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A General Framework for Predicting CCN Activity of Organic Molecules from Functional Group Data

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Motivation: 0.4 W m^{-2} in indirect forcing

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How important is organic aerosol hygroscopicity to aerosol indirect forcing?

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"The simulation results show that the uncertainty in organics aerosol hygroscopicity, based on current understanding and our model formulation, may lead to an uncertainty of about 0.4 W m^{-2} ... . This uncertainty is comparable to or even larger than those due to autoconversion parameterization and tuning parameters related to entrainment, drizzle and snow formation."

Levels of representation of organic aerosol

By mass/source	By age/oxidation state	By molecular structure
direct emissions	physical age, photochemical age	explicit speciation
product schemes	principle components HOA/OOA/LV-OOA ...	functional group composition
volatility basis set approach	O:C and H:C ratio	master chemical mechanism
	explicit oxidation state	

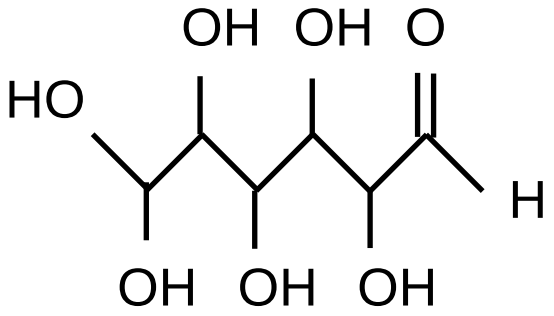
Increasing level of scientific understanding

Increasing complexity, increasing uncertainty

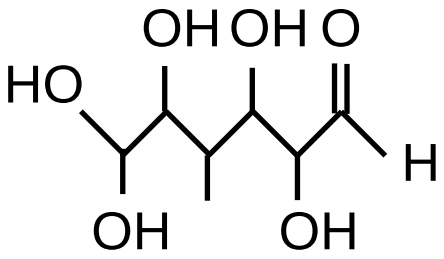
Can we predict the water uptake/CCN properties of a substance from molecular composition?

Hydrophobic and insoluble

Hydrophilic and water soluble



We can represent this molecule as



$$v = 115\,\frac{\mathrm{cm}^{-3}}{\mathrm{mol}}, 6 \times (C), 5 \times (-\mathrm{OH}), 1 \times (=\mathrm{O}), 1 \times (\mathrm{CH_2})$$

molar volume, # carbon, #hydroxyl, #carbonyl, #CH_2

Our objective is to find a relationship for

CCN activity = function(molar volume, #carbons, sum[#moiety(i)])

Why do we need such a relationship?

By mass/source	By age/oxidation state	By molecular structure
direct emissions	physical age, photochemical age	explicit speciation
product schemes	principle components HOA/OOA/LV-OOA ...	functional group composition
volatility basis set approach	O:C and H:C ratio	master chemical mechanism
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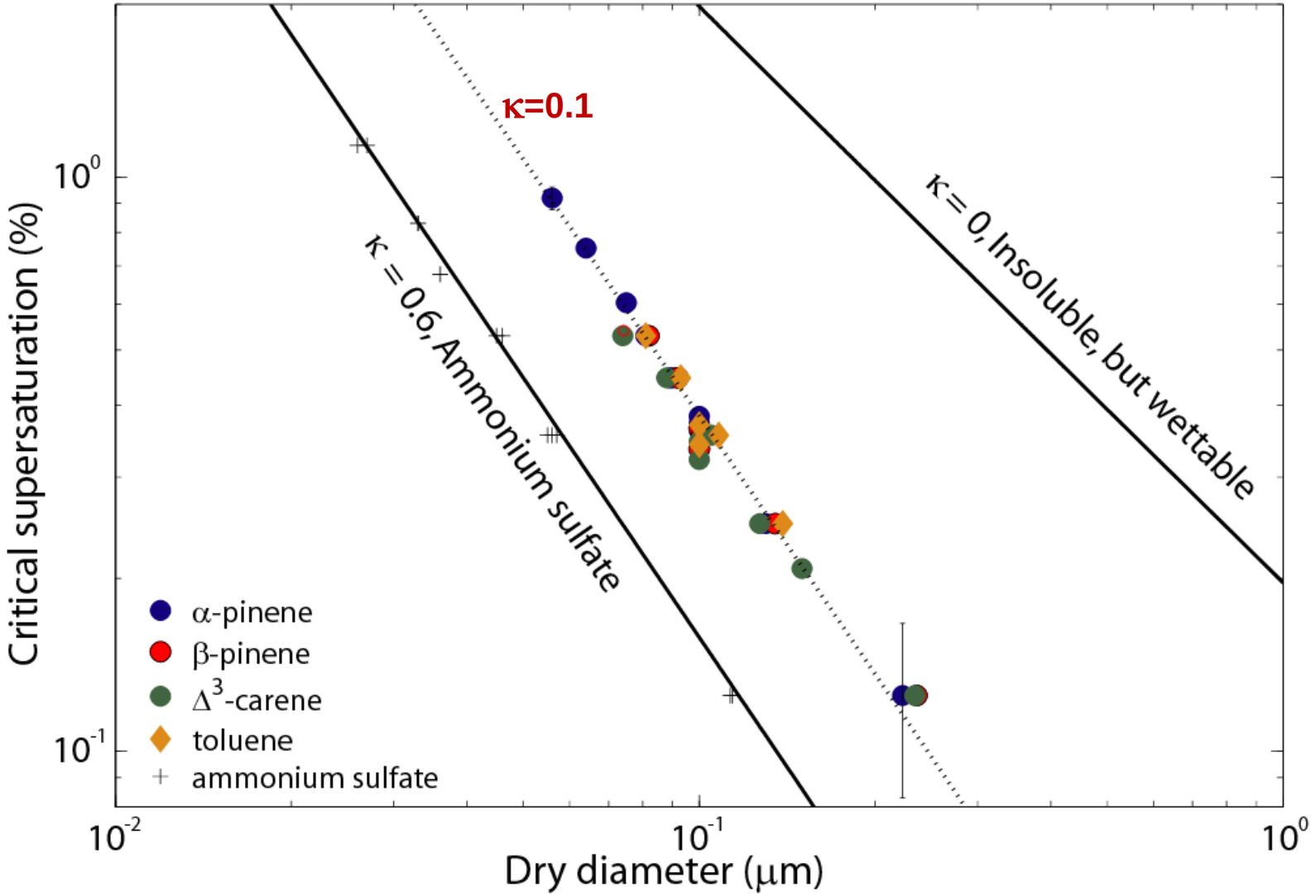
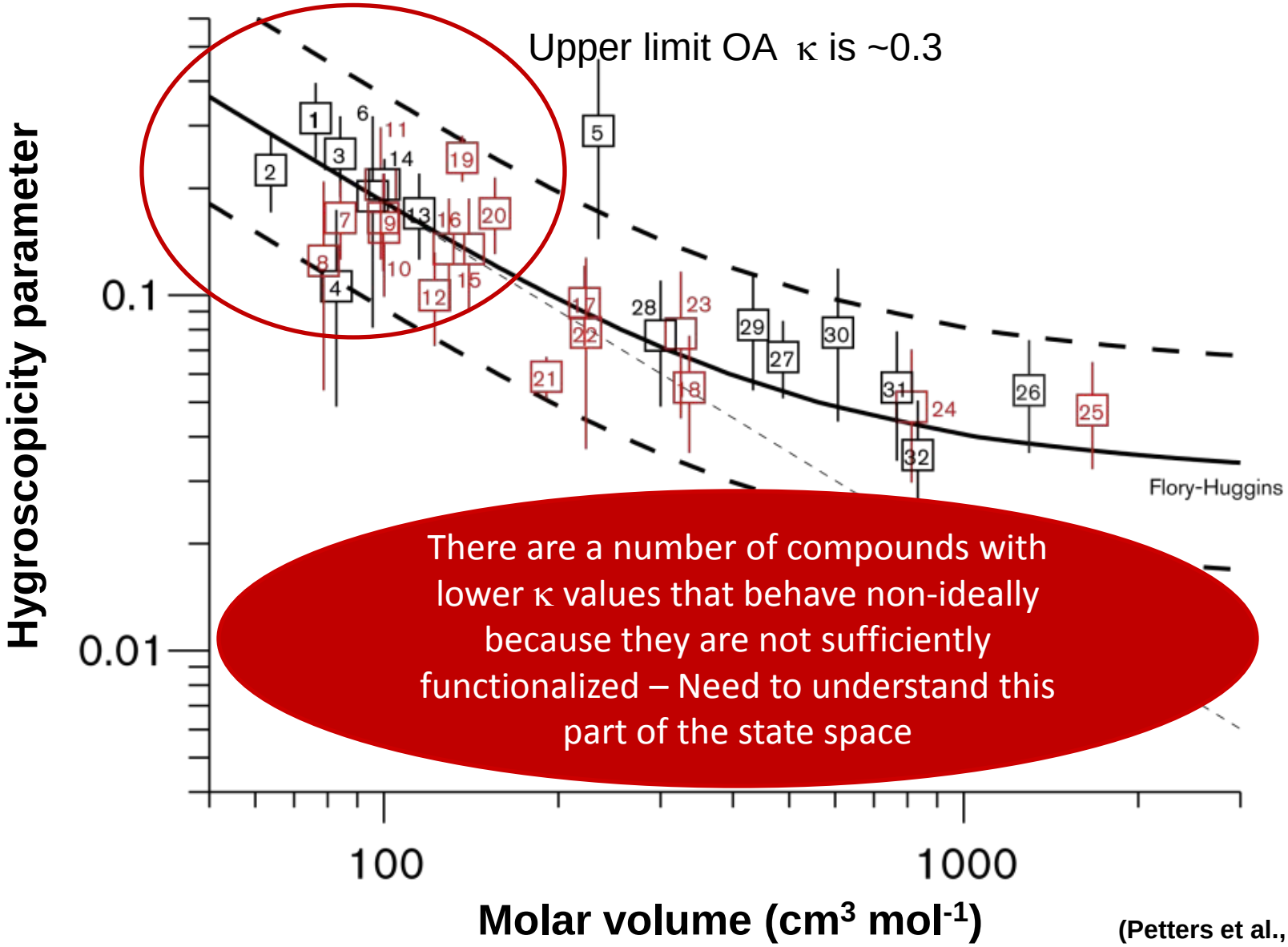
1. Parameterization of CCN activity example for SOA for monoterpene + O_3



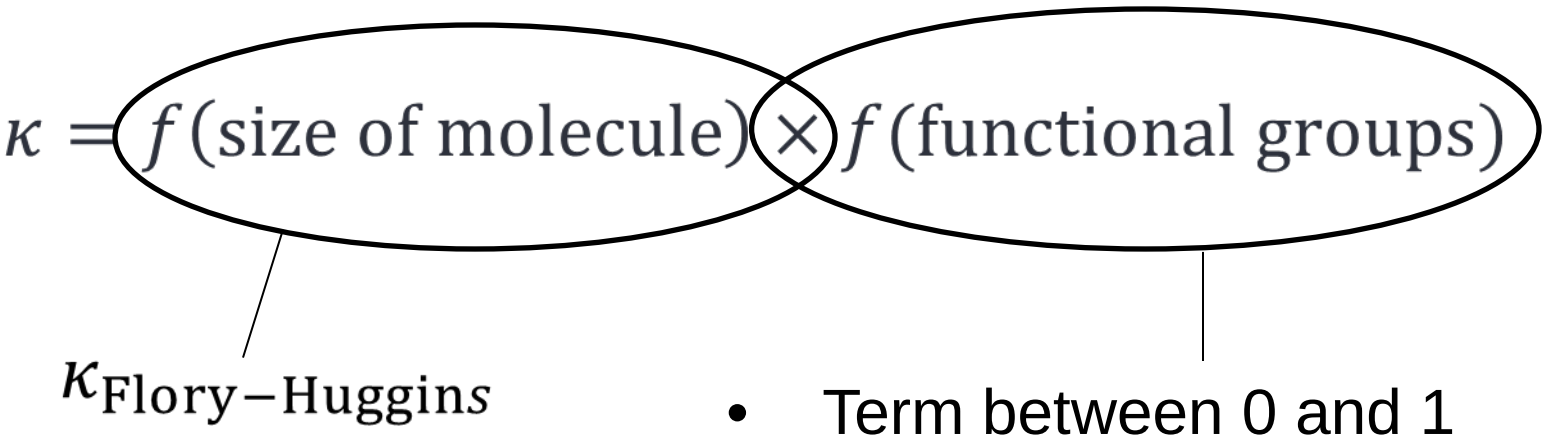
(Prenni et al., 2007, JGR)

2. For sufficiently water soluble compounds OA κ is controlled by molar volume



(Petters et al., 2009, GRL)

Seek an equation that works also for less soluble compounds



- Term between 0 and 1
- 1 for “soluble” compounds
- Account for different types of functional groups (e.g. “acid”, “nitrate”, “hydroxyl”...)
- Need experimental framework to constrain this term

3. Use model SOA systems to synthesize molecules with known moieties

Example system: linear 1-alkene + O_3 +

- H_2O
- Methanol
- Propanol

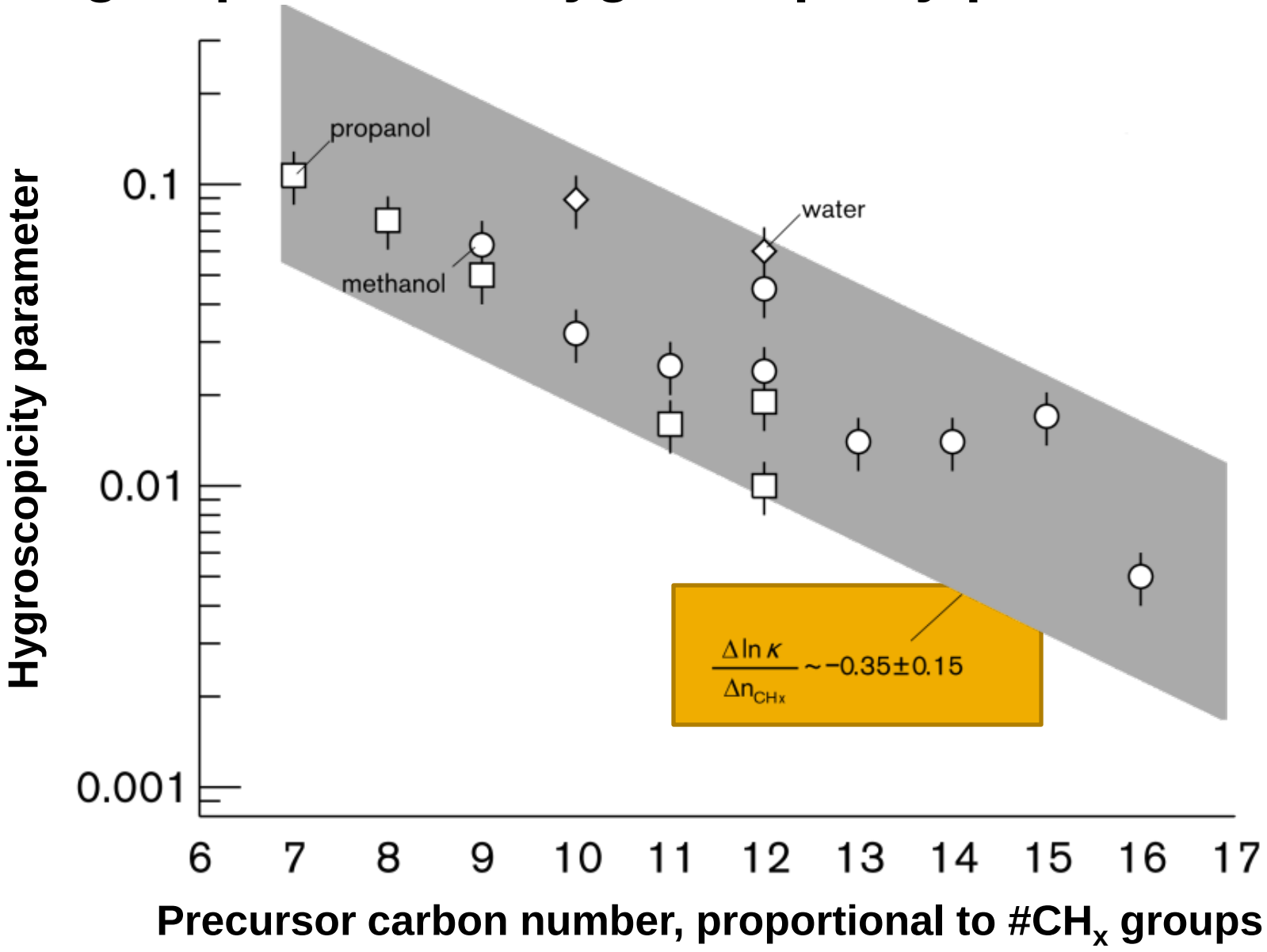
$HOO(GO)CH-(CH_2)_R-CH_3$

oxidized tail with functionality reflecting the SCI reactant

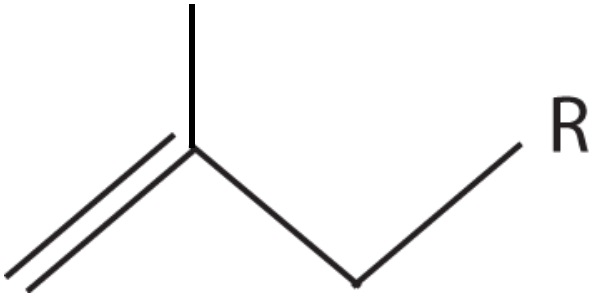
Number of CH_2 groups depends on precursor chain length

(Tobias and Ziemann, ES&T, 2001)

3. Empirical relationship between # of CH_x groups and the hygroscopicity parameter

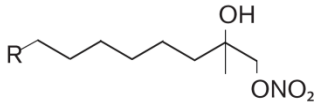


3. Second example: synthesize molecules with different # of OH groups

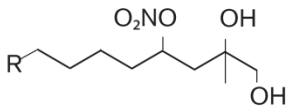


2-methyl-1alkene + OH/NO_x

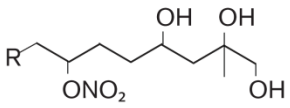
(Matsunaga et al., PNAS, 2010)



β-hydroxynitrates



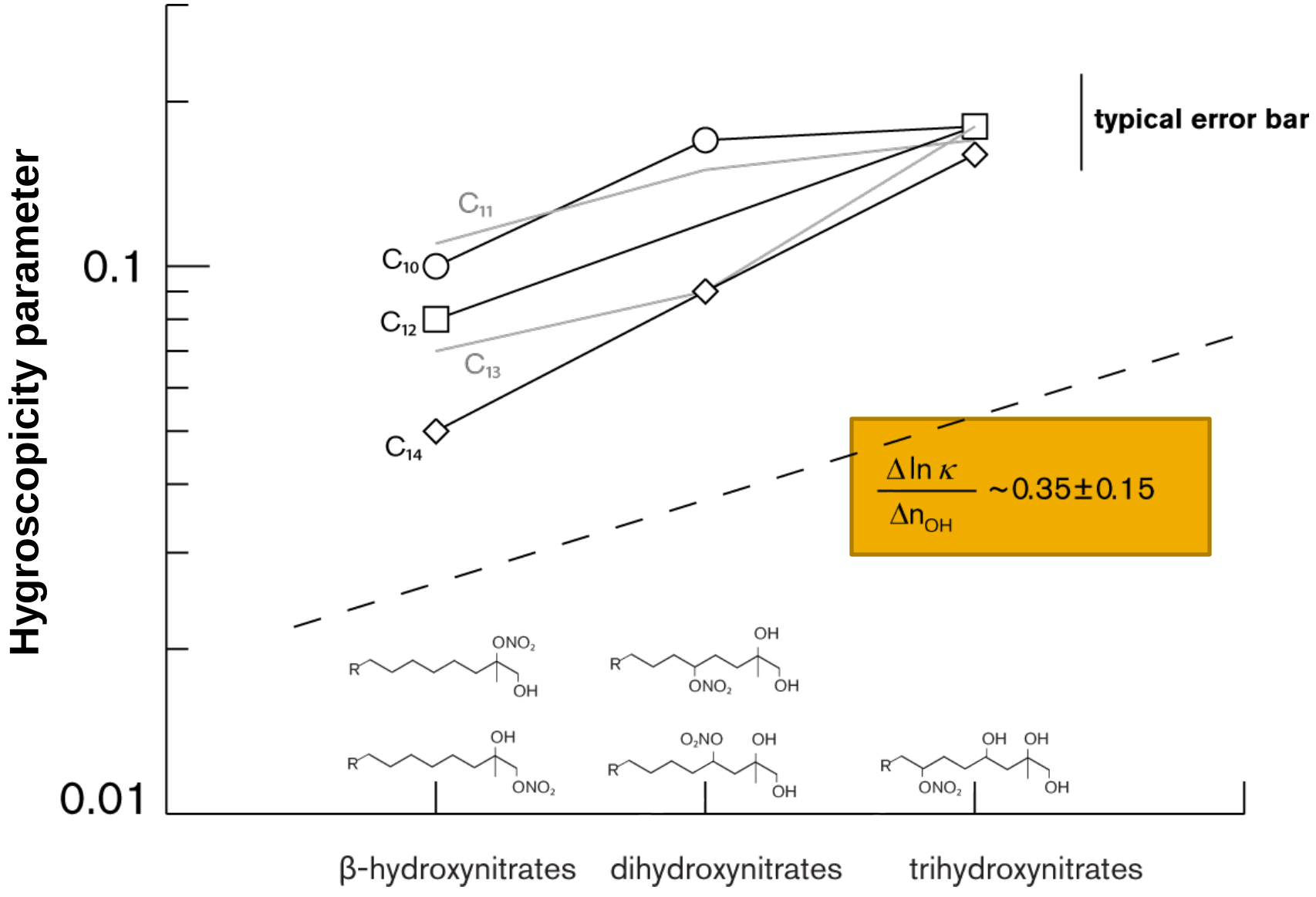
dihydroxynitrates



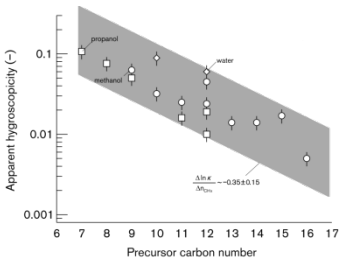
trihydroxynitrates

Use offline HPLC-CCN technique to measure CCN activity of individual compounds: See poster *Hygroscopicity frequency distributions of secondary organic aerosols* by Sarah Suda

3. Empirical relationship between # of OH groups and the hygroscopicity parameter



4. The empirical relationships can be used to construct the following framework



detrimental effect of CH_x on kappa

number of effective CH_x groups (≥0)

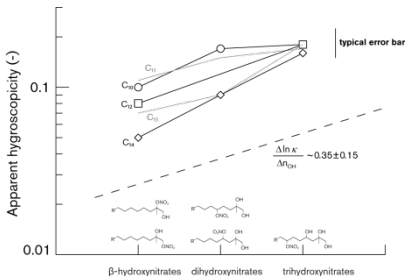
$$\kappa = \kappa_{\text{Flory Huggins}} \exp(cn_e)$$

$$n_e = n_c - \sum \alpha_i n_i$$

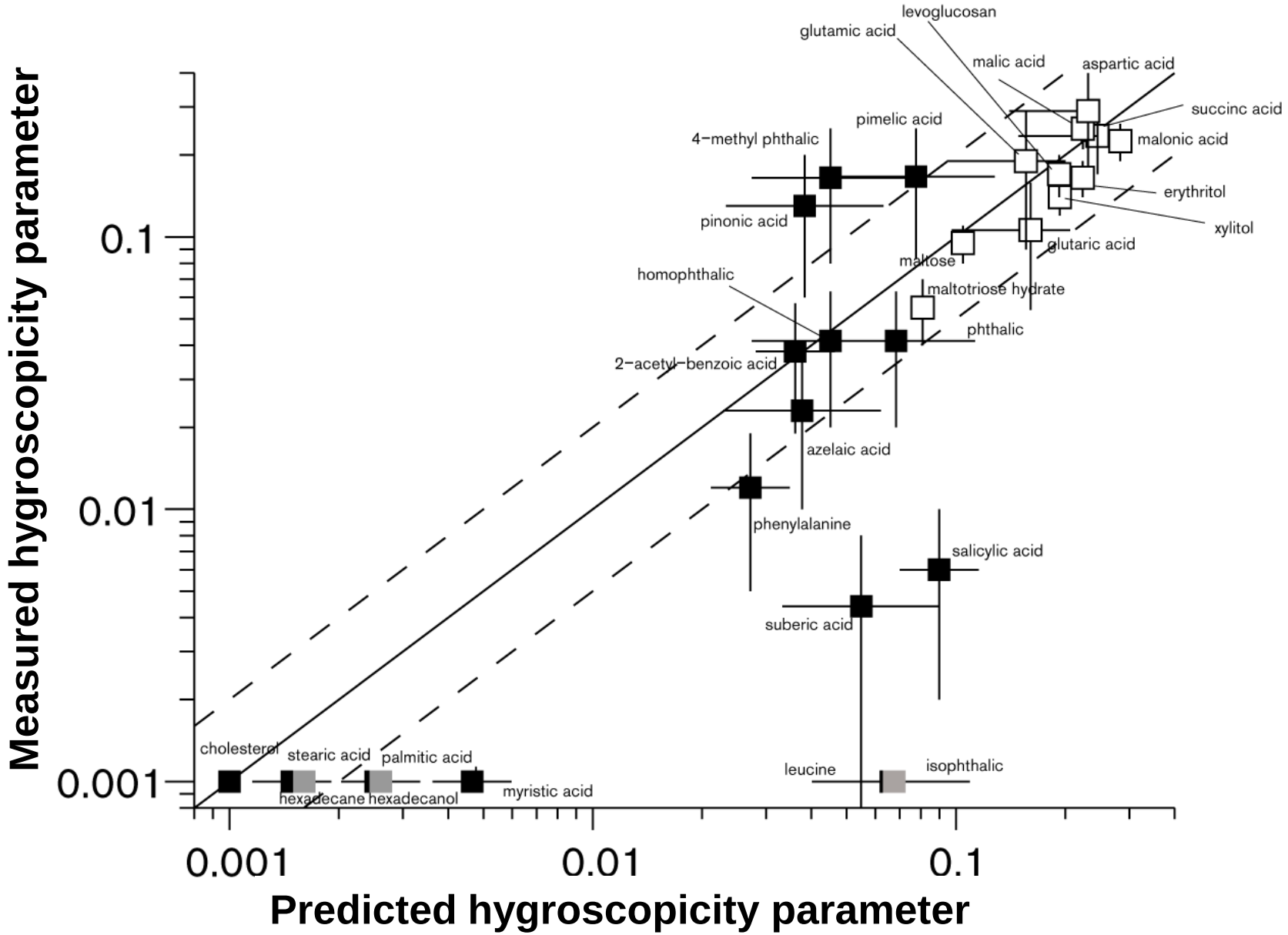
number of carbon atoms

ability of functional group to negate CH_x

number of that group type



4. Test of fidelity with current parameters against CCN data from pure compounds



Conclusions

- For sufficiently functionalized molecules Flory-Huggins theory presents a reasonable baseline
- Developed a simple mathematical framework to compute kappa from
  - number of carbon atoms/molar volume
  - number of functional groups of type i
  - a functional group dependent interaction parameter
- Experiments with model SOA systems can be used to populate the parameter space of the relationship