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## **Comment on acp-2021-173**

Anonymous Referee #1

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Referee comment on "Ambient aerosol properties in the remote atmosphere from global-scale in situ measurements" by Charles A. Brock et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-173-RC1>, 2021

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### **Review of the manuscript "Ambient aerosol properties in the remote atmosphere from globalscale in-situ measurements"**

The short assessment of this study is: impressive spatial coverage, comprehensive and state of the art set of experimental methods, and appropriate approaches to merge and integrate these. All this leads to a great data set on chemical, physical and optical properties of atmospheric aerosols. Definitely, suitable and important to be published in this journal.

The length of this review is by no means in contradiction with above positive assessment. By contrast, the expectation that this data set is going to be a benchmark that will most likely be used for a long time and in many future studies. Therefore, I consider it valuable to clarify several items and maybe adjust one or two assumptions in the calculations. It is one of several strengths of this manuscript that the entire chain of assumptions and calculations required to infer optical aerosol properties from primary observations is quite completely and transparently presented. Addressing at least some of the comments below, which are virtually all of minor or even technical nature, could help in putting additional emphasis on the basic starting point assumptions, and to clarify a few things. There may be one or two items where I question an assumption (e.g. BC refractive index or "F<sub>org</sub>"; see specific comments). Even if adjusting would likely lead to little change only, I encourage to consider it all the same. There is considerable chance that any assumption made in this study will be pickup up in many follow-up studies, given the quality of this work, also for calculations where it might have more impact than in this work. Keeping this in mind should help in gauging the effort put in addressing or discarding below comments.

### **More general and more important comments**

Sect. 2.3, L262-280: As far as I can judge, the approach for approximating composition resolved size distributions to handle light scattering and light absorption is well thought. However, the underlying basic motivation / physics behind the approach could be communicated more clearly to the readers less experienced in aerosol optics. I suggest to introduce the distinct concepts behind handling scattering and absorption, possibly before dwelling on where composition and mixing state data are taken from (see also comment below, which addresses visualization in Fig. 2). For example, when it comes to light scattering, there is no way around describing aerosol size distribution and hygroscopic growth with sufficient accuracy, whereas replacing the volume associated with BC by the same volume of "NR-PM" as measured by the AMS introduces very limited error (BTW: I do not think that the approach chosen for this study leads to "double counting" of BC (line 275); instead it simply is material substitution for the light scattering calculations plus some volume error from sizing errors associated with BC particles). By contrast, first order approximation for calculating absorption simply is: summation over all absorbing components of the product "component specific mass absorption cross section times mass concentration" (with 2<sup>nd</sup> order corrections for size mixing state effects which lead to deviation from volume-based absorption and hamper additivity of light absorption for internal mixtures), while volume/size of externally mixed non-absorbing particles is absolutely irrelevant.

Section 2.3: The approach to obtain a good approximation of size-resolved aerosol composition and mixing state appears to be appropriate, though certain aspects are not perfectly clear. Given that different methods are combined in different manner for different size bins and particle types (in order to account for size and composition dependent detection efficiency of each method), I suggest to base the discussion on Figure 3 and to start with the basic assumptions before providing details. E.g.:

- Purpose: Prepare the ground for calculating RH dependence of size distribution and aerosol light scattering (as a function of RH) □ step1: assign approximate mixing state and composition to each size bin in order to infer hygroscopic growth factors and refractive index (and density) in next steps. (If I understand correctly, this composition information is not used for inferring light absorption (otherwise, it would be inappropriate to substitute e.g. EC with different species).

- All size ranges: aerosol volume taken from AMP

- 0.05-0.14  $\mu\text{m}$ : Internal mixture. Composition exclusively based on AMS measurement. This means that the aerosol volume associated with refractory components that remain undetected by the AMS (BC, dust, NaCl, ...) is substituted with AMS measured bulk composition.

- The three size bins in 0.25 to 4  $\mu\text{m}$  range: Measured volume is split into contributions by 9 particle types based on PALMS particle type classification. Then explain for each particle class how composition of respective volume is approximated, only including approximations common to calculating kappa and refractive index (here an SI figure or SI table resolved by particle type may be very useful and much clearer than a linear text

block).

- 0.14 to 0.25  $\mu\text{m}$  size bin: measured volume is split to contributions from two sub-groups of PALMS-derived particle types. One sub-group is treated as internal mixture with AMS composition imposed, the other sub-group is retained as external mixture with PALMS-derived particle type specific composition imposed.

- extrapolation for small and large particles...

Inferring kappa:

- Equation 4: this is an explicit variant of the ZSR mixing rule, as applied for inferring the kappa of some PALMS-derived particle classes. It is a very basic implementation which parametrizes kappa based on "inorganic to organic" ratio. Such a simplification can perform very well, given that the major contributors to inorganic volume are measured and lumped together, and alike for all major contributors to organic volume. However, footnote "B" in Table 2 suggests that sulfate is the only species considered for calculating  $F_{\text{org}}$ . This will lead to systematic bias if other inorganic ions such as nitrate make a substantial contribution to inorganic volume. It remains unclear how/whether nitrate volume is appropriately accounted for in size classes relying on PALMS composition data. Please clarify.

- The hygroscopic growth has discontinuities at size bin boundaries, particularly where switching from AMS to PALMS for composition constraints. Does this cause any problems with wet size distribution shapes, or is this unimportant because discontinuity is small or because final optical parameters are integrated over all sizes?

- Minor: Sulfuric acid or nitric acid contain considerable residual water at "dry RH" (in cabin conditions), such that the effective kappa value would be considerably smaller (more comparable to e.g. corresponding ammonium salts). Anyway, volume fractions of these acids are likely low, such that propagated uncertainties are unimportant.

Inferring refractive index (Sect. 2.7 and Table 2):

- The equation composition dependence applied to some PALMS particle classes ( $(1-F_{org}) * 1.479 + F_{org} * 1.480 + 0i$ ) appears to be a precision overkill given considerably larger absolute uncertainties. Furthermore, is it important to consider nitrate salts, which does not appear to be the case, for refractive index estimates (see related comment on hygroscopic growth)?

- "SP2: Black Carbon" and "SP2: Coating": please clarify whether these refractive indices feed into general calculation of scattering coefficient and/or absorption coefficient, or whether they are exclusively used for inferring BC particle mixing state from SP2 raw data. The Moteki 2010 value does not appear to be appropriate for absorption calculations and questionable for general applicability to light scattering calculations because it is only based on a single light scattering cross section measurement at 1'064 nm for BC heated to sublimation temperature by a strong laser ("single" in the sense of one parameter rather than single data point).

Line 354ff: Treatment of e.g. the "PALMS-derived sulfate/organic" particles with respect to optical calculations remains somewhat unclear. The equation in the "refractive index" column of Table 2 is a simplified two-component volume mixing rule (only distinguishing "inorganics" and "organics" with refractive indices of ammonium bisulfate and OA assigned, respectively). This brings back the question: are inorganic salts other than sulfate salts considered for calculating "F<sub>org</sub>"? Furthermore, is this 2-component mixing rule applied to big and small sulfate/organic particles (and equally treated types) or is the full AMS-composition considered for the small ones as implied by the compositional model? Besides clarifications, I suggest some reordering and rewording along the line (depending how calculations were done actually): "Scattering was calculated for the wavelengths of 340, 380, 405, 440, 532, 550, 670, 870, 940, and 1020 nm, which match common wavelengths for the AERONET sunphotometers and satellite measurements of AOD. The refractive indices in Table 2 are not adjusted for wavelength; this is a small potential bias in the context of other assumptions and approximations in the calculation. All particle types were treated as spherical in shape and internally homogeneous for optical calculations. For particles that are a multi-component mixture based on the simplified composition and mixing state representation introduced in Sect. 2.3, the dry particle refractive index is calculated as the volume-weighted mean refractive index of contributing components. This calculation is further simplified for this and that particle type using this and that equation/approach....". – Note: this volume-based mixing rule is also applied to the small particles for which composition is constrained with AMS only (if I understand correctly; this is not clearly stated in the manuscript).

Suggestions for some additions/reorganization of Figure 2:

i) Explicitly indicate which subsets of the flow chart are used to compute light scattering and light absorption, respectively. Maybe even split in two separate panels as inputs hardly have any overlap.

ii) How is contribution of BC particles to asymmetry parameter handled? Is BC particle contribution completely ignored? Is this expected to have a significant effect? If yes, rather systematic positive or negative bias (depending on value of calculated asymmetry parameter)?

iii) What optical model is used for water-soluble brown carbon absorption? (See also separate comment.)

iv) How is hygroscopic growth effect on BrC and BC absorption treated? (RH also as input for absorption calculations? Explicitly include in the figure that treated independent of RH.

v) How is dust absorption treated? Indicated even if set to zero, as this would also be an important piece of information.

vi) Top right box: Why/how is pressure required? "H<sub>2</sub>O" likely stands for "water vapour partial pressure (as opposed to total liquid water content or liquid water associated with non-activated aerosol particles; see e.g. "H<sub>2</sub>O" label in Fig. 10). I assume that temperature is only required to infer RH from water vapour partial pressure, whereas nothing else is treated as temperature dependent? It might be worthwhile to emphasize the top right box is exclusively required to deliver RH to hygroscopic growth calculations, i.e. simplify it to "(ambient) RH".

Line 371: Any peculiar reason for using the idealistic core-shell morphology assumption as opposed to fractal-like shapes? Size dependence of MAC tends to be stronger for compact spheres than for loose compact spheres (e.g. Romshoo 2021). Additionally, the refractive index used for BC is inappropriate as it is a value to get light scattering by BC at 1064 nm and at 4'000 K within the SP2 instrument right, whereas it wasn't determined to get light absorption by BC right (which is not accessible to standard SP2 measurements). What matters in the end are the resulting coated BC MAC values (or the alternatively the product bare BC core MAC value times absorption enhancement factor due to lensing). Values resulting from the calculations made in this study should be reported and be put in context of previous values in the literature, even if it simply remains on the level of confirming plausibility of the result.

Romshoo, B., Müller, T., Pfeifer, S., Saturno, J., Nowak, A., Ciupek, K., Quincey, P., and Wiedensohler, A.: Radiative properties of coated black carbon aggregates: numerical simulations and radiative forcing estimates, *Atmos. Chem. Phys. Discuss.* [preprint],

<https://doi.org/10.5194/acp-2020-1290>, in review, 2021.

Lines 383 to 397: BrC data are only available on 5 – 15 minutes time resolution, while the aerosol variability occurred on shorter time scales. Furthermore, a time resolution of 60s is chosen for the reported data set. Therefore, the BrC absorption data are “resampled” to higher time resolution with making use of covariance between BrC and BC and between BrC and biomass burning aerosol mass concentrations. While I fully support such an approach, I do not consider the actual implementation appropriate because it does not conserve the mean BrC mass measured on the original time intervals. I suggest to choose an approach in which covariance with one or both aforementioned parameters is used to introduce variation of BrC absorption around the measured mean value over the original sampling interval in such a manner that mean BrC absorption is conserved for each original interval.

### **Minor comments**

Figure 3: This figure is useful. Some minor suggestion:

i) The inlet size range could additionally be indicated with arrow at top.

ii) It might be worthwhile to indicate the size ranges across which AMS and PALMS provide composition information (currently only shown across which size range information of these instruments is used).

iii) Maybe “AMS bulk composition” because no size-resolve data are used (in contrast to PALMS for which size-resolved information is retained).

iv) For the 0.14 to 0.25 size class: “meteoric” appears twice, oil combustion appears to be missing?

L57-59: Just a side remark: interaction between different molecules in gas and liquid condensed phase is of chemical *and physical* nature: Raoult’s law shifts the phase partitioning for species that are miscible with a liquid aerosol phase present in the system without involving chemical reactions, i.e. also for non-reactive vapours. See volatility basis set approach for phase partitioning in e.g. Donahue et al. (2006).

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics. *Environ. Sci. Technol.*, 40, 2635-2643, doi:10.1021/es052297c, 2006.

L63: "dilution" could be added to this comprehensive list (as it can cause evaporation feedback for semi-volatile species through the physical effect mentioned in the previous comment). Distinction between solid and liquid condensed phase is also important in this context.

L86: Recent overview article on polarimetric retrievals:

Dubovik, O., Li, Z., Mishchenko, M. I., Tanré, D., Karol, Y., Bojkov, B., Cairns, B., Diner, D. J., Espinosa, W. R., Goloub, P., Gu, X., Hasekamp, O., Hong, J., Hou, W., Knobelspiesse, K. D., Landgraf, J., Li, L., Litvinov, P., Liu, Y., Lopatin, A., Marbach, T., Maring, H., Martins, V., Meijer, Y., Milinevsky, G., Mukai, S., Parol, F., Qiao, Y., Remer, L., Rietjens, J., Sano, I., Stammes, P., Stamnes, S., Sun, X., Tabary, P., Travis, L. D., Waquet, F., Xu, F., Yan, C., and Yin, D.: Polarimetric remote sensing of atmospheric aerosols: Instruments, methodologies, results, and perspectives. *J. Quant. Spectrosc. Radiat. Transf.*, 224, 474-511, doi:10.1016/j.jqsrt.2018.11.024, 2019.

L164: Petzold et al. (2013) recommend using "rBC" when reporting BC mass quantified using laser-induced incandescence. For the purpose of this manuscript, it is probably more useful to stay with "BC mass", except for dropping a remark in the methods section that BC mass is obtained through measurement of operationally defined "rBC mass".

Petzold, A., Ogren, J. A., Fiebig, M., Laj, P., Li, S. M., Baltensperger, U., Holzer-Popp, T., Kinne, S., Pappalardo, G., Sugimoto, N., Wehrli, C., Wiedensohler, A., and Zhang, X. Y.: Recommendations for reporting "black carbon" measurements. *Atmos. Chem. Phys.*, 13, 8365-8379, doi:10.5194/acp-13-8365-2013, 2013.

L167-168: "BC mass concentration data, corrected to reflect accumulation mode BC outside of the detection-range of the instrument" – How was this done? Extrapolation via lognormal fit? At large diameter tail only, or also for small BC cores? Is it important to state time resolution of the correction factor?

L166-168: "BC mass concentration data, [...], are reported on a 1 s time basis (with frequent null detections at this rate at the concentrations found in ATom)" – All okay with this. However, important to provide good instructions in the meta data to users of the data base on how (not to) handle zero entries when aggregating 1s data to lower time resolution.

L182-187: only "cloud free" conditions are reported, whereas "haze" category is included. Is this going to be taken up in the discussion section when it comes to the question of comparing these in-situ data with remote sensing data? I.e., are remote sensing data typically "cloud free only" inclusive or exclusive "haze"?

L208: PALMS uses laser ablation to desorb and ionize, correct? Can all particle types be vaporized (i.e. also transparent particles)? Some hint is given on L213 that detection efficiency might be composition dependent (or was this only about size dependence), while no statement is made about resulting impacts on averaged composition in a size bin.

L218ff: "Thus, to calculate optical and hygroscopic properties, we do not assume a weighted internal mixture of the chemical components, but rather treat the total aerosol as an externally mixed collection of independent size distributions, each composed of one PALMS compositional type mapped onto the particle size distributions." – Important piece of information. Shouldn't this better be moved to where Figure 2 is discussed?

L225: "Further, the AMS composition is applied to the sulfate/organic, biomass burning, EC, and unclassified particle types for the 0.14–0.25  $\mu\text{m}$  PALMS size range". – How is this to be understood? Are they all thrown into one bucket and composition is assigned based on AMS data (which does not exclude that composition of these aerosol types still differs after this process because they are prevalent at different times)? What happens to e.g. EC, which is not detected by the AMS, i.e. are the "EC particles ending up as "EC-free" (which may not necessarily be an issue)?

L230: "As noted by Hodzic et al. (2020), in background conditions during ATom a substantial fraction of the AMS organic aerosol (OA) concentrations were below detection limit, and included negative values. We substitute negative AMS values with zeros when calculating optical or hygroscopic properties (Sect. 2.5)" – One should first pre-average the data to intervals sufficiently long to reduce negative organic readings to a minor fraction such that replacing negatives by zeros does not really make a change in the average composition inferred from these pre-averaged data. If replacing the negatives by zeros is done before any averaging, then this will introduce a systematic high bias in average organic fraction and bias calculated hygroscopic growth through its dependence on organic to inorganic ratio.

L234 – L238: This descriptions sounds as if PALMS data were aggregated by "air mass or plume" type most of the time, with few exceptions only, when truly time-resolved composition is provided? Please clarify. I additionally suggest to refer to Fig. 3 where regional averaging is also addressed.

L263: "D<sub>p</sub>" appears to be reserved for total particles geometric diameter throughout most of the manuscript. Here it is used for a BC mass equivalent core diameter, which differs from total particle diameter for internally mixed BC (in which case optical sizing by the SP2 provides something like D<sub>p</sub>). I suggest using a distinct symbol for BC core mass

equivalent diameter to avoid ambiguity. Strictly speaking, the SP2 arrow in Fig. 3 also lives on a different diameter axis.

L279: This should read: "for the purpose of calculating aerosol hygroscopic growth and light scattering" (I doubt that PALMS data go into BC light absorption calculations.)

Equations 3: This equation appears to be quite randomly picked among those equations used to come up with hygroscopic growth (most of which are provided in Table 2, except for the ZSR mixing rule approach applied to AMS data on top level, which is quite hidden on lines 307/308). The ZSR mixing rule deserves at least as much emphasis as Equation 3. (PS: Equation 4 is the explicit variant of ZSR mixing rule applied to some PALMS-derived particle classes).

Line 318: "The overall project-mean value of  $\kappa$  from the AMS measurements was  $0.53 \pm 0.19$ ". This value appears to be at the high end of AMS-based literature data (given that potential sea salt contribution is not considered in this value). Is this a result of small organic fraction and/or high fraction of acids, which got a high kappa assigned in pure form (on average)?

Line 323: "For a pure organic aerosol ( $F_{org}=1$ ), this yields  $\kappa_{org} = 0.17$ , close to the AMS project-wide value of  $\kappa_{org} = 0.18$  from Eq. 3"; good to put approaches chosen for different size ranges in context to each other. However, while consistency for pure organic aerosol is given (just skipping O/C dependence in PALMS size range), Equation 4 based kappa have a low bias compared with AMS-kappa for pure inorganic aerosol ( $F_{org} = 0$ ), as the lowest among all sulfate and inorganic kappa values is chosen for  $\kappa_{inorg}$  in Equation 4. Is this of relevance or anyway within uncertainties? (The potential bias in  $F_{inorg}$ , which I addressed in a previous comment, may be of greater impact.)

Line 324: Statements such as "The project-wide mean value of  $\kappa$  from Eq. 4 for particles with  $D_p > 0.25 \mu\text{m}$  was  $0.36 \pm 0.05$ ." are potentially misleading, because this "kappa value" only applies for a subset of particles in this size class. The grand average kappa over all particles within a size class would be more relevant as a most basic parameter for comparison with other studies.

Treatment of the coarse tail of the size distribution taken from the CAS on Lines 255-260 and Lines 330-338: Some duplication of the approach on how water content correction is applied to infer dry size distribution from the measurement at ambient RH. I suggest blend these blocks together. Furthermore, it is not quite clear whether data reduction is done in a single or two step process, i.e. where and how compositional constraints are used. Single step would be directly relating dry size distribution to scattering signal using a forward kernel constrained with observed composition to approximate hygroscopic growth and refractive index as a function of RH (wet size distribution would then be an intermediate side product of the forward kernel applied to the inverted dry size distribution). Two step approach would be: first inferring wet size distribution from

scattering signal (done with or without using composition constraints for water content and refractive index estimates?) and then dividing wet diameters by hygroscopic growth factors based on composition constraints (no more need of refractive indices in second step).

Section 2.6: I suggest adding a remark that AMS-derived kappa values are chosen to infer critical dry diameters as these fall into the size range where composition is best constrained with the AMS (Fig. 3).

Line 353: the scattering efficiency also depends on the imaginary part of the refractive index. Why is it not considered? Could possibly be important for the larger and absorbing particles, e.g. dust.

Line 360: This sentence belongs into the next paragraph. And I suggest something along the line: "In order to calculate scattering coefficient of the aerosol at fixed RH values of 70, 80, and 85% RH, the effects of hygroscopic growth were considered. The diameter of every particle was adjusted based on the growth factor calculated as described in Sect. 2.5, and the refractive index was adjusted to the volume weighted mean of dry particle and water refractive indices.

Line 366 onwards: I suggest a separate sub-section for the method to calculate absorption including a few introductory sentences on the basic approach behind it, also commenting on which parts of Table 2 and Figure 2 are used for it and which parts are not required.

Line 374: "We assume that hygroscopic growth on coated BC particles does not appreciably change the absorption coefficient through additional lensing effects, since substantial coatings on the aged BC particles already existed." – This statement implicitly includes expert knowledge that absorption enhancement saturates for thick coatings. Might be useful to state this explicitly. I would support this assumption even outside the saturation range with the following two arguments. Uncoated BC does not undergo hygroscopic growth hence no absorption enhancement. Moderately coated BC will undergo hygroscopic growth, however, opposite effects of increasing shell thickness and decreasing shell refractive index will approximately compensate each other, thereby leaving a small net effect. PS: These assumptions are not perfect, but reliable experimental characterization of humidity dependence of aerosol absorption unfortunately remains an open challenge to the best of my knowledge.

Line 377: Why is it considered unimportant to treat absorption accurately in dust plumes (where dust contributes substantially to absorption)? E.g. line 46 does not read like dust is not generally unimportant for the ATom data set. (More comments on dust absorption are provided below.)

Line 389: “[...] approximately account for unmeasured BrC that is extractable in organic solvents [...]”: this statement is imprecise and should be reformulated to: “[...] approximately account for unmeasured BrC that is not extractable in water [...]”. The unmeasured BrC may include material that is exclusively extractable in organic solvents but insoluble in water (while it does not include BrC that is soluble in both water and organic solvents). The unmeasured BrC may also include amorphous carbon “tar BrC” that is insoluble, i.e. neither soluble in organic nor polar solvents (e.g. Corbin et al., 2019). For the same reason, “organic-soluble BrC” on line 399 should be replaced by “water-insoluble BrC”.

Corbin, J. C., Czech, H., Massabò, D., de Mongeot, F. B., Jakobi, G., Liu, F., Lobo, P., Mennucci, C., Mensah, A. A., Orasche, J., Pieber, S. M., Prévôt, A. S. H., Stengel, B., Tay, L. L., Zanatta, M., Zimmermann, R., El Haddad, I., and Gysel, M.: Infrared-absorbing carbonaceous tar can dominate light absorption by marine-engine exhaust. *npj Clim. Atmos. Sci.*, 2, 12, doi:10.1038/s41612-019-0069-5, 2019.

Lines 388-390: It is good that first order approximations are made to account for unmeasured BrC and for the difference between mass specific absorption in bulk solution versus airborne particulate form. The conversion factor to infer particulate absorption from bulk solution data implicitly includes particle morphology assumptions and an optical model, likely homogeneous spheres and Mie theory, respectively. This should be reflected in Figure 2 (see separate comments made on Figure 2).

Lines 400-404: Did I understand correctly, that the water extracted absorbance measurement is only used to quantify absorption by BrC at 365 nm? Or was it also used to constrain the AAE of 5, which is used to extrapolate BrC absorption to longer wavelength? If assumed, then provide suitable references, if constrained by measurements, then don't forget to state this (also updating at line 462). Furthermore, absorption by soluble BrC typically vanishes at visible red and NIR wavelength. Is it justified to extrapolate BrC absorption with an AAE of 5 all the way up to NIR wavelength?

Figure 4a: Logarithmic axis scaling could possibly provide a better visualization of the level of agreement for lower concentrations.

Figures 4a and 4b: It would be useful to have error bars on the data points (for both calculated and measured values).

Line 438: Shouldn't total scattering per component rather than total extinction per component be used as weighting factor for phase function averaging? It may be worthwhile to drop a remark here on how BC-particle contribution to phase function is treated (or neglected). See also above comment.

Line 440-446: Is total scattering in the approach used to calculate the fine mode fraction identical to total scattering calculated with the standard approach? I suspect it comes out slightly different due to different "effective refractive index"? I'm just curious, while I don't see need to adjust anything. Even if slightly inconsistent, it is in the end irrelevant as reported fine mode fraction is a normalized quantity, and the major uncertainty comes from splitting the two size ranges.

Line 460: Is the approach used to determine the extinction Angström exponent also applied to determine the scattering Angström exponent in equivalent manner?

Line 460: Approximating spectral dependence with a power law typically works very well over limited wavelength ranges. However, a rather wide range from 340 nm to 1020 nm is used here, in which case the power law approximation loses out in performance to precisely describe the spectral dependence. As a consequence of this, Angström exponent values become increasingly dependent on the specific approach chosen to infer it from spectral measurements: which wavelength range is covered, which discrete wavelength values are included in the fit, are data log-transformed before fitting, etc.? One peculiar approach to assess sensitivity could be to additionally determine the Angström exponent for two wavelength pairs (e.g. for 340/670 and for 550/1020). If the result is insensitive to choosing different approaches, then it is worthwhile to say so. If not, then it should be stated how exactly the least square fit was done and, more importantly, whether this peculiar approach was on purpose chosen to be identical with standard approaches in e.g. AERONET data processing routines (or some other standard data products or model outputs). BTW: Angström exponent results are not presented or discussed in the main text of the manuscript, correct?

Line 461-464: AAE BrC is kept fixed and AAE BC likely isn't too variable either. Thus, overall AAE essentially just reflects the relative amounts of BrC compared to BC, correct? Or does calculated AAE BC exhibit considerable regional variation? In any case, calculated AAE BC should be reported to confirm plausibility of calculated values (after updating the refractive index of BC as requested elsewhere). Actually, I actually wonder whether one should just assume a value of around  $1 \pm 0.2$  for AAE BC. Most importantly, it should be quantified how input uncertainties (e.g. a factor of 3 for BrC absorption; see line 400) propagate through to AAE uncertainty (this should be quite straight forward).

Line 474: Here it is argued that dust plumes must also be considered for (A)AOD calculations. Does this go together with the approach to neglect absorption by dust in the calculations?

Line 478: Interpolation is applied if no more than two vertical layers are filtered due to cloud screening. This seems fine, in particular in the interest of increasing data coverage, except for one potential caveat. Such conditions would be removed via cloud screening from columnar remote sensing measurements. I would expect above-average RH in the cloud-free layers of profiles with clouds in some layers. Could this lead to a systematic RH bias between the data set of this study and remote sensing data sets that may be used for future comparison, or is it likely a minor effect?

Figure 5: When comparing panel d with panel f and panel c with panel e, it looks like considerable covariance of biomass burning and sulfate/organic extinction. Does this suggest that true biomass burning particles do mostly show up in the biomass burning class but also bleed over significantly into the sulfate/organic particle class? Would that affect the interpretation given on lines 495 to 498? More generally, the dust particle class also has quite some co-variance with above two classes, whereas sea salt class exhibits a very distinct spatial pattern. Are source and transport patterns of true biomass burning, sulfate/organic and dust particles more correlated with each other than with sea salt source patterns, or is the applied methodology very good in isolating sea salt particles, while distinction between biomass burning, sulfate/organic and dust is more ambiguous? The authors have much greater experience in strength and limitations of the particle typing approach they applied than the general reader of this manuscript has. Therefore, they should convey their expert interpretation relating to above questions.

Figure 6:

i) Fitting a slope with axis intercept is not a suitable means to assess "overall" closure performance. This type of regression analysis heavily up-weighs higher concentration values and heavily down-weighs lower concentration values. Hence, the regression slope only represents the performance for the higher AOD values. It might be useful to add a sub-panel with a histogram of ratios, possibly even segregated by upper and lower half of AERONET (or DC-8) AOD values.

ii) There is always a question whether using linear or logarithmic axis scaling (or both). Linear axis scaling puts visual emphasis on absolute values and errors. In its current form the graph nicely shows that the two methods both agree well in terms of distinguishing low AOD from high AOD. Logarithmic axis scaling puts emphasis on relative errors (and helps for visualizing values varying by several orders in magnitude). In this example, choosing logarithmic axis scaling (and adding further grid lines in parallel to the 1:1-line corresponding to fixed ratios) would likely allow for a better visual assessment of closure performance in relative terms at low AOD values, where the fit and 1:1 lines both appear to lay systematically off the data points (little in absolute terms, a lot in relative terms). In the end, axis-scaling type is always a subjective decision. However, discussion of closure results should always clearly distinguish between the two basic questions: "ability to distinguish low from high values" and "level of relative agreement across the full range (or defined sub-ranges) of observed absolute values".

Figure 7: The data points appear to scatter quite symmetrically about the LOWESS fit, in a visualization with logarithmic axis scaling. I have no experience with LOWESS but this fit result looks counter intuitive as "linear" sounds like "putting emphasis on absolute deviation" (unless data were log-transformed before applying LOWESS). Anyway, it looks like the LOWESS provides local modal/median values rather than local mean values. Depending on atmospheric process or on what is to be emphasized with the fit curve, one or the other type of value can be more relevant. It could be considered to provide two types "smoothed fit" to show both local mode and mean (local median and local averaging are simple ways to get such curves). Providing two different curves has the advantage

that potential future users of the fit curve, which may want to compare it with their own data, will have to assess which one to choose and how to fit their data to ensure consistency of the comparison.

Lines 553 to 556 / thresholds for "in plume" conditions: choosing rather high thresholds, as done here is perfectly suitable to separate conditions where bulk aerosol properties represent the plume aerosol type. However, the "free troposphere" conditions contain, as a consequence, all more dilute biomass and dust plumes. It would be interesting to know whether "free tropospheric conditions without BB/dust plume", could be unambiguously isolated with suitable low thresholds. However, this may not be possible as transition between "dilute plume" to "no plume" may be continuous or due to limited sample number. Based on this comment, line 604 should read "[...] exclude data from strong BB and dust plumes [...]" (and equivalently in caption of Fig. 11).

Figure 9: A duplicate of this figure with showing percentage contribution of each particle type (and water) to total extinction shown on the abscissa could be added to the SI. This would visualize relative contributions of different aerosol types at higher altitudes, which is not accessible in the current graph.

Fig. 10b: Scattering by dust is one or two orders in magnitude greater than absorption by BC for dust plumes. This means that absorption by dust could exceed absorption by BC in these plumes, unless dust SSA is really high. This brings me back to earlier comments on the role of dust absorption. Would it be possible to approximately consider dust absorption in the optical model by simply applying literature values of dust SSA to calculated dust scattering (if dust SSA isn't excessively size or source area dependent)?

First paragraph in Sect. 3.3.2: I perfectly agree with the arguments made for need to get composition and size right. Only one small caveat: number size distribution instead of volume size distribution, as presented in Fig. 11, would provide better insight when it comes to CCN and aerosol-cloud interactions. Would it be possible to add particle-type resolved number size distributions to the SI?

Lines 640 to 645: I would refrain from interpreting altitude dependence of accumulation mode modal diameter. Cloud processing and wet removal may affect size in addition to condensation.

Figures 12 c & f: The GSD of the accumulation mode decreases at altitudes below ~2 km with a concurrent increase of the coarse mode GSD. The latter trend is explained with SSA versus dust. I wonder whether the former is real, or to some extent a fitting artefact which leads to reduced accumulation mode GSD when coarse SSA is present?

Figure 13: A fair estimate of uncertainties should be added to calculated values shown in

this figure. For example, a factor of 3 uncertainty is state for BrC absorption in the methods section, whereas I expect lower uncertainty for absorption by BC. Therefore, the ratio of BC to BrC absorption seen in this figure must not be over-interpreted, whereas single scattering albedo may have relatively small error with little contribution from BrC absorption uncertainty. The authors have a discussion section on limitation, caveats and uncertainties, which is very good to have, and in which they argue against feasibility of error propagation with reasonable effort. This is fair enough; however, some additional guidance of the reader on how to interpret or not to interpret results in one or the other figure could be helpful.

Line 665 to 668: This statement almost motivates an SI figure showing vertical profiles of MAC and MSC.

### **Technical comments**

L95: Define acronyms (ATom) at first incident in the text (excluding abstract).

L111: "ATom"

L141-142: Avoid exclusive use of "size" when reporting quantitative numbers. Instead explicitly state "radius" or "diameter".

L174: please add: [...] was then converted to aerosol absorption as described in Section XY.

L194: refer forward to Sects. 2.5 & 2.6 for hygroscopic growth and CCN activity and to Sect. 2.7 for optical properties (i.e. for additional simplifications made to infer kappa and refractive index from composition).

L208 & 215: "particle volume size distributions"

L352: use common term for the quantity calculated - "scattering" alone is quite undefined - and provide units (to further minimize potential risk of ambiguity).

Lines 401-403: Calculation of extinction is a bit hidden. I suggest a separate paragraph and including equation number, just to give it a little more weight.

Lines 419-422: This belongs into the previous subsection.

Equation 7: "I" on the right hand side of the equation also requires a subscript "i". And, strictly speaking, all  $\theta$  in the denominator should be replaced by e.g.  $\theta'$  in order to disambiguate the integration variable, which runs over the range from 0 and  $\pi$ , from the  $\theta$  in numerator and on the left hand side, which has a fixed value between 0 and  $\pi$ .

Equation 10: I suggest to explicitly include wavelength and reference wavelength on the left hand side of the equation.

Equation 11: Using "i" as index for layer here and as index for chemical component elsewhere in the manuscript, bears a (small) risk of causing confusion. I suggest using a different index for the layers. With "AOD" on the left hand side, "x" on the right hand side can exclusively be a placeholder for extinction. I suggest to provide the AOD variant of the equation only and comment that AAOD is obtained with substituting extinction by absorption.

Figure 5: Color scale font size is really at the lower limit.

Line 562: "water dominates"

Line 576: also refer to Fig. 10a

Figure 10 caption:

i) Add a "combustion=HFO-combustion".

ii) It should be stated that all rows except BrC Abs and BC Abs represent scattering only (based on the basic assumptions behind the optical calculations).

iii) "H<sub>2</sub>O" could also be expanded to "contribution of light scattering enhancement by particulate water relative to dry particle properties". (Elsewhere, "H<sub>2</sub>O" is used for water vapour.)

iv) Where has the "unclassified" PALMS class gone?

Line 581: I suggest: "[...] absorption from BC, which includes the enhancement by substantial coating as shown to be present by the SP2, is also a significant contributor [...]"

Figs. 9 and 11 and line ~200: Which PALMS classes are included in "industrial combustion"? Generally, labelling should be harmonized across figures and throughout the manuscript.

Fig. 12d: Fix Aitken mode color.

Line 654: I suggest: "The  $\sigma_g$  of the lognormal distribution is  $>2$  in the lowest 2 km of the profile, where sea salt dominates, but  $<2$  in the middle [...]"

Figure 13: Please put emphasis on the wavelength!

Line 676: Maybe: "[...] due to the shift of modal diameter to smaller sizes [...]"