Estimating Brown Carbon concentrations by Multi-wavelength Thermal-Optical Analysis

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Methods to Calculate Aerosol Radiation Absorption

$$ATN_{\lambda} = ln\left(\frac{FT_{\lambda,f}}{FT_{\lambda,i}}\right) \quad (1)$$

$$b_{ATN}(_{\lambda}) = ATN_{\lambda} \times \left(\frac{A}{V}\right) \quad (2)$$

$$\frac{b_{ATN}(\lambda_1)}{b_{ATN}(\lambda_2)} = \left(\frac{\lambda_1}{\lambda_2}\right)^{-AAE} \quad (3)$$

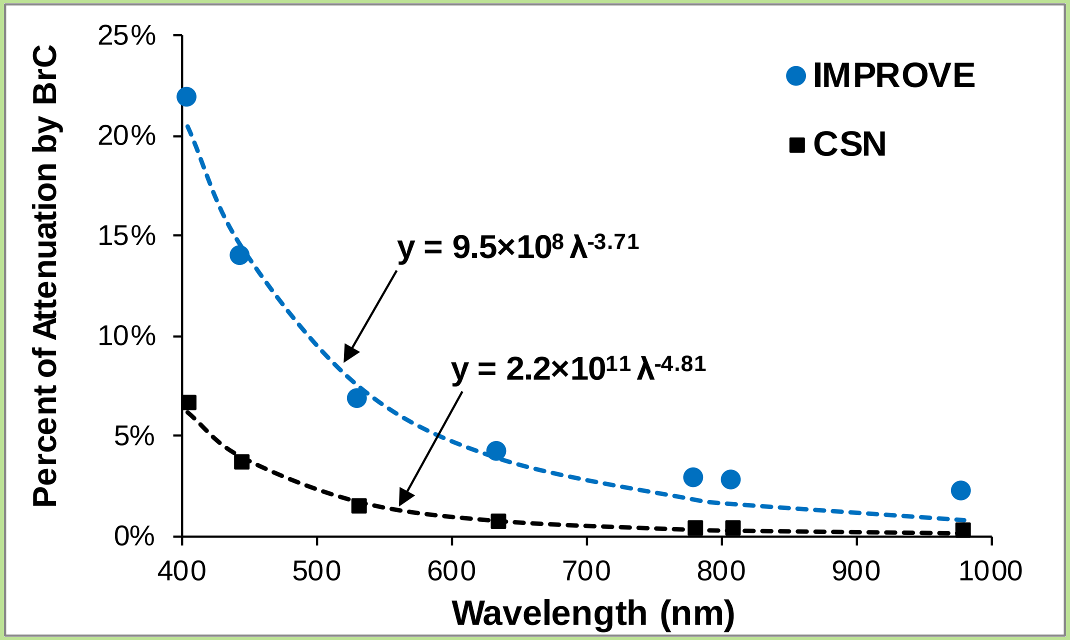
$$ATN_{\lambda} = q_{BC} \times \lambda^{-AAE_{BC}} + q_{BrC} \times \lambda^{-AAE_{BrC}} \quad (4)$$

Where:

- ATN is the radiation attenuation
- $FT_{\lambda,i}$ and $FT_{\lambda,f}$ represent the filter transmittance before and after thermal carbon analysis, respectively
- b_{ATN} is the attenuation coefficient
- A is the filter deposit area (3.53 cm^2)
- V is the 25 mm IMPROVE sample volume (33.12 m^2)
- AAE is the absorption Angström exponent
- q_{BC} and q_{BrC} represent the fitting coefficients

Enhanced light attenuation by BrC is found at shorter wavelengths

(average attenuation due to BrC_{405} is 6.7% for CSN and 21.9% for IMPROVE in 2016)



DRI Model 2015 Multiwavelength Carbon Analyzer

The wavelength ratios at 405 and 635 nm are used to derive the power-law fit of b_{ATN}

Attenuation coefficient (b_{ATN}) is not easily related to BrC mass

- Challenge:

  -- BrC is not a single compound and $MAC_{BrC(\lambda)}$ varies with compound

- Solution:

  -- Measure MAC for several BrC surrogate compounds, and express BrC as surrogate-equivalent mass concentrations (BrC_e)

$$^{*}BrC_{(\lambda)} = b_{ATN}/MAC_{BrC(\lambda)};\ b_{ATN_{(\lambda)}} = ATN_{\lambda} \times \left(\frac{A}{V}\right);\ ATN_{\lambda} = \ln\left(\frac{FT_{\lambda,f}}{FT_{\lambda,i}}\right)$$

Properties that should be considered to select BrC standards

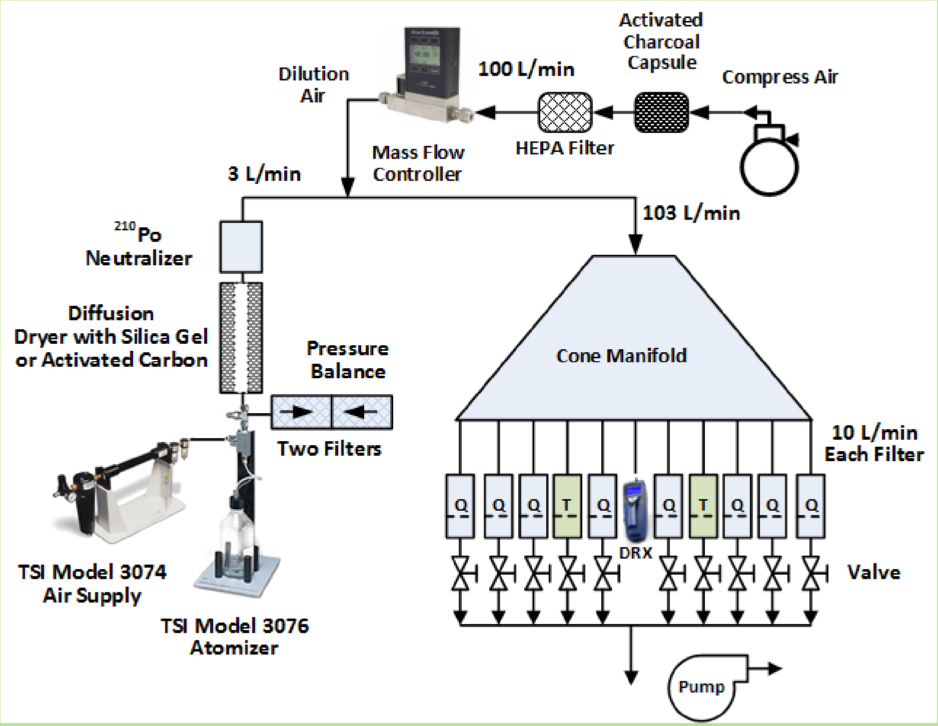
- Atmospheric aerosol relevant
- Light absorbing OC
- Low volatility and chemically stable
- Low toxicity
- Easy to nebulize (for laboratory testing)
- Commercially available with reasonable cost

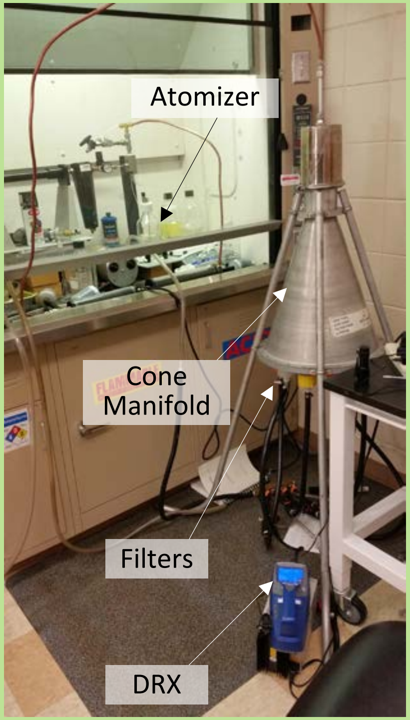
Approximately 20 BrC compounds were considered

BrC Compound	Molecular Formula
• **Humic-Like Substances (HULIS)**	
Fulvic Acid	$C_{14}H_{12}O_8$
Humic Acid (Suwannee River, GA)	$C_{187}H_{186}O_{89}N_9S_1$
Humic Acid Sodium Salt	$C_9H_8Na_2O_4$
• **Nitro-aromatics - Aged Smoke (SOA)**	
2-nitrophenol	$C_6H_5NO_3$
4-nitrophenol	$C_6H_5NO_3$
2,4-dinitrophenol	$C_6H_4N_2O_5$
3-methyl-4-nitrophenol	$C_7H_7NO_3$
4-nitrocatechol	$C_6H_5NO_4$
3-methyl-5-nitrocatechol	$C_7H_7NO_4$
3-methyl-6-nitrocatechol	$C_7H_7NO_4$
4-methyl-5-nitrocatechol	$C_7H_7NO_4$
• **PAHs - Fresh Smoke**	
Fluoranthene (C16)	$C_{16}H_{10}$
Pyrene (C16)	$C_{16}H_{10}$
Chrysene (C18)	$C_{18}H_{12}$
Retene (C18)	$C_{18}H_{18}$
Perylene (C20)	$C_{20}H_{12}$
Bbenzo[a]pyrene (C20)	$C_{20}H_{12}$
Indeno[1,2,3-cd]pyrene (C22)	$C_{22}H_{12}$
Anthanthrene (C22)	$C_{22}H_{12}$
Coronene (C24)	$C_{24}H_{12}$

BrC solutions are nebulized and sampled onto filter substrates

(loadings of 1 to 1024 μm/filter)



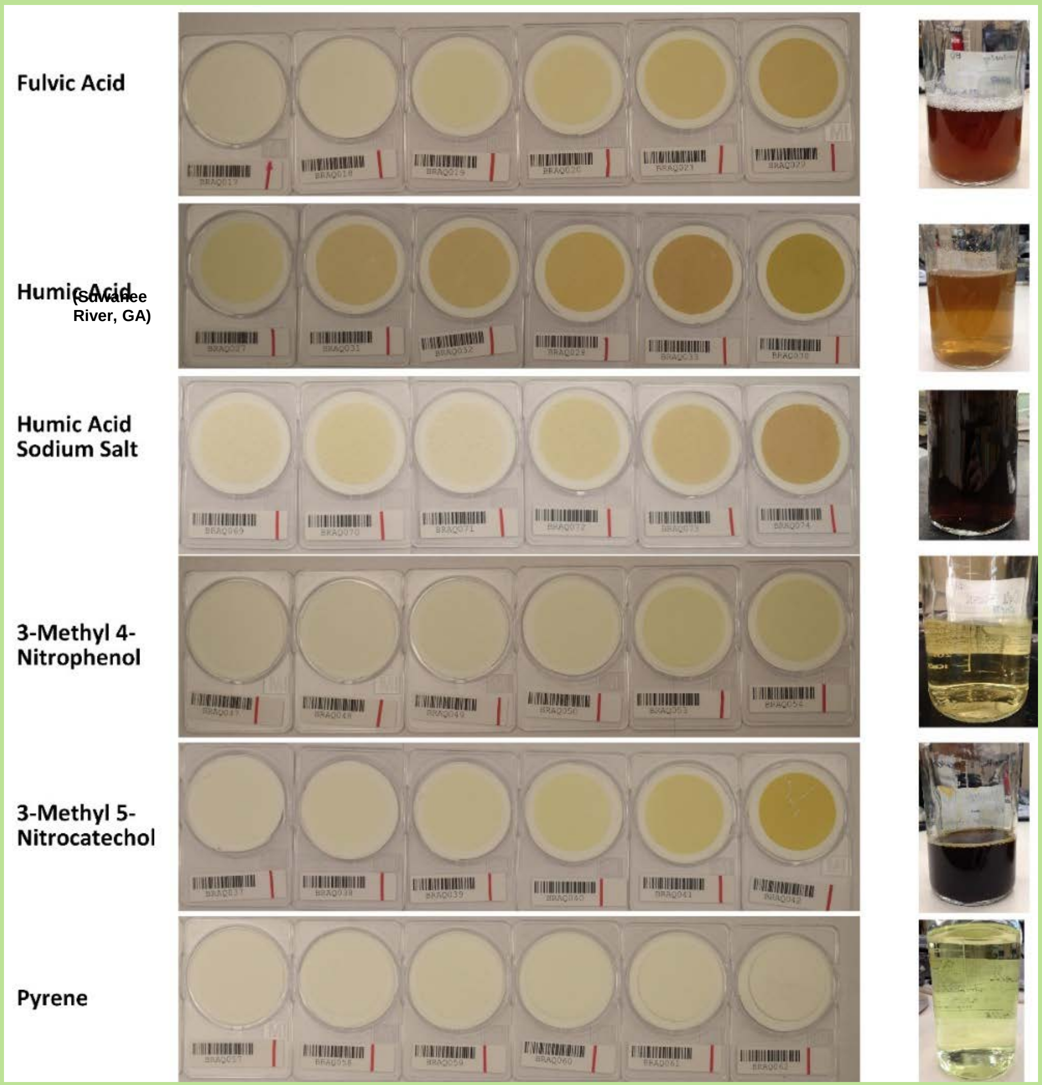


Sampling flow rates and time are adjusted to collect different loadings (i.e., 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, and 1024 μg/filter)

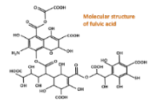
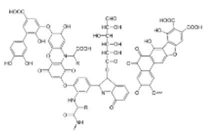
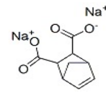
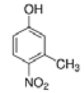
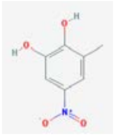
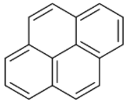
BrC standards exhibit different “brownness”

Filter samples with increasing loading

BrC in Solution



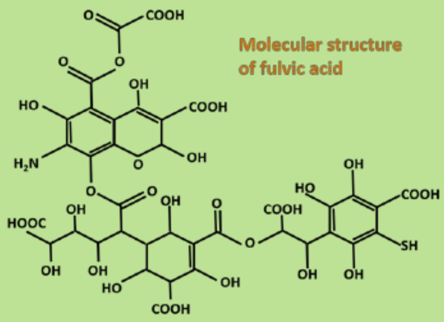
Large variations found for MACs and AAEs in tested brown carbon surrogates

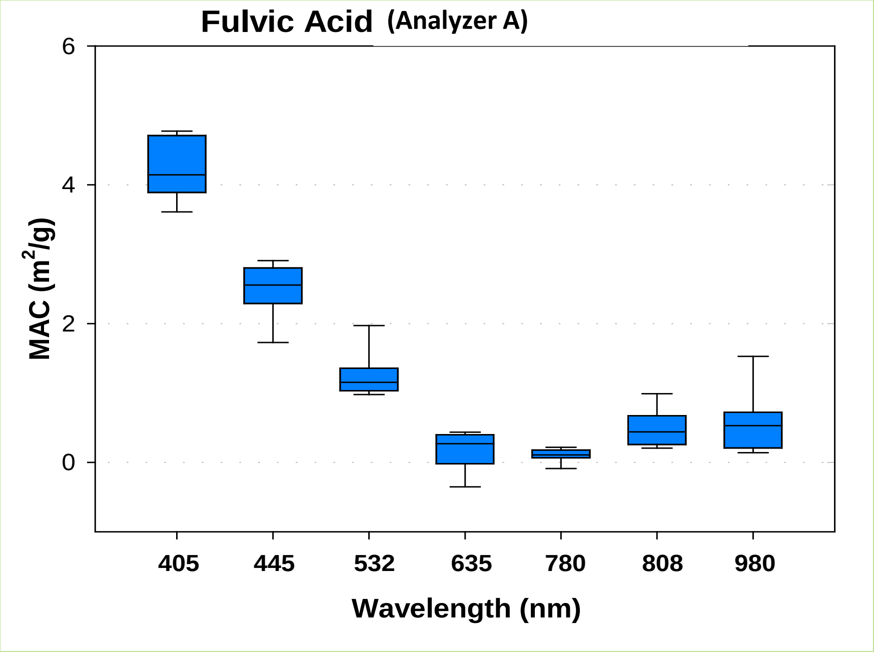
Brown Carbon Compound (formula)	Molecular Structure	405 nm MAC (m^2/g)	AAE
Humic-like Substance (HULIS)			
Fulvic acid ($C_{14}H_{12}O_8$)		4.5	5.4
Humic acid (Suwannee River, GA) ($C_{187}H_{186}O_{89}N_9S_1$)		3.9	N/A
Humic acid sodium salt (HASS) ($C_9H_8Na_2O_4$)		15.4	4.3
Nitro-aeromatics- Aged Smoke (SOA)			
3-methyl-4-nitrophenol ($C_7H_7NO_3$)		2.2	9.7
3-methyl-5-nitrocatechol PAHs- Fresh Smoke ($C_7H_7NO_4$)		15.1	8.4
PAHs- Fresh Smoke			
Pyrene ($C_{16}H_{10}$)		0.1	1.3

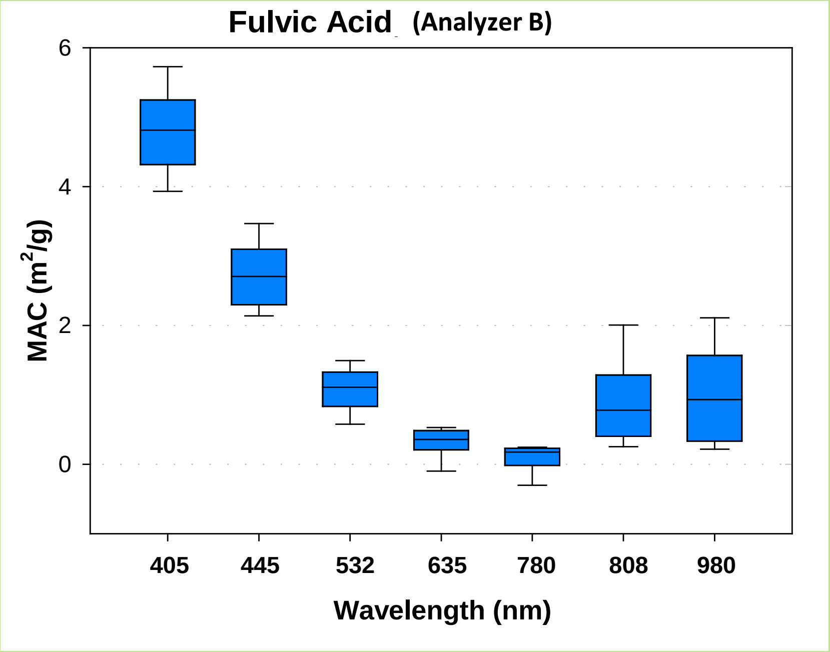
*MAC: Mass absorption coefficient; AAE: Absorption Ångström Exponent; $b_{ATN(405)}/b_{ATN(635)} = \left(\frac{405}{635}\right)^{-AAE}$

MAC$_{405}$ of fulvic acid (4.5 m^2/g) are wavelength dependent

(AAE = ~5.4)

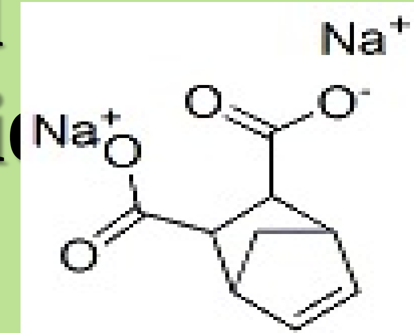


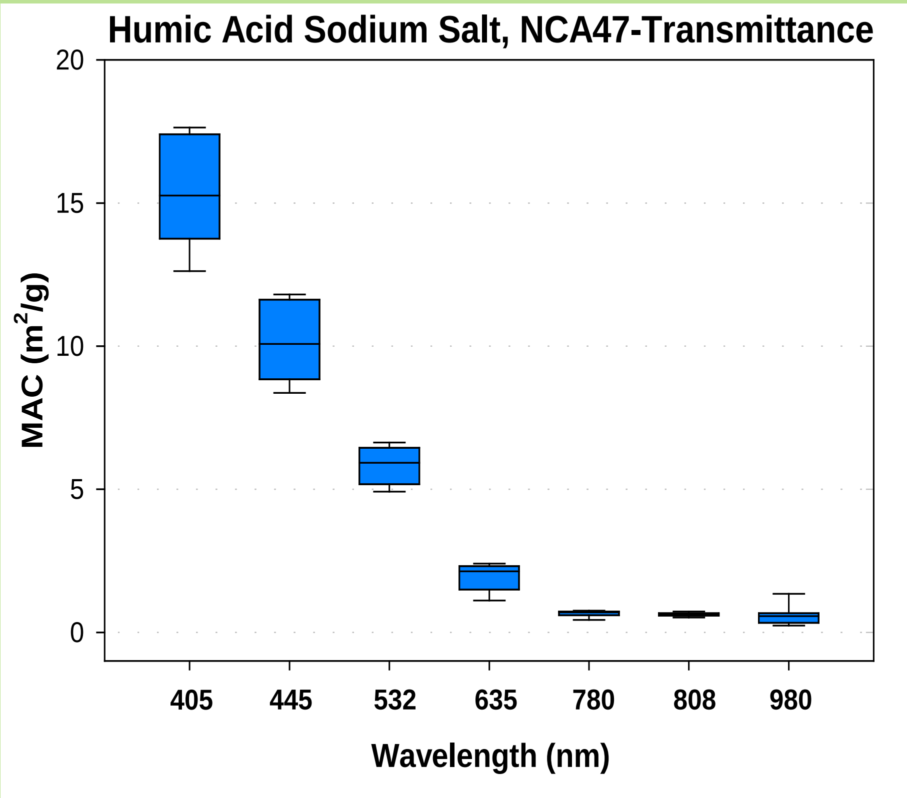


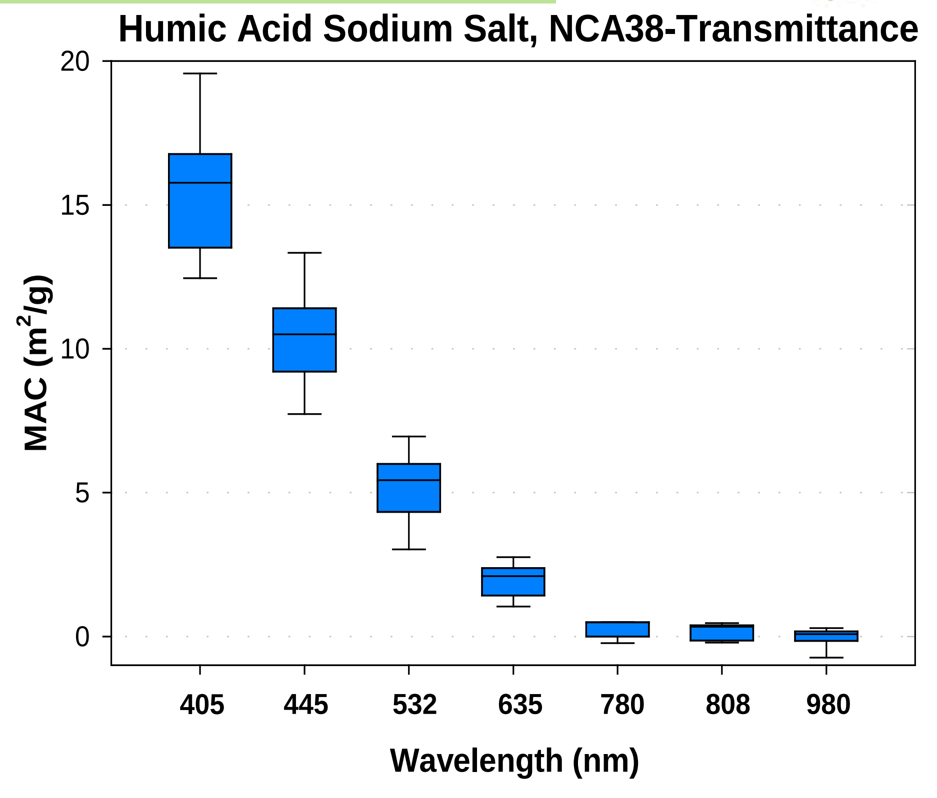


MAC: Mass Absorption Coefficient

Humic acid sodium salt (HASS) yield larger MAC_{405} (15.4 m^2/g) and lower AAE (~4.3) than fulvic aci

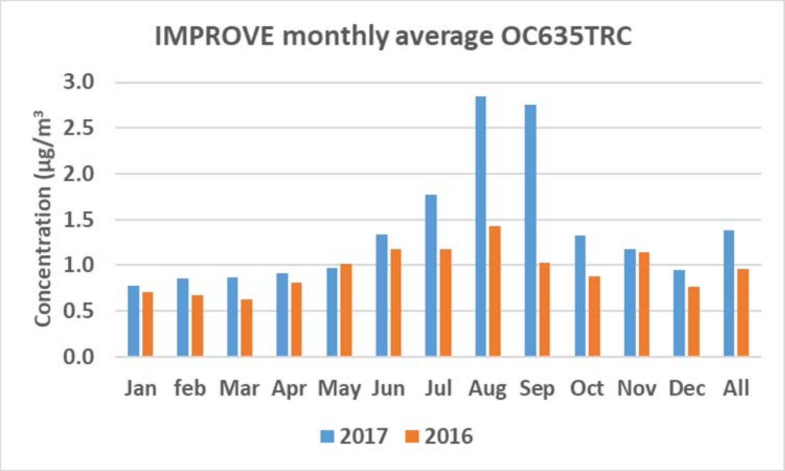




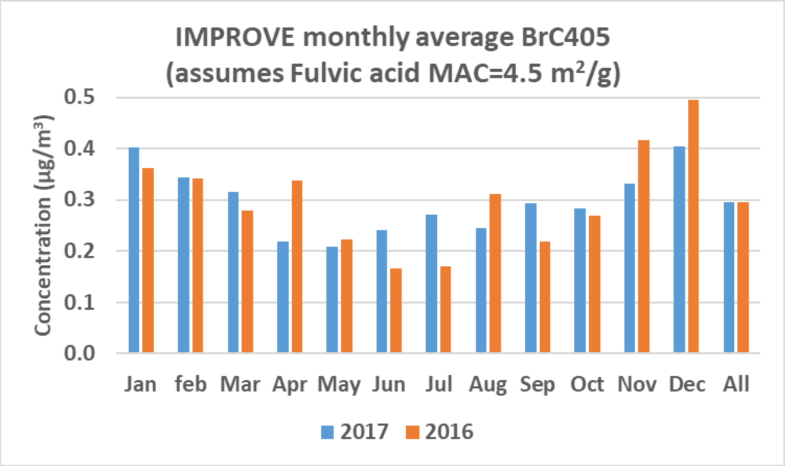


Used as standard to calibrate Integrated Plate Method by the Europeans

BrC$_e$ concentrations were estimated, assuming fulvic acid or humic acid sodium salt (2016 and 2017 IMPROVE and CSN data sets)



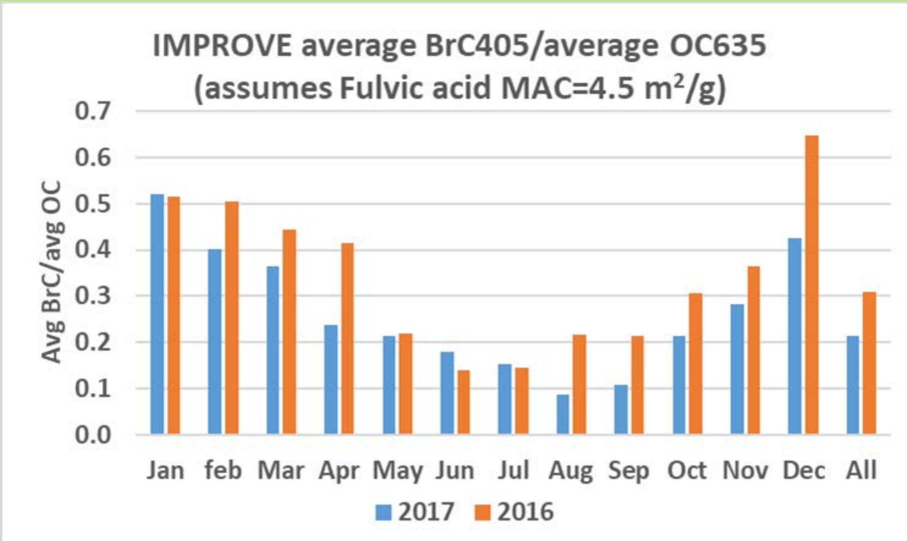
IMPROVE 2017 OC higher than 2016 for every month, especially in summer



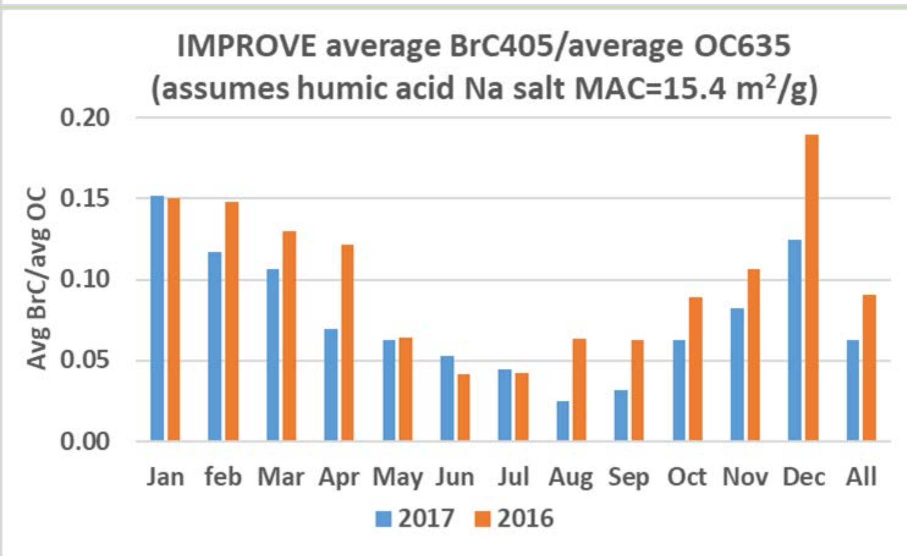
Average BrC concentrations about the same between 2016 and 2017

BrC$_e$ accounts for ~5-30% of monthly average OC depending on the assumption on MAC$_{405}$

(156 sites)

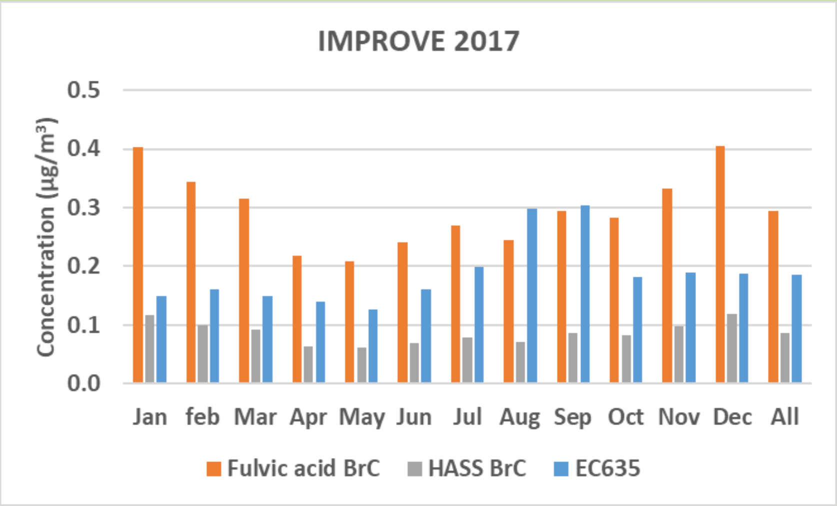


Attributing BrC$_e$ light absorption to fulvic acid (MAC$_{405}$=4.5 m^2/g), BrC$_e$ averages 20-30% of OC.

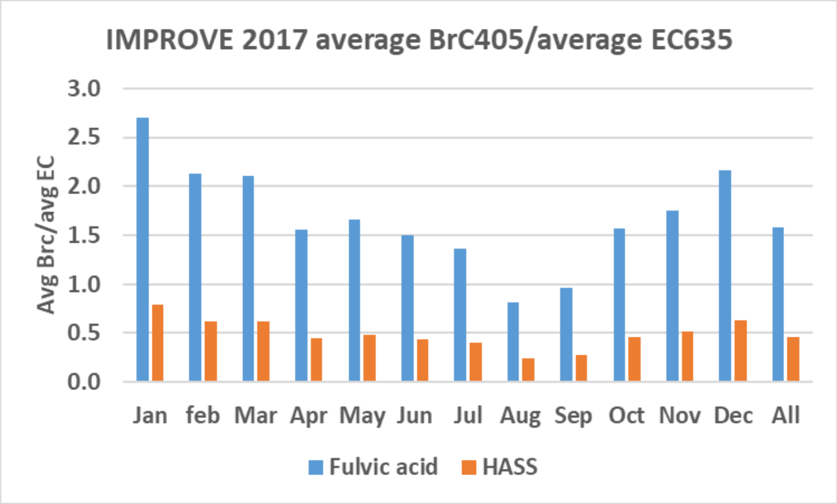


Attributing BrC$_e$ light absorption to humic acid sodium salt (MAC$_{405}$=15.4 m^2/g), BrC averages 5-10% of OC.

BrC_e concentrations may be lower or higher than EC depending on BrC composition



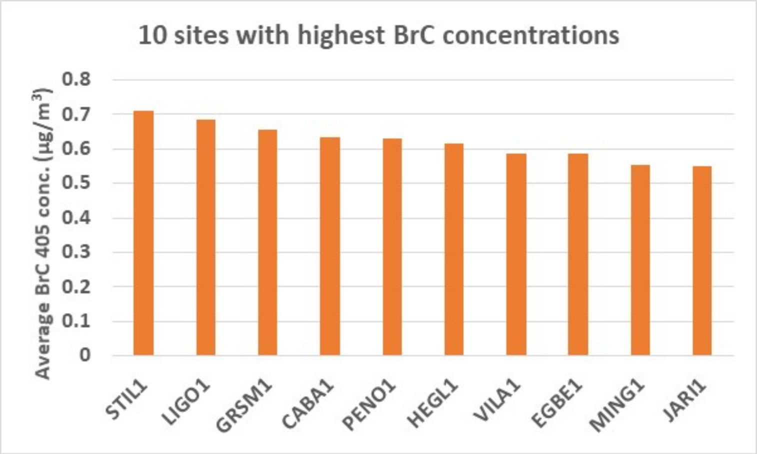
Depending upon composition of BrC, BrC concentrations are comparable in magnitude to EC concentrations



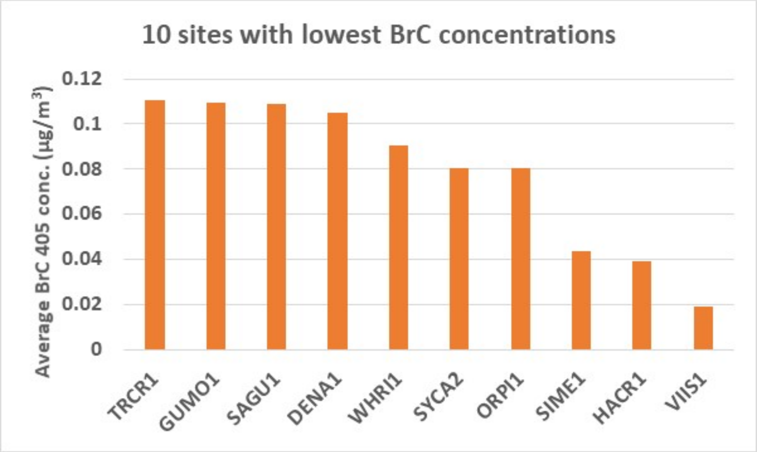
With BrC_e assumed to be fulvic acid, BrC_e on average is greater than EC; if humic acid sodium salt is assumed, BrC_e about half EC on average

No specific spatial distributions were found for the 10 highest BrC_e sites

(Assumes BrC_e is fulvic acid for 2016 IMPROVE data)



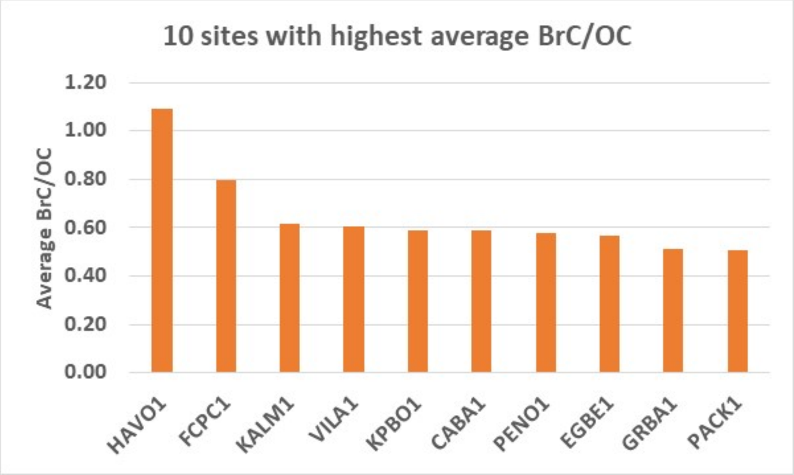
STIL=Stilllwater, OK
LIGO= Linville Gorge, NC
GRSM= Great Smoky Mtns, NC
CABA=Casco Bay, ME
PENO= Penobscot, ME
HEGL=Hercules Glade, MO
VILA= Viking Lake, IO
Egbert, Ontario
Mingo, MO
James River, VA



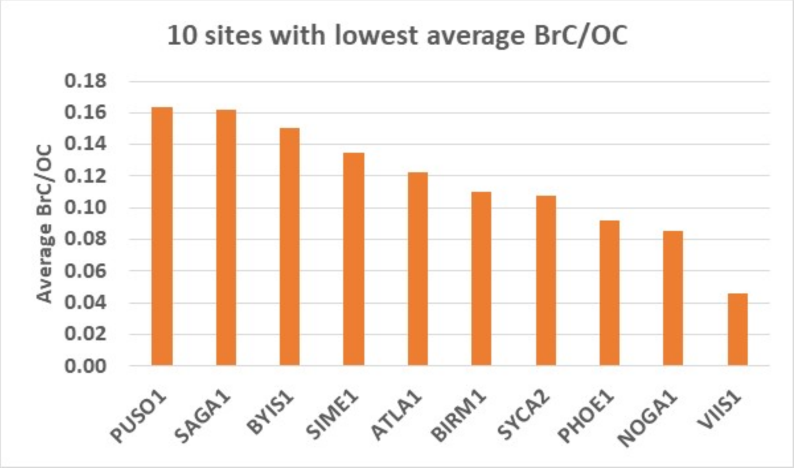
Low BrC concentrations tend to be western sites
TRCR= Trapper Creek-Denali, AK
GUMO= Guadelupe Mountains, TX
SAGU=Saguaro, AZ
DENA= Denali, AK
WHRI=White River, CO
SYCA= Sycamore Canyon, AZ
ORPI=Organ Pipe, AZ
SIME=Simeonof, AK
HACR=Haleakala Crater, HI
VIIS= Virgin Islands

BrC_e accounts for ~50-100% of OC at the 10 highest sites

(Assumes BrC_e is fulvic acid for the 2016 IMPROVE data)



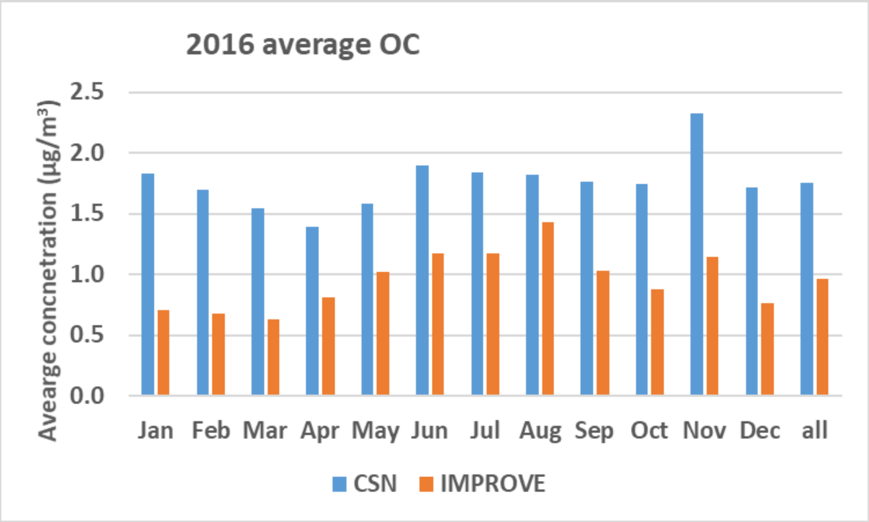
HAVO= Hawaii Volcanoes, HI
FCPC=Forest County Potawatami, WI
KALM= Kalmiopsis, OR
VILA=Viking Lake, IA
KPBO=Kenai Peninsula Burough, AK
CABA=Casco Bay, ME
PENO=Penobscot, ME
EGBE=Egbert, Ontario
GRBA=Great Basin, NV
PACK=Pack Monadnock Summit, NH



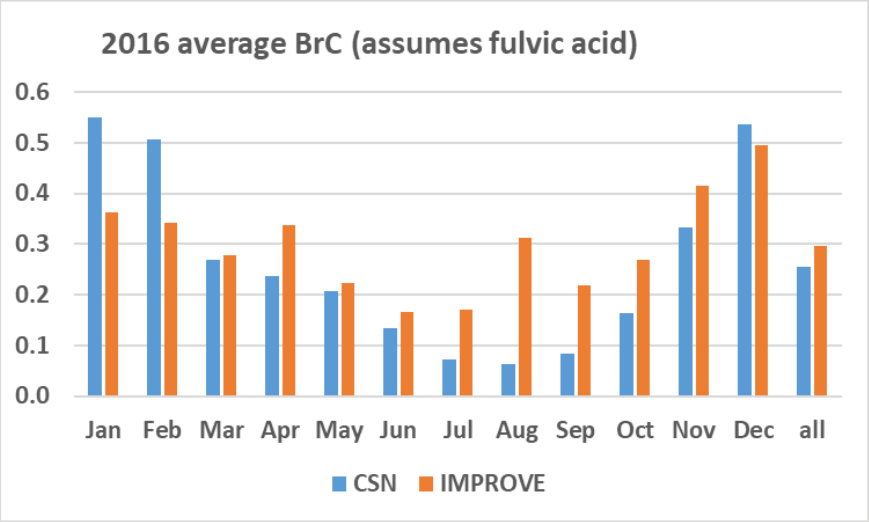
Urban Areas tend to have low BrC/OC ratios
PUSO= Puget Sound, WA
SAGA=San Gabriel, CA
BYIS=South Korea
SIME=Simeonof, AK
ATLA= Atlanta, GA
BIRM=Birmingham, AL
SYCA=Sycamore Canyon, AZ
PHOE=Phoenix, AZ
NOGA=Nogales, AZ
VIIS= Virgin Islands

Monthly average BrC_e ranged ~0.2 to 0.5 µg/m3 for IMPROVE and 0.06 to 0.5 µg/m3 for CSN

(Assumes BrC_e is fulvic acid for 2016 dates)



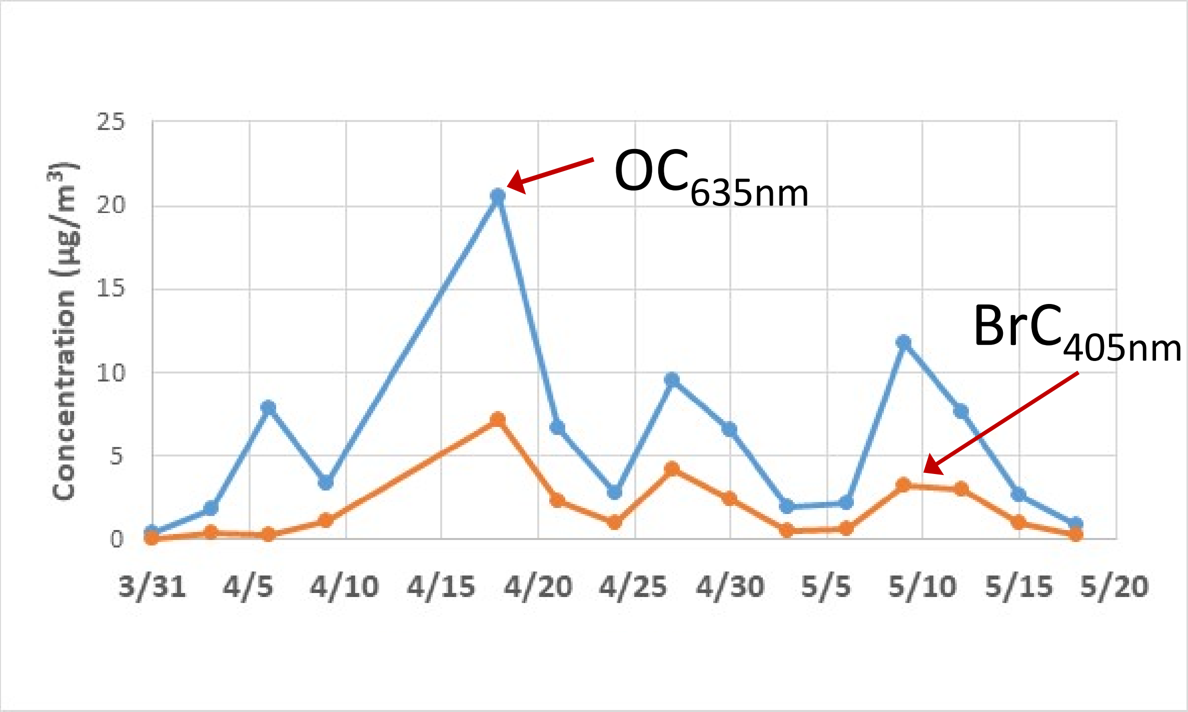
Not surprisingly, CSN has significantly higher OC than IMPROVE



But- IMPROVE has on average higher BrC than CSN (less in winter, more in summer)

BrC_e concentration exceeding 7 μg/m^3 was found during the 2016 Everglade fire

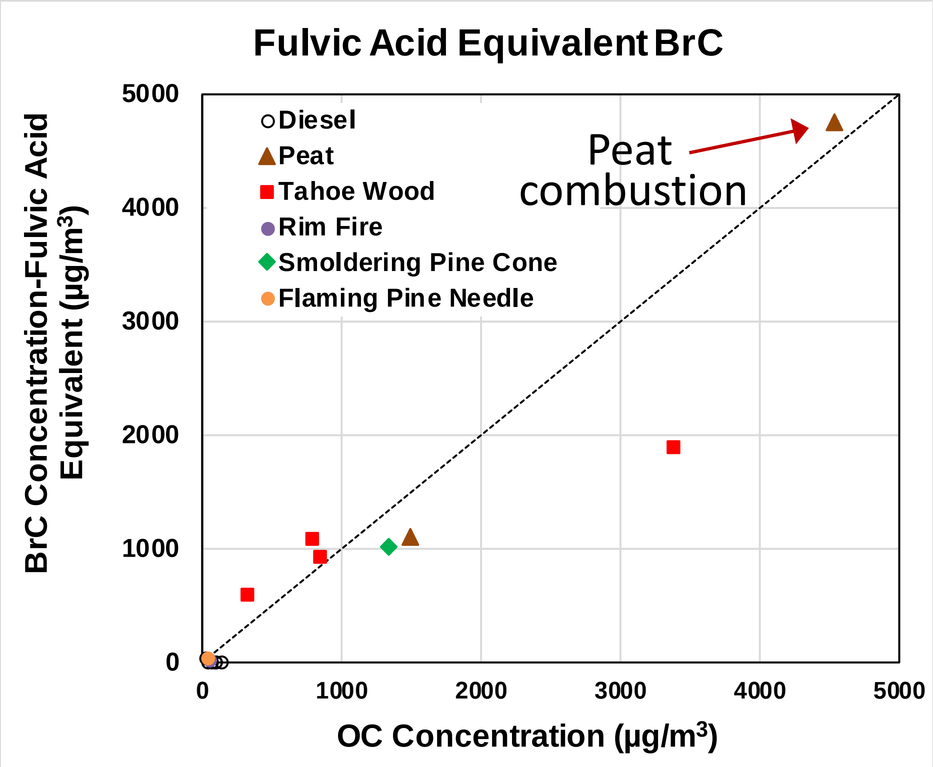
(Florida, USA)

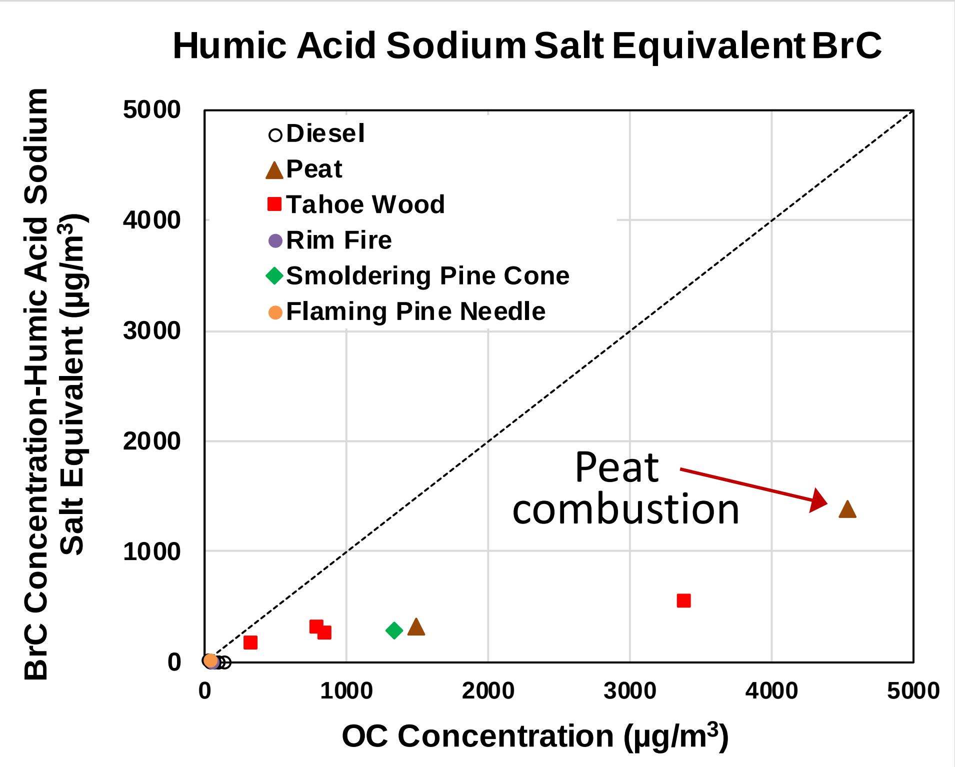


BrC and OC track well during Everglade area fires in spring 2016

(Assumes BrC_e is fulvic acid)

Equivalent BrC varied in source samples





Summary/Conclusions

- Selected BrC compounds can be used to estimate wavelength dependent Mass Absorption Coefficients (MACs) based on filter transmission
- MACs and attenuation coefficients can be used to estimate BrC mass concentration for ambient IMPROVE and CSN samples
- Calculated BrC_e mass highly dependent upon MAC used, which can vary greatly from compound to compound
- Fulvic acid and humic acid sodium salt produced repeatable results
- Total light absorption from BrC is a more defensible estimate than the estimated BrC equivalent mass concentration