PhD Thesis

Investigation of the inherent and apparent optical properties of atmospheric aerosol and the untangling of the absorption spectrum using the photoacoustic method

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1. Introduction

One of the most significant scientific goals of our time is the reliable and precise determination of the anthropogenic climate modifying impacts. Despite the fact that the role of atmospheric aerosol is comparable to that of greenhouse gases regarding the shifts in the radiative balance of the Earth-atmosphere system, considering their inherent (freshly after emission) and the apparent (in the atmospheric equilibrium state) optical properties there is only limited and mostly uncertain data available. Our knowledge on absorption properties is incomplete and unprecise regarding both carbonaceous aerosol being dominant in number-concentration while having strong specific absorption and mineral dust being dominant in mass-concentration while having low specific absorption. This has major impact on the uncertainties regarding the estimations on the global climate forcing of aerosol. Atmospheric aerosol are in the focus of scientific interest not only because of their climatic impact but also their effect on air quality. Based on our current knowledge, however, atmospheric soot aerosol are negligible in mass-concentration, they are the largest contributors to the toxicity of particulate matter. The investigation of human health impacts and the apportionment of emitting sources is one of the biggest scientific challenges of our time. Latest researches have shown significant relationship between the chemical composition and the optical absorption spectra of aerosol, which can be measured in real time. This opens novel possibilities in the field of the real-time source apportionment of these aerosol.

The fact that, despite of its significance, we do not have sufficient information on the absorption response of atmospheric aerosol can be traced back to several reasons, like the lack of instrumentation, which is capable of providing reliable data with sufficient sensitivity, the difficulties of the laboratory modelling of aerosol, and also the error originating from the comparability of the data deriving from the application of different measurement techniques. It is a further problem that the physical-chemical properties of aerosol go through severe changes as a result of atmospheric processes, which significantly limit the quantitative analysis of the so called apparent optical response and chemical properties derived from ambient measurements carried out on aerosol in their equilibrium state.

As the majority of the scientific ‘vox populi’ agrees that photoacoustic spectroscopy is the most promising measurement technique for the investigation of the wavelength dependent absorption response of ambient aerosol, in the last few years lot of research groups and companies have been working on the development of aerosol instrumentation based on this method. The Photoacoustic Group of the University of Szeged has been researching aerosol optical absorption since 2003. I joined this research in 2010. During my doctoral work I have been focusing on the laboratory and field investigation of the absorption properties of climate relevant aerosol compounds.

2. Scientific goals

Based on the above mentioned statements I am setting my objective to precisely and accurately determine the inherent optical absorption properties of climate relevant aerosol compounds under controlled laboratory conditions in aerosol phase, and also to untangle and quantify of the relationship between the real-time determined, apparent absorption spectra and physical-chemical properties of ambient aerosol.

In order to reach the set objectives I have carried out the following tasks:

1. Determination of the inherent absorption spectra of artificially generated carbonaceous aerosol with great accuracy; the investigation of the possibility of the applicability of the studied spectral characteristics in the real-time source apportionment of particulate matter.

2. Determination of the aerosol-phase absorption spectra of ambient humic-like substance (HULIS) extracted from filter samples collected among ambient conditions; comparison of the measured data with literature values computed using various measurement techniques. Comparing the absorption spectra of HULIS aerosol determined by the photoacoustic method and that by UV-VIS spectroscopic measurements.

3. Aerosol phase investigation of the absorption properties of characteristic mineral dust components of particulate matter, the comparison of the measurement results with literature data computed from measurements carried out on bulk-phase and thin film samples.

4. Determination of the apparent absorption properties of real atmospheric aerosol during wintry urban field measurements; the studying of the daily fluctuation of the AAE.

5. The untangling and quantification of the relationships between the AAE values computed among field measurement conditions and the physical-chemical properties of the investigated aerosol.

3. The applied methods

3.1 Laboratory study: Aerosol generating methods

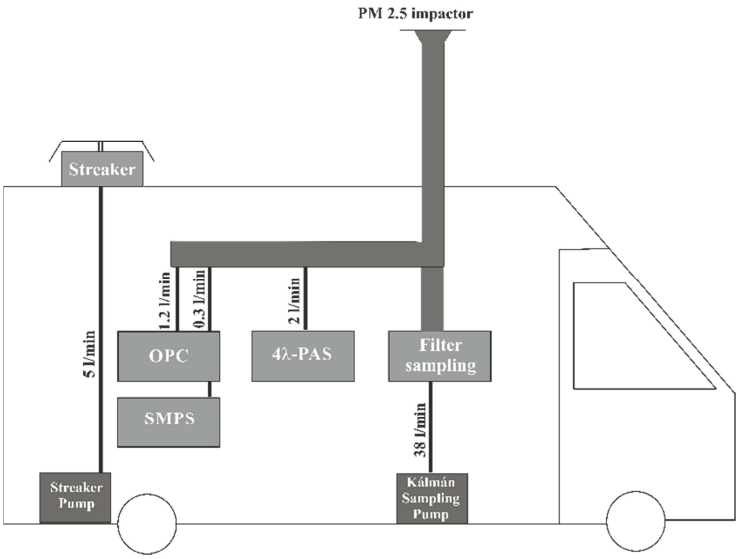
I carried out the generation of ***carbonaceous aerosol*** partly by methods, which model combustion, partly among real combustion conditions. For the prior I applied two commercially available soot generators (Miniature Combustion Aerosol Standard (mini-CAST) and Palas GFG 1000), and also a method based on laser ablation, which has been developed by the co-operation of the Photoacoustic Research Group and the Ablation Research Group of the University of Szeged Faculty of Science and Informatics Department of Optics and Quantum Electronics. The investigation of the mini-CAST aerosol was carried out at the Karlsruhe Institute of Technology, Institute of Meteorology und Climate Research. I investigated real combustion aerosol (diesel and wood stove aerosol) at the Paul Scherrer Institute in Switzerland.

I investigated ***atmospheric humic like substance (HULIS)*** in aerosol phase by atomizing the acetonitrile solution extracted of the samples collected among real ambient conditions.

The re-dispersing of ***mineral dust components*** was carried out by an automatized vibration unit blown by synthetic air.

3.2. Field study: sampling

I have carried out field measurements during January 12-26, 2011, in the city center of Szeged next to the measurement station of the Csongrád County Government Office in an air- and humidity-conditioned, specially designed professional mobile measurement platform. The standardized PM2.5 sampling unit was placed on the top of the platform 5 m from the ground. All instruments and filter sampling for chemical analysis took sample from this impactor (1st graph).



1. graph. Schematic setup of the mobile platform

3.3. Applied instruments

I have described the absorption properties with optical absorption coefficient (OAC), mass specific absorption coefficient (MAC), Aerosol Angström Exponent used for the description of the wavelength dependency of the spectrum, and in case of mineral dust complex refractive index.

- Measurement of OAC at 266, 355, 532 and 1064 nm was carried out by the Four Wavelength Photoacoustic System (4-λ PAS),
- Measurement of mass was carried out by a Tapered Element Oscillating Microbalance (TEOM)
- I used the Scanning Mobility Particle Sizer (SMPS) and the Optical Particle Sizer (OPC) for the determination of size distribution
- Complex refractive indices was computed by the inverse Mie-iteration method using the measured size distribution data and refractive index data from the literature

4. Summary

The optical absorption spectrum is the only physical parameter that can be measured in real-time and which can carry information considering climatic impact, emitting sources and physiological effects. Thus, the investigation of optical absorption properties is one of the most timely and significant scientific goals of our time. Whereas we already acquire satisfying information on the scattering properties of atmospheric aerosol, our knowledge regarding its absorbing components is quite limited and imperfect. During my doctoral work I have been focusing on the precise determination and the thorough investigation of the explanation of the absorption spectra by the means of either laboratory studying artificially generated or re-dispersed real aerosol samples, and also real-time measurement of atmospheric aerosol.

Abstract of the PhD dissertation. Phrasing the new results.

I. I have determined the Absorption Angström Exponent (AAE) values of artificially generated carbon aerosol during laboratory measurements. The AAE values determined at all operating wavelengths of the Four Wavelength Photoacoustic Spectrometer were computed as 1.04±0.11, 1.25±0.14 and 1.80±0.20 in case of the soot generating methods modelling combustion processes like laser-ablation, mini-CAST and Palas GFG 1000. During the laboratory photoacoustic investigation of real combustion processes, the aerosol emitted by a diesel vehicle and wood combustion the AAE values were determined as 1.30±0.14 és 1.95±0.21. Measurements carried out at multiple wavelengths have proved that the different aerosol samples can be well distinguished from each other based on their AAE values. Furthermore their AAE values show wavelength dependence with the only exception of laser-ablation. According to the laboratory photoacoustic measurements I have concluded that the different combustion-based soot generating methods well model real combustion processes considering optical response. From this point of view the mini-CAST generator which is based on propane burning in a diffusion flame is capable of modelling diesel emission with the setup described in my dissertation. However, Palas GFG 100, which is based on spark discharge on graphite electrodes, well models the mixed aerosol emission most characteristic of winter urban areas.

With the means of laser ablation black carbon (BC) particles can be generated. While comparing the results of the photoacoustic laboratory measurements with the data gained from field measurements I have concluded that that the AAE values computed during laboratory measurements are in good agreement with that of field measurements among such time periods (rush hour or non-traffic) when only one of the emitting sources (traffic or wood burning) is dominant. According to this I took cognizance of the fact that the effect of atmospheric processes was negligible in case of my field measurements. . **[1,12,16]**

II. During the laboratory investigation of atmospheric humic like substances (HULIS) isolated from filters collected during an autumn measurement campaign I have concluded that HULIS has negligible mass specific optical absorption coefficient values (MAC) in the visible range ($2.97*10^{-2}\pm2.67*10^{-3}m^2/g$ @532 nm), however towards shorter wavelengths it steadily increases. The UV range MAC value of HULIS is comparable ($4.925\pm0.5418m^2/g$ @266 nm) to that of the main absorbing component of atmospheric aerosol, black carbon (BC). Moreover I have determined the wavelength dependency of the MAC values of HULIS. The AAE values of the HULIS sample were the following on the specific wavelength ranges of 1064-532nm, 532-355nm and 355-266nm: 2.23±0.23, 5.87±0.49 and 9.48±0.76. The result is tune with values determined during liquid-state measurements available in literature, however I was the first to determine these values during aerosol-phase measurements.

While comparing my results with data determined in case of HULIS samples collected at the same site during the summer, I came to the conclusion that the absorption spectra of HULIS determined in aerosol-phase (just as that in liquid-phase) can be an indicator of the emitting sources and/or the processes of formation. I have compared the results of my photoacoustic aerosol-phase measurements with liquid-phase measurement, as a result of which, I have experimentally confirmed that the optical properties (MAC and AAE) of HULIS measured in liquid-phase can be extended to particles in case the morphology of the particles can be estimated by spherical shape and the size of particles is small compared to the wavelength of excitation. **[2]**

III. By the means of photoacoustic measurements I have determined the mass specific optical absorption coefficient (MAC) values of soil-originating mineral dust (MD) components like clay minerals (illite, kaolin and bentonite), oxides (quartz, hematite and rutile) and carbonates (limestone). I have derived refractive index (k) values from the computed data. The investigated samples have remarkable optical absorption mostly in the ultraviolet range. In this range hematite and rutile have the highest k values (1.26±0.31 és 1.1±0.28 @266 nm). Compared with the values of carbon containing aerosol the imaginary parts of the complex refractive indices are negligible to BC, however comparable to the k values of BrC. Considering k values the oxides are followed by clay mineral compounds (illite, kaolin and bentonite):$1.1*10^{-2}\pm2.8*10^{-3}$, $4.2*10^{-2}\pm1.05*10^{-2}$ and $3.1*10^{-2}\pm7.75*10^{-3}$ @266 nm, while quartz and limestone have the lowest optical absorption values $6.5*10^{-3}\pm1.63*10^{-3}$ and $3.0*10^{-3}\pm7.5*10^{-4}$ @266 nm). The k values of these components are two orders of magnitude lower than that of carbon aerosol (BC, BrC).

By the means of measurements I have demonstrated that the photoacoustic method, thanks to its advantageous characteristics (online, in-situ, insensitive-to-scattering and zero-background measurement technique), can be successfully applied for the precise and accurate aerosol-phase determination of the absorption properties of mineral dust components with low optical absorption coefficients. I have experimentally demonstrated that taking particle losses into consideration enhances the reliability of the measurement results. I have compared the determined values with data from the literature. The basis of the compresence were the literature values adapted for my specific measurement conditions. The literature values have been determined by off-line methods in bulk-phase in case of different sample preparation, while my data have been determined in aerosol-phase among standardized conditions. I have confirmed that this method can be applied in case of the bulk-particle transformation of optical properties, if the same sample is used, previously prepared under the same standardized conditions. The results can be used during the modelling of the global climate forcing of mineral dust. **[3, 5,9,13]**

IV. During field measurements carried out in Szeged I have demonstrated that the photoacoustically measured AAE values have a daily fluctuation, which can be explained by the daily fluctuation of traffic emission activity. Moreover I have shown and quantified the wavelength dependency of the AAE values in the complete measurement range of the photoacoustic instrument. I have been measuring the other characteristic parameters of atmospheric aerosol simultaneously, like size distribution and chemical properties (levoglucosan-, carbon-content). I have set forth that the ratios computed from the measured parameters (N_{100}/N_{20}, LG/TC, $OC_{wood\ burning}/EC_{traffic}$) are more suitable to monitor the relative activity of the emitting sources than the measured parameters themselves. **[5, 10, 14]**

V. I have revealed the relationships between the AAE values derived from the absorption determined by the photoacoustic method and the source-specific physical and chemical properties of atmospheric aerosol. By revealing the strong correlations between the AAE values and ratio of organic soot originating from wood burning and inorganic soot originating from traffic activity I have verified that the value of AAE is mostly determined by the relative changes in the activity of the emitting sources. I have further confirmed that the strength of the relationship of the different parameters strongly depend on the applied wavelengths. I have shown the strongest correlation in the ultraviolet range. The correlation factors of the relation between the AAE@355-266nm and the N_{100}/N_{20}; LG/TC; and $OC_{wood\ burning}/EC_{traffic}$ ratios were computed to be R=0.93; R=0.95; 0.96. By using the Aethalometer model I have concluded and demonstrated that photoacoustic measurements carried out on multiple wavelengths including the UV range create the opportunity of the selective, real-time identification of the emitting sources. **[5, 10, 14]**

Referred articles connected to the new measurement result

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