

Response to reviewer#2

Thanks for the reviewer's helpful suggestions! The comments are addressed point-by-point and responses are listed below.

Comment 1: General comments: The present manuscript describes a method for deriving the real part of the refractive index by means of a differential mobility selector (DMA) and scattering intensities measured with a SP2. The derivation of the real part of the refractive index of a quasi-mono disperse aerosol is not completely new. What is new, however, is the application with the use of the SP2, which in a unique way can also determine the mixing state of the aerosol within certain limits. This ensures that errors caused by unknown imaginary parts of the refractive index are minimized. The method shown is limited to non-absorbent particles.

Reply 1: We agree with the anonymous reviewer's comments.

Comment 2: The reviewer thinks that the current limitations and consequences have not been adequately presented. In particular, a consideration of the uncertainties in violation of the restrictions (weakly absorbing particles) is lacking.

Reply 2: Thanks for the comments. The reviewer provides a good view in uncertainties analysis of our proposed method.

There are some brown carbon (BrC) that absorb the light intensity in the near infrared range. The imaginary part of the refractive index at a given wavelength λ (k_λ) of the BrC can be calculated as:

$$k_{\lambda 1} = k_{\lambda 2} \times \left(\frac{\lambda_2}{\lambda_1}\right)^w \quad (1),$$

Where w is defined by mass of BC to organic aerosol ratio (R) (Saleh et al., 2015)with:

$$w = \frac{0.21}{R+0.07} \quad (2).$$

Based on the work of Saleh et al. (2015), the k_{550} can be expressed as:

$$k_{550} = 0.016 \times \log_{10}(R) + 0.04 \quad (3).$$

The values R ranges between 0.09 and 0.35 for different types of aerosols (Saleh

et al., 2015). Based on equation (8), (9) and (10), the k_{1024} ranges between 0.01 and 0.024. The maximum value 0.024 is used for further analysis.

The uncertainties of the retrieved RRI when ignoring the effect of BrC are analyzed. Firstly, The scattering light intensity at a given diameter with a refractive index of $1.46 + 0.024i$ is calculated using the Mie model. Then the corresponding RRI are retrieved with given diameter and the calculated light intensity. The retrieved aerosol RRI for different aerosol diameter are shown in fig. 7(b). For the light absorbing particles, their scattering light intensity is smaller than that of the pure scattering particles with the same diameter and RRI. Therefore, the retrieved aerosol RRI is underestimated for most of the conditions. The differences between the given RRI value (1.46) and retrieved RRI value are lower than 0.006 for all of the diameters as shown in fig. 7(b) in the manuscript. The BrC component have little influence on the retrieved aerosol RRI.

We added some discussions in section 4.2 on the uncertainties when the aerosols contain a small amount of BC cores that are below the detection threshold of SP2. Monte Carlo simulations were applied to investigate the influence of the BC core on the retrieved ambient aerosol RRI. These particles can lead to less than 0.02 overestimation of the aerosol RRI for most of the conditions. More details are shown in **Reply 4**.

Some corresponding discussions were added in section 4.2.3 and 4.2.4 in the text.

Comment 3: In laboratory experiments, as shown with ammonium sulfate and ammonium chloride, this is easily possible. The application to a complex ambient aerosol, on the other hand, was not treated sufficiently. The example shown in chapter 4.1 shows results of measurements in Beijing, where a complex mixed aerosol is present (that measurement place was characterized as urban roadside; line 96).

Reply 3: We thank the anonymous reviewer's comments and suggestions. In this work, we mainly focus on the method of measuring the aerosol size-resolved real part of the refractive index (RRI). The ammonium sulfate is used for calibration, and the ammonium chloride is used for validation. These studies are easy but power

demonstrations that our proposed is applicable of measuring the BC-free aerosol. More results about field measurements using this method can refers to another work at <https://www.atmos-chem-phys-discuss.net/acp-2019-250/>.

Comment 4: An error estimation is missing: a) what happens with weakly absorbing organic droplets, b) what happens with internally mixing particles with a small soot core when the incandescence signal is below the detection threshold of SP2. How large are the expected errors in the real part of the refractive index?

Reply 4: We do appreciate the comments. The reviewer provides a good view in uncertainties analysis of our proposed method. We added discussions on this point in section 4.2.

For the organic droplets, the light absorption of these components is ignorable as detailed in reply 2.

There are some particles with a small soot core and the incandescence signals are below the detection threshold of SP2. The derived aerosol RRI should be influenced by small soot core. Uncertainties might be resulted when deriving the RRI for these BC-contained aerosols.

For the BC-contained aerosol, Aquadag soot particles with effective density of 1.8 g/cm^3 is used to determine the lower limit of the BC particle diameter when the incandescence signals can be detected by SP2. The calibration procedure is conducted the same as that of the ammonia sulfate in the manuscript. The diameters (D_p) of the aerosol passing through the DMA are manually changed from 60 to 400 nm with a step of 20 nm. The relationships between the measured incandescence signal height and the D_p are shown in fig. R2. From fig. R2, we conclude that our SP2 is not capable of measuring the Aquadag soot particles lower than 80 nm.

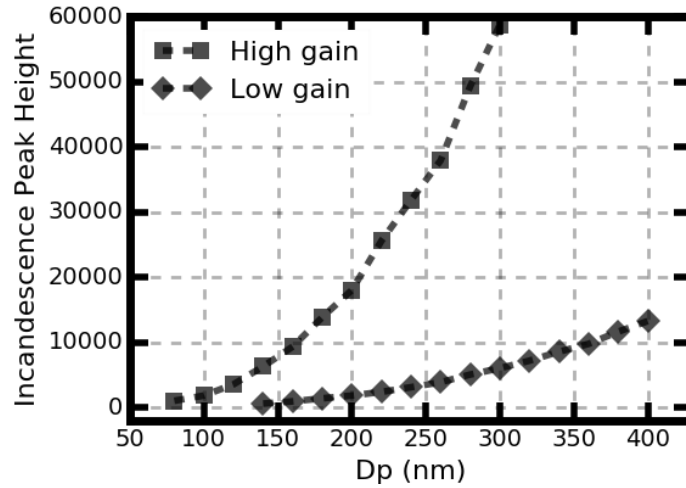


Figure R2. The calibrated relationship between the incandescence peak height and the BC diameter for both the incandescence high gain channel and the incandescence low gain channel.

We derived the aerosol equivalent refractive index when the aerosol have BC cores lower than 80 nm with two steps. 1, the scattering strength of the BC-containing aerosols are calculated based on Mie scattering theory with a given core and total diameter. 2, the scattering strength are used to deriving the equivalent refractive index with assuming that the BC-containing aerosols are pure scattering aerosols.

Monte Carlo simulations were applied to investigate the influence of the BC core on the retrieved ambient aerosol RRI. Firstly, the aerosol diameter are first chosen between 200 nm and 500 nm. Then the core diameter are random determined lower than 80 nm. The core diameters flow the log-normal distribution with the mean core diameter of 120 nm (Raatikainen et al., 2017). When calculating the scattering strength, the complex refractive index of the core $1.8+0.54i$ (Zhao et al., 2018) is used. The complex refractive of the shell adopts the measured mean values ($1.46+0i$) during the field measurements. The scattering strength can be calculated with the above information and the Mie scattering Model. Then with the calculated scattering strength, the equivalent real part of the refractive index (RRI) can be derived with assuming that the aerosols are pure scattering aerosols. If the core diameter is zero, the derived aerosol equivalent aerosol RRI should be 1.46.

For each aerosol diameter, the Monte Carlo simulations were conducted for

10000 times. Figure. R3 gives the retrieved aerosol equivalent RRI at different diameters. Results show that the retrieved aerosol equivalent RRI are larger than 1.46 for all of the given aerosol diameters. When the aerosols have BC core, the scattering strength are larger than that of pure scattering aerosols with the same aerosol diameter. The derived mean equivalent RRI tend to be closer to 1.46 when the aerosol diameter is larger, where the BC core contributes less and the influence of the BC core are smaller. The derived mean aerosol equivalent RRI is 1.47 and 1.462 at 200 nm and 500 nm respectively. At the same time, the uncertainties associated with the equivalent RRI are larger when the aerosol diameter is smaller. We conclude that the uncertainties associated with BC core are smaller than 0.01 when the aerosol diameter are larger than 250 nm. The maximum of the difference of the derived RRI is 0.02.

The above corresponding discussions were added in the uncertainties analysis part in section 4.2.2 of the manuscript.

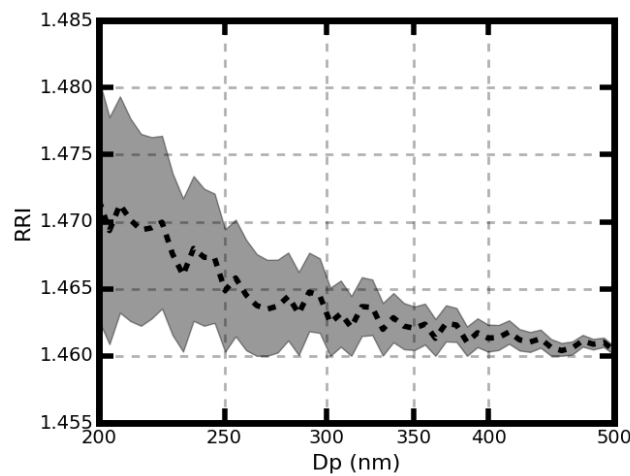


Figure R3. The retrieved equivalent aerosol RRI at different aerosol diameter. The filled color represents the 5th and 95th percentiles.

Comment 5: The reviewer believes that this work can make a good step in the optical characterization of sub-micrometer particles using the SP2, and that subsequent work can build on it. Therefore, the reviewer thinks that the manuscript can be published after a major revision.

Reply 5: We thank the reviewer's comments.

Comment: Specific comments: Title: The method shown is very general, but applied to SP2 in the present study. The study is thus adapted to the size range, the size resolution and the optical geometry of the SP2. The author should consider whether the application of the method to SP2 should be mentioned in the title.

Reply: Thanks for the comment. We have changed the title of the manuscript.

Comment: Introduction: Can the author give a first estimate on the accuracy of RRI measurements required to make statements on the chemical composition?

Reply: Traditionally, the ambient aerosol RRI is calculated using some main inorganic aerosol component and the influence of organic is ignored. However, the organic component contributes more than 20% of the total aerosol component in the North China Plain (Hu et al., 2012; Liu et al., 2014). RRI of the organic aerosol changes significantly between 1.36 and 1.66 (Moise et al., 2015). Ignoring the organic component may lead to significantly uncertainties when estimating the aerosol RRI.

In the introduction part, we added some information about the uncertainties of calculating the aerosol RRI using the measured aerosol chemical composition due to aerosol organic component.

We found that the aerosol RRI was determined by aerosol density rather than the aerosol chemical composition, which is discussed in detail in another paper <https://www.atmos-chem-phys-discuss.net/acp-2019-250/>.

Comment: Line 36: Typo: “Hänel”

Reply: Thanks for the comments. We have changed the manuscript correspondingly.

Comment: Lines 89, 90: The measurements provide the necessary data in five minute intervals. However, no conclusion can yet be drawn that the RRI can be derived with a time resolution of five minutes.

Reply: Thanks for the comments. We have changed the corresponding descriptions.

Comment: Line 121: to be precise, the power is about 1 W/m² circulating power in cavity

Reply: Thanks for the comments. We have changed the manuscript corresponding.

Comment: Line 131: what is the unit of the peak height H.

Reply: Thanks for the comments. The avalanche photo-detector measures the light signals and changes the signals series to a light scattering of incandescent intensity time series. There is no unit for these signals. Correspondingly, there is no unit for the peak height H.

Comment: Lines 133,134: How were BC containing particles ruled out for ambient measurements.

Reply: The BC containing particles are ruled out by not counting the scattering signal peak height of these aerosol particles when the incandescent peak height is larger than 500. The manuscript is changed correspondingly.

Comment: Section 3.1: Shouldn't the signals be the same value at 45° and 135° due to the circulating wave in the cavity?

Reply: Yes, the received signals intensity are at 45° and 135° due to the circulating wave in the cavity. When calculating the scattering intensity, the aerosol scattering coefficient at both 45° and 135° in the cavity are considered.

Comment: Line 145: To avoid misunderstandings: The SP2 can determine the scattering signal in a certain scattering angle range. But not the scattering coefficient!

Reply: Thanks for the comment. We add some sentence to distinguish the light scattering intensity by aerosols and the measured light scattering signals by SP2 at the manuscript.

Comment: Figure 2: Is the scattering strength the same as the scattering intensity S?
Please use consistent notations.

Reply: Thanks for the comments. We have changed the manuscript accordingly. All of the scattering strength are changed into scattering intensity S .

Comment: Line 151: monotonously instead of homogeneously.

Reply: Thanks for the comment. We have changed the manuscript correspondingly.

Comment: Line 159: Establishing the threshold value at 1000 seems somewhat arbitrary. Is there a justification for this?

Reply: Thanks for the comment. This value is selected based on the analyzing the noise of the incandescence signals. The value 1000 depends on the instrument's stability. When recording the aerosol incandescence signals, the instrument gets the maximum values of 60000. In calibration studies using ammonium sulfate, the fit maximum incandescence signal peak height is 720, which is only 1.2% of the measurement range. This can be caused by signal noise. This value can be different for different instruments. We added some descriptions at the manuscript correspondingly.

Comment: It would be better to read to bring figure S2 und figure 3 together.

Reply: Thanks for the comment. We have changed the figure and manuscript correspondingly.

Comment: Lines 166 and 167: Refer to figure S1

Reply: Thanks for the comment. We have changed the manuscript correspondingly.

Comment: Line 175: Please check that sentence. I can't see different marker for different diameters.

Reply: Thanks for the comment. This sentence is misleading. We changed this sentence into: The H_0 values of corresponding to different elementary charges are labeled with different markers in fig. 3.

Comment: Is fig. 2 the correct figure?

Reply: The figure number is not right. We have changed it into fig. 3 in the manuscript.

Comment: Line 177: What is “PH0”?

Reply: Thanks for the comment. We have changed the PH_0 into H_0 , it is the geometric mean value of H .

Comment: Line 180: Shouldn't it be Fig 3.

Reply: Thanks for the comment. The text in the manuscript has been changed correspondingly.

Comment: Lines 180,181 and Figure 3: Check if the peak height is plotted versus the mobility diameter Z_p and not versus the geometric diameter D_p ?

Reply: Thanks for the comment. We have checked the result and find the peak height is plotted versus the mobility diameter D_p , but not the electoral mobility diameter.

Comment: Line 184: “ D_p superscript tilde” not defined

Reply: Thanks for the comment. We have changed the manuscript correspondingly. The $\widetilde{D_p}$ is the corresponding diameter of the aerosols that share the same Z_p but different charges with those particles that have diameter of D_p with one charge.

Comment: Line 184: There is no dashed line in figure 2

Reply: Thanks for the comment. The figure number is not correctly labeled here and we have changed it into figure 3(a).

Comment: Lines 194 and 200 : Please bring references for the refractive index.

Reply: Thanks for the comment. We have changed the manuscript correspondingly.

Comment: Figure 4a: Should be scattering intensity instead of scattering strength

Reply: Thanks for the comment. We have changed the figure.

Comment: Lines 192 – 208, Figure 4: For the reader it is not obvious at first sight which value was calibrated! What is the value of the calibration factor C? The reviewer thinks it is worth giving a short summary list of all steps necessary for deriving RRI. For an absolute calibration, the slope of about unity is more important than the references to the correlation coefficient. The high correlation coefficient is, as written, a good indicator for the potentially high accuracy of this method.

Reply: Thanks for the comment. We changed the figure 4. When comparing the scattering peak height and the scattering intensity, C is assuming to be unity in this study. The values of C and the slope should change proportionally. We agree with the reviewer that the slope is more important than the correlation coefficient. Some discussions about the slope at the end of section 3.2 were added to the manuscript. At the same time, we added a short summary of the step for deriving the RRI at the end of section 3.1.

Comment: Line 211: It would be good to have some additional information, e.g. the mean BC concentration and the number of fractions of internally/externally mixed particles and coated particles provided by SP2. How was it ensured that the purely externally mixed non-absorbent particles were used in the calculation of the RRI?

Reply: Thanks for the comment. We added the information of the BC mass concentrations integrated by the SP2 in the manuscript. It is $6.31 \mu\text{g}/\text{m}^3$. The corresponding aerosol scattering coefficient is 385 Mm^{-1} .

The number fractions of internally mixed particles and coated particles retrieved from SP2 were provided here. The measured mean mixing states of the ambient aerosol are shown in fig. R4.

From fig. R4(a), the BC core diameter (D_c) is lower than the D_p for most of the particles when the aerosol D_p is larger than 150 nm. There are a lot of particles with D_c larger than D_p when the aerosol is lower than 150 nm, which reflects the complex morphology of these BC-contained aerosols (Peng et al., 2017; Peng et al., 2016).

There are two mode for the BC-contained aerosol, with one thinly coated or uncoated aerosol mode locating near the D_c equaling D_p line and another thickly coated aerosol mode appearing that the D_c locates between 100 nm and 150 nm, which is in accordance with the previous study of the BC mixing states (Wu et al., 2018). The measured total aerosol PNSD, the measured BC-contained aerosol PNSD, the BC-free aerosol PNSD and the ratio of the BC-contained aerosol to total aerosol PNSD between 80 nm and 560 nm are shown in fig. 4(b). The PNSD for the BC-contained aerosols are calculated from the measurement from SP2. As for the PNSD for the BC-free aerosol, these values between 180 nm and 560 nm come from the measurement of SP2 and these values between 80 nm and 180 nm is calculated by subtracting the total aerosol PNSD to the PNSD of the BC-contained aerosol. Results show that both the total aerosol PNSD and BC-free aerosol PNSD peak around 120 nm. As for the BC-contained aerosol PNSD, it peaks at around 170nm. The ambient aerosol are mainly composed of BC-free aerosol and the BC-contained aerosol contributes less than 0.20 of the total aerosol over the measured size range. The ratio increases from about 0.03 to 0.2 when the aerosol diameter increases from 80 nm to 300 nm. The ratio decreases with the increment of diameter when the diameter is larger than 300 nm. Therefore, the ambient BC-contained aerosol only contributes to less than 20% of the total aerosols. The measured mean PNSD and particle mass size distribution (PMSD) of the rBC is shown in fig. 4(c). The PNSD and PMSD of the rBC peaks at 120 nm and 330 nm respectively. The measured PNSD and PMSD of the rBC is in accordance with many previous studies of the rBC distribution (Schwarz et al., 2006; Sharma et al., 2017).

The above information would help know the surrounding condition of the measurement sites. These results will be presented in another paper in preparation and are not included in this manuscript.

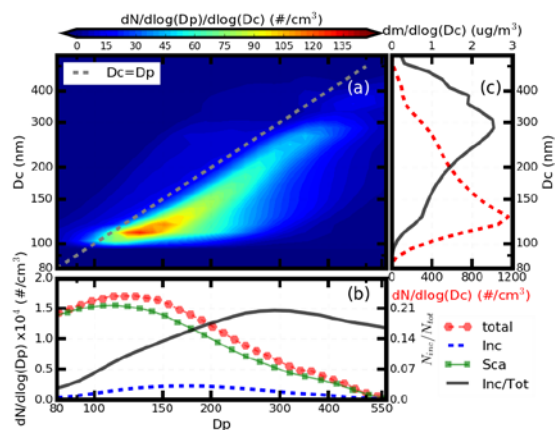


Figure R4. (a) Measured number concentration distributions for different aerosol diameters with different D_c . (b) measured total aerosol PNSD, the BC-free aerosol PNSD, the BC-contained aerosol PNSD and the ratio between the BC-contained aerosol to total aerosol number concentrations are shown in red dashed line marked with hexagon, in green line marked with square, blue dashed line and in dark solid line respectively. (c) the measured number size distribution of the rBC for different D_c is shown in red dashed line and the measured mass size distribution for different D_c is shown in dark solid line.

Comment: Line 216: Can the authors estimate the fraction of the light scattering size distribution that is covered.

Reply: Thanks for the comment. The fraction of the light scattering size distribution in the range between 200 nm and 450 nm is 0.63. We added the estimated result in the manuscript.

Comment: Lines 22ff: The uncertainty of the transfer function is covered by the H fitting, since the transfer function is a system function and relatively stable and also covered by a DMA calibration with size standards. How are other influences taken into account, e.g. uncertainties in sheath air flow or CPC counting efficiency?

Reply: Thanks for the comment. The uncertainties in sheath air flow would influence the transfer function. However, the flow rate of the sheath flow is controlled by a

circulatory system, which is very stable and the uncertainties is lower than 1% to our knowledge. This low fluctuation of sheath flow would have little influence on the aerosol transfer function when the Q_{sh} in equation 3 changes by 1%. At the same time, the CPC counting efficiency has no impact on the retrieving of aerosol RRI.

Based on equation 6, the aerosol RRI are influenced by the aerosol diameter and the scattering intensity. The uncertainties of the aerosol diameter resulted from the DMA transfer function, which were fully resolved by using the Gaussian distribution to fit the aerosol scattering signal height distribution. Another source of the uncertainties comes from the measured scattering peak height by SP2, which was discussed in detail in section 4.2.

Comment: Line 225: HW not defined.

Reply: Thanks for the comment. The HW is the half width of the transfer function. We have changed the manuscript correspondingly.

Comment: Line 227 to 229: Does this mean that the additional broadening by the H distribution function is 1.073?

Reply: Yes.

Comment: Lines 230,231: Can the authors give more details about the uncertainty analysis?

Reply: Thanks for the comment. More details about the uncertainty analysis are added in the manuscript.

The steps of conducting the uncertainties are as follows. Firstly, the theoretical scattering intensity that can be measured by the SP2 for a given aerosol diameter and RRI are calculated. The scattering intensity are changed by $\pm 6.8\%$ (the uncertainties of the measured scattering intensity by SP2) and the corresponding RRI can be derived using the given aerosol diameter and the changed scattering intensity. Finally, the derived RRI are compared with the initial aerosol RRI. The uncertainties are

analyzed for different aerosol diameter and different RRI.

Comment: Lines 243, 244: How can it be ensured in a mixed aerosol that BC containing particles are excluded and how big would the error be if small amounts of BC affect the measurement?

Reply: Thanks for the comment. This has been addressed in general comment 4. We have added some text in section 4.2 to discuss this.

Hu, M., Peng, J., Sun, K., Yue, D., Guo, S., Wiedensohler, A., Wu, Z. (2012) Estimation of size-resolved ambient particle density based on the measurement of aerosol number, mass, and chemical size distributions in the winter in Beijing. *Environ Sci Technol* 46, 9941-9947.

Liu, H.J., Zhao, C.S., Nekat, B., Ma, N., Wiedensohler, A., van Pinxteren, D., Spindler, G., Müller, K., Herrmann, H. (2014) Aerosol hygroscopicity derived from size-segregated chemical composition and its parameterization in the North China Plain. *Atmospheric Chemistry and Physics* 14, 2525-2539.

Moise, T., Flores, J.M., Rudich, Y. (2015) Optical properties of secondary organic aerosols and their changes by chemical processes. *Chemical Reviews* 115, 4400-4439.

Peng, J., Hu, M., Guo, S., Du, Z., Shang, D., Zheng, J., Zheng, J., Zeng, L., Shao, M., Wu, Y., Collins, D., Zhang, R. (2017) Aging and hygroscopicity variation of black carbon particles in Beijing measured by a quasi-atmospheric aerosol evolution study (QUALITY) chamber. *Atmospheric Chemistry and Physics Discussions*, 1-32.

Peng, J., Hu, M., Guo, S., Du, Z., Zheng, J., Shang, D., Levy Zamora, M., Zeng, L., Shao, M., Wu, Y.-S., Zheng, J., Wang, Y., Glen, C.R., Collins, D.R., Molina, M.J., Zhang, R. (2016) Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments. *Proceedings of the National Academy of Sciences* 113, 4266-4271.

Raatikainen, T., Brus, D., Hooda, R.K., Hyvärinen, A.-P., Asmi, E., Sharma, V.P., Arola, A., Lihavainen, H. (2017) Size-selected black carbon mass distributions and

mixing state in polluted and clean environments of northern India. *Atmospheric Chemistry and Physics* 17, 371-383.

Saleh, R., Marks, M., Heo, J., Adams, P.J., Donahue, N.M., Robinson, A.L. (2015) Contribution of brown carbon and lensing to the direct radiative effect of carbonaceous aerosols from biomass and biofuel burning emissions. *Journal of Geophysical Research: Atmospheres* 120, 10,285-210,296.

Schwarz, J.P., Gao, R.S., Fahey, D.W., Thomson, D.S., Watts, L.A., Wilson, J.C., Reeves, J.M., Darbeheshti, M., Baumgardner, D.G., Kok, G.L., Chung, S.H., Schulz, M., Hendricks, J., Lauer, A., Kärcher, B., Slowik, J.G., Rosenlof, K.H., Thompson, T.L., Langford, A.O., Loewenstein, M., Aikin, K.C. (2006) Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere. *Journal of Geophysical Research* 111.

Sharma, S., Leaitch, W.R., Huang, L., Veber, D., Kolonjari, F., Zhang, W., Hanna, S.J., Bertram, A.K., Ogren, J.A. (2017) An evaluation of three methods for measuring black carbon in Alert, Canada. *Atmospheric Chemistry and Physics* 17, 15225-15243.

Wu, Y., Xia, Y., Huang, R., Deng, Z., Tian, P., Xia, X., Zhang, R. (2018) A novel study of the morphology and effective density of externally mixed black carbon aerosols in ambient air using a size-resolved single-particle soot photometer (SP2). *Atmos. Meas. Tech. Discuss.* 2018, 1-18.

Zhao, G., Zhao, C., Kuang, Y., Bian, Y., Tao, J., Shen, C., Yu, Y. (2018) Calculating the aerosol asymmetry factor based on measurements from the humidified nephelometer system. *Atmospheric Chemistry and Physics* 18, 9049-9060.