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Interactive comment

# Interactive comment on "Droplet activation behaviour of atmospheric black carbon particles in fog as a function of their size and mixing state" by Ghislain Motos et al.

#### Ghislain Motos et al.

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Received and published: 23 January 2019

RESPONSES TO THE REFEREES AND CHANGES MADE TO THE MANUSCRIPT.

The authors would like to thank the three referees for their constructive comments which helped to make the paper clearer and easier to understand. This document presents, for each comment from the referees, a response and a note clarifying what has been changed in the manuscript. Indications of page and line numbers refer to the revised version of the manuscript (without track changes).

Answers of the authors to the interactive comment of Anonymous Referee #2 (Referee





#### Comment 2)

#### Anonymous review of manuscript: General remarks

The authors report results from a case study comprising four separate fog events observed in an urban environment in Zurich. Overall, the manuscript is well written and the data analysis has been conducted with great care. The results show that soluble coating on top of an insoluble black carbon (BC) cores indeed increases their ability to serve as condensation nuclei for fog droplets, and the threshold coating thickness decreases with increasing BC core size. Furthermore, the authors demonstrate that a simple -Köhler model can be used to predict the fog droplet activation when the particle size, coating thickness and hygroscopicity of the coating material are known. Understanding the mixing state of ambient BC and its impact and fate in the atmosphere has been of great interest to aerosol community, and thus, the manuscript by Motos et al. is well within the scope of ACP. That said, the main findings of this study are more incremental rather than novel and (as such) provide a little new insight into the studied topic. Therefore, I would like to see more discussion concentrating on the implications of the results, e.g., how black carbon and its aging are currently treated in particle-resolved models (that were also mentioned in the conclusions) and how these new results could possibly improve these aspects. In other words, there is definitely no need to shift the focus of the paper from experimental research into modelling, but instead, highlight the importance of the results and point out more concretely how aerosol community could benefit from them. In my opinion, this would improve the impact of the paper substantially. Otherwise, I only have a few minor comments and suggestions to be considered by the authors.

Response: We thank the referee for the in this article and the suggestions to highlight the potential benefits our main results can bring to the aerosol community. Another paper focusing on the activation of BC in liquid clouds has recently been submitted to ACPD (https://www.atmos-chem-phys-discuss.net/acp-2018-1054/). It combines results from measurements at a high altitude site of clouds with medium to high peak

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supersaturation with the results of the present paper of fog with low peak supersaturation. A broader discussion of the activation of BC (in different environments and at different supersaturations) including potential benefits and implications for the modelling community are discussed in more detail in this other paper.

Changes: Here we added the following sentences to Sect. 3.5, p. 19, I. 32: "Several mixing state-resolved modelling studies simulated scavenged fractions based on the estimation of the critical supersaturation using the Köhler theory combined with the ZSR mixing rule (e.g. Matsui, 2016; Ching et al., 2018). The present study suggests that such modelling approaches are valid, at least for fog with low peak supersaturation, and encourages future use of them."

Specific comments from Referee #2:

Comment: "Page 3, Line 21: A relatively recent paper by Maalick et al. (2016) presents results from LEM simulations concentrating on the effect of BC on the evolution and lifetime of radiation fog. Although this specific paper does not directly deal with BC mixing state, it points out an important aspect of BC in aerosol-cloud/fog interactions and could be cited in this paragraph (if the authors wish)."

Response: Agreed by the authors.

Changes: We added the reference to the paragraph mentioned in the comment (p. 3, I. 19): "Although BC can dissipate fog through the semi-direct effect (evaporation of fog droplets due to absorption of solar radiation by BC particles and subsequent droplet evaporation), high concentrations of other CCN were shown to influence fog lifetime in a stronger manner (Maalick et al., 2016). Because these CCN form droplets more efficiently, they lead to increased radiative cooling and decreased droplet removal through sedimentation, thus enhancing fog lifetime."

Comment: "Page 3, Line 35: The study by Dalirian et al. (2018) has been conducted by atomizing BC particles from aqueous solutions and then coating them with organics

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by using a tube furnace. Therefore, it should be referred to as laboratory study rather than a conventional chamber measurement."

Response: We thank the referee for these important details.

Changes: We modified "chamber experiments" by "laboratory studies" in the paragraph mentioned. We also added the following paragraph to Sect. 3.5, p. 19, l. 37: "Dalirian et al. (2018) conducted a laboratory study during which they atomized BC particles from aqueous solutions and then coated them with organics by using a tube furnace."

Comment: "Page 5, Line 26: Later in the paper, the authors are referring to uncertainties in CCN calibration (Sect. 3.1). Therefore, it would be good to briefly describe how the instru-ment was actually calibrated and how the possible instrumental limitations are affecting the measurement uncertainties especially at the lowest and highest supersaturations."

Changes: The following paragraph was added to the experimental section (Sect. 2.2.1), p. 5, l. 32: "The CCNC was calibrated before and after the campaign on 13 August 2015 and 23 March 2016, respectively, using size-selected ammonium sulfate. Both calibration curves agreed within 5% (relative) with each other and are in good agreement with the instrument history for the range between 0.1% and 1.0% SS. This agreement is better than the estimated calibration accuracy of ~10%. As discussed later, the CCNC was also operated at SS = 1.33% during the campaign. Higher uncertainty of  $\pm$ 20% was assigned to this supersaturation to give allowance for extrapolation uncertainty, which may have caused larger bias for data derived from measurements at this SS."

Comment: "Page 8, Line 24: Here, the authors define that the hygroscopicity of the soluble coating  $\kappa$ coating is equal to  $\kappa$ median, which according to Sect. 2.3.4 is directly inferred from CCNC measurements. To my understanding, the value obtained from CCNC data is representative for all particles of equal size, and thus, reflects the possible presence of non-hygroscopic black carbon. This would mean that

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 $\kappa$ median-> $\kappa$ coating only when the fraction of BC containing particles ! According to the manuscript BC-free particles "represent majority of the particles" (Page 14, Line 15), and therefore, the definition of  $\kappa$ coating :=  $\kappa$ median would be justified. Is this rationale correct or have I misunderstood the applied notation? In any case, I'd like to ask the authors to describe the reasoning behind  $\kappa$ coating :=  $\kappa$ median more carefully to improve readability and to avoid any danger of misunderstanding. This leads me to another question: can you quantify "majority of the particles"? For example, would it be useful/possible to have a plot estimating the number or volume fraction of particles with BC core as a function of dry particle size (e.g. in supplemen-tary material)?"

Changes: We added the following paragraph to Sect. 2.3.2 p. 9, l. 16: "[...]We treated our particles as two-component mixtures considering an insoluble BC core ( $\kappa = 0$ ) and a soluble coating to which we assigned the size-resolved median  $\kappa$  value ( $\kappa$ coating:= $\kappa$ median) obtained from sCCNC measurements:  $\kappa$ median was retrieved from the diameter at which 50% activation is reached for a certain SS applied in the CCNC (see Sect. 2.3.4). Figure 7, which will be discussed later, indicates that  $\kappa$ median is virtually not affected by variations in the number fraction of locally emitted BC particles. Instead,  $\kappa$ median is representative of the hygroscopicity of the background aerosol, which has a very small BC mass fraction (e.g: Hueglin et al, 2005), and was therefore chosen as approximation for the coating hygroscopicity. [...]"

Comment: "Page 11, Line 15: The authors state that the anomalies in the sizedependence of  $\kappa$  are likely due to the increased uncertainties in CCNC calibration at the lowest and highest supersaturation. In the next two paragraphs, however, the results from these two supersaturations are being discussed more detailed and the authors even use the measured value of  $\kappa$ median = 0.6 (at SS = 1.33%) to support their hypothesis on night-time accommodation of ammonium nitrate. Frankly, this would not make much sense if the anomalies in the size dependence of were solely due to calibration uncertainties. It should be addressed more carefully how the CCNC calibration uncertainties effect the data and data interpretation.

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Response: This apparent confusion is resolved by the fact that the first statement refers to a small deviation, whereas the following two paragraphs refer to substantially higher  $\kappa$ . The text has been modified to avoid this confusion. Moreover, most of the discussion in the two paragraphs is based on temporal patterns, which only relies on precision rather than accuracy of the data.

Changes: First of all, we added uncertainties to the values shown in Table 1. The statement about size dependence of  $\kappa$  was reworded (p. 12, l. 17): "[...] Mean aerosol hygroscopicity increased with increasing particle size (Table 1), a feature which is often observed for atmospheric aerosols (Swietlicki et al., 2008). Note, the aforementioned trend of  $\kappa$  median with particle size is broken for the data from measurements at lowest and highest supersaturations; however, this minor deviation from the trend at either end is likely an artefact caused by systematic bias within the specified calibration uncertainties at these two extreme supersaturations [...]."

We also included a value of uncertainty in the following paragraph, Sect. 3.1, p. 12, l. 38: "The fact that the retrieved  $\kappa$ median value increased up to 0.6 (uncertainty: ±20%) thereby almost reaching the  $\kappa$  value of ammonium nitrate (~0.67 for 0.3% <SS< 1%; Petters and Kreidenweis, 2007), supports this hypothesis."

Concerning the uncertainty of eBC data from the aethalometer, we added the following paragraph p. 7, I. 32: "The Environmental Technology Verification Report for the Aethalometer reported an instrument precision of  $\pm 15\%$  (https://www.epa.gov/etv/pubs/01\_vr\_aderson\_aeth.pdf). However, the uncertainty of aethalometer data, largely dominated by the estimate of the mass-specific attenuation coefficient, can reach values as high as 50%."

Concerning the uncertainty of CCNC data in Table 1 (see Sect. 2.2.1, p. 5, I. 38): The uncertainties on CCN concentrations measured by the CCNC (Table 1) are based on the study of Rose et al. (2008); they are higher at SS below 0.14%, following the instructions from the ACTRIS standard operation procedures

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#### (http://fp7.actris.eu/Portals/97/deliverables/PU/WP3\_D3.13\_M24.pdf).

Comment "Page 11, Line 36: The authors have done great job assessing the contribution of different sources (traffic and wood burning) on the mixing state and presence of non-hygroscopic particles. However, it feels that such a comprehensive analysis and presentation shifts the attention away from the focal points of the manuscript. I would like to ask the authors to consider condensing this part of the manuscript by moving "less important" parts and maybe some of the figures to the supplementary material and to concentrate especially on those periods relevant for analyzed fog events."

Response: Agreed by the authors.

Changes: We moved Figure 5 and the corresponding discussion to the Supplement. We added the following text to Sect. 3.2, p. 13, l. 16 instead: Based on the diurnal cycles of particle and BC concentrations and two different indicators of the source of carbonaceous aerosol (the absorption Ångström exponent and the organics to eBC mass ratio), we conclude that these concentration peaks were caused by traffic emissions, rather than the second most common source of BC in Zurich, wood burning (Zotter et al., 2017; additional discussion attached to Figure S5 in the Supplement).

Comment "Page 15, Line 6: According to Fig. 3, the range between the 95% confidence intervals also illustrates the range of variation during the fog events. Therefore, the derived uncertainty of SSpeak (Table 2) could be somewhat interpreted as an indicator of temporal variation. In my opinion, these uncertainty estimates should be discussed, or at the very least, mentioned in this paragraph.

Response: Indeed, the range between the 95% intervals indeed illustrate temporal variability during a fog event. The authors agree with the reviewer that it should thus not be included in the uncertainty calculation of the mean SSpeak during a fog event. Instead, uncertainties are dominated by extrapolation errors.

Changes: We revised the uncertainty calculations accordingly (see also answer to next

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comment) and added the following clarification to Sect 2.3.4, p. 10, l. 35: "As discussed later and shown in Figure 3c,  $\kappa$ median is essentially independent of size for diameters between around 80 nm and 200 nm (between 75 nm and 178 nm for the 14 December event shown in the figure). The uncertainty of  $\kappa$ median extrapolated to the activation cut-off diameters,  $\kappa$ median(D\_half^fog) and  $\kappa$ median(D\_50^fog), is dominated by extrapolation errors, which are estimated to be potentially as large as 40%.

Comment "Page 38, Figure 9: The figure caption says, "The variability in the fogactivated fraction induced by the choice of  $\kappa$ coating (retrieved  $\kappa$ median  $\pm$  0.05) is represented by horizontal bars". Why is an arbitrary (?) uncertainty of 0.05 used and not the uncertainty indicated by the 95% confidence intervals like in Table 2?

Response: The uncertainty analysis for panels b)-e) in Fig. 9 of the revised manuscript was redone. The horizontal error bars now show Poisson-based statistical uncertainties of the activated fractions. We also changed the error bars of SSpeak according to the updated uncertainty estimates (see previous comment). The uncertainty of the  $\kappa$  values, while being important for inferred cloud peak supersaturation, has virtually no influence on the outcome of the closure as changing the  $\kappa$  value has two compensating effects. This is now discussed in detail in the Supplement by means of the new Figure S9 and summarizing statements in the main manuscript.

Changes: Figure 9 (Fig.1 in this author comment) including caption were updated.

The new Figure S9 (Fig.2 in this author comment) in the Supplement and associated discussion were added.

The following summarizing statement was added to Sect. 3.5, p. 18, l. 24: "It is important to note that the closure for the activation of BC-containing particles is insensitive to changes in  $\kappa$  coating as changing  $\kappa$  coating has two compensating effects (see Figure S9 and corresponding discussion in the supplement)."

In addition, the following discussion was attached to Figure S9 in the supplement: "Dis-

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cussion of Figure S9: To infer the critical supersaturation of individual BC-containing particles, the hygroscopicity parameter of the coatings,  $\kappa$ coating, was assumed to be equal to the median hygroscopicity measured for the total aerosol ( $\kappa$ median; see Sect. 2.3.2). Here, we performed a sensitivity analysis to test the sensitivity of the BC activation closure result to the assumed value of  $\kappa$ coating: the analysis shown in Figure 9a and 9b and explained in Sect. 3.5 was repeated with using  $\kappa$ coating disturbed by  $\pm 0.05$ . Figure S9b shows that changing  $\kappa$ coating alters the retrieved fog peak supersaturation (solid horizontal lines) as well as the vertical position of the curves indicating the activated fractions. These changes virtually compensate each other such that the observed 50% activated fraction for BC-containing particles is reached at a supersaturation closely mating the fog peak supersaturation for all three  $\kappa$ coating scenarios. This means that successful closure between observed and predicted cloud droplet activation of BC is successfully achieved independent of the exact choice of  $\kappa$ coating."

Technical comments:

Comment "Page 5, Line 17: This sentence needs some minor rephrasing as something seems to be lacking, e.g., "from 20 to 593 nm in 5.5 min, after which the monodisperse aerosol"

Changes: Manuscript corrected.

Comment "Page 5, Line 30: "was used behind the total inlet" Should this say interstitial inlet instead of total inlet?

Changes: Manuscript corrected, we thank the referee.

Comment "Page 16, Line 5: The sentence starting as "The BC cores with" is not easy to understand and could be rephrased to improve readability.

Changes: This sentence (p. 17, l. 13) was changed to: "The BC cores associated to core diameter DrBC below 212 nm and a thin/moderate coating remained smaller than the minimum overall particle diameter required for activation: according to Figure

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8, this diameter was around 280 nm during the 14 December event, even for BC-free (water-soluble) particles."

Comment "Figures: Is it possible to increase the font sizes especially in Figures 3, 5, 7 and 11.

Response: Agreed by the authors.

Changes: The changes were implemented in the manuscript.

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**Fig. 1.** Figure 9: (a): SScrit of individual particles sampled behind the total inlet (grey dots) and interstitial inlet (dots coloured by  $\Delta$ coating) as a function of their DrBC during the 14 December fog event

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**Fig. 2.** Figure S9: Sensitivity analysis of BC activated fraction in fog to assumed coating hygroscopicity. Same as Figure 9a and b for the 14 December fog event plus additional activation curves derived with

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