Supplement of

Wildfire plume ageing in the Photochemical Large Aerosol Chamber (PHOTO-LAC)

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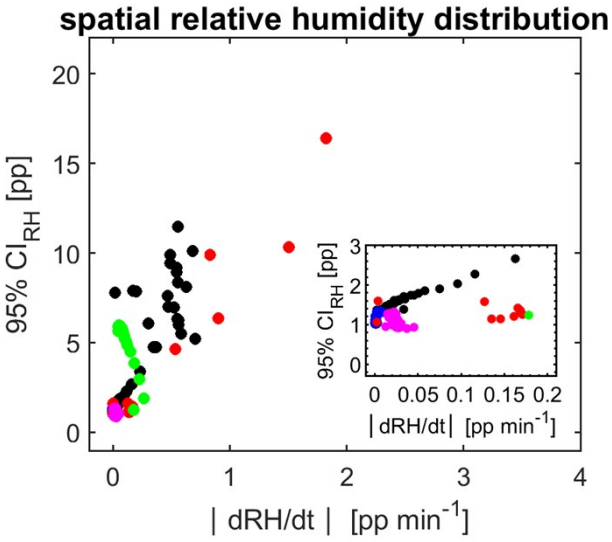
Table S1 Repeated analysis of photochemically-aged BB aerosol (from BB6) with average and 95% confidence interval for the number of assigned sum formula, the modified aromaticity index (AI_{mod}), organic matter to organic carbon ratio (OM:OC) and elemental ratios H:C and O:C

	sum formula number	AI_{mod}	OM:OC	H:C	O:C
Analysis1	4314	0.37	2.44	1.31	0.15
Analysis2	4126	0.37	2.44	1.31	0.16
Analysis3	3368	0.38	2.43	1.29	0.17
Average	3936	0.38	2.44	1.30	0.16
95% CI	982	0.01	0.01	0.02	0.01



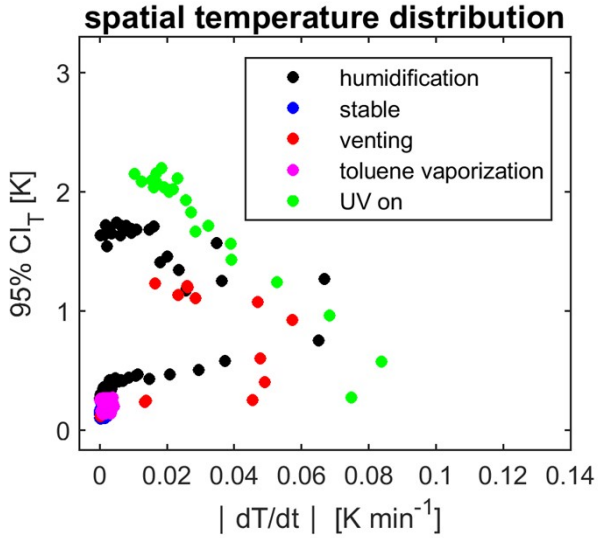


Fig. S1 95% Confidence interval (95% CI)of relative humidity (RH) and temperature (T) from twelve RH and T sensor measurements in PHOTO-LAC dependent on change over time for various operation conditions.

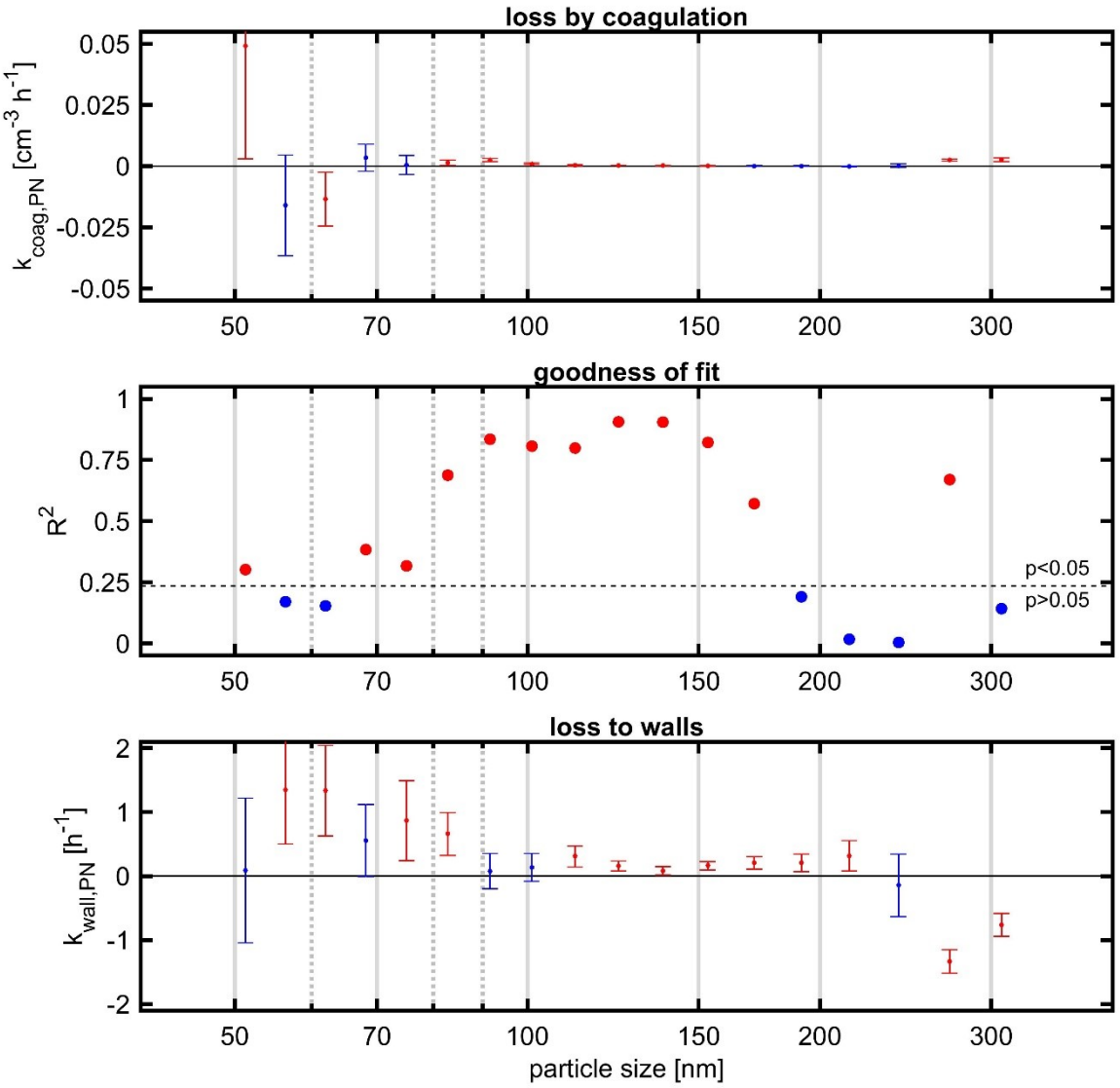


Fig. S2. Loss rate individual particle sizes due to coagulation or loss to the inner walls according to equation $dPN/dt = -k_{coag,PN} \cdot N^2 - k_{wall,PN} \cdot N$ with goodness of fit represented by explained variance R^2 between measured and fitted data. Red colour indicates statistically significant difference from zero at 5% level.

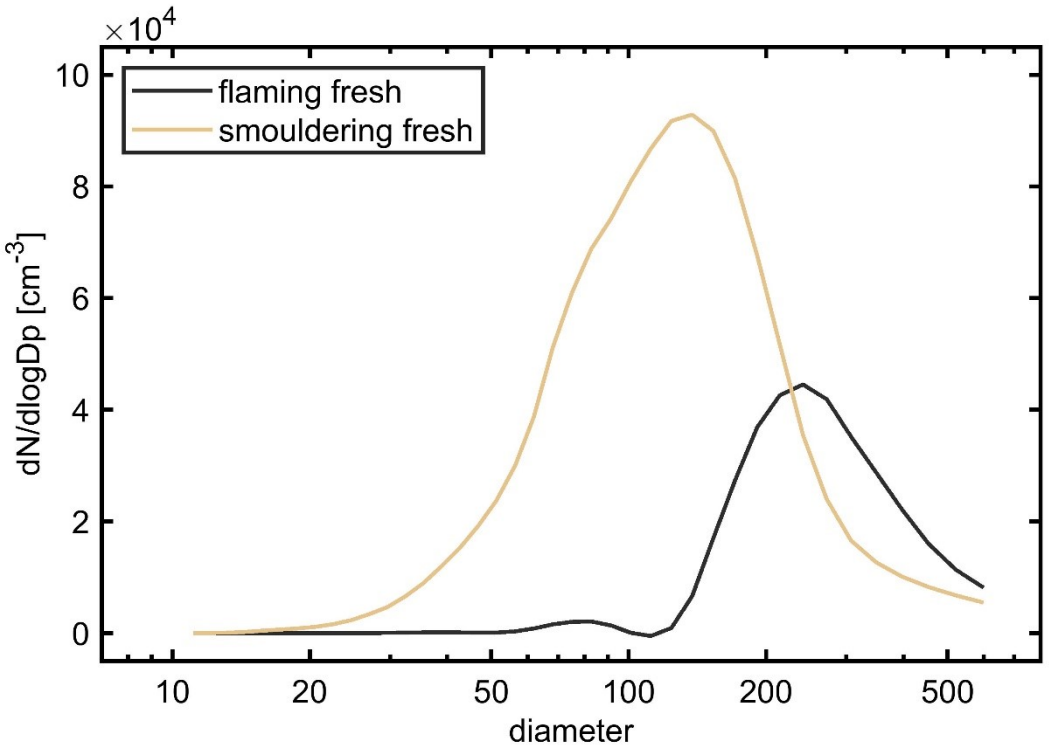


Fig.S3 Size distributions of fresh flaming and smouldering BB aerosol from experiments BB1 and BB6 referring to Table 1 of the main manuscript.

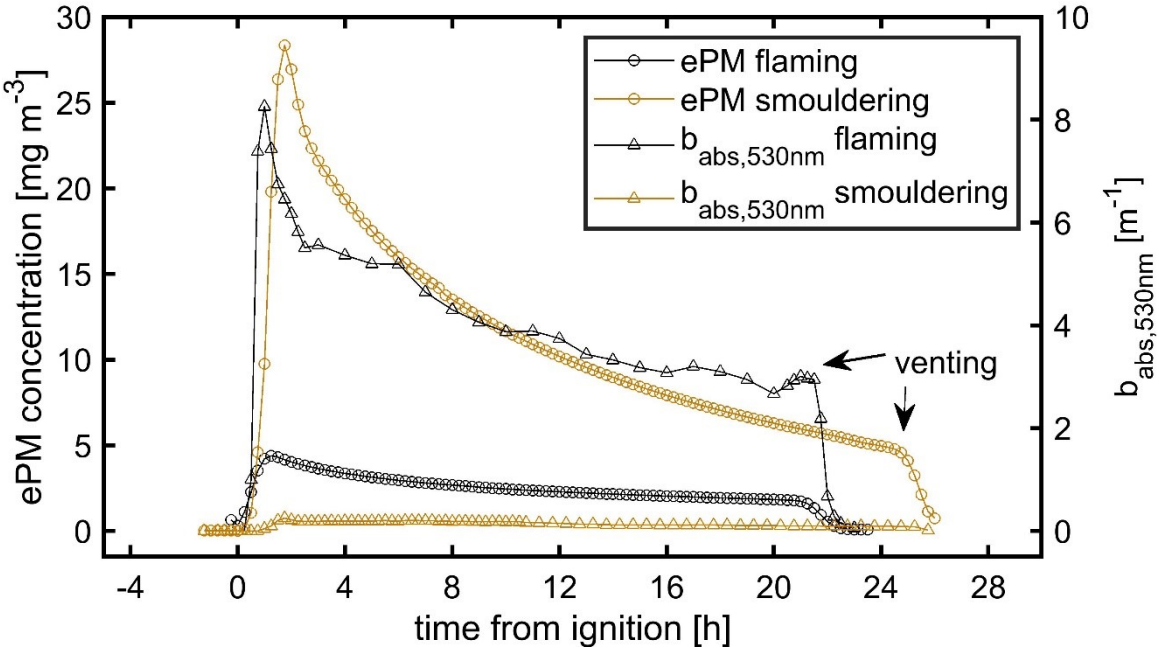


Fig. S4. ePM and-b_{abs} from BB under flaming (black) and smouldering (brown) conditions derived from nephelometer (circles) and aethalometer at 530 nm (triangles). Declining concentrations of flaming aerosol after 22 h and smouldering aerosol after 25 h results from PHOTO-LAC venting.

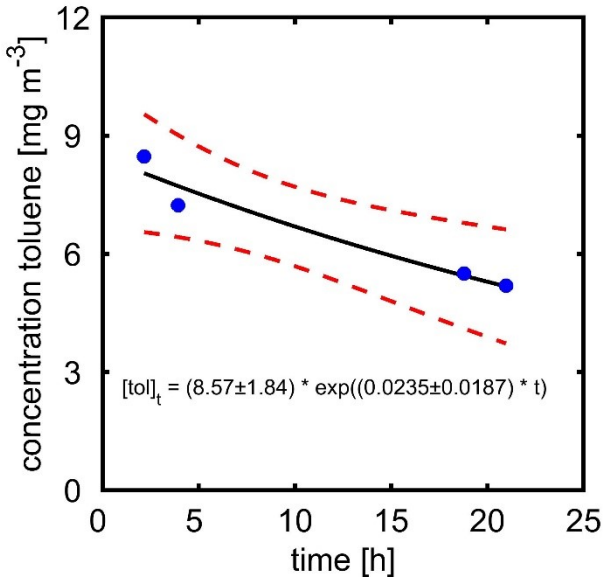


Fig. S5. Toluene loss over time with 95% non-simultaneous functional confidence band.

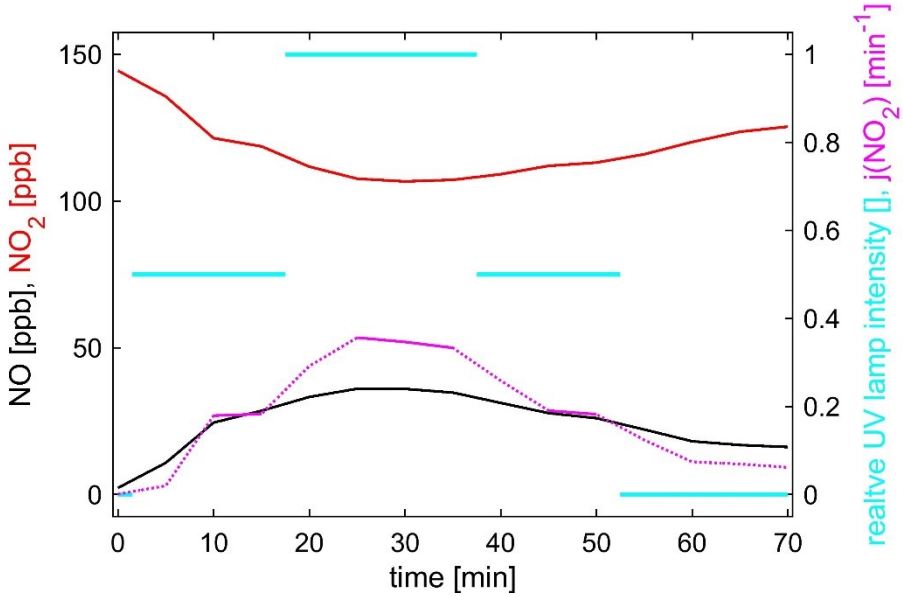


Fig. S6. Temporal concentrations of NO and NO_2 at 50% and 100% UV light intensity. The final photolysis rate $j(NO_2)$ was obtained from periods indicated by solid lines.

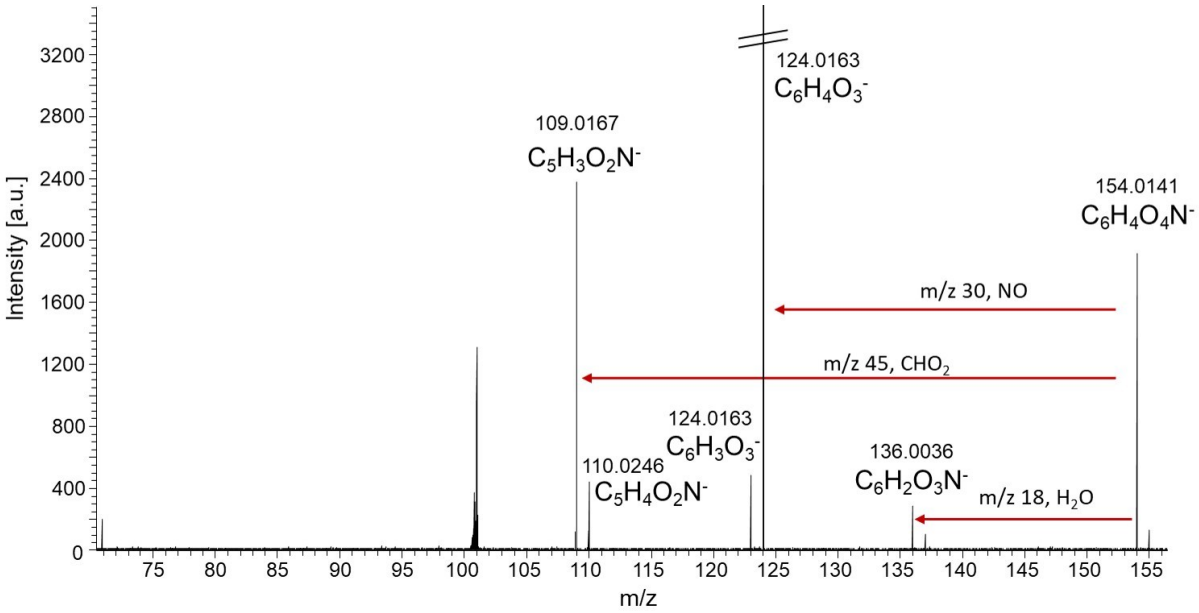


Fig. S7. Collision-induced dissociation (CID) of *m/z* 154 in aerosol from toluene photooxidation (tol4). The most intense fragment was observed at *m/z* 124.016 corresponds to NO neutral loss, indicating the presence of 4-nitro-catechol. The signal at *m/z* 101 belong to electronic noise.

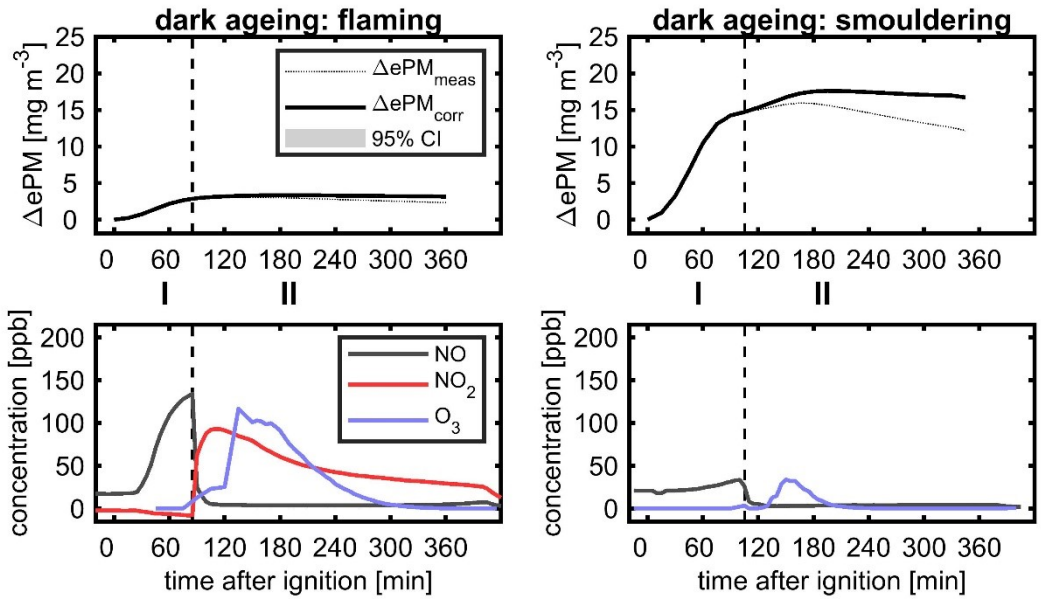


Fig. S8 short dark ageing of flaming (left) smouldering BB aerosol (right) with temporal evolution of equivalent particle mass (ePM; top) and gases NO, NO_2 and O_3 (bottom) for (I) generation of BB aerosol and (II) ozone addition. In order to facilitate formation of $\cdot NO_3$, after conversion of NO to NO_2 the same amount of O_3 is added 30 min later. For smouldering condition, no NO2 data is available.

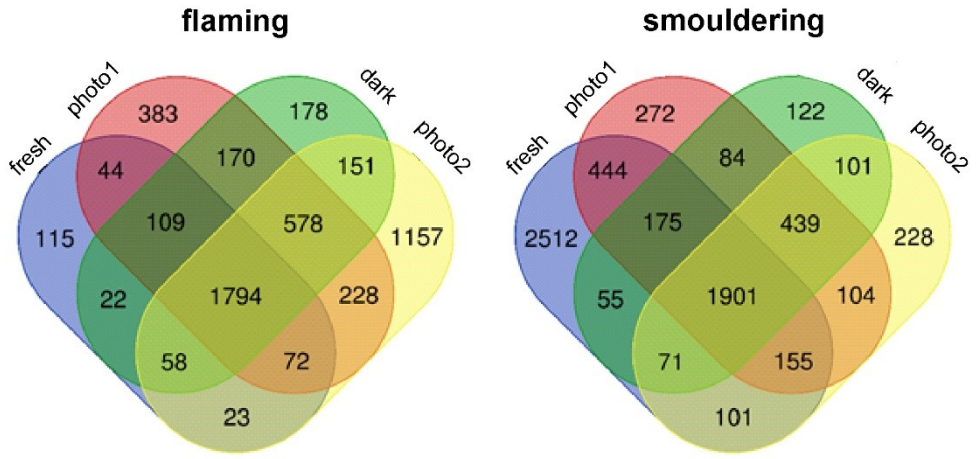


Fig. S9. Venn diagrams of APPI high resolution mass spectra from long ageing with alternating photochemical (photo1 and photo 2) and dark ageing (dark) conditions.