

Quantification of Aerosol Species
with the AMS:
Background and Recent lab
results relevant for OA

Presented by Manjula Canagaratna

AMS Clinic, Boulder, CO

June 18,2015

Mass Loading Calculations

$$C = \frac{10^{12}}{IE} \frac{1}{Q} \frac{MW}{N_A} \cdot I$$

$$\frac{IE_s}{MW_s} = RIE_s \frac{IE_{NO_3}}{MW_{NO_3}}$$

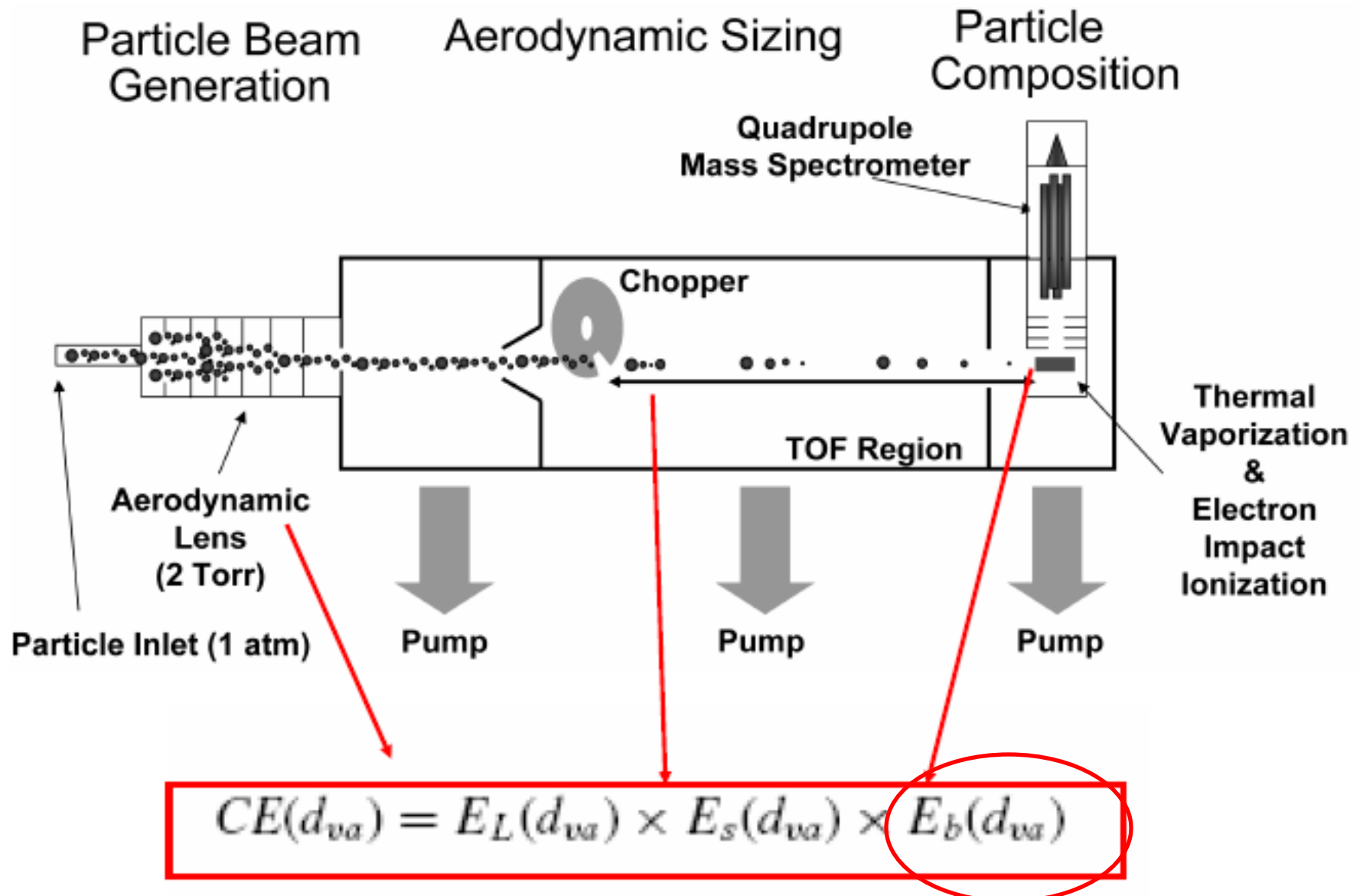
Primary Calibration

$$C_s = \frac{10^{12} MW_{NO_3}}{CE_s RIE_s IE_{NO_3} Q N_A} \sum_{all\ i} I_{s,i}$$

Nitrate
Equiv.
Mass

$CE_s RIE_s$ is largest uncertainty in mass concentration calculations

Collection Efficiency Definition



CE: From Lab and Field Work

E_b is dominant contribution to CE

E_b affected by

- 1) nitrate content
- 2) acidity/neutralization
- 3) Relative humidity in the sampling line
- 4) organic liquid content

MUCH (ALL?) OF THIS IS DRIVEN BY PHASE DEPENDENCE:

Solids Bounce, Liquids Don't Bounce

"Impactor 101", same is true for ELPI (Virtanen et al. Nature 2010)

References: Matthews et al., Quinn et al., Middlebrook et al.

CE (Collection Efficiency)

Lab CEs: (*Matthews et al., Docherty et al.*)

Pure $\text{NH}_4\text{NO}_3 = 1$

Pure $(\text{NH}_4)_2\text{SO}_4 = 0.3$

CEs for mixed NO_3 and SO_4 particles vary with NO_3 content, humidity, and liquid organic coating

Lab SOA > 0.2 (Range observed, dependence on f_{44})

Ambient CEs: (*Middlebrook et al.*)

CE = 0.5 (+/-0.15) with empirical composition dependence

Pure lab particles are poor models for ambient mixed particles, but similar trends observed with humidity and NO_3

Ambient particles are solid/ mix of solid and liquid/glassy phase states

(State of particles in ambient or in AMS after transmission through lens)

RIE (Relative Ionization Efficiency)

$RIE_{NO_3} \sim 1.1$

(Accounts for ions other than m/z 30 and 46)

$RIE_{NH_4} \sim 3-5$

$RIE_{SO_4} \sim 1.2$

RIE_{SO_4} can be measured for each instrument.

Complicated by non-unit CE

1) Get RIE_{NH_4} from NO_3 cal

2) Use RIE_{NH_4} from step 1 to calculate input NH_4 mass and then input SO_4 for sulfate calibration.

Determination of CE, RIE for Organics

Complication: Ambient OA is made up of thousands of individual organic species.
What do we use as a calibrant?

Ambient Measurements:

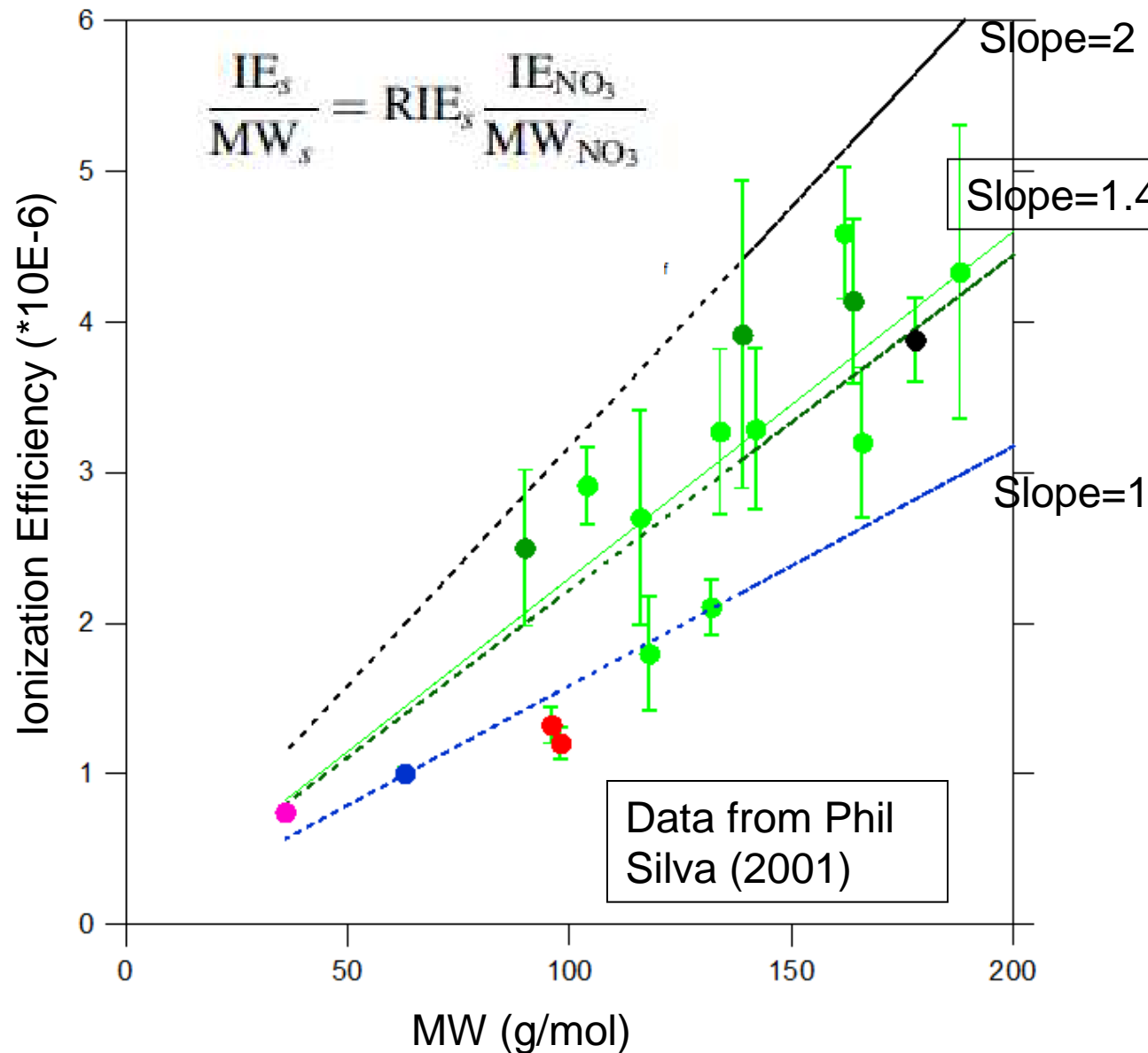
Usually $CE * RIE_{Org} = (0.5 * 1.4) = 0.7$

Assume CE_{Org} same as sulfate due to internal mixture

$$RIE_{Org} = 1.4$$

(Value published in Canagaratna et al. (2007) and is based on unpublished laboratory work by Silva et al. (2001).

Lab measurements of RIE_{Org}



Calibration Species:
inorganic and organic acids (oxidized species –surrogates of OOA)

Lab particles not necessarily good models for ambient.

In practice, ambient organic mass concentrations typically evaluated by comparing with other measurements (total mass, OM/OC ratios).

Examples will be discussed in next talk
By Jose

MW dependence of RIE_{org}

*More on this topic
later this morning*

Time spent in ionization region (t) is inversely proportional to sqrt(MW). RIE is directly proportional to t

$$\text{Kinetic Energy} = \frac{1}{2} mv^2 \propto \frac{1}{2} MW(1/t)^2$$

$$\text{RIE} \propto t \propto (1/\text{sqrt}(MW))$$

Expect MW dependence in RIE

How could this affect AMS mass concentration measurements ?

Original AMS data from Phil Silva doesn't show clear MW dependence within measurement uncertainties for Oxidized organic species MW <200

Measurement Uncertainties: RIE_{Org}

Basic Idea: Compare measured OM with **known** input OM

Producing **known** input mass is hard

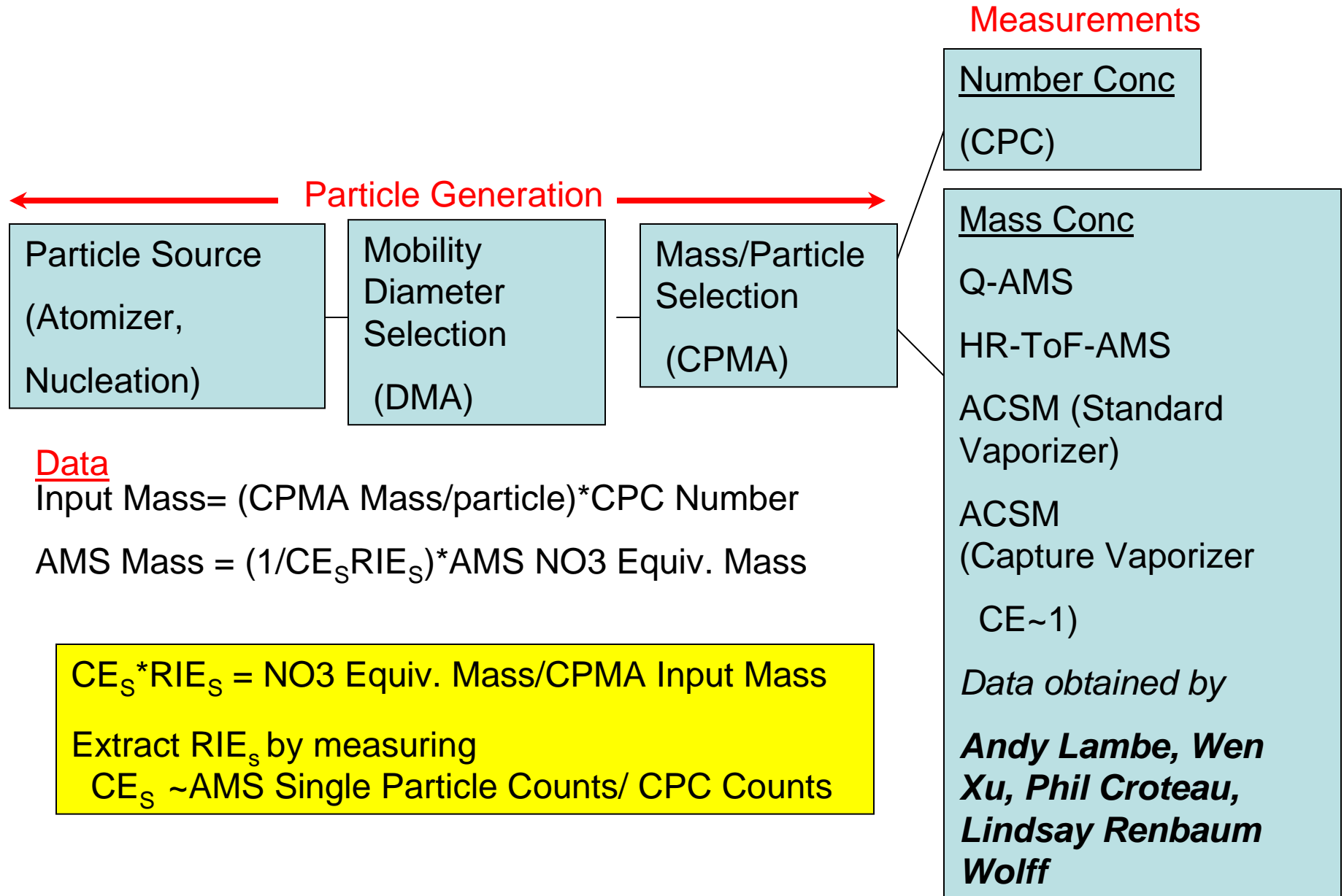
- Atomizing organics (H₂O vs. other solvents)
- Calculating mass of input particles properly even with DMA size-selected particles
 - Accounting for Q>1 particles in DMA output (Used single particle from TOF)
 - asphericity (shape factors)
- loss of volatiles in lens
- Non-unit CE due to bounce

New measurements with control of input OM mass

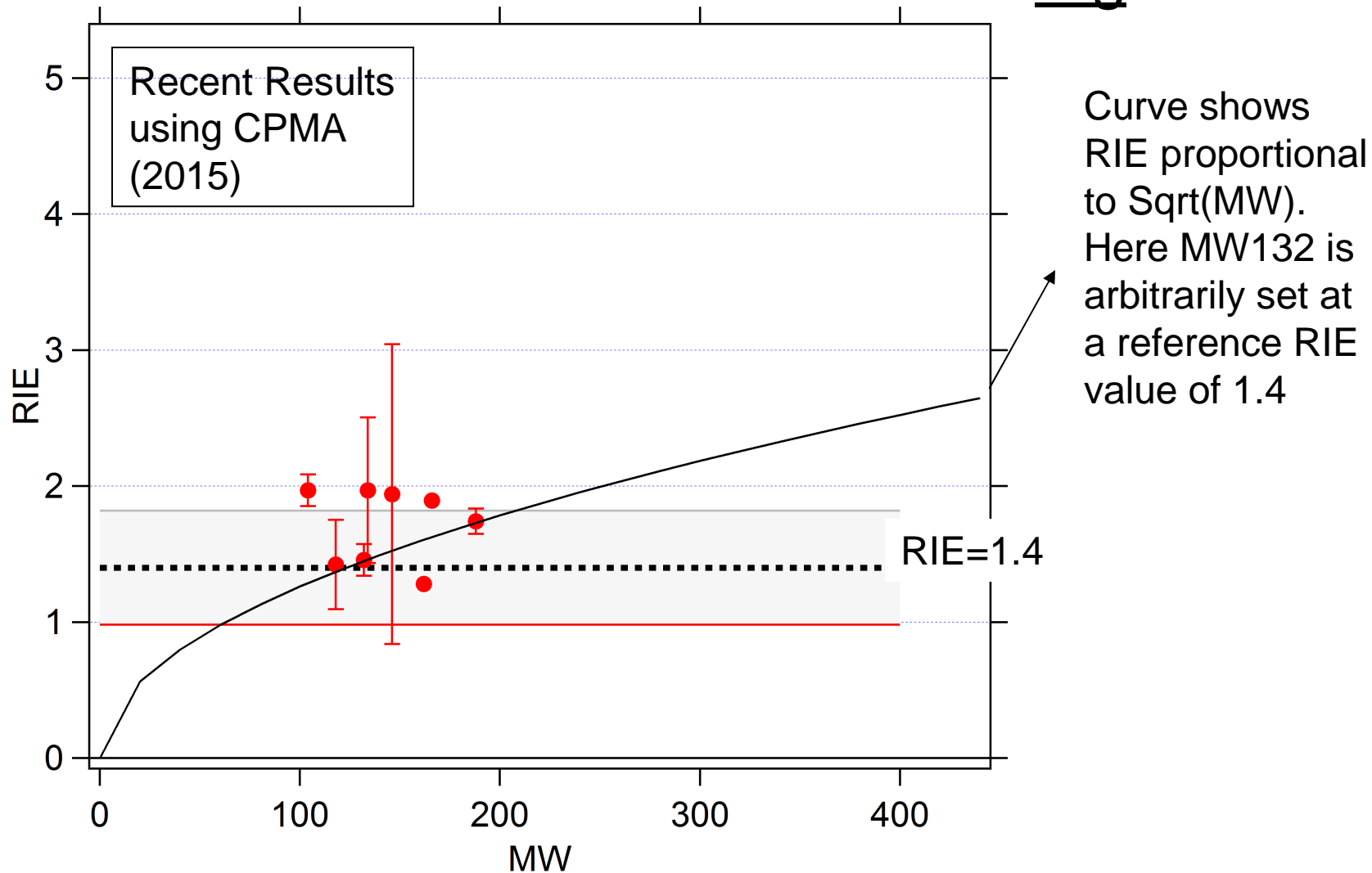


Use Centrifugal Particle Mass Analyzer (CPMA) to control of input mass/particle

Experimental setup



MW dependence of RIE_{org}

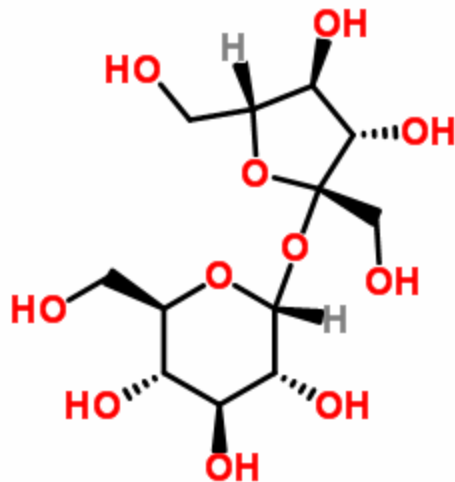


Oxidized Organic standards <200 MW don't show obvious non-linear RIE trend with MW. More work to be done with more "atmospherically relevant" standards

Role of Thermal Decomposition

Thermal Decomposition reduces effective MW of parent molecules in vapor phase

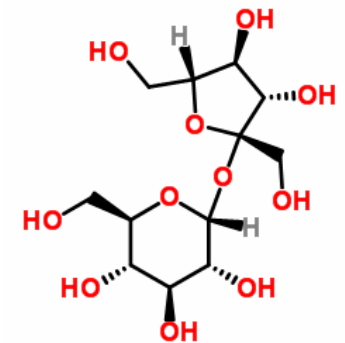
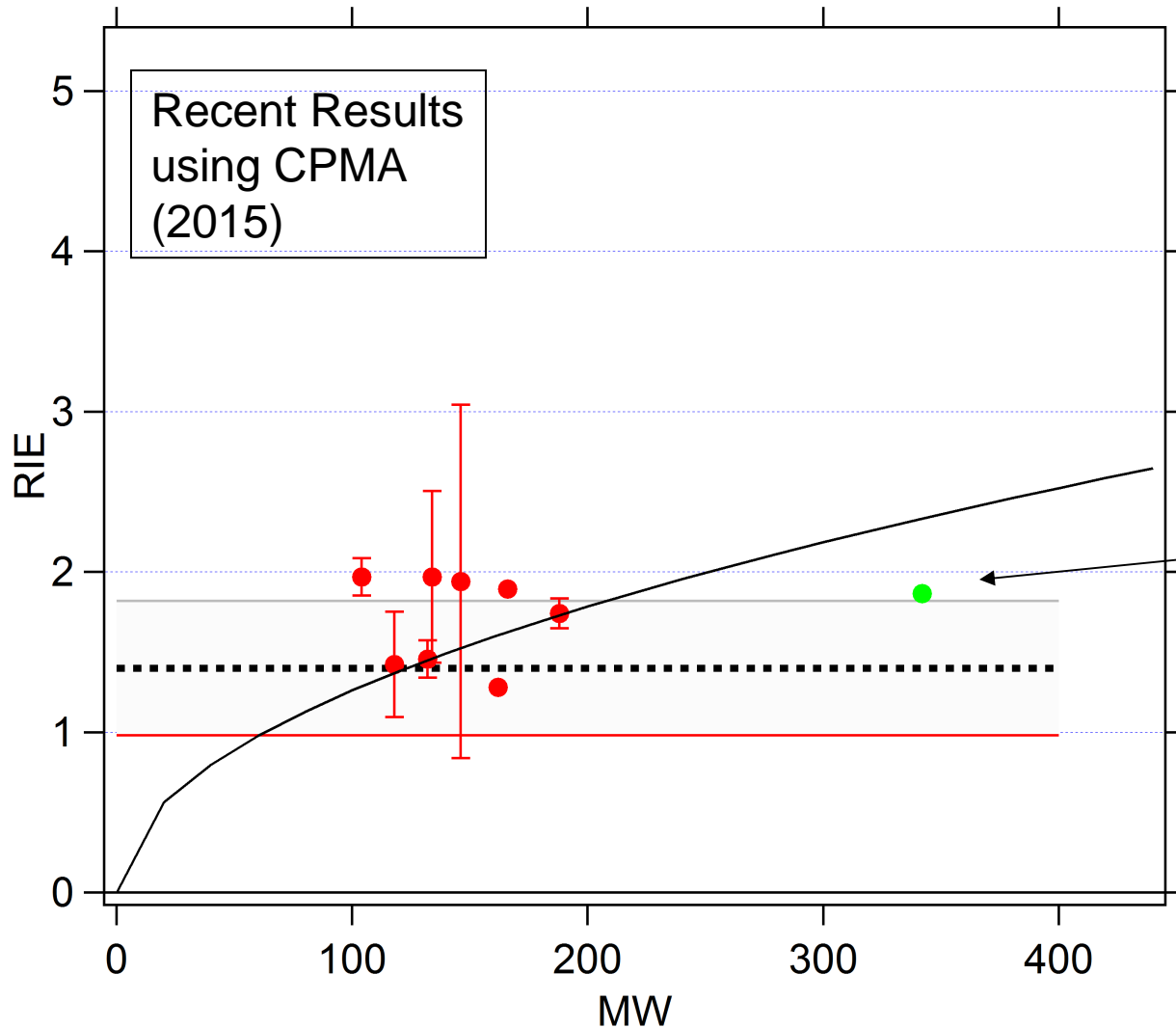
- Acidic species lose CO₂, H₂O, CO
- Alcohols lose H₂O
- Oligomeric species likely decompose into monomers



Sucrose, MW=342

MW dependence of RIE unlikely to be a big effect for Ambient OOA

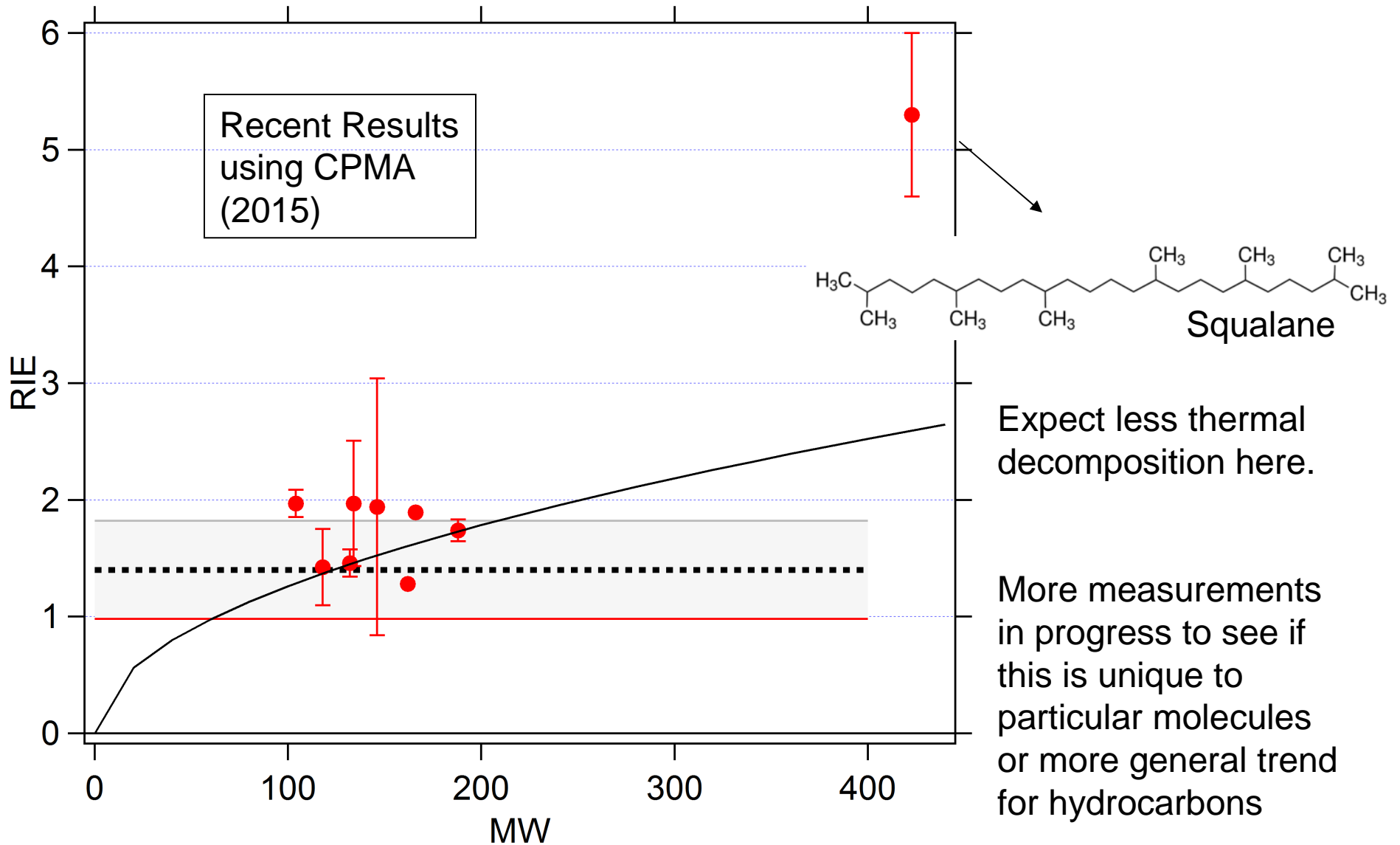
MW dependence of RIE_{org}



Sucrose

Large MW species that thermally decomposes has similar RIE to smaller oxidized organics

MW dependence of RIE_{org}



Work in progress

- Measuring RIEs of large MW hydrocarbons which are less likely to thermally decompose.
- Measure RIEs for more oxidized organic species that are more atmospherically relevant (PAM SOA, ambient OA)
- Compare/Analyze data from all AMS instruments (standard vs. capture vaporizer)