American Association for Aerosol Research

Session 3AP

Predicting Real Refractive Index of Organic Aerosols from Elemental Composition (O:C & H:C)

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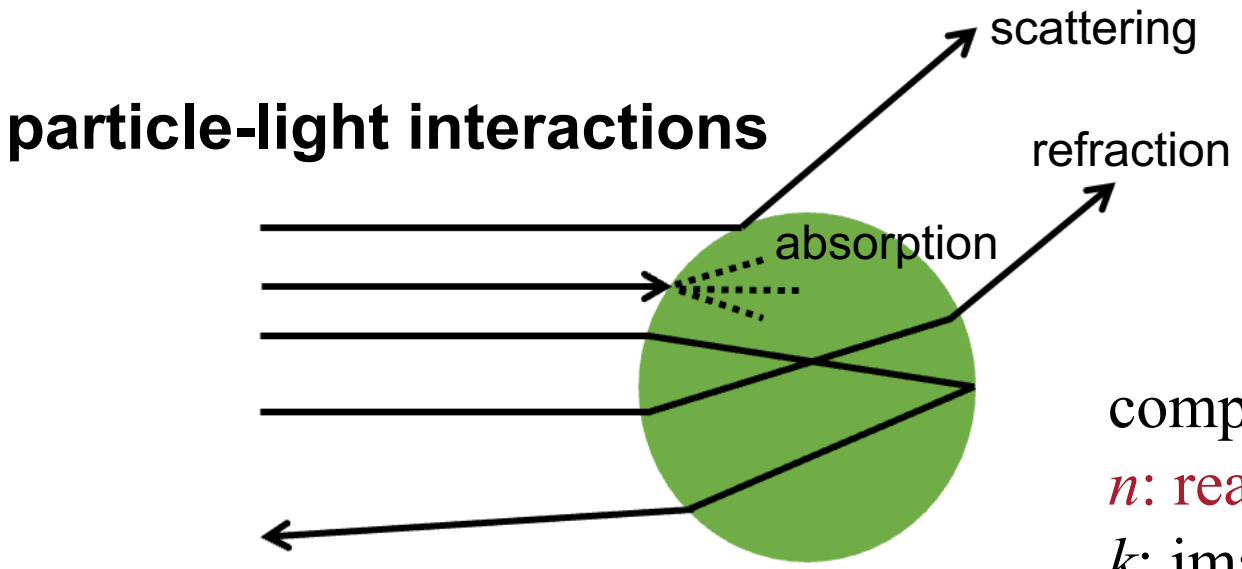
What is real refractive index (*n*) of a particle?



n: a dimensionless number that gives the indication of the **light bending ability (changing speed)** of that medium.

complex refractive index $m = n + ik$

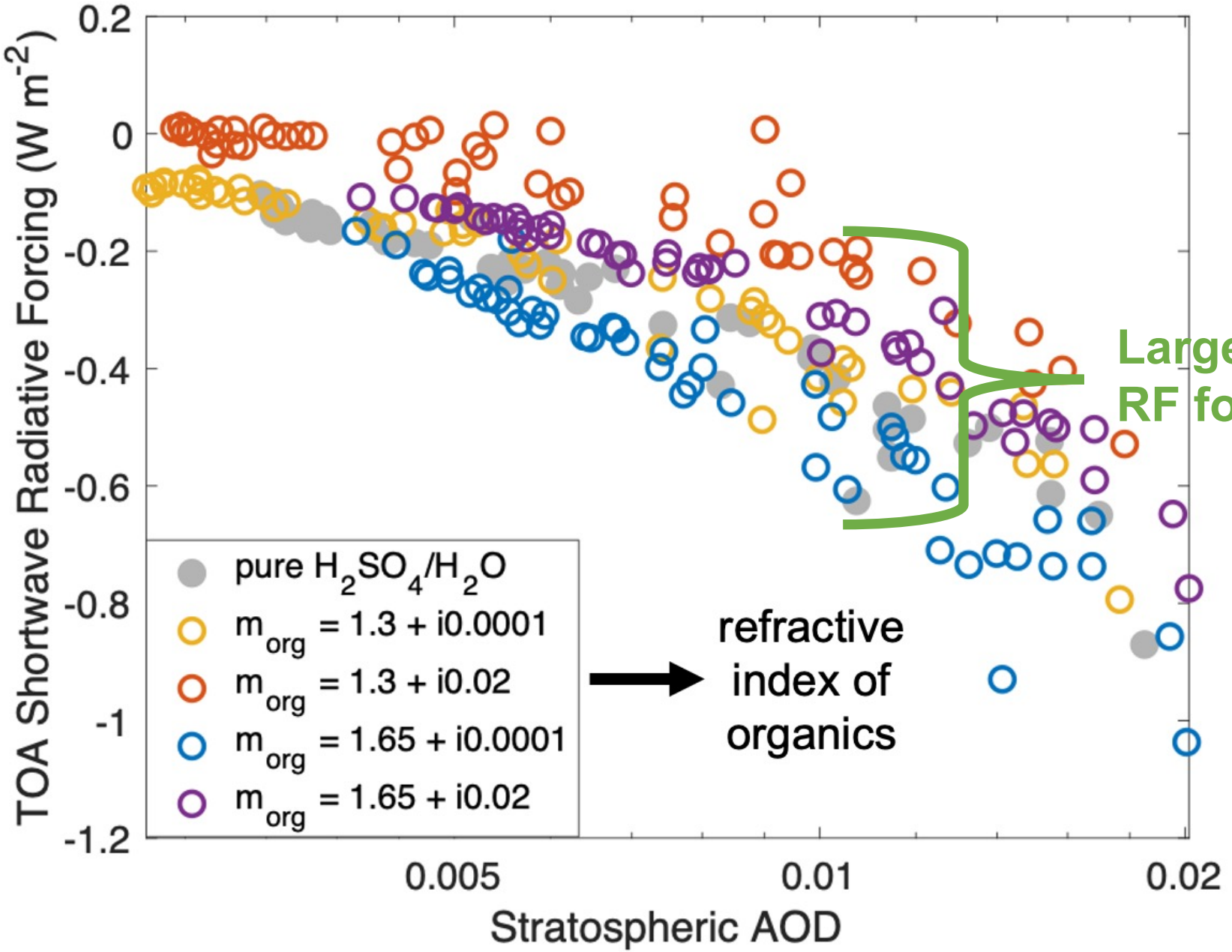
n: real refractive index (scattering of light)

k: imaginary refractive index (absorption of light)

- ✓ both *n* and *k* are functions of wavelength (λ)
- ✓ Lorentz-Lorenz equation relates *n* to the mean polarizability (α), mass density (ρ), and molecular weight (M) of the compound (*Born & Wolf, 1980*):

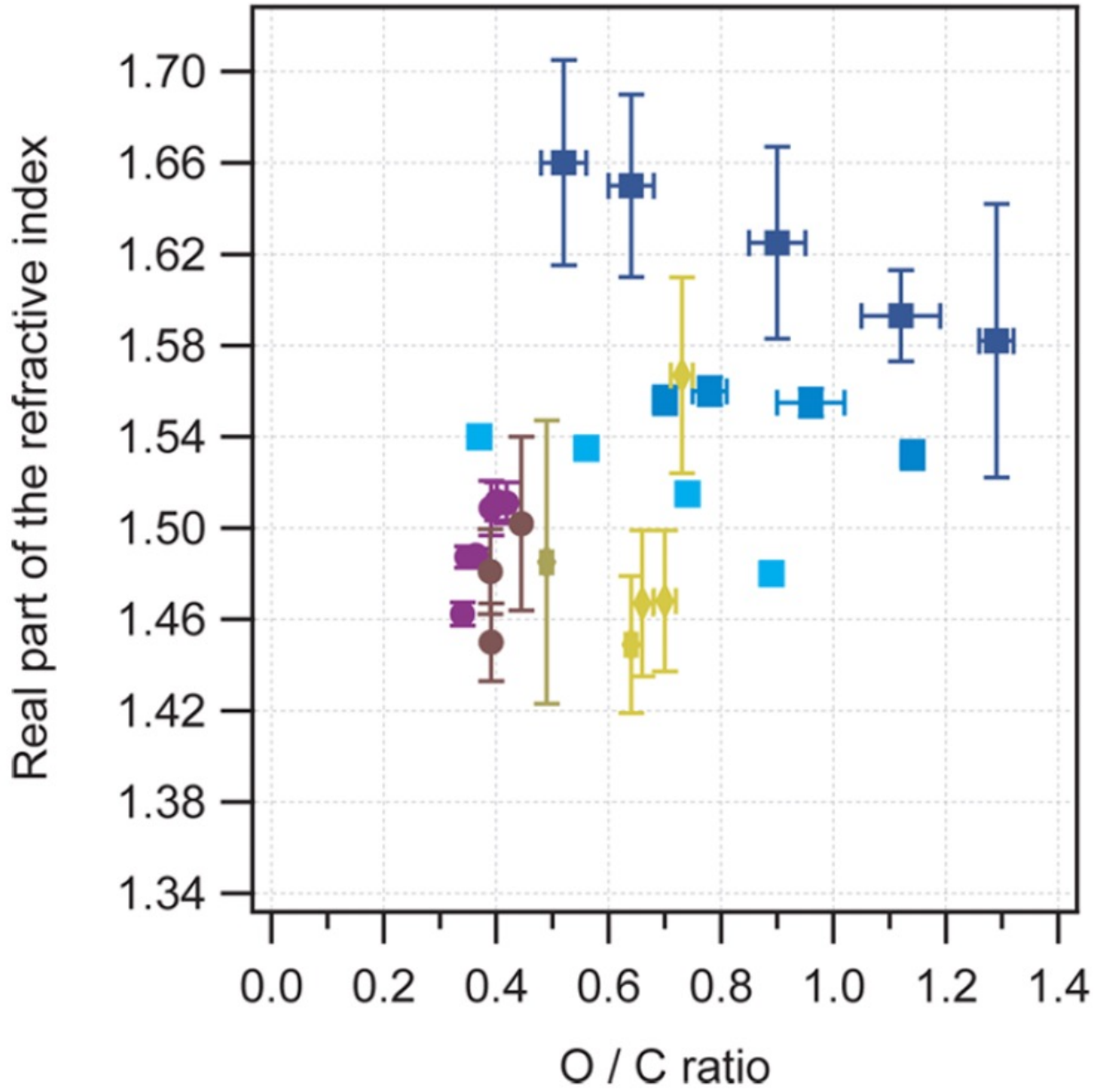
$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N_A \rho \frac{\alpha}{M}$$

For a given AOD, aerosol radiative forcing is still highly dependent on the refractive index



[Li et al., 2021]

n of organic aerosols (OA) varies significantly depending on the chemical compositions



Mixture of α-pinene, limonene and p-xylene-d_{10}
Flores et al. (2014b)
BSOA exposed to p-xylene-d_{10}
Flores et al. (2014b)
Naphthalene
Lambe et al. (2013)
Guaiacol
Lambe et al. (2013)
Toluene
Nakayama et al. (2013)
1,3,5-trimethylbenzene
Nakayama et al. (2013)
Tricyclo[5.2.1.$0^{2,6}$]decane
Lambe et al. (2013)

[Moise et al., chemical review, 2015]

Various *n* prediction methods for organic components (and potentially for OA)

- **Redmond and Thompson et al., 2011:** Quantitative Structure–Property Relationship (QSPR) (**need to know the molecular formula**)

$$RI_{589\ nm} = 0.031717\mu + 0.0006087\alpha - 3.0227\left(\frac{\rho_m}{M}\right) + 1.38709$$

(μ: degree of unsaturation; α: molecular polarizability; ρ_m: density; M: molecular weight)

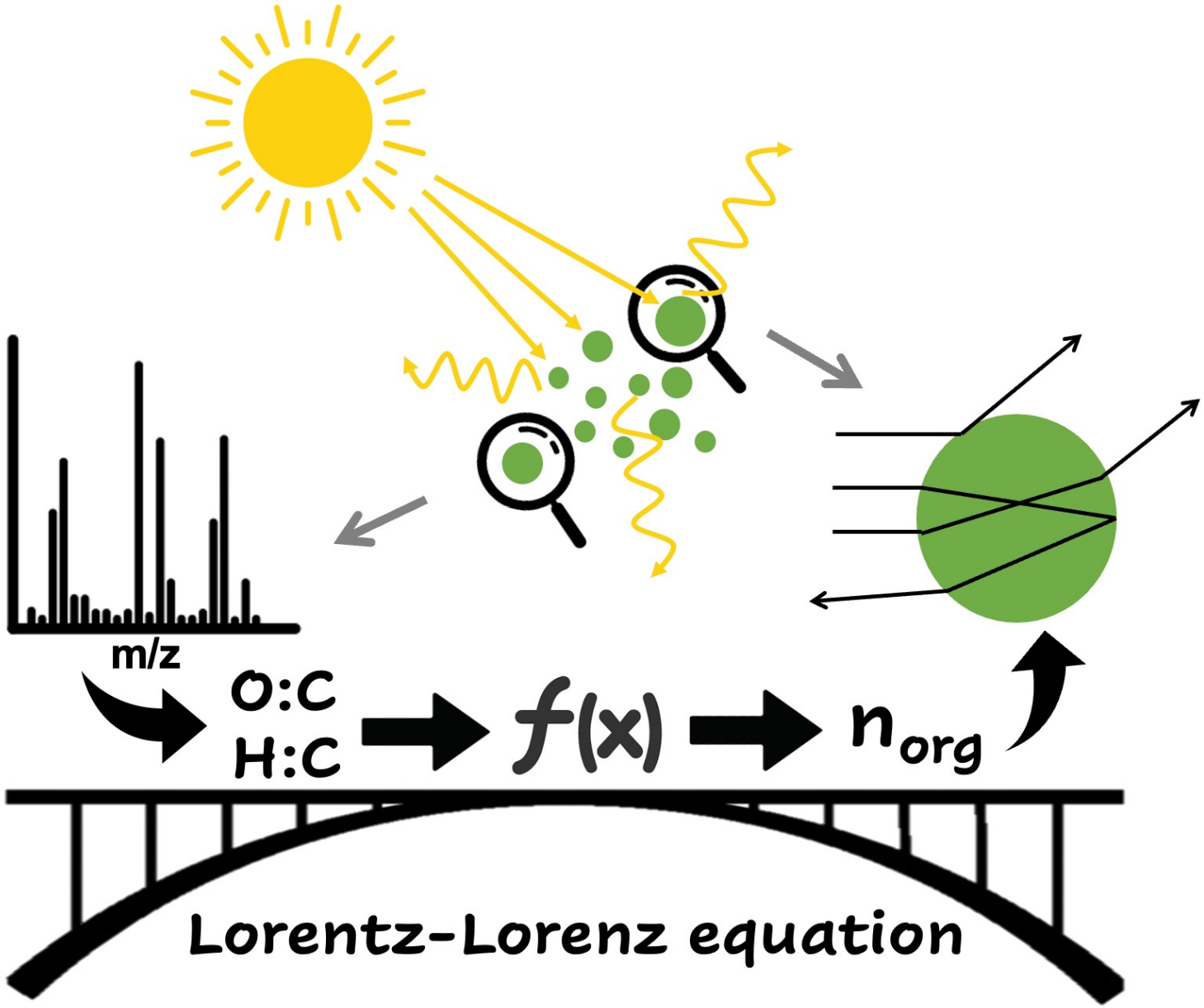
- **Cai et al., 2017:** Group Contribution (GC) models (**need to know molecular formula and chemical functionality, Lorentz-Lorenz equation**)

$$\sum_i x_i \frac{\alpha_i}{V_{m,i}} = \frac{3}{4\pi}\left(\frac{n^2-1}{n^2+2}\right)$$

- **Bouteloup & Mathieu, 2018:** Geometrical Fragment (GF) approach (**higher accuracy, need to know molecular formula and chemical functionality, Lorentz-Lorenz equation**)

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \frac{\sum_k x_k R_k}{\sum_k x_k V_k}$$

GOAL: develop a semi-empirical model to predicts *n* of OA using elemental ratios



$$\frac{n^2-1}{n^2+2}=\frac{4\pi}{3}N_A\rho\frac{\alpha}{M}$$

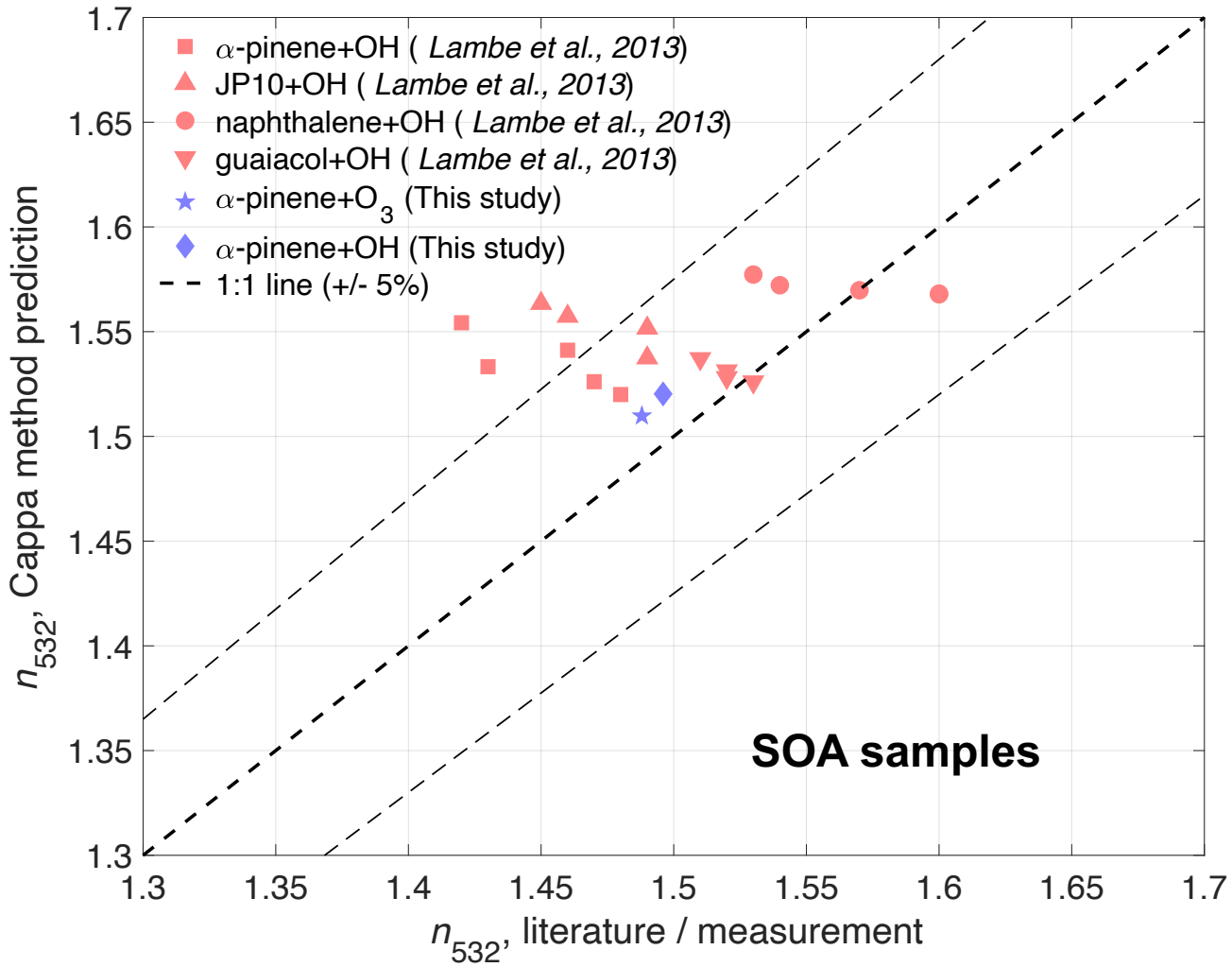
The Lorentz-Lorenz equation relates real refractive index *n* to the mean polarizability (α), mass density (ρ), and molecular weight (*M*) of the compound (*Born & Wolf, 1980*)

Inspired by Cappa et al. (2011), our objectives are twofold: 1) to improve accuracy and 2) to expand the wavelength prediction range

Cappa et al., 2011: calculate the *n* at 532 nm from O:C and H:C based on the Lorentz-Lorenz equation. Fit molecular polarizability, molar mass, and mass density all together with 3 parameters (significantly overpredicts *n* for SOA samples)

Cappa parameterization:

$$\frac{n^2-1}{n^2+2} = \frac{1}{3} \cdot \frac{x1+x2 \cdot O{:}C+x3 \cdot H{:}C}{1+1 \cdot O{:}C+1 \cdot H{:}C}$$



Theory and model training

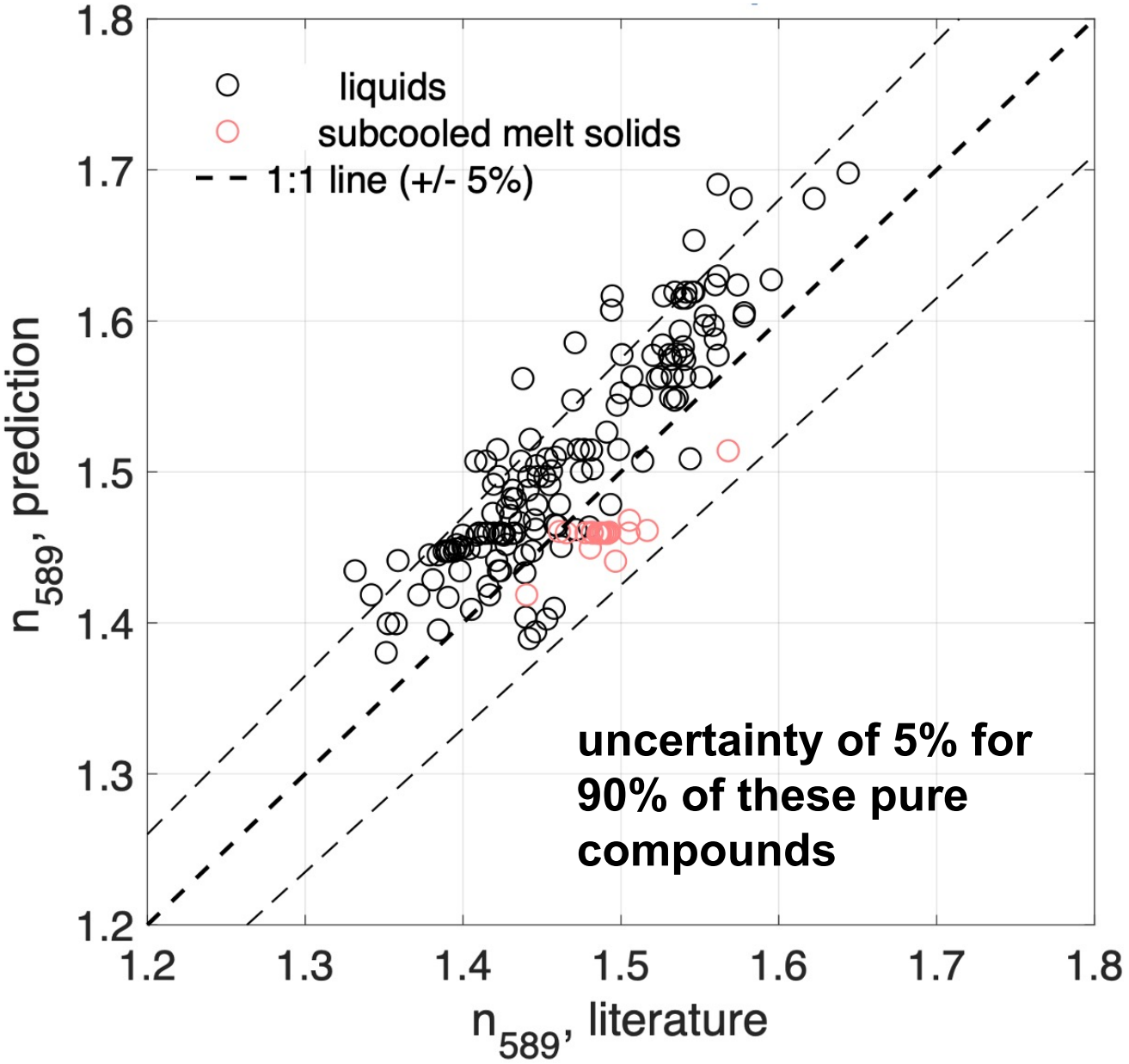
- Theory
  - Lorentz-Lorenz equation: $\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} N\alpha = \frac{4\pi}{3} N_A \rho \frac{\alpha}{M}$
  - Polarizability (*Bosque and Sales*, 2002): $\alpha = a_1 \cdot \#C + a_2 \cdot \#O + a_3 \cdot \#H$
  - Molecular weight: $M = 12 \cdot \#C + 16 \cdot \#O + 1 \cdot \#H$
  - Density (*Kuwata et al.*, 2012): $\rho = \frac{12 \cdot \#C + 16 \cdot \#O + 1 \cdot \#H}{b_1 \cdot \#C + b_2 \cdot \#O + b_3 \cdot \#H} = \frac{12 + 16 \cdot O{:}C + 1 \cdot H{:}C}{b_1 + b_2 \cdot O{:}C + b_3 \cdot H{:}C}$
- Prediction equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} (N_A \cdot 10^{-24}) \cdot \frac{\boldsymbol{a_1} + \boldsymbol{a_2} \cdot O{:}C + \boldsymbol{a_3} \cdot H{:}C}{\boldsymbol{b_1} + \boldsymbol{b_2} \cdot O{:}C + \boldsymbol{b_3} \cdot H{:}C}$$

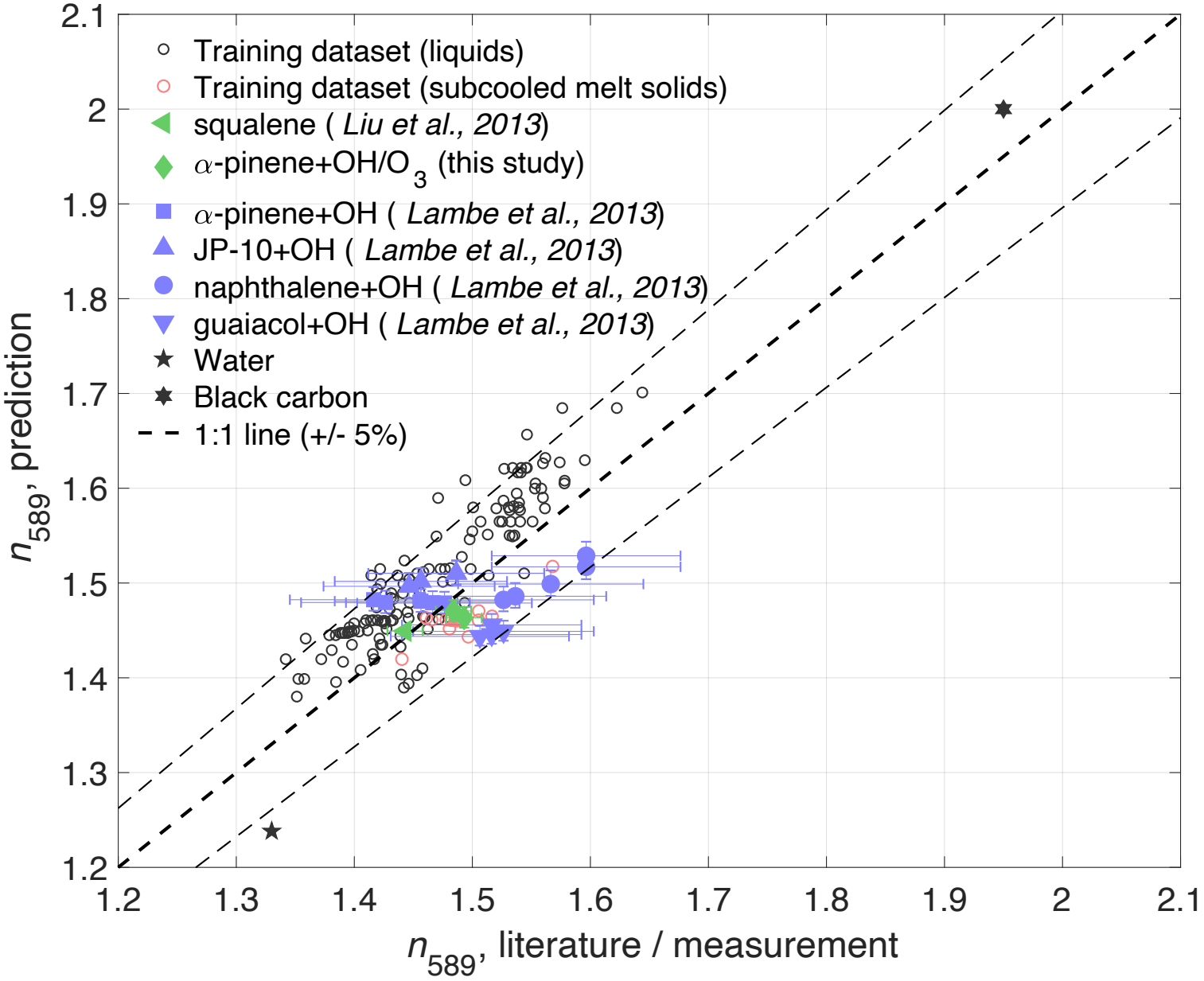
- Model training (fit polarizability and density separately, each with 3 coefficients) :
  - Training dataset: 160 pure organic components composed of C, O, and H with known density, and real refractive index at 589 nm: 140 liquids (CRC handbook) + 20 subcooled melt solids (*Cai et al., 2016*)
  - Train liquids and melt solids separately and apply weighted average to these two set of coefficients

Model training results

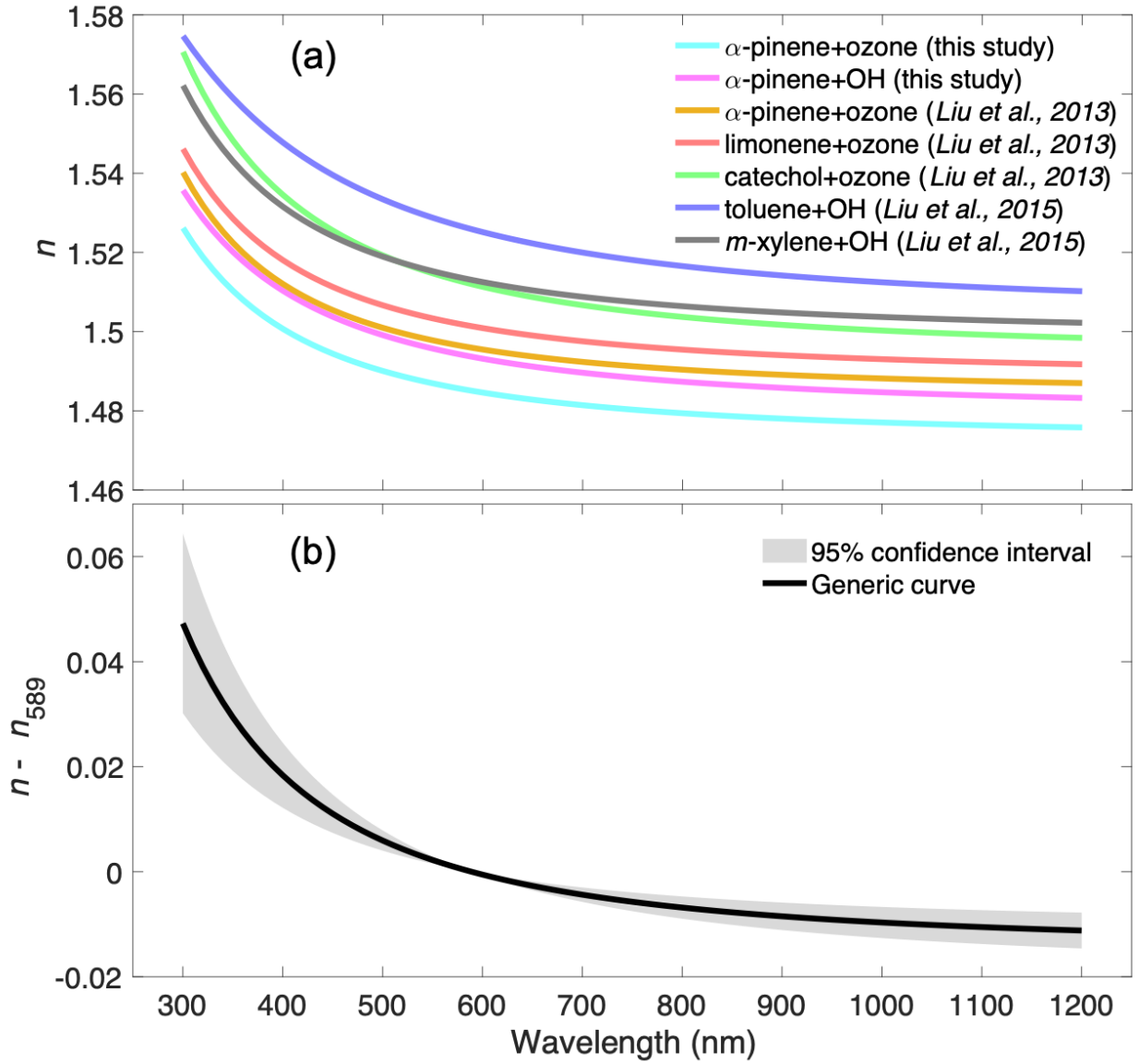
$$\frac{{n_{589nm}}^2 - 1}{{n_{589nm}}^2 + 2} = \frac{4\pi}{3}(N_A \cdot 10^{-24}) \cdot \frac{1.57 + 0.64 \cdot (O:C) + 0.13 \cdot (H:C)}{6.76 + 7.80 \cdot (O:C) + 5.07 \cdot (H:C)}$$

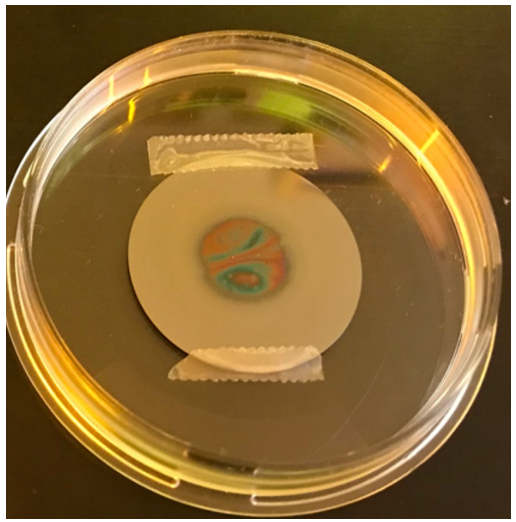


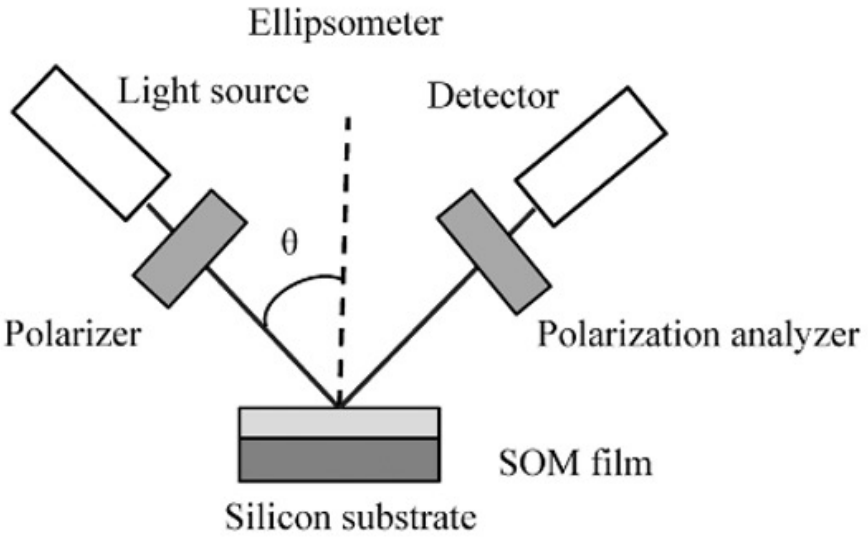
Uncertainty of 5% for the whole validation data set (various SOA samples)



The predictions can be expanded to a wide spectrum between 300 nm and 1200 nm

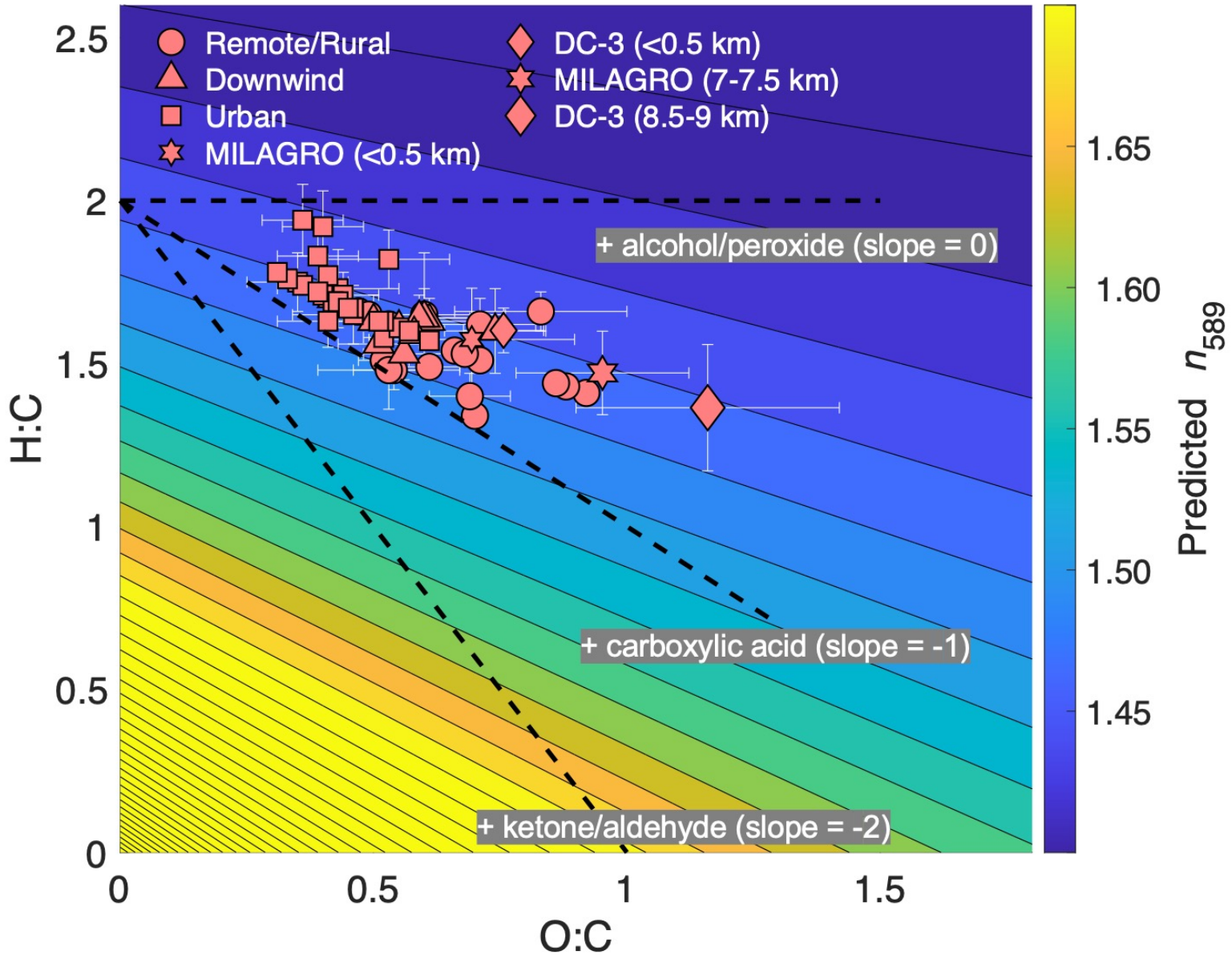






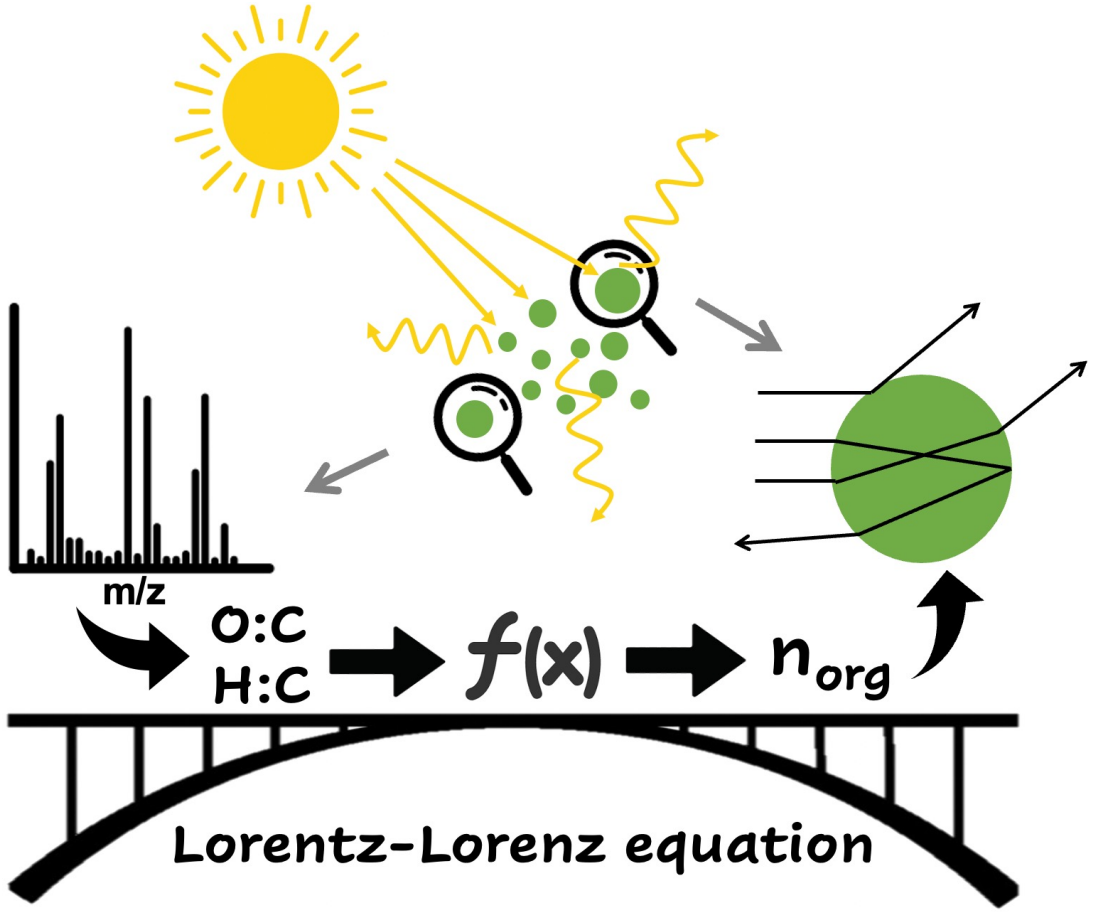
$$n(\lambda) - n_{589nm} = 4.98\times10^{3}/\lambda^{2} + 0.603\times10^{8}/\lambda^{4} - 0.0139$$

The model predicts small variation (1.43-1.51) in *n* at 589 nm for typical O:C and H:C values of OA in the atmosphere (only C, H, O are considered in this model!!!)

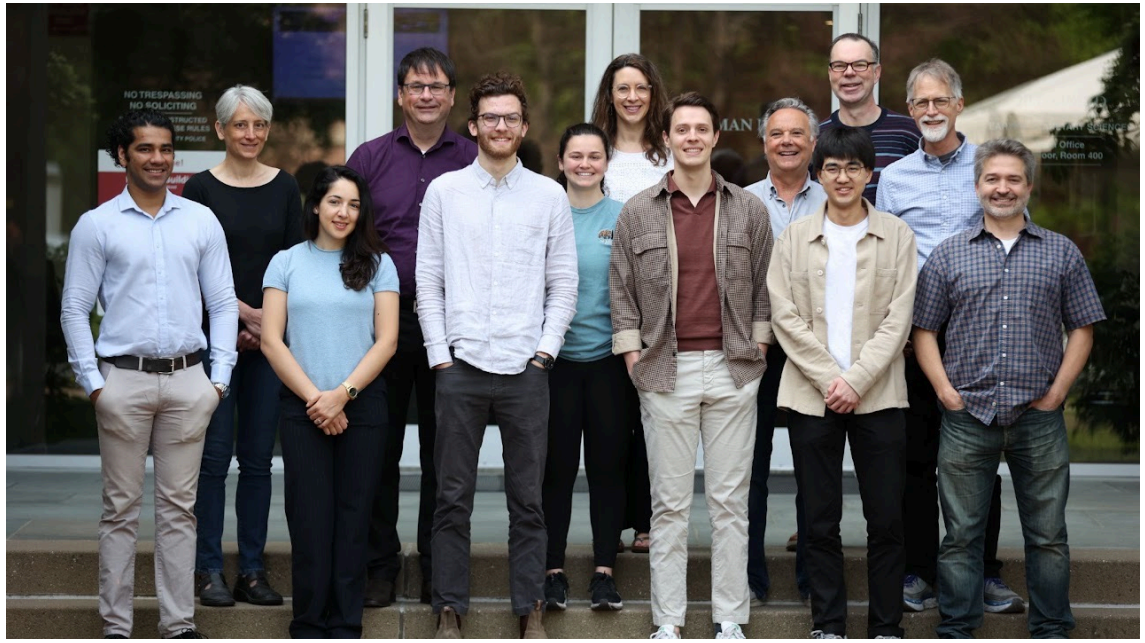


Take home messages

1. A semi-empirical model was developed to predict the real refractive index (*n*) of organic aerosols (**consisting mainly of C, H, and O**) using O:C and H:C elemental ratios
2. The model accuracy (**≥95%**) was validated with measurements of various secondary organic aerosols
3. The predictions can be expanded to predict *n*-values in a wide spectrum between **300 and 1,200 nm**
4. The model predicts **small variation in *n* at 589 nm** for typical O:C and H:C values of organic aerosols in the atmosphere
5. A goal for future research is to further incorporate the N:C and S:C ratios into the model framework.



Acknowledgements



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Yaowei Li and Bin Bai contributed equally to this work.

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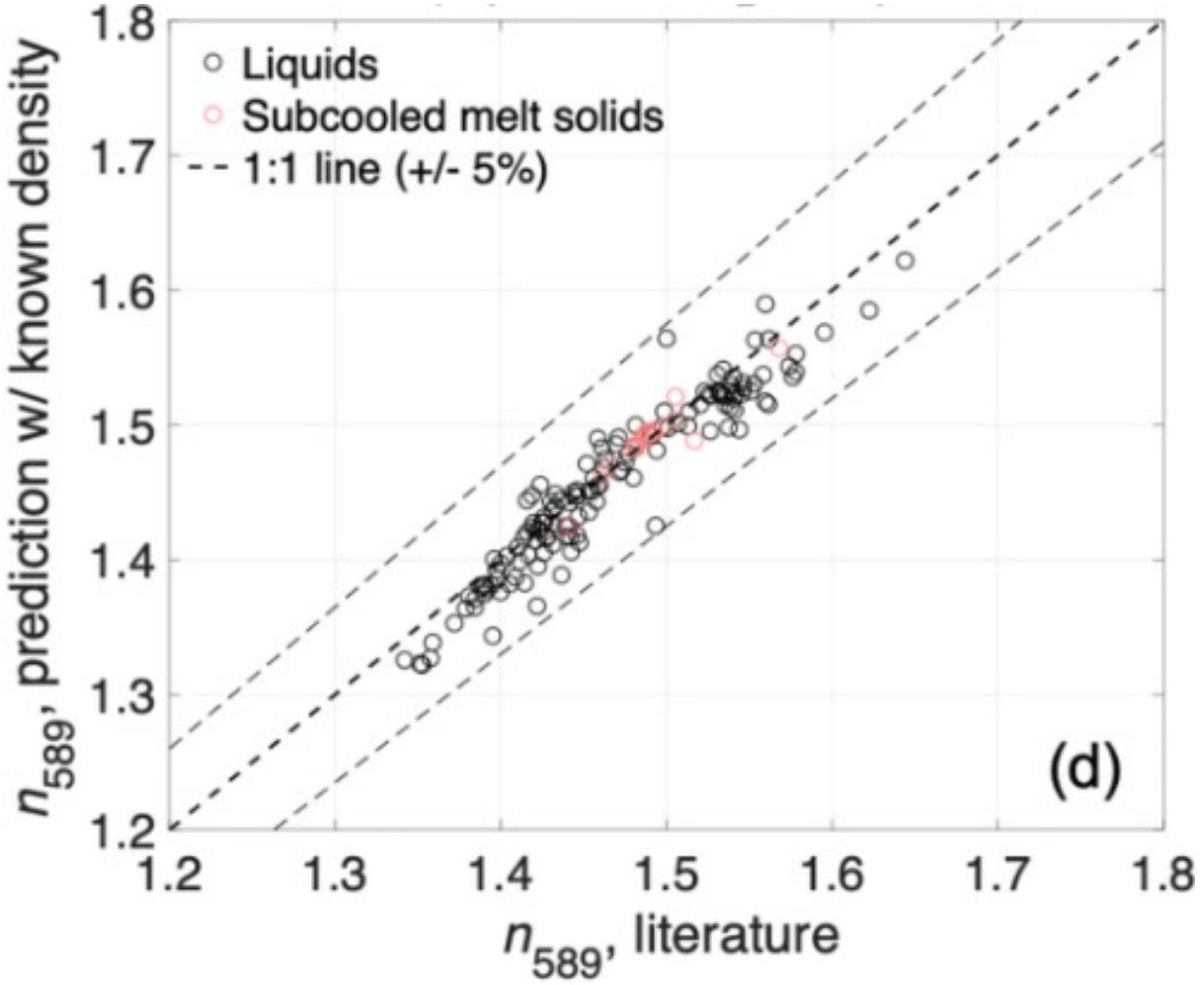
If material density ρ is known, the modified prediction equation with higher accuracy:

$$\frac{{n_{589\mathrm{nm}}}^2 - 1}{{n_{589\mathrm{nm}}}^2 + 2} = \frac{4\pi}{3}\left(N_A\rho \cdot 10^{-24}\right) \cdot \frac{1.57 + 0.64 \cdot (O:C) + 0.13 \cdot (H:C)}{12 + 16 \cdot (O:C) + 1 \cdot (H:C)}$$



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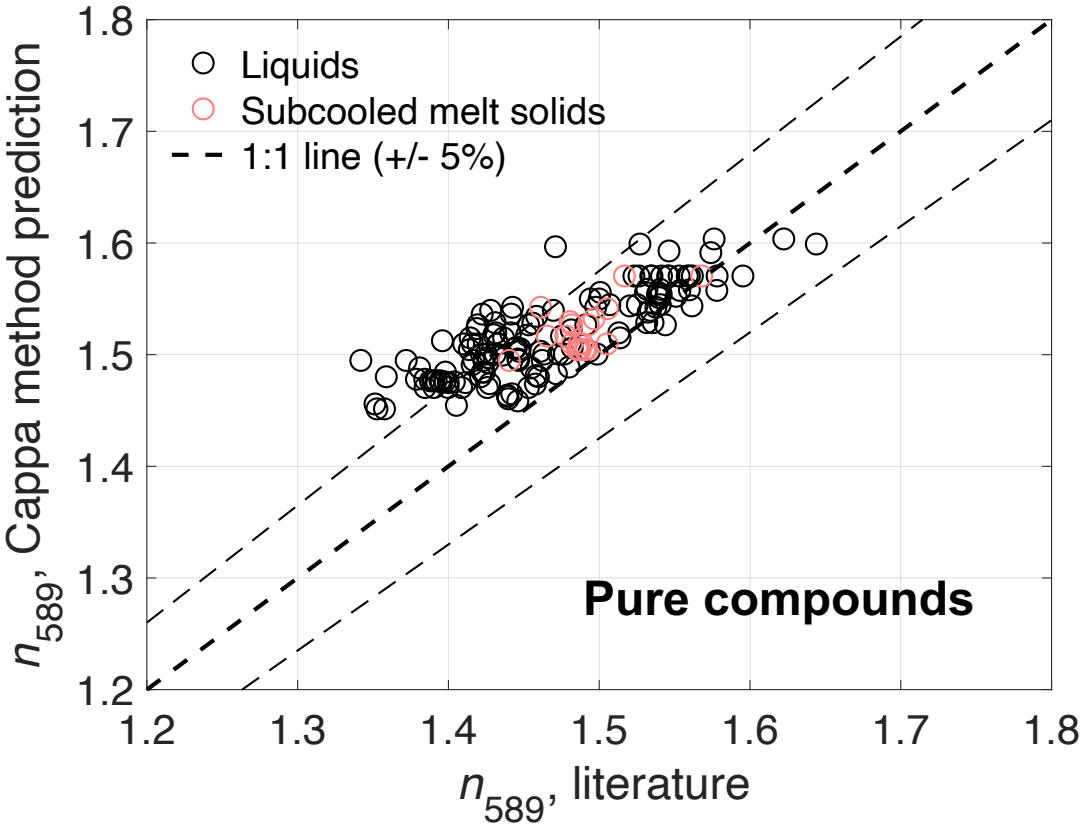

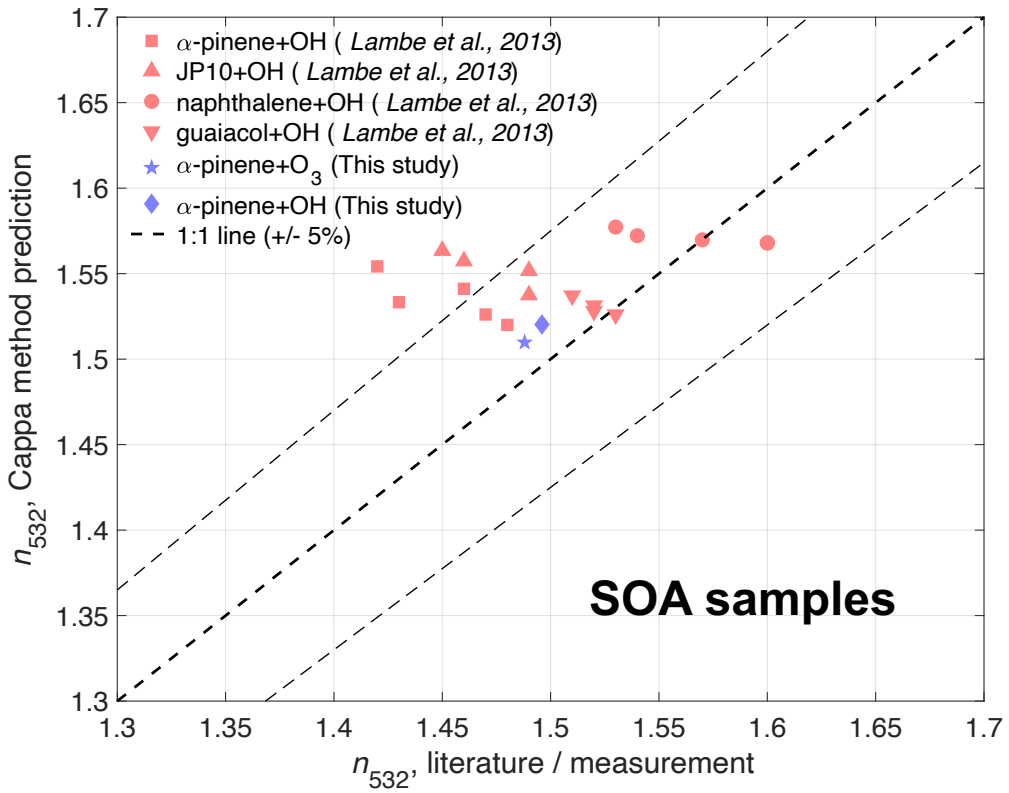

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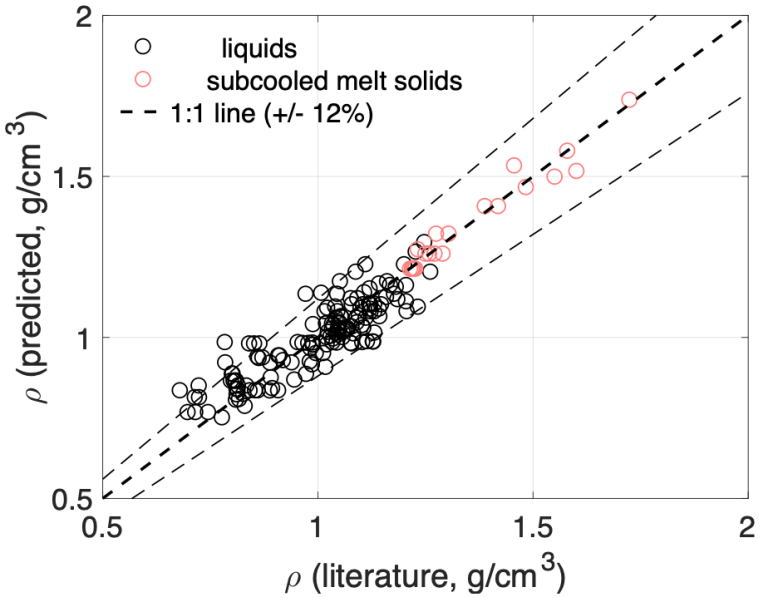
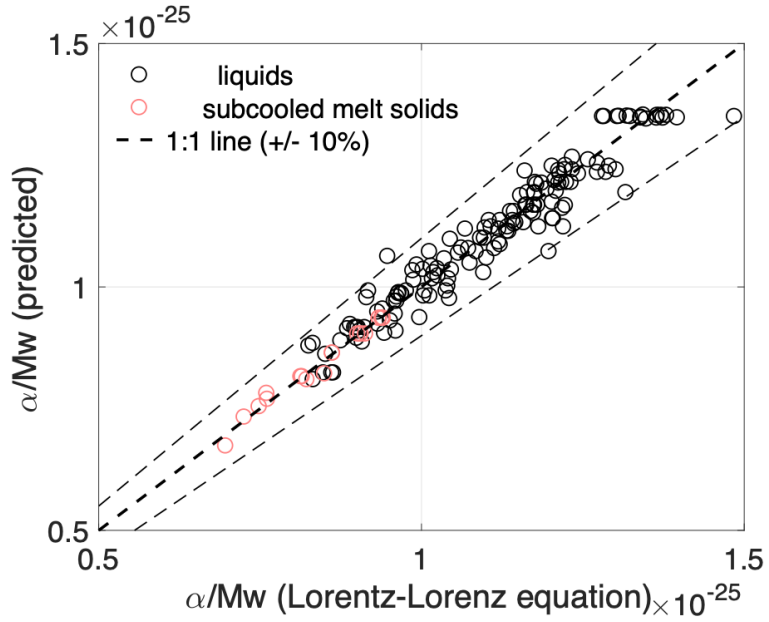
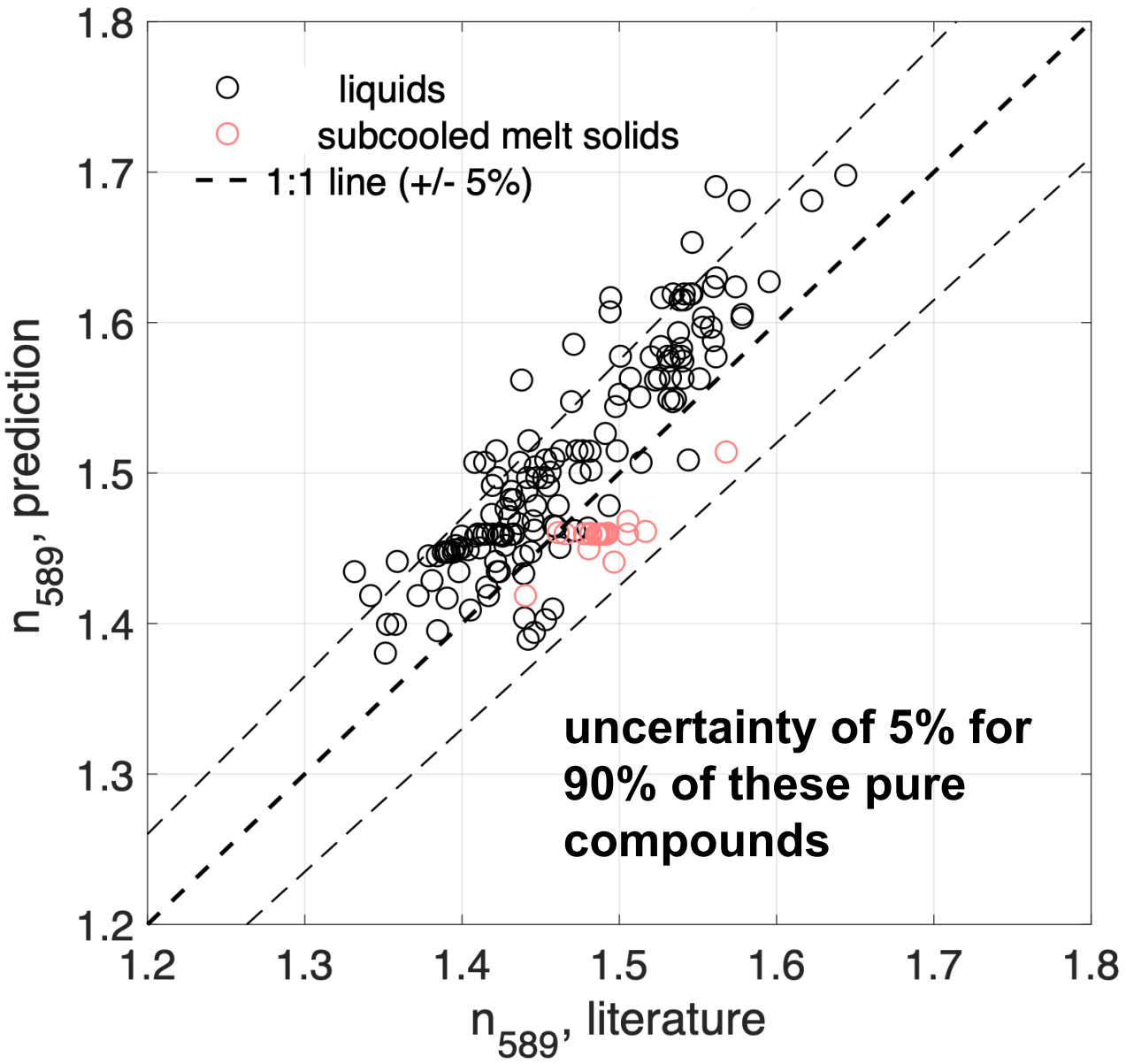






Various *n* prediction methods for organic components (and potentially for OA)

- Quantitative Structure–Property Relationship (QSPR): multi-linear fit (no physical basis) of the degree of unsaturation (μ), molecular polarizability (α), and ρ_m/M (need to know the molecular formula) *Redmond and Thompson et al., 2011*

$$RI_{589\ nm} = 0.031717\mu + 0.0006087\alpha - 3.0227\left(\frac{\rho_m}{M}\right) + 1.38709$$

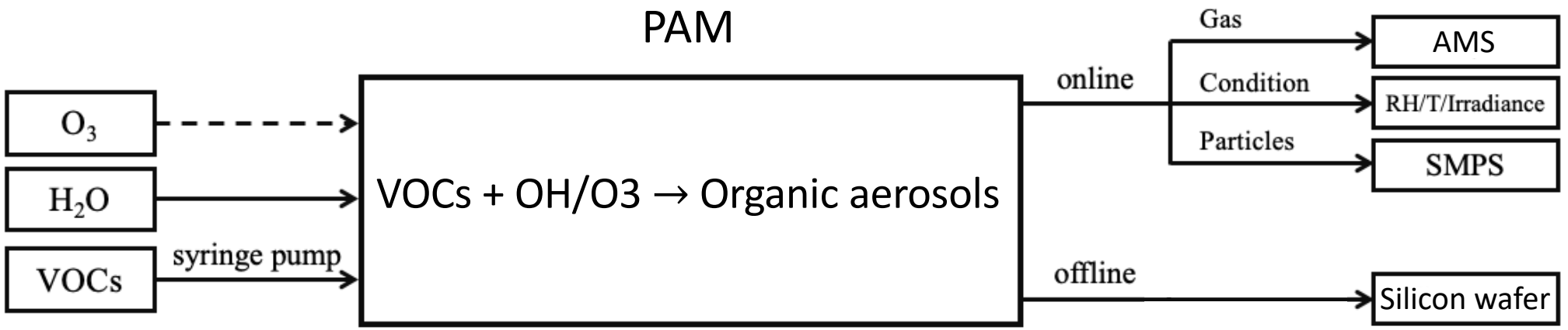
- Group Contribution (GC) models: Lorentz-Lorenz equation, contributions of different functional groups (high accuracy but need to know molecular formula and chemical functionality) *Cai et al., 2017*

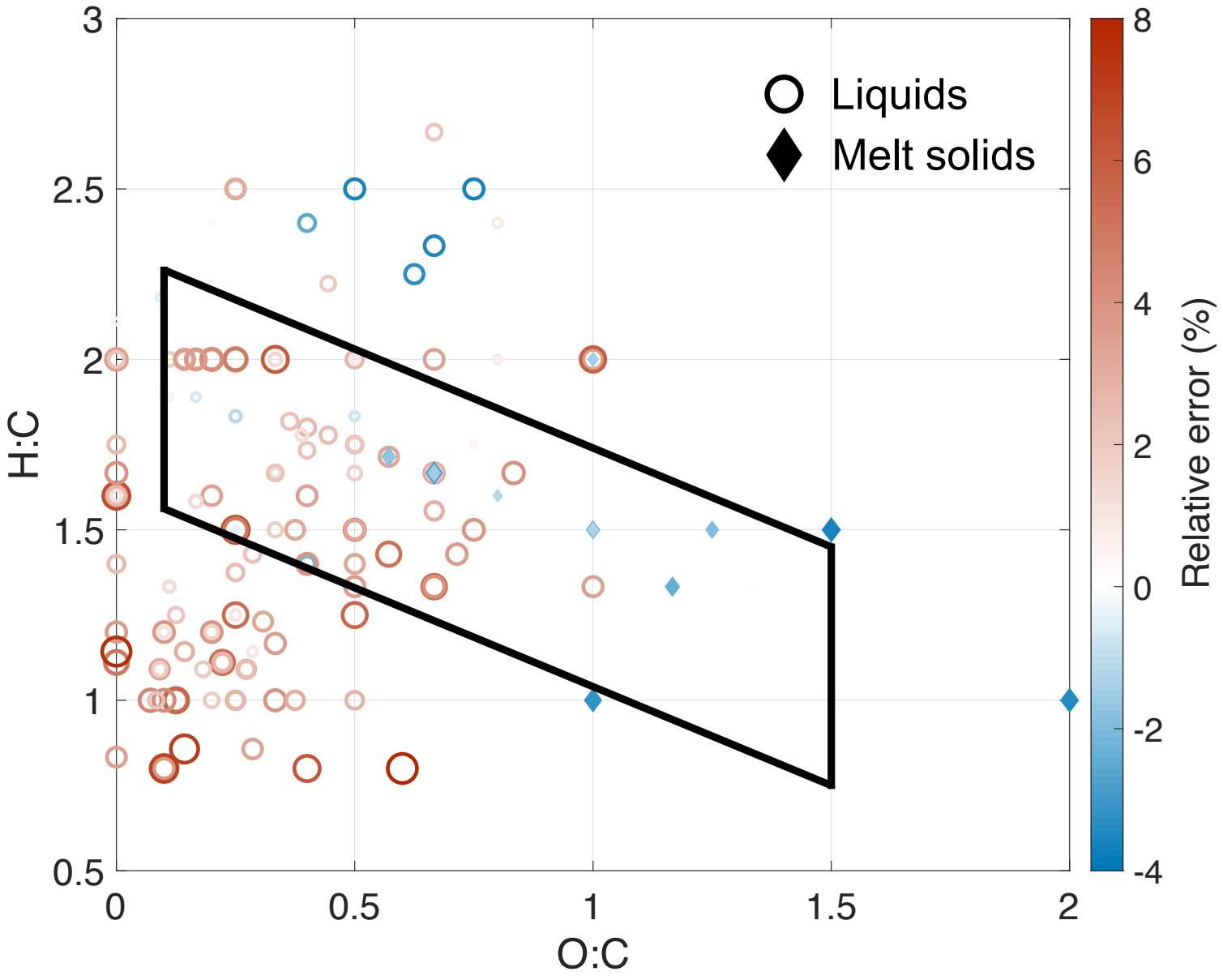
$$\sum_i x_i \frac{\alpha_i}{V_{m,i}} = \frac{3}{4\pi}\left(\frac{n^2-1}{n^2+2}\right)$$

- Geometrical Fragment (GF) approach: Lorentz-Lorenz equation; fit molecular polarizability (α) and molar volume (V_m) separately; contributions of different functional groups (high accuracy but need to know molecular formula and chemical functionality) *Bouteloup & Mathieu, 2018*

$$\frac{n_D^2-1}{n_D^2+2} = \frac{\sum_k x_k R_k}{\sum_k x_k V_k}$$

Typical Operation Diagram




Liquids
Melt solids
H:C
O:C
Relative error (%)
3
2.5
2
1.5
1
0.5
0
0.5
1
1.5
2
8
6
4
2
0
-2
-4