Optical Studies of Brown Carbon (BrC) Formation

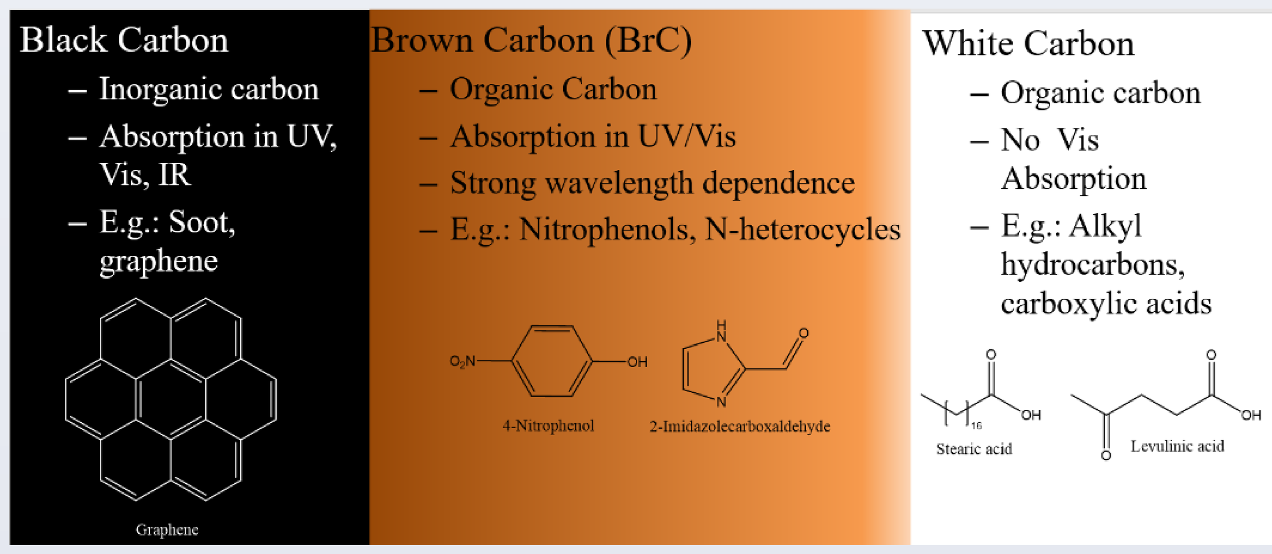
Zach Schiffman[1,2], Kevin Jansen[1,2], Margaret Tolbert[1,2]

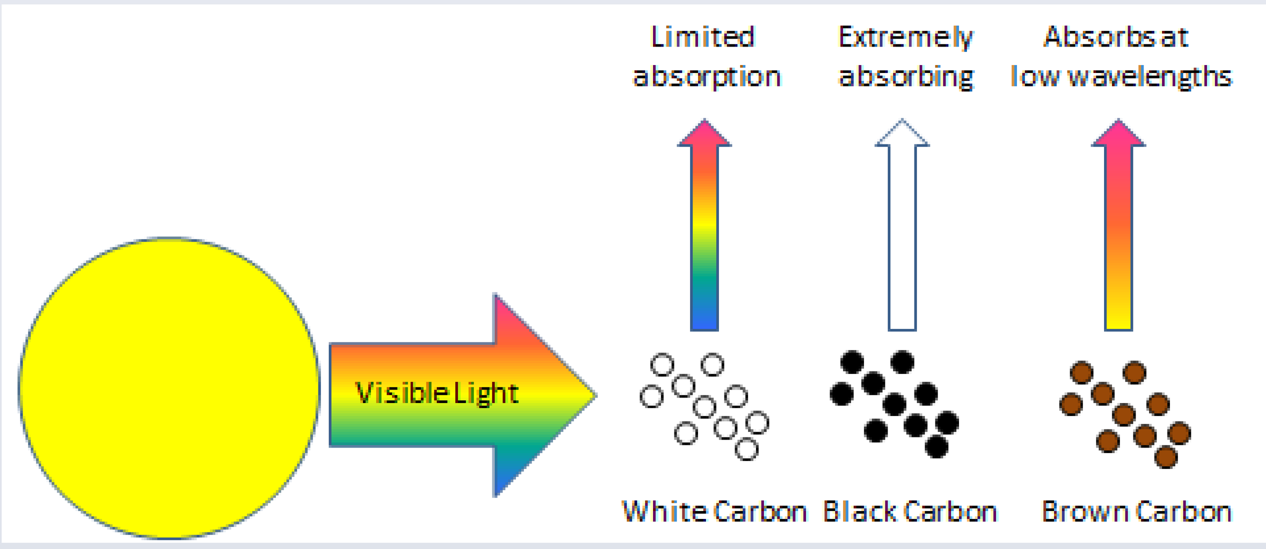
[1]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder CO 80309 USA
[2]Department of Chemistry, University of Colorado, Boulder CO 80309 USA
Contact: Zachary.Schiffman@colorado.edu

I. INTRODUCTION

- Hazes of carbon-containing aerosol can absorb visible light and lead to warming climate effects

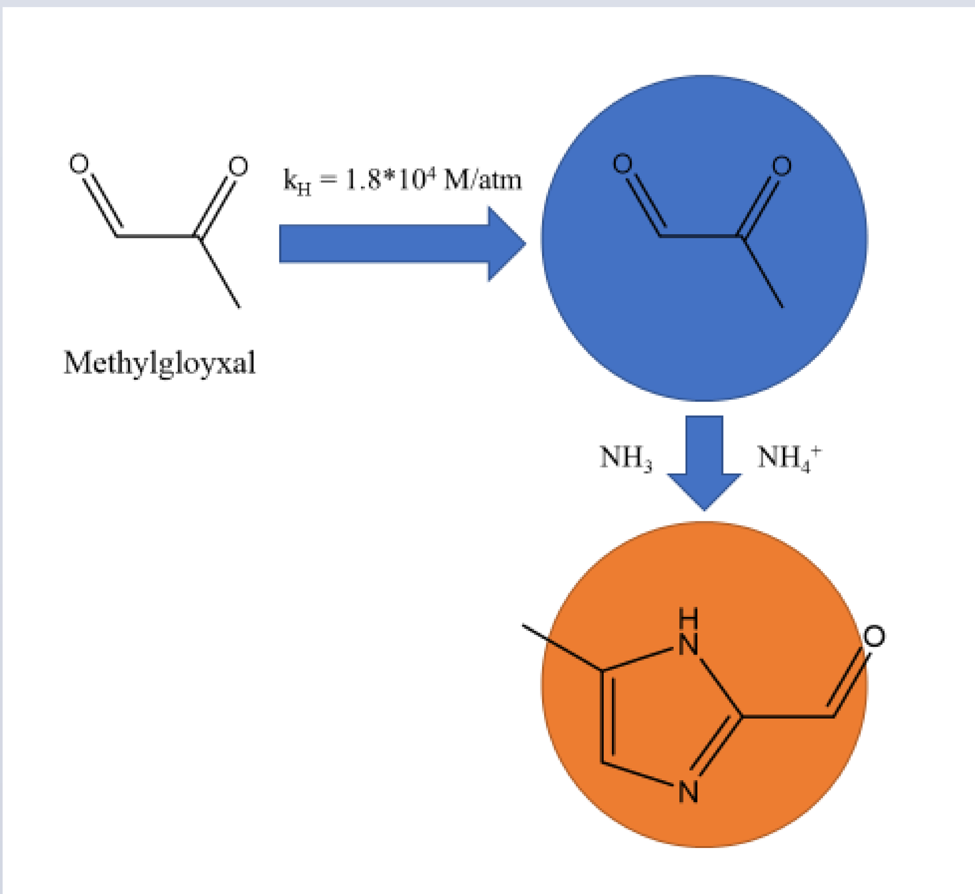
Brown carbon can impact both the air quality and visibility in our atmosphere. [1]





Categorization of carbon aerosol by level of absorption.

- Methylglyoxal (MeGly) is a volatile organic compound (VOC) released primarily from the oxidation of isoprene over land, as high as 140 Tg/yr , with an atmospheric lifetime of approximately 1.6 hours from losses to photolysis, OH oxidation, and secondary organic aerosol (SOA) formation [2]
- Produces 8 Tg/yr of secondary organic aerosol (SOA) [2]



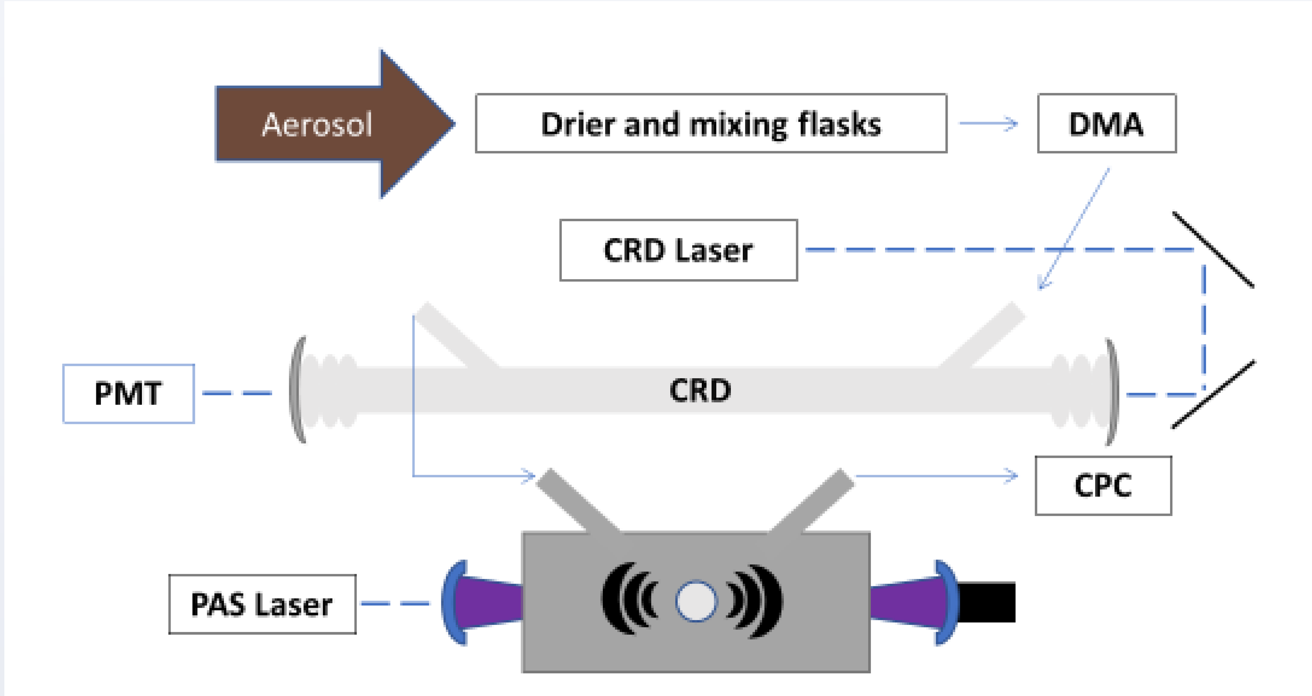
Methylglyoxal readily hydrates into aqueous droplets, allowing for reaction with ammonium or ammonia [3,4]

- The reaction of methylglyoxal with ammonium (NH_4^+) in the atmosphere can lead to the production of brown carbon aerosol [5]
- BrC derived from MeGly is among the darkest BrC in the atmosphere [5]

How important is methylglyoxal brown carbon in the radiative balance of Earth's atmosphere?

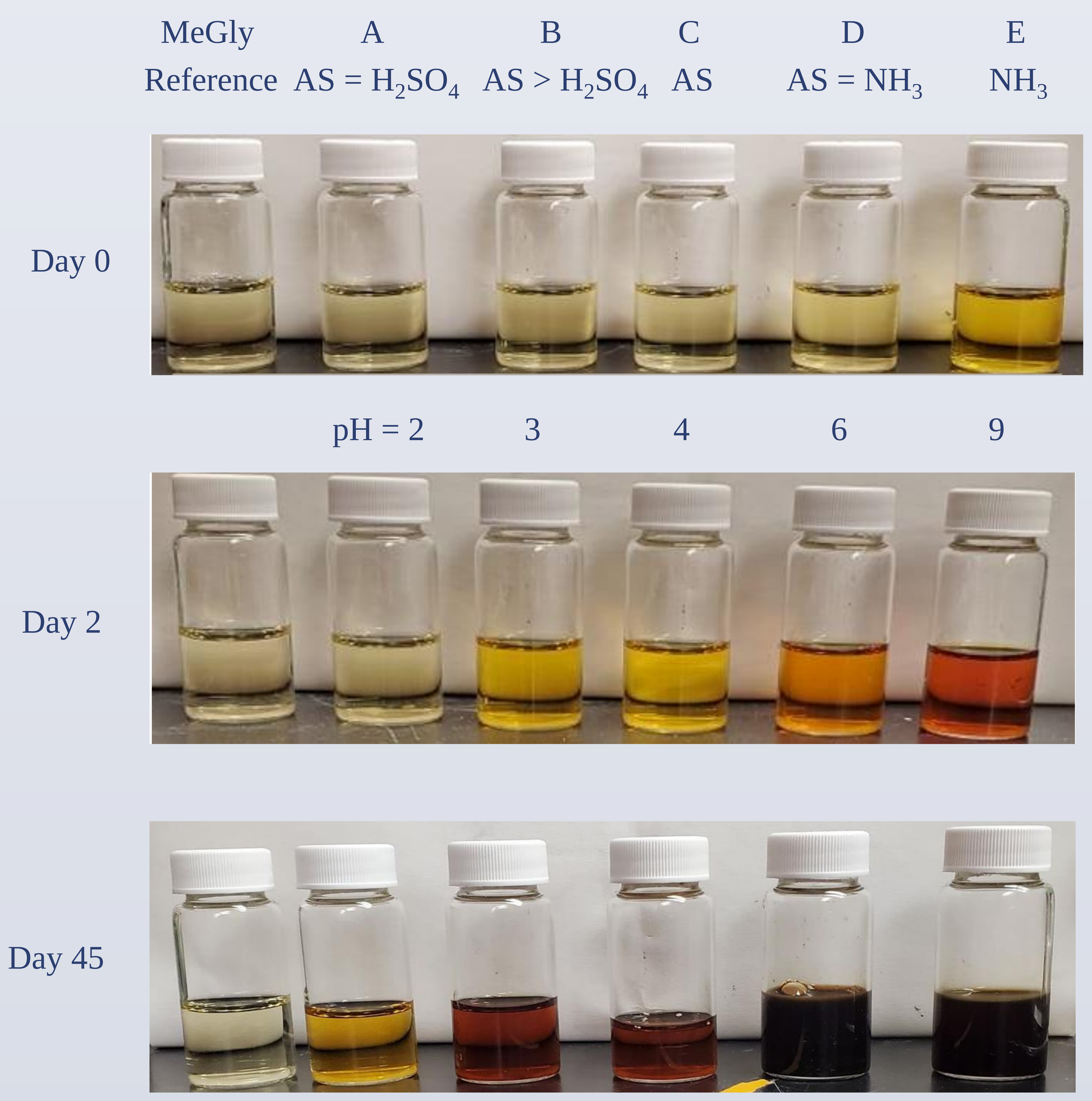
What is the effect of aerosol pH on the rate of methylglyoxal BrC formation?

II. EXPERIMENTAL SETUP

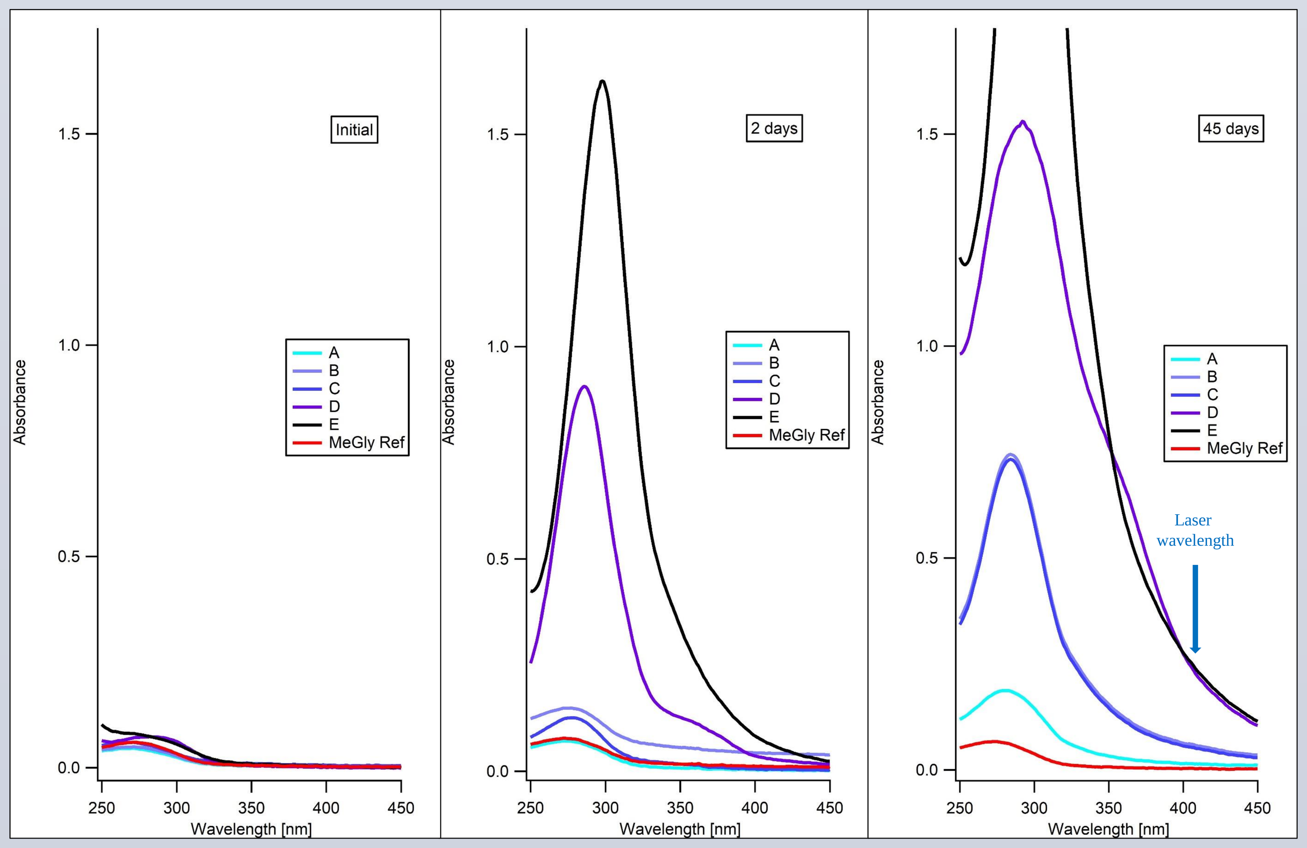


- In addition to PAS/CRD Aerosol studies, the bulk solutions were subjected to UV-Vis spectroscopy at intervals over time to monitor the dark aqueous formation of brown carbon.

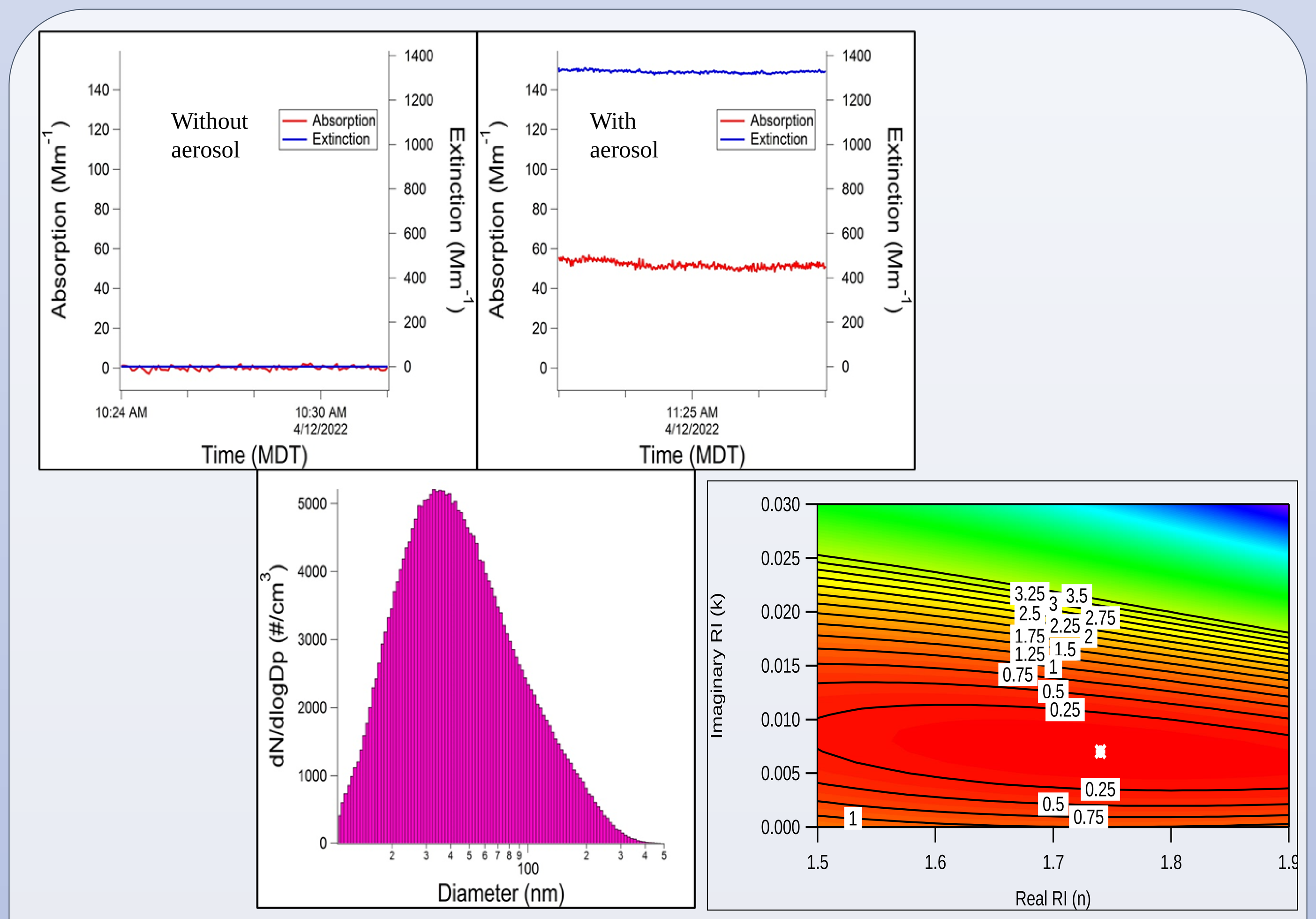
III. RESULTS



Evolution of MeGly/NH_4^+/NH_3 BrC over time at various pH levels by mixing methylglyoxal (MeGly) with varying combinations of ammonium sulfate (AS), sulfuric acid (H_2SO_4), ammonia (NH_3), and sodium sulfate (Na_2SO_4).



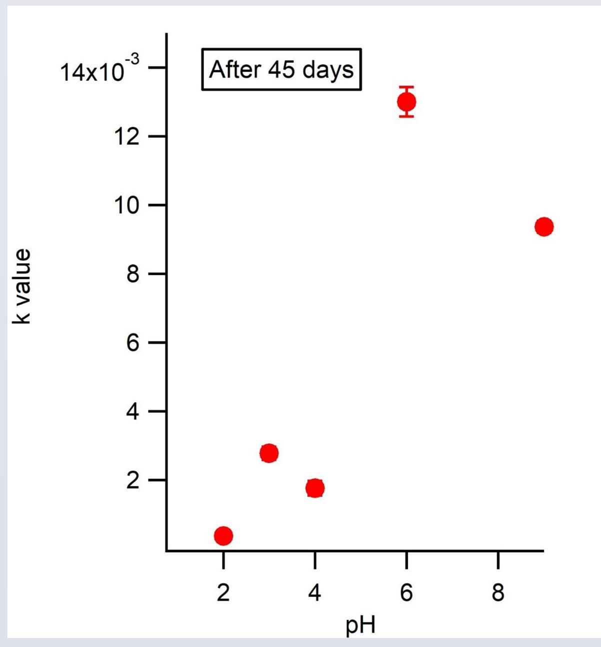
Evolution of BrC UV-Vis spectra over time.



Once absorption and extinction (top), and the size distribution (bottom left) have been measured, the optical properties, or "refractive indices," for the particles can be determined using Mie Theory (bottom right). Because the refractive index is a fundamental property of the aerosol, these values can be used to calculate optical effects of BrC under various atmospheric conditions.

$$R.I. = n + ik$$

Extinction Absorbance



Substance	*k* value
Ammonium sulfate	~0
Our BrC	**0.0004 – 0.013**
Nigrosin	0.19 – 0.24
BC	0.44 – 0.79

Imaginary value of refractive index, measured after 45 days of dark aging, as a function of pH.

IV. CONCLUSIONS

- We find absorption increases overall as the solutions age in the dark.
- We find that brown carbon produced from methylglyoxal and ammonium/ammonia solutions display higher rates of browning as the pH of their reactants is increased
- Presence of ammonia increases *k* value while high concentrations of sulfuric acid decreases *k* value
- Atmospheric aerosol is found to exist at acidic pH levels < 4; this can help constrain our models of aerosol absorption. [6]
- By retrieving the refractive indices of aerosols produced and reacted under varying conditions of atmospheric composition, we can improve prediction of aerosols' effect on radiative balance, air quality, and climate variability and change.

V. REFERENCES

[1] NOAA. (2015). The Chemistry of Atmospheric Brown Carbon. Climate Program Office.

[2] Fu, T., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., & Henze, D. K. (2008). Global budgets of atmospheric glyoxal and methylglyoxal , and implications for formation of secondary organic aerosols. 113.

[3] Loeffler, K. W., Koehler, C. A., Paul, N. M., & De Haan, D. O. (2006). Oligomer formation in evaporating aqueous glyoxal and methyl glyoxal solutions. Environmental Science and Technology, 40(20), 6318–6323.

[4] de Haan, D. O., Jimenez, N. G., de Loera, A., Cazaunau, M., Gratien, A., Pangui, E., & Doussin, J. F. (2018). Methylglyoxal Uptake Coefficients on Aqueous Aerosol Surfaces. *Journal of Physical Chemistry A*, *122*(21), 4854–4860. https://doi.org/10.1021/acs.jpca.8b00533

[5] Powelson, M. H., Espelien, B. M., Hawkins, L. N., Galloway, M. M., & De Haan, D. O. (2014). Brown carbon formation by aqueous-phase carbonyl compound reactions with amines and ammonium sulfate. Environmental Science and Technology, 48(2), 985–993.

[6] Freedman, Ott, and Marak. (2019). Role of pH in Aerosol Processes and Measurement Challenges. Journal of Physical Chemistry A, 123(7), 1275–1284.

VI. ACKNOWLEDGEMENTS

This work was partially funded by NASA grant and by CIRES.