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Optical properties and simple forcing efficiency of the organic aerosols and black carbon emitted by residential wood burning in rural central Europe

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1. Principles of instrument operation

We provide a general description of the Aethalometer AE33 compensation algorithm and operation principles of the total carbon analyzer (TCA08), mobility particle size spectrometers (MPSSs), and high-volume PM sampler used in the field measurements. For more specifications, the reader is referred to complementary studies and documentation from the instrument manufacturers (Aerosol Magee Scientific, 2018, 2022; Drinovec et al., 2015; Wiedensohler, 1988).

1.1 Aethalometer AE33 algorithm

The calculations in the Aethalometer AE33 transform the change of the attenuation ($\Delta ATN_1(\lambda)$) into absorption coefficient ($b_{abs}(\lambda)^{non\ comp.}$) using a correction factor for the multiple scattering of light (*C*, filter material dependent, Eq. S1) and additional variables: the spot area (*s*), the airflow through spot 1 (F_1), and a leakage factor (ζ). According to the manufacturer, the value of *C* depends on the filter material (Aerosol Magee Scientific, 2018). However, various studies indicate that the aerosol type affects light scattering in filter-based absorption photometers. In a recent study, Drinovec et al. (2022) compared the AE33 attenuation to a newly developed Photothermal Aerosol Absorption Monitor (PTAAM), which measures at two wavelengths (532 and 1064 nm). The PTAAM was designed to eliminate light scattering artifacts during aerosol light absorption measurements. This characteristic favors the evaluation of artifacts in filter-based absorption photometers like the AE33. During field measurements, the PTAAM-AE33 comparison resulted in *C* factors of 3.28 (532 nm) and 2.57 (1064 nm); in laboratory analyses, *C* ranged between ~2.5 to ~5.5 depending on the volume size of soot particles (100 – 500 nm). In a field measurement campaign in Melpitz, Germany, collocated measurements of light absorption coefficients by AE33 and Multi-Angle Absorption Photometer (MAAP) showed that the light absorption estimated from the AE33 was 20 to 50% above the MAAP absorption at 637 nm (interpolated for AE33). The overestimation has resulted in median AE33-MAAP scaling factors of 2.25 (ranging between 1.74 (P.10) and 2.97 (P.90)) at the Melpitz research station and 1.87 (ranging between 1.15 (P.10) and 2.83 (P.90)) at Melpitz village station. The dual-spot system in the AE33 serves to calculate correction factor *k* to compensate for the filter-loading effect produced by the shadowing of particles accumulated on the filter. The absorption is loading-compensated ($b_{abs}(\lambda)^{comp.}$, Eq. S2) and used together with predetermined values of BC mass absorption cross sections ($MAC(\lambda)$) to estimate the mass concentrations of equivalent black carbon at multiple wavelengths ($eBC(\lambda)$, Eq. S3) (Drinovec et al., 2015).

$$b_{abs}(\lambda)^{non\ comp.} = \frac{s*(\Delta ATN_1(\lambda)/100)}{F_1*(1-\zeta)*C*\Delta t}. \quad \text{(S1)}$$

$$b_{abs}(\lambda)^{comp.} = \frac{b_{abs}(\lambda)^{non\ comp.}}{(1-k(\lambda)*ATN_1(\lambda))}. \quad \text{(S2)}$$

$$eBC(\lambda) = \frac{b_{abs}(\lambda)^{comp.}}{MAC(\lambda)}. \quad \text{(S3)}$$

1.2 Total carbon analyzer (TCA08)

Using an online thermal method, the total carbon analyzer TCA08 estimates total carbon (TC) concentrations in aerosol particles. The instrument integrates two analytical chambers that sequentially alternate between sample collection and sample analysis, i.e., while one chamber collects a new aerosol sample (sampling time ranging

from 20 min to 24 h), the second chamber performs the thermal analysis of the sample previously collected (17 min for analysis). The aerosols are deposited on a quartz-fiber filter, forming one sample-laden spot. Once the sample-collection period finishes, the filter is heated almost instantaneously up to 940 °C to combust all the carbonaceous compounds (organic and elemental carbon). An infrared sensor measures the concentration of CO_2 present in the carrier gas (filtered ambient air) before ($CO_2^{ambient}$) and after (CO_2^{signal}) the combustion step. Subsequently, both concentrations are integrated over the heating time, together with the CO_2 from the blank filter (CO_2^{blank}) to estimate the total carbon concentration of the sample (Rigler et al., 2020).

1.3 Mobility Particle Size Spectrometer (MPSS)

The MPSS determines the particle number size distribution of atmospheric aerosol particles. The instrument contains three consecutive main components: a bipolar diffusion charger (neutralizer), a differential mobility analyzer (DMA), and a condensation particle counter (CPC). At first, the particles are led to a bipolar charge equilibrium through a radioactive source in the bipolar charger. The charged aerosols pass to the DMA, which consists of a cylindrical capacitor where the particles are separated according to their electrical mobility (Z_p). The electrical mobility depends on the particle charge, diameter, the corresponding Cunningham slip correction factor, and the gas viscosity. Since the shape and dimensions of the DMA are well known, it is possible to estimate and administer specific voltages to the electrodes to transport the particles with definite electrical mobilities from the entrance of the DMA to the annular slit in the center of the capacitor. The distribution of Z_p is determined by scanning the voltage over the entire range of electrical particle mobility of interest. Lastly, the CPC counts the number concentration of particles with specific Z_p. Small particles (diameter < ~100 nm) need a size enlargement to be optically detected in the CPC; in the butanol-type, this is achieved by heating and saturation of the aerosol particles with butanol vapor. Next, in a cooling section, the butanol condenses onto the particles and forms bigger droplets (~10 μm). The droplets are brought to a focusing nozzle, and an optical laser counts them individually (Wiedensohler et al., 2012, 2018). In the water-type CPC, the aerosols are preconditioned in a humid section of the tube, saturating the sample. Next, a heated section of the tube increases the water vapor pressure, supersaturating the sample and starting condensation on the aerosol particles. Finally, a cooling section allows complete condensation and growth (TSI Inc, 2023).

1.4 Digitel sampler (DHA-80)

In the high-volume sampler Digitel DHA-80, the aerosol particles are continuously collected through a PM_{10} inlet and deposited over a circular filter collocated in the instrument flow chamber. The upper section of the flow chamber functions as a diffuser with a regular cross-section to guarantee uniform loading of the filters. During each sampling, the instrument measures the air flow transported through the filter (ranging from 100 to 1000 L min^{-1}) and records the total sampling time. The pressure drop across the filter is controlled, as well as the internal air pressure and temperature. The DHA-80 operates according to the standard EN12341 “ambient air – gravimetric method for determining the PM_{10} or $PM_{2.5}$ mass concentration of suspended particulate matter” (Digitel Enviro-Sense, 2021).

2. Comparison of the calculated OA mass with OC mass concentrations (OA/OC ratios)

The OA/OC ratios were calculated as the slope from the orthogonal fit between OA_{MPSS} and OC_{TCA} (Fig. S1a), and OA_{MPSS} and $OC_{filters}$ (Fig. S1b). The total carbon measured by the TCA was determined following the procedure from Rigler et al. (2020, Eq. S4).

$$[OC]_{TCA} = ([TC]_{TCA} - [eBC]_{AE33}) \quad \text{(S4)}$$

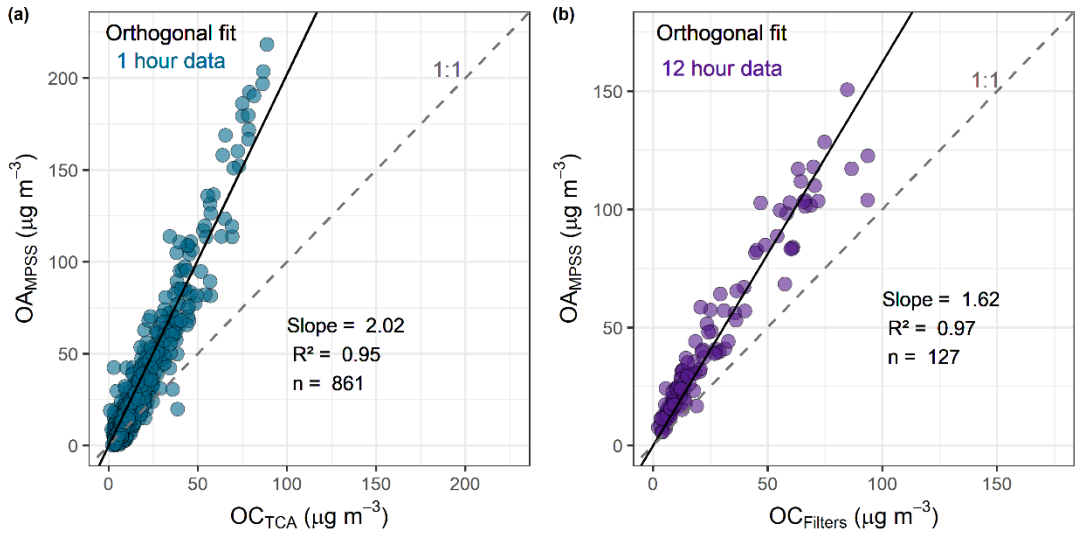

Figure S1. Scatterplots and orthogonal regressions (solid black lines) for the comparison of (a) OA_{MPSS} and OC_{TCA}, and (b) OA_{MPSS} and $OC_{filters}$. The figures include the regression slope, the coefficient of determination (R^2), and the number of observations (n). The intercepts were forced through zero.

3. Mie modeling

Below are the equations used to estimate the particle volumetric fractions and shell refractive index via mixing rule.

Particle mass:

$$M_{Total\ particle} = M_{OC} + M_{InA} + M_{BC}, \quad \text{(S5)}$$

Particle volume fractions:

$$V_{f,OC} = \frac{\frac{M_{OC}}{\rho_{OA}}}{\frac{M_{Total\ particle}}{\rho_{Total\ particle}}}, \quad \text{(S6)}$$

$$V_{f,InA} = \frac{\frac{M_{InA}}{\rho_{InA}}}{\frac{M_{Total\ particle}}{\rho_{Total\ particle}}}, \quad \text{(S7)}$$

$$V_{f,BC} = \frac{\frac{M_{BC}}{\rho_{BC}}}{\frac{M_{Total\ particle}}{\rho_{Total\ particle}}}, \quad \text{(S8)}$$

Shell refractive index:

$$k_{Shell} = \frac{(k_{OA} * V_{f,OC}) + (k_{InA} * V_{f,InA})}{(V_{f,OC} + V_{f,InA})}, \quad \text{(S9)}$$

Where M_{OC}, M_{InA}, and M_{BC} are the mass concentrations , $V_{f,OC}$, $V_{f,InA}$, and $V_{f,BC}$ are the volumetric fractions, and ρ_{OA}, ρ_{InA}, and ρ_{OC} are the aerosol densities of organic carbon, inorganic aerosols, and black carbon,

respectively; k_{Shell} is the particle shell refractive index; $M_{Total\ particle}$ and $\rho_{Total\ particle}$ are the total particle mass and density.

Table S1. Complex refractive indexes of black carbon, organic aerosols, and inorganic aerosols used in Mie modeling

λ (nm)	BC		Ref	OA		Ref	InA		Ref
	n	k		n	k		n	k	
370	1.92	0.67	Kim et al., 2015	1.59	0.11	Kim et al., 2015	1.4	<0.01	Shamjad et al., 2012
470	1.92	0.67		1.47	0.11				
520	1.96	0.65		1.47	0.04				
590	1.96	0.65		1.47	0.04				
660	2	0.63		1.47	0				
880	2	0.63		1.47	0				

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