Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplementary Information

No Evidence for Brown Carbon Formation in Ambient Particles Undergoing Atmospherically Relevant Drying

Vikram Pratap[1], Michael A. Battaglia Jr.[1], Annmarie G. Carlton[2], Christopher J. Hennigan[1]*

[1]Department of Chemical, Biochemical and Environmental Engineering, University of Maryland, Baltimore County
[2]Department of Chemistry, University of California, Irvine

Corresponding Author: *Phone: (410) 455-3515; fax: (410) 455-6500; e-mail: hennigan@umbc.edu

Contents of this file

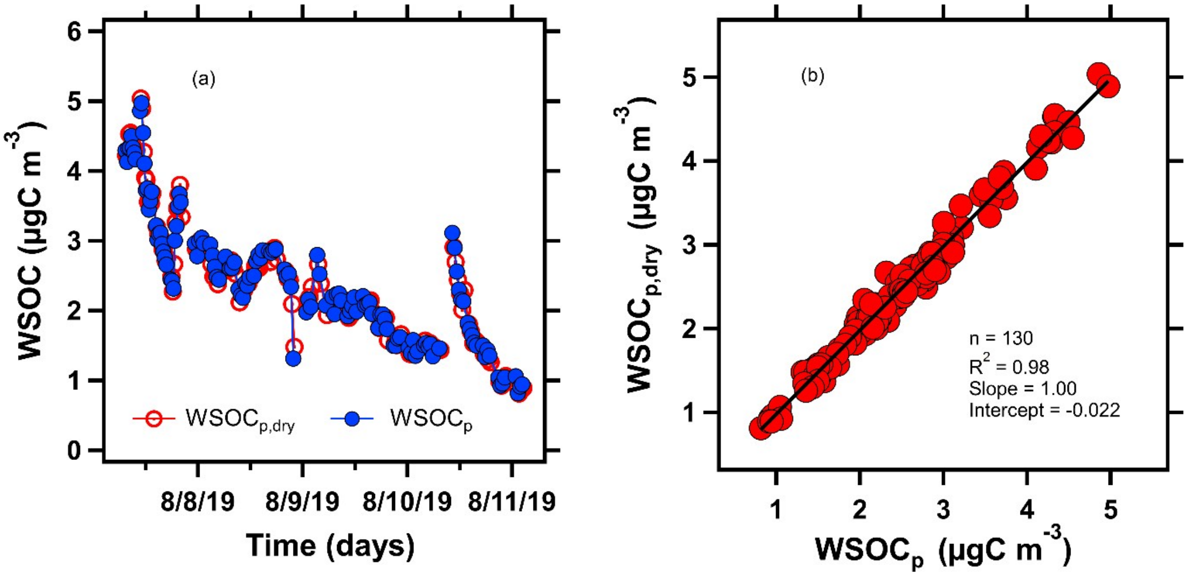

Figure S1: Control experiment plots, where the dry channel was empty (no silica gel). (a) WSOC$_p$ data for dry and ambient channel plotted against time. (b) WSOC$_{p,dry}$ (dry channel WSOC) is compared with WSOC$_p$ (ambient channel WSOC). The slope of the straight line fitted to the data is 1.00, indicating no bias between the channels.

Text S1 Calibration details of TOC analyzer and LWCC

The TOC analyzer is calibrated in factory service or if our verification step fails. Before each sampling campaign, the TOC analyzer is tested for verification. In the verification process before the starting of the campaign, we prepared sucrose solutions of known concentrations within a concentration range that includes our measurement range. Those sucrose solutions were then measured for TOC using the TOC analyzer. The sucrose solutions had a theoretical TOC (expected TOC) which was compared with the measured TOC. Figure S2(a) shows the verification curve for the TOC analyzer. The data exhibits a linear response with a slope of 0.97, intercept of 0.042, and $R^2 = 0.999$. This verification confirms that the factory calibration remained valid throughout the ambient measurements.

The LWCC was also factory calibrated and tested for performance. We performed verification of the LWCC using different diluted solutions of coffee, with absorbance values covering the range of our measurements. Filtered coffee solutions of different concentration were prepared, and the absorbance was measured through the LWCC in the same configuration as was used for the WSOC measurements. Figure S2(b) shows the verification plot. The data are highly linear, with $R^2 =1$.

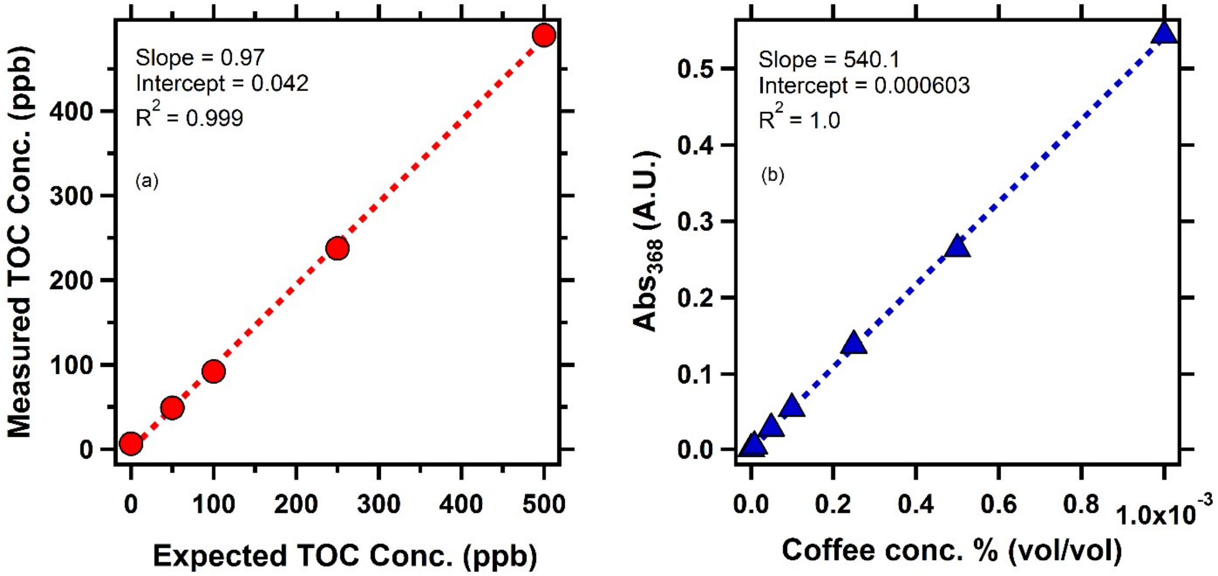

Figure S2: Verification curves of the TOC analyzer and LWCC

Text S2 Gly and MeGly EXPERIMENTS

A series of aerosol drying experiments were conducted with atomized solutions of glyoxal (Gly) and methylglyoxal (MeGly) in 20 mM $(NH_4)_2SO_4$. The experiments were performed using a similar setup as the one used in the ambient sampling. The schematic of the experimental setup is shown in Figure S3. Gly and MeGly were obtained from Sigma-Aldrich as 40% w/w aqueous solutions. ACS grade $(NH_4)_2SO_4$ was acquired from Fisher Scientific. All of the chemicals were used as they were received without further processing. Compressed air was generated using an oil-free compressor, and the air was cleaned using activated carbon (GE Healthcare, carbon cap 150) and a HEPA filter. The particles were generated in an atomizer (TSI model 9302) and passed through a trap to remove larger particles. The aerosol stream was then merged with the make-up air to achieve flow balance. In low humidity experiments, the make-up air flow was increased to achieve a target RH after the dryer. The TOC and LWCC analysis of the collected aerosol are the same as described in Section II of the manuscript.

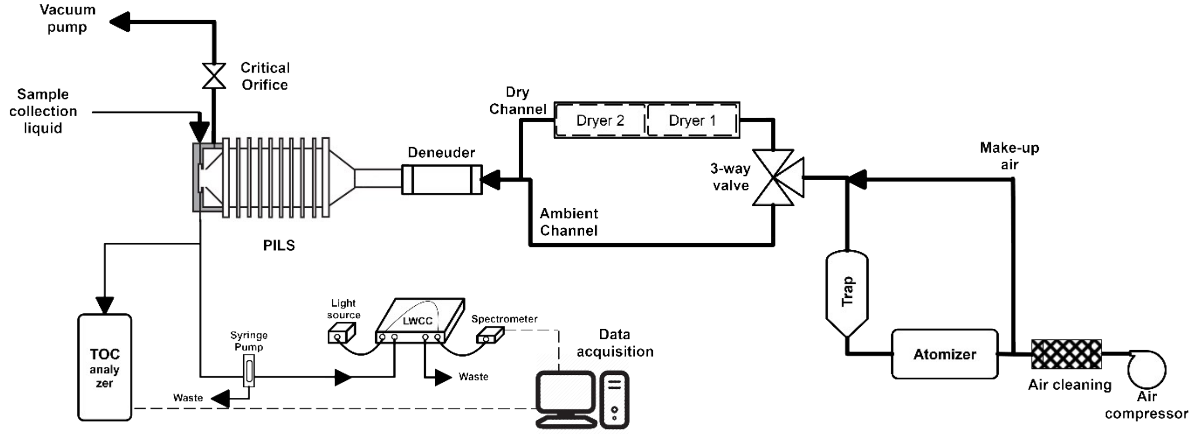

Figure S3: Schematic of the experimental setup for the glyoxal and methylglyoxal laboratory experiments.

All the experiments were conducted with mixed solutions consisting of 10 mM organic (Gly or MeGly) and 20 mM $(NH_4)_2SO_4$ concentrations. Table S1 shows the list of the experiments and associated details. Note the loss of $WSOC_p$ due to the evaporation of organics in the dry channel was observed for all experiments ($WSOC_{p,dry} < WSOC_p$). The MeGly loss to evaporation was significantly higher than that for Gly, which is consistent with previous studies [1]. Also, the MeGly absorbance was generally larger than the Gly absorbance, indicating a higher potential of MeGly in BrC formation [2]. Comparison of the absolute Abs_{368} between the bypass and dried channels is not applicable here since significant organic mass was lost when the atomized particles were dried. Therefore, we compare instead the organic mass-normalized Abs_{368} between the two channels to evaluate the effect of particle drying on BrC formation. The last column of table S1 shows the dry to bypass ratio of the mass-normalized Abs_{368}, and is plotted in figure S8. Figure S8 shows the enhancement in absorbance when the RH of the experiments was reduced from 50% for both Gly and MeGly. For comparison, the RH of the bypass channel was 86%. It can be seen that the dry to bypass MAC (mass absorption coefficient) ratio for Gly remained ~1.0 at 50% RH, but was enhanced by ~25% when the RH was reduced to 33%. For MeGly, there was an enhancement of 50% at 50% RH, and the enhancement further increased to 70% at an RH of 25%. These results suggest the enhancement of BrC with the reduction in RH, likely due to the more concentrated reaction mixture in the particles increasing the condensed-phase reaction rates.

Table S1: Details of the experiments performed with Gly and MeGly at different RH

	Dry channel RH (%)	$Abs_{dry,368}$ (A.U.)	$Abs_{p,368}$ (A.U.)	$WSOC_{p,dry}^{\$}$ (ppb-C)	$WSOC_p^{\$}$ (ppb-C)	$Abs_{dry,368}$/ $WSOC_{p,dry}$ (A.U.)(ppb^{-1})	$Abs_{p,368}$/ $WSOC_p$ (A.U.)(ppb^{-1})	Dry/ Ambient[#]

Exp-1	Gly + AS	50	5.1×10^{-3}	5.2×10^{-3}	9925	10350	5.1×10^{-7}	5.0×10^{-7}	1.02
Exp-2	MeGly + AS	50	3.7×10^{-2}	4.2×10^{-2}	2890	4723	1.2×10^{-5}	8.8×10^{-6}	1.42
Exp-3	Gly + AS	33	6.1×10^{-3}	5.6×10^{-3}	3530	3905	1.7×10^{-6}	1.4×10^{-6}	1.22
Exp-4	MeGly + AS	25	8.6×10^{-3}	9.0×10^{-3}	98	173	8.7×10^{-5}	5.2×10^{-5}	1.68

[*] AS = $(NH_4)_2SO_4$

[$] Aqueous concentrations measured in the collected PILS samples

[#] Dry/Ambient = $(\mathrm{Abs}_{dry,368}/\mathrm{WSOC}_{p,dry})/(\mathrm{Abs}_{p,368}/\mathrm{WSOC}_p)$

Text S3 ABSORBANCE ESTIMATION IN AN AMBIENT PARTICLE

To estimate the approximate contribution of Gly and MeGly to the total absorbance, we calculated the mass absorption coefficient (MAC) of the ambient aerosol and used MAC to estimate the absorbance signal strength equivalent to the total added concentration of Gly and MeGly assuming the high end of reported ambient concentrations. MAC is the wavelength-specific absorbance per unit mass and is calculated according to Chen & Bond, (2010) as:

$$MAC(\lambda) = \frac{A_{10}^{solution}(\lambda) \times \ln 10}{b \times C_{mass}} \ \mathrm{cm^2\ g^{-1}}$$

where, $A_{10}^{solution}(\lambda)$ is the base 10 absorbance at a given wavelength, b is the optical path length in cm, and C_{mass} is the concentration in solution in g cm^{-3}. For example, for an average ambient measurement from this study, $\mathrm{WSOC_p}$ = 2.3 µgC m^{-3} and $\mathrm{Abs}_{p,368} = 4.5 \times 10^{-3}$, b = 50 cm, C_{mass} in the PILS sample is 16×10^{-9} g cm^{-3}, would yield a MAC equal to 13000 cm^2 g^{-1}. Using MAC = 13000 cm^2 g^{-1}, and 50 ng m^{-3} Gly + 50 ng m^{-3} MeGly(45 ngC m^{-3} total) would provide $\mathrm{Abs}_{p,368} = 1.0 \times 10^{-4}$, which is an order of magnitude smaller than the LOD of the LWCC employed in our study. The $\mathrm{Abs}_{p,368}$ of 1.0×10^{-4} is likely an upper bound of the Gly and MeGly contribution. Even though the MAC value estimated here is larger than most laboratory studies, it is reasonable with respect to studies on ambient BrC [3–5].

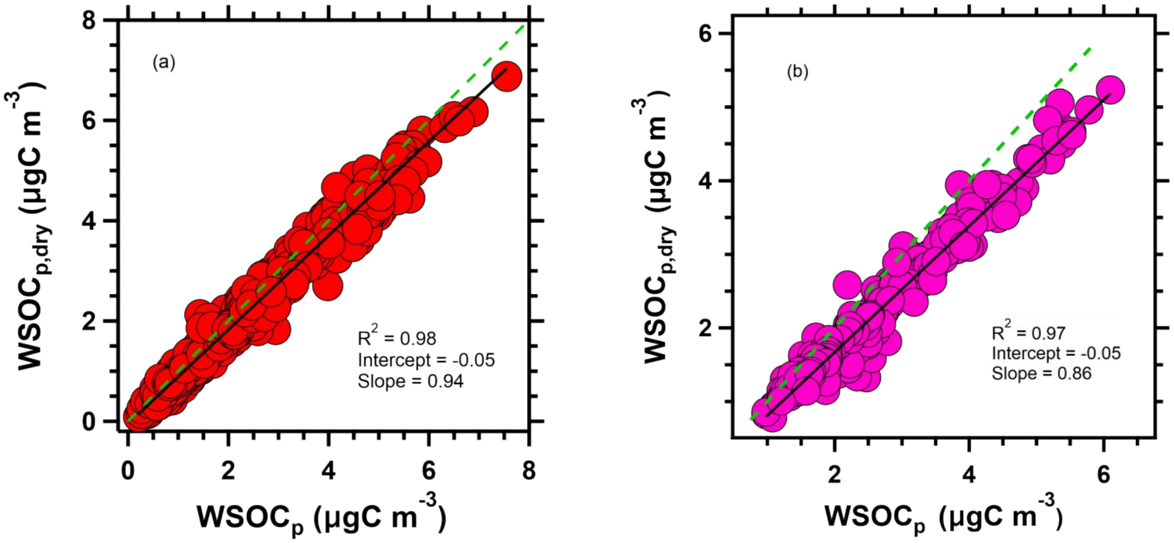

Figure S4: $WSOC_p$ and $WSOC_{p,dry}$ are plotted and fitted to a straight line (black). Dashed green lines are 1:1. (a) Sampling conducted at an average RH = 41%, (b) Sampling conducted at an average RH = 35%.

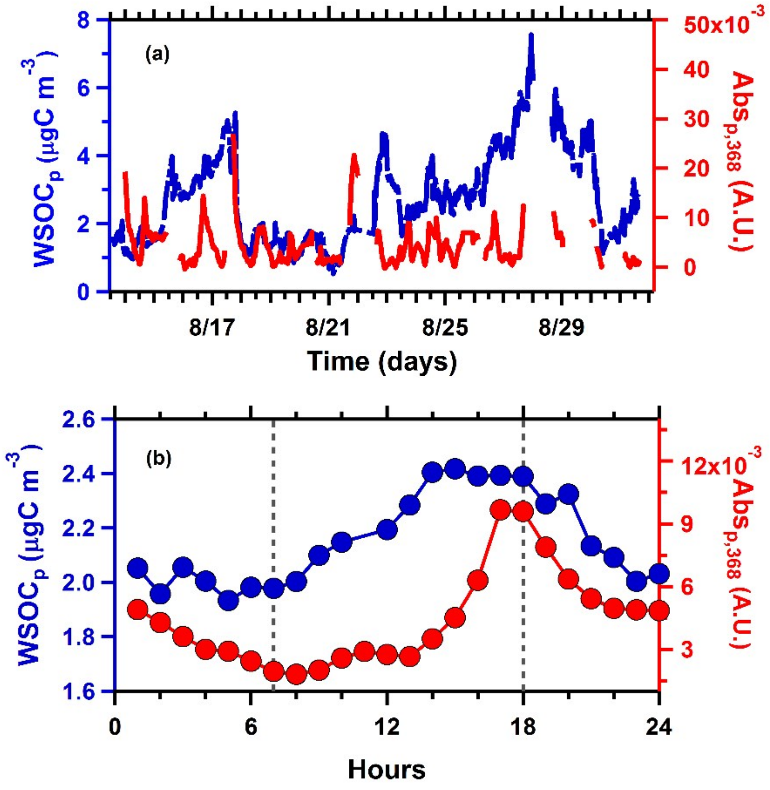

Figure S5 The brief $WSOC_p$ spike above 6.0 µg-C m^{-3} on 27-Aug was not included in the diurnal profile averaging to prevent the influence of this maximum.

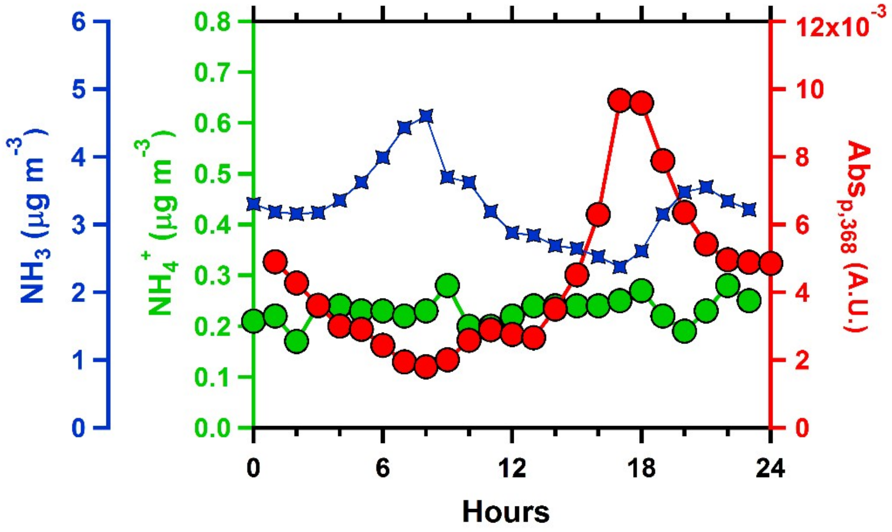

Figure S6: Diurnal profiles of particulate NH_4^+, gas-phase NH_3, and $Abs_{p,368}$.

References:

1 D. O. De Haan, a L. Corrigan, M. a Tolbert, J. L. Jimenez, S. E. Wood and J. J. Turley, *Environ. Sci. Technol.*, 2009, **43**, 8184–8190.

2 M. H. Powelson, B. M. Espelien, L. N. Hawkins, M. M. Galloway and D. O. De Haan, *Environ. Sci. Technol.*, 2014, **48**, 985–993.

3 Y. Chen and T. C. Bond, *Atmos. Chem. Phys.*, 2010, **10**, 1773–1787.

4 H. Sun, L. Biedermann and T. C. Bond, *Geophys. Res. Lett.*, 2007, **34**, 1–5.

5 J. P. S. Wong, M. Tsagaraki, I. Tsiodra, N. Mihalopoulos, K. Violaki, M. Kanakidou, J. Sciare, A. Nenes and R. J. Weber, *Atmos. Chem. Phys.*, 2019, **19**, 7319–7334.