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Accuracy assessment of aerosol source apportionment by dual wavelength photoacoustic measurements

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ABSTRACT

Aerosol source apportionment is a major challenge for air quality monitoring. Due to the frequently observed correlation between the chemical properties of aerosol particles and the wavelength dependence of their optical absorption coefficient, the photoacoustic (PA) method (similarly to alternative optical absorption measurement techniques) offers the unique possibility of real time source apportionment under certain circumstances. However, so far, the selection of lasers into a multi-wavelength PA system for source apportionment was based only on rule of thumb type estimations (like "one should use the highest available light powers with the widest possible wavelength separation"). Here we introduce a simulation method to estimate the accuracy of source apportionment and to be used for the optimised selection of the light sources of a dual wavelength PA system in cases, when light absorbing carbonaceous aerosol (LAC) originates from two distinct sources and dominates the atmospheric aerosol load. The method has two phases and it can be applied either on actual measurement results or on simulated datasets. In the first "calibration" phase the parameters of a non-linear calibration curve are determined, which describes the correlation between the ratio of optical absorption coefficients (*OAC*s) measured photoacoustically at two wavelengths and the ratio of the source specific segregated mass concentrations (mass concentration ratio, *MCR*) measured by an independent calibration method. During the second "measurement" phase these calibration parameters are used to estimate the *MCRs* solely from the photoacoustically measured *OAC* ratios. The relative uncertainty of this estimation is used to grade dual wavelength PA systems. Executions of this simulation on different *MCR*, *OAC* datasets have proved that with a fairly simple PA system (which consists of a 405 and a 1064 nm diode laser having modulated light power of 150 and 300 mW, respectively) *MCR* determination is feasible with at least 10% relative accuracy whenever the mass concentration of LAC exceeds 1 $\mu g/m^3$.

1. Introduction

During serious pollution events, atmospheric aerosol is quite often an external mixture of aerosol components originating from various sources. An important task of air quality monitoring is the development of real time aerosol source apportionment methods for specifying the proportional contribution of distinct sources to air pollution. These methods typically utilise the differences in the

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physical and/or chemical properties of the individual aerosol components, however, the routine application of majority of them such as the aerosol mass spectrometer (Kleinman et al., 2007; Lack, Lovejoy, Baynard, Pettersson, & Ravishankara, 2006) or the semi continuous EC/OC ratio measurement (Chow, Watson, Crow, Lowenthal, & Merrifield, 2001) are limited by their high prices and laboratory costs.

For light absorbing atmospheric aerosol components including many of those with harmful health effects, there is a relationship between the wavelength dependency of optical absorption and the chemical composition (Ajtai et al., 2011; Chakrabarty et al., 2010; Favez et al., 2010; Flowers et al., 2010; Harrison et al., 2013; Lewis, Arnott, Moosmüller, & Wold, 2008; Massabò et al., 2015; Moosmüller, Chakrabarty, Ehlers, & Arnott, 2011; Sandradewi et al., 2008). Furthermore in case of light absorbing carbonaceous aerosol (LAC) the wavelength dependency of both the segregated optical absorption coefficient (*OAC*) and the segregated mass specific optical absorption coefficient (σ) of a specific aerosol component can be accurately quantified by the so called Absorption Angström Exponent (*AAE*) (Ångström, 1929):

$$\frac{OAC_{\lambda_1}}{OAC_{\lambda_2}} = \frac{\sigma_{\lambda_1}}{\sigma_{\lambda_2}} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-AAE} \tag{1}$$

where λ_1 and λ_2 are the wavelengths of the optical absorption measurement.

During a recent field campaign under urban wintry conditions (Utry et al., 2014) *OAC*s were measured by a four-wavelength (i.e. 266, 355, 532 and 1064 nm) photoacoustic (PA) system and depending on the selected wavelength pairs various degrees of correlations were found between the *OAC* ratios (i.e. practically the *AAE* values) and the ratio of the source specific segregated mass concentrations (mass concentration ratio, *MCR*). The fact that the strength of the correlation depends on the selected PA measurement wavelengths can be partially attributed to the degree of laser wavelength separation and also to the signal-to-noise levels at each of the measurement wavelengths. Indeed, while the noise level of the PA measurement is wavelength independent, the PA signal generated by a given optical absorption coefficient is linearly proportional to the light power available at that wavelength. Furthermore as it is also confirmed by earlier studies (Bond, Covert, Kramlich, Larson, & Charlson, 2002; Filep et al., 2013; Rissler et al., 2006; Schneider et al., 2006; Wehner & Wiedensohler, 2003), *MCR* determination can be based not only on off-line Chemical Analysis of Filter collected aerosol Samples (CAFS) but also on quasi real time Number Size Distribution Measurement (NSDM). Since an NSDM cycle can be completed within 15 min while 12 h long filter sampling is typically required in order to collect sufficient amount of aerosol samples for reliable CAFS, synchronising the averaging time of the PA measurement and correlating the photoacoustically measured *OAC* values with the results of NSDM rather than CAFS has clear advantages:

- From the point of view of the PA system's stability 15 min is approximately an optimum duration of PA signal averaging to achieve maximum signal to noise ratio as it follows from Allan-variance analysis of various PA systems (unpublished results).
- With a state-of-the-art PA system and with a 15 min averaging time, the repeatability of the *OAC* measurement is in the range of 0.1 Mm^{-1}, i.e. during a typical urban measurement *OAC* is measured with a relative uncertainty of at least a few percent,
- According to our experience, in most of the cases neither the meteorological conditions nor the *MCR* nor the optical properties of the atmospheric aerosol change during a 15 min measurement period,
- When NSDM is used as a reference method, a short measurement campaign is sufficient to collect the necessary amount of measurement points necessary for determining a reliable correlation between the size distribution data and the *OAC* values (e.g. during a 2-week campaign - in principle - more than 1000 data points can be collected).

In a recent publication (Ajtai et al., 2015) correlations between *OAC*s and *MCR*s were further analysed and a non-linear calibration curve was introduced that quantifies the correlation between the *OAC* ratios and *MCR* values. The current simulation is based on these results.

Despite of the growing number of publications on multi-wavelength PA measurements under field conditions, to the best of the authors' knowledge the influence of wavelength selection on the accuracy of source apportionment has not been investigated systematically yet. The presented simulation method can be used to predict and compare the source apportionment accuracy of dual wavelength PA systems.

2. The simulation method

The proposed simulation method mimics a field campaign; has a calibration and a measurement phase (Fig. 1) and is executed under the following premises:

- The "measured" atmospheric aerosol load is dominated by two LAC components mixed externally (i.e. no internal mixing or chemical interaction between the components occur and consequently the total mass concentration of LAC is the sum of the mass concentration of these two components). This is a typical case e.g. for urban measurements under wintry conditions when atmospheric aerosol load is dominated by fossil fuel and wood burning aerosols,
- Each of the two aerosol components has well-defined and markedly different optical absorption parameters (i.e. mass specific optical absorption coefficients at a reference wavelength and *AAE* values) which do not vary in time,
- It is assumed that during the "calibration" phase *MCR* is determined either by NSDM or CAFS (actually in the following the PA noise level is assumed to correspond to a 15-min averaging time and consequently the use of NSDM is assumed, but one could