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Title: Mass specific optical absorption coefficients of mineral dust components measured by a multi wavelength photoacoustic spectrometer

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Reviewer #1:

Reviewers' comments: This manuscript presents mass absorption coefficient measurements for a range of mineral dust components. Measurements were made on re-suspended particles using a multi-wavelength photoacoustic spectrometer, with corrections applied for particle transport losses based on the MPI particle loss calculator program. Results were compared to idealized calculations based on Mie theory using literature values of refractive index. This paper is a good application of the author's homebuilt photoacoustic spectrometer and aside from some minor comments, I have few technical suggestions for improvement. It is relatively simple in scope and in my opinion its most significant weakness is that the technical or scientific breakthroughs presented are not extensive. This will limit its impact, but I do nevertheless believe the paper should be considered for publication in AMT following consideration of the following comments.

Authors' response: First of all, we would like to express the authors' thanks for this review. The authors are in unison regarding that all the implementing comments and suggestions in the revised MS have really improved its scientific level and also its impact on the field.

Specific comments:

Could the authors use their results to derive the wavelength-dependent complex refractive indices for each of the mineral components as a useful addition to Table 1?

Authors' response: Indeed besides the mass specific absorption coefficients, κ values (the imaginary part of the complex refractive indices) can also be deduced from our measured data. Therefore, according to the suggestion of the reviewer we added another Table (Table 2) to the

manuscript which includes the following data for each investigated mineral dust component: κ (deduced from our measurement), n (literature value used in the calculation of κ) and κ (literature value for inter-comparison purposes).

Furthermore we added the following text on page 11 from line 286-296:

“Values of κ were also calculated from the measured and particle loss corrected data by using a simple Mie-theory based retrieval algorithm (Guyon et al.,2003, Hoffer et al., 2006). First, the Mie code takes the n values from the literature and the measured and particle loss corrected size distribution data as input parameters, then calculates the absorption coefficient. Thereafter this value is compared to the measured absorption coefficients and following that the initial κ value is increased stepwise until the calculated and measured optical coefficients agree to within 0.5%. The κ value associated to this agreement represents the imaginary part of the investigated sample.”

page 12, line 309-311:

“The MACs and the imaginary parts of the complex refractive indices deduced from the measured data are listed in Table 1 and Table 2, respectively.”

Furthermore we also added the following Table 2 with the corresponding Table caption:

page 12, line 322-325:

“Table 2. Imaginary parts of the complex refractive indices (κ) of the measured MD components. For the sake of clarity these data are supplemented with the n and κ values taken from the literature, where the former ones are used in the κ calculation while the latter ones are shown in this Table for inter-comparison purposes.”

We also added the following text on page 16, line 374-378:

“The κ values deduced from the presented measurements are compared to the values deriving from the literature (Table 2.) For some mineral dust components the difference between these values are within the combined uncertainty of the measurement and the calculation (e.g. in case of bentonite, hematite and rutile) while for other cases (such as for illite and kaolin significant differences (above the uncertainty level) can be observed.”

These will of course be sensitive to the size distribution. Some indication of how uncertainty propagates from the size distribution to the r.i. retrieval would be interesting.

Authors' response: Following the suggestion of the reviewer we investigated the propagation of errors in the retrieval and the results of which are also described in the revised MS:

We added the following text on page 16, line 379-393 (this will be a part of a new paragraph in the Discussion section which especially deals with the uncertainties and errors in the deduced parameters):

“The uncertainties of the calculated parameters are affected by the fluctuations in the concentration of the generated aerosol, the noise of the PA measurements, the errors of the size distributions as well as the uncertainty of literature values used in the retrieval procedure. In order to estimate the resulting uncertainty of the calculated parameters, a sensitivity study of the input parameters was performed.

The uncertainty of the measured OAC values was determined directly from the uncertainty of the PA measurement including concentration instability. In case of MAC values the uncertainty of about $\pm 20\%$ and $\pm 5\%$ were used for OAC and mass concentration measurement respectively where the OAC uncertainty includes the concentration instability as well. The quadrature sum of these individual errors was found to be about 21%. The uncertainty of the modelled OAC values are not determined here due to the lack of available information about the error of the literature R_i data. Error propagation of size distribution for the R_i retrieval was also investigated separately and we found that the uncertainty of the size distributions are between $\pm 15\%$ and the uncertainty of the OAC values are between $\pm 20\%$ translate directly in the computed κ . Therefore, the resulting quadratic error of computed κ were found to be about 25%.”

At first read of section 2.4, I was surprised that only calculation was used to determine particle losses with no experimental validation. Where experiments not possible? A note explaining why this was the case would be useful. I would have consider this a major deficiency if it were not for the degree of agreement observed in Figure 3.

Authors' response: We definitely agree with the Reviewer that the validation of the particle loss correction should further increase the reliability of the presented results. Anyway, the experimental validation of the particle losses in a real experimental set-up comes up against many technical difficulties such as the differences in volumetric flow rates of the applied instruments as well as the SMPS, which really limits the reliability of such validation. In our case it was a further limitation that our SMPS is not able to operate in selection mode in which the monodisperse subsection of the generated aerosol stream could be quantitatively investigated. Moreover, according to our preliminary calculation, the mass concentration of the selected subsection of the generated sample would also be beyond our detection limit which further limited the possibilities of such a validation. However there were at least two reasons why we accepted the results of the PLC algorithm in this study. One is that our experimental set-up is much less complicated (i.e. not including double U turn or so) than in which the independent validations procedure of this PLC algorithm was performed (Von der Weiden et al., 2009). The other is based our real measurement results (which are not presented in this study) in which we generated dust aerosol stream with significantly different size distribution resulted in significantly different particle loss transfer function for calculation, however, the resulted χ become identical. This is kind of indirect validation of the reliability of PLC algorithm.

Accordingly we added the following text on page 9 from line 244 to line 249

“The uncertainty of the particle loss calculator was determined independently in another study (Von der Weiden, 2009). Since the experimental set-up presented here is much less complicated (i.e. devoid of double bend configuration with sharp curvature) than the one used in the validation procedure and all the applied instruments use low flow sampling in the laminar flow region where the reliability of this PLC algorithm is more adequate, we used this uncertainty in this study.”

The legend for Figure 3 indicates that error bars are from the uncertainty in PA measurements. Does this include contribution from the stability of the aerosol generation source and stability of the background measurement? How stable were these measurements?

Authors' response: We agree with the Reviewer in that the explanation of the related error bars are misleading since it is suggested that the error bars are only indicating errors due to the PA signal instability. Actually the errors marked by the bars also represent quadratic uncertainties of the instrumentations including concentration instability.

Therefore, according to this suggestion, we described the measurement protocol as well as the uncertainty of the presented data including concentration instability in the revised MS.

Page 14, line 341

“Figure 3. Aerosol optical absorption coefficients. The points represent OAC data calculated from PA signals with error bars representing the uncertainty of the OAC data (see text in details)”

Page 5 from line 202-207

i.e.” In the measurement mode a complete 15-minute-long measurement cycle includes a 10-minute sampling and a 5-minute background measurement period. Generally, 8 measurement cycles were used for data evaluation. The initial transient period was not evaluated. Depending on the investigated mineral dust component and the applied wavelength, the fluctuation of the PA signal including concentration instability was found to be in-between 15% and 22%”

Page 16, line 379-393:

“The uncertainties of the calculated parameters are affected by the fluctuations in the concentration of the generated aerosol, the noise of the PA measurements, the errors of the size distributions as well as the uncertainty of literature values used in the retrieval procedure. In order to estimate the resulted uncertainty of the calculated parameters, a sensitivity study of the input parameters was performed. The uncertainty of the measured OAC values was determined directly by the uncertainty of the PA measurement including concentration instability. In case of

MAC values the uncertainty of about $\pm 20\%$ and $\pm 5\%$ were used for OAC and mass concentration measurements respectively, where the OAC uncertainty includes the concentration instability as well. The quadrature sum of these individual errors was found to be about 21%. The uncertainty of the modelled OAC values are not determined here due to the lack of available information about the error of the literature R_i data. Error propagation of size distribution for the R_i retrieval was also investigated separately and it was found that the uncertainty of the size distribution in between $\pm 15\%$ translates directly in the computed χ . Therefore, the resulted quadratic error of computed κ were found to be about 25%.”

Can the authors add a comment to justify use of Mie model for particle that are clearly non spherical? Is there any prior works that suggest this to be a valid approach?

Authors' reply: We definitely agree with the reviewer that using the Mie model for non-spherical particles such as dust minerals means limitation to the calculations. So according to this suggestion we explain the legacy and the limitation of Mie code for the retrieval of optical absorption coefficient and the imaginary part of refractive indices in the revised MS

Therefore we added the following text on page 11, line 293-306::

”However, it is noteworthy, that although the application of Mie-theory for non-spherical particles limits the reliability of the computed data, many prior works used this approach to calculate the spectral responses of dust minerals (Conant et al.,2003;DeSouza-Machado et al.,2006;Moffet and Prather, 2005;Wang et al.,2002). This is because the most widely used shape sensitive models such as T-matrix or DDA (Discrete dipole approximation) are also not using the real morphology of the investigated aerosol sample but they are based on mathematically well characterized geometrical approximation (Kalashnikova and Sokolik, 2004; Tegen and Lacis, 1996). (Kalashnikova and Sokolik, 2004; Tegen and Lacis, 1996). Kalashnikova and Sokolik demonstrated that the deviation between the spherical and non-spherical approaches become significant above the approximate size parameter of 5 and only in case of the asymmetry parameter and the scattering phase function which are mainly governed by the coherent scattering

physical process, while the absorption which is an incoherent physical phenomena, the deviation is much less significant even above size parameter higher than about 5.”

And

page 19, line 440-444:

i.e.” Using the Mie-theory based simulation and assuming spherical particles we determined the refractive indices of the measured components and we also made comparison between the measured and the simulated OAC data with the quoted limitations described in details in section 2.4”

Section 2.3: What fraction of the total photoacoustic signal was the background signal typically? (i.e. was this a small or a large corrections) What RH where measurement performed at?

In order to answer these questions we added the following to the MS:

p 16, line 370-374:

“In our study, the ratio of the total photoacoustic signal to background signal was varied between 1.4 and 3.3 depending on the investigated components and the applied wavelengths. The signal to noise ratio was higher than 20 even in the less absorptive components such limestone and quartz, therefore all the presented data have high reliability.”

And

page 7, line 171-174

“The relative humidity (RH) of the air stream including suspended particles in the buffer chamber was measured during the whole measurement campaign and found to be below RH~30 in each sample. All the presented measurement result were performed at room temperature and atmospheric pressure.”

Page 9027, line 11-15: this statement is confusing. For an aerosol sample with e.g. 10 Mm-1 absorption and Mm-10 scattering, the SSA is 0.5 not 0.9 as stated.

We agree with the reviewer that the cited statement is not valid; therefore we corrected this in the revised MS.

page 1 line 49-51:

“Generally speaking, light absorption is one of the most difficult aerosol parameters to be measured even when optical absorption has the same magnitude as scattering, i.e. the single scattering albedo (SSA) is around 0.5.”

Page 9029, lines 17-19: can a reference be provided for this statement? While true for submicron particles, how large do particles need to be before heat transfer into the particle bulk during photoacoustic cycles becomes important?

We really agree with the reviewer in that the dust minerals sample presented here cannot be typified as volumetric absorber with exhaustive confidence and using this classification is confused and might mislead the readers. Since we cannot support this statement adequately, under this suggestion, we neglect this classification in the revised MS.

Anyway, we made some calculation for the size dependency of the heat transfer period and found that the characteristic time interval for the heat transfer become commensurable with the time interval determined by modulation frequency of the excitation (photoacoustic cycle) only when the characteristic diameter of the investigated composite are higher than 3.4 μm even in the case of clay minerals having the highest heat capacity. This calculation is based on the relation defined by Chan (1975).