Modeling organic aerosol-cloud interactions

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Project Goals and Methods

- Address current limited understanding of the effects of **organic species** on the role of atmospheric aerosols in warm and cold cloud formation
- Improve understanding of the product mix resulting from formation of **secondary organic aerosol** (SOA), and the role of SOA in cloud formation
- Condense information into form(s) suitable for **atmospheric modeling**

- Our **approach** as been to conduct a large number of experiments (> 60) varying the precursor organic compound + oxidant:
  - Carbon chain length (size of carbon “backbone”)
  - Oxidant (ozone; NO_3; OH in presence of NO_x; OH in absence of NO_x; reaction of stabilized Criegee intermediate with water, alcohols, and aldehydes)
- Followed by analyses of composition and cloud-forming potential using both conventional and novel techniques

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Compositional analyses

***Motivation**:*

SOA and oxidized primary organic aerosol (POA) systems are too complex to be effectively analyzed by molecular methods (GC-MS and LC-MS)

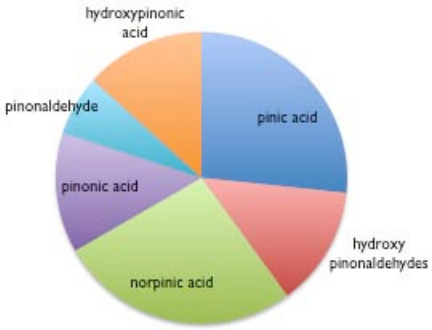
***Approach**:*

Develop and apply new spectrophotometric analyses for identification and quantification of **functional groups**

- Expect the type and number of functional groups to play a key role in compound hygroscopicity
- Applied to filter samples (so can be readily extended from lab systems to ambient samples)

- Have methods for quantification of **carboxyl, hydroxy, carbonyl, nitrate, peroxy, and ester groups**
  - Qualitative and quantitative results are consistent with known reaction mechanisms
  - Also compare well with measured elemental composition (C, H, O, N)

Example: α-pinene + O_3

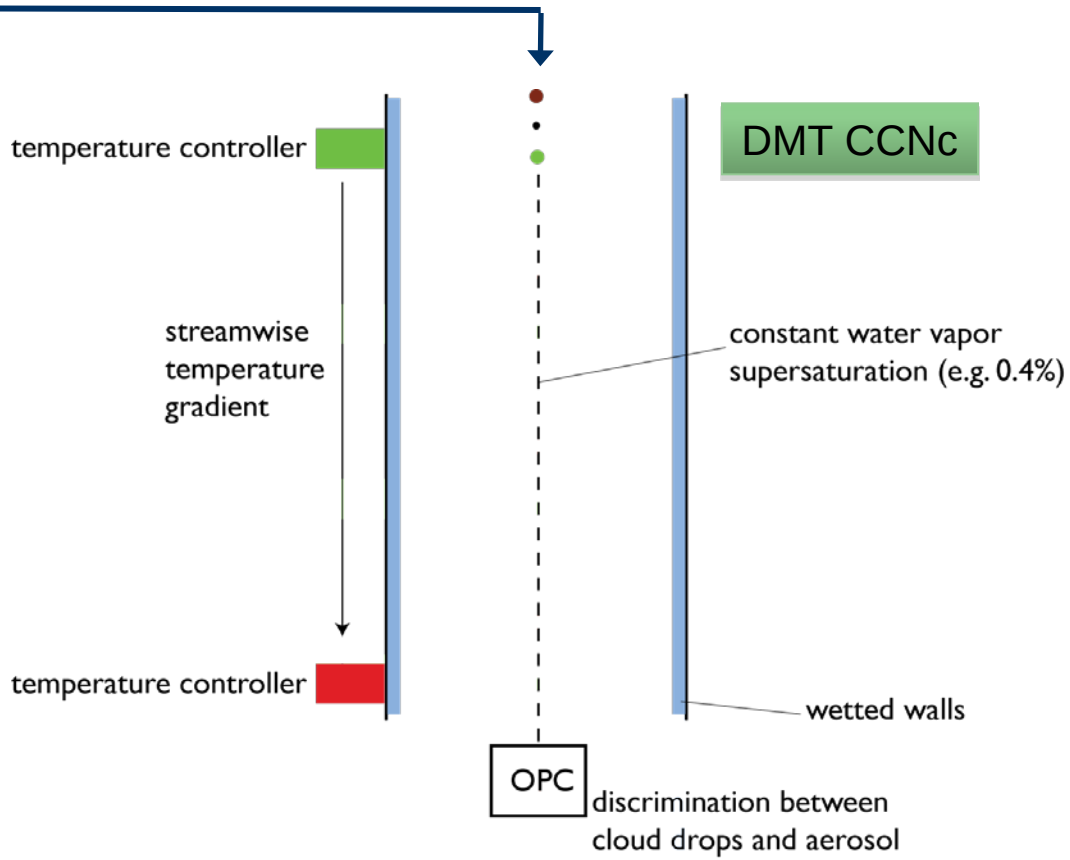


- ***Major products (Yu et al., 1999)***:
  pinic acid, pinonaldehyde, hydroxy pinonaldehydes
  pinonic acid, hydroxy pinonic acid, and norpinic ac

- Applying estimated relative amounts in aerosol phase of these products, obtain overall O:C ~0.4
- Comparison of relative abundance of functional groups from the literature,
  and from our new methods:

	Carboxyl C(O)OH	Carbonyl C(O)	Hydroxyl COH	Ester C(O)OR	Peroxide COO	Methylene CH_2	O:C
	0.15	0.08	0.03	0	0	0.74	0.4
new	**0.12**	**0.12**	**0.03**	**0.06**	**0.02**	**0.65**	**0.55**

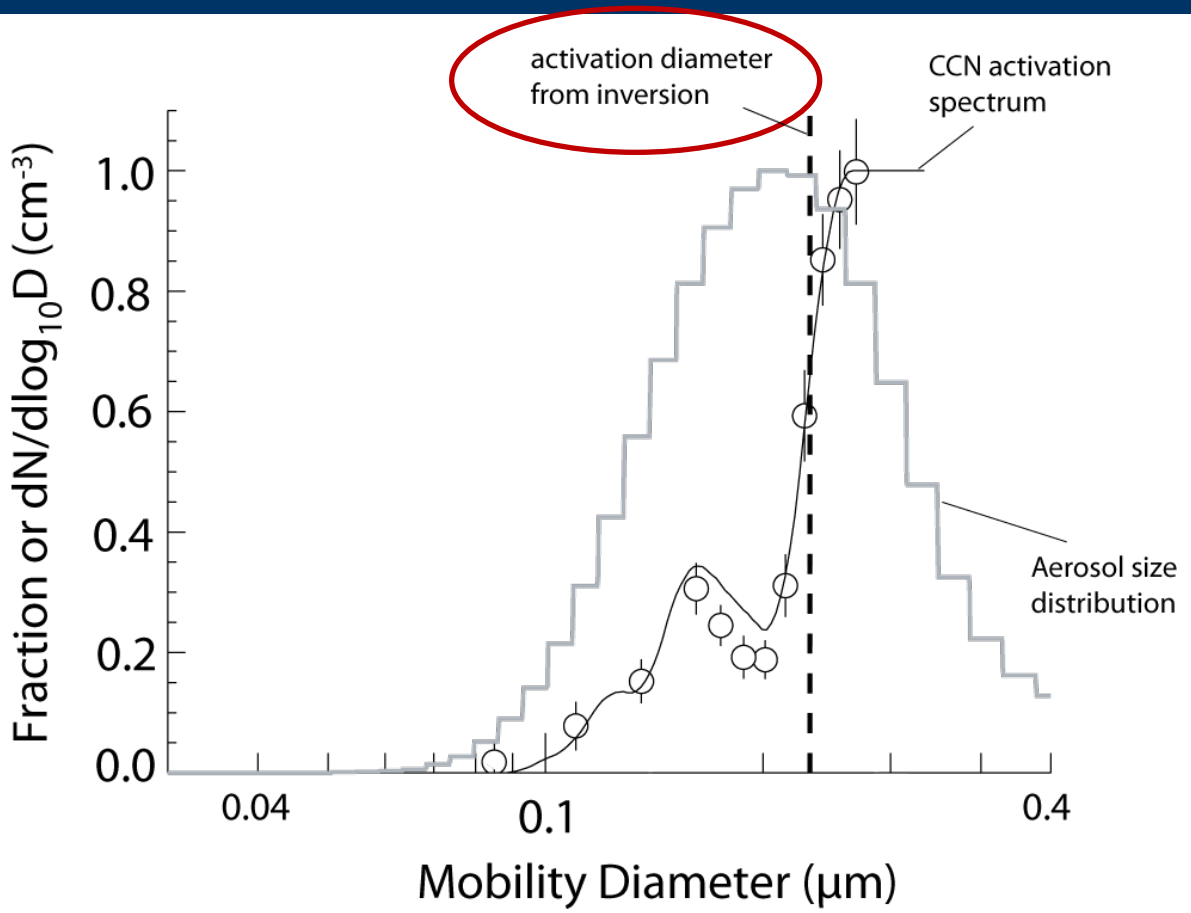
Size resolved cloud condensation nuclei



Use DMA + CPC + CCNc
to measure size distribution

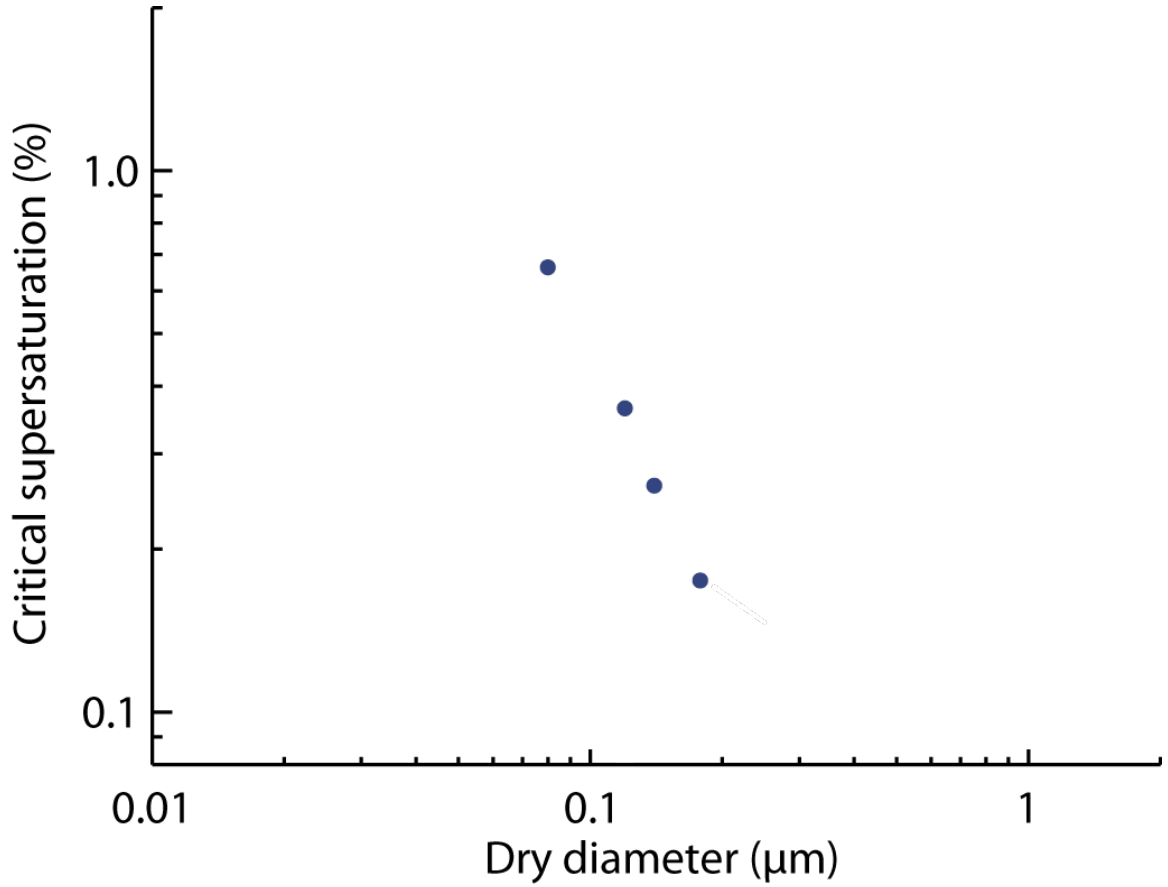
and CCN distribution at
constant supersaturation

Example activation spectrum at s = 0.53%

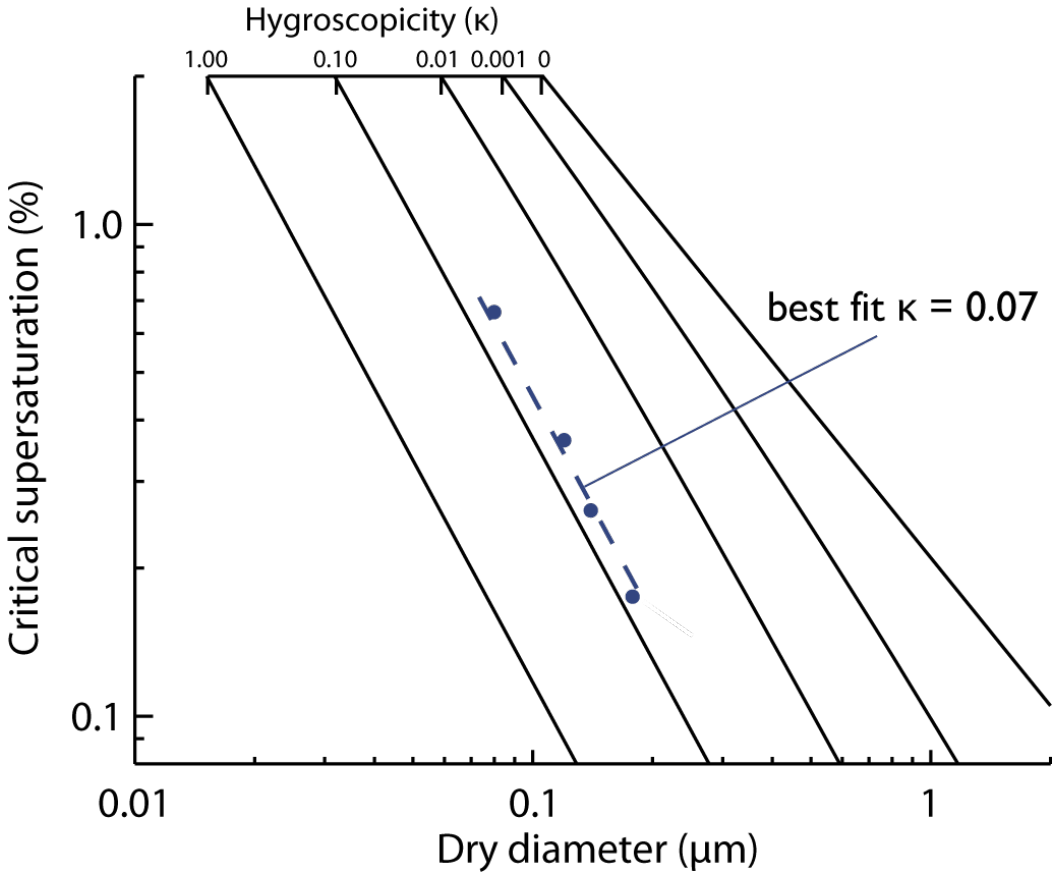


[Method described in Petters et al., 2007 AS&T and 2009 J

Data in supersaturation / activation diameter space



Data in supersaturation / activation diameter space, parameterized (κ)



Petters and Kreidenweis, ACP, 2007; 2008

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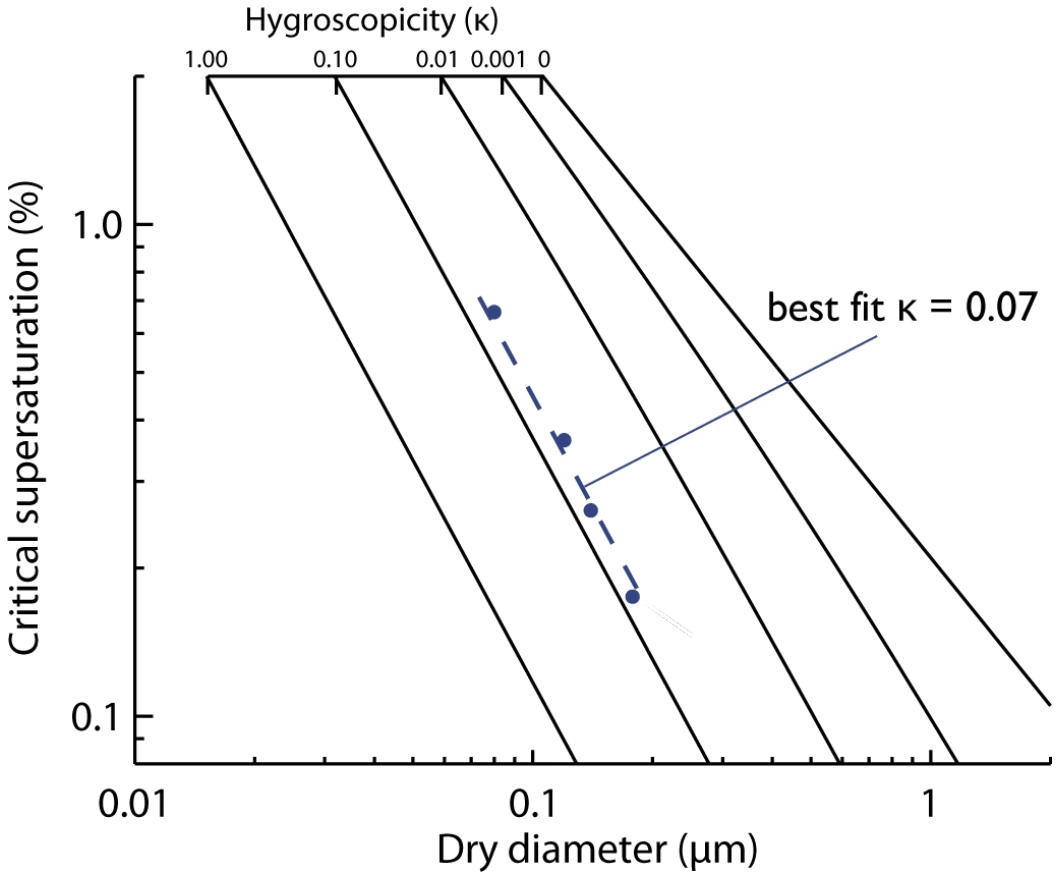


Will express all "CCN activity" findings in terms of κ

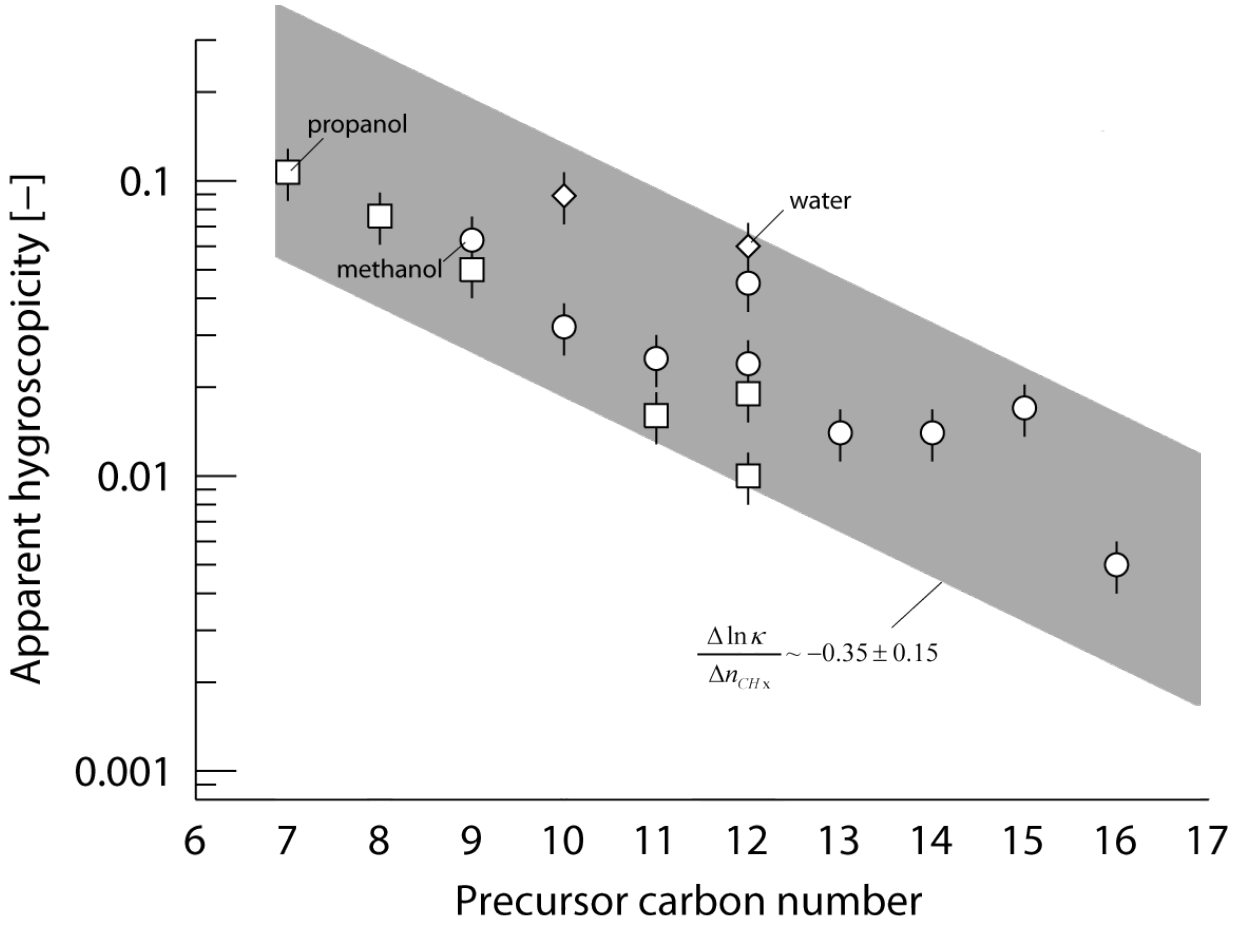
Seek

$$\frac{\partial \kappa}{\partial(\text{carbon number})}$$

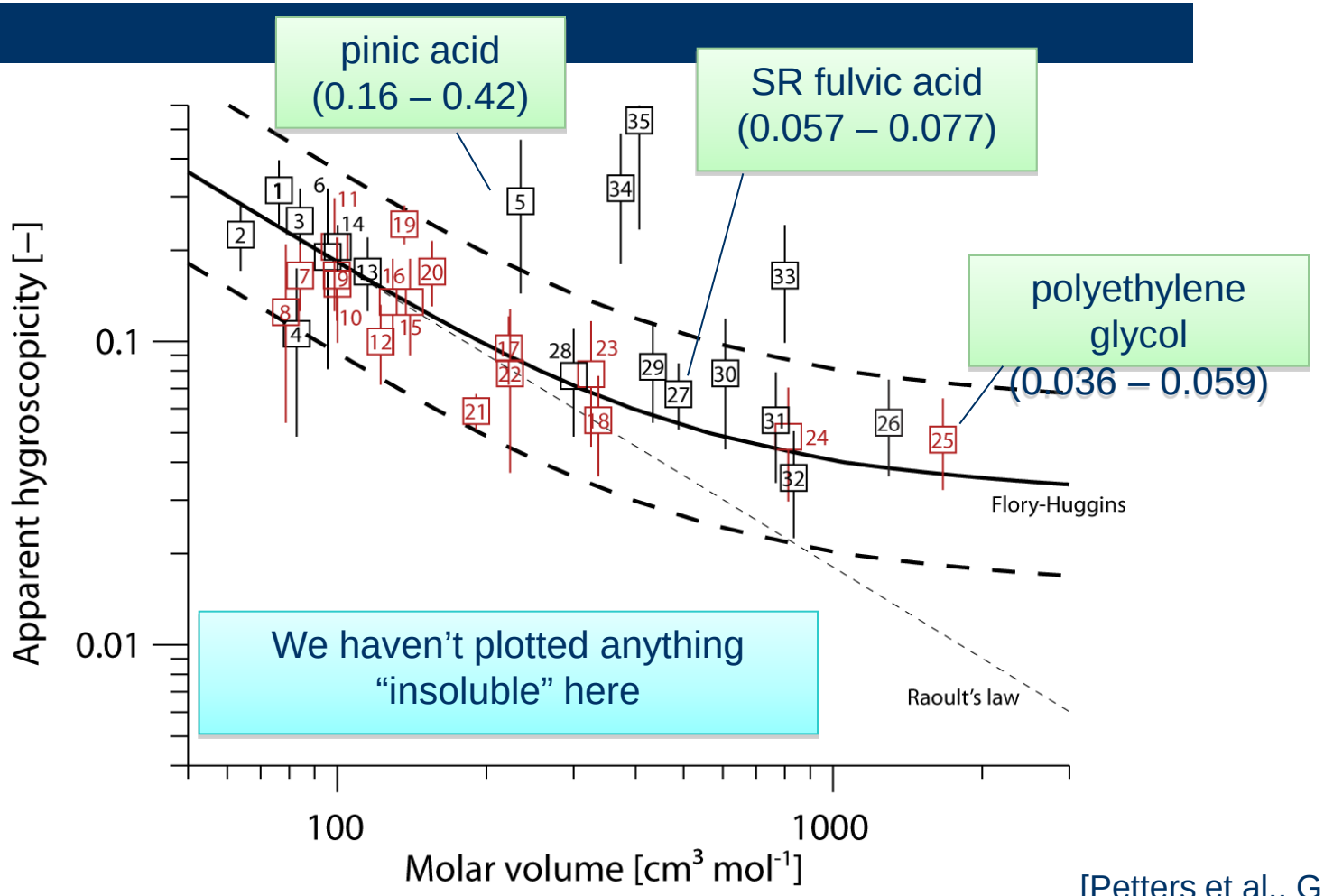
$$\frac{\partial \kappa}{\partial(\text{functional group})}$$

Begin with individual organic molecules: add functional groups to these; then create SOA from known

Example partial derivative



Expect κ to decrease with molecular weight (except for polymers)



[Petters et al., GRL, 2009]

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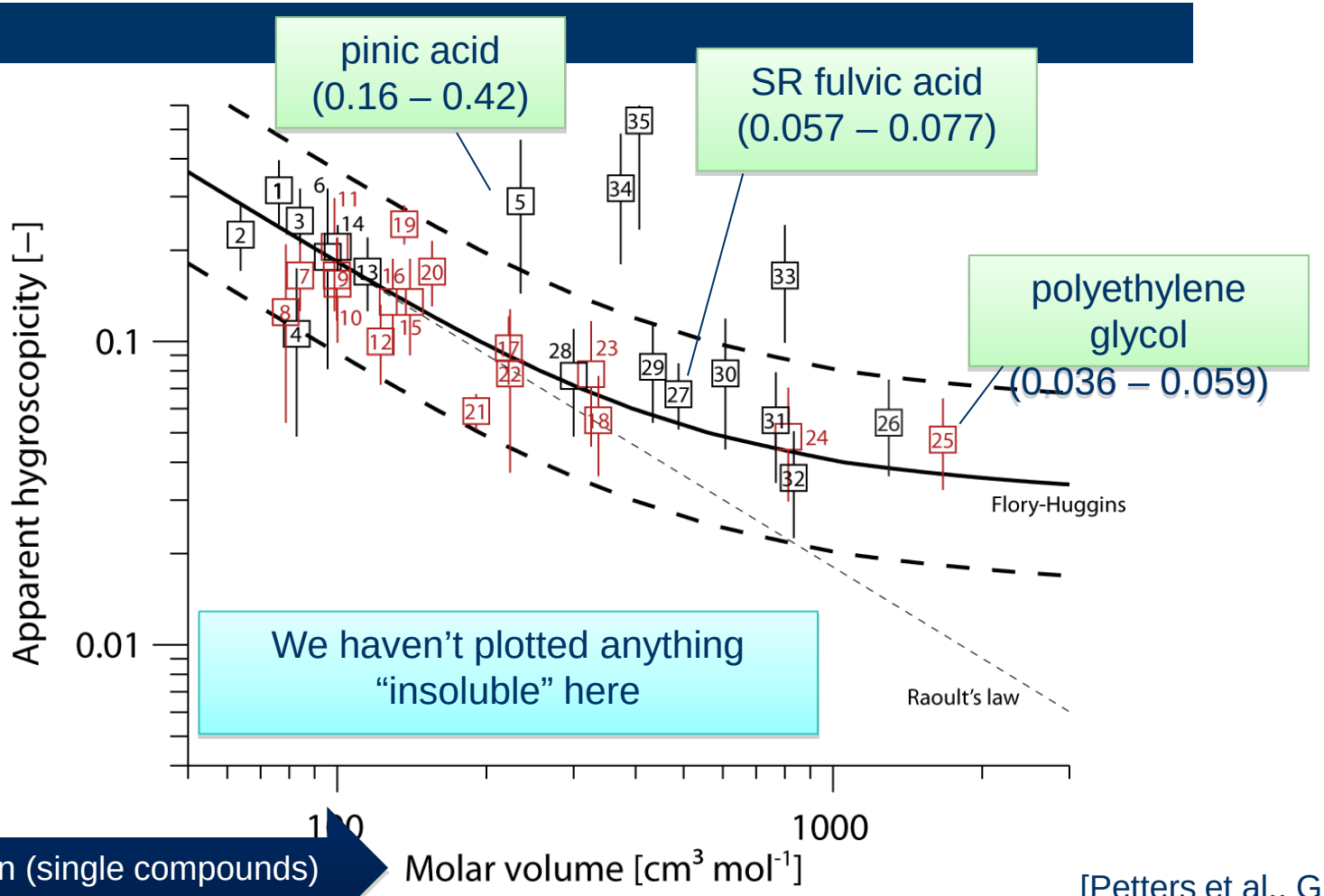
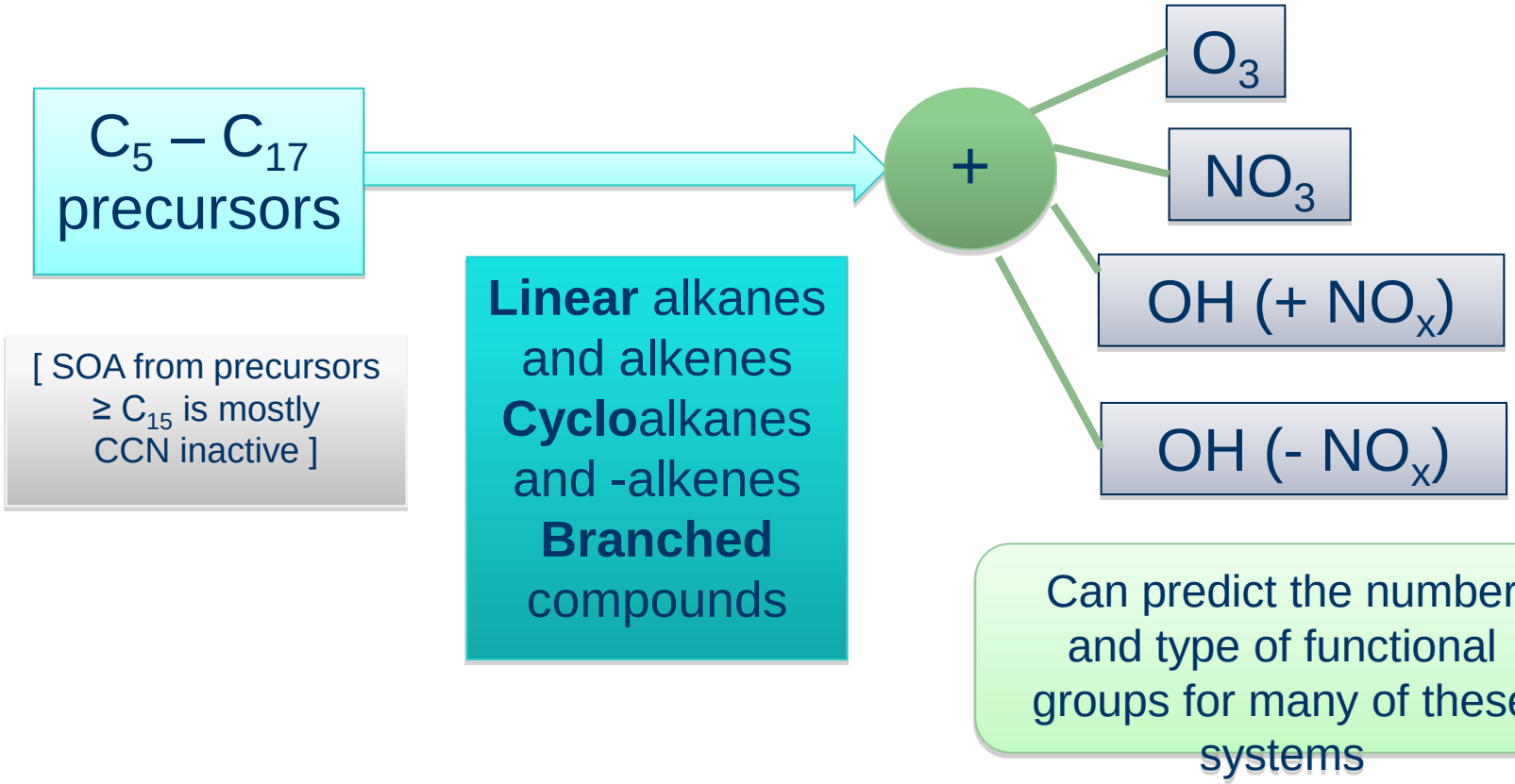


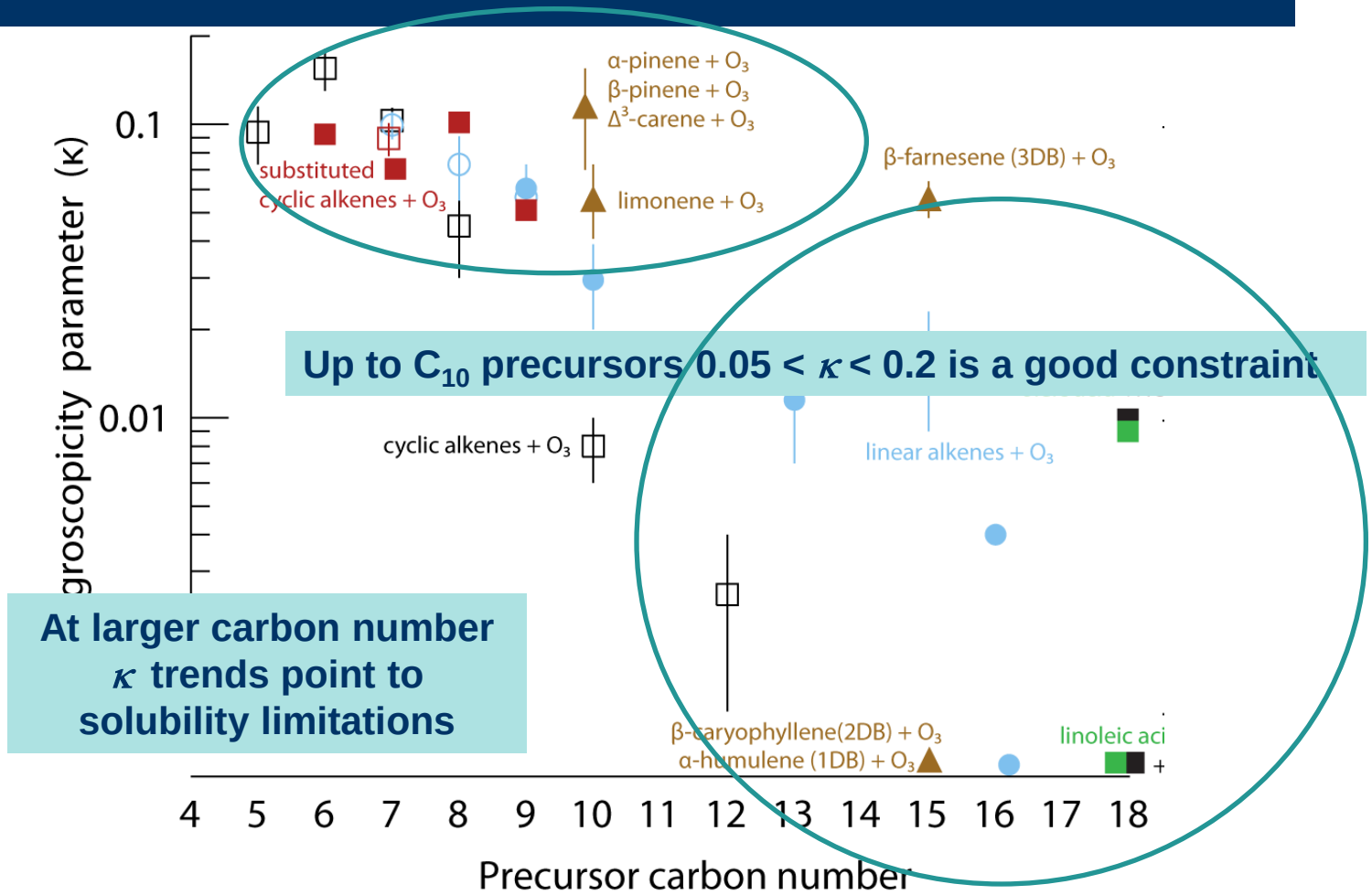
Known (single compounds)

[Petters et al., GRL, 2009]

SOA systems studied thus far



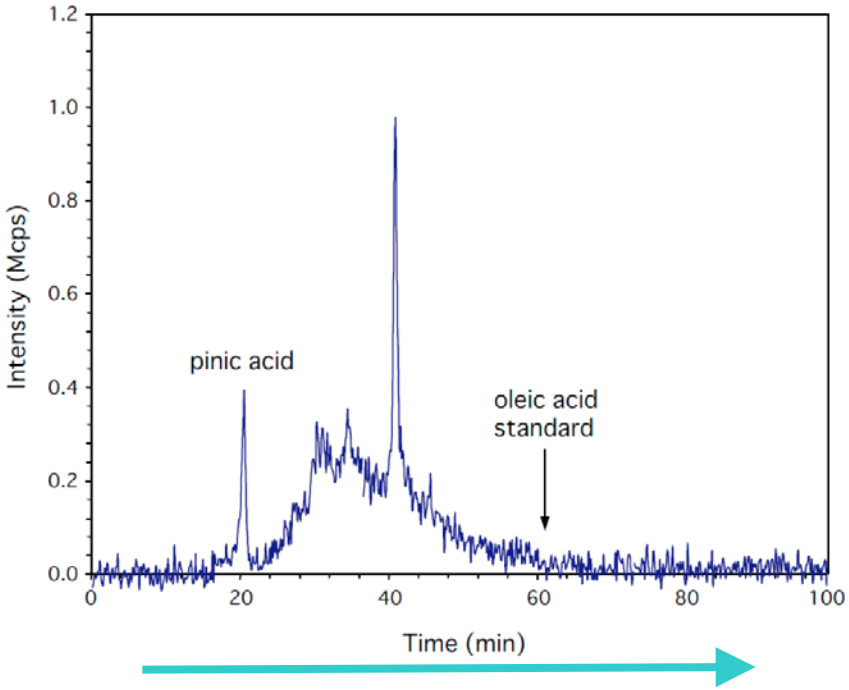
Ozone chemistry with cyclic alkenes, linear alkenes, and monoterpenes



At larger carbon number κ trends point to solubility limitations

Further clarification of structure-κ links (proof-of-concept)

total ion current, TDPBMS

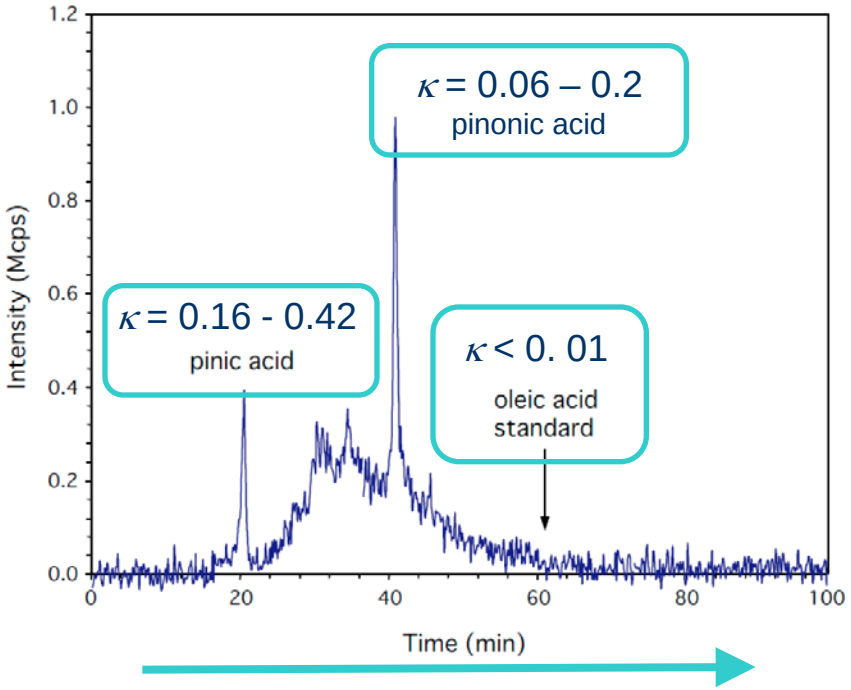


- HPLC in a reversed-phase mode
- SOA created in chamber, collected on filter
- Extracted in ethylacetate & dried; dissolved in acetonitrile
- In HPLC, separated via gradient elution method using a water/acetonitrile mixture ramped linearly from 0.95/0.05 to 0/100

decreasing polarity, water solubility, κ

Method achieved separation of κ

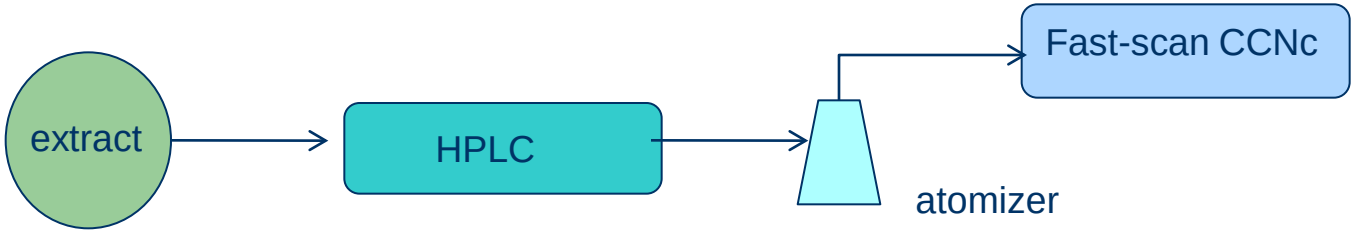
total ion current, TDPBMS

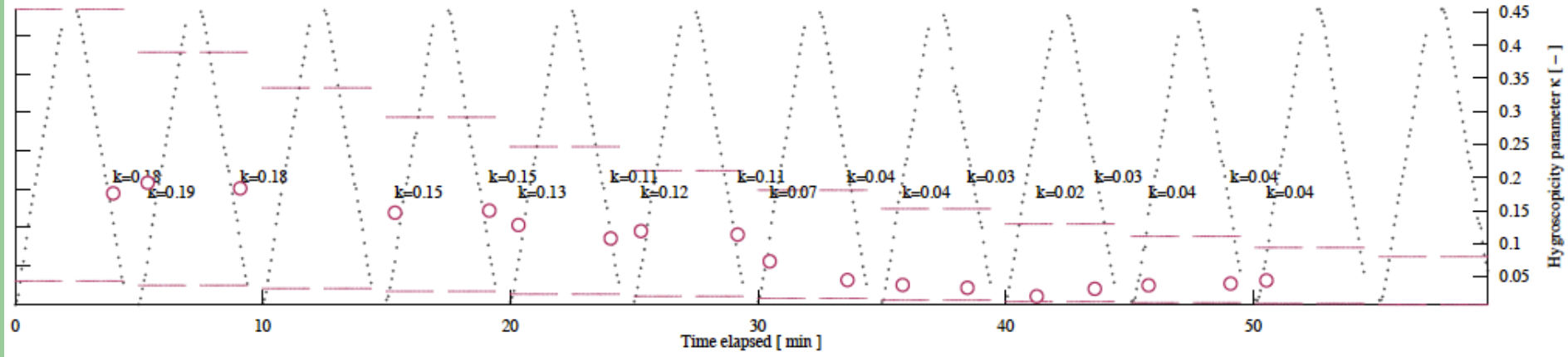


decreasing polarity, water solubility, κ

Distribution of κ in α-pinene SOA

α-pinene + O_3 dark reaction, in UCR smog chamber





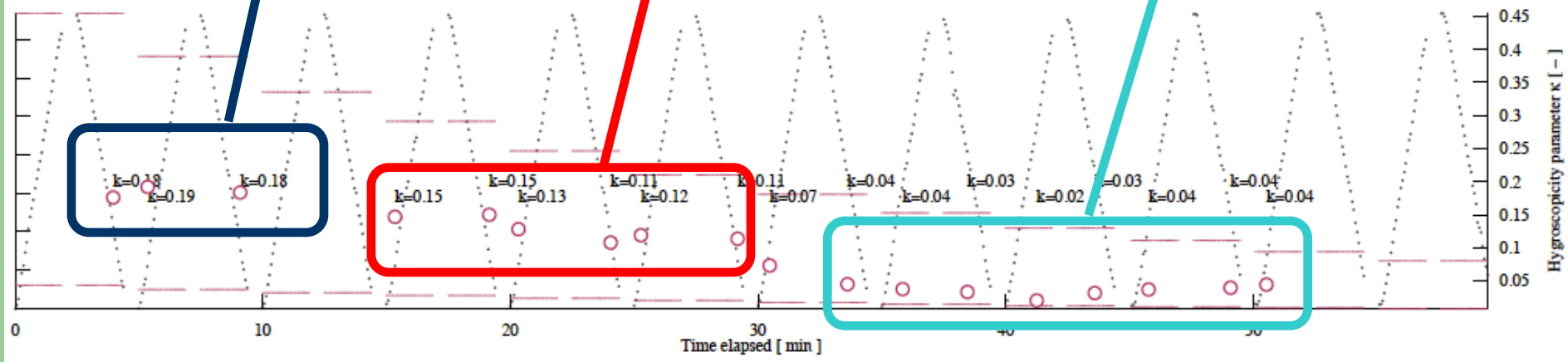
Elution time →

Distribution of κ in α-pinene SOA

κ = 0.19 – 0.18

κ = 0.11 – 0.15

κ = 0.02 – 0.04



Elution time →

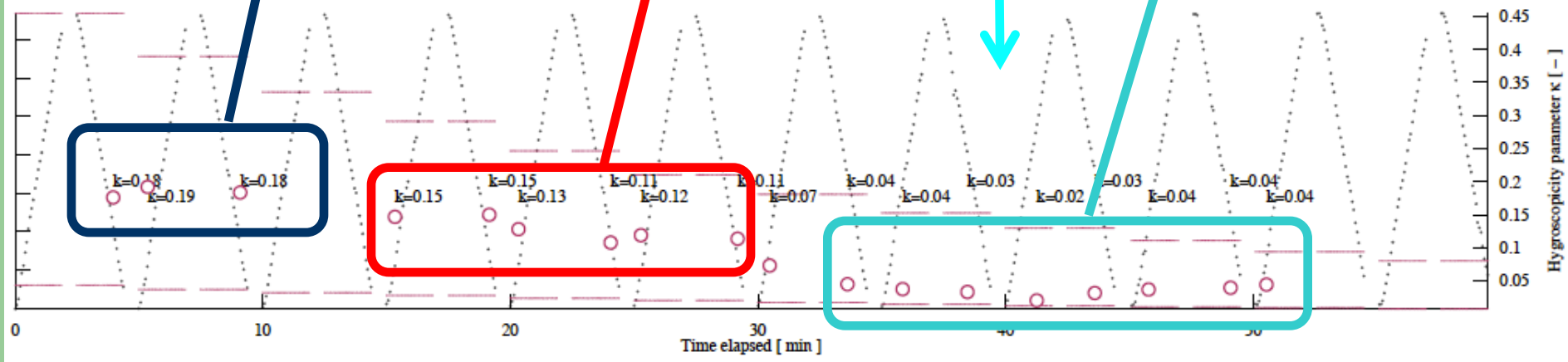
Distribution of κ in α-pinene SOA

pinonic acid κ = 0.025?
too volatile; must be part of an oligomer

κ = 0.19 – 0.18

κ = 0.11 – 0.15

κ = 0.02 – 0.04



Elution time →

Distribution of κ in α-pinene SOA

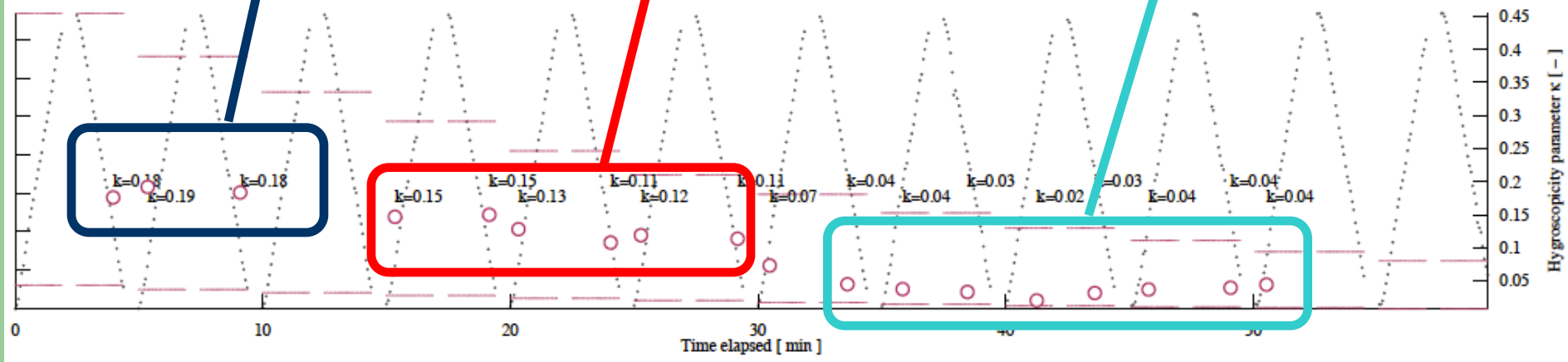
κ_{meas} = 0.12 ± 0.01

K_{avg} (HPLC) = 0.12

κ = 0.19 – 0.18

κ = 0.11 – 0.15

κ = 0.02 – 0.04



Elution time →

Summary

- Have developed new methods for
  - quantifying number and type of functional groups in a sample of organic aerosol
  - Separating aerosol samples by κ
    (concept demonstrated; method in development)
  - Linking κ to molecular structure (C number, functional groups)
- Findings thus far:
  - κ decreases with precursor carbon number within a "series" of similar molecules
  - $\kappa \sim 0.1$ is a good model for SOA from 'small' precursors ($< C_8$-C_{10}).
  - SOA from most precursors $\geq C_{15}$ effectively CCN inactive
- Developing a framework for predicting κ that can be coupled to chemical mechanism models