Supporting information for:

Production of particulate brown carbon during atmospheric aging of wood-burning emissions

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Wall loss correction

Solving the equations in Section 3.1 requires the determination of the time-dependent concentrations of the different absorbing species, which may be governed by their photochemical production or decay as well as by diffusion, electrostatic and gravitational losses to the walls. Assuming all particles are equally lost to the walls, an inert, non-volatile species, *X*, follows a first order decay:

$$X(t) = X(t_0) \cdot \exp(\tau^{-1}(t - t_0))$$
(S1)

Here, t and t_0 denote the time of interest and reference time, respectively. The time constant τ is the lifetime of X with respect to particle wall losses. We determined τ by fitting $b_{abs}(t, 880nm)$ to Equation S1. Only the last period of each experiment was chosen for fitting, when secondary organic aerosol production rates are smaller. On average, τ equals 3.9 ± 0.8 hours for our chamber. The wall loss corrected absorption coefficient, $b_{abs}^{WLC}(t, 880 nm)$, varied less than 8% throughout the experiment, with higher values in the first period of

measurements. Therefore we conclude that the first order decay is an appropriate approach for the wall loss correction of inert particulate properties. We ascribe the residual variations of $b_{abs}^{WLC}(t, 880 nm)$ to a combination of uncertainties, including the aethalometer compensation parameter and possible small changes of MAC_{BC}(880nm) with aging.

For the extrapolation of our data to ambient environments we computed the average SOA mass formed as a function of OH exposure during the different experiments. This step requires the correction of OA mass for particle wall losses, which has been achieved by assuming two cases: (1) condensable oxidized gases do not interact with wall-deposited particles and (2) condensable oxidized gases condense at similar rates onto the suspended and wall-deposited particles (Pierce et al., 2008). We did not consider the deposition of oxidized vapors onto the clean Teflon walls, which would require knowledge of the saturation vapor pressures of the compounds, the condensed phase bulk properties and the vapor-wall equilibration rates. It is likely that the large particle condensational sinks utilized here (with a particle surface area concentration of several hundreds of μm^2 cm⁻³), outcompeted vapor deposition onto the walls. Therefore, we consider the vapor deposition to the clean Teflon wall to be of a minor importance compared to burn-to-burn variability and other experimental uncertainties.

Solving the mass balance equations of the suspended organic aerosol, $[OA_{sus}(t)]$, and the organic aerosol on the walls yields the expressions in Equations (S2) and (S3), when considering scenario (1) and (2), respectively:

$$\begin{bmatrix} M_{OA,wlc,1}(t) \end{bmatrix} = \begin{bmatrix} M_{OA,sus}(t) \end{bmatrix}_{0}^{t} \begin{bmatrix} \tau^{-1} \end{bmatrix} \begin{bmatrix} M_{OA,sus}(t) \end{bmatrix} dt$$
(S2)

$$\left[M_{OA,wlc,2}(t)\right] = \left[M_{OA,sus}(t)\right]^* \exp(\tau^{-1}t)$$
(S3)

Here, $[M_{OA,wlc}(t)]$ is the wall-loss-corrected OA concentration. The results presented in Figure 8 in the manuscript are the average time-series of all experiments considering both scenarios, and associated ranges entail both the experiment-to-experiment variability and the uncertainties related to wall loss corrections.

Supplementary figures



Figure S1: Absorption coefficients of fresh and aged emissions measured at 6 different wavelengths (i.e. 370 - 880 nm) using the aethalometer. The OA is measured using an AMS. Dotted lines are primary-subtracted OA (SOA) and absorption coefficient ($b_{absSOA}(370$ nm)) . The black boxes mark the times where the primary, slightly aged (Aged1, OH exposure ~1x10⁷molecules cm⁻³ h) and heavily aged filters (Aged2, OH exposure ~ 4x10⁷ molecules cm⁻³ h) were collected.



Figure S2: (a) Probability density function (PDF) comparing the MAC values determined by normalizing MWAA absorption measurements of offline primary (filter A), slightly aged (filter B: Aged1) and aged filter (filter C: Aged2) samples to EC (EUSAAR2) measurements of the same samples (bold line). A literature value for pure BC is also shown (Bond et al., 2006) (dashed blue line). (b) PDF comparing aethalometer attenutation measurements at 880 nm and MWAA absorption measurements at 850 nm to retrieve the aethalometer *C* value.



Figure S3: Wall-loss-corrected aethalometer absorption coefficient at 880 nm normalized to start-of-experiment absorption. The lack of any trend in this plot illustrates that the wall loss correction is appropriate and that only a negligible absorption increase occurs due to additional lensing by SOA.



Figure S4: SMPS measurements (top), lognormal fits (middle; f_{POA} =0.51), and fit residuals (bottom) of the size distribution of biomass burning organic aerosol during a typical aging experiment.



Figure S5: Absorption coefficients of fresh wood burning emissions measured using an aethalometer normalized to the eBC mass as a function of wavelength. In the legend each color denotes the $\alpha_{BC+POA}(370nm,880nm)$ for an individual experiment. The dashed lines mark the literature range of α values obtained for primary biomass burning emissions.



Figure S6: Relationship of $\alpha_{BC+POA+SOA}(370nm, 880nm)$ to f_{OA} for seven wavelengths, with symbol sizes indicating OH exposure.



Figure S7: Analysis of the fitting errors of $\alpha(\lambda, 880\text{nm})$ of primary emissions as a function of f_{0A} . Panel A shows the α residual as a probability density function. Panel B is an image plot of the $\alpha(\lambda, 880\text{nm})$ uncertainty as a function of f_{0A} estimated based on error propagation, using Equation 13 and assuming MAC_{POA}(λ), MAC_{BC}(λ) and f_{0A} to be independent variables (assuming negligible covariance between these quantities). The image plot in panel B shows that at short wavelengths and low fractions of OA, the estimated error on α is less than 0.1. However, with increasing OA fraction and at longer wavelength the uncertainty increases. It should be noted that this increasing uncertainty is not greater than 0.5 even at OA fractions of 0.99, corresponding to an α of ~ 2.2.



Figure S8: Power law fits through the average MAC of BC, POA and SOA calculated from Aethalometer measurements plotted as a function of wavelength. Note that $MAC_{SOA}(880nm)$ and $MAC_{POA}(880nm)$ are zero by definition.



Figure S9: Probability distributions of α and ln(A) describing the optical properties of BC, POA and SOA. Parameters for representing these distributions as a bivariate normal joint density function are shown in Table S1.

Parameters for representing these unstandards as a structure of $f(\mathbf{X}) = \frac{|\Sigma|^{-\frac{1}{2}}}{2\pi} \exp\left(-\frac{1}{2}(\mathbf{X}-\mu)^{\mathrm{T}}\Sigma^{-1}(\mathbf{X}-\mu)\right)$, where $\mu = \begin{pmatrix} \mu_{\alpha} \\ \mu_{\ln(A)} \end{pmatrix}$; represents the average α and $\ln(A)$ values and $\Sigma = \begin{pmatrix} \sigma_{\alpha}^2 & \rho \sigma_{\alpha} \sigma_{\ln(A)} \\ \rho \sigma_{\alpha} \sigma_{\ln(A)} & \sigma_{\ln(A)}^2 \end{pmatrix}$ is the covariance matrix. As α and $\ln(A)$ are determined from fitting the MAC vs. λ , their covariance is high. Therefore the selection of these parameters to represent the MAC profiles of BC, POA and SOA, should not be done independently but by using the probability density function above and the parameters in Table S1.

	BC	РОА	SOA
μ	$\binom{1.2}{10.0}$	$\binom{4.6}{29.2}$	$\binom{5.6}{33.3}$
Σ	$\begin{pmatrix} 0.09 & 0.054 \\ 0.054 & 0.61 \end{pmatrix}$	$\begin{pmatrix} 0.64 & 2.6 \\ 2.6 & 4.1 \end{pmatrix}$	$\begin{pmatrix} 1.36 & 11.4 \\ 11.4 & 8.35 \end{pmatrix}$

Table S1: Parameters for normal joint density function.



Figure S10: MAC_{SOA} as a function of OH exposure color coded according to the wavelength.



Figure S11: Absorbance measurements from UV-visible analysis of water extracted filters from several wood burning experiments showing very good repeatability (consistent within 10%).



Figure S12: MAC_{bulk} (bulk absorbance of extracts normalized to AMS-measured OA) of primary, slightly aged (Aged1, OH exposure ~ $1x10^7$ molecules cm⁻³ h) and aged emissions (Aged2, OH exposure ~ $4x10^7$ molecules cm⁻³ h) for (A) water and (B) methanol extracts. The bold lines indicate the medians, and the dashed lines mark the 25th and 75th percentiles. At 450–500 nm, the methanol-extract absorption shows a constant absorptivity feature which was not present before aging, suggesting that the absorbing species may be partially-oxidized (partially-solubilized) primary OA, or reflect light-absorbing SOA.



Figure S13: MAC_{OA} at $\lambda = 370$ nm calculated from aethalometer measurements vs. k_{OA} at $\lambda = 370$ nm from the UV-visible measurements of the methanol extracts.



Figure S14. Similar to Figure 7 in the main text, but plotted against f_{0A} for comparison to the other figures in this work.

References

Pierce, J. R., Engelhart, G. J., Hildebrandt, L., Weitkamp, E. A., Pathak, R. K., Donahue, N. M., Robinson, A. L., Adams, P. J. and Pandis, S. N.: Constraining particle evolution from wall losses, coagulation, and condensation-evaporation in smog-chamber experiments: optimal estimation based on size distribution measurements, Aerosol Sci. Technol., 42, 1001–1015, doi:10.1080/02786820802389251, 2008.

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