Extreme pH Affects the Formation and Destruction of Light Absorbing Brown Carbon Aerosol

Impact of pH on the Formation and Bleaching of Brown Carbon Aerosol

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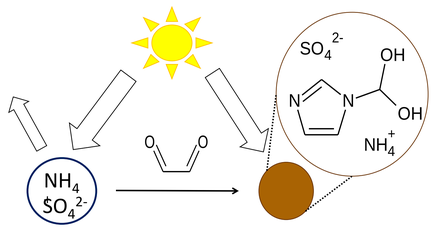
Introduction

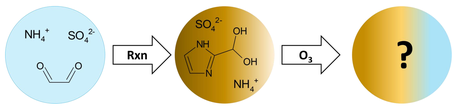
Objective: Determine optical and chemical properties of absorbing organic aerosol, or Brown Carbon (BrC), as it is oxidized by ozone under atmospherically relevant pH conditions

Motivation:

- The Brown Carbon budget, particularly its lifetime and magnitude of absorption, are highly uncertain
- Di-carbonyl compounds, such as glyoxal, can react with N-containing compounds to form UV-Vis absorbing BrC aerosol

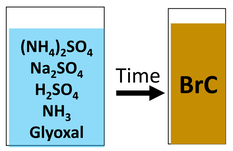


- Little is known about the rate and extent of BrC bleaching due to oxidation

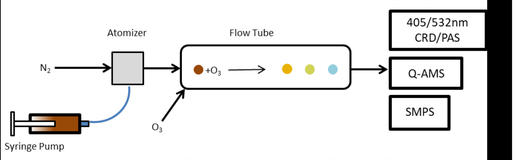


- There is a need to simulate both BrC formation and oxidation under more atmospherically relevant pH conditions

Methods

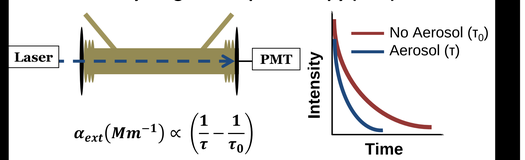


- Solutions of various inorganics and glyoxal are mixed and either aged or analyzed immediately
- Aged solutions are analyzed over time with a UV-Vis spectrometer
- BrC solutions are pH adjusted post-reaction and atomized, passing BrC aerosol into a O_3 flow tube to simulate atmospheric aging.

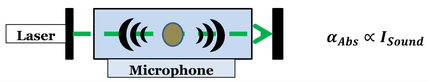


Instrumentation for Determination of Optical Properties

Cavity-Ring Down Spectroscopy (CRD)

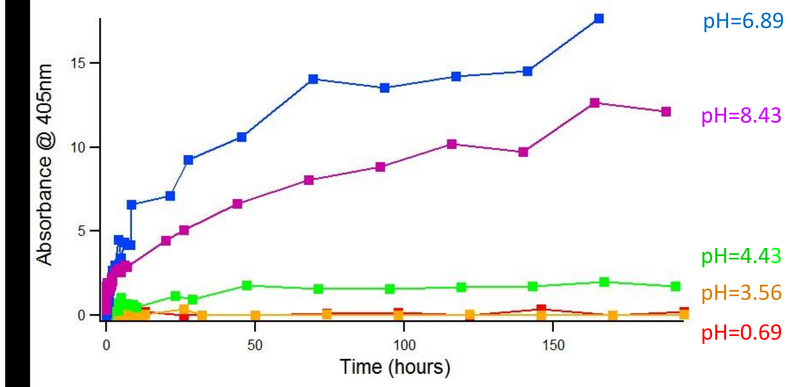


Photoacoustic Spectroscopy (PAS)



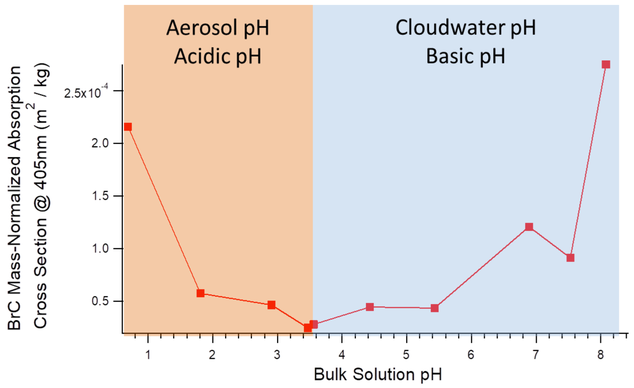
BrC Formation Under Various pH Conditions

Brown Absorption Grows in Over Time in Aqueous Solutions



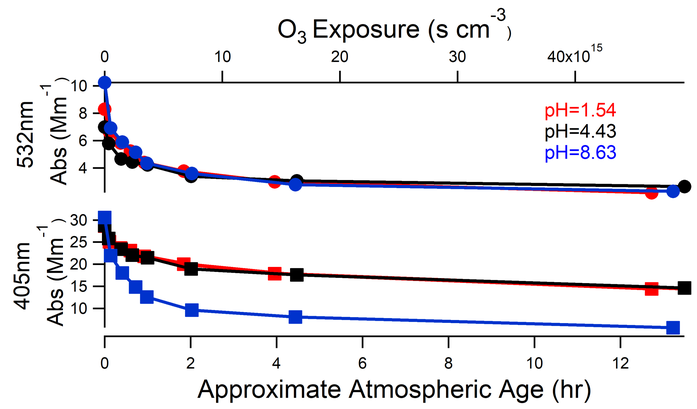
- Rate of formation of BrC Chromophores increases with pH
  - Acidic solutions (<pH=4) inhibit BrC formation

BrC Formation in Aerosols Favors Extreme pH Conditions

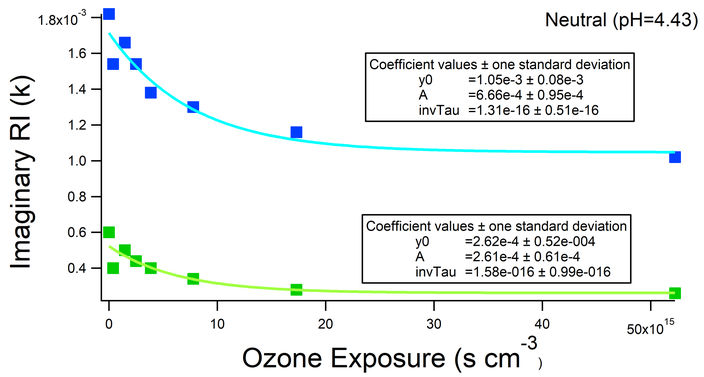


- BrC Absorption Detected Using Photoaccoustics
  - Most absorbing BrC formed in highly acidic and basic conditions
- Rapid drying of aerosol samples likely caused MAC values to be small

Aerosol Bleaching During Ozonolysis



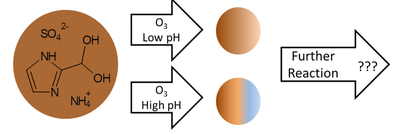
- BrC Absorption decays quickly over 12 hour timescale
- Recalcitrant fraction due to O_3 resistant BrC or new BrC formation
  - Rate and extent of aerosol bleaching varies with wavelength
  - Acidic pH Conditions limits BrC bleaching at shorter wavelengths



- We retrieve refractive indexes (RI) for BrC material using a full aerosol size distribution
- Imaginary RI, while low, matches similar retrieved RI's
- Psuedo-1st order reaction used to retrieve ozonolysis rate constant and O_3 uptake coefficients

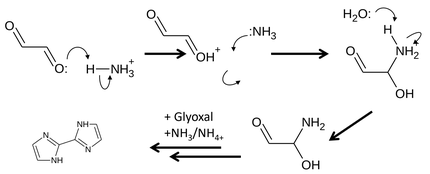
Conclusions and Significance

- pH affects both the formation and bleaching of Brown Carbon
- BrC formation is favored under extreme pH conditions when in the aerosol phase
- First values for pH dependent RI and O_3 uptake coefficients reported for glyoxal-based BrC
- Subsequent reactions and reactions with other atmospheric oxidants need to be further constrained

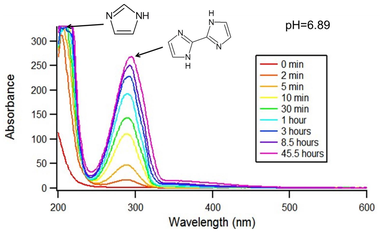


Additional Information

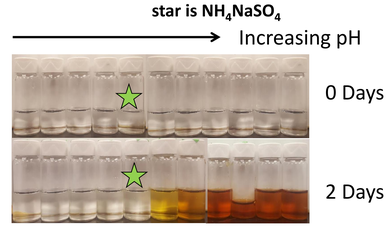
Acid Catalyzed BrC Formation Mechanism



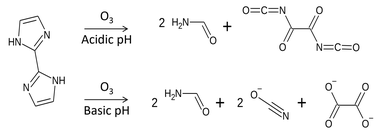
UVVis Spectrum of Aging Bulk Phase BrC Solution



Evolution of BrC samples over time. Sample with green star is NH_4NaSO_4



Example of pH dependent Ozonolysis products



PASCARD Validation

	Ammonium Sulfate	Nigrosin
Our 405nm Laser	1.53 ± 0i	1.55 ± 0.18i
Literature 405nm	1.53 ± 0i	1.66 ± 0.19i
Our 532nm Laser	1.53 ± 0i	1.63 ± 0.29i
Literature 532nm Laser	1.53 ± 0.01i	1.68 ± 0.32i

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References: Volkamer, R. et al. Geophys. Res. Lett. 2007, 34, L19807., Rossignol, S et al. *Environ. Sci. Technol.* **2014**, *48* (6), 3218–3227., Schill, G. P. et al. *Environ. Sci. Technol.* **2014**, *48* (3), 1675–1682, Zarzana, K. J.; et al. *Environ. Sci. Technol.* **2012**, *46* (9), 4845–4851, De Haan et al. *Environ. Sci. Technol.* **2017**, *51* (13), 7458–7466. Liggio, et al. *Environ. Sci. Technol.* **2005**, *39 (6),* 1532-1541.