



Light Absorption and Chemical Composition of Primary and Secondary Organic Aerosol

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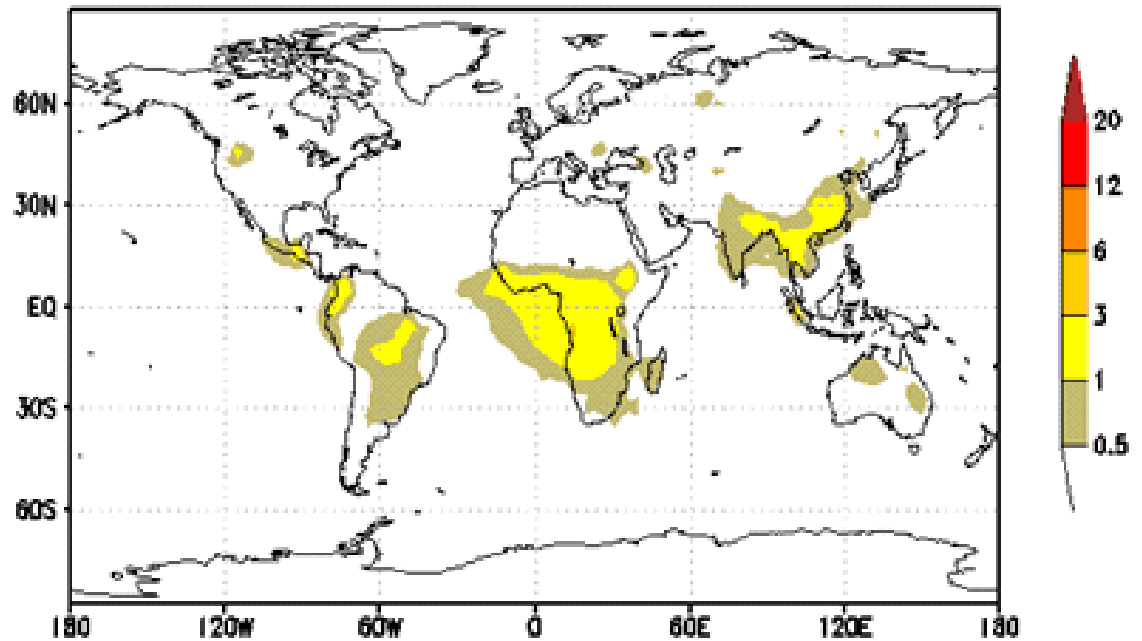
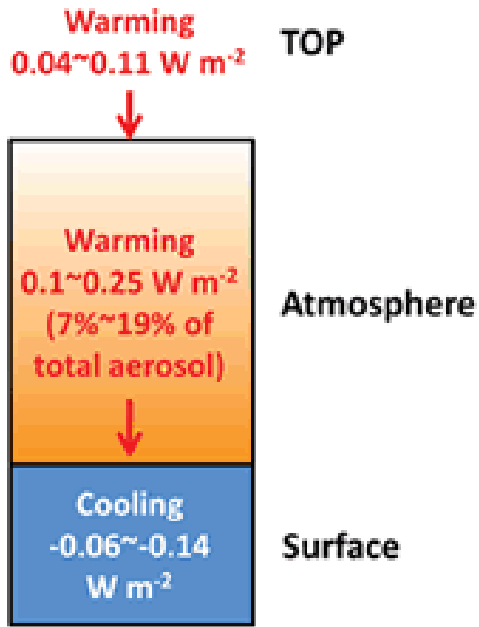
The 1st Regional GEOS-Chem Asia Meeting

Nanjing, Jiangsu, China

May 21-23, 2018

Background

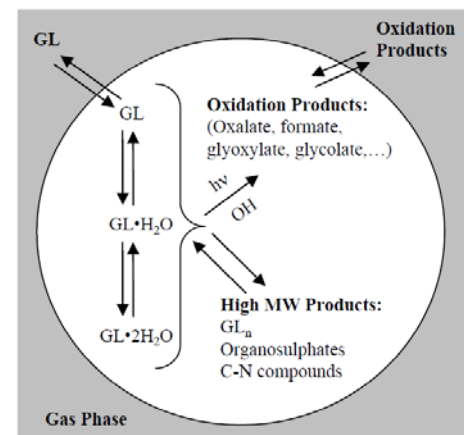
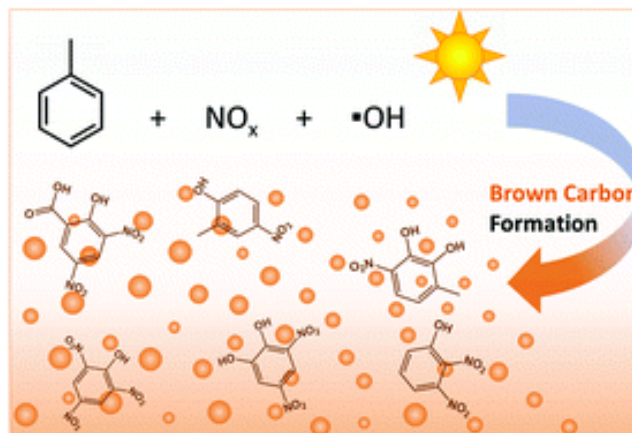
Warming Effect of BrC



- BC contributes 72% of the global atmospheric absorption
- Strong BrC contributes > 20–50% of the global atmospheric absorption over regions dominated by seasonal biomass burnings and biofuel combustion
- Overall, BrC > ¼ BC absorption on a global basis.

Background

BrC Sources



Lin et al., 2015, PCCP

Galloway et al., 2009, ACP



Background

Particle-based

VS

Extract-based

Light Absorption Measurement

Photoacoustic Spectrometer (PASS-3),
Aethalometer: b_{abs}

UV/Vis spectrometer: A_{abs}
(Solvent extraction)

Imaginary Part of the Refractive Index (k_{OA})

Mie theory:

Optimized k_{OA} resulting in best theoretical fit
to measured b_{abs}

Inputs:

BC, OA size distribution (SP2 and SMPS)
BC refractive index (existed measurements)
Real part of RI (existed measurements or
from PASS-3 scattering coefficient
measurement)

Major Uncertainties:

BC mass concentration and size distribution;
Assumptions on mixing state of OA and BC.

Empirical equation:

$$k_{\text{OA}} = \frac{\rho \times \lambda \times \text{MAC}_{\lambda}}{4 \times \pi \times \text{OM}}$$

MAC_{λ} calculation:

$$\text{Abs}_{\lambda} = (A_{\lambda} - A_{700}) \times \frac{v_l}{v_a \times L} \ln(10)$$

$$\text{MAC}_{\lambda} = \frac{\text{Abs}_{\lambda}}{C_{\text{oc}}}$$

Advantage: Reflect the absorption of pure
OM, no influence from BC or EC;

Disadvantage: Cannot reflect BrC absorption
in suspended particles.



Background

Particle-based

VS

Extract-based

Composition Measurement

HR-ToF-AMS:

H:C ratio, primary
O:C ratio, secondary

PASS-3 and Aethalometer:

b_{abs}

H:C/O:C ratio vs. b_{abs}

GC-MS, LC-DAD-ToFMS:

Molecular composition

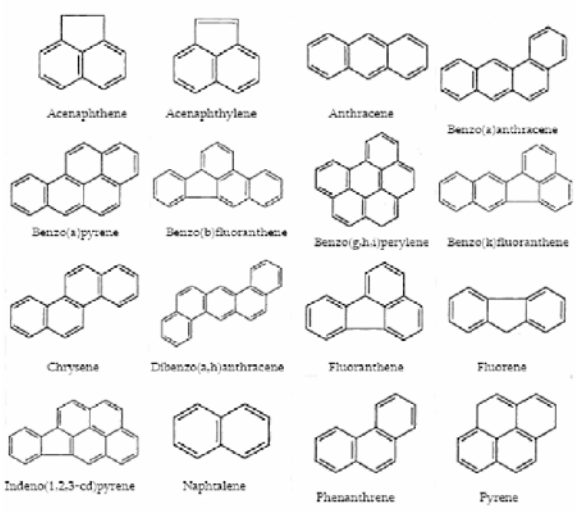
UV/Vis spectrometer:

A_{abs}

Attribute A_{abs} to light-absorbing molecules.

Background

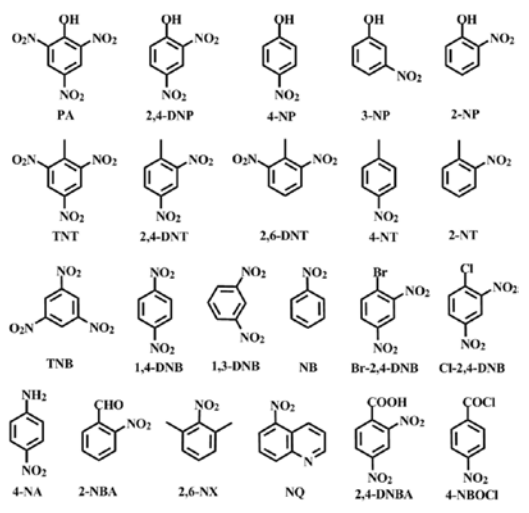
Light-absorbing Organic Molecules



PAHs

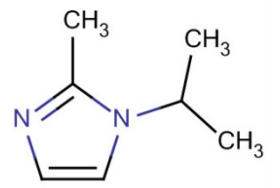
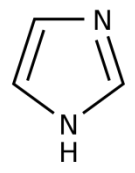
Nearly all combustion processes.....

Half-life: ~20 h



Nitro aromatics

Biomass burning;
Gas-phase oxidation



Imidazole

Reactive uptake of GL or Methyl-GL on AS

Half-life: minutes to hours



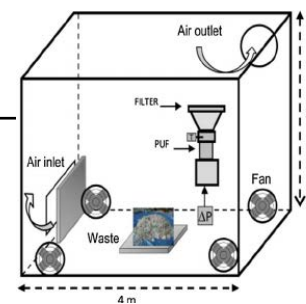
Objective

- ✓ **Light-absorbing properties of organic matter from biomass burning and SOA formation**
- ✓ **Relationship of BrC absorption vs. burn condition**
- ✓ **Contribution of BrC molecules to OA mass and bulk absorption**

Biomass burning

Sample information for prescribed and laboratory burns

Location	Fuel type	Field burn sample No.	Lab burn sample No.
Agriculture Field			
Nez Perce, ID	Kentucky Bluegrass ("KBG")	6	3
Nez Perce, ID	Wheat stubble ("Wheat")	2	3
Walla Walla, WA	Chemically fallowed wheat stubble ("Wheat + Herbicide")	6	3
Forest Field			
Eglin Air Force Base, FL	Grass/forb/shrub/wood debris ("Forest burn")	4	9
Eglin Air Force Base, FL	Grass/forb/shrub ("Grass burn")	2	0

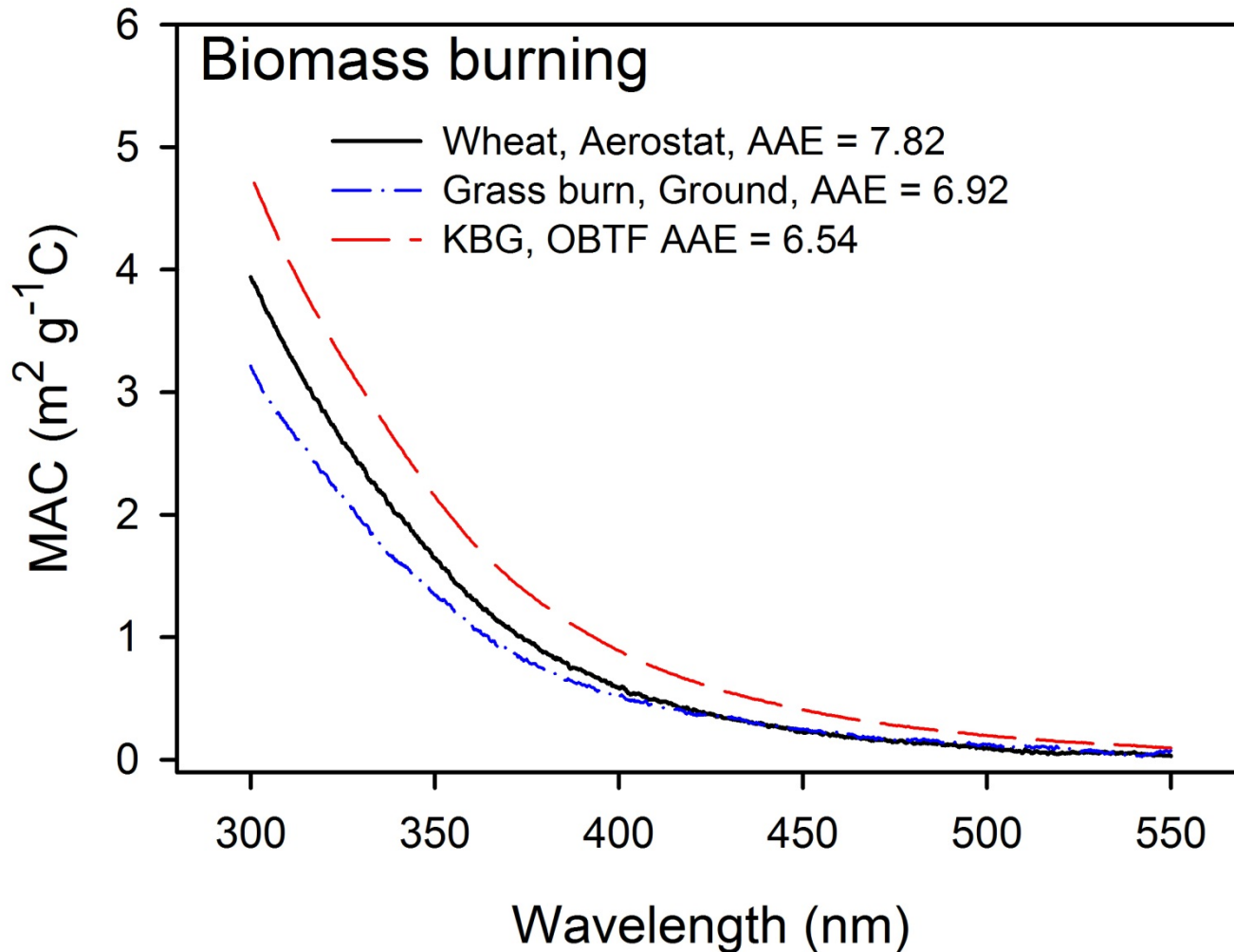


Open Burn Test Facility (OBTF)



Biomass burning

Typical absorption spectra



The MAC at 365 nm was usually used as proxy for BrC absorption.

1. Far from short UV region, avoiding the interference from non-organic compounds in aqueous extracts;
2. High correlated with the sum of absorption over 300 – 400 nm.



Biomass burning

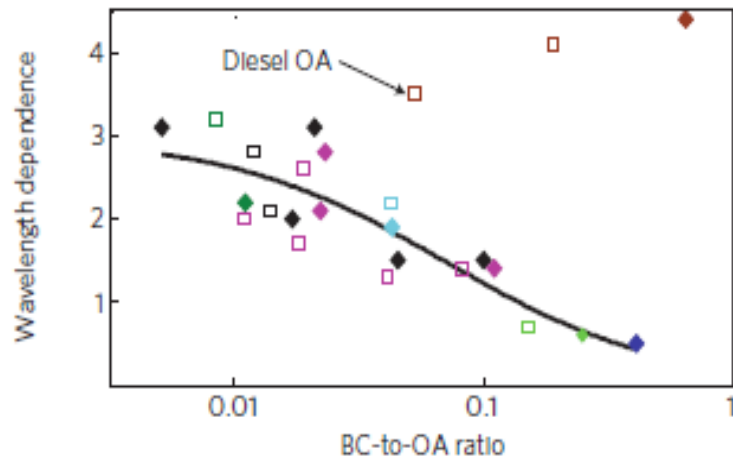
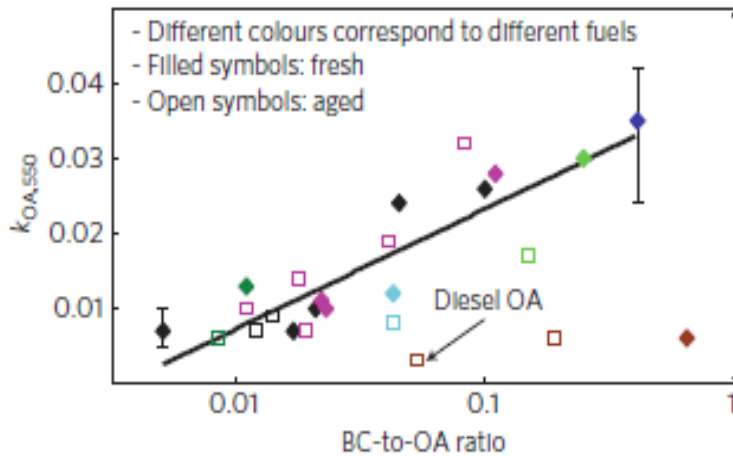
Light absorbing properties of methanol extractable OC from biomass burning

Fuel type	Sampling type	EC/OC	Extraction Efficiency (%)	MAC ₃₆₅ (m ² g ⁻¹ C)	AAE (300 - 550 nm)
KBG	Aerostat	0.036 ± 0.011	93.4 ± 0.84	1.38 ± 0.033	7.03 ± 0.068
	Ground	0.032 ± 0.015	94.7 ± 1.91	1.32 ± 0.17	7.12 ± 0.15
	OBTF	0.17 ± 0.091	94.5 ± 2.01	1.80 ± 0.15	6.25 ± 0.26
Wheat	Aerostat	0.084	90.1	1.19	7.82
	Ground	0.018	90.8	1.06	8.11
	OBTF	0.33 ± 0.18	94.5 ± 2.97	1.28 ± 0.12	5.28 ± 0.96
Wheat + Herbicide	Aerostat	0.046 ± 0.019	90.8 ± 3.59	1.05 ± 0.059	7.77 ± 0.51
	Ground	0.016 ± 0.0081	95.1 ± 1.18	1.00 ± 0.076	7.93 ± 0.64
	OBTF	0.13 ± 0.022	91.5 ± 3.17	2.09 ± 0.12	5.83 ± 0.69
Forest burn	Aerostat	0.041	96.5	1.10	7.08
	Ground	0.026 ± 0.0095	97.5 ± 1.13	1.04 ± 0.084	7.37 ± 0.078
	OBTF	0.21 ± 0.16	97.0 ± 1.87	1.13 ± 0.15	7.36 ± 0.59
Grass burn	Aerostat	0.086	95.1	0.90	6.43
	Ground	0.089	95.3	0.97	6.92

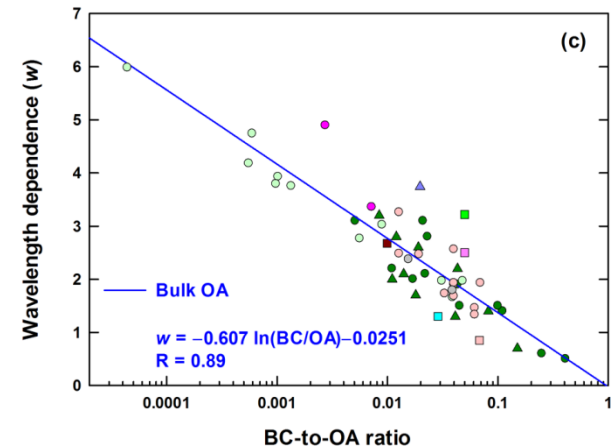
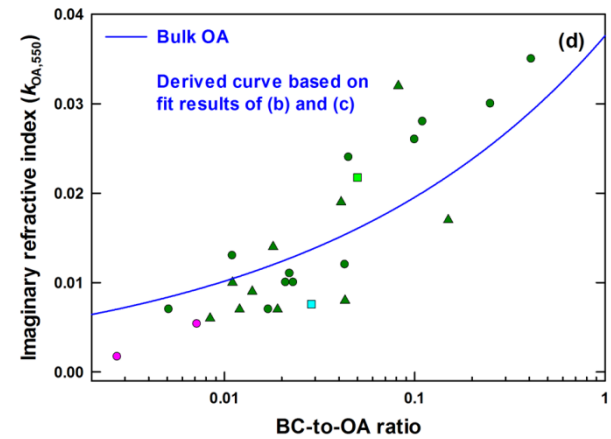
Xie et al., 2017, Sci. Rep.

Biomass burning

Dependence of Light Absorption on BC-OC ratio



*Saleh et al., 2014,
Nature. Geosci.*

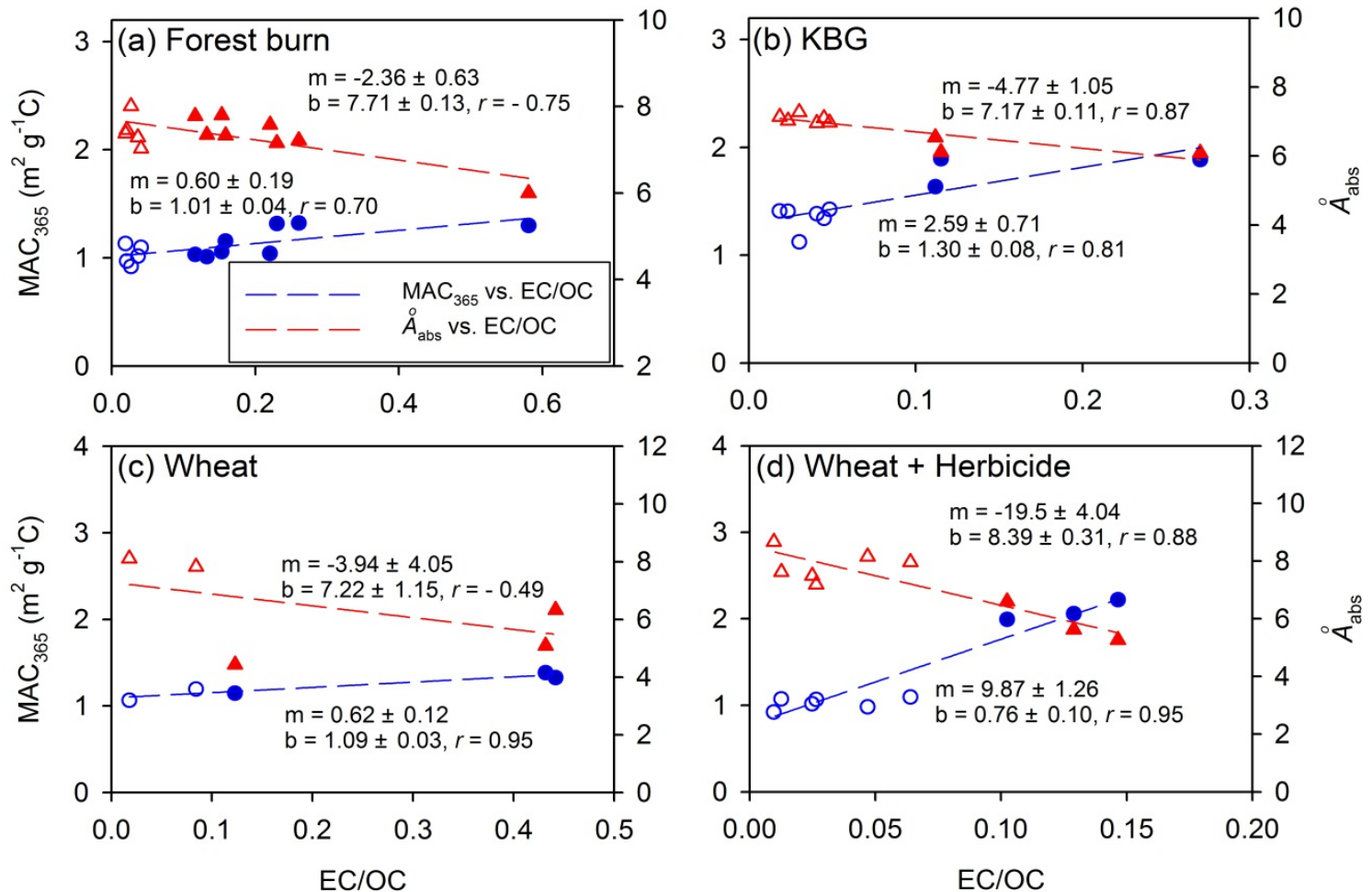


*Lu et al., 2015, Environ.
Sci. Technol.*



Biomass burning

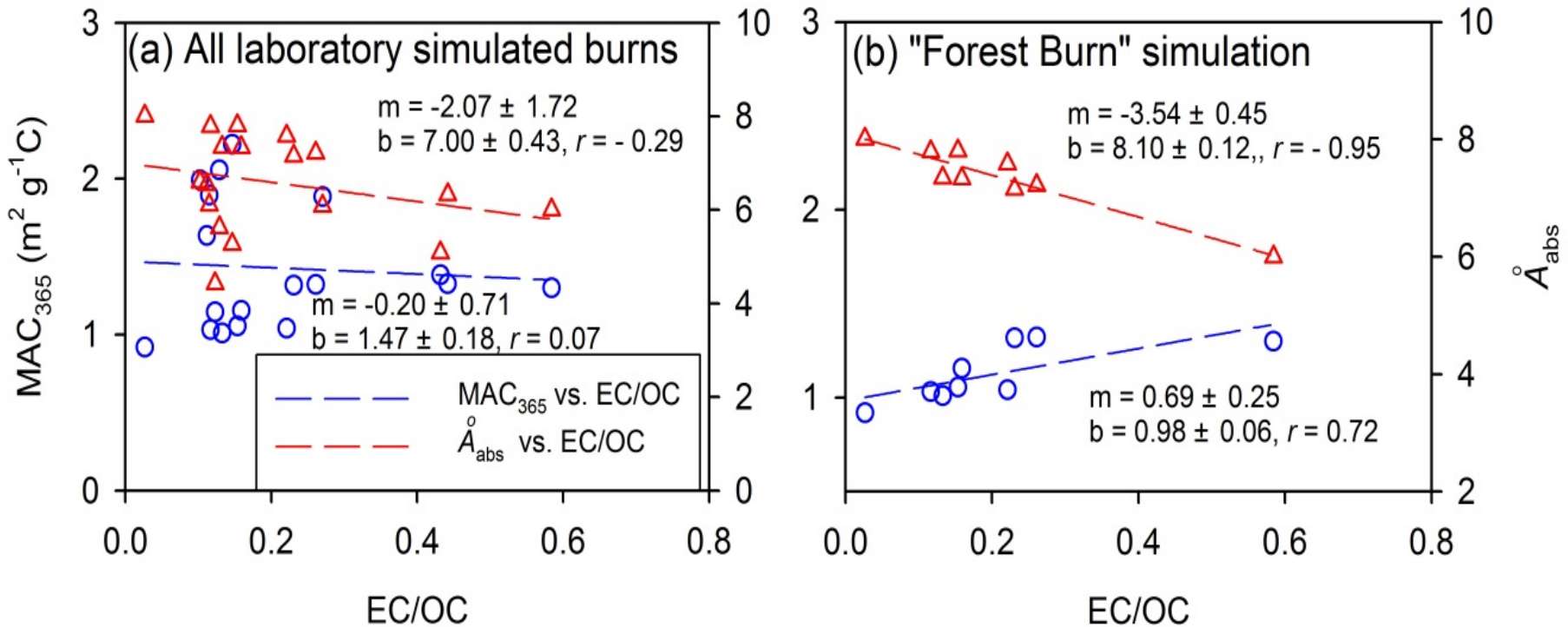
Dependence of Light Absorption on EC-OC ratio



Xie et al., 2017, Sci. Rep.

Biomass burning

Dependence of Light Absorption on EC-OC ratio



The light absorption of BrC from biomass burning is not only dependent on **burn condition**, but also **fuel species**.



Biomass burning

Similar fuel species burned in different seasons

Experiment	Phase	Fuels	EC/OC	MAC ₃₆₅ (m ² g ⁻¹ C)	MAC ₅₅₀ (m ² g ⁻¹ C)	Åabs
Burn 1	Flaming	hardwood/loblolly pine (N=3)	0.042 ± 0.014	1.47 ± 0.25	0.15 ± 0.065	5.68 ± 0.70
	Smoldering	hardwood/loblolly pine (N=3)	0.0098 ± 0.0024	1.00 ± 0.11	0.054 ± 0.015	6.83 ± 0.52
Burn 2	Flaming	hardwood/loblolly pine (N=4)	0.049 ± 0.011	4.07 ± 0.15	0.17 ± 0.0051	7.38 ± 0.069
	Smoldering	hardwood/loblolly pine (N=4)	0.0075 ± 0.0026	3.25 ± 0.35	0.12 ± 0.033	7.95 ± 0.22

Fuel: hardwood/loblolly pine
Burn type: Lab burn (OBTF)

Burn 1:
Date: 04/16/2016
Temp: 12 °C
RH: 49%

Burn 2:
Date: 07/14/2016
Temp: 29 °C
RH: 70%

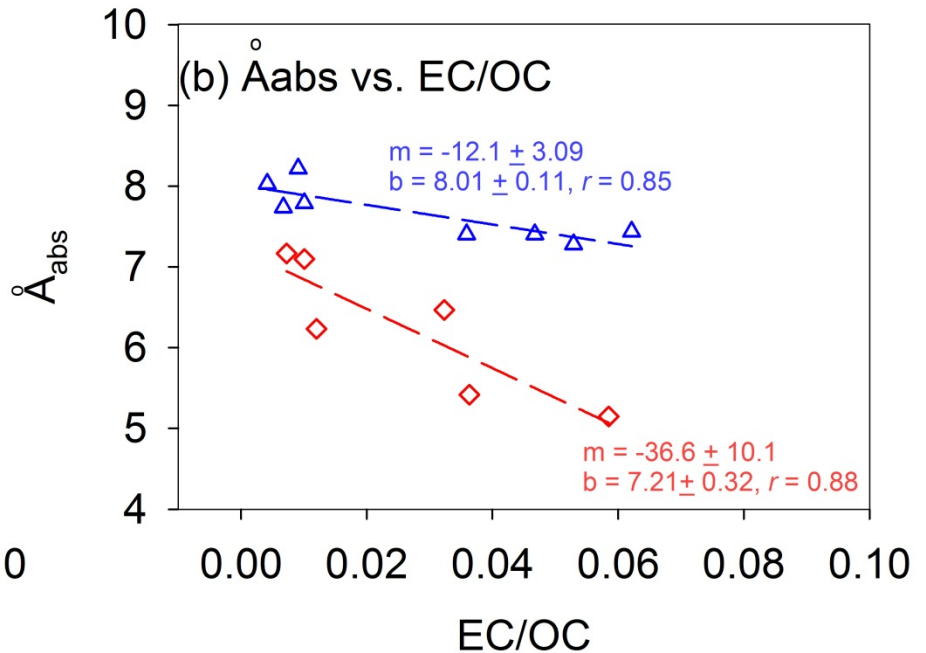
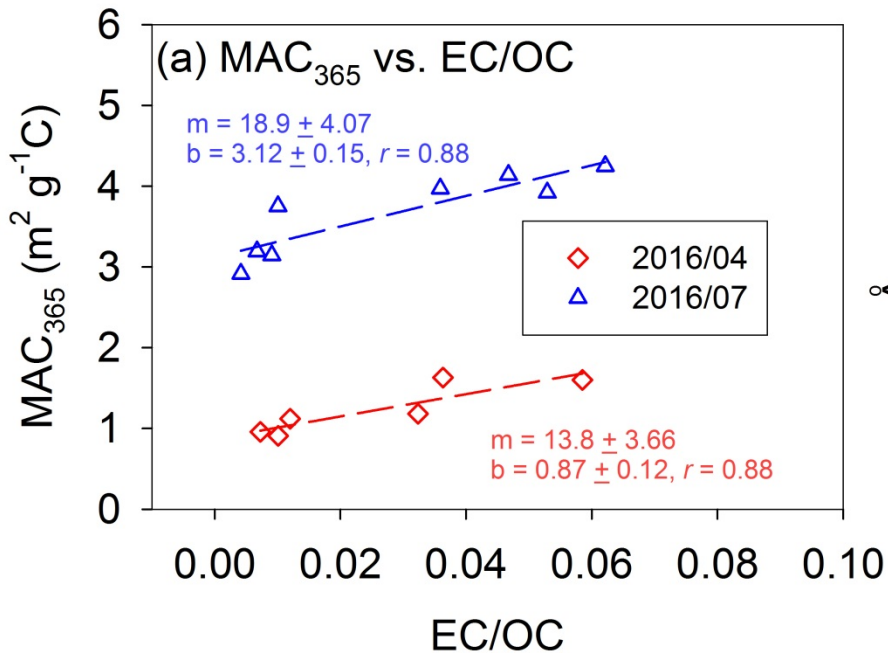


US EPA at Research Triangle Park, NC



Biomass burning

Similar fuel species burned in different seasons

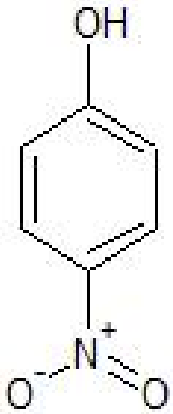


Xie et al., submitted

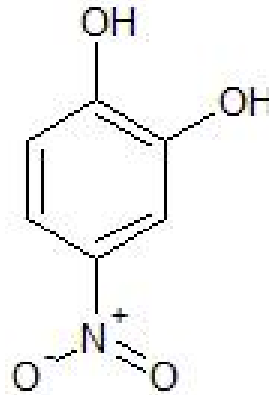
Ambient temperature might also have an impact on BrC absorption of biomass burning.

Biomass burning

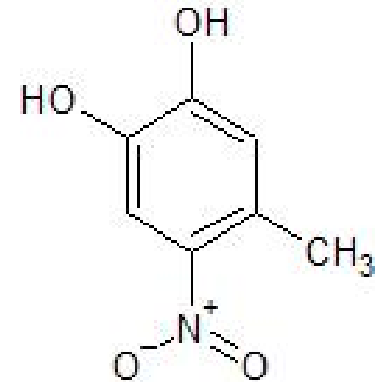
Molecular Composition of BrC



4-Nitrophenol
(C₆H₅NO₃)



4-Nitrocatechol
(C₆H₅NO₄)



Methyl-nitrocatechol
(C₇H₇NO₄)

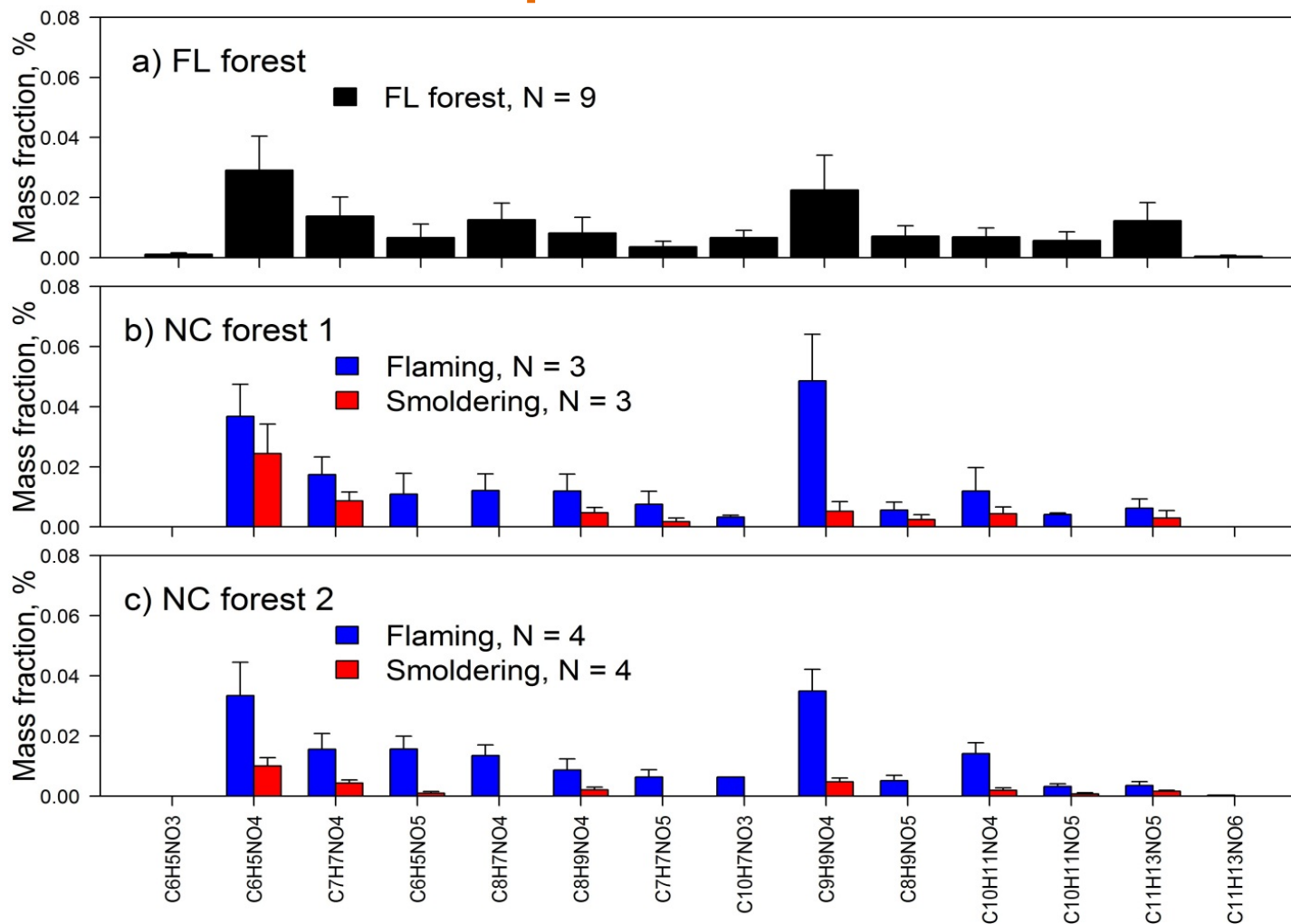
Biomass burning impacted atmosphere:

Cloud water, (**Desyaterik et al., 2013, JGR**)

Ambient aerosol, (**Claeys et al., 2012; Zhang et al., 2013, EST; Teich et al., 2017, EST**)

Biomass burning

Molecular composition of Nitroaromatics



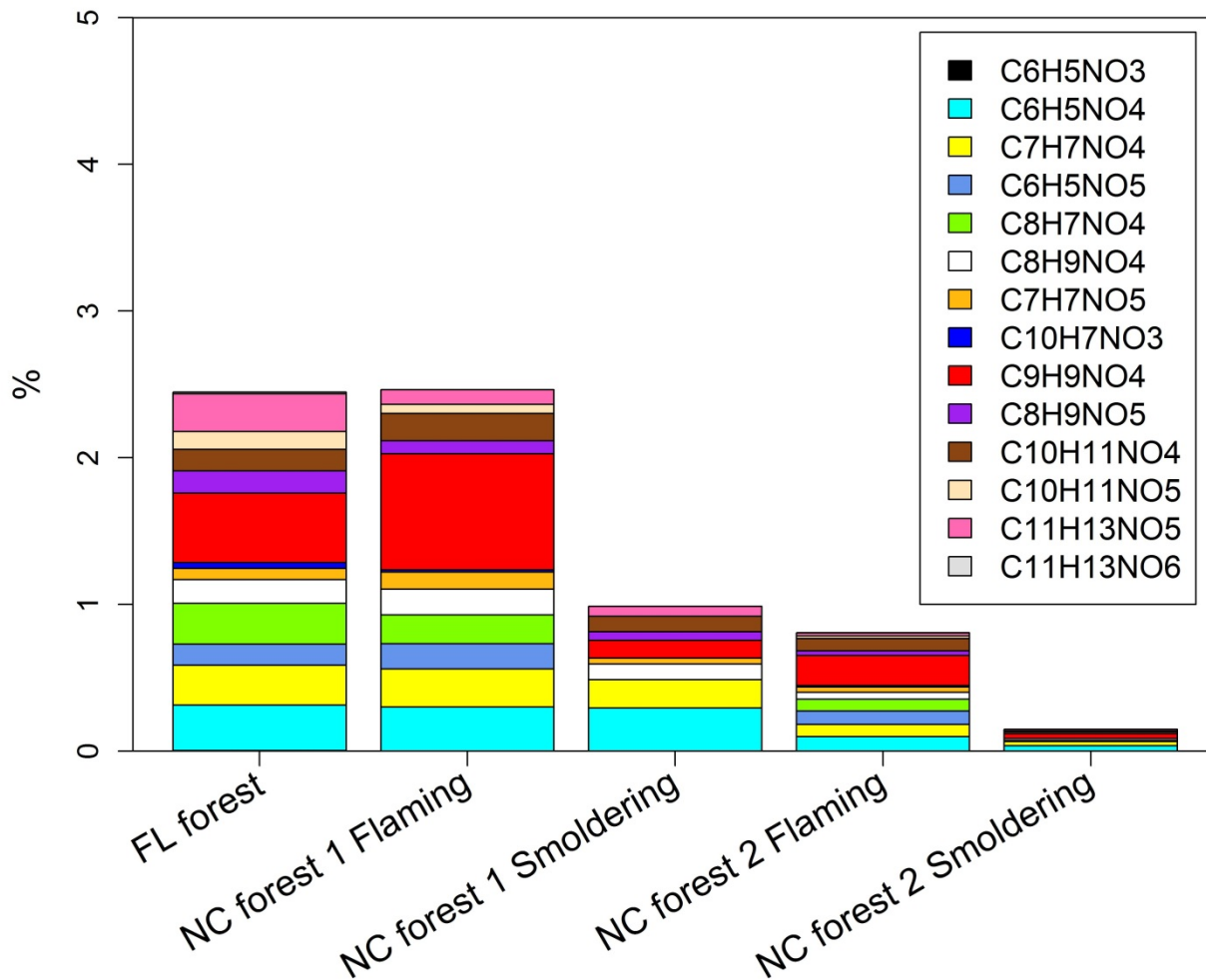
Mass contribution to OA: 0.037 – 0.21%

Xie et al., submitted



Biomass burning

Contribution to bulk Abs_{365}



Abs_{365} contribution: 0.12 – 2.44%

Mass contribution to OA: 0.037 – 0.21%

Nitroaromatics are strong BrC chromophores.



Chamber reactions



Biogenic VOCs: α -pinene, isoprene and β -caryophyllene;

Aromatic VOCs: 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, *m*-xylene, toluene, ethylbenzene, benzene, naphthalene and *m*-cresol;

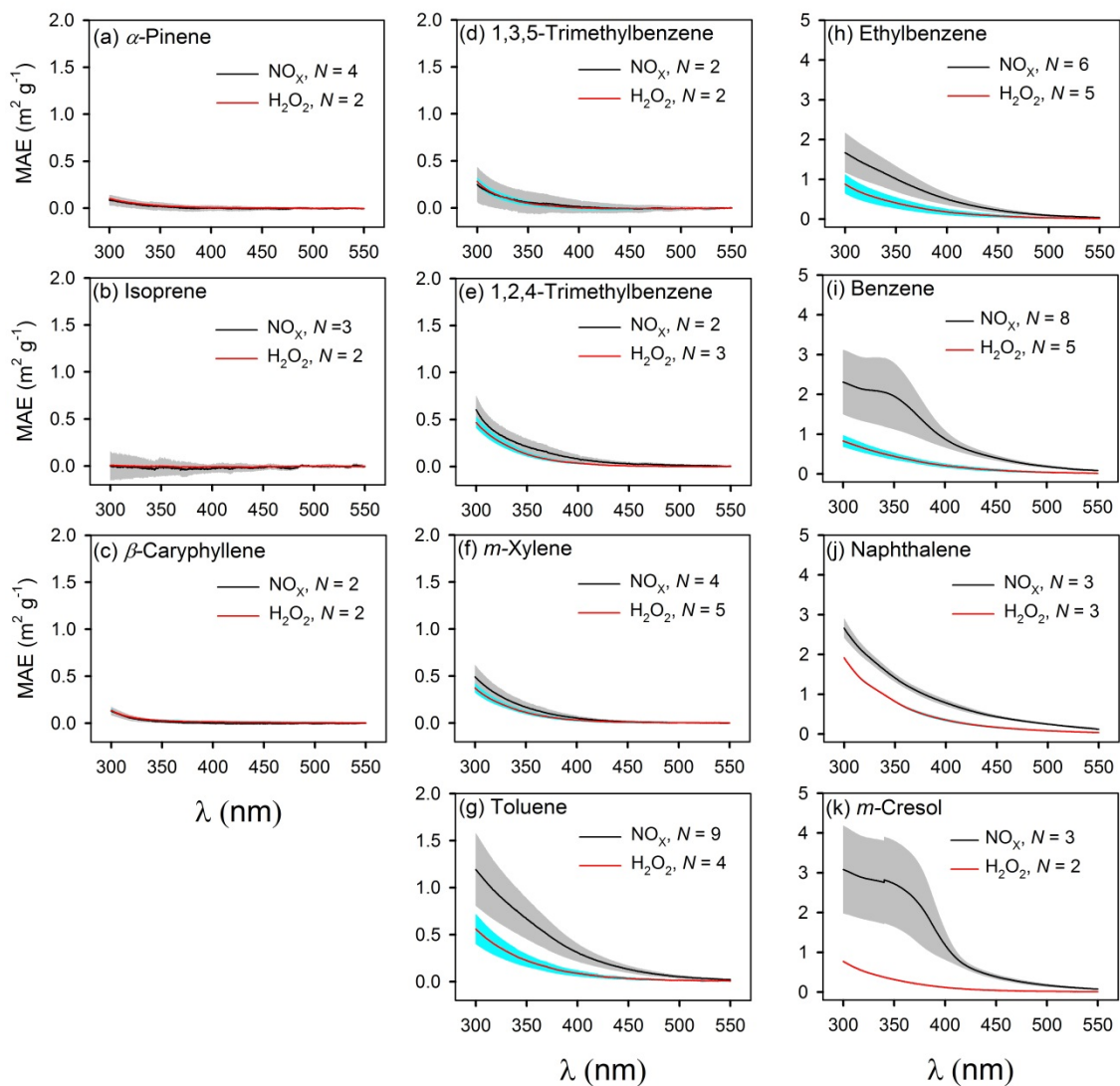
Aerosol Seed: Neutral ammonium sulfate;

Oxidant: NO_x ; $\cdot\text{OH}$ (H_2O_2)

Smog chamber at US EPA, RTP, NC

Chamber reactions

Light absorption spectra

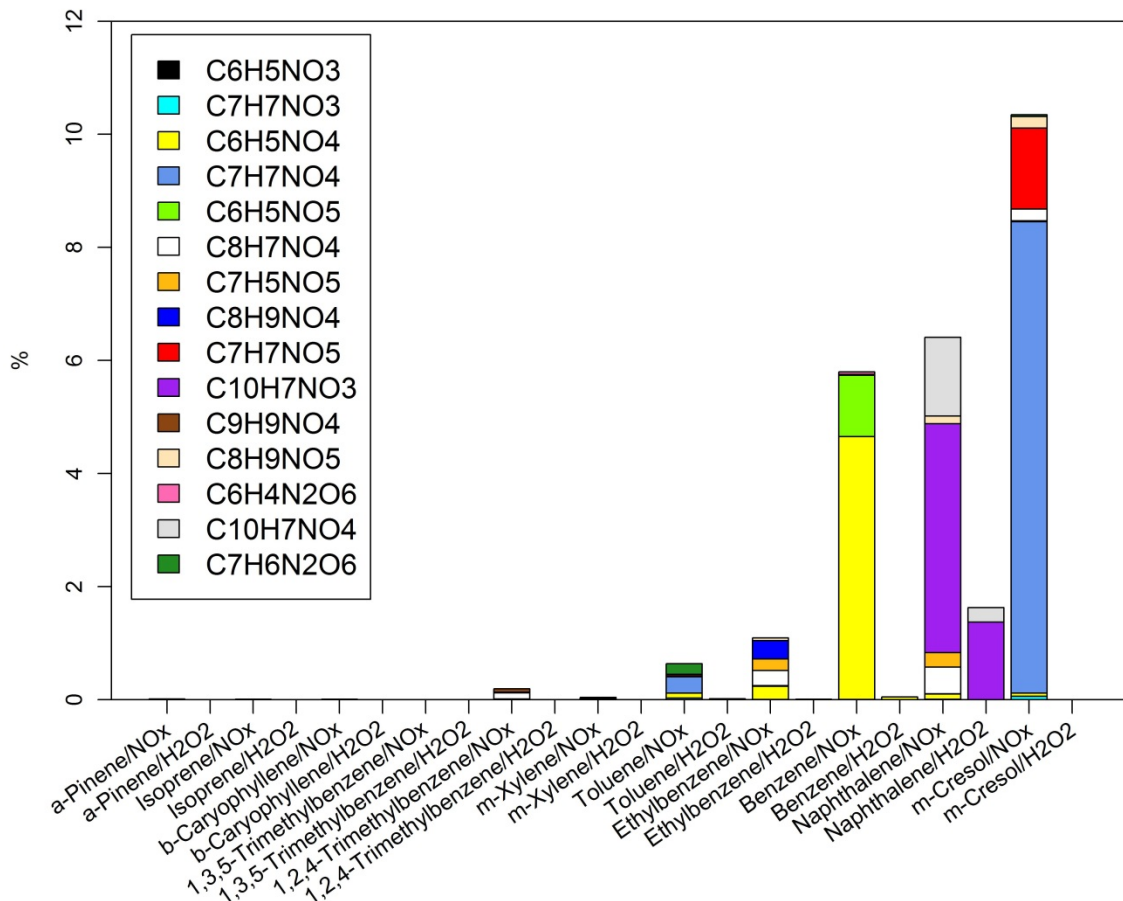


1. Photo-oxidation of **biogenic VOCs** may **not** generate light-absorbing SOA on **neutral seed** $[(\text{NH}_4)_2\text{SO}_4]$;
2. The **aromatic SOA** contains BrC, for which the **light-absorption** is sensitive to differences in molecular structures of SOA precursors and the **availability of NO_x** ;
3. Reveals the potential significance of **aromatic VOCs** as important **precursors** for secondary BrC;
4. **Secondary BrC** should have more impacts on aerosol absorption in **urban atmosphere** with abundant **aromatic VOCs** and **NO_x** .



Chamber reactions

Molecular Composition of Nitroaromatics

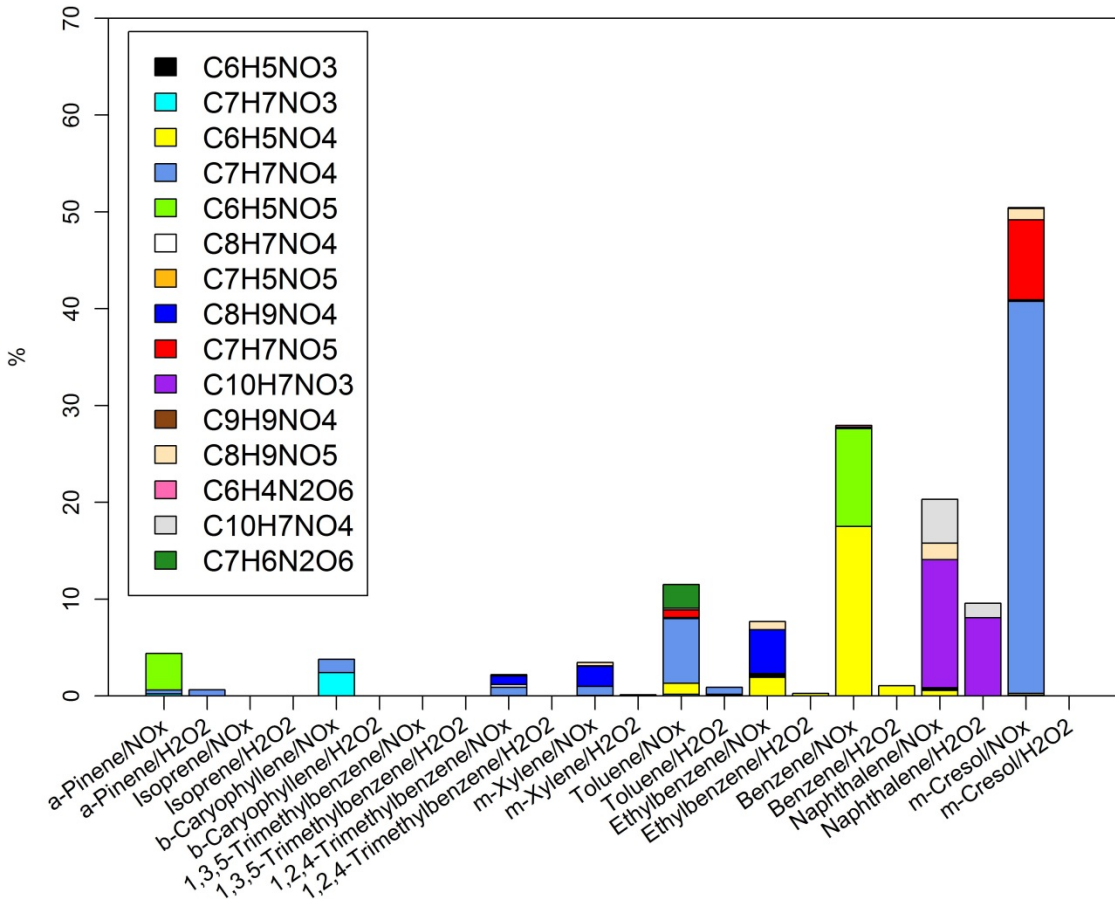


1. Nitroaromatics were mostly identified in reactions with NO_x, except Naphthalene/H₂O₂ reactions.
2. The *m*-cresol/NO_x SOA has the highest average mass contribution from total NACs ($10.4 \pm 6.74\%$), followed by naphthalene/NO_x ($6.41 \pm 2.08\%$) and benzene/NO_x ($5.81 \pm 3.82\%$) SOA
3. Formula with high mass contributions, *m*-cresol/NO_x SOA : C₇H₇NO₄ and C₇H₇NO₅; naphthalene/NO_x: C₁₀H₇NO₃ and C₁₀H₇NO₄; benzene/NO_x: C₆H₅NO₄ and C₆H₅NO₅.



Chamber reactions

Contribution to bulk Abs₃₆₅



1. m-Cresol/NO_x: 50.4%
2. Naphthalene/NO_x: 20.3%
3. Naphthalene/H₂O₂: 9.58%
4. Benzene/NO_x: 27.9%
5. Ethylbenzene/NO_x: 7.69%
6. Toluene/NO_x: 11.5%

Mass contribution: up to 10%



Chamber reactions

Uncertainties

1. Surrogates
2. Chamber reactions vs. Atmospheric photo-chemical reactions
3. For source apportionment, the impact from atmospheric processing (G/P partitioning, photo-bleaching) and other sources should be evaluated.



Future work

1. Identification of BrC chromophores in both emission and ambient aerosols;
2. HMW and highly conjugated compounds
3.



Thanks!