



## Abstract

Mass specific optical absorption coefficients of various mineral dust components including silicate clays (illite, kaolin and bentonite), oxides (quartz, hematite and rutile), and carbonate (limestone) were determined at wavelengths of 1064, 532, 355 and 266 nm. These values were calculated from aerosol optical absorption coefficients measured by a multi-wavelength photoacoustic (PA) instrument, the mass concentration and the number size distribution of the generated aerosol samples as well as the size transfer functions of the measuring instruments. These results are expected to have considerable importance in global radiative forcing calculations. They can also serve as reference for validating calculated wavelength dependent imaginary parts ( $\kappa$ ) of complex refractive indices which up to now have been typically deduced from bulk phase measurements by using indirect measurement methods. Accordingly, the presented comparison of the measured and calculated aerosol optical absorption spectra revealed the strong need for standardized sample preparation and measurement methodology in case of bulk phase measurements.

## 1 Introduction

Mineral dust (MD) in the atmosphere affects the radiative budget of the Earth both directly and indirectly. It absorbs and scatters the solar and terrestrial radiations in the near-infrared-visible-near-UV wavelength range, and its overall forcing effect is influenced by its chemical composition, temporal and spatial distribution as well as its optical properties. As a consequence of this complex dependence, current knowledge on both the sign and the magnitude of the MD induced radiative forcing is largely uncertain (Claquin et al., 1998). Some studies estimate that the forcing effect of MD compares to or even exceeds the cumulative forcing effect of all other aerosol originated from anthropogenic sources (Sokolik and Toon, 1996). Therefore, there is a strong need for measurement methods which can characterise the optical properties of MD accurately.

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7, 9025–9046, 2014

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(Claquin et al., 1998; Nickovic et al., 2012). Various efforts have already been made to calculate the optical properties of MD from the optical properties of its components, e.g. by using the effective medium approximation (Sokolik et al., 1993; Sokolik and Toon, 1999). Most often these calculations are based on the Mie-theory, and approximate the particles as being spherical and homogeneous. In these calculations the size distribution and the  $Ri$  of each component play a crucial role. Although refractive indexes of most abundant MD components are measured and tabulated over broad, climate relevant wavelength ranges, these data are typically derived from bulk phase indirect measurements, wherefore they have limited reliability. Furthermore, these measurement results are not validated by aerosol phase measurements, i.e. the actual microphysical aerosol conditions such as size and morphology are neither taken into account nor validated. Very often  $Ri$  data (and especially  $\kappa$ ) differ significantly even when measured at the same or very close wavelengths in the bulk phase due to the differences in the applied measurement methodology and sample treatment (Rao, 2002; Arakawa et al., 1997). There are serious concerns especially about the reliability of  $\kappa$  values determined by the most commonly applied diffuse reflectance based techniques. Claquin et al. (1998) found that the variation of  $\kappa$  determined by different methodologies manifests in significant uncertainties in radiative forcing calculations, and thus not only the magnitude but also the sign of the calculated radiative forcing parameter is uncertain.

Another potential application of accurate optical absorption data in a wide wavelength range could be the so called inverse problem, i.e. the determination of the chemical composition and thus the sources of MD (Müller et al., 2011) from its measured optical properties. This analysis is based on the fact that unlike scattering, which is mainly driven by aerosol size and morphology, absorption has rather strong sensitivity to the chemical composition too (Andreae and Gelencsér, 2006; Moosmüller et al., 2009).

The photoacoustic (PA) measurement technique has already proved its applicability under laboratory and field conditions in case of strongly absorbing aerosol components such as black carbon, brown carbon and HULIS (HumicLike Substances). These

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measurements have proved that contrary to the differential and the filter based methods the PA technique has a potential for the accurate in-situ determination of aerosol light absorption at multiple wavelengths due to its unique advantages such as filter-free sampling, linear proportionality of the PA signal with the aerosol optical absorption coefficient (AOC) and immunity to scattering (Andreae, 2001). On the other hand, application of the PA technique for the measurement of MD or MD components is a real challenge not only because of the high SSA and strong wavelength dependence of  $\kappa$  as described above, but also because of the relatively large size of the measured particles. Indeed, while the typical size of atmospheric black and brown carbon is in the range of a few hundred nanometres or even below, the size of the MD particles is mostly in the micron range. Consequently, the size transfer function of the detection system has to be taken into account accurately, especially for large particles, since already a few of them can considerably modify the aerosol mass concentration in the PA cell with which the PA signal is linearly proportional as described below.

Photoacoustic determination of optical absorption by aerosol is based on the absorption of periodically modulated light and the subsequent non-radiative relaxation of excited aerosol particles. Due to the high thermal conductivity and the small size of climate relevant ambient aerosol particles the energy absorbed by them is transferred promptly (adiabatically) to the surroundings. The subsequent thermal expansion induces periodic pressure variation, which is proportional to the concentration and the absorption cross section of light absorbing particles, can be detected and converted into a measurable electronic signal by an acoustic transducer (typically a microphone). The AOC can be deduced from the measured PA signal by using a conversion factor determined by an independent calibration of the PA system. The major advantages of this method against the alternatives are selectivity, sensitivity as well as accuracy. Selectivity means that PA is not only a zero background technique, i.e. in the absence of light absorption no PA signal is generated, but in addition to that the PA response is inherently unaffected by the non-absorbing aerosol particles present in the sampled aerosol stream, and also by the non-absorbing compounds of the individual aerosol

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particles (Moosmüller et al., 2009; Bozóki et al., 2011). The accuracy of the method stems from both its scattering insensitivity and its free-floating operation (i.e. from filter free sampling). The accuracy of the recently published PA instruments for aerosol measurement is in the range of a few percent, which is at least an order of magnitude better than that of the most commonly used filter based instruments, even when their readings are corrected posteriorly after the measurement (Andreae and Gelencsér, 2006).

To the authors' best knowledge, this paper presents the aerosol phase mass specific optical absorption (MAC) spectra of the most abundant mineralogical MD components for the first time. However it is worthy of note that single scattering albedo of several mineral dust samples was also previously determined by the combination of multi-wavelength photoacoustic spectroscopy and nephelometry (Moosmüller et al., 2012). These spectra are measured by our recently developed multi-wavelength photoacoustic spectrometer (4 $\lambda$ -PAS) in the shortwave climate relevant and the photochemically active UV-Vis-near-IR spectral region. Furthermore, the Mie-theory based simulated AOC spectra are generated by using bulk-phase  $R_i$  values derived from published literature and the measured number size distributions corrected by the size transfer function of the measuring system. These theoretical curves are compared with measured AOC spectra, and based on these comparisons the PA method is argued to be a powerful tool for verifying theoretical calculations.

## 2 Experimental and methods

### 2.1 Sample preparation

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. Kaolin was obtained from Zettlitz (Germany). It contained clay mineral kaolinite as the

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main component up to 90 %, accompanied by some micaceous minerals and small amounts of quartz. We used a fine-grained washed kaolin sample with a characteristic particle size of 1.2–1.4  $\mu\text{m}$ . The source of montmorillonite was bentonite from Mád (Hungary). The mined bentonite had a grain size of less than 90  $\mu\text{m}$ , activated by 5 %  $\text{Na}_2\text{CO}_3$  and enriched in montmorillonite. A high purity quartz sample ( $\text{SiO}_2 > 99\%$ ) was ground and the sieve fraction  $< 200\ \mu\text{m}$  was used. Hematite ( $\text{Fe}_2\text{O}_3$ ) produced by Reanal Private Ltd. (Hungary) had a degree of purity  $> 95\%$ . Rutile (Bayertitan R-U-2) produced by Bayer AG contained 98 %  $\text{TiO}_2$ ; it is an alumina lattice modified sample, its relative light scattering power is 96 and its specific gravity is  $4.1\ \text{g cm}^{-3}$ . Limestone (calcium carbonate –  $\text{CaCO}_3$ ) was collected in the Pilis Mountains (Hungary) then grained to produce fine powder.

## 2.2 Sample generation

MD particles were re-dispersed from the prepared powder sample and added to the buffer chamber for instruments sampling in the experimental setup depicted in Fig. 1.

Prior to the measurements, aerosol samples were desiccated in a vessel partly filled with silica gel for at least 24 h. A small amount of mineral powder was placed into the Erlenmeyer vessel and then into an automatic shaker. Synthetic air was blown through the shaker at a constant flow rate of  $10\ \text{L min}^{-1}$ . The re-dispersed aerosol was fed into a buffer chamber. Pressure was kept at atmospheric level by an exhaust pipe implemented into the buffer chamber. Each instrument sucked the aerosol loaded air mass directly from the chamber.

## 2.3 Instrumentation for aerosol characterisation

The AOC was measured simultaneously at four wavelengths by a multi-wavelength photoacoustic spectrometer (4 $\lambda$ -PAS). It contained four measuring cells with each of them being illuminated through one of the operational wavelengths of 266, 355, 532 or 1064 nm. With the help of a magnetic valve controlled by the electronics of the











## 4 Discussion

The SEM pictures are largely similar to those reported in literature (Bohor and Hughes, 1971; Dong et al., 2014) and show that apart from rutile, which has a more or less compact and spheroid shape, all other particles show a high degree of irregularity with versatile and unclassifiable shapes.

Although all the instruments were placed as close to the buffer chamber as possible to minimize the curves and lengths of the tubes, there is a relatively large difference in the number size distribution measured directly at the exit of the buffer volume and the PA detection cell, especially for particles with a characteristic diameter above  $1\ \mu\text{m}$ . On the other hand, the corrected size distribution data also show that almost all particles below  $1.2\ \mu\text{m}$  get into the PA detector. Thus, the measured and simulated results based on these data are climate relevant. Furthermore, it is also important to note that neglecting the particle loss in the instrumentation modifies the calculated optical spectra quite drastically, as shown in Fig. 3. It affects not only their overall magnitude, but also their shape as described in other works (Filep et al., 2012).

The MAC data listed in Table 1 and shown in Fig. 1 prove that in accordance with the expectations, the measured MD components are volumetric absorbers. As it is expected, their MAC values are several orders of magnitude smaller than those of BC and BrC. On the other hand, the PA signals were measured with a high signal to noise ratio even for the smallest MAC values, consequently all the presented data have high reliability.

As far as the measured and the calculated AOC spectra shown in Fig. 3 are concerned, it must be first of all emphasised that the presented research does not intend to provide a quantitative comparison of the theoretical and experimental results or to validate the optical models or the  $\kappa$  data used in the modelling, because of the lack of detailed information on sample preparation and on measurement methods applied on bulk samples for the determination of  $\kappa$ . Rather, as the presented AOC values are based on a direct and aerosol phase measurement of absorption using standardised

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data by Arakawa et al. (1997) in this case. Rutile provides a good example for the fact that even the same measurement method can result in strongly different spectra, most probably either due to differences in the sample preparation methods or due to differences in the samples themselves.

## 5 Summary and conclusions

The mass specific optical absorption coefficient is determined for the most abundant MD components by using a recently developed multi-wavelength photoacoustic system. For modelling the AOC values by the Mie-theory based simulation we used the measured and particle losses corrected number size distribution, as well as tabulated  $R_i$  data based on bulk or thin film phase, indirect measurement method taken from the published literature. Using the Mie-theory based simulation and assuming spherical particles we have made comparison between the measured and the simulated AOC data. We also experimentally demonstrated here that the reliability of both the measured and the simulated AOC values can be further increased by using particle corrected measurement data.

In some cases we have found good agreement between the photoacoustically measured and the simulated AOC data, while in other cases we could give plausible explanations for the differences. Nevertheless, due to the limited availability of information on the applied measurement techniques, on sample preparation and the detailed description of the measurement conditions in case of bulk samples, the scientific goal of this work was not the quantitative comparison of the measured and the simulated AOC values. Rather, we wanted to measure aerosol phase optical absorption using a direct and light scattering immune technique. Due to being free from all analytical and methodological artefacts (that may occur when using competitive techniques), the values measured and presented here can be used as reference in the validation of optical absorption measurements conducted on bulk phase samples. Furthermore, the data deduced from the presented experiments open up novel possibilities to experimentally

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investigate the effect of the bulk-aerosol transition when the bulk phase data are used in aerosol forcing calculations.

*Acknowledgement.* Financial support by the Hungarian Scientific Research Foundation (OTKA, project no. K101905) is gratefully acknowledged. The European Union and the European Social Fund have provided financial support to the project under the project no. TÁMOP-4.2.2.A-11/1/KONV-2012-0047 and TÁMOP FUTURICT 4.2.2.C-11/1/KONV-2012-0013. The research of Noémi Utry was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP 4.2.4. A/2-11-1-2012-0001 “National Excellence Program”.

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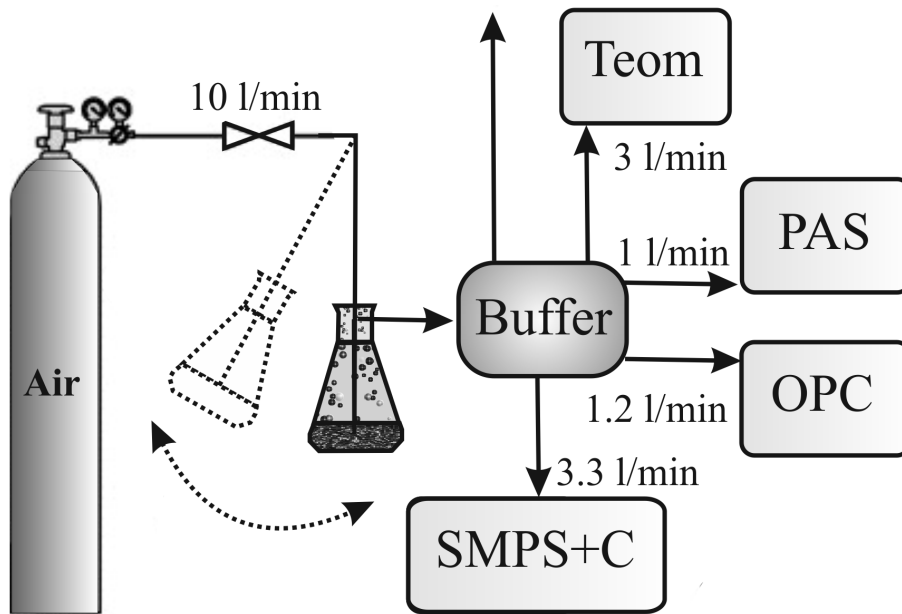
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**Figure 1.** Schematic diagram of the experimental setup.

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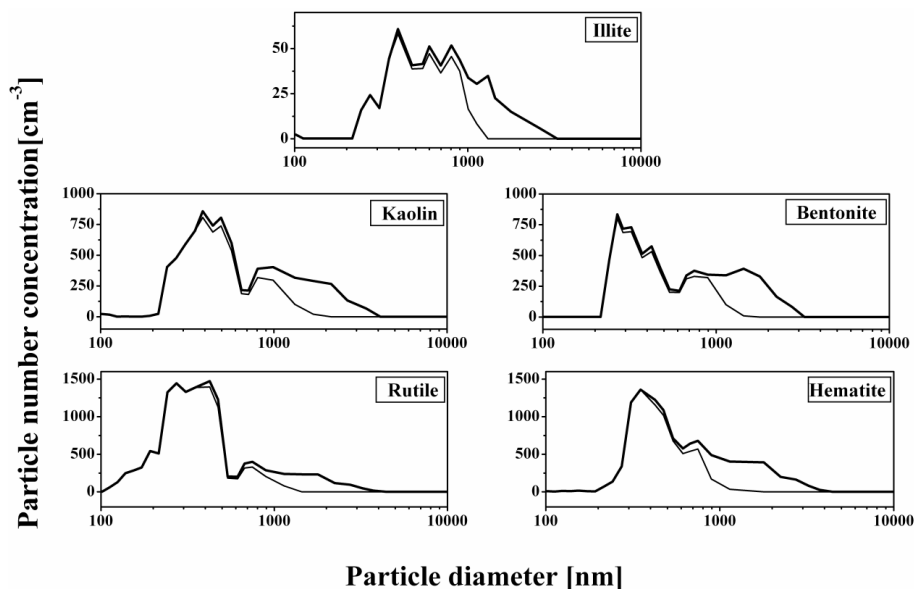
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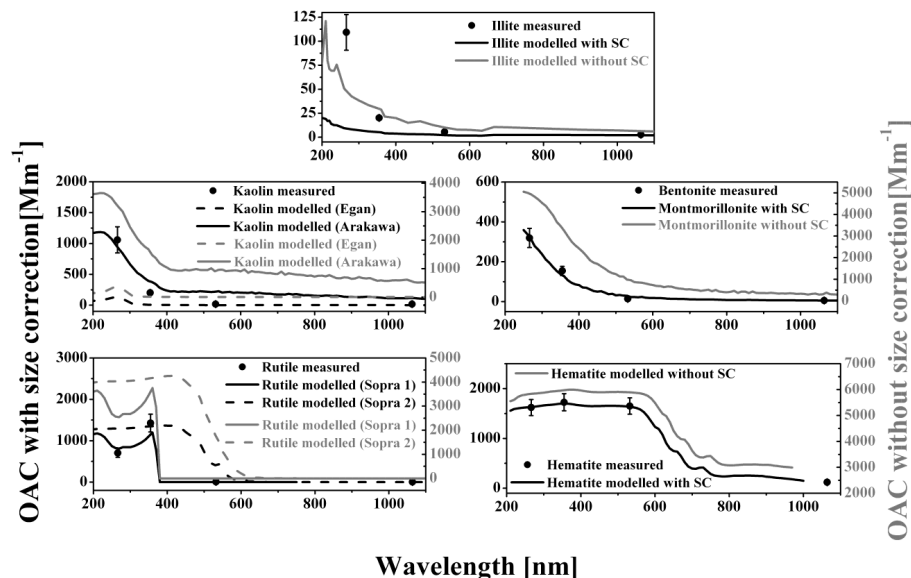


**Figure 2.** Number size distributions: in the buffer chamber measured by the SMPS and the OPC instruments (thick line) and in the PA cell calculated from the SMPS + OPC data by taking into account the calculated size transfer function of the PA system (thin line).

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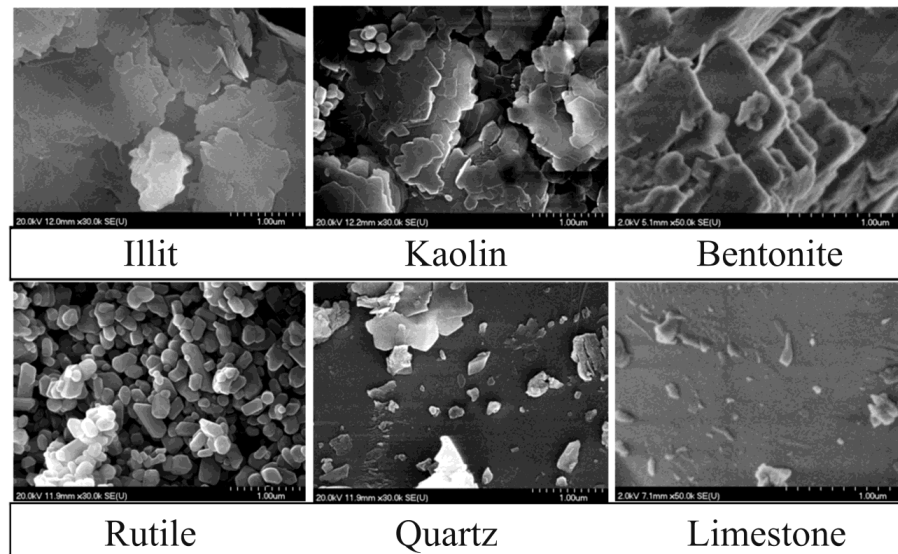
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**Figure 3.** Aerosol optical absorption coefficients. The points represent AOC data calculated from PA signals with error bars representing the uncertainty of the PA measurements; the black and grey lines represent the Mie-theory based calculations with or without size correction (SC-taking into account the size transfer function of the PA system), respectively. The dashed grey lines represent the results of calculations by using alternative RI parameters (see text for details).

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**Figure 4.** SEM pictures of collected aerosol samples.

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