revised manuscript. Instead we refer the reader to the study by Moteki et al. (2009) for more detailed investigations on the structure of different BC materials (this has already been done in response to the above comment).