

# Composition and Chemical Identity of BrC

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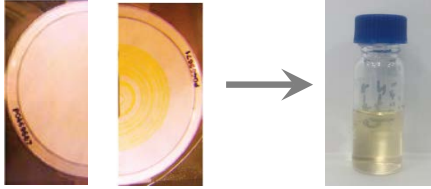
<sup>2</sup> *Department of Chemistry, University of California, Irvine, CA*

<sup>3</sup> *Weizmann Institute of Science, Rehovot, Israel*



# LC-PDA-MS Analysis

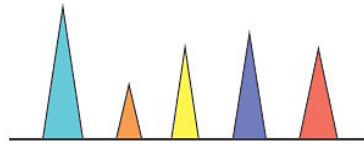
Lin et al, 2015, *PCCP*



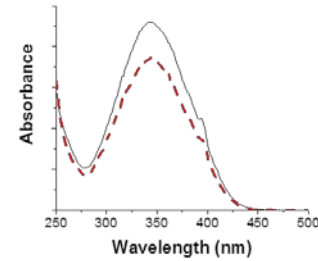
SOA  
(Toluene/OH/NO<sub>x</sub>)

>10 μg

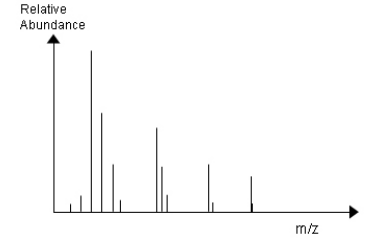
HPLC  
Separation



UV-Vis  
spectrometer



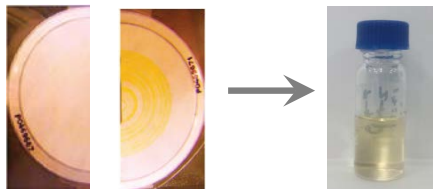
High resolution  
ESI/APPI-MS, MS<sup>n</sup>



- Spectrum and formula for separated BrC fractions

# LC-PDA-MS Analysis

Lin et al, 2015, *PCCP*



SOA  
(Toluene/OH/NO<sub>x</sub>)

>10 μg

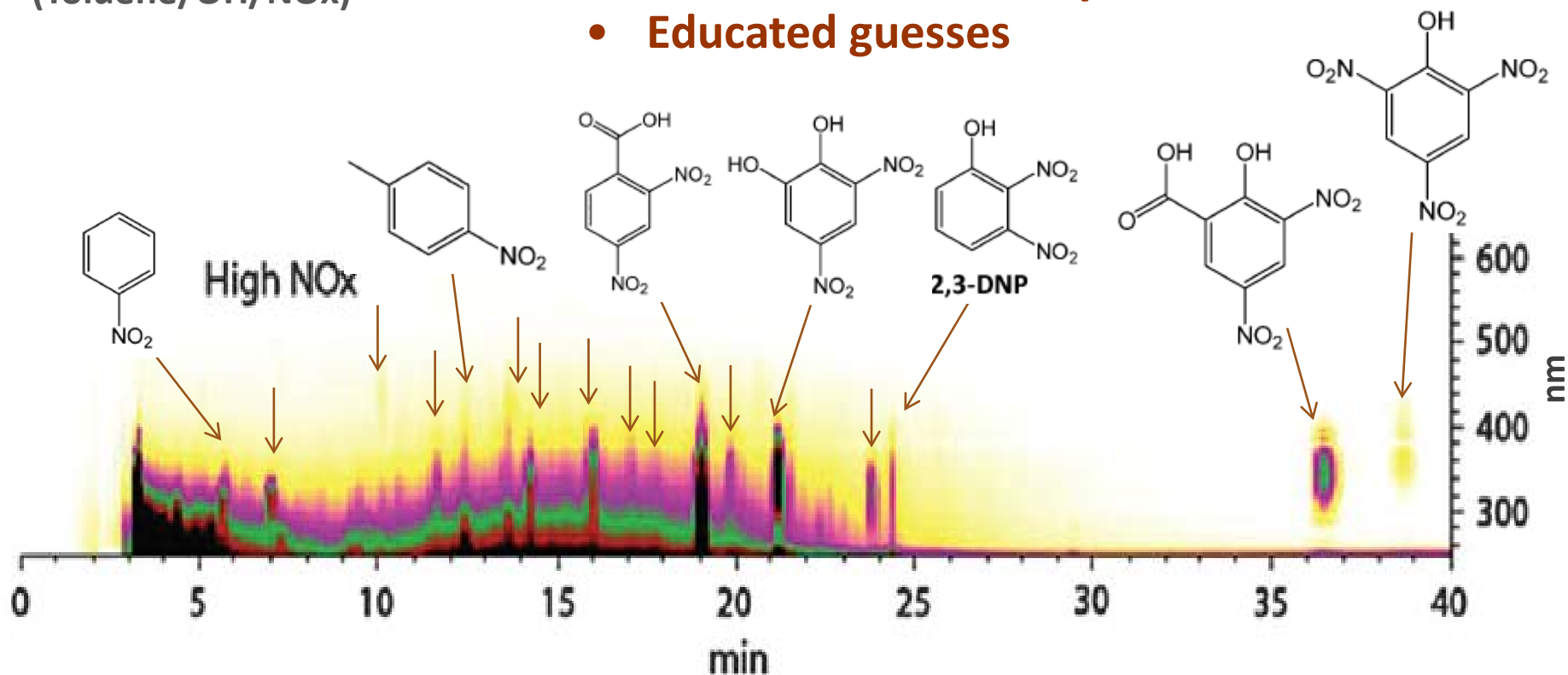
HPLC  
Separation

UV-Vis  
spectrometer

High resolution  
ESI/APPI-MS, MS<sup>n</sup>

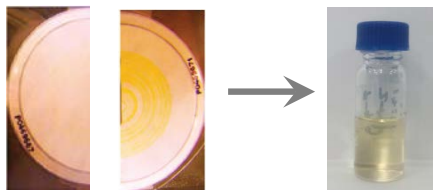
□ Assessment of BrC components based on:

- Comparison with standards
- Theoretical Chemistry Calculations
- Educated guesses



# LC-PDA-MS Analysis

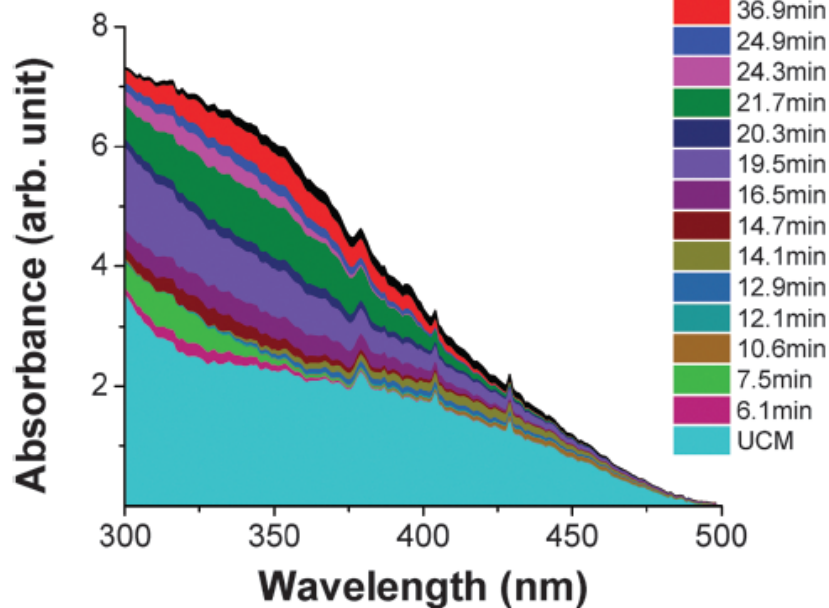
Lin et al, 2015, *PCCP*



SOA

>10  $\mu\text{g}$

(Toluene/OH/NO<sub>x</sub>)

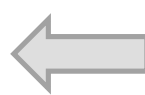


HPLC Separation

UV-Vis spectrometer

High resolution ESI/APPI-MS, MS<sup>n</sup>

PDA spectrum @RT(min)	Formula and candidate compound	Proposed structures
RT = 39.1min $\lambda_{\text{max}} = 366\text{nm}$ 	C <sub>6</sub> H <sub>3</sub> N <sub>3</sub> O <sub>7</sub> , picric acid	
RT = 36.9min $\lambda_{\text{max}} = 345\text{nm}$ 	C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>7</sub> , 3,5-dinitrosalicylic acid	
RT = 24.9min $\lambda_{\text{max}} = 340\text{nm}$ 	<sup>14</sup> C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> O <sub>6</sub> , methyl-dinitrocatechol	
RT = 24.3min $\lambda_{\text{max}} = 325\text{nm}$ 	C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>5</sub> , dinitrophenols (DNP)	
	C <sub>7</sub> H <sub>7</sub> NO <sub>3</sub> , nitroresols	



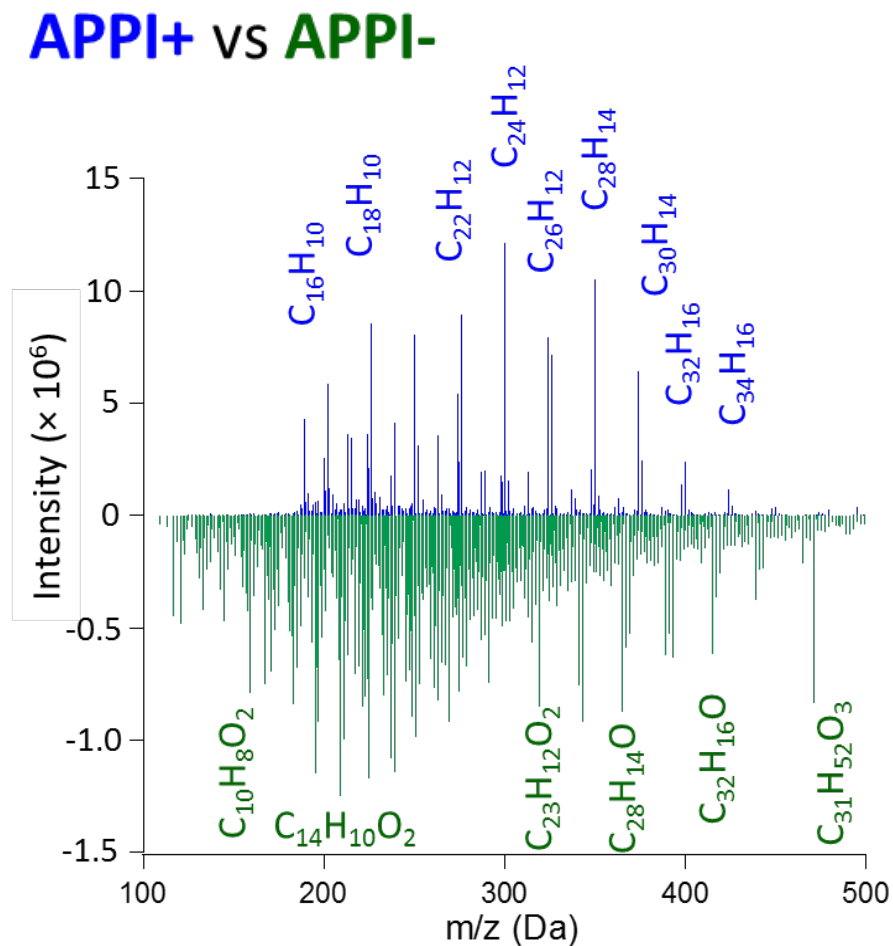
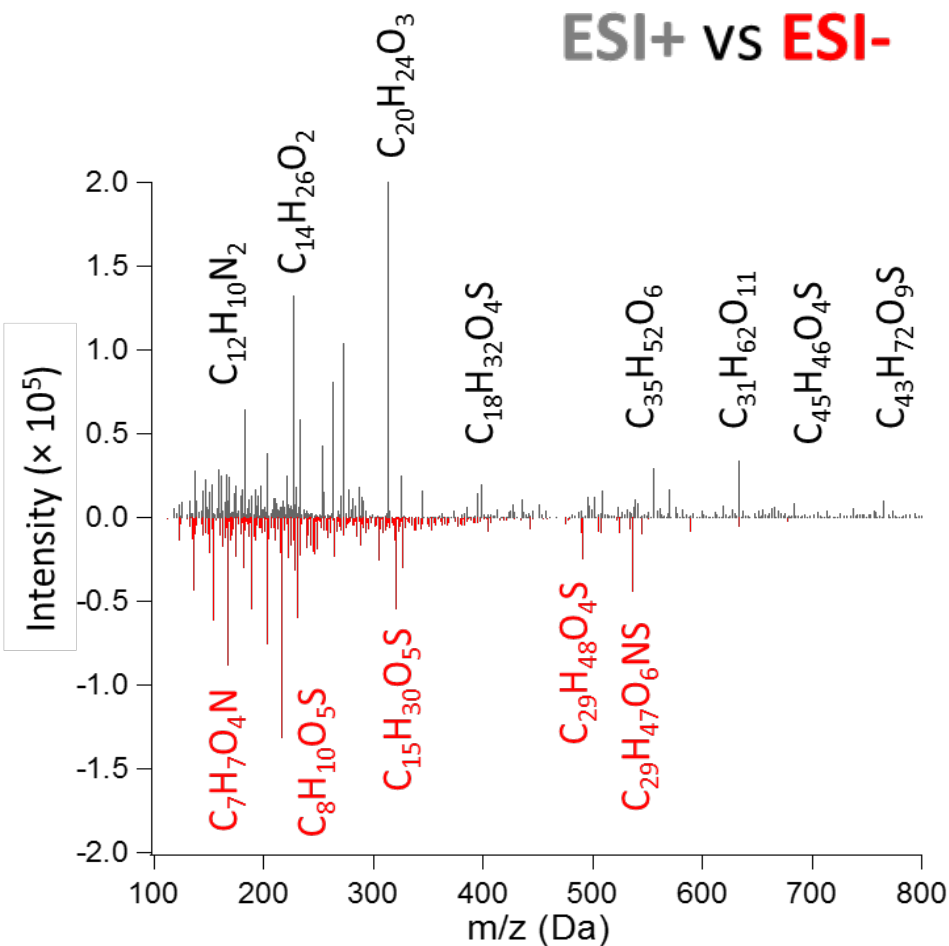
- ~50% of MAC attributed to individual BrC chromophores

... 15 chromophores

# Multi-Modal Ionization

(Real-world BBOA sample, FIREX 2016)

Lin et al, 2018, *Anal. Chem.*



**Polar compounds: organo-sulfates, organo-nitrates, carboxylic acids, etc.**

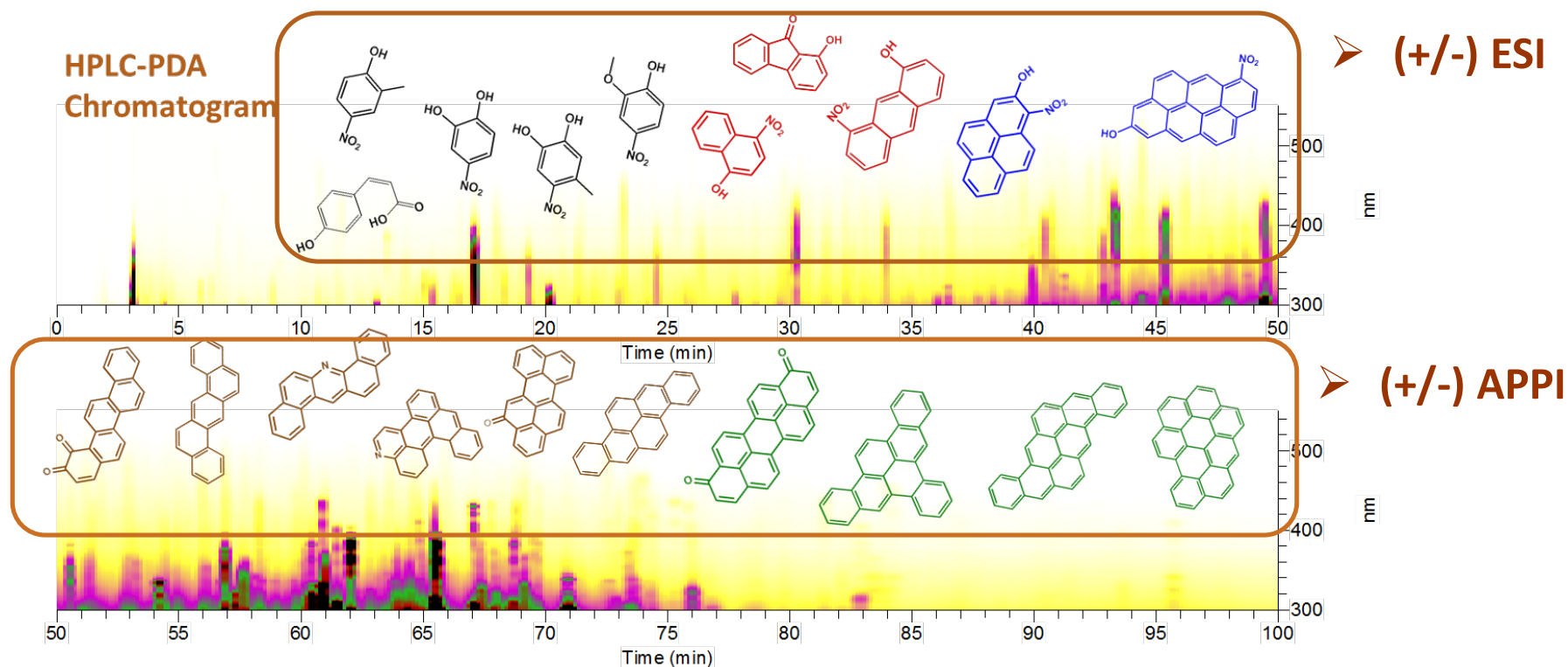
**Non- and less-polar compounds: PAH, N- and O-heterocyclic species, ketones, alcohols.**

# Separation $\Rightarrow$ Analysis of BrC Chromophores

- Detection of BrC chromophores in complex biomass burning samples collected in test burns



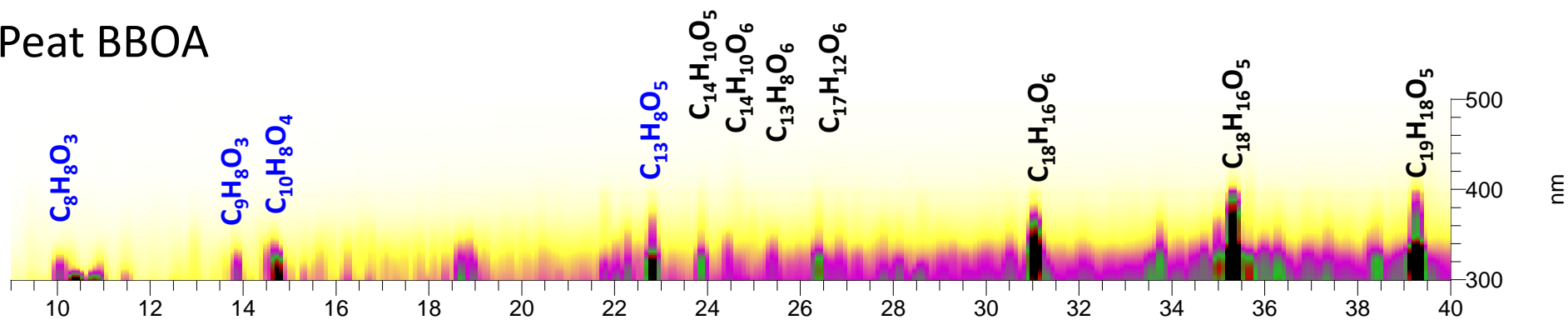
Lin et al, 2016, *ES&T*



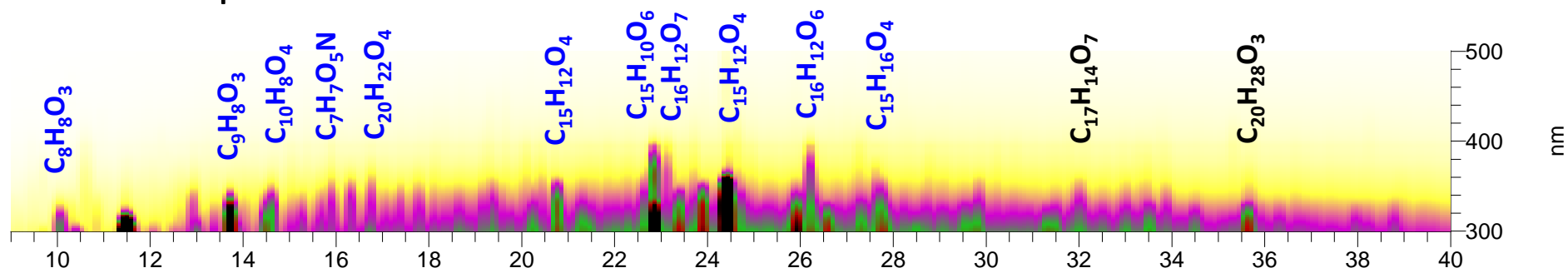
- use of different ionization modes

# Common and Source-specific Chromophores

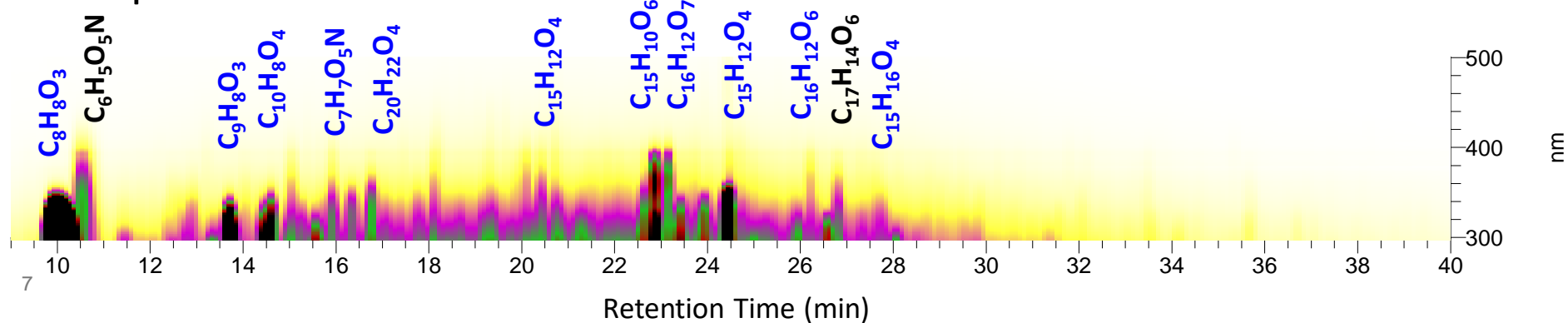
Peat BBOA



Ponderosa pine BBOA

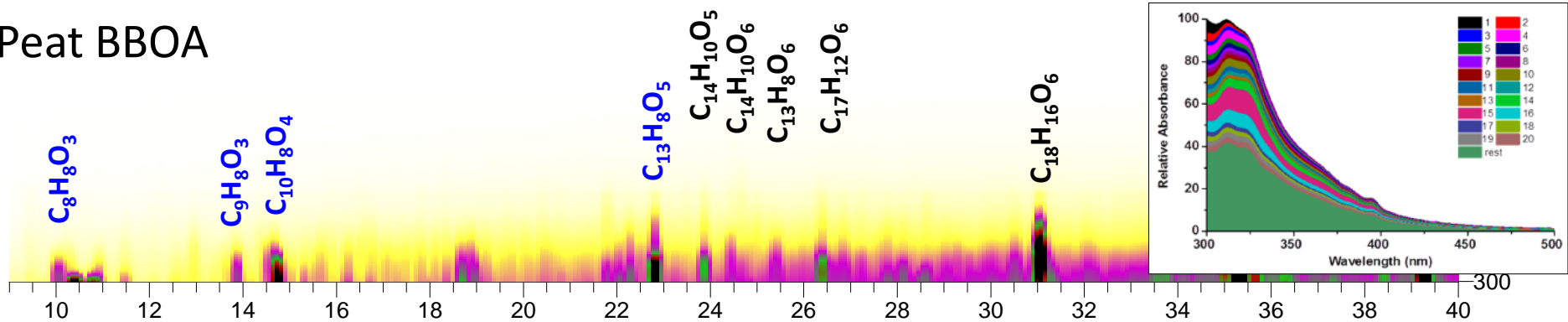


Black spruce BBOA

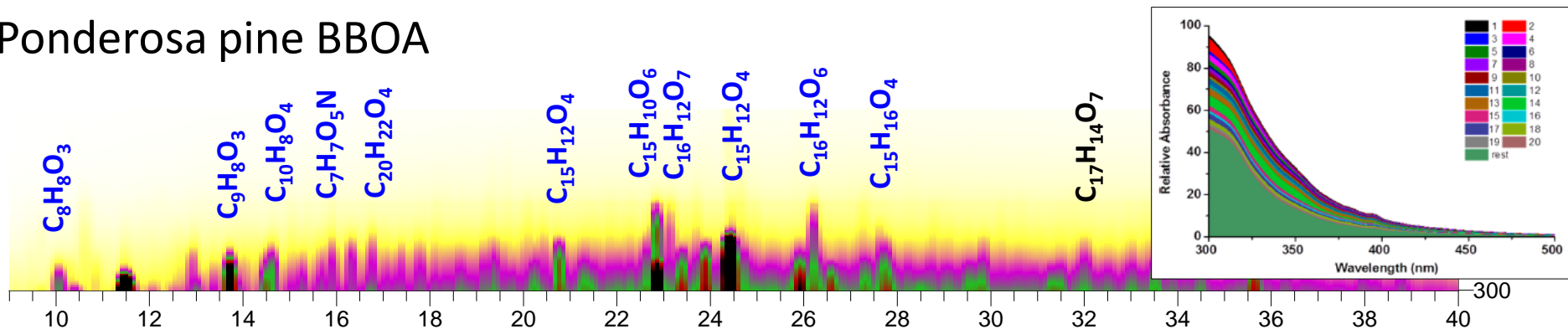


# Common and Source-specific Chromophores

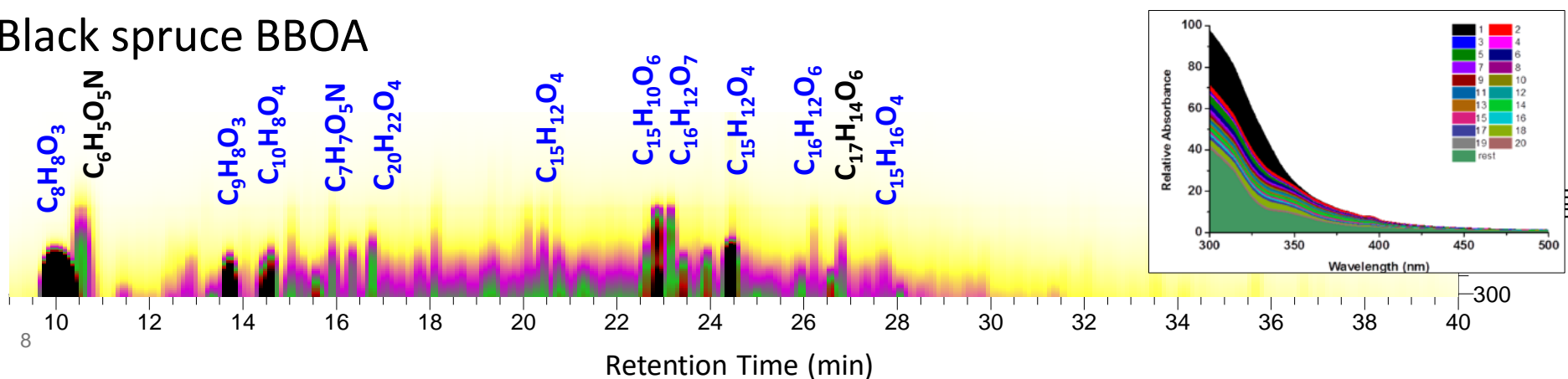
Peat BBOA



Ponderosa pine BBOA

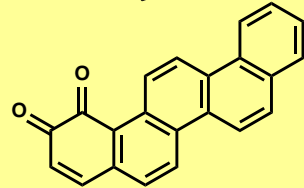
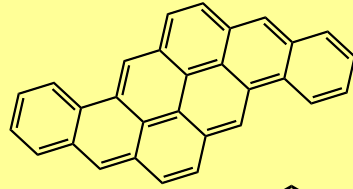
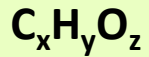
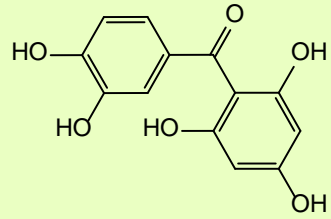
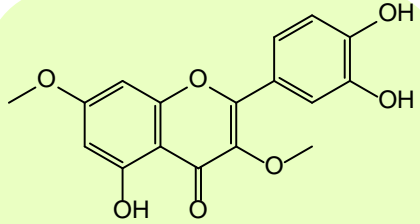


Black spruce BBOA

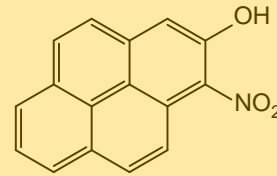
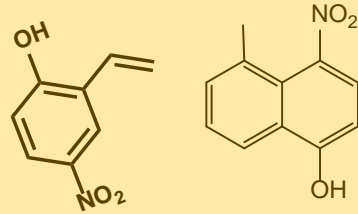




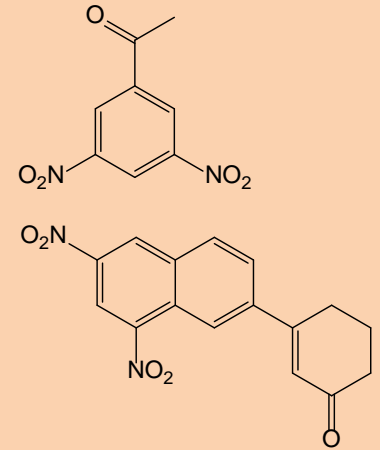
# Characteristic BrC Chromophores



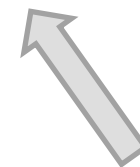
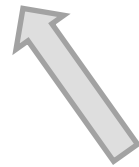
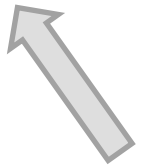
**PAHs &  
Derivatives**



**Nitro Aromatics**



**Dinitro-aromatics**



**Smoldering burns**  
(low T; low MCE)



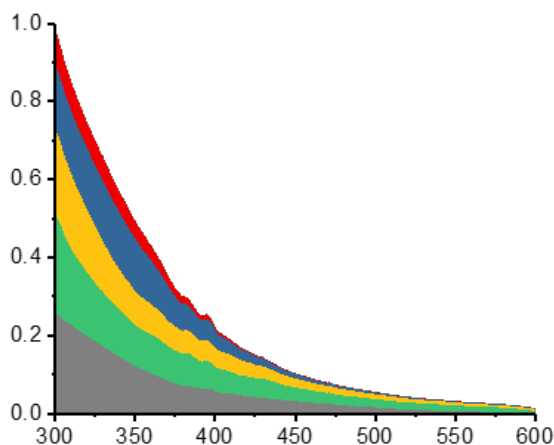
**Flaming burns**  
(high T; high MCE)



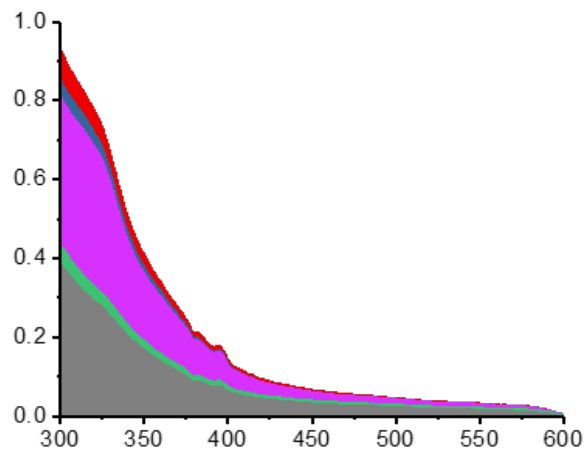
**Combustion in Engines**

# Comparing BrC samples

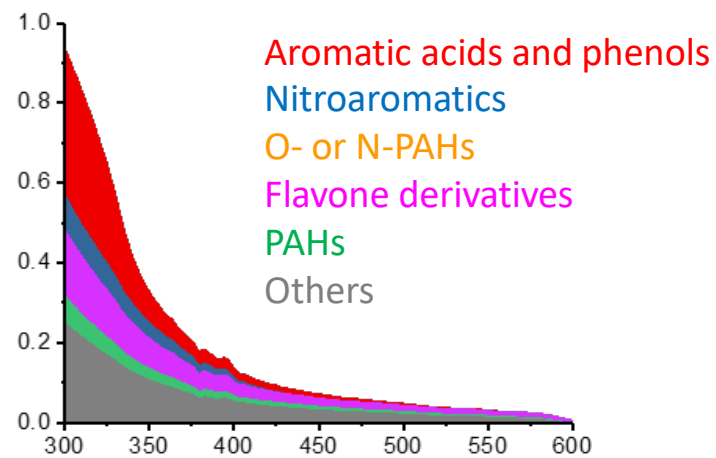
## Sagebrush BBOA



## Peat BBOA

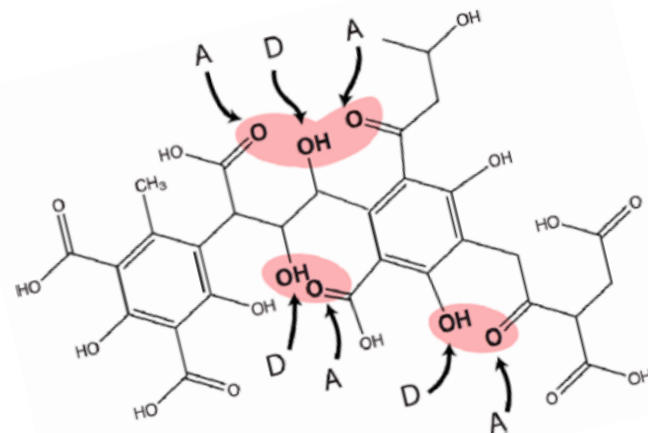


## Black Spruce BBOA



- BrC chromophores are source-specific..!
- >50% of *MAC* attributed to individual BrC chromophores
- Unresolved fractions:  
weak chromophores,  
charge-transfer complexes

Phillips and Smith, *EST* 2014

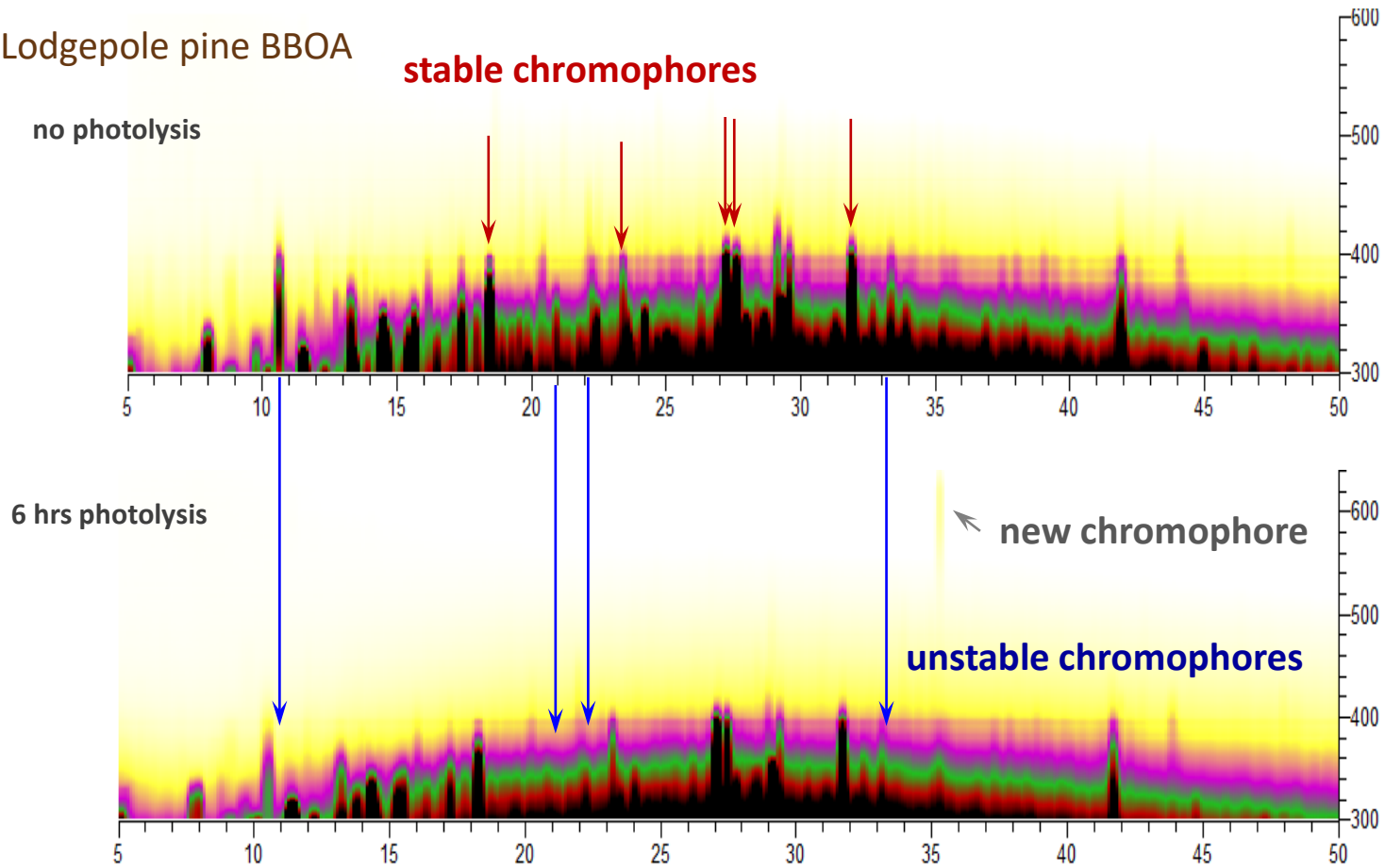


# Ageing of BrC by Photolysis

- Different chromophores have different resistance to photolysis

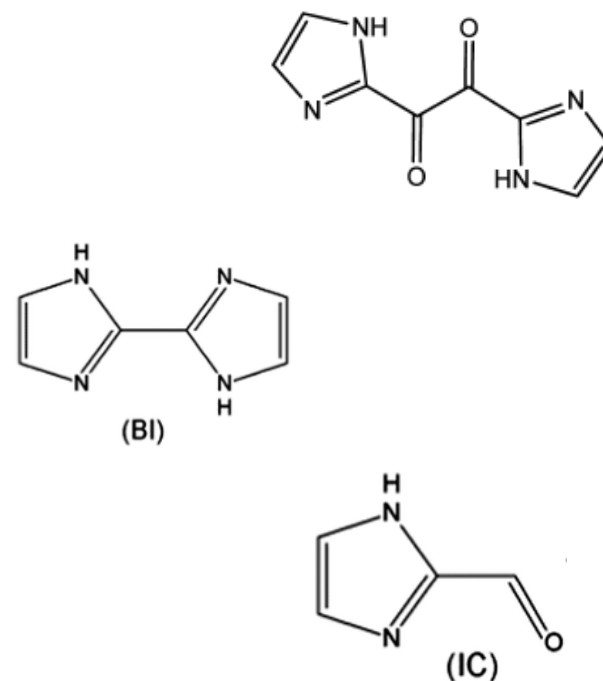
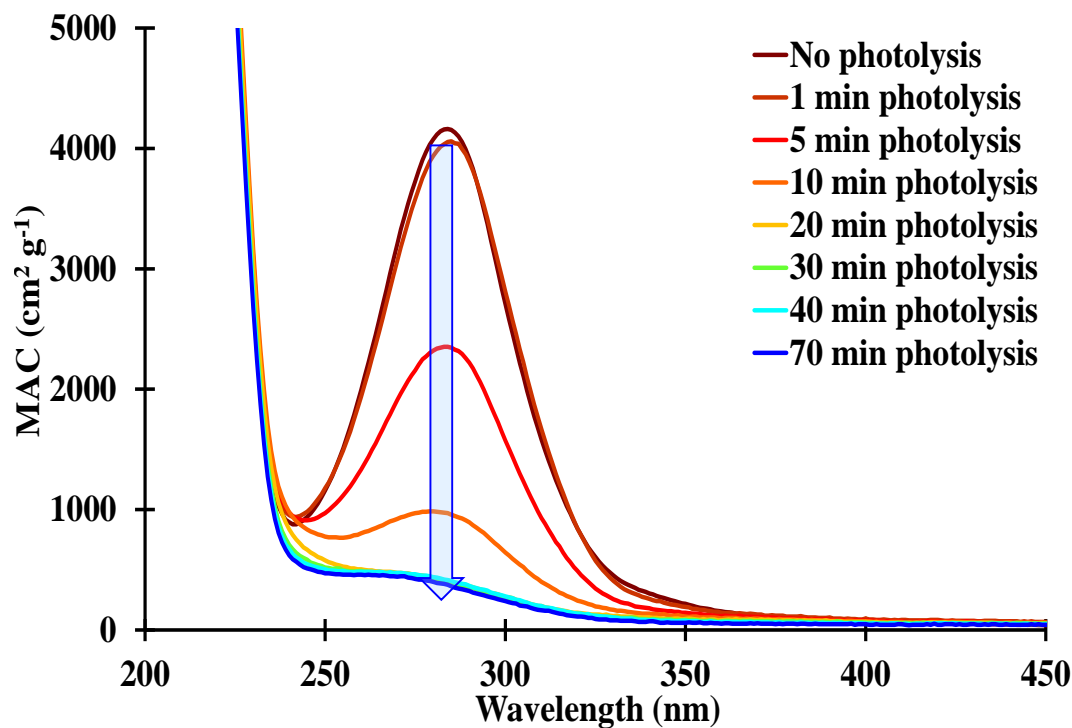
Fleming et al, 2019, *ACP Discussion*

Lodgepole pine BBOA



# Ageing of BrC by Photolysis

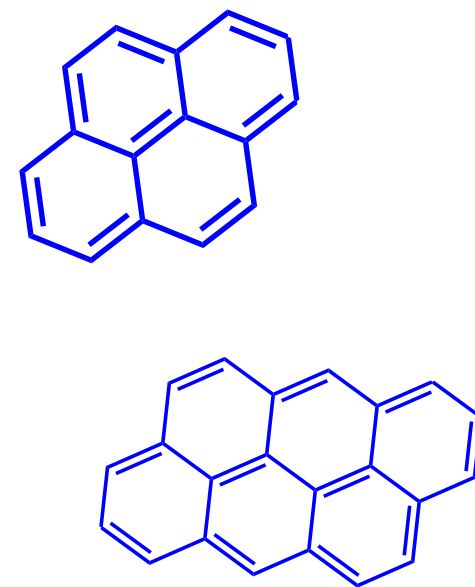
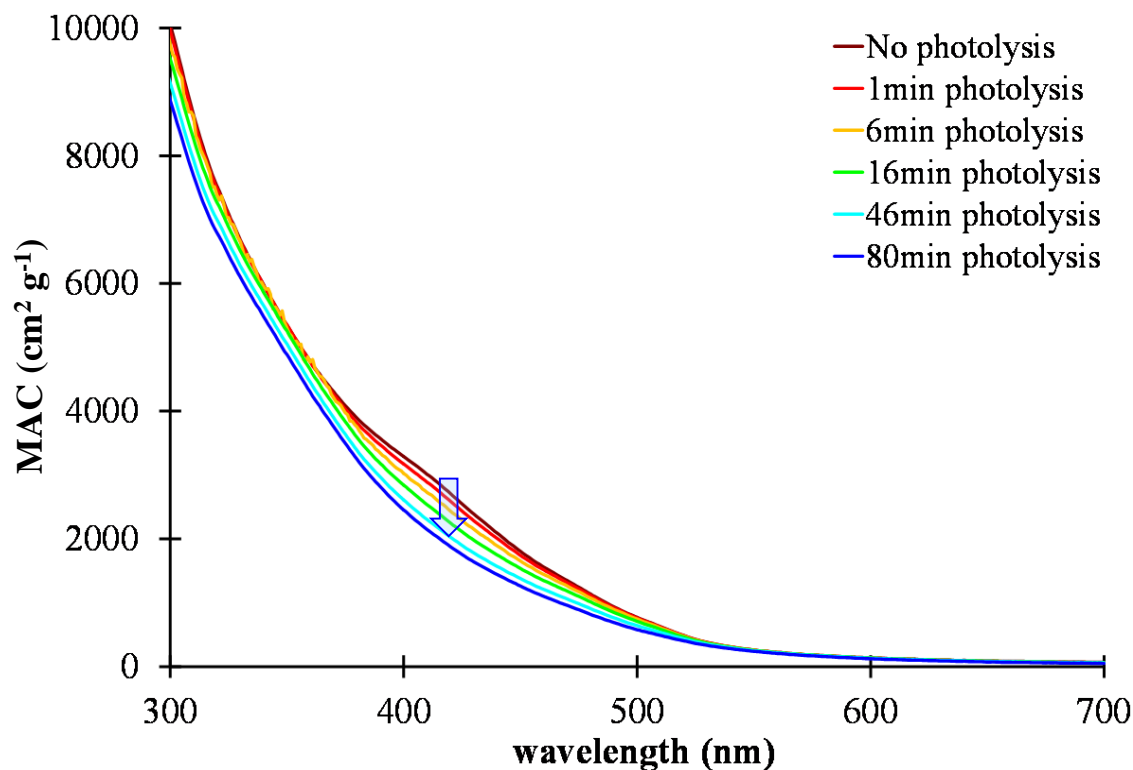
- Imidazole based chromophores are unstable  
*Effective lifetime: minutes-hours*



Lee et al, *EST* 2014

# Ageing of BrC by Photolysis

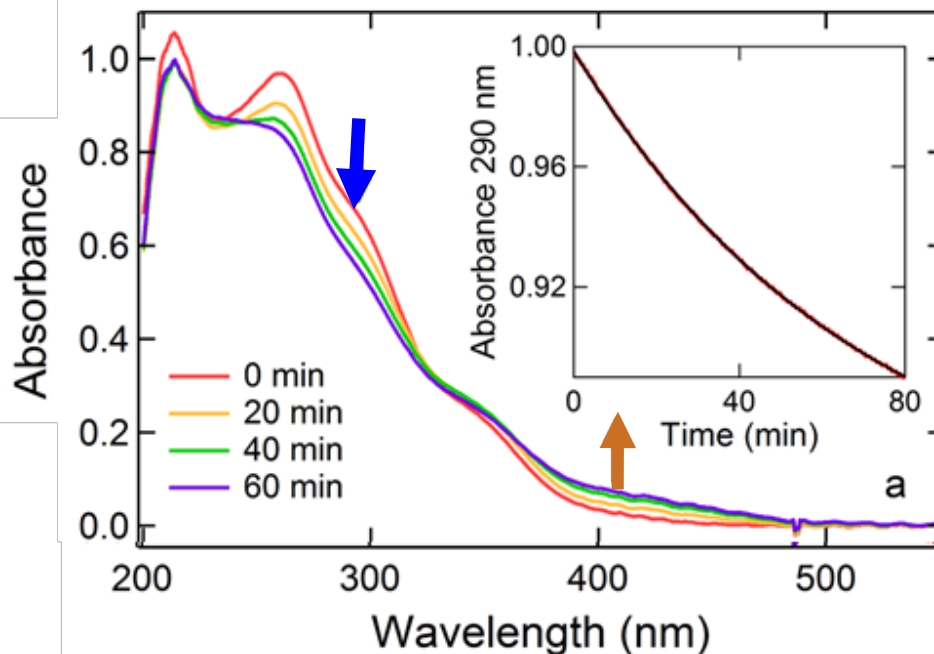
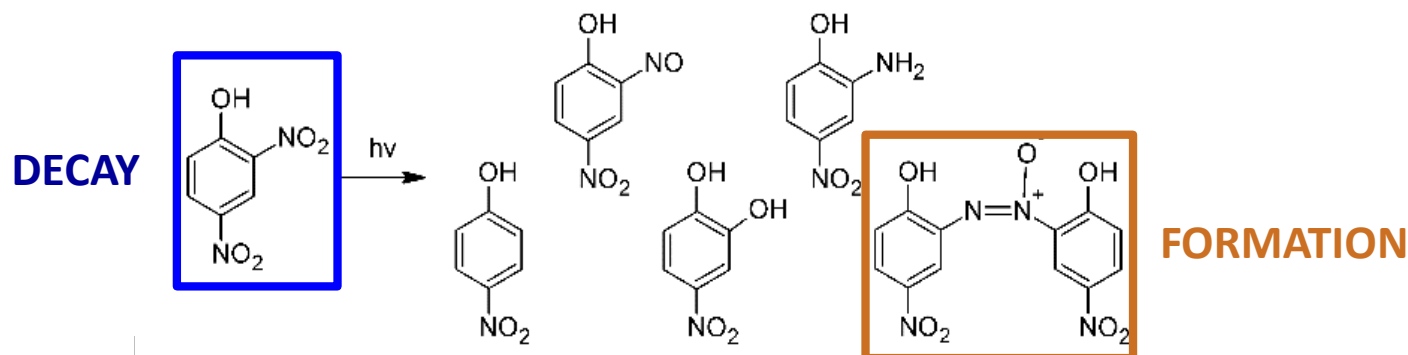
- Nitro-PAH chromophores are stable  
*Effective lifetime: 1-2 days*



Lee et al, *EST* 2014

# Ageing of BrC by Photolysis

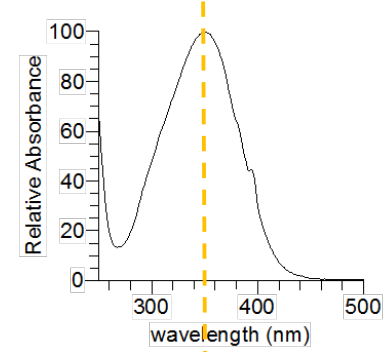
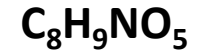
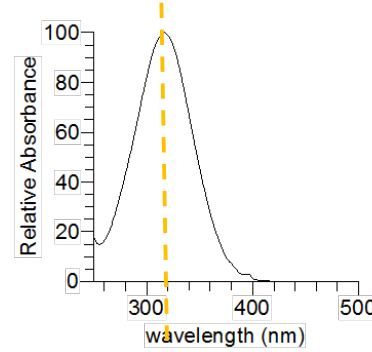
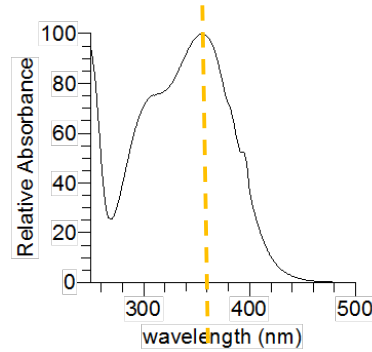
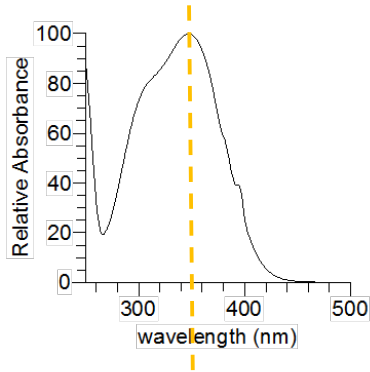
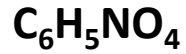
- Dinitro-phenols show dual effect:



Hinks et al, *PCCP* 2016

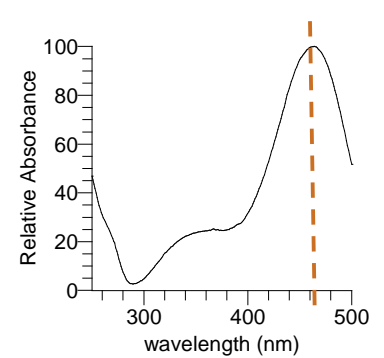
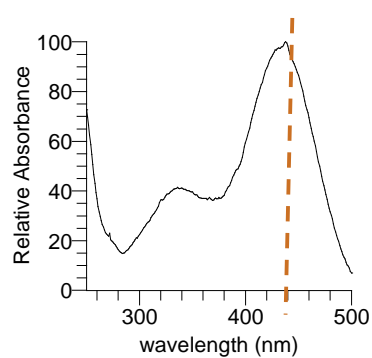
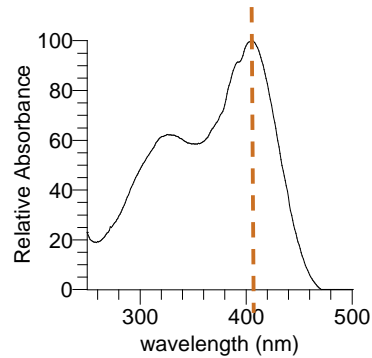
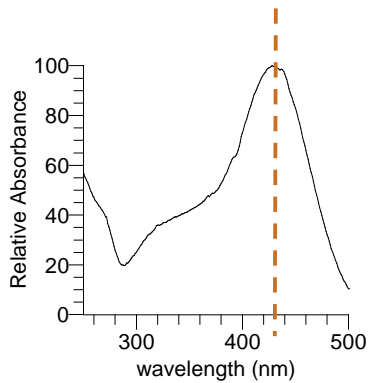
# Effect of pH on UV-Vis spectra of BrC

pH  $\leq$  3



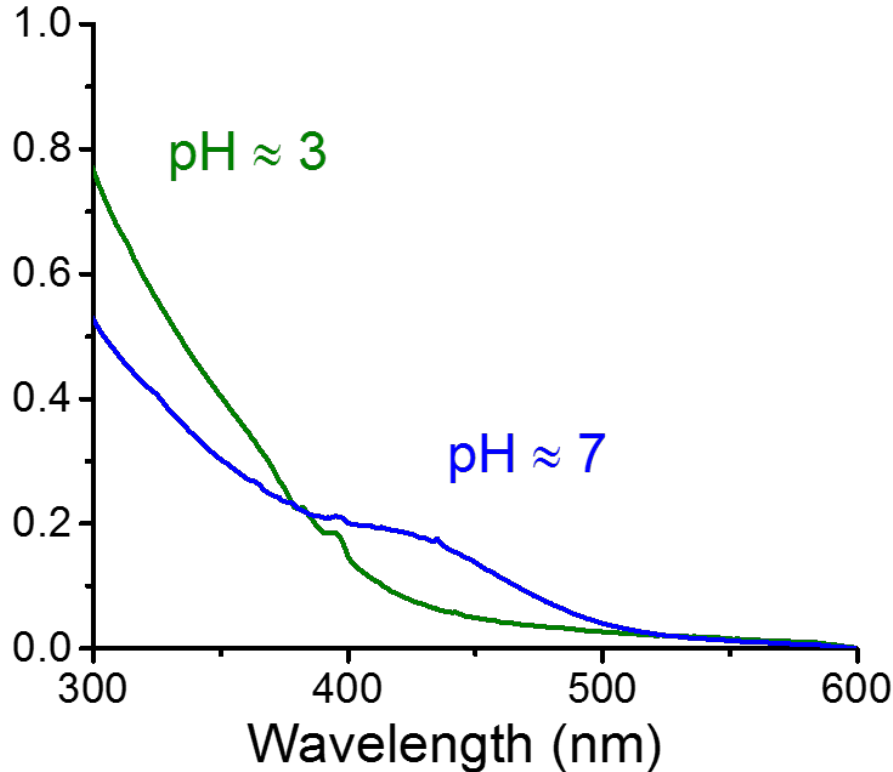
pH  $\geq$  6

Deprotonated (anionic) forms



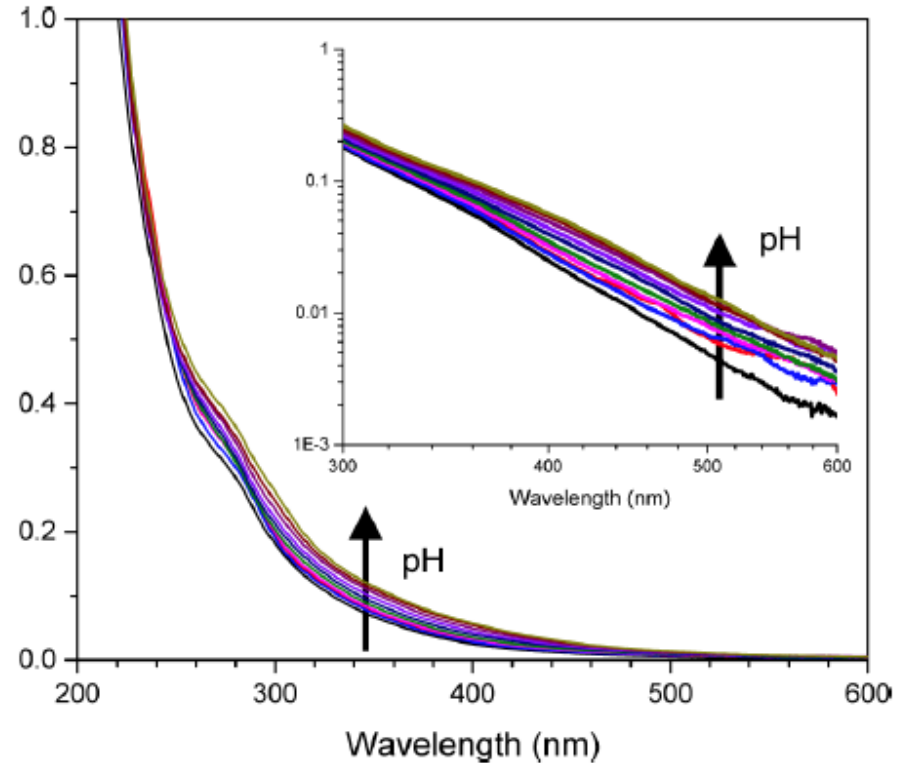
# Effect of pH on UV-Vis spectra of BrC

- Light absorption by BrC depends strongly on pH



- **BBOA** dominated by nitro-aromatics

Lin et al, 2018, *ES&T*



- **CT complexes** in HULIS

Phillips and Smith, *EST* 2017



# Summary

- **Diverse BrC chromophores define ~50% of MAC**
- **Common & Source-specific BrC chromophores**
- **Nitro-aromatics and PAH derivatives dominate absorption spectra of BBOA**
- **Lifetimes vary for different BrC chromophores**
- **Aerosol acidity affects absorption by BrC**

# Summary

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## Outlook

- **Assessment of common vs source-specific BrC, their formation and evolution mechanisms**
- **Quantitative detection of strong chromophores**
- **Effects of particle internal composition on BrC properties**

