

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

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H. Moosmüller:

Reviewers' comments: This manuscript contains interesting work on much needed spectral absorption properties of mineral dust aerosols and their mineral components. Currently, there are large discrepancies between published imaginary refractive indices for mineral dust components. These discrepancies seem to be largely due to the use of samples that have not been analyzed for chemical and mineralogical composition and the use of different, largely bulk measurement methods. In terms of the first problem the authors of this manuscript don't do any better, for example "limestone was collected in the Pilis Mountains of Hungary"; chemical and mineralogical analyses are totally absent. In terms of measurement methods, this manuscript adds a very different method, the photoacoustic instrument to the mix. The primary measurement products are MACs for largely sub-micron particles at four wavelengths. So what? What are these MACs good for? They can't be used for radiative transfer calculations because ambient particles, even after long-range (e.g., intercontinental) transport, are typically substantially larger (Formenti et al., 2011; table 3). The one important use that I could see is to derive imaginary parts of the spectral refractive index from these measurements, which should be possible if the particles are truly volume absorbers. To this subject, the authors state "The MAC data listed in Table 1 and shown in Figure 1 prove that in accordance with the expectations, the measured MD components are volumetric absorbers." With fig. 1 not containing any MAC data, the authors need to do a much better job in explaining why these sub-micron particles are volume absorbers! If these particles are indeed volume absorber (as I suspect), the authors may be able to use small particle absorption theory (Bohren and Huffman, 1998; p. 136, eq. 5.11) to retrieve the imaginary part of the refractive index. While the use of Mie theory for

these highly non-spherical particles is suspect, it may actually work well for calculating the absorption of volume absorbers; but this needs to be substantiated, otherwise Mie results should not be included.

Authors' response: First of all the authors give thanks for Hans Moosmüller for this review since according to our perception this review really highlighted the weak points of the MS and take into account these suggestions it really improved the quality of this MS.

1. These discrepancies seem to be largely due to the use of samples that have not been analyzed for chemical and mineralogical composition and the use of different, largely bulk measurement methods. In terms of the first problem the authors of this manuscript don't do any better, for example "limestone was collected in the Pilis Mountains of Hungary"; chemical and mineralogical analyses are totally absent.

Authors' response: We really agree with the reviewer that the chemical purity of the investigated components might limit the reliability and also the general applicability of the presented data. Therefore, we extended the chemical description of the investigated material according to our all available information from these specific components.

Therefore we added the following to the MS:

page 6, line 141-161:

" In this study MD components, phyllosilicates (illite, kaolin and bentonite), oxides (quartz, hematite and rutile), and carbonate (limestone) were investigated. High purity illite was obtained from a Hungarian source Füzérradvány and measured as received. Its mineral composition is illite 75, montmorillonite 5, quartz 14, kaolinite 1 and feldspar 4% and its chemical composition is SiO₂ 47.5, Al₂O₃ 29.0, Fe₂O₃ 1.2, CaO 1.8, MgO 3.0, K₂O 6.8, Na₂O 1.1, loss of ignition 8.5 and total 98.9%. Kaolin was obtained from Zettlitz (Germany). It contains clay mineral kaolinite as the main component up to 90 %, accompanied by some micaceous minerals and small amounts of quartz. Chemical composition of kaolin is MgO 0.27, CaO 0.29, SiO₂ 46.9, Al₂O₃ 37.4, Fe₂O₃ 0.65, K₂O 0.84, Na₂O 0.44, TiO₂ 0.18, H₂O 12.95 and total 99.92%. We used a fine-grained washed kaolin sample with a characteristic particle size of 1.2–1.4 μm. The source

of montmorillonite was bentonite from Mád (Hungary). Its mineral composition is montmorillonite 86, quartz 3, feldspar 5% and its chemical composition is SiO₂ 63.8, Al₂O₃ 16.0, Fe₂O₃ 5.0, CaO 2.4, MgO 1.2, K₂O 0.8, Na₂O 1.1, TiO₂ 0.6, loss of ignition 8.9 and total 99.8%. The mined bentonite had a grain size of less than 90 μm, activated by 5% Na₂CO₃ and enriched in montmorillonite. A high purity quartz sample (SiO₂ > 99%) was ground and the sieve fraction < 200 μm was used. Hematite (Fe₂O₃) produced by Reanal Private Ltd. (Hungary) had a degree of purity > 95 %. Rutile (Bayertitan R-U-2) produced by Bayer AG contained 98% TiO₂; it is an alumina lattice modified sample, its relative light scattering power is 96 and its specific gravity is 4.1 g cm⁻³. Limestone (calcium carbonate with CaCO₃ content 98%) was collected in the Pilis Mountains (Hungary) then grained to produce fine powder.”

2. The primary measurement products are MACs for largely sub-micron particles at four wavelengths. So what? What are these MACs good for? They can't be used for radiative transfer calculations because ambient particles, even after long-range (e.g., intercontinental) transport, are typically substantially larger (Formenti et al., 2011; table 3). The one important use that I could see is to derive imaginary parts of the spectral refractive index from these measurements, which should be possible if the particles are truly volume absorbers.

Author's response: We really agree with the reviewer in that aside from the mass specific absorption coefficient the more climate relevant parameter i.e. the imaginary part of the complex refractive indices can also be deduced from the measured data. Therefore, according to this suggestion, we also implemented a table (Table 2) which includes the complex refractive indices of the investigated minerals deduced from our measured data with the complete description of their derivation. However, we also agree with the reviewer in that the nomenclature “climate relevant” used here is laxity and should be used more quantitatively always defined the actual parameter to which the climate relevance is used in the revised MS. We really agree with the reviewer that the submicron mineral dust aerosol only covers the part of the total amount of the ambient dust, therefore the climate relevance in the context of the size cannot be used here. However, we presented the results of dust minerals except for mineral dust which is only a part of that having smaller but not well defined characteristic size inside the real mineral dust aerosol.

Therefore, according to this suggestion, we omit the climate relevance as the classification of the presented data in the context of size throughout the revised MS. However, it is also noteworthy, that although, the submicron mineral dust particles is not the most climate relevant fraction of the total dust both the mineral dust and especially also its components having characteristic size below 1 μm are in the focus of many prior works (Mogili et al., 2007; Kalashnikova and Sokolik, 2003; Linke et al., 2006).

Therefore, however, we also partly agree with the reviewer that climate relevance of these parameters is really limited into the submicron particles which are only a part of a total amount in the mineral dust aerosol.

3. To this subject, the authors state “The MAC data listed in Table 1 and shown in Figure 1 prove that in accordance with the expectations, the measured MD components are volumetric absorbers.” With fig. 1 not containing any MAC data, the authors need to do a much better job in explaining why these sub-micron particles are volume absorbers!

Authors’ response: We really agree with the reviewer that the dust minerals sample presented here cannot be typified as volumetric absorber with exhaustive confidence especially in the UV wavelengths and using this classification is confusing and might mislead the readers. Inasmuch, we cannot support this statement adequately here, consequently and based on this suggestion, we neglect the usage of “volumetric absorber” in the argumentation throughout the revised MS.

4. While the use of Mie theory for these highly non-spherical particles is suspect, it may actually work well for calculating the absorption of volume absorbers; but this needs to be substantiated, otherwise Mie results should not be included.

Authors’ response: We really agree with the reviewer that using the Mie theory such highly non-spherical particles as the mineral components means limitation on the reliability and also the general applicability of the measured data. However, despite of these limitations many earlier studies used this approach to calculate the spectral responses of ambient dust aerosol (Müller et al., 2011; Conant et al., 2003; DeSouza-Machado et al., 2006; Moffet and Prather, 2005; Wang et al., 2002). Since the most commonly applied shape sensitive models such as T-matrix and DDA

also did not used the real morphological condition but its simplified geometrical approximation and the deviations between the results of the two approaches become significant above the size parameter of about 5 and only in the asymmetry parameter and the scattering phase function both of that are driven by the coherent physical processes such as scattering. While the parameters driven by the absorption which is an incoherent physical phenomena this deviation is negligible even at about size parameter higher than 5. Therefore, we really agree with the reviewer in that both the legacy and the limitation as well as the complete description of the applied spherical methodology should be included in the revised MS.

Therefore we added the following text to the manuscript:

page 11, line 286-293:

“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, and 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.”

And also

page 12, line 309-310:

“The MACs and the imaginary part of the complex refractive indices of the measured components deduced from the presented measurements are listed in Table 1 and Table 2, respectively.”

And also

page 11, line 293-306:

i.e ”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.”

Additional more minor comments are:

- 1) **L43-44 and L69: What is this climate relevant spectral region? Are the authors talking about the tropospheric solar spectrum (300 – 2300 nm) or are they also including the thermal infrared?**

Authors' response: we really agree with the reviewer that climate relevancy in the context of spectral region used here is not adequate and needs to be reduced to the wavelength region defined by the operational wavelengths of the applied instrument. Therefore, according to this suggestion, we modify these sentences in the revised MS.

Instead of this sentence:

“These spectra are measured by our recently developed multi-wavelength photoacoustic spectrometer (4λ-PAS) in the shortwave climate relevant and the photochemically active UV-Vis-near-IR spectral region.”

We implemented:

page 5, line 129-131:

“These spectra are measured by our recently developed multi-wavelength photoacoustic spectrometer (4λ-PAS) in the UV-Vis-near-IR spectral region.”

We deleted this sentence:“Thus, the measured and simulated results based on these data are climate relevant.”

- 2) **Querry’s work on hematite refractive index is generally misquoted. Querry (1987) quoted here does not contain any work on hematite, the correct reference is Querry (1985)**

Authors’ response: We really agree with the reviewer in that this reference is generally misquoted in our works and should be repaired in the revised MS.