Investigating the effects of atmospheric aging on the direct radiative properties and climate impacts of black- and brown- carbon aerosol

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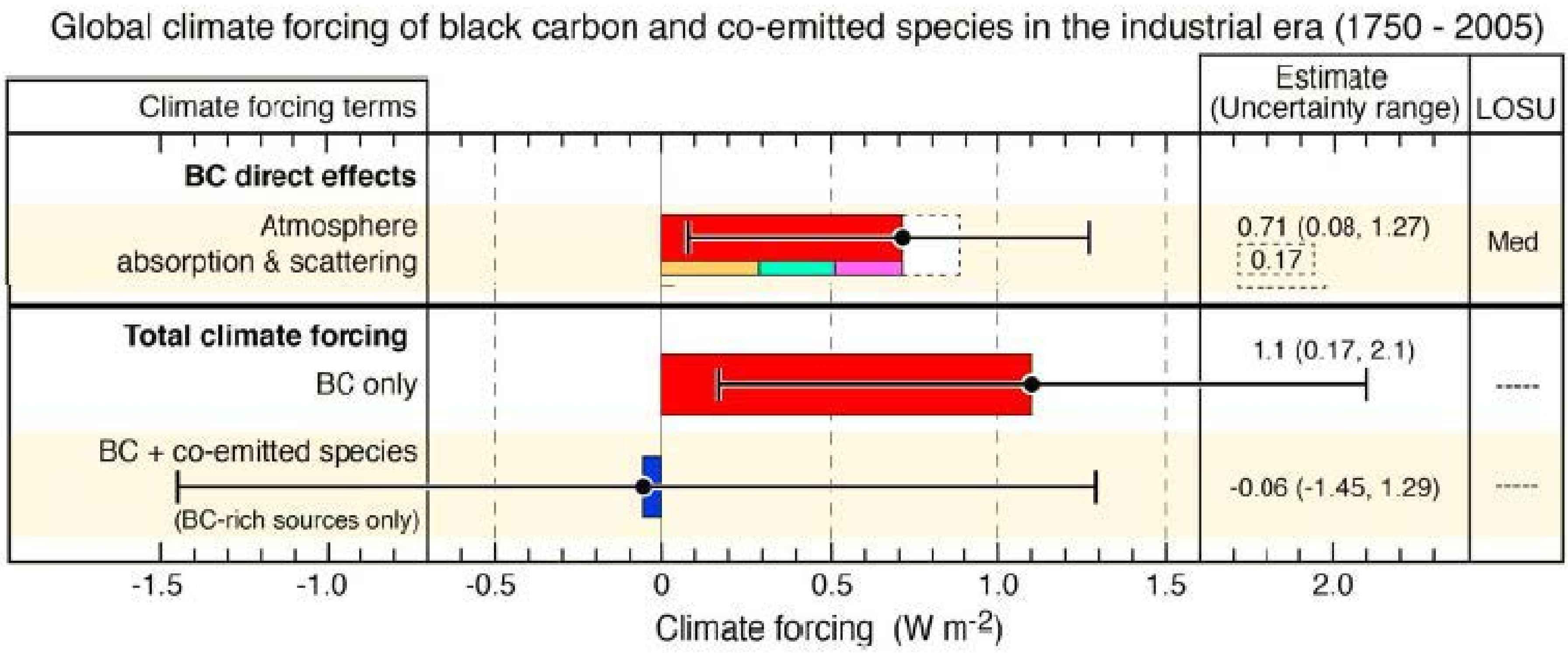
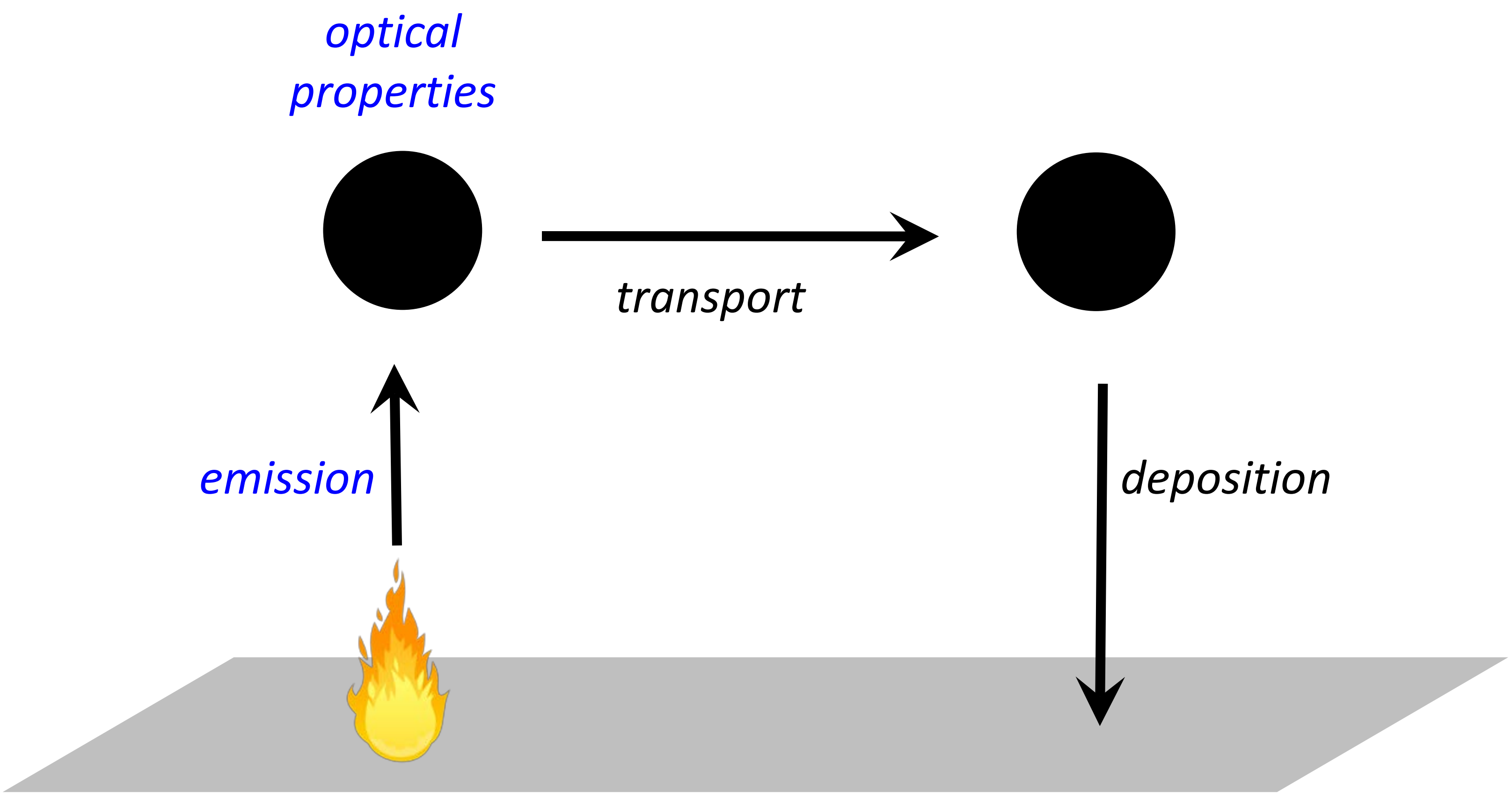
BC climate forcing: Large, complex, uncertain

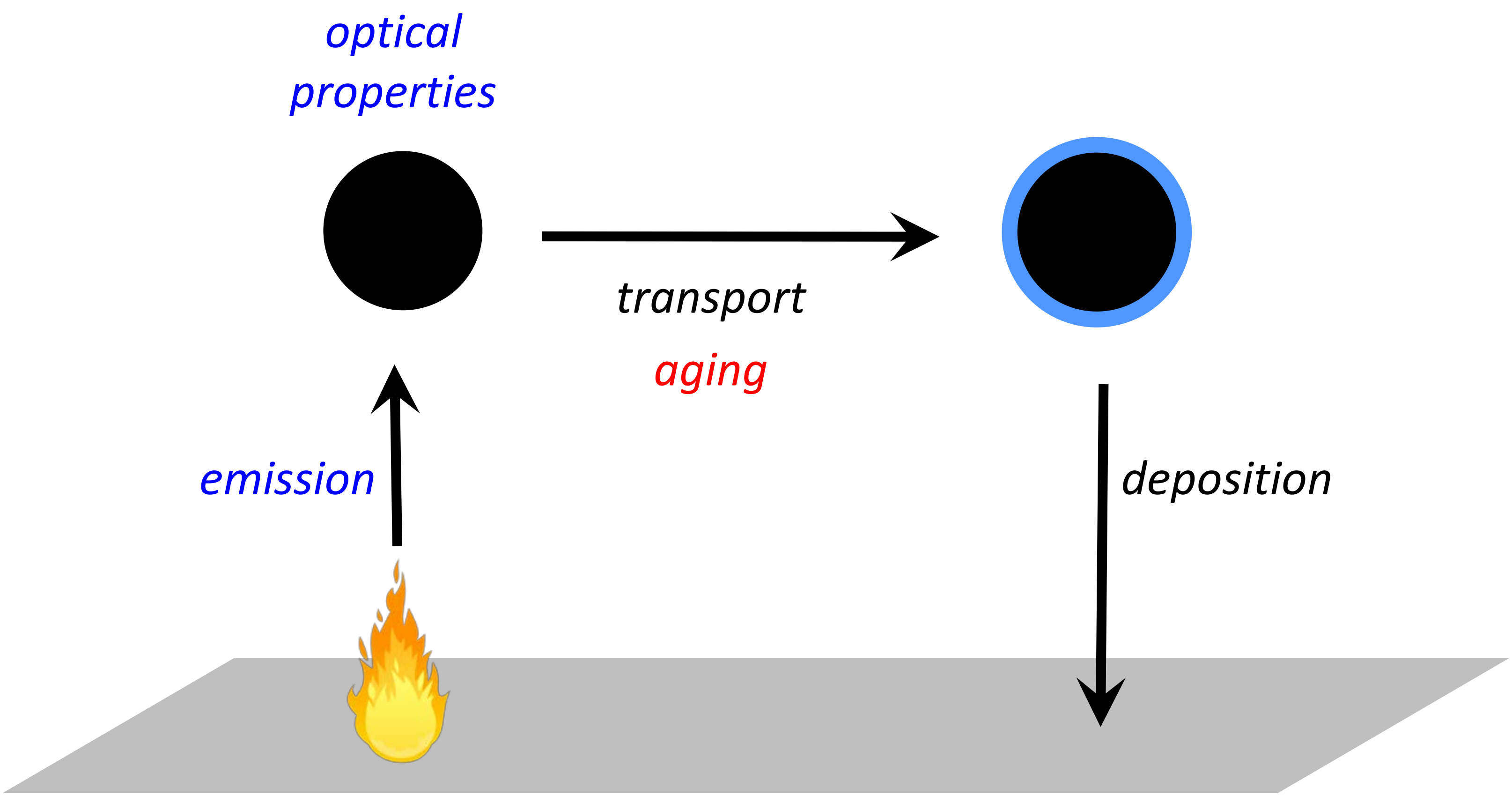


[Bond et al., 2013]

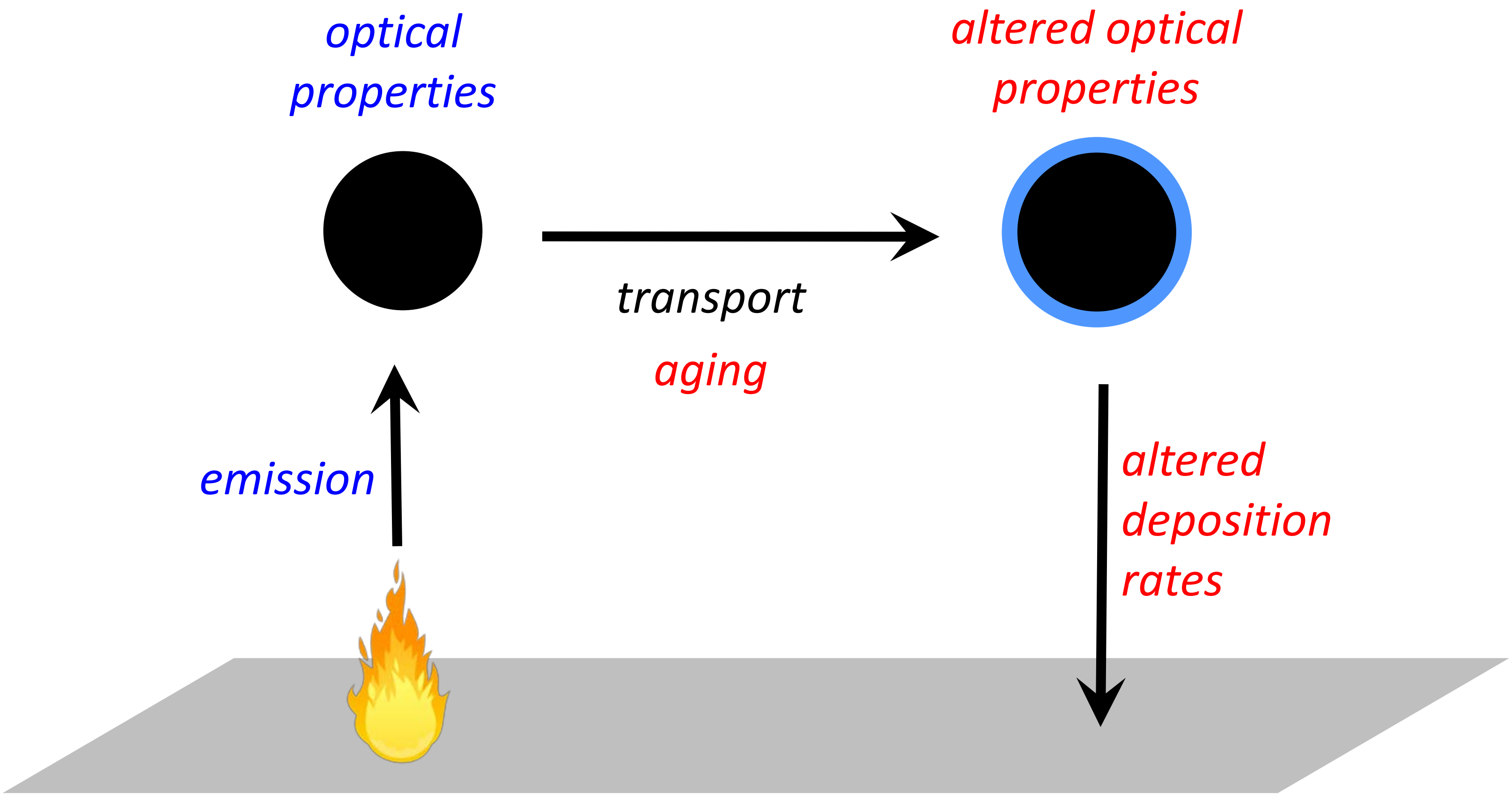
Simple lifecycle of atmospheric BC



Simple lifecycle of atmospheric BC

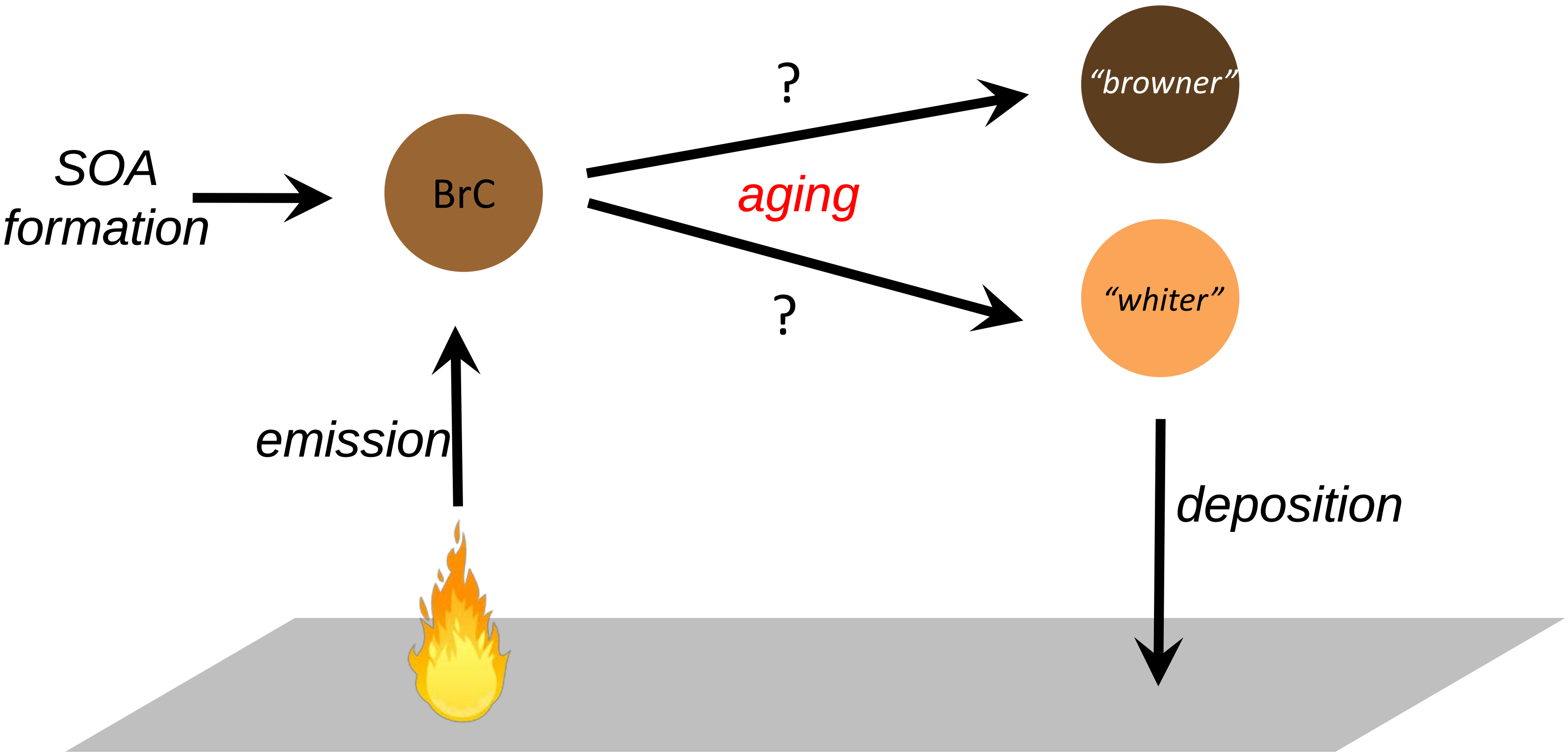


Simple lifecycle of atmospheric BC



Simple lifecycle of atmospheric BrC

"Brown carbon": OC that absorbs in the UV/visible (distinct molecules)



This project

Black/brown carbon aerosol is chemically dynamic, subject to atmospheric aging reactions; these can lead to dramatic changes in physicochemical properties, and therefore climate forcing effects.

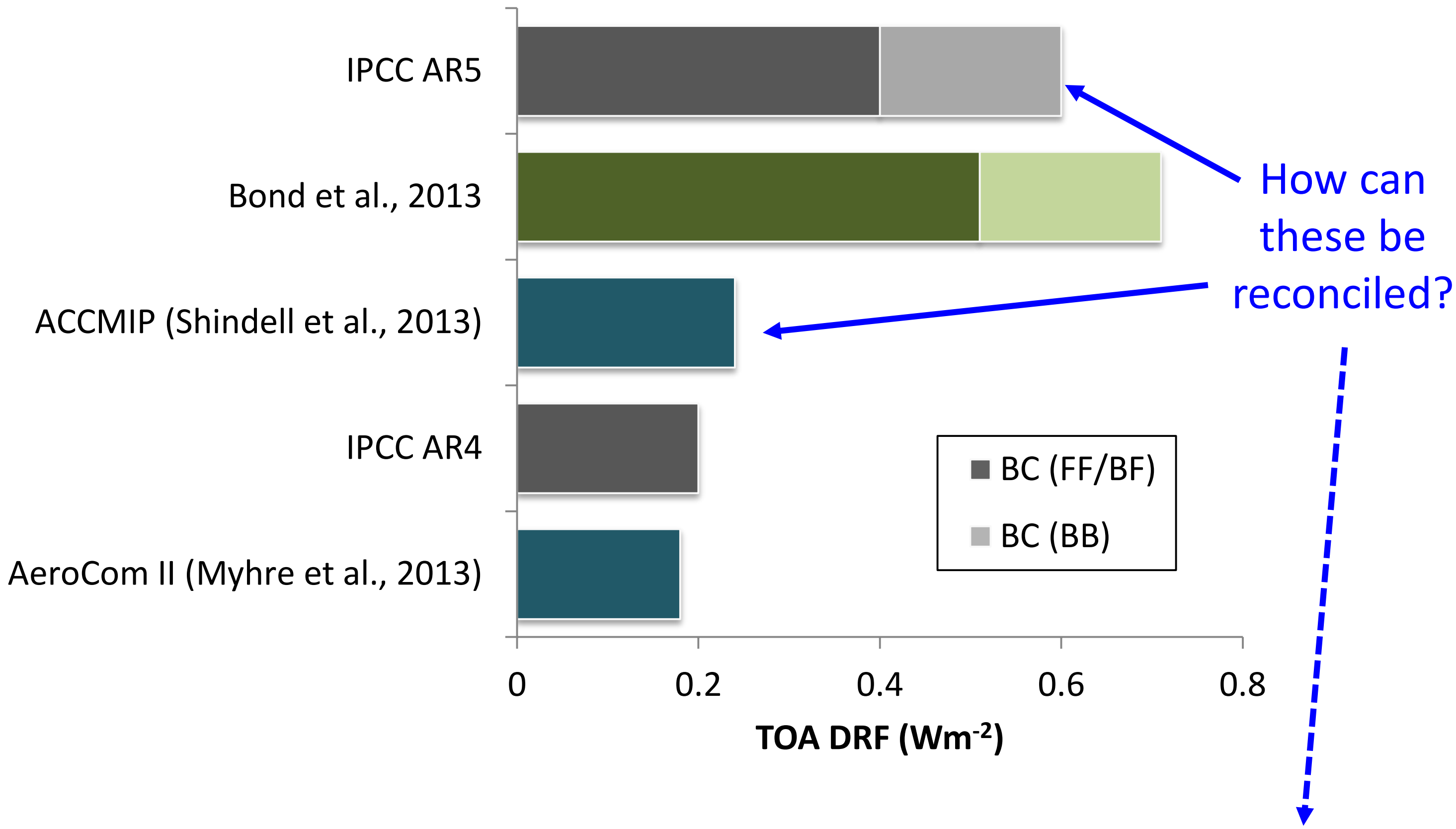
A complete understanding of this aging, and representation of this aging within models, is necessary for the accurate simulation of global direct radiative forcing.

Major questions:

- what are the most important atmospheric aging transformations of BC/BrC?
- what effects does aging have on climate-relevant properties of BC/BrC?
- how do these aging reactions impact BC/BrC direct radiative forcing?

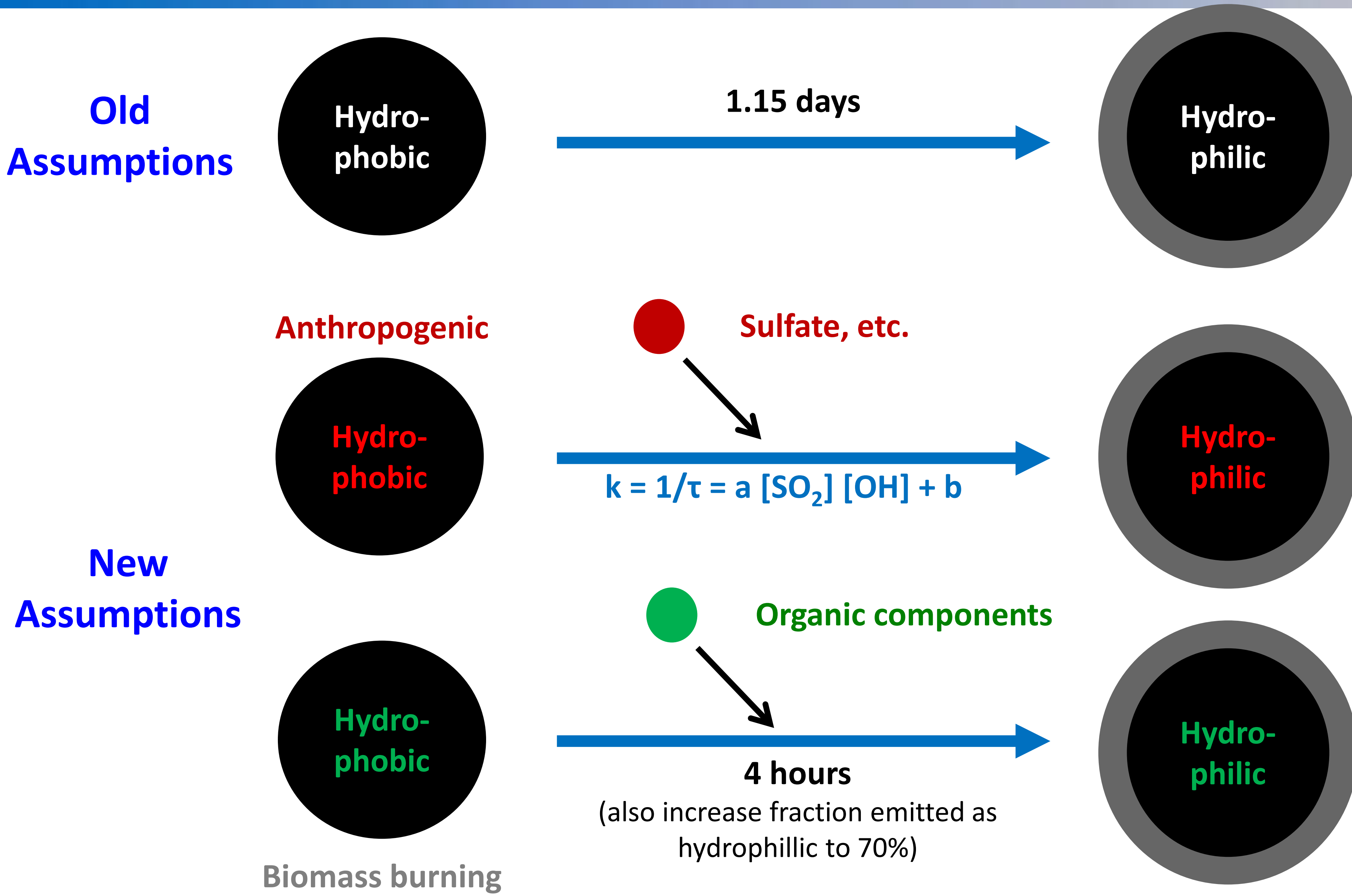
IPCC AR5 Estimates that Black Carbon is the 2nd Largest Warming Agent in the Atmosphere.

(but that's not what models say)



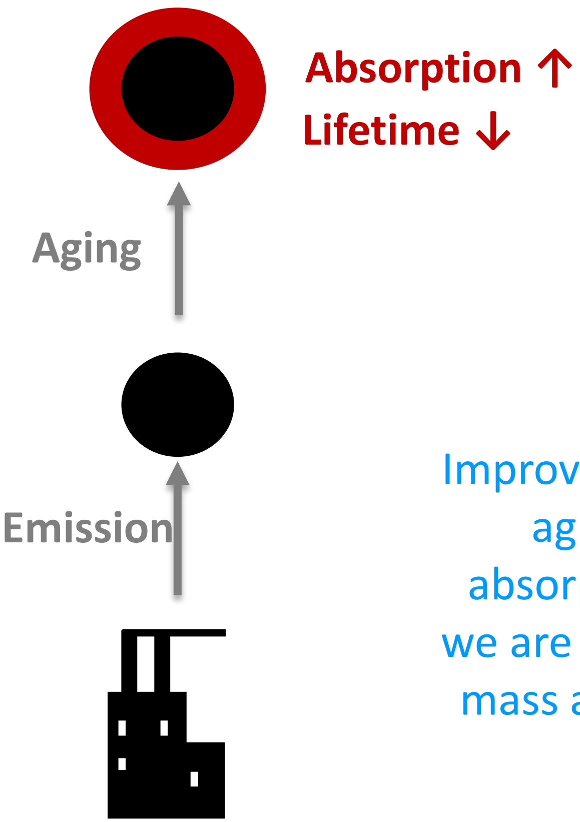
At the same time, AeroCom models overestimate BC over Americas by factor ~8 [Koch et al., 2009], overestimate remote HIPPO BC by factor ~5 [Schwarz et al., 2010].

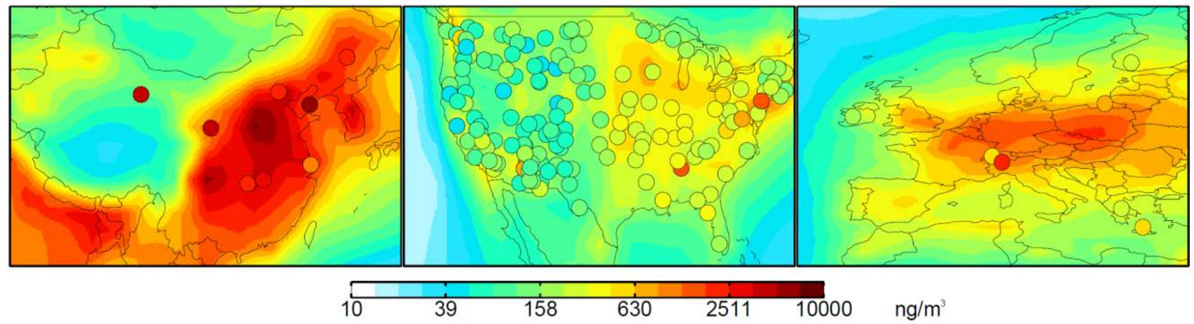
New Model Aging Processes for BC



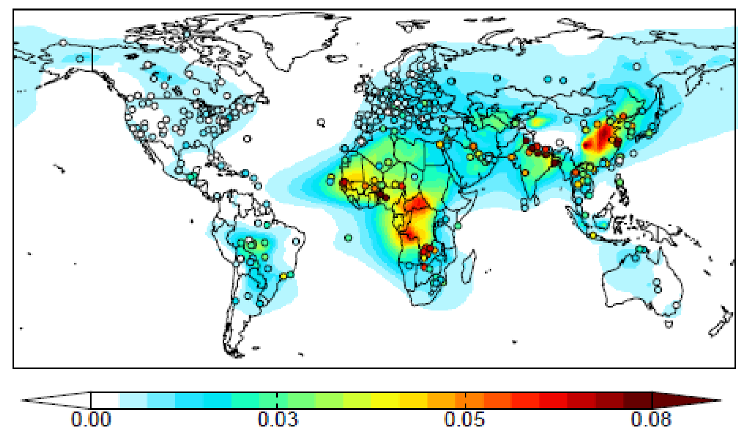
Based on several lab and field studies, esp Liu et al. (2010); Akage et al. (2012)

Aging Processes Reconcile Both Mass and Absorption Constraints





Improving our description of aging and including absorption enhancement, we are able to simulate both mass and absorption of BC

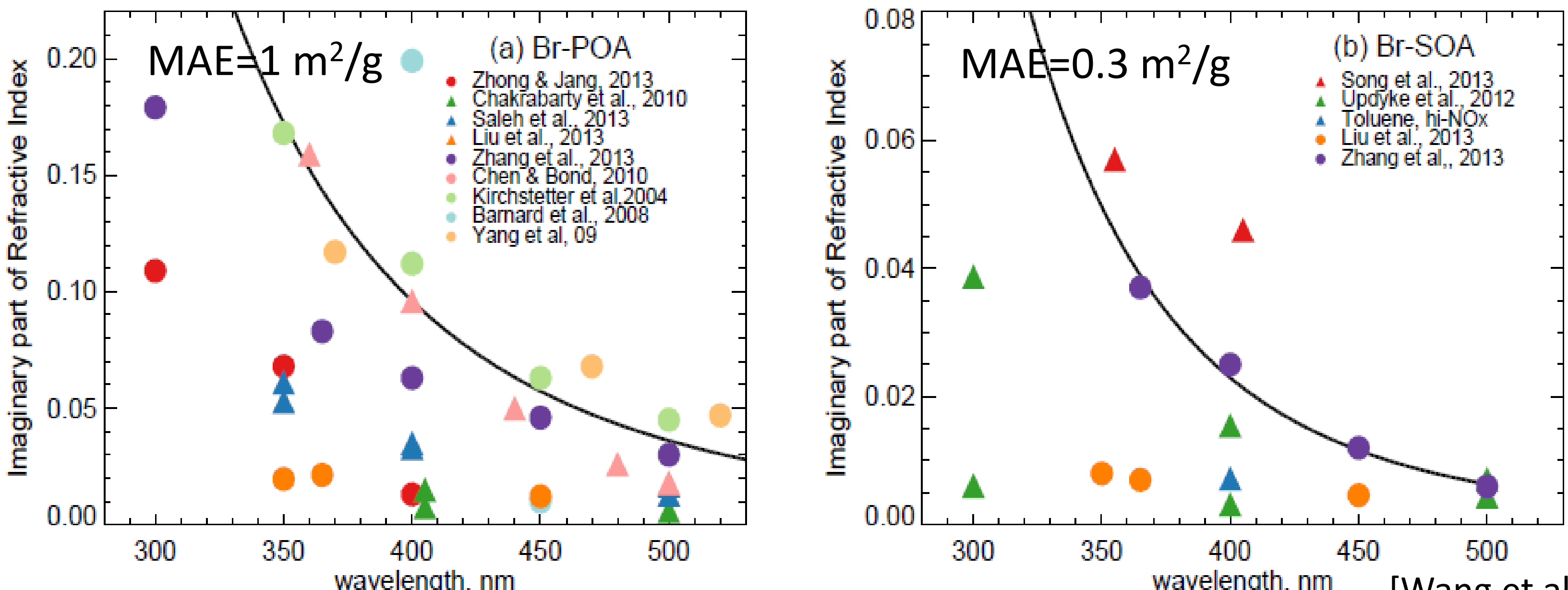


We estimate that the BC DRF (0.21 W/m^2) is much less than AR5 estimate (0.6 W/m^2). Suggests that controlling BC is less effective for climate mitigation.

[Wang et al., ACP, 2014]

How Important is Brown Carbon?

Modelling studies estimate that BrC contributes 20% to 40% of total carbonaceous aerosol absorption and that its direct radiative effect (DRE) ranges from +0.1 to + 0.6 Wm^{-2}
(Feng et al., 2013; Lin et al., 2014; Wang et al., 2014; Saleh et al., 2015; Jo et al., 2016)

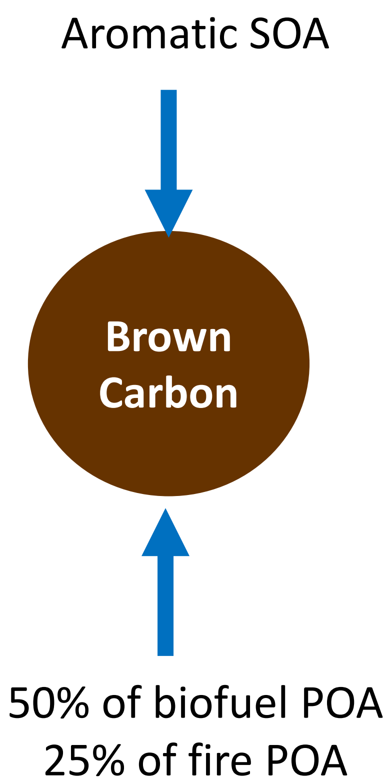


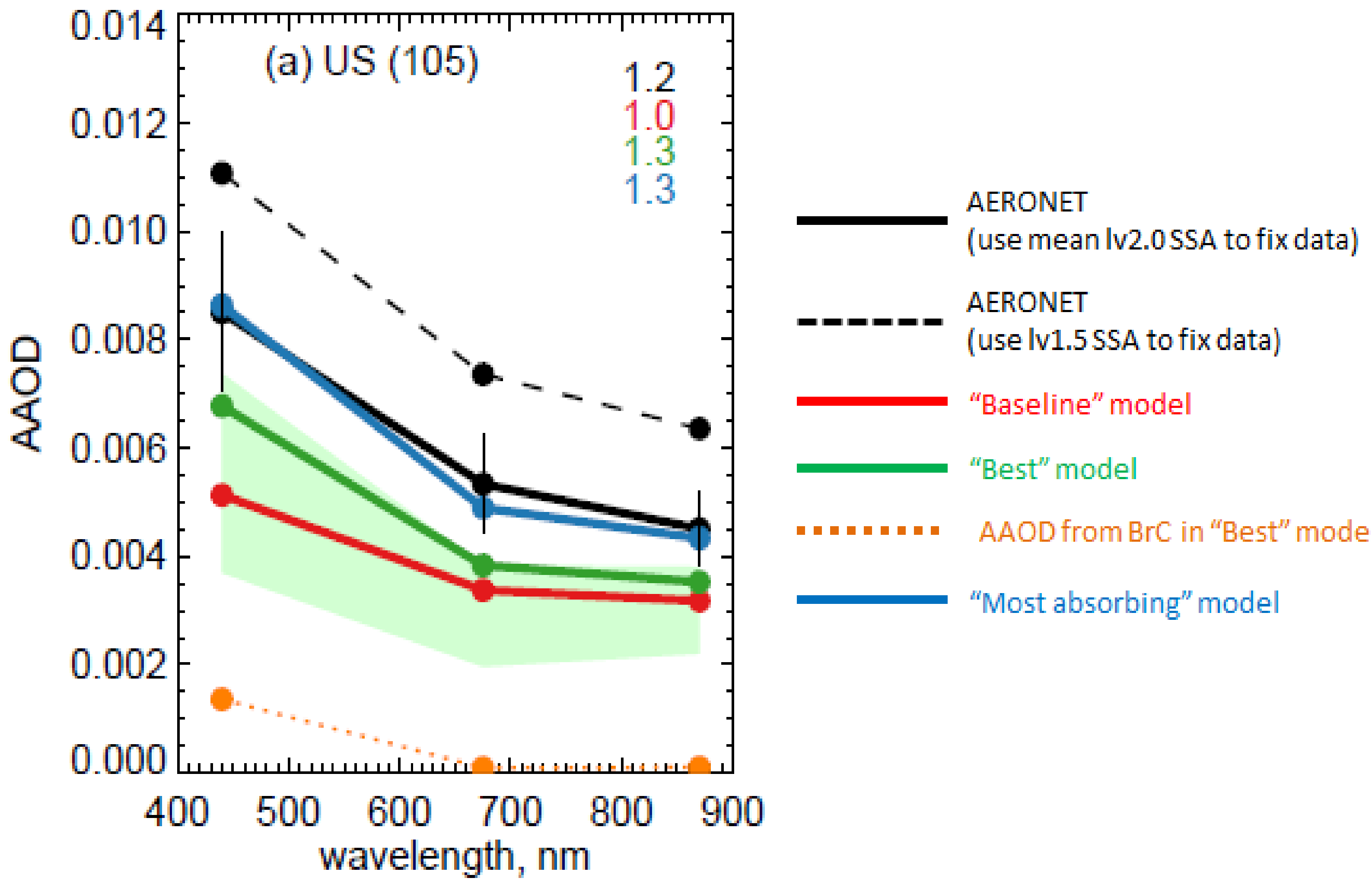
[Wang et al., ACP, 2014]

But sources and properties are so uncertain, we need observational constraints.

Including Brown Carbon is Critical to Capturing the Spectral Dependence of AERONET AAOD

*AAOD product here using lev2 SSA with lev1.5 AOD



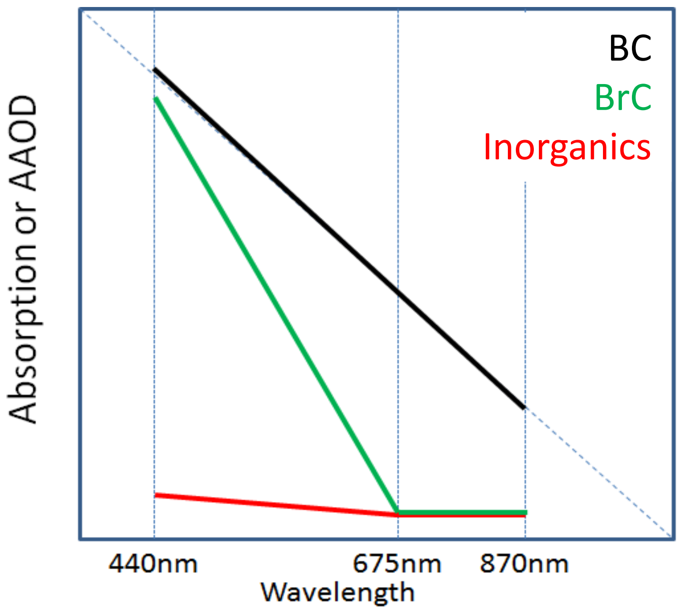


But given uncertainties in BC absorption, this constitutes a qualitative constraint at best

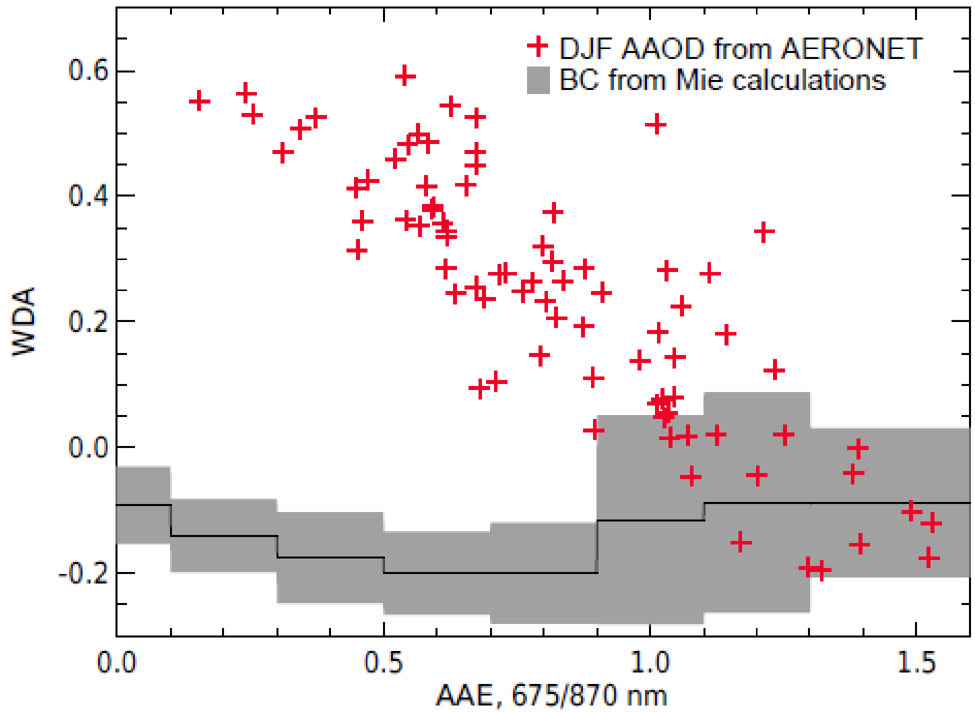
[Wang et al., ACP, 2014]

How to Separate BrC from Absorption Measurements?

Schematic of wavelength dependence of absorption



$$AAE = -\frac{\ln\left(\frac{abs(\lambda_1)}{abs(\lambda_2)}\right)}{\ln\left(\frac{\lambda_1}{\lambda_2}\right)}$$

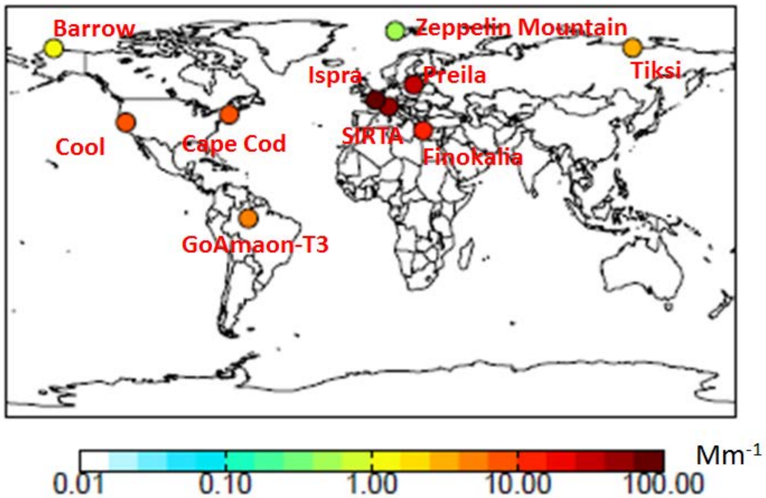


$$WDA = AAE_{440/870} - AAE_{675/870}$$

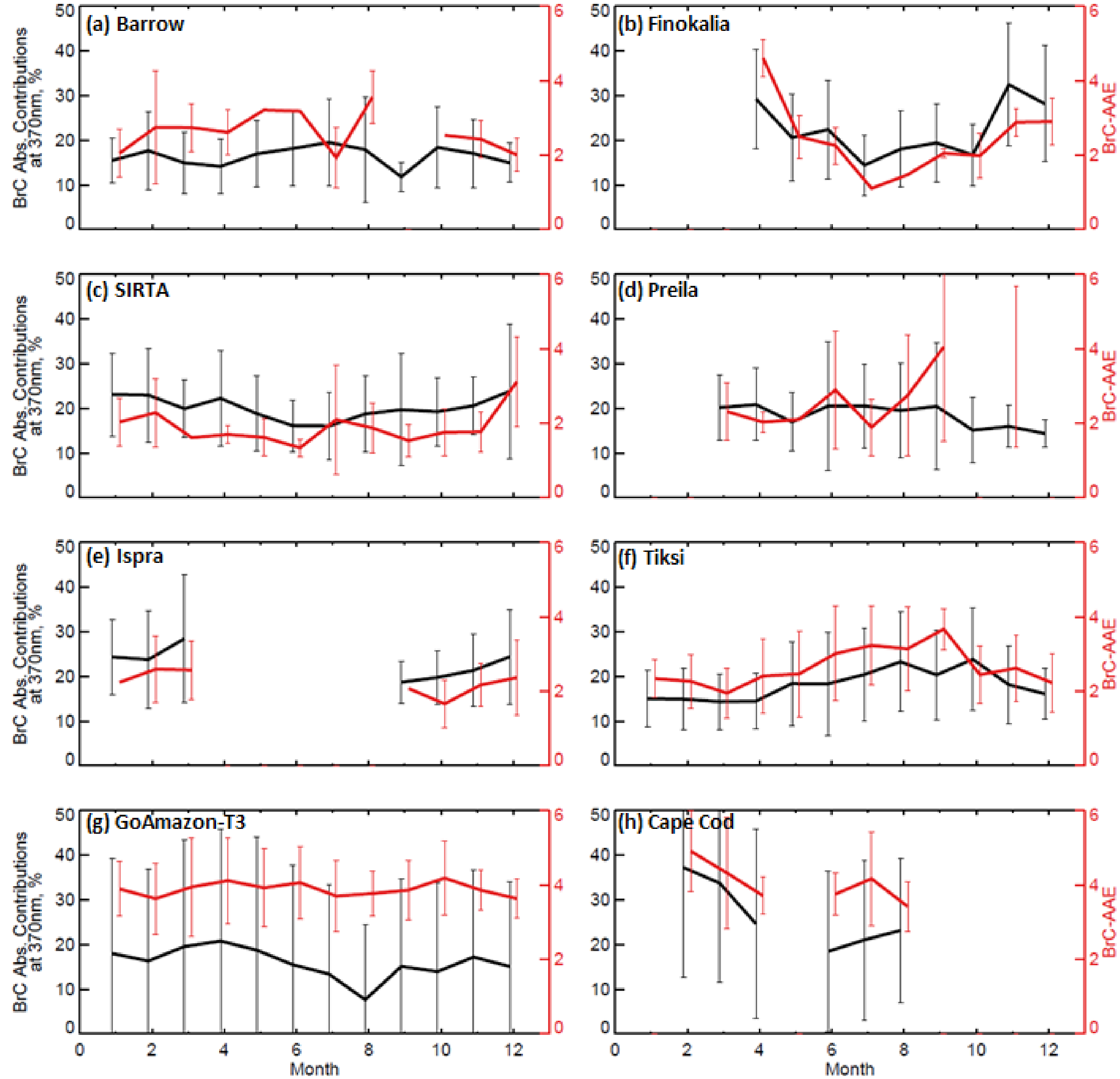
Many studies assume AAE of BC=1 and estimate BrC, but this is a poor assumption. Instead we estimate the wavelength dependence of BC absorption, and use this to estimate BrC absorption.

[Wang et al. ACP, 2016]

Globally BrC makes up 10-35% of Absorption



(370 nm)



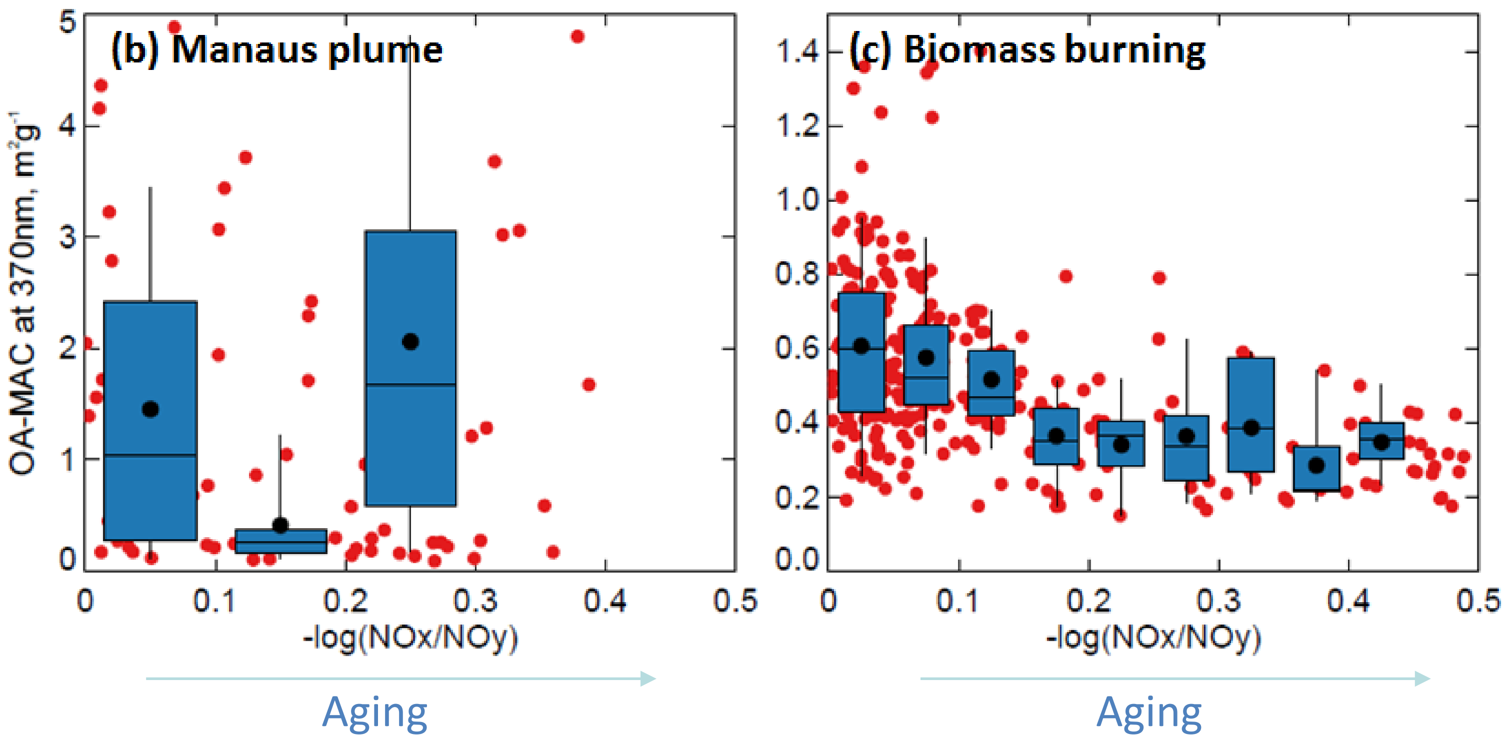
[Wang et al., ACP, 2016]

Does BrC Photochemically "Whiten" in the Atmosphere?

GoAmazon Site in Manacapuru

Jan-Mar 2015 (urban influence)

Aug-Oct 2014 (fire influence)



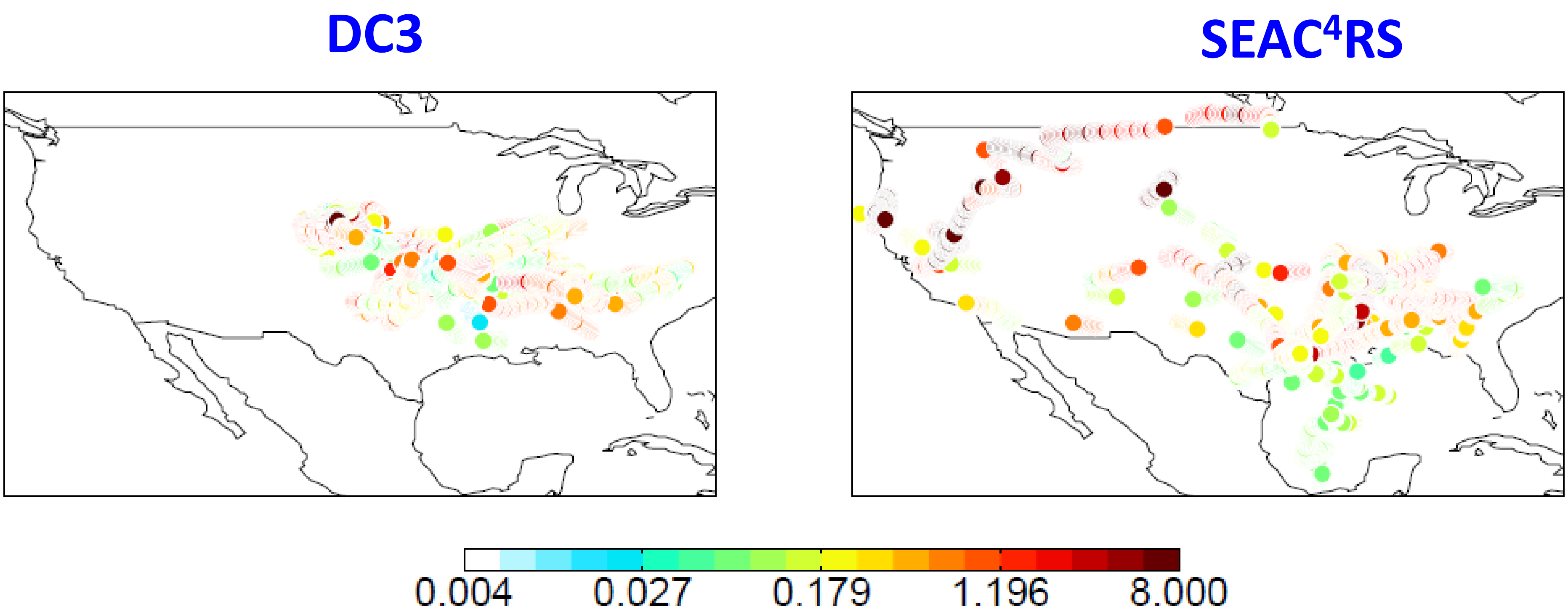
Suggests that urban/fossil BrC absorption is not photochemically altered (we conclude the same for Cape Cod), but that BrC from fires whitens with a lifetime of ~1 day (consistent with Forrister et al., 2015). Possible means of bringing models into better agreement with observational constraints?

[Wang et al., ACP, 2016]

On-Going Work: Exploring the Radiative Impacts of BrC

Building a BrC simulation for GEOS-Chem

- Optical properties as a function of BC:OA of source
- Impact of including whitening
- Testing against observations of OA mass and OA absorption
- Estimating the DRE with range of assumptions

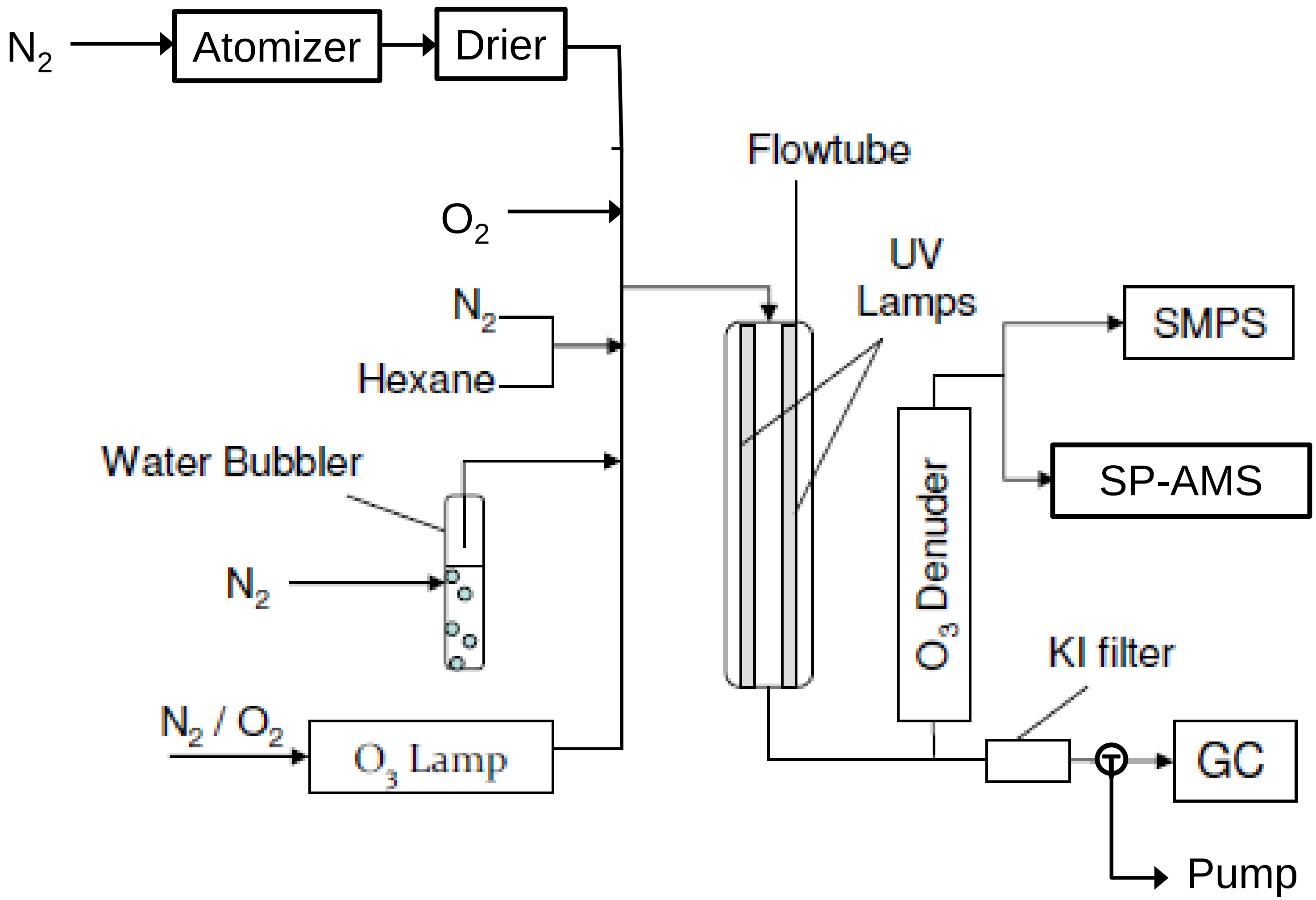


Absorption from Organic Aerosols at 365nm, Mm^{-1}

[Wang et al., in prep]

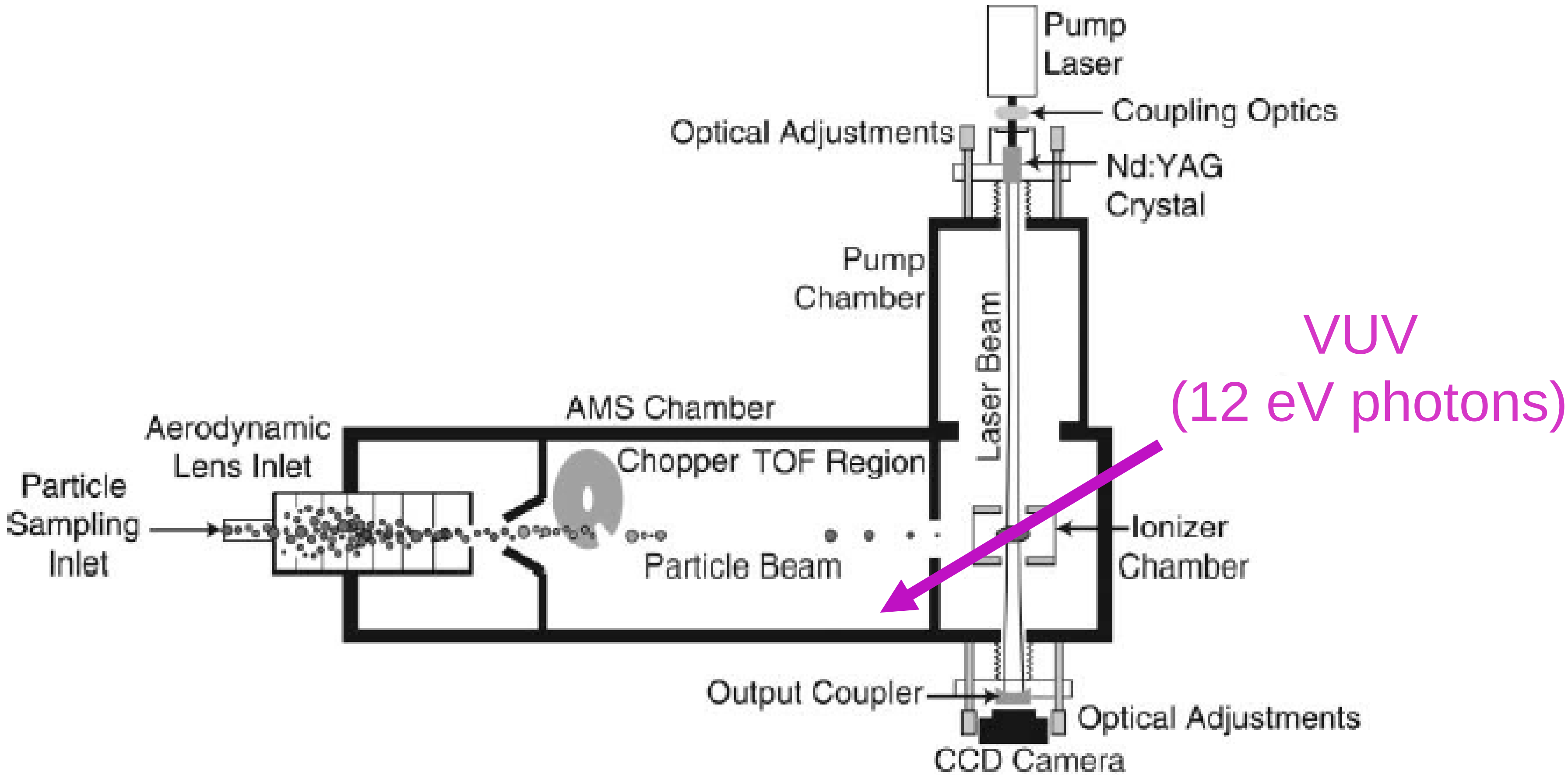
Heteogeneous oxidation of BC

with Kevin Wilson (LBNL), Manjula Canagartna and Paola Massoli (ARI)



[Browne, et al., 2015]

SP-AMS with VUV ionization



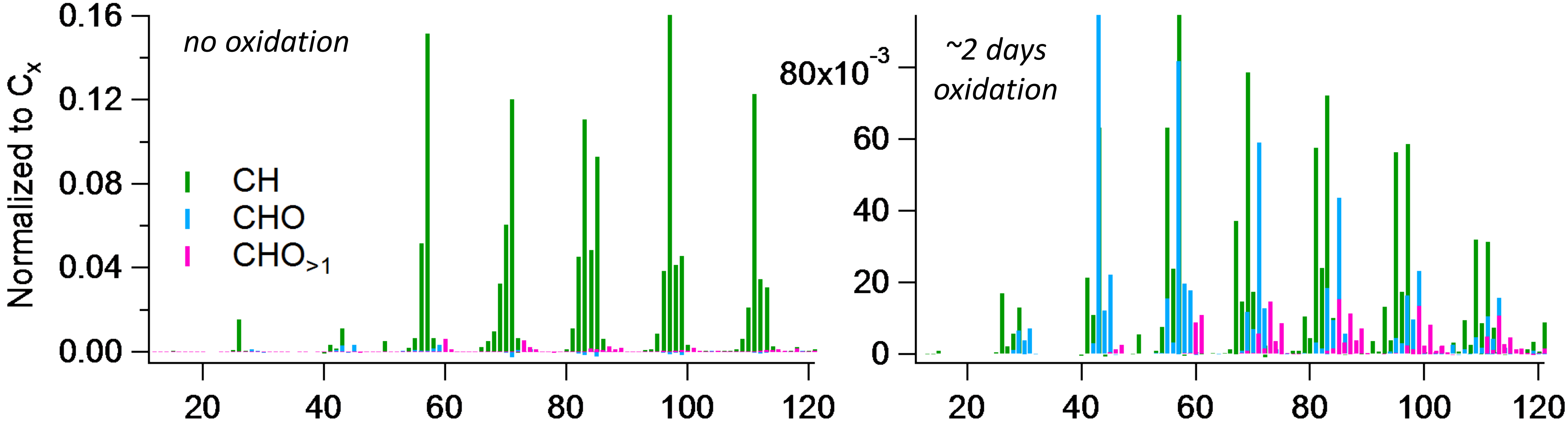
Ionization efficiencies

PAHs: 7-8 eV

Most organics: 9-10 eV

BC fragments (e.g. C_3): ~11.5 eV

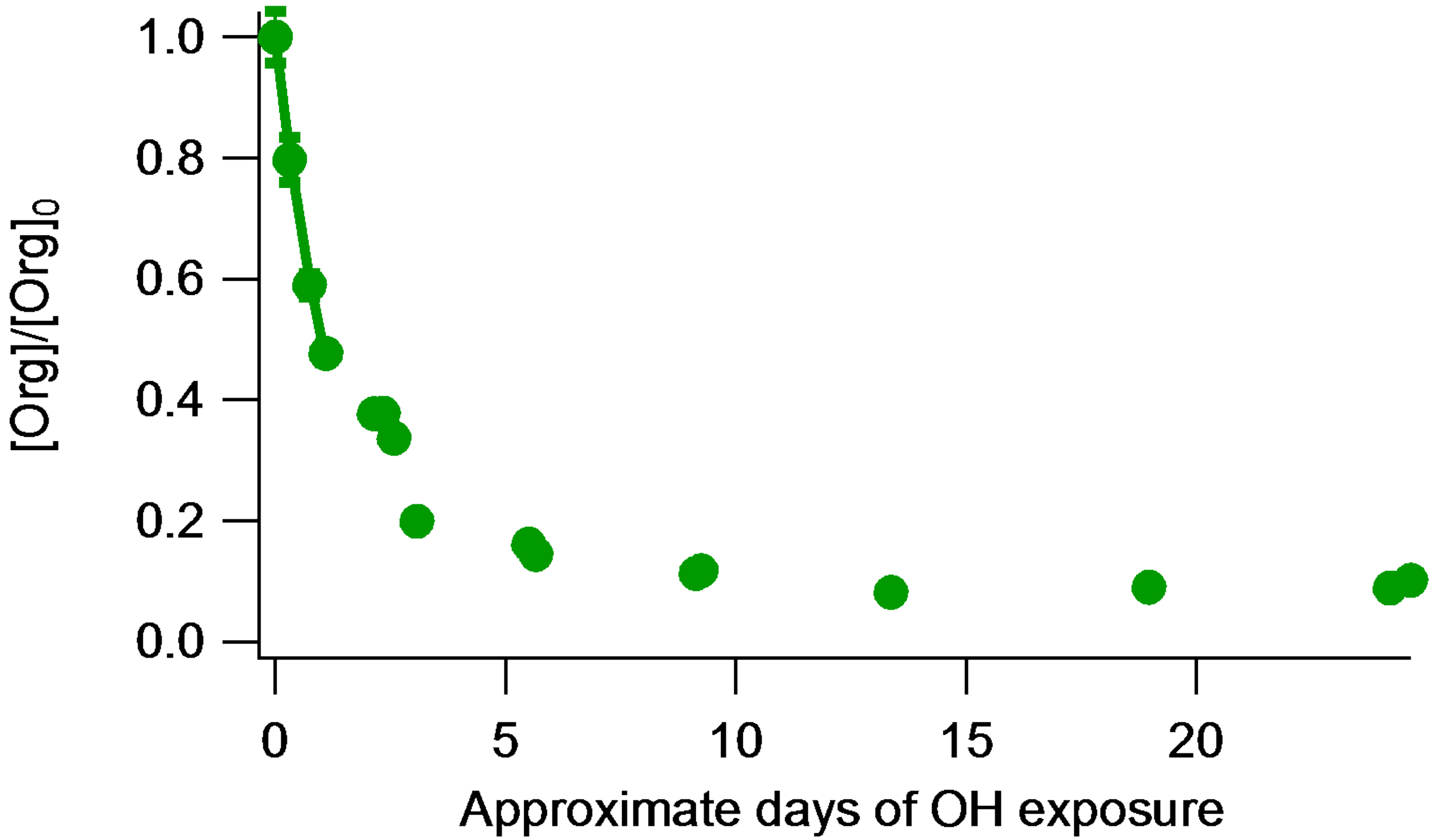
Changes to adsorbed organic species



Organics associated with BC (representing small fraction of total particles) undergo dramatic chemical changes

[Browne, et al., 2015]

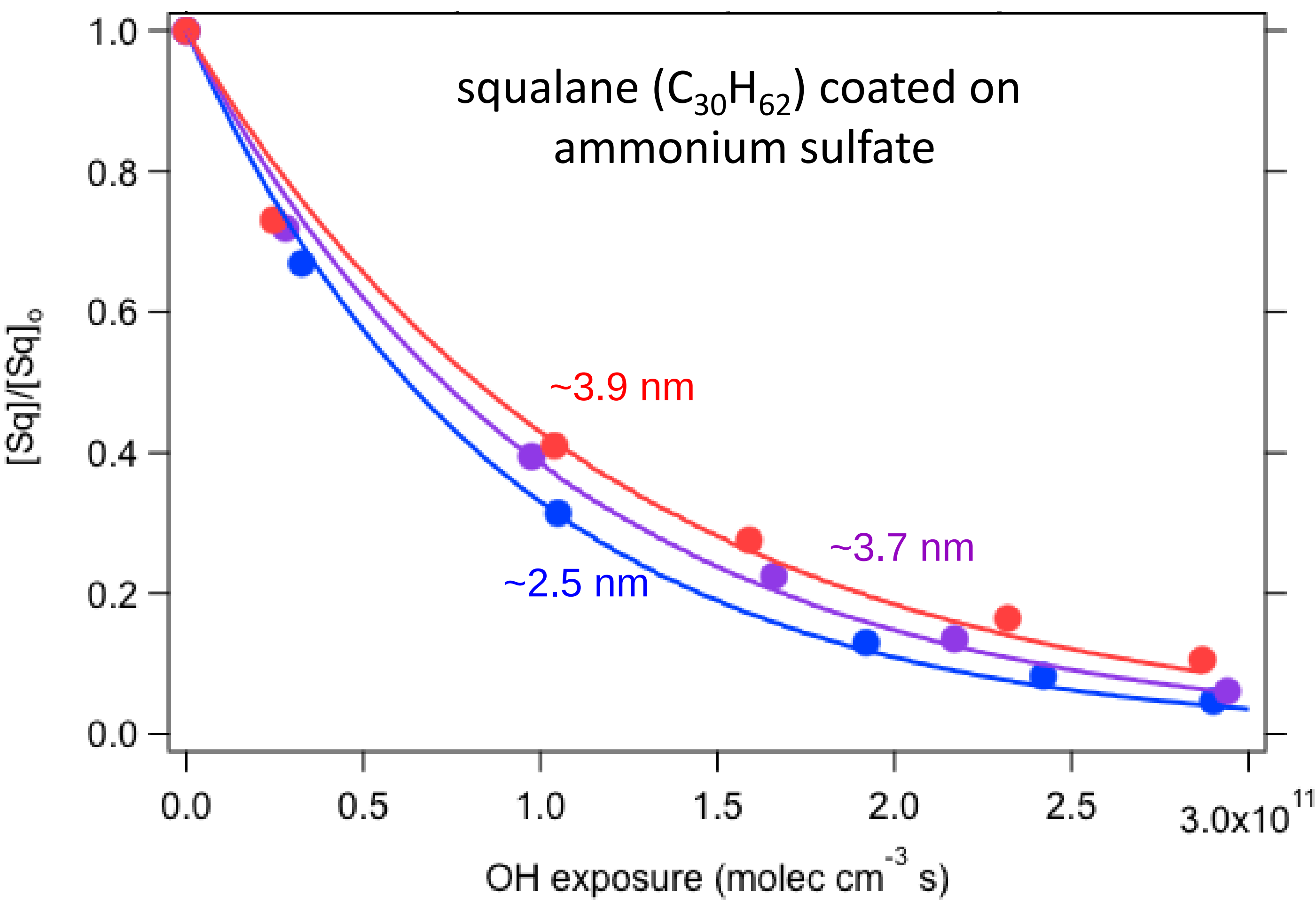
Rapid loss of organic species



Lifetime of adsorbed organics is short

[Browne, et al., 2015]

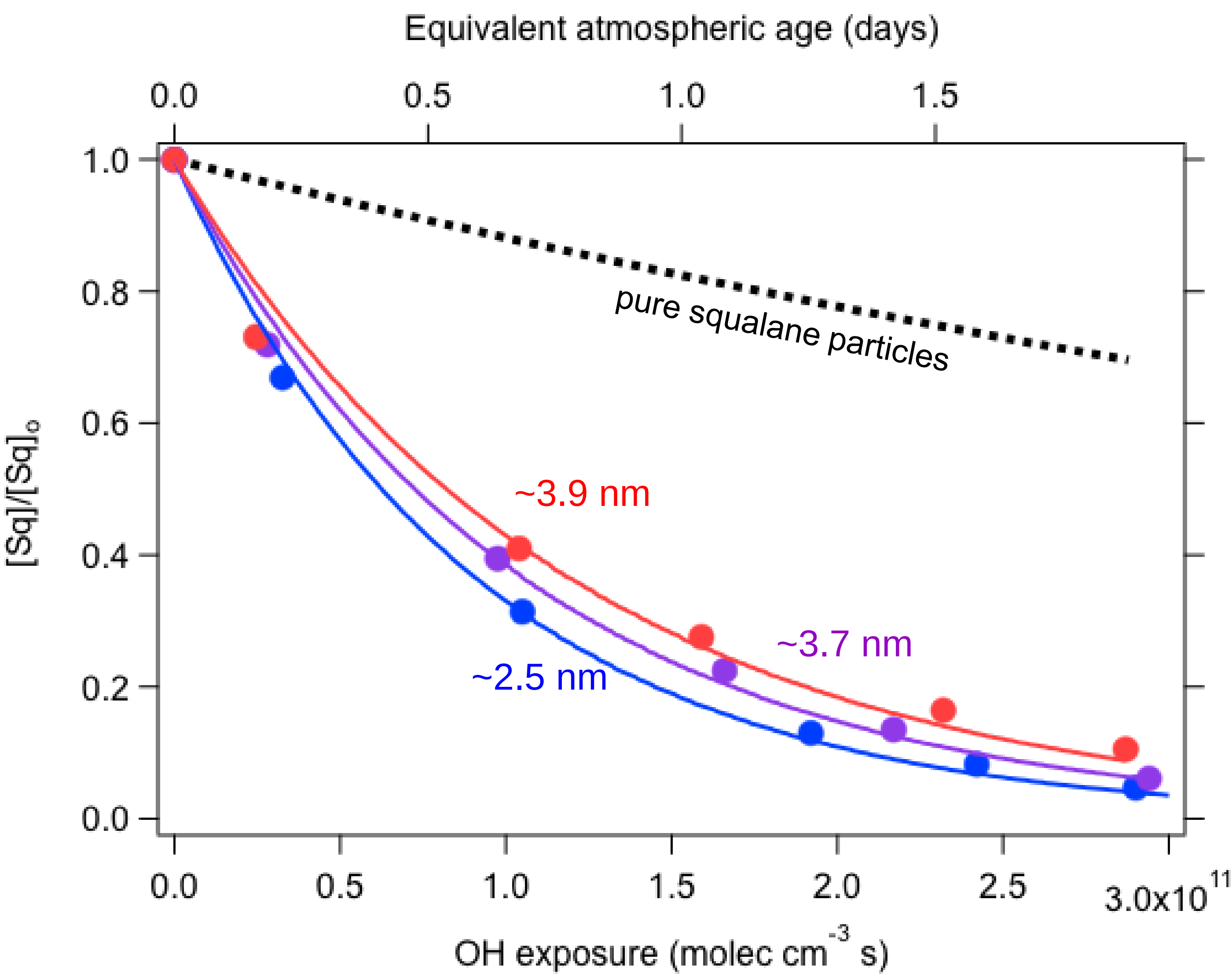
Heterogeneous oxidation of thin coatings



Thinner coating → faster reaction

[Lim et al. in prep]

Heterogeneous oxidation of thin coatings



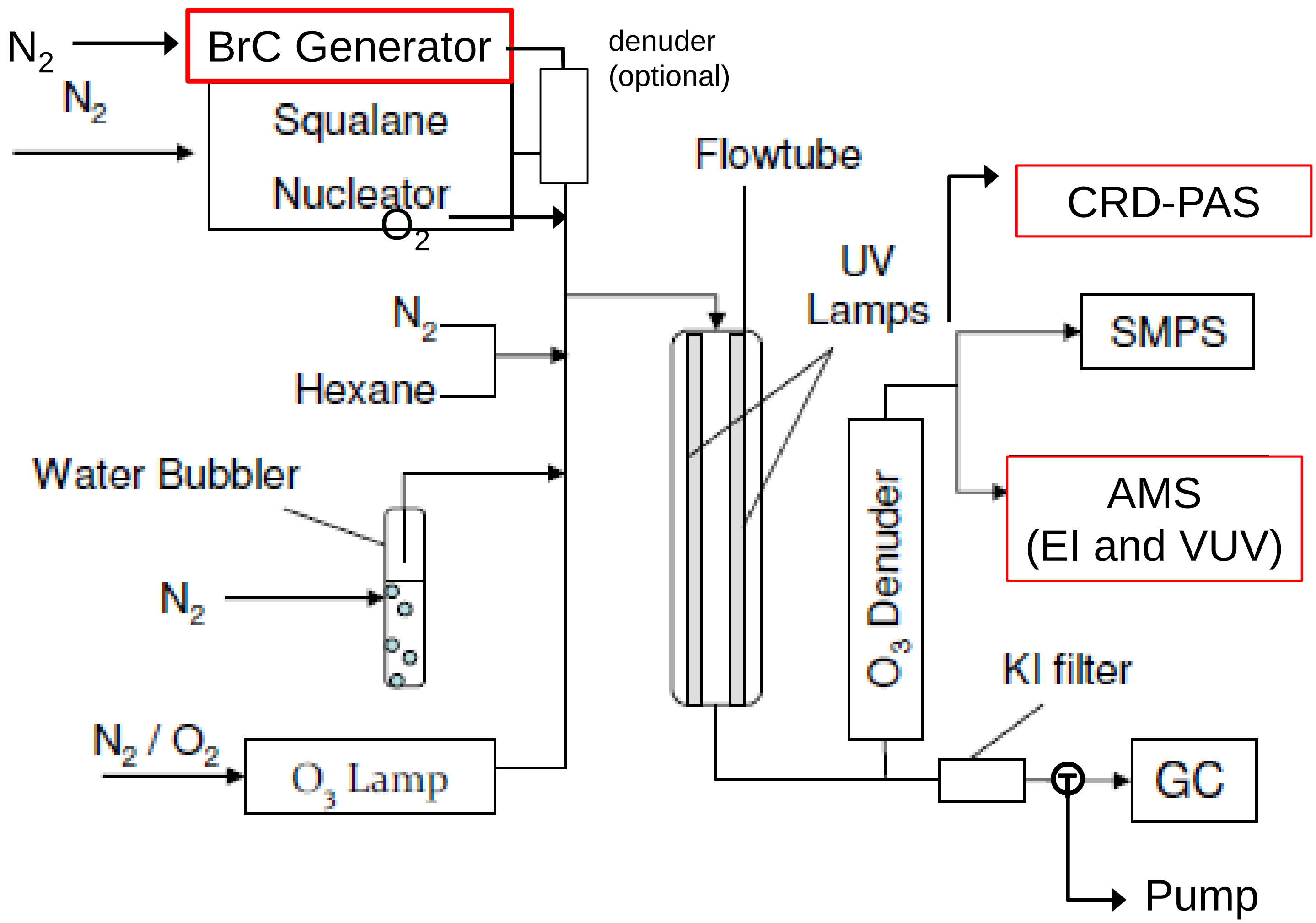
Thinner coating ⟶ faster reaction

Coated particles react far faster (x10) than pure particles

[Lim et al. in prep]

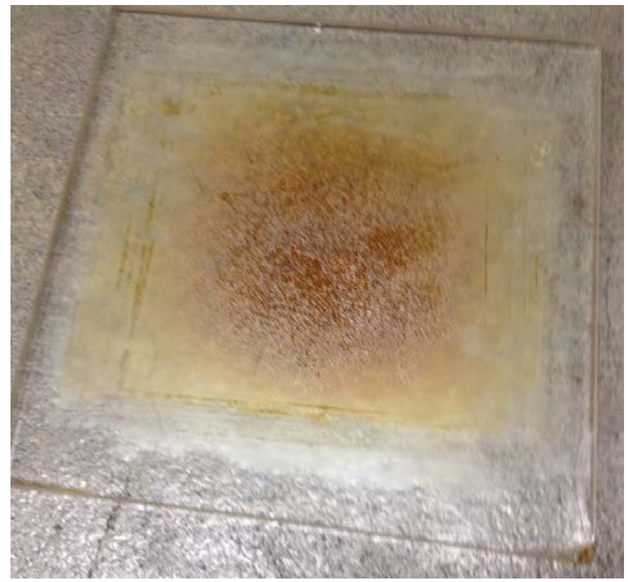
Heterogeneous oxidation of Brown Carbon

with Xiaolu Zhang, Chris Cappa (UCD); Kevin Wilson, Tom Kirchstetter (LBNL)



"Brown carbon generator"

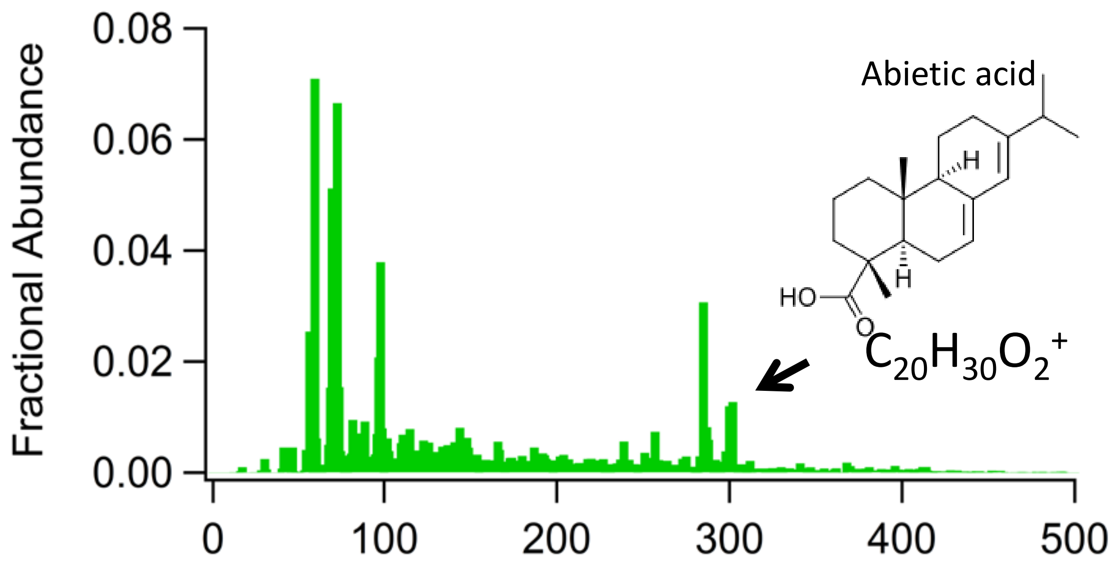
Heated biomass: Smoldering only, no BC



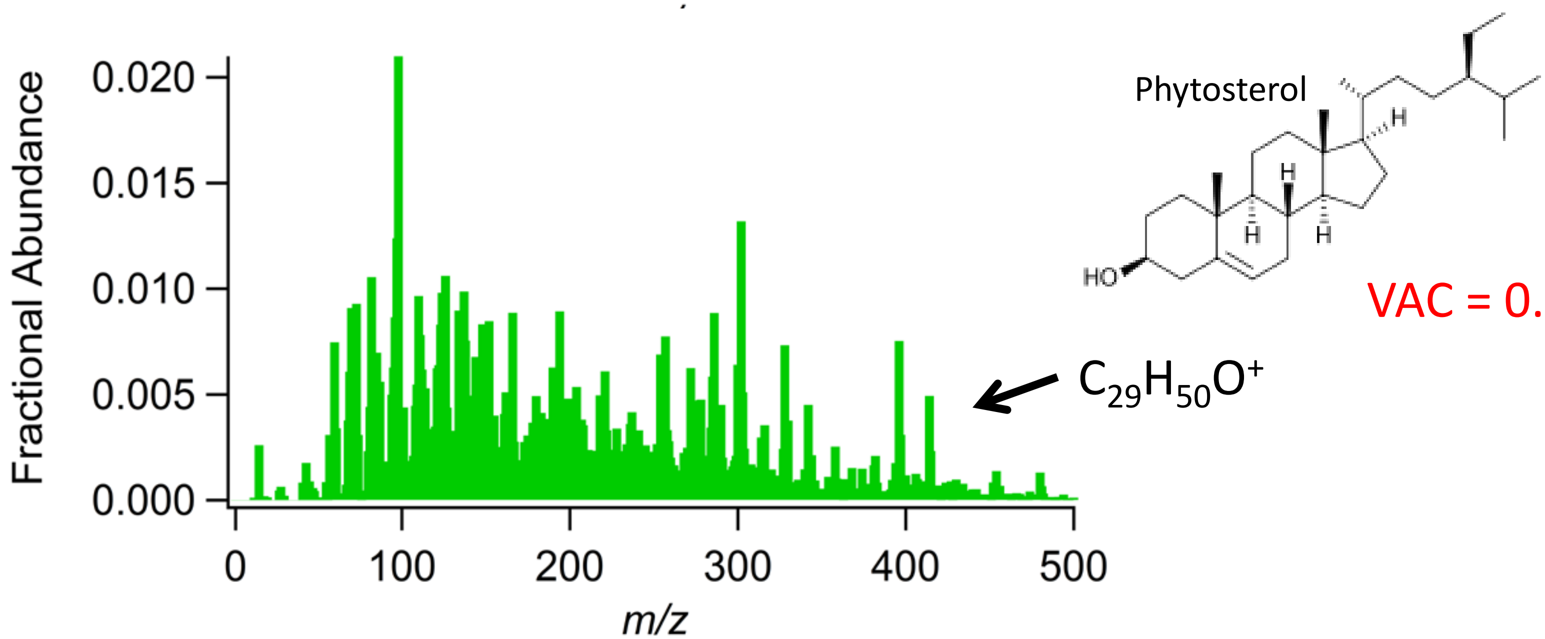
Single-scattering albedo (SSA)
@405 nm: ~0.99
Volume-absorption coefficient (VAC)
@405 nm: ~0.20 $m^3\ cm^{-3}$

Tom Kirchstetter (LBNL)

Primary BrC is complex and highly variable

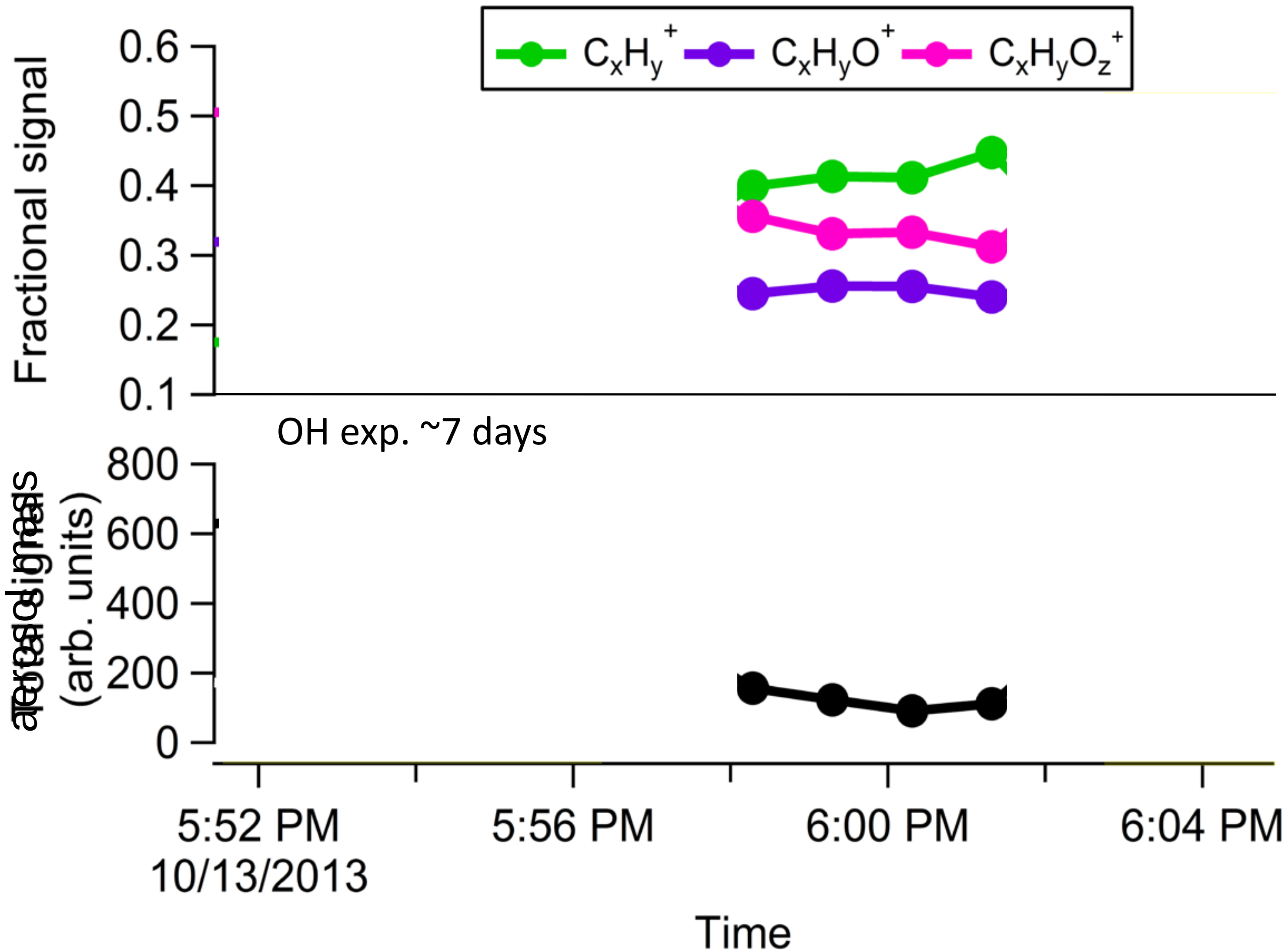


VAC = 0.05 m²/cm³

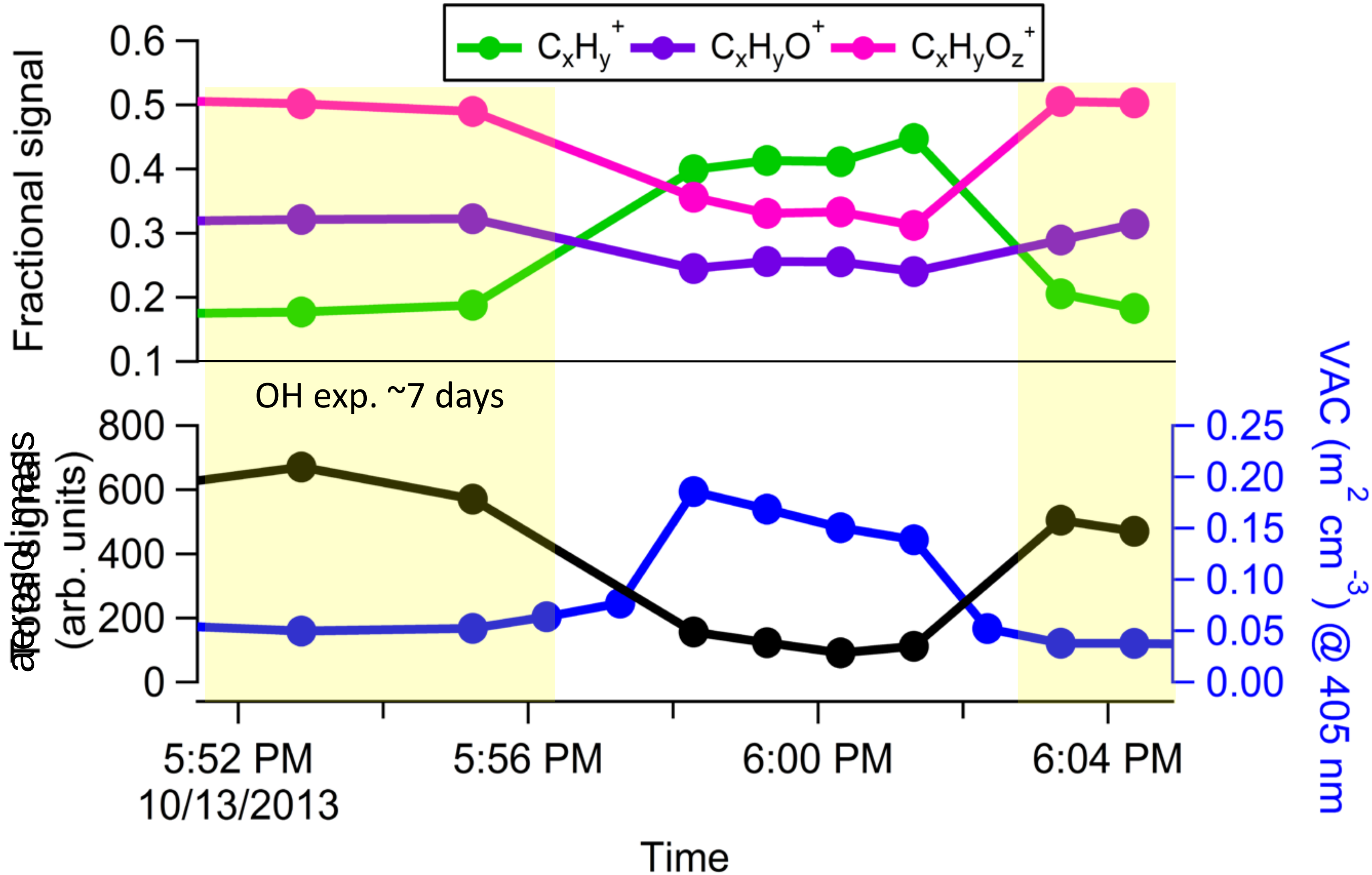


VAC = 0.30 m²/cm³

SOA formation from POA + vapors + OH



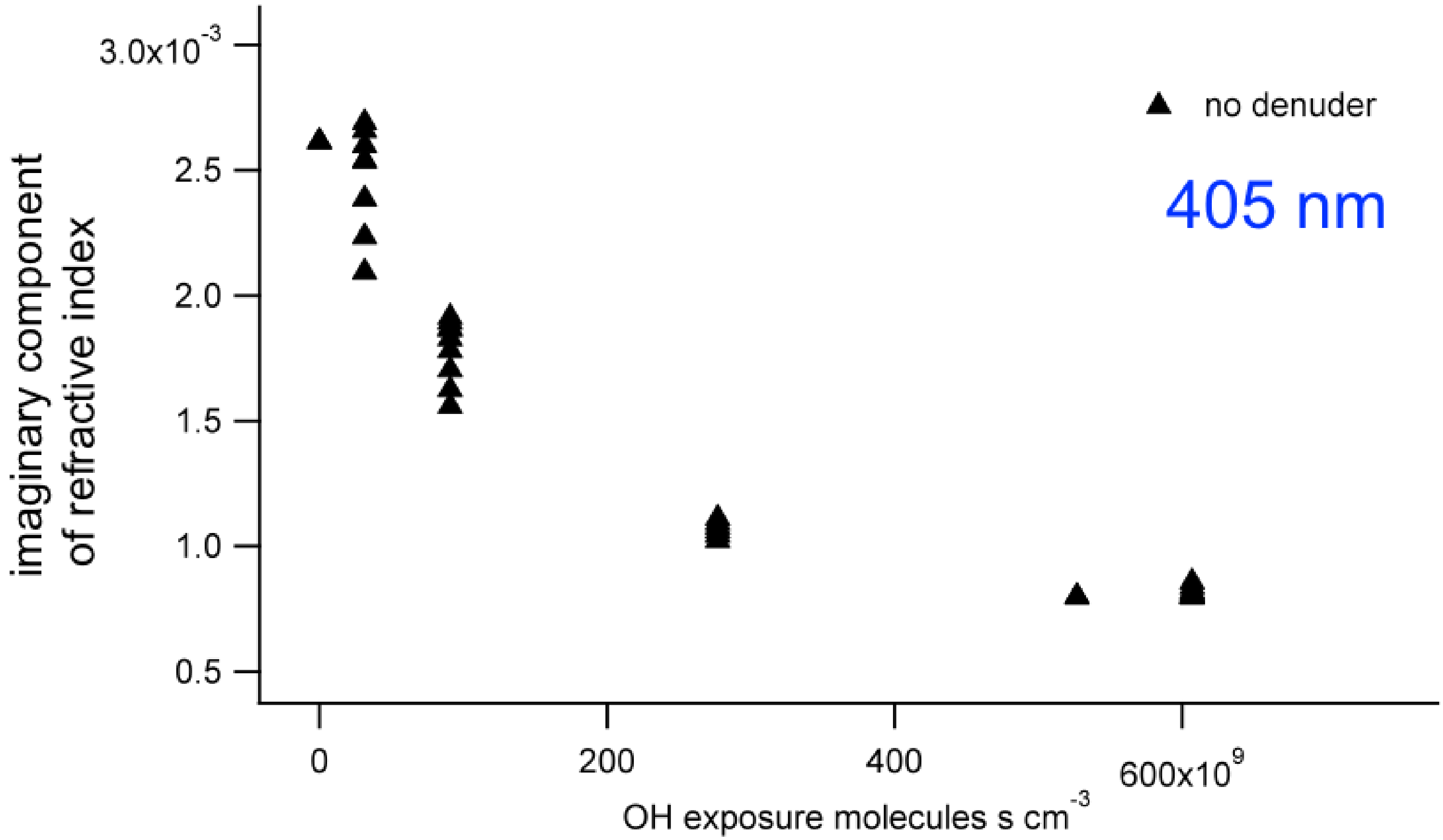
SOA formation from POA + vapors + OH



SOA is much less “brown” than POA

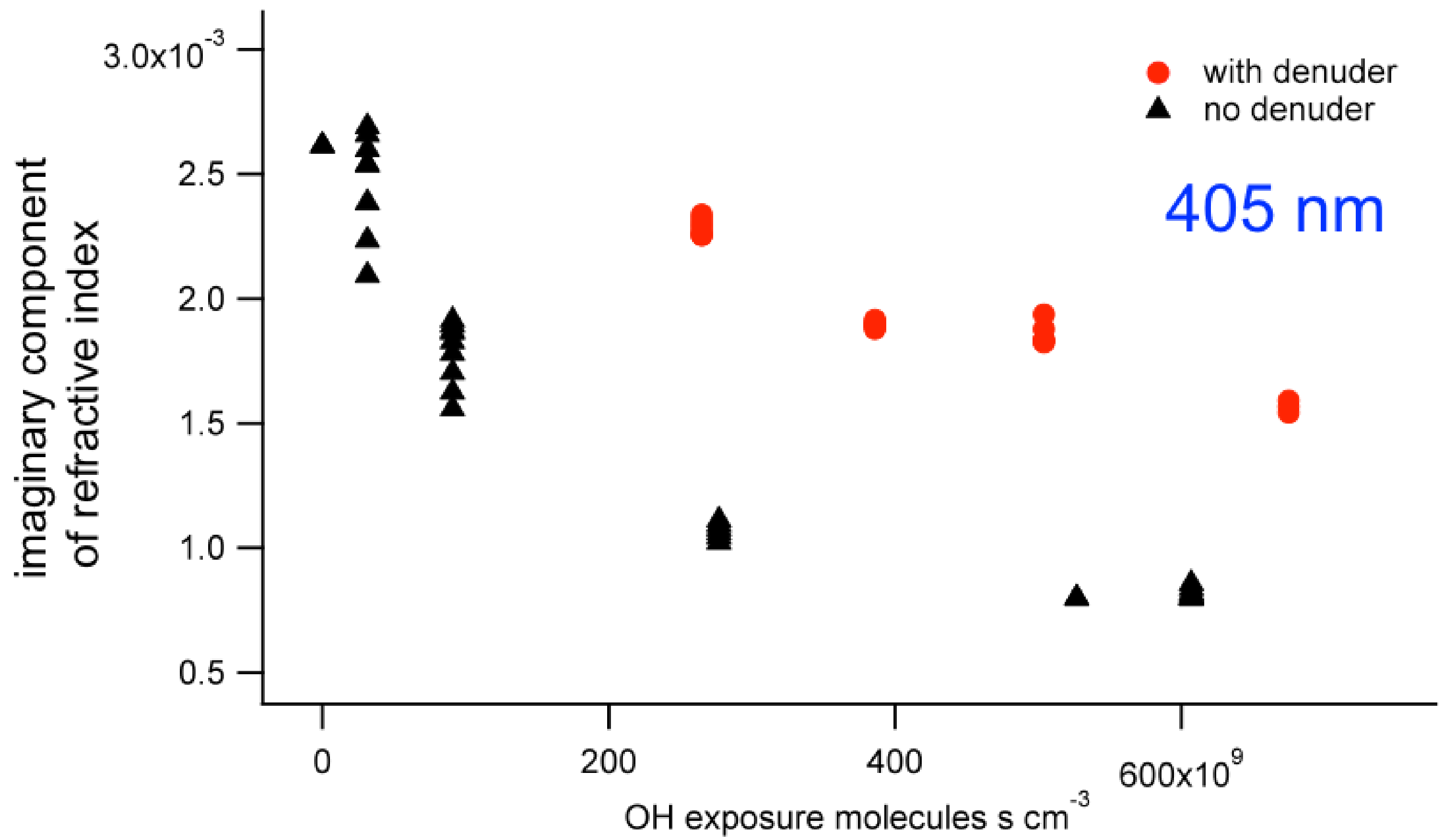
(also more hygroscopic)

Optical properties vs. degree of aging



SOA formation □less absorption (SOA is less brown than POA)

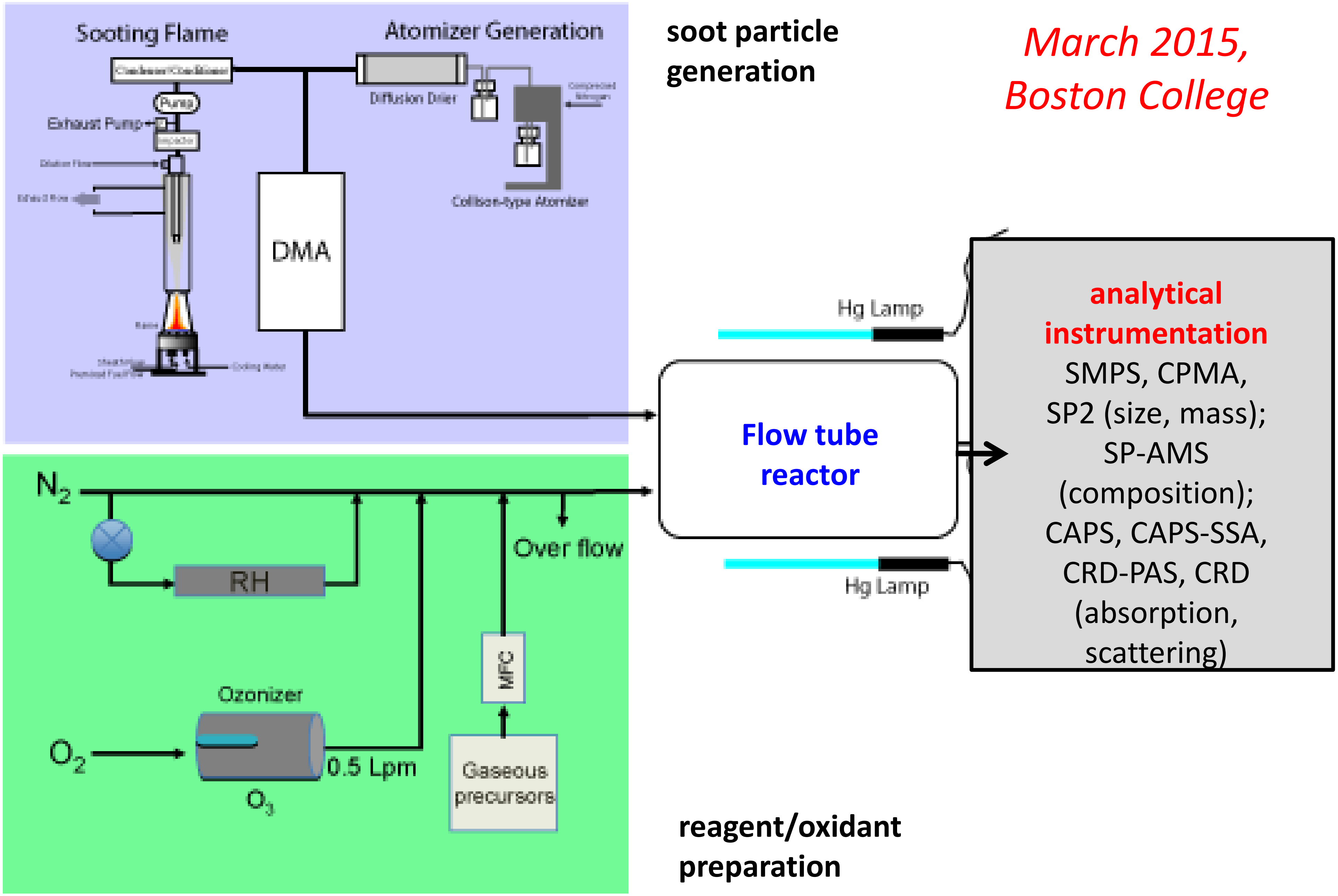
Optical properties vs. degree of aging



SOA formation □less absorption (SOA is less brown than POA)

POA aging □less absorption (bleaching)

BC+coating experimental intensive



BC-coatings: Experimental matrix

BC source

- soot from inverted diffusion flame (denuded at 300^{o}C)
    - CH_4, ethylene
- also atomized black carbon spheres

Particle size

- mostly polydisperse, 30-300 nm

Aging type

- OH/O_3 only (heterogeneous ox.)
- OH + SO_2 (sulfuric acid coating)
- OH/O_3 + VOCs (SOA coating: isoprene, α-pinene, or naphthalene)
- mixed (SOA+sulfuric acid, multiple SOA types)

Degree of oxidation

- 2-4 [OH] levels per system

Ongoing work: parameterization

Changes to composition/hygroscopicity + optics
as a function of atmospheric exposure

Key optical parameters determined, included in a “lookup table”
(or interpolated function) based on experimental results

Inputs		Outputs
particle size relative humidity wavelength composition (BC:org:SO_4)	→	mass extinction efficiency single scattering albedo asymmetry parameter

Summary/conclusions

- Modeling results: Better descriptions of BC aging can reconcile models with observational constraints on both mass loadings of BC and aerosol absorption; resulting estimate of the BC DRF is lower than AR5

- Observational analysis: We develop a new indirect method for estimating BrC absorption from multi-wavelength measurements. Key results: BrC contributes 10-35% of UV absorption, BrC from biomass burning appears to "whiten" with atmospheric aging.

- Laboratory results: Heterogeneous oxidation an efficient way to change organic components of soot; oxidation can dramatically decrease "brown-ness" of BrC

- Next steps:
    - Explore how uncertainty in BrC sources, evolution impacts DRF
    - Laboratory results → implementation in models

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U. Hawaii: Anthony Clarke

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U. Sao Paulo: Paulo Artaxo

PNNL: Lizabeth Alexander

Brookhaven: Arthur Sedlacek, Thomas Watson, Stephen Springston

Los Alamos: Allison Aiken, Manvendra Dubey

<u>Publications from this Project</u>:

Heald et al., ACP, 2014
Wang et al., ACP, 2014
Wang et al., ACP, 2016
Browne et al., JPCA, 2015
3 more in preparation

Lambe et al., ES&T, 2013
Sedlacek et al. AS&T, 2015
Lambe et al., J. Aerosol Sci., 2015
Onasch et al., AS&T, 2015

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