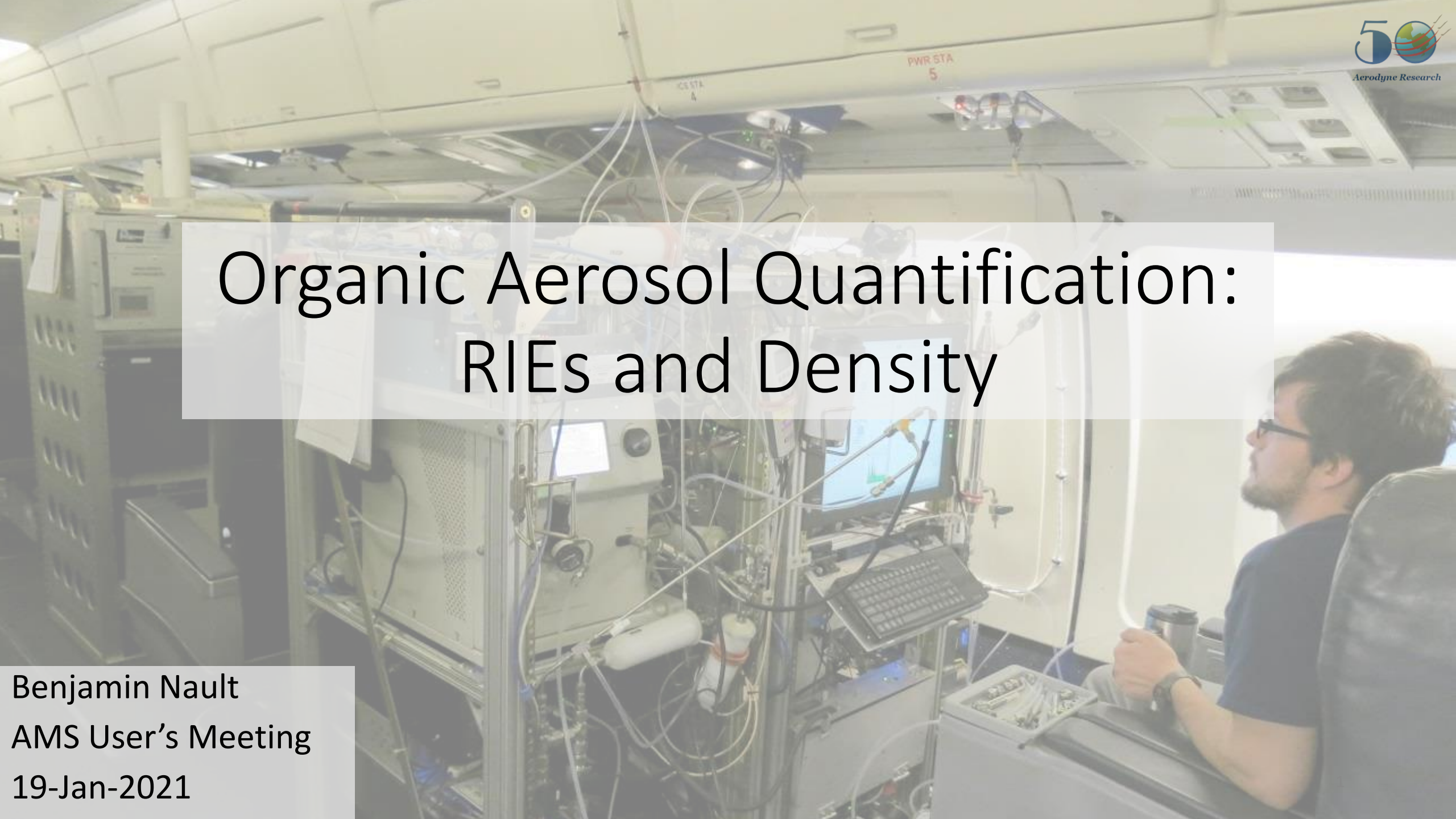

Organic Aerosol Quantification: RIEs and Density

Benjamin Nault

AMS User's Meeting

19-Jan-2021

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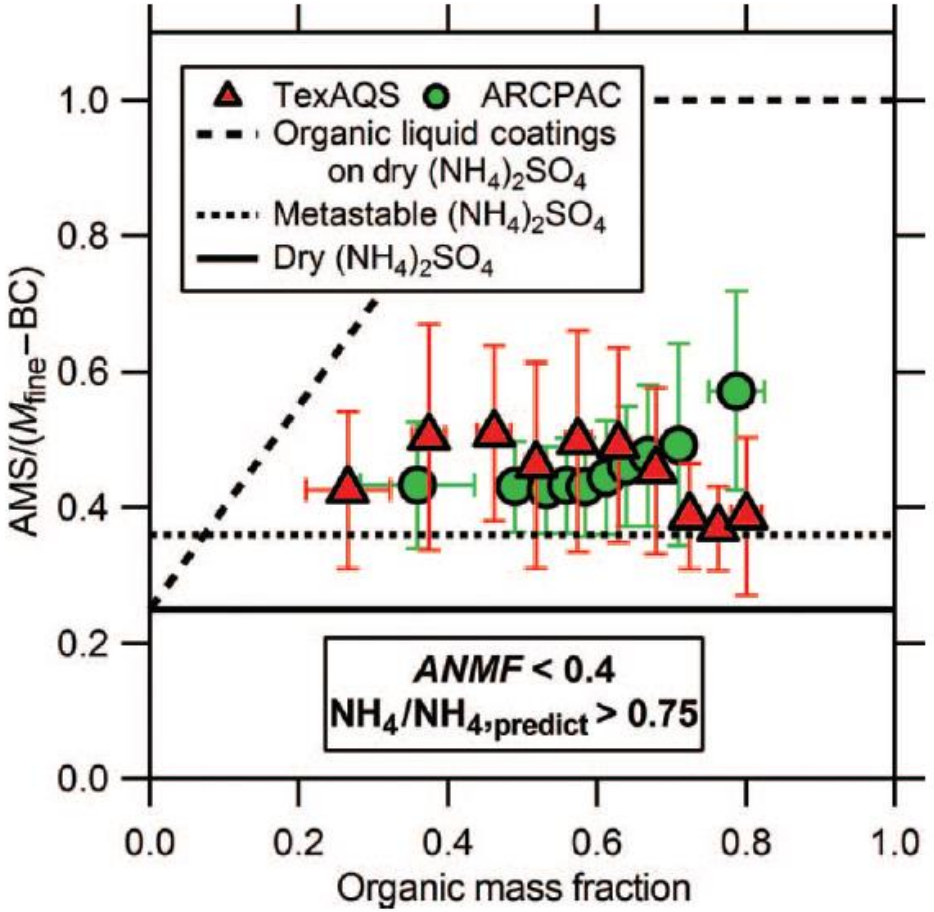
Why RIE and density matter for quantification

$$OA(\mu g\, m^{-3}) = \frac{10^{12}}{CE_{OA}} \frac{MW_{NO_3}}{RIE_{OA} IE_{NO_3} QN_A} \sum_{all\ i} I_{OA,i}$$

$$Volume\ (\mu m^3\ cm^3) = \frac{OA_{mass}}{\rho_{OA}}$$



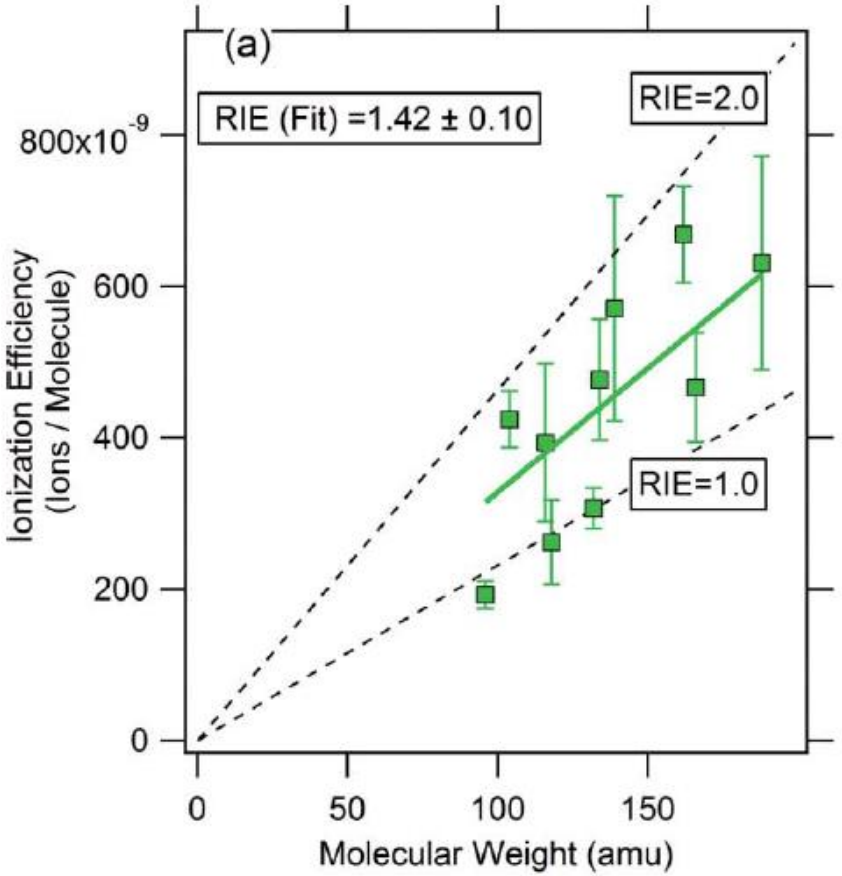
CE for ambient data does not depend on OA

NOT CASE FOR PURE OA

(SOURCE/CHAMBER EXPT)

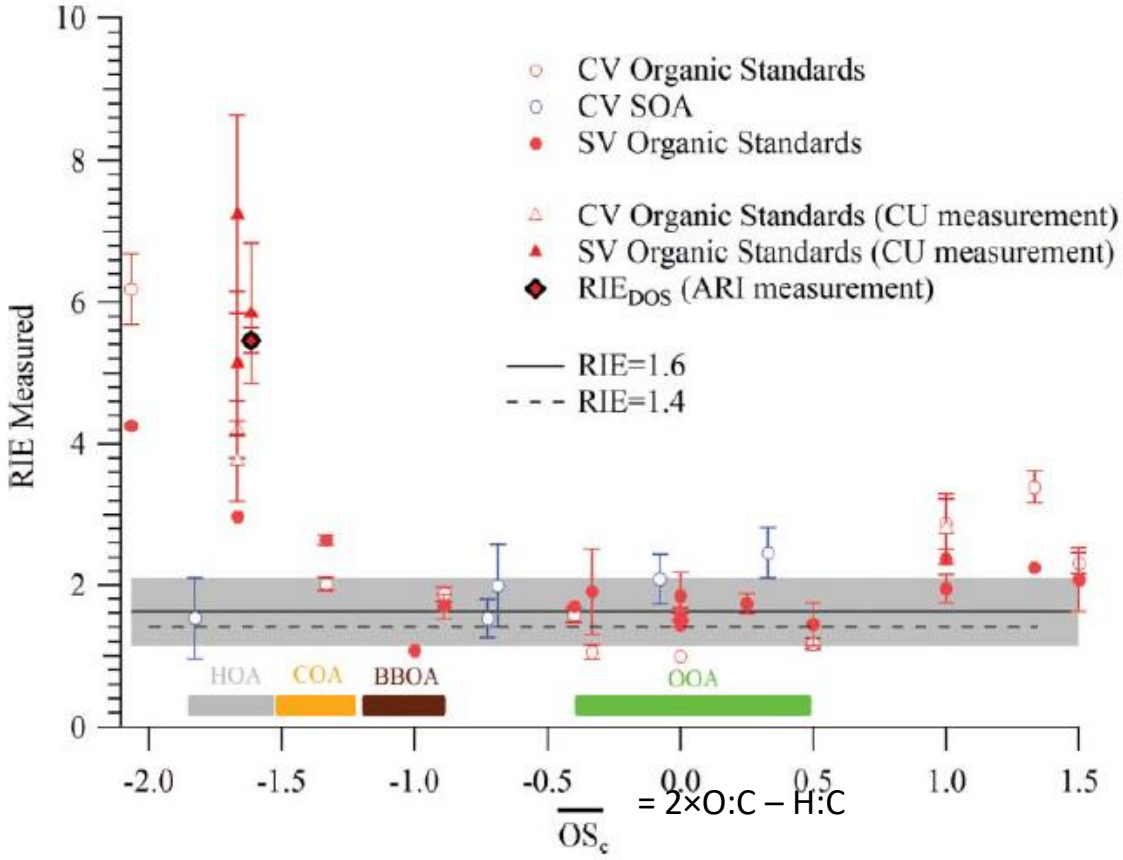
Middlebrook et al., AST, 2012

Organic Aerosol RIE overview from prior lab studies



Compilation of Org standards leads to RIE ~1.4

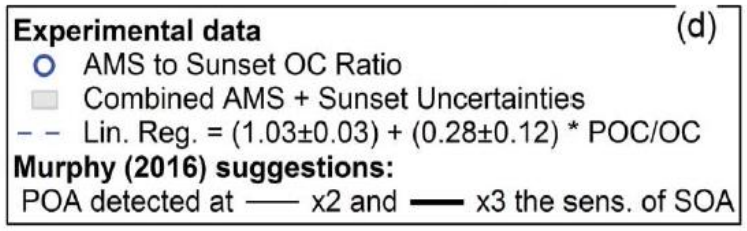
Jimenez et al., AST, 2016

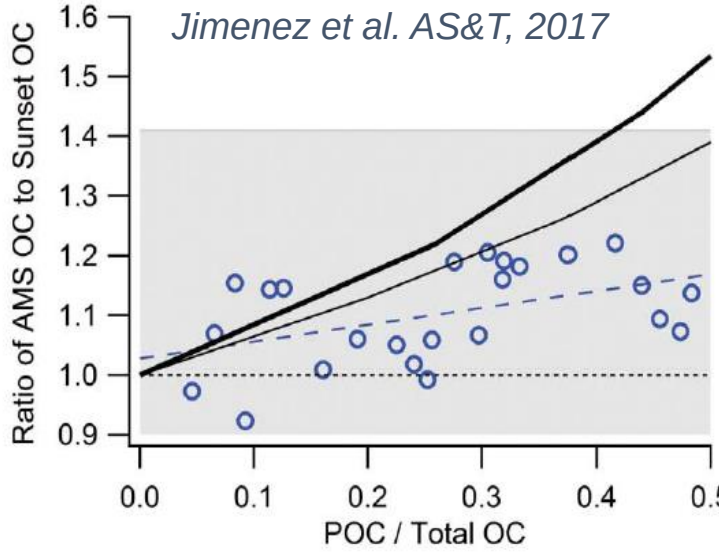


Further analysis indicates RIE 1.6±0.5 (but more analysis of ambient studies needed to verify)

Xu et al., AST, 2018

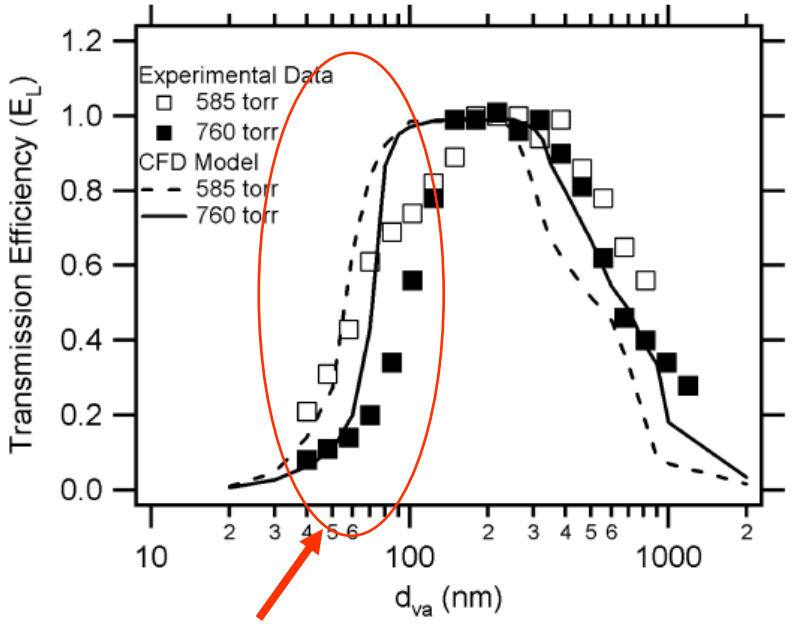
Is there evidence for higher RIE for reduced compounds?





More ambient measurements needed to derive variable RIE parameterizations

Large biases not observed for ambient OA mass calculated with constant RIE =1.4 (even for high POA content)



Offsetting of RIE by CE differences?
RIE (POA) > RIE (SOA)
CE (POA) < CE (SOA)

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Online Chemical Characterization of Food-Cooking Organic Aerosols: Implications for Source Apportionment

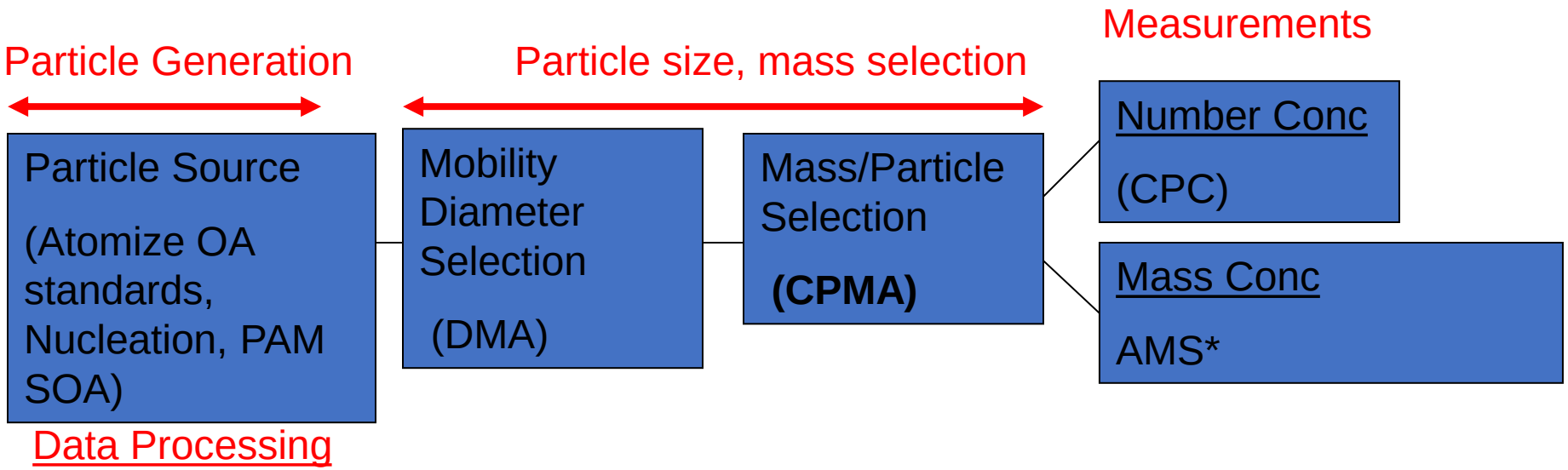
Ernesto Reyes-Villegas,*,† Thomas Bannan,† Michael Le Breton,†,§ Archit Mehra,† Michael Priestley,† Carl Percival,†,∥ Hugh Coe,† and James D. Allan*,†,‡

RIE ~1.6 – 3.1

Questions/Goals of this study

- Can we empirically parameterize variation in Org RIE, particularly for complex OA mixtures?
- How well does the lab Org RIE standards match RIE of complex OA (ambient, chamber SOA, emissions)?
  - Extend Wen's work to see if RIE from ambient material (extracted from filters) follow the trends from laboratory standards
- Investigate current parameterizations for OA density (density can be also directly obtained from RIE cal set-up)

Protocol to measure OA RIE



Data Processing

Input Mass= (CPMA Mass/particle)*CPC Number

AMS Mass = $(1/CE_S RIE_S)$*AMS NO3 Equiv. Mass

CE_S*RIE_S = NO_3 Equiv. Mass/CPMA Input Mass

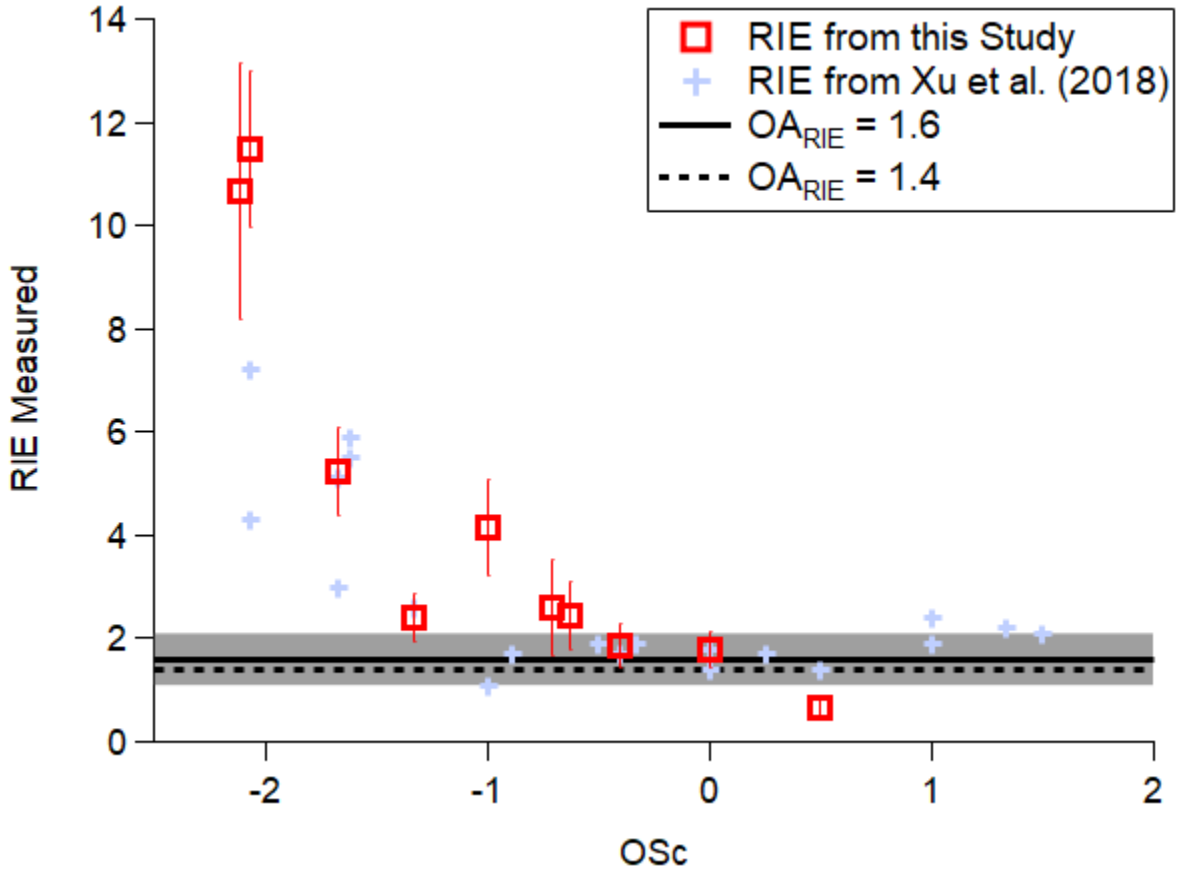
CE_S ~AMS pTOF Single Particle Counts/ CPC
OR
AMS LS Particle Counts/ CPC

Taken from:
Xu et al. AS&T,(2018)
Users' Meetings

Standard OA used for this experiment

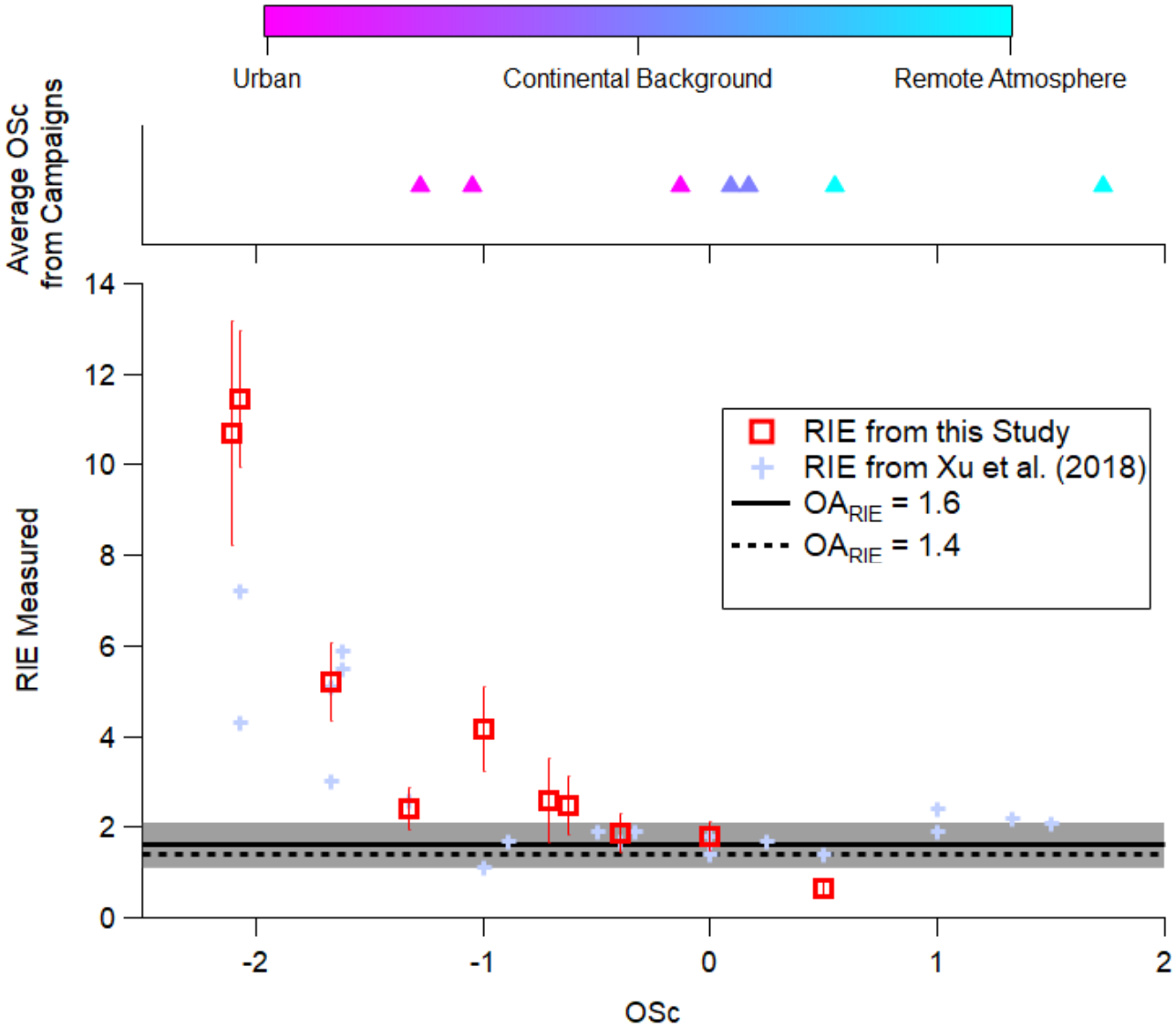
Species	Density	O:C	H:C
Levoglucosan	1.69	0.83	1.67
Xylitol	1.52	1.00	2.40
Oleic Acid	0.90	0.11	1.89
Squalane	0.81	0.00	2.07
Sebacic Acid	1.21	0.40	1.80
Anthracene	1.25	0.00	0.71
Succinic Acid	1.56	1.00	1.50
1,2,6-Hexanetriol	1.11	0.50	2.33
Pyrene	1.27	0.00	0.63
Octadecane	0.78	0.00	2.11
Oxidation experiments	Variable	Variable	Variable

Extending RIE vs OSc measurements to more species



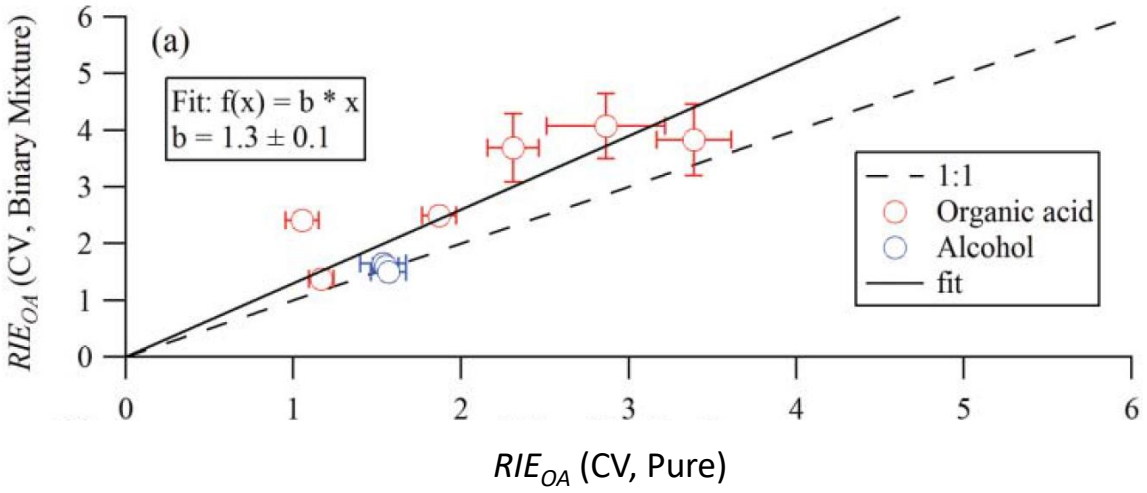
- OA standards in atomized in acetonitrile to extend OSc range
- Lower OSc compounds have higher variability (investigating why)
- -1 < OSc < 1 reproducible with different solvents and a different range of copounds

Change in RIE vs OSc may impact bulk OA analysis



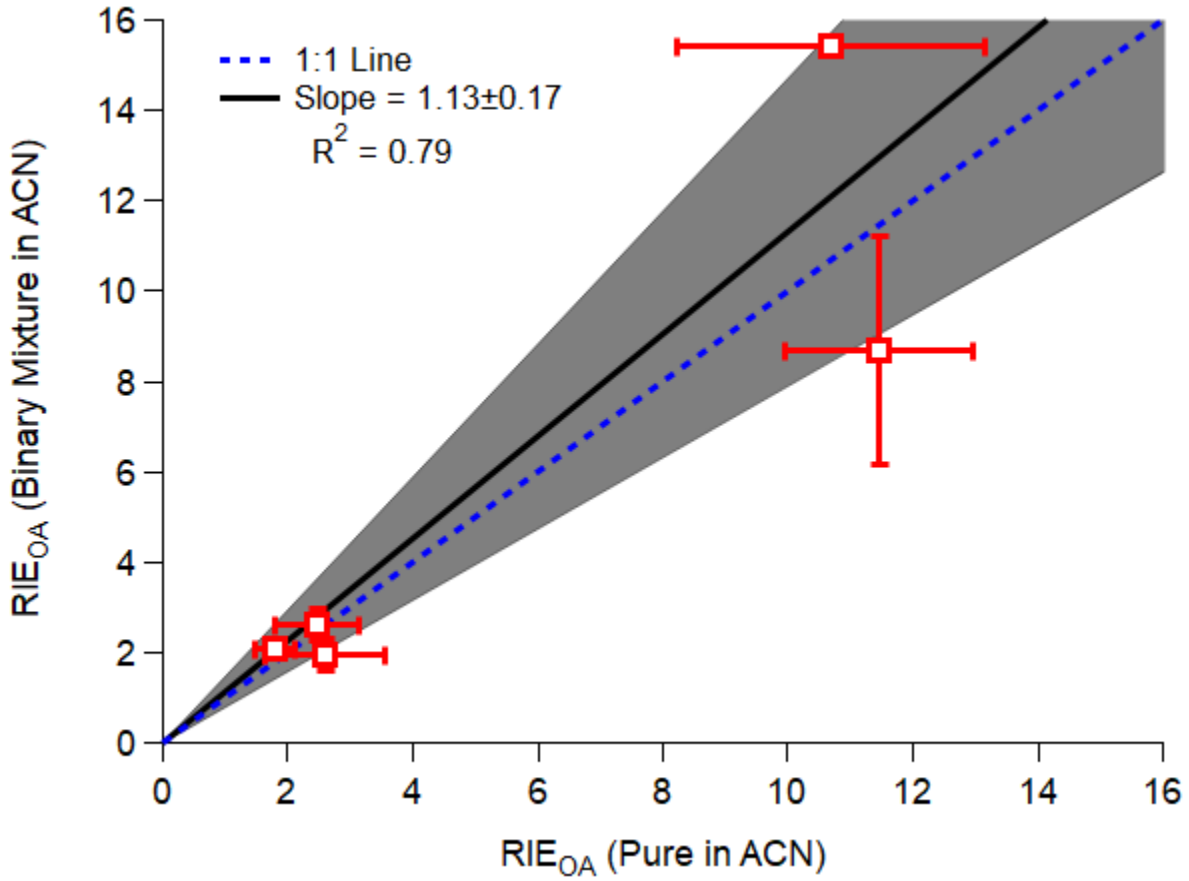
- Urban bulk OA has lower OSc than continental background and remote atmosphere due to emissions of hydrocarbon-like aerosol
- Will be investigating comparisons of different comparisons (e.g., volume, scatter, OC/OM) from prior studies
- Will investigate if having and a predictable RIE vs OSc in complex OA mixtures improves agreement
- Need to add biomass burning and more studies
- **If planning on measuring "continental background" to remote atmosphere, either can safely assume current default RIE = 1.4 agrees to 38% or use levoglucosan to calibrate**

Using mixtures with internal calibrant for direct measure of OA RIE



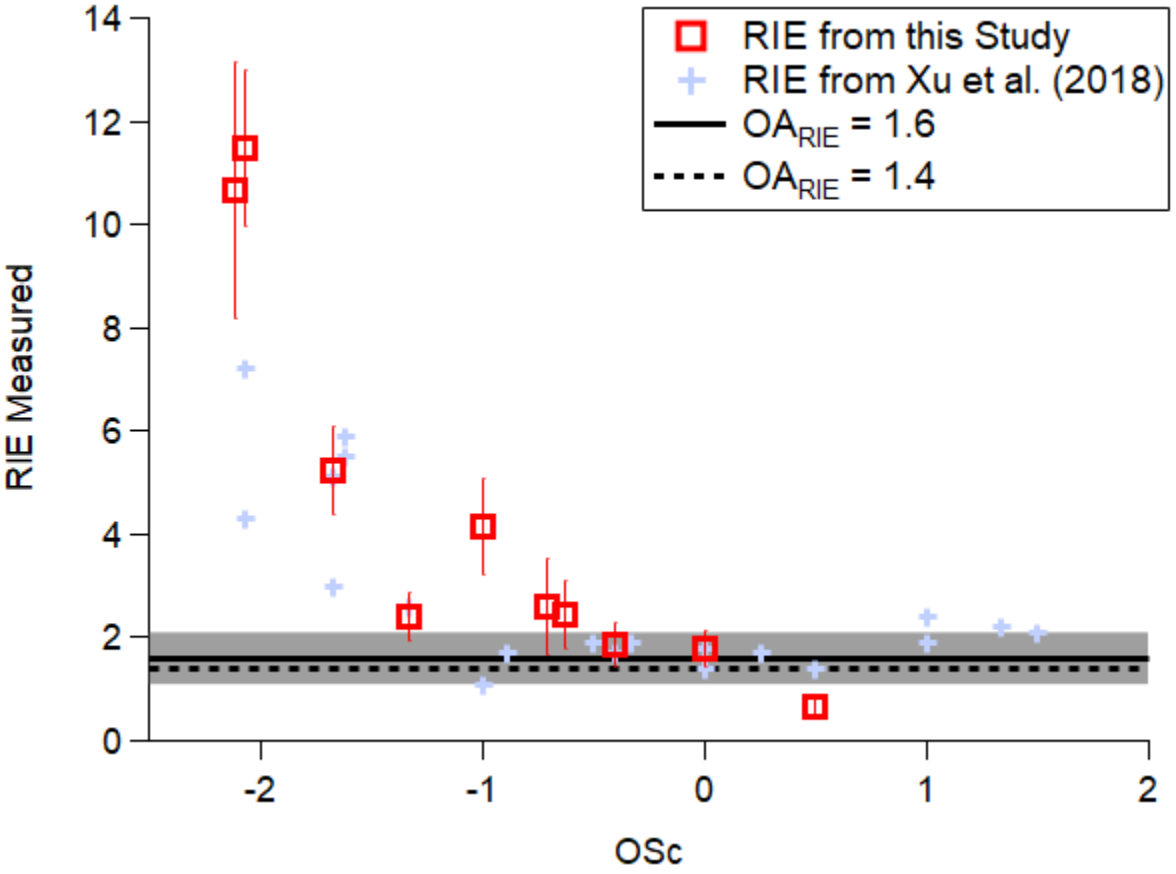
Xu et al. (2018) showed for non-organic acids, binary mixture (organic + ammonium nitrate) reproduces RIE observed in single component (organic) systems.

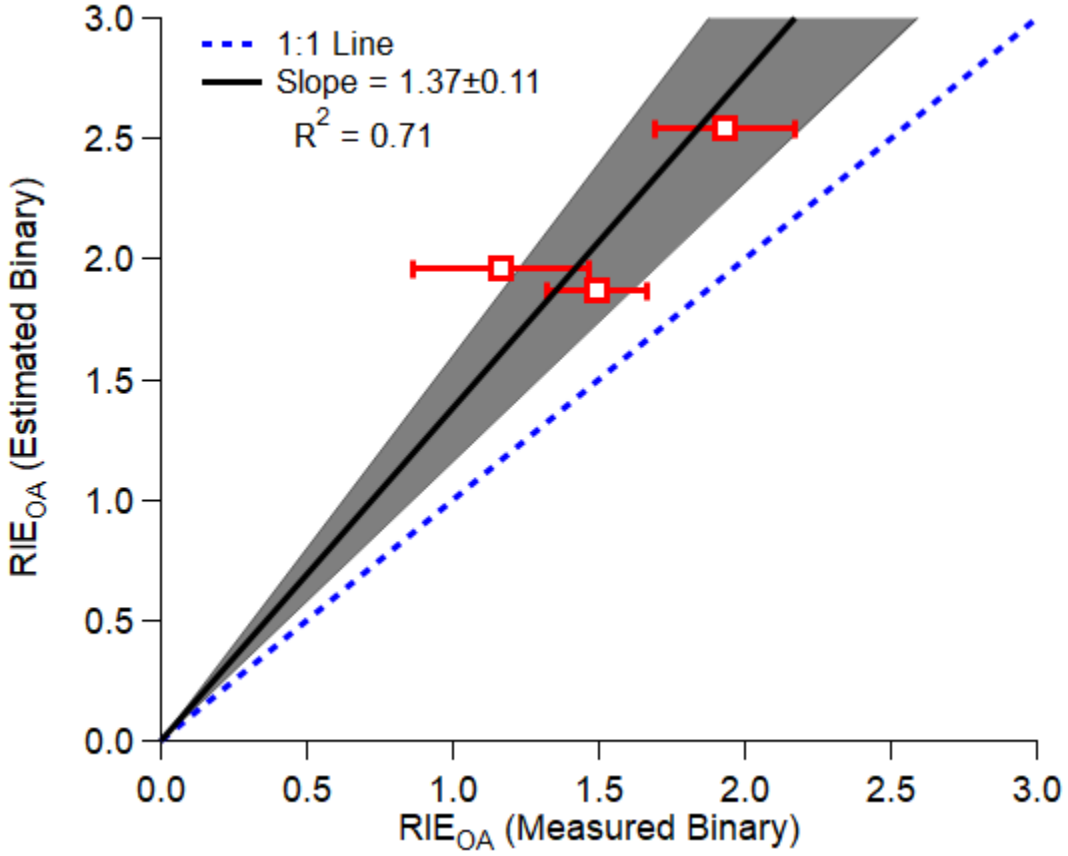
Organic acids DO NOT work due to organic acid + NH4 reaction.



Expanding the compounds investigated, generally observe agreement within 13% between binary mixture (organic + ammonium nitrate) vs single component

RIE measurements of binary organic aerosol— Mixture of Levoglucosan and other OA to directly measure RIE of complex mixtures





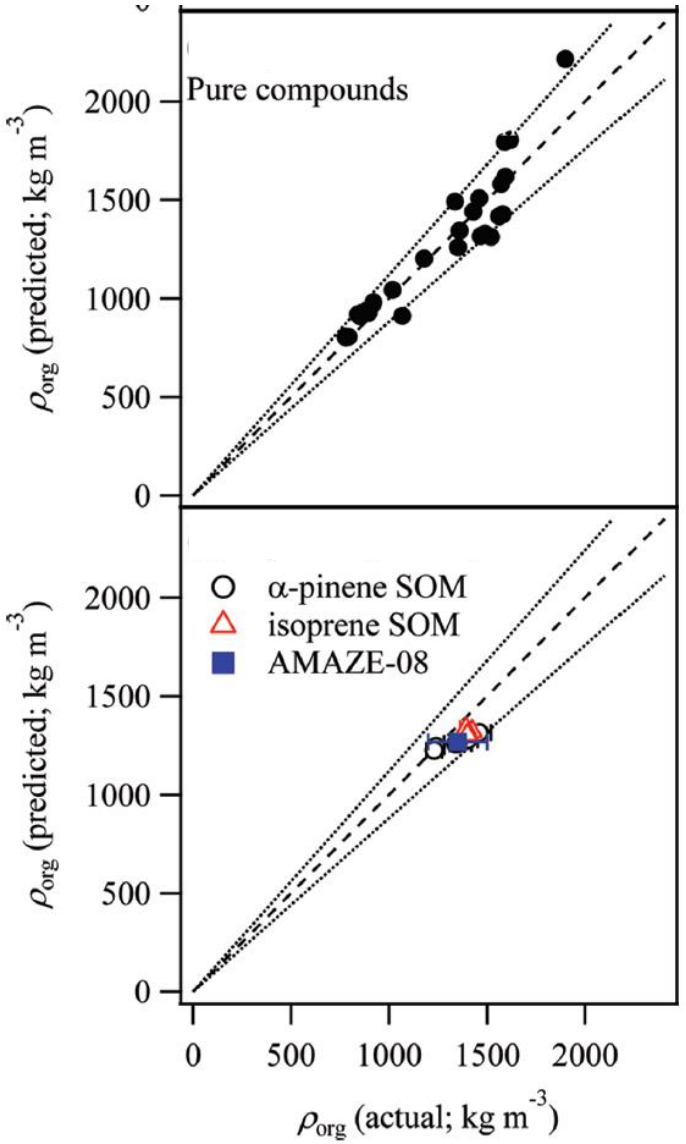
Binary = Levo + Other

Only a limited number of solutions have been evaluated. More solutions for higher OSc/RIE will be made to further evaluate the accuracy of the RIE vs OSc relationship.

Further work to be done….

- **Levoglucosan is reproducible in water or organic solvent and w/ or w/out ammonium nitrate (as levoglucosan has CE ~ 1)**
- **For higher RIE, oleic acid appears reproducible and has CE ~1. Standard most easily made in organic solvent**
- Further experiments to investigate standards in different solutions and mixtures being conducted to investigate reproducibility
- Evaluate prior ambient studies, where the CE cut-off is well known, to see if there is evidence/constraint of RIE on comparisons
- Evaluate RIE of different ambient filter OA fractions to investigate RIE vs. OSc to compare lab calibrations w/ ambient OA

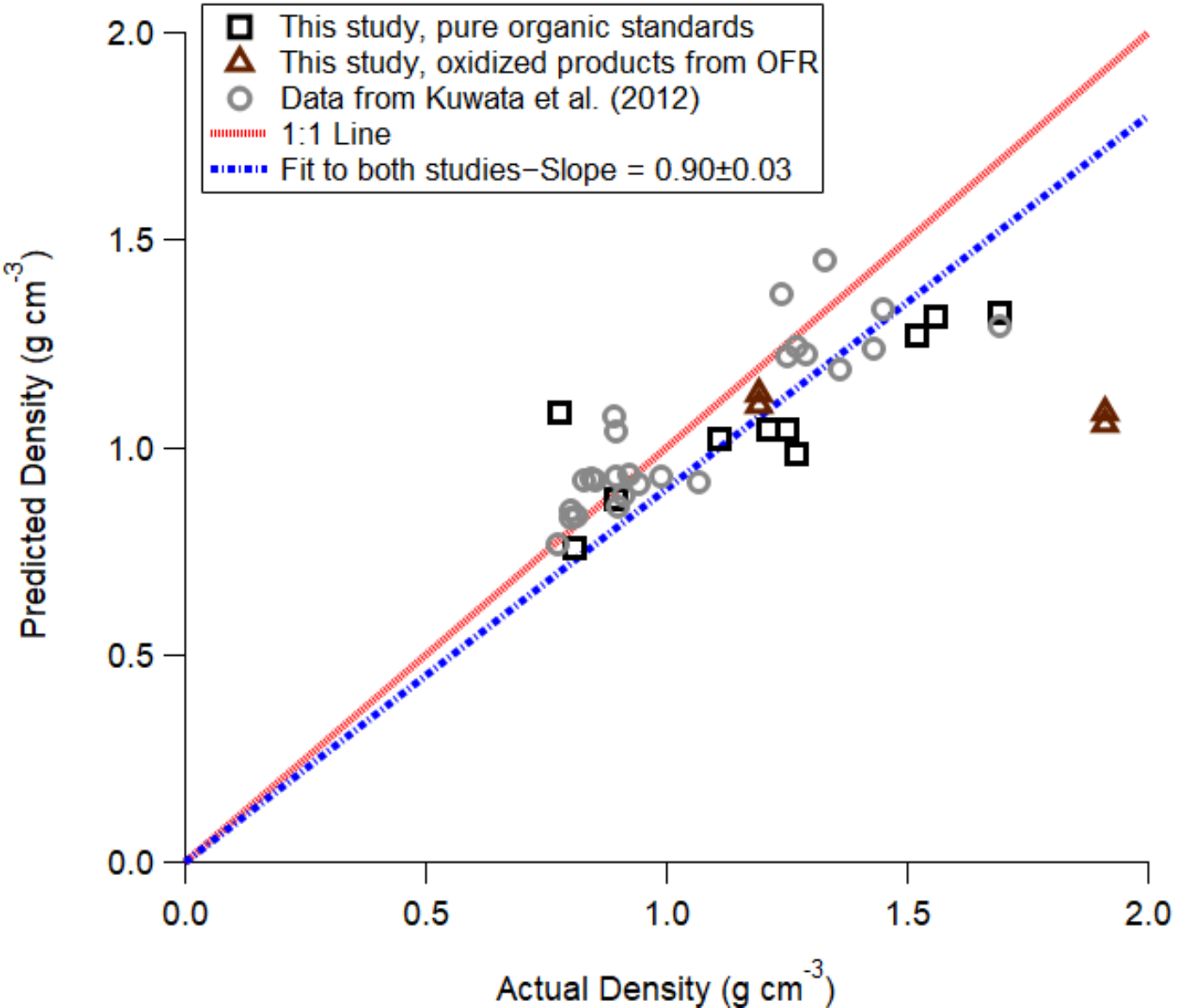
Organic Aerosol Density—Kuwata et al. (2012)



$$\rho_{OA} = \frac{12 + H{:}C + 16 \times O{:}C}{7 + 5 \times H{:}C + 4.15 \times O{:}C}$$

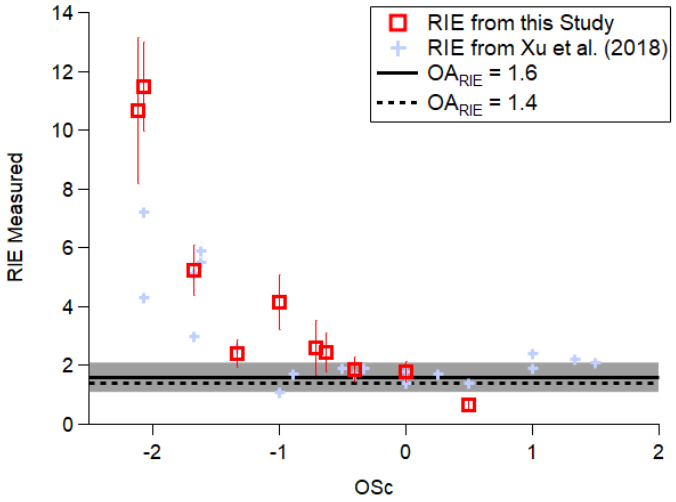
- Kuwata et al. (2012) showed that OA density could be predicted using the observed H:C and O:C values from AMS
- HOWEVER, they created a correction value to improve the agreement
- FURTHER, this was done prior to the Canagaratna et al. (2015) improved elemental analysis and without any nitrogen containing compounds

Kuwata parameterization maybe underpredicting density

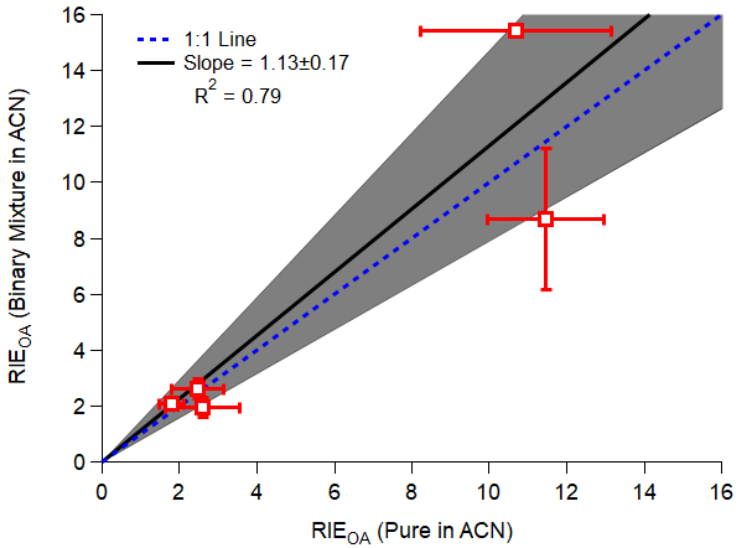


- After correcting the O:C and H:C from Kuwata et al. (2012) and adding results from recent laboratory study (both pure OA standards and OA produced by oxidation), new fit shows ~10% lower predicted vs observed density
- More studies will be conducted to investigate

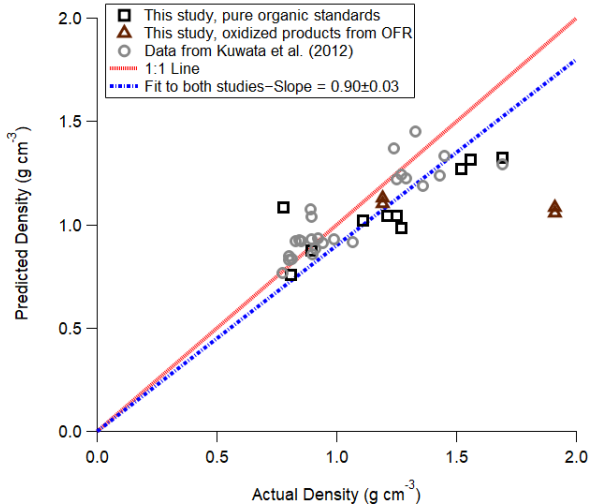
Conclusions so far



- Is lab generated standard OA RIE vs OSc relationship observable in ambient OA



- Binary mixtures can be used to eliminate CE.
- A “simple” RIE calibrant could be identified to represent OSc < -0.5. Best candidates are levoglucosan alone, binary internal mixtures of alcohol + ammonium nitrate, or OA standard with levoglucosan (will identify more)



- Current parameterization may under-predict density.
- More studies to follow