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No evidence for brown carbon formation in ambient particles undergoing atmospherically relevant drying†

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Recent laboratory studies have reported the formation of light-absorbing organic carbon compounds (brown carbon, BrC) in particles undergoing drying. Atmospheric particles undergo cycles of humidification and drying during vertical transport and through daily variations in temperature and humidity, which implies particle drying could potentially be an important source of BrC globally. In this work, we investigated BrC formation in ambient particles undergoing drying at a site in the eastern United States during summer. Aerosol BrC concentrations were linked to secondary organic aerosol (SOA) formation, consistent with seasonal expectations for this region. Measurements of water-soluble organic aerosol concentrations and light absorption (365 nm) were alternated between an unperturbed channel and a channel that dried particles to 41% or 35% relative humidity (RH), depending on the system configuration. The RH maintained in the dry channels was below most ambient RH levels observed throughout the study. We did not observe BrC formation in particles that were dried to either RH level. The results were consistent across two summers, spanning ~5 weeks of measurements that included a wide range of RH conditions and organic and inorganic aerosol loadings. This work suggests that mechanisms aside from humidification-drying cycles are more important contributors to ambient particle BrC loadings. The implications of this work on the atmospheric budget of BrC are discussed.

Environmental significance

Organic carbon in atmospheric particles can perturb solar insolation and hence, alter radiation budgets. Recent laboratory studies have shown that light-absorbing organic carbon (BrC) may be produced from chemical reactions in particles when dried. Atmospheric particles undergo natural drying during daily cycles in relative humidity (RH) and through changes in RH encountered during vertical transport. This may form brown carbon if the processes identified in the lab studies are widespread. We investigated this phenomenon in the eastern United States and did not find evidence of BrC formation in atmospheric particles that were dried from ambient RH to 35% and 41% RH. This suggests that other processes are more important contributors to BrC formation in ambient particles.

1. Introduction

Brown carbon (BrC) is defined as the organic carbon that absorbs radiation in the near UV-Vis spectrum (300–400 nm).[1–4] It has a positive radiative forcing effect on climate, and is increasingly found to be a significant light-absorption component of ambient particles.[1,5–8] On a global scale, radiative forcing by BrC is estimated to be approximately 25% of the radiative forcing by black carbon, though it can have a significantly higher contribution in regions strongly impacted by biomass burning emissions.[1,7,9]

Brown carbon is primarily produced from incomplete and smoldering biomass combustion, which includes wildfires, prescribed fires, wood and other biofuels used for cooking, heating, and other energy demands.[10] Brown carbon is also generated through secondary pathways involving a variety of precursors, such as glyoxal,[11,12] methylglyoxal,[12–15] isoprene,[16] monoterpenes,[17] and lignin.[18] The formation of secondary BrC compounds has been reported in both laboratory and ambient studies.[19–22] For example, in the southeastern United States, secondary BrC was dominated by organic aerosol from biogenic sources.[21] On the other hand, secondary BrC in an urban location in the western United States (Los Angeles) was dominated by anthropogenic sources, and had several times higher absorption (normalized by carbon mass) than the BrC in the

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Southeast, suggesting significant differences between BrC sources and/or formation processes.[19,21] Additionally, particulate water-soluble organic carbon ($WSOC_p$) concentrations exhibited very different correlations with BrC absorbance in these locations, reinforcing geospatial differences among BrC sources and formation processes in the atmosphere.[21] The prevalence of BrC throughout the troposphere provides further evidence of the importance of secondary processes contributing to BrC formation.[5,23,24] Humic-like substances (HULIS) observed in clouds are strongly absorbing, and are also likely secondary in nature.[25,26]

Glyoxal (Gly) and methylglyoxal (MeGly) are well-known precursors in secondary BrC formation. The BrC formation reaction likely requires the presence of nitrogen-containing species like amines and ammonium sulfate (AS).[27] The BrC formation occurs through an aldol-condensation reaction in the aqueous phase, requires sulfate or acidic conditions, first forms imidazole oligomers eventually leading to light absorbing compounds (BrC).[11–13,15,27–31] This reaction is not considered oxidant driven and is confirmed by several laboratory studies.[11–13,15,27–31] Early studies of this pathway focused on bulk reactions where Gly/MeGly and AS were mixed into an aqueous solution and analyzed for BrC (absorbance) over a period of time. The reactions in the bulk phase were found to be extremely slow, as light absorption increased over a period of days.[11–13,30] Recent work focused on investigating BrC formation in drying/evaporating droplets, which was more relevant to ambient aerosols.[14,29,32] These studies confirmed at least an order of magnitude faster rate of BrC formation compared to the bulk reactions.[14,29,32–34] For example, Lee *et al.* (2013)[34] reported BrC formation within a few seconds in Gly + AS particles dried at an RH of ≤35%. The enhancement in BrC formation in evaporating droplets occurs as the concentration of reactants in aqueous droplets increase with water evaporation, increasing reaction rates. Therefore, the process of drying may also have an impact on BrC formation in ambient particles. The liquid water content of particles in the atmosphere changes throughout the day with natural variations in temperature and relative humidity.[35] Vertical transport also perturbs aerosol liquid water content due to the associated temperature and RH gradients. Similarly, most clouds are non-precipitating,[36] thus particles that go through a cloud cycle experience large changes in their liquid water content and in the aqueous phase concentrations of their components. Such humidification-drying cycles may have a profound effect on secondary BrC formation.[14,29,33,34] To our knowledge, BrC formation in ambient particles undergoing drying has not been investigated previously. Herein, we characterize this phenomenon in the eastern United States during the summer, a time and region where secondary BrC formation is known to occur.[20,21]

2. Materials and methods

Ambient particle sampling was carried out on the campus of the University of Maryland, Baltimore County (UMBC).[37,38] The experimental setup was based upon El-Sayed *et al.* (2015),[37] but modified to simultaneously measure $WSOC_p$ and absorbance ($\lambda = 365$ nm) of the water-soluble aerosol components (Fig. 1). The experimental setup was installed inside a temperature-controlled building on UMBC's campus. In addition to $WSOC_p$ and absorbance, gas-phase ammonia and inorganic aerosol composition (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) were measured. Sampling was conducted in two phases. Approximately 3–4 weeks of data were collected during the period of 17 July to 31 August, 2018 (phase I), and 1–2 weeks from 13 to 23 August, 2019 (phase II). In the first phase, one dryer provided an average dry channel RH of 41% (Fig. 1), while two dryers were installed in the second phase to yield an average dry channel RH of 35% (Fig. 2). The average drying RH of 41 ± 4% was selected to simulate the natural drying of particles in the atmosphere. This was in agreement with the average daytime RH of ~45% recorded in a previous summer campaign

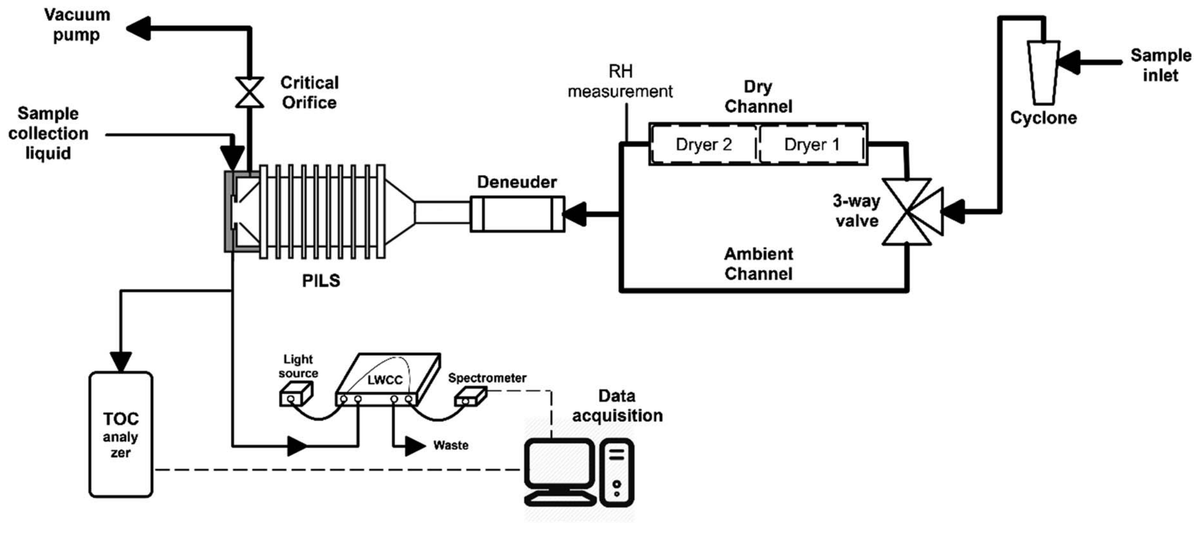

Fig. 1 Schematic of the sampling setup. Note that one dryer was used in the dry channel during phase I (summer 2018), while two dryers were used during phase II (summer 2019).

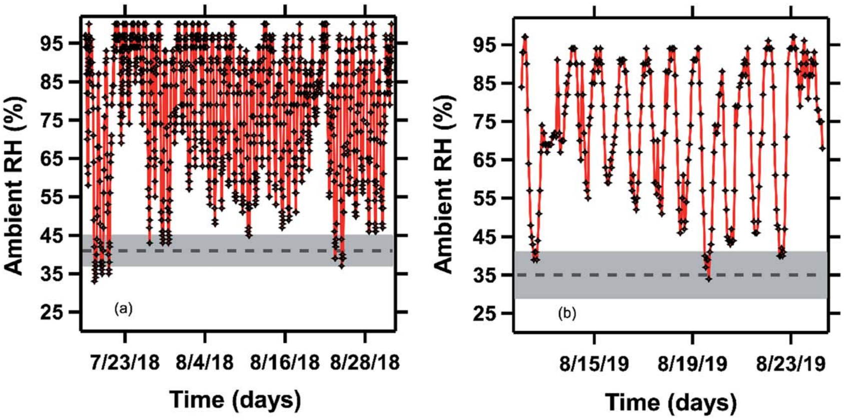

Fig. 2 Hourly ambient relative humidity levels during (a) phase I (17-July-2018 to 31-Aug-2018), and (b) phase II (13-Aug-2019 to 23-Aug-2019) of the study. The dashed line shows the 41% RH maintained in the dry channel during phase I sampling, and the gray shaded region represents the average ± 1σ RH range of 37–45%. Note, only ~2% hourly data fell below 41% RH. In phase II sampling, the average drying RH was 35% (dashed line), and the shaded region is average ± 1σ RH range of 29–41%. The data were downloaded from NOAA's Baltimore Washington International airport meteorology station, located 7 km south of UMBC (https://www.ncdc.noaa.gov/cdo-web/search?datasetid=GHCND).

in Baltimore.[39] During the present study, in phase I, the average minimum daytime RH was 55% ± 13%, and only ~2% of hourly data were below an RH of 41% (Fig. 2). During phase II, the average minimum daytime RH was 51% ± 13%, with only ~0.1% of hourly RH values below 35%. Therefore, the experimental results typically dried ambient particle below observed minimum values experienced at the surface during our study. Even though the ambient RH rarely falls below 40% in Baltimore, MD during the summer, the phase II sampling was conducted at a reduced RH of 35% in an attempt to probe the BrC formation process observed in laboratory studies.[34]

The experimental setup is shown in Fig. 1. Ambient particles were sampled at a flow rate of 12 lpm and alternated through two different channels ("ambient" and "dry") every 15 minutes using an automated three-way valve (Brechtel manufacturing). In the ambient channel, particles passed unperturbed through a copper tube (1/2″ O.D.), while in the dry channel, they passed through a silica gel diffusion dryer.[34] Both sample paths were connected to an activated carbon (AC) denuder to remove VOCs and any evaporated WSOC from the sample stream. Note that RH levels were not measured downstream of the AC denuder. AC adsorbs water, which can affect the removal of VOCs, especially volatile hydrocarbons.[40] However, we do not anticipate RH changes through this component of the experimental setup since the gas residence time in the denuder (~1 s) is much shorter than the equilibration timescale for water vapor adsorption to AC (hours).[40] Particles were continuously collected into an aqueous solution *via* a Particle-into Liquid Sampler (PILS, Brechtel manufacturing).[41] The liquid PILS sample, which was continuously generated at 1.4 mL min^{-1}, was split and sent to a TOC analyzer (Sievers 900 portable, GE Analytical Instruments) and a liquid waveguide capillary cell (LWCC, WPI, model 3050). The TOC analyzer was operated in turbo mode and provided WSOC measurements with 4-s resolution. The LWCC has an effective path length of 50 cm and was coupled to a monochromatic 365 nm UV light source (Oceanoptics, LLS-LED) and a spectrometer (Oceanoptics, FLAME-S, 200–800 nm) *via* fiber optic cables (QP400-2-SR, Oceanoptics). A longer path length of 50 cm in the LWCC provides enhanced sensitivity to capture the differences in absorbance between the dry and ambient channels.[42] Since BrC is operationally defined, multiple approaches have been used in the past to measure BrC across a broad spectral range of 280–700 nm. Studies have defined BrC based upon the absorbance at ~300 nm,[12,15,34,43] ~365 nm (ref. 12, 20, 34 and 43) or an integrated range between 300–500 nm.[15,44] A wide range of BrC precursors (glyoxal, methylglyoxal, glycoaldehyde, hydroxy acetone, *etc.*) produce chromophores that absorb at different wavelengths.[12] Speciation of BrC compounds formed from MeGly + AS mixtures resulted in the majority of BrC compounds exhibiting peak absorption at ~300 nm, and >70% of total absorbance was observed in the 300–500 nm range.[15] Hecobian *et al.*, reported average absorption in a narrow range of 360–370 nm as a measure of brown carbon.[20] They found that the absorbance at 365 nm was strongly correlated with the integrated absorption over 300–400 nm, but avoided interferences from non-organic compounds, as the basis for recommending 365 nm for the BrC measurement. We followed the approach developed by Hecobian *et al.*,[20] which appears to be in agreement with many previous studies.[12,34,43] Absorption spectra were recorded over a range of 350–400 nm using Oceanview spectroscopy software 1.6.3 (Oceanoptics), and the absorbance is reported at 368 ± 5 nm. Absorbance was measured in a semi-continuous mode where the PILS sample was injected into the LWCC *via* a syringe pump (Tricontinent, C3000), providing an absorbance measurement every 15 minutes. The measurements through the dry and ambient channels were termed $WSOC_p$ ($Abs_{p,368}$) and $WSOC_{p,dry}$ ($Abs_{dry,368}$), respectively. The LWCC was cleaned with 0.6 M HCl and 18.2 MΩ deionized water every three days during the sampling.[20] Dynamic blanks were taken every 24 hours for both the TOC analyzer and LWCC. The ambient measurements were blank-corrected. Limits of detection (LOD) were calculated as 3× the standard deviation of the blanks and were 0.21 μg C m^{-3} and 1.0×10^{-3} A.U., respectively. Calibration details of the TOC analyzer and LWCC are provided in the ESI (Text S1†). The experimental setup was tested with a control experiment where the sampling was performed with empty (no silica gel) dry channel, with one and two dryers installed in the dry channel flow path. We did not find any difference between the two channels during these control experiments (Fig. S1†), in agreement with our past studies (see Fig. S3 in El-Sayed *et al.* (2016)),[39] indicating that differences between the two measurement channels observed during ambient sampling were the result of physical and/or chemical changes to the particles induced by aerosol water evaporation.

3. Results and discussion

3.1 Drying induced BrC formation

The comparison of the absorbance measured for the ambient ($Abs_{p,368}$) and dry ($Abs_{dry,368}$) channels is shown in Fig. 3. For both dry channel configurations (one or two driers, Fig. 3a and b, respectively), comparison of $Abs_{p,368}$ and $Abs_{dry,368}$ yielded a slope of 1.00 and an R^2 value of 0.99. This demonstrates no difference in BrC at either of the drying levels. Fig. 4 shows a time series of the absolute difference in absorbance between the two channels ($\Delta Abs_{368} = Abs_{dry,368} - Abs_{p,368}$). The ΔAbs_{368} values showed no temporal pattern, and no correlation with meteorological conditions or aerosol chemical components in either of the measurement phases. The mean ΔAbs_{368} values were -1.1×10^{-4} and 1.0×10^{-4} at 41% and 35% RHs, respectively, which are much lower than the measurement LOD (1.0×10^{-3} A.U.). As discussed in Section 2, BrC is operationally defined, with measurements of absorbance at different wavelengths.[12,15,34,43] It is possible that an enhancement in absorbance at ∼300 nm due to particle drying would have been observed in our study. However, based on prior studies that have observed strong correlations between absorbance at 365 nm and integrated absorbance across 300–400 nm, our observations suggest that there was no generation of BrC in ambient particles undergoing drying.

To investigate further, and evaluate the production of BrC in particles undergoing drying in our experimental setup, we also conducted laboratory experiments with Gly and MeGly in aqueous ammonium sulfate solutions (10 mM + 20 mM) similar to Lee *et al.*, 2013.[34] The details of the experiments are discussed in the ESI (Text S2†). Briefly, mixtures of glyoxal/methylglyoxal and ammonium sulfate were atomized and alternated through the ambient and dry channels while Abs_{368} and $WSOC_p$ measurements were carried out with the same system used for the ambient sampling. The RH through the bypass (ambient) channel was ∼85%, while two different RH levels were investigated for the dry channel. Fig. 5 shows the results of the experiments. In the case of Gly, no enhancement in absorbance was observed when particles were dried to 50% RH, but drying to ∼33% RH did produce a measurable enhancement in absorbance. On the other hand, MeGly showed an enhancement of ∼40% in A.U. at drying to 50% RH. The enhancement further increased to ∼70% when dried at ∼25% RH. On average,

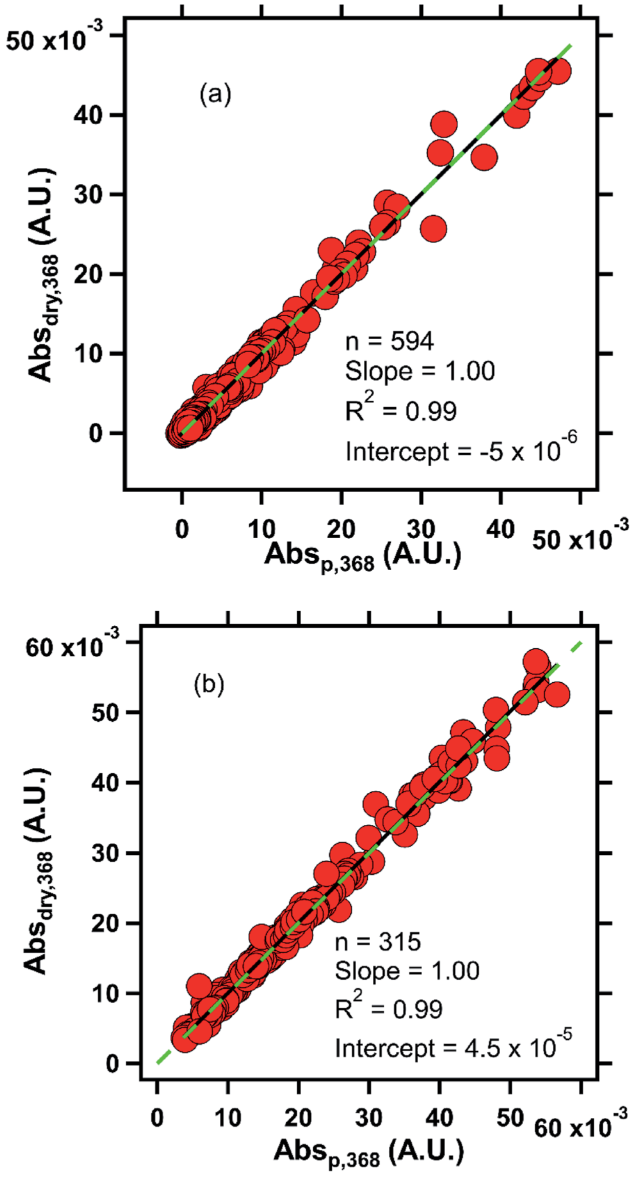

Fig. 3 Comparison of the ambient and dry channel absorbance measurements during (a) phase-I sampling (dry channel RH = 41%) conducted between 17-July-2018 to 31-Aug-2018, and (b) phase-II sampling (dry channel RH = 35%) conducted between 13-Aug-2019 to 23-Aug-2019. The 1:1 line (green dashed line) is shown for visual reference, and the solid black line is the linear fit to the data using least-squares regression analysis.

we found a 20% enhancement (per mass basis) in BrC absorbance for both Gly and MeGly systems when the RH was reduced from 50% to ∼30% in the dry channel. The study by Lee *et al.*, (2013)[34] also implemented moderate drying (RH ≤ 35%); however, a direct quantitative comparison with their work is not possible. The kinetics of BrC formation in bulk solutions of Gly and MeGly with AS can be quite slow, as absorption evolves over a period of days.[11–13] The delay between solution preparation and atomization/particle collection would need to be standardized for such a comparison. The time-dependent mass absorption coefficient (per C mass basis) is not available, which would add uncertainty to such comparisons. Further, the RH

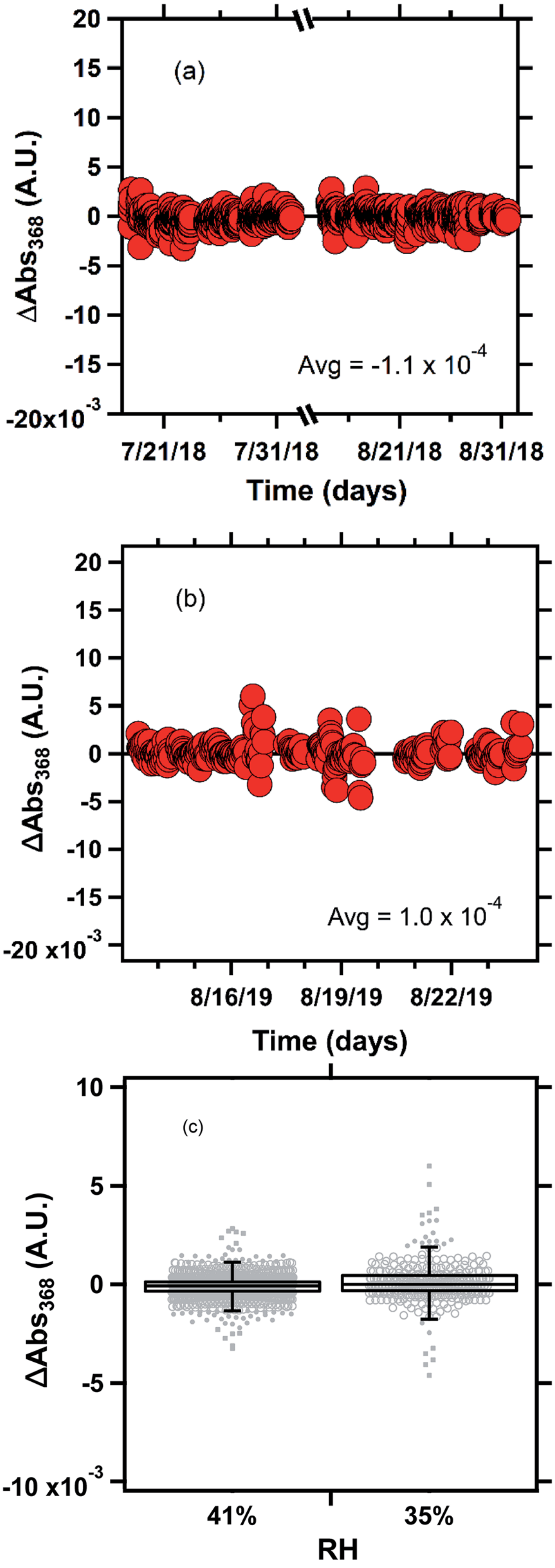

Fig. 4 (a and b) Time series of ΔAbs_{368} (ΔAbs_{368} = $Abs_{dry,368}$ − $Abs_{p,368}$) during the phase I and phase II sampling periods, respectively. Note the broken *x*-axis in panel (a) corresponds to a ~10 day period when the instrument was off-line for maintenance. No difference in BrC concentration was observed at both RH levels. (c) Box plot of ΔAbs_{368} (ΔAbs_{368} = $Abs_{dry,368}$ − $Abs_{p,368}$) of ambient samples collected at two different RHs – 41% and 35%.

and drying times would need to be standardized to enable quantitative comparisons between experiments. However, these experiments demonstrate qualitative agreement with prior studies that observed BrC formation (or increased rates of BrC formation) in particles undergoing drying. The results also demonstrate the capability of our experimental setup to generate BrC in particles undergoing drying, providing an important contrast for the ambient observations.

Overall, these results suggest that, even if BrC formation occurs in drying ambient particles, the effect is quite minor. The most likely cause of this observation is the low concentrations of BrC precursors in ambient particles. Gly and MeGly are formed in high abundances from the oxidation of biogenic and aromatic emissions, and are thought to be important secondary BrC precursors.[12–14,45] Based upon Gly and MeGly concentrations in ambient particles (each typically in the range of 0–50 ng m^{-3}),[23,46,47] we estimated that they may contribute a combined $\Delta Abs_{p,368}$ = 1.0 × 10^{-4} during one drying cycle, which is smaller than the LOD of the LWCC employed in our study (see ESI for details of this estimate – Text S3†).[48–50] In these laboratory experiments, the $WSOC_p$ concentration was reduced by 4% (Gly) and 39% (MeGly) at 50% RH and 10% (Gly) and 43% (MeGly) at ~30% RH (Table S1†). This is in line with the relative $WSOC_p$ reductions we observed in ambient sampling (Fig. S4†), and is consistent with $WSOC_p$ reductions due to drying in prior studies from our group.[38] The absolute organic aerosol concentrations in the laboratory Gly and MeGly experiments were orders of magnitude (35 to 3600 μg m^{-3}) above ambient levels (0.1 to 10 μg m^{-3}) when the mM aqueous Gly and MeGly solutions were atomized (Table S1 and Text S3†). As discussed above, the laboratory experimental conditions were based upon prior studies,[34] and the high concentrations employed likely

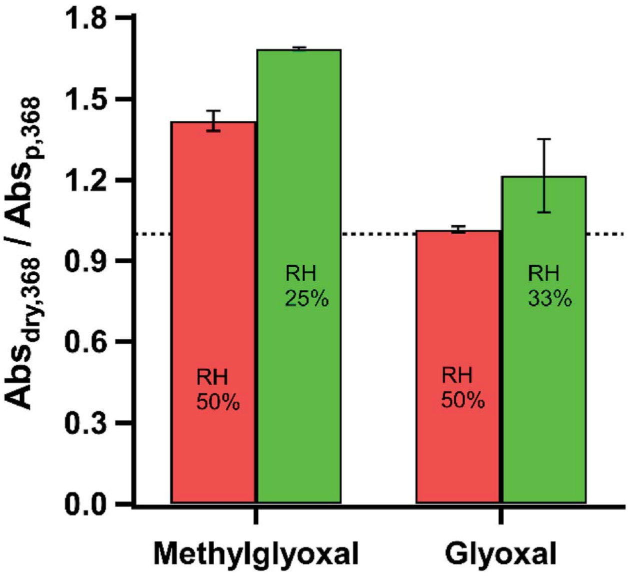

Fig. 5 The ratio of dry to bypass MAC is shown for Gly and MeGly experiments conducted at different RH levels (RH of the dry channel is given in the figure as percentages). The dashed black line at *y* = 1 is provided for visual guidance.

contributed to the marked absorption enhancements not observed in ambient particles.

3.2 WSOC and total absorbance

Previous observations during the summer have shown that some fraction of $WSOC_p$ (5–30%) evaporates as a result of particle drying.[38,39] The average $WSOC_{p,dry}/WSOC_p$ ratio was ~0.90 and 0.84 at RHs of 41% and 35%, respectively (Fig. S4†). These results indicate the reversible uptake of WSOC to aerosol water (reversible aqSOA), in agreement with our previous observations at this site.[38,39] Gly and MeGly reversibly partition to aerosol water,[29,51] and may contribute to the reduced $WSOC_p$ we observe in the dry channel.[39] However, our results suggest that even though some $WSOC_p$ is evaporating in the dry channel, chemical formation of BrC is negligible.

Associations between $WSOC_p$ and BrC can provide insight into primary emissions and secondary formation processes in a given location.[19–21] A time series of $WSOC_p$ and $Abs_{p,368}$ is plotted in Fig. S5(a).† Overall, the absorbance levels were quite low (average = 0.0045), which reflects the summertime conditions during which biomass burning influence was low and the source of BrC was predominantly through secondary formation, consistent with previous studies.[20] At times, $Abs_{p,368}$ and $WSOC_p$ were correlated, but not during periods when the $WSOC_p$ concentration was highest. Even though elevated $WSOC_p$ was likely due to SOA formation, a process that can also be associated with BrC formation,[13,43] other competing processes like photobleaching[52–54] during the daytime may lead to the loss of secondary BrC.

The diurnal trends of $WSOC_p$ and $Abs_{p,368}$ are shown in Fig. S5(b).† The $WSOC_p$ profile is relatively flat, while absorbance appears to fall by ~60% in the early morning hours (00:00 to 8:00 am). A shoulder is observed for both $WSOC_p$ and absorbance during the morning rush-hour, suggesting an influence of traffic.[21] The mid-day peak of $WSOC_p$ indicates photochemical SOA formation as a major contributor to diurnal variability of $WSOC_p$.[55] $Abs_{p,368}$ has a similar afternoon peak, but appears to lag behind $WSOC_p$, suggesting the BrC formed is from secondary processes.[20] The lag may be due to slower kinetics of BrC formation or photobleaching during mid-day hours when the actinic flux is greatest.[12] Organonitrogen compounds, often formed from reactions of organic molecules with NH_4^+ or NH_3, contribute greatly to BrC levels.[15,27] The diurnal profiles of BrC, NH_4^+ and NH_3 are compared in Fig. S6.† The average concentration of NH_4^+ does not fluctuate much throughout the day, consistent with the regional nature and the strong influence of sulfate on NH_4^+ concentrations in the eastern U.S.[56] Interestingly, the NH_3 concentration appears to be anti-correlated with BrC; however, it is unlikely that this relationship is causative. The gas-phase NH_3 concentration is driven by many factors that have not been directly linked to secondary BrC formation, including emissions, gas-particle partitioning, boundary layer dynamics, aerosol liquid water content, and particle acidity.[57] The magnitude of concentration changes (2–3 $\mu g\ m^{-3}$ for NH_3 *vs.* 7–8 $\times 10^{-3}$ A.U. for $Abs_{p,368}$) further suggests that the apparent anti-correlation does not indicate a causal relationship. Future studies may be required to confirm this hypothesis.

4. Conclusions

This represents, to our knowledge, the first study to characterize BrC formation in ambient particles undergoing drying. We did not find evidence of BrC formation in ambient particles dried to ~35% RH, lower than almost all ambient RH values observed at the surface during our study. The reason for this observation is most likely the low concentrations of BrC precursors in ambient particles. The low concentration of BrC precursor chemicals may not be a constraint in fogs and clouds. Liquid water content in fog and clouds is several orders of magnitude higher than the ambient particles, enabling significantly higher uptake (mass basis) of BrC producing chemicals.[58,59] The drying of fog and cloud droplets can lead to an extremely concentrated mixture that may form BrC.[32,60] Multiple cycles of this processing may lead to a buildup of BrC in an air mass, which may ultimately alter the overall atmospheric BrC budget. Alternately, cloud processing in strong convective systems may be a significant source of free-tropospheric BrC,[24] though the overall contribution of cloud processing to global BrC levels remains highly uncertain.[1,61,62] Future studies should also characterize the lifetime of secondary BrC formed through drying processes, since photobleaching represents a major sink for BrC, reducing its direct radiative effect (DRE).[7,8,63] The photochemical lifetime of ambient BrC (dominated by biomass burning) is estimated to be ~1 day, though laboratory experiments have shown that secondary BrC may have shorter lifetimes.[64,65] A significant amount of primary BrC from biomass burning (including residential wood burning) is emitted in wintertime.[21] Therefore, the summertime was appropriate to investigate drying induced BrC formation when the contributions of biomass burning were minimal. The effects of aerosol liquid water uptake and evaporation on primary BrC emitted from biomass burning have been investigated in conjunction with photolysis (photobleaching).[62] However, studies isolating the effects of humidification and drying on the transformation of primary BrC emitted from biomass burning have not been performed and need to be evaluated in future studies.

Conflicts of interest

Authors declare no competing financial interests.

Acknowledgements

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