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Generation and UV-VIS-NIR spectral responses of organo-mineral aerosol for modelling soil derived dust

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HIGHLIGHTS

- Complete monolayer coating of humic acid (HA) was created on clay particles.
- Freshly emitted soil derived dust can be modelled by this method.
- Absorption EF, κ of complex refractive index, SSA, coating thickness were determined.
- Coating promotes the dispersion of particles and cause EF~6–7 in the UV–VIS range.
- Base soluble HA fraction of MD may have important role in global radiative transfer.

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ABSTRACT

Various optical properties of laboratory constructed clay minerals coated by humic acid were determined in this study. For the preparation of organo-clay complexes, an adsorption method was conducted in Ca^{2+} dominated aquaeous solutions, which provides the opportunity to generate solely internally mixed aerosol particles with complete surface covering. The wavelength dependent optical absorption and scattering coefficients of the syntetised organo-clay complexes and the single clay components were measured in-situ in aerosol phase, using multi-wavelength photoacoustic and scattering instruments. Other climate relevant optical properties such as mass absorption and scattering coefficients, absorption enhancement factor, the imaginary part of complex refractive index, single scattering albedo and coating thickness were also deduced from the measured data. The estimated thickness of humic acid coating was about 10–20 nm. Even such relatively thin shell substantially enhanced the measured absorption of the clay particles with an enhancement factor of about 3–7 in the visible-near ultraviolet range, while caused smaller changes in the mass scattering values. As a cumulative effect, the coating decreased the single scattering albedo of the clay particles; from 0.99 ± 0.04 to 0.93 ± 0.04 in case of illite and from 0.99 ± 0.04 to 0.90 ± 0.03 in case of kaolin at 525 nm. The HA coating slightly modified the shape, the particles became less excentric. We presented a new method capable of generating solely internally mixed particles. Applying this method we experimentally demonstrated the strong effect of a light absorbing coating on the optical properties of dust particle.

1. Introduction

As one of the major terrestrial sources of atmospheric aerosols, mineral dust (MD) plays an important role in the global and regional climate by scattering and absorbing solar radiation, known as the direct radiative effect (Sokolik and Toon, 1996). Mineral dust can also affect the global radiation balance indirectly through interaction with clouds acting as cloud nucleation nuclei (CCN) (Sassen, 2002). The net radiative effect of dust aerosol is still highly unclear (Claquin et al., 1998). It depends on several factors including particle composition, size, shape and mixing state, all of which can show extreme complexity. Atmospheric MD is a mixture of different minerals. Furthermore, MD can be internally mixed with other components such as surface active organic matter

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(Simoneit et al., 1980, Havers et al., 1998). The presence of organic films can impact the size, shape and optical properties of the particles (Falkovich et al., 2004, Laskina et al., 2013), thus can alter the radiative effect of the dust aerosol.

A class of organic molecules extracted from atmospheric aerosol particles and isolated from fog and cloud water has been termed *HUmic-LIke Substances (HULIS)* due to their physical and chemical similarities with terrestrial and aquatic humic substances (Graber and Rudich, 2006, and references therein). *Humic substances (HS)* are the largest constituents of soil organic matter (~60%) and are considered as a key component of the terrestrial ecosystem (Jones and Bryan, 1998). Humic and humic-like substances are probably the most abundant organic macromolecules that occur in nature (Pédrot et al., 2010).

One feature common to HULIS and HS is the high surface activity. Due to the acidic functional groups of these organics and the high reactivity of the surface of minerals, they form organo-mineral complexes (Johnston and Tombácz, 2002). Clay-sized organo-mineral complexes comprise 50–75% of soil organic matter in cold and temperate soils (Christensen 2001) while field studies have shown that they are also present in atmospheric mineral dust (Havers et al., 1998, Falkovich et al., 2004). Another common characteristic of them is that they contain a wide variety of molecular components, therefore they can only be defined on an operational basis. HS are subdivided into three operationally defined fractions: fulvic acid (water soluble at all pHs); humic acid (base soluble, acid (pH 1) insoluble); and humin (insoluble at all pHs). Like HS, HULIS can be categorized into two major groups based on their solubility, namely Water Soluble and Total (WS and T) HULIS.

Also differences between HULIS and HS, including smaller average molecular weight, lower aromatic moiety content, lower light absorption efficiency as well as others, are demonstrated (Graber and Rudich, 2006). Different sources and formation processes are proposed that may explain such differences. It is also possible that some of the differences stem from the extraction and isolation methods utilized. HULISws represents an important fraction (30–50%) of the Water Soluble Organic Carbon (WSOC) mass, therefore the vast majority of studies relate to HULISws. HULISws include the fraction compatible with fulvic acid of HS and many low molecular weight organic and inorganic species, and exclude the (base-soluble) fraction equivalent with the humic acid of HS. The characterization of the base-soluble (humic acid-equivalent) fraction of HULIS is highly desirable if we consider (1) The atmospheric organo-mineral complexes may originate from a primary source, namely from the soil itself. The major consituent of soil organic matter is humic acid. Therefore humic-acid equivalent fraction can be predicted to be present in atmospheric dust due to the soil dust emission (Dang and Hegg, 2014) (2) The humic acid equivalent fraction of aerosol tend to have higher light absorption potential in the UV–visible range than HULISws (Graber and Rudich, 2006).

However it is noteworthy that once it has been emitted into the atmosphere, atmospheric processes like physical-chemical aging alter the inherent properties of soil derived humic acid. In order to understand the effects of different aging processes, the original properties of the freshly emitted particles need to be obtained.

The recent increase in soil dust emission caused by increasing agricultural activity makes the study of organo-mineral particles a highly current issue (O'Sullivan et al., 2014). MD particles coated by HS have been investigated in several laboratory studies (Hatch et al., 2008, Laskina et al., 2013, Alexander et al., 2015). The generation of internally mixed particles was carried out using the condensation method. These studies mainly focused on the impact of HS on the cloud condensation nuclei (CCN) activity, the shape, the infrared and Raman spectra and the visible scattering properties. The effect of HS coating on the UV–visible light absorption properties of MD has not been studied experimentally yet.

The absorption properties of aerosol are important parameters both for remote sensing methods and for the investigation of the climatic change. Climate models require accurate knowledge of the aerosol complex refractive index (*Ri)* (Kaufman et al., 2002, Bellouin et al., 2005, Bates et al., 2006). The real (n) and imaginary part (k) of the complex refractive index are directly associated with light scattering and absorption, respectively. The n value is generally well constrained, less composition dependent than the imaginary part and only slightly varies with wavelength. In contrast, k widely varies widely *mineral* to *mineral* and has a strong wavelength dependency covering three orders of magnitude in the whole shortwave spectral region (McConnell et al., 2010, Otto et al., 2007, Utry et al., 2015).

Another problem arises from the fact that light absorption is one of the most difficult aerosol parameters to measure. Traditional in-situ filter-based instruments have been shown to have moderate uncertainties in case of strongly absorbing aerosol (Arnott et al., 2005, Bond et al., 1999, Virkkula 2005) and large uncertainties in case of weakly absorbing and/or mixed aerosol ensembles (Cappaet al. 2008, Lack et al., 2008). Photoacoustic spectroscopy, i.e. energy transfer from a modulated light source to an acoustic wave by optical absorption, is a unique method to measure the light absorption coefficient of aerosols directly and without the filter sampling artefacts (Roessler and Faxvog, 1980). The photoacoustic (PA) signal is linearly proportional to light absorption and it is completely insensitive to light scattering. The PA measurement technique has already proved its applicability under laboratory and field conditions in case of black carbon, brown carbon, HULIS (Cappa et al., 2008, Lack et al., 2012, Chakrabarty et al., 2011, Moosmüller et al., 2009, Ajtai et al. 2010a). Due to the insensitivity to scattering and its filter-free sampling, a PA system can be used to determine the absorption coefficient with high reliability even in case of weakly absorbing mineral dust components (e.g. clay minerals) (Moosmüller et al., 2012, Utry et al., 2015). Furthermore, this technique has recently been validated for the accurate measurement of the absorption enhancement caused by the particle coating (Lack et al., 2009).

To date, all laboratory studies of the absorption enhancement have focused solely on the role of non-absorbing coatings on a strongly absorbing core (mainly BC) (Lack et al., 2009). In that case, the shell acts as a lens and focuses more photons onto the core than how much would reach it otherwise (Fuller et al., 1999). The absorption enhancement has not been studied experimentally in the reverse case, when absorbing shells cover the mildly absorbing cores, like humic-clay complexes. This type of mixing is also presumed to lead to absorption enhancement, but instead of the lense effect, another phenomenon takes place. If the shell absorbs light, it is expected to partially or completely shield the core from photons (Lack and Cappa, 2010). In other words, the optical properties of the originally weakly absorbing core can be more or less masked by the absorbing coating.

As a follow up to our previous work, where the optical absorption properties of single mineral dust components were measured by photoacoustic method, we prepared and investigated two-component organo-clay complexes in this present study. Our focus here was on clay particles that fall in the accumulation (or clay-sized) mode. It is expected that illite and kaolin are particularly abundant in these small dust particles (Prospero, 1999), therefore we used these two types of clays. The organo-clay complexes were used here as simplified models of freshly emitted soil derived MD particles.

The organo-clay complexes were prepared by an adsorption