Modeling the Explicit Chemistry of Anthropogenic and Biogenic Organic Aerosols

Objective: Explain and predict SOA characteristics from known chemistry.

Climate Relevant SOA Property(s) Investigated: Mass, composition, optics, lifetimes

Lead personnel: Sasha Madronich & Julia Lee-Taylor (NCAR)

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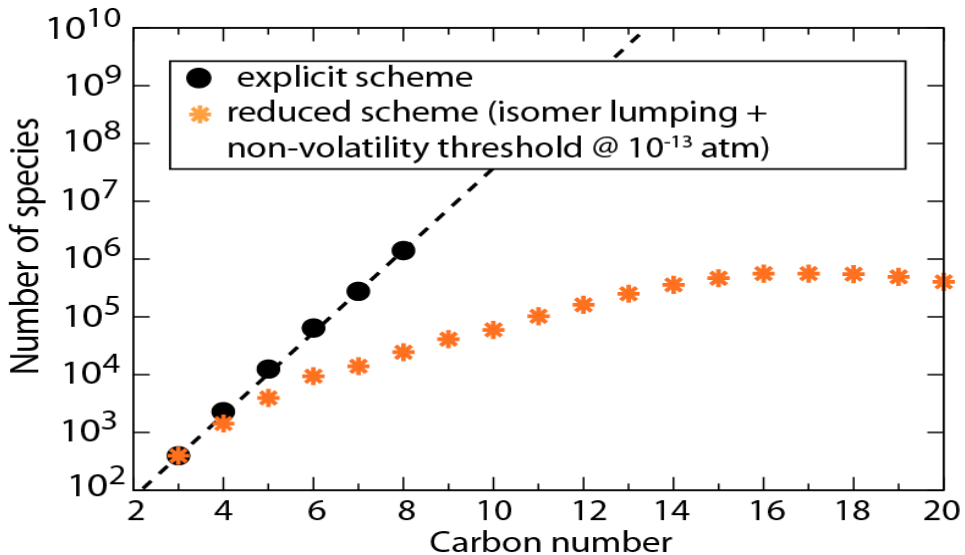
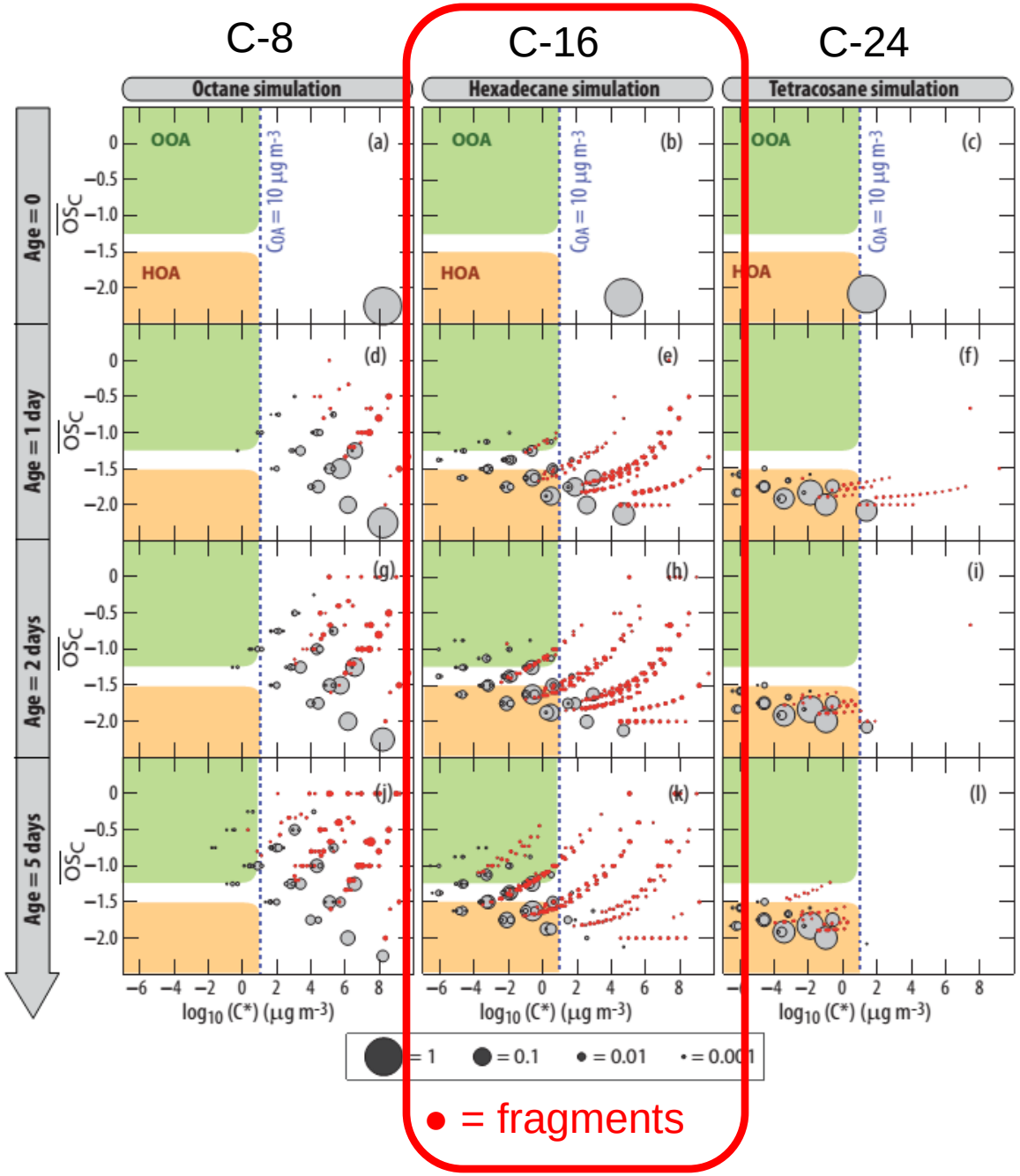
Generator of Explicit Chemical Kinetics of Organics in the Atmosphere (GECKO-A)



GECKO-A

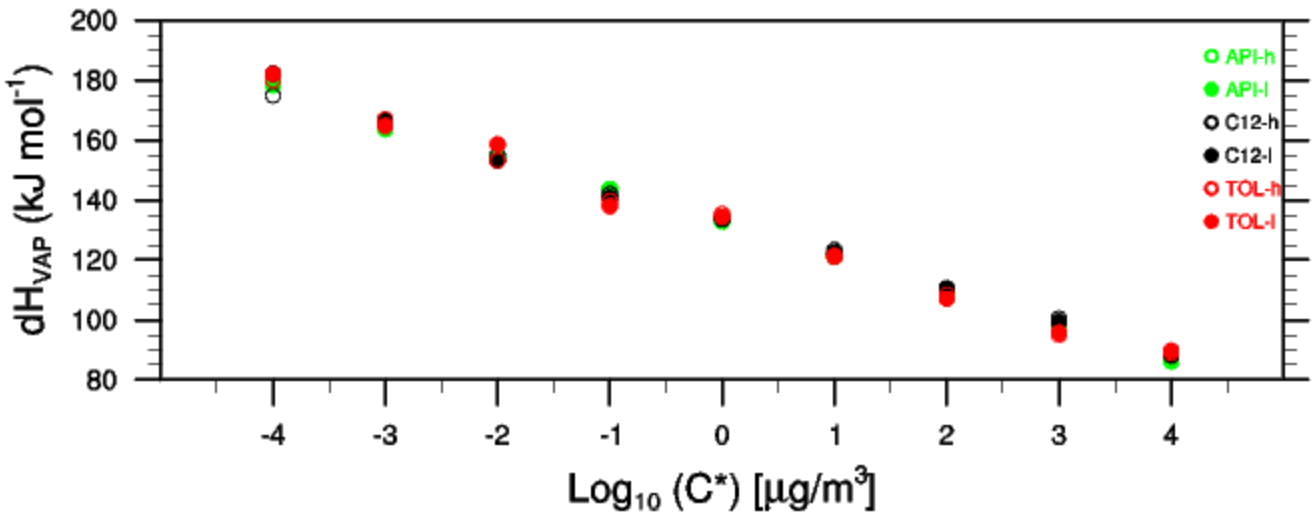
Evolution of n-alkanes

(at high NOx)

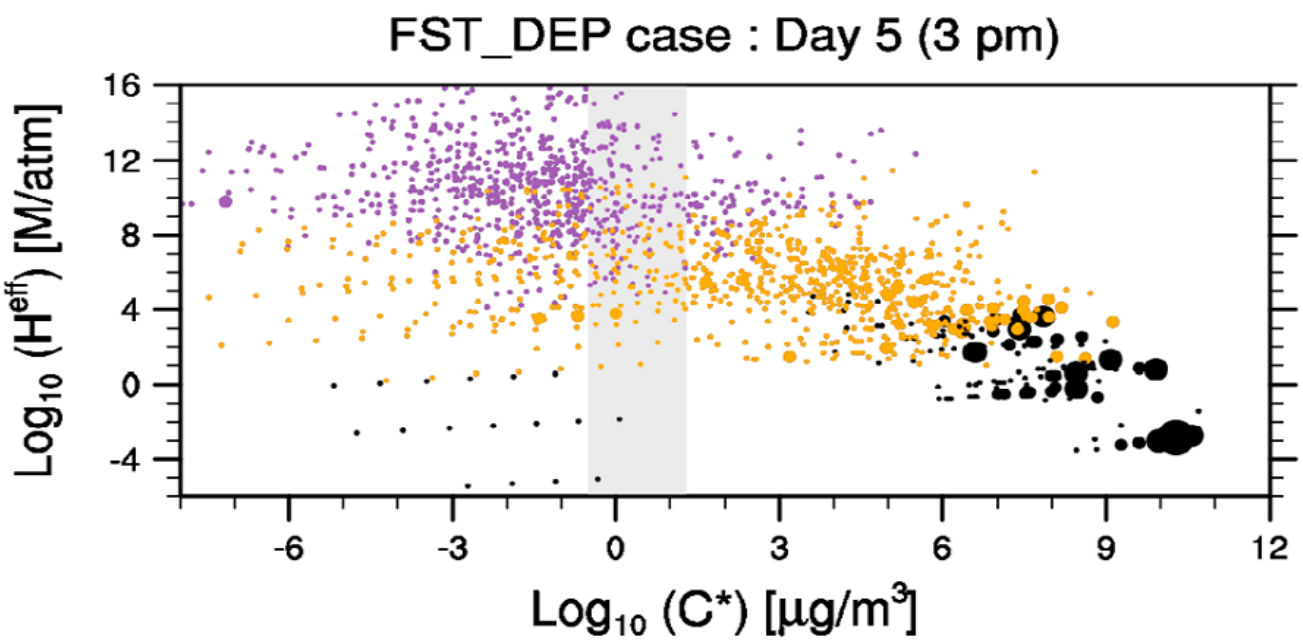


GECKO-A Estimation of Thermodynamic Properties

Enthalpies of vaporization

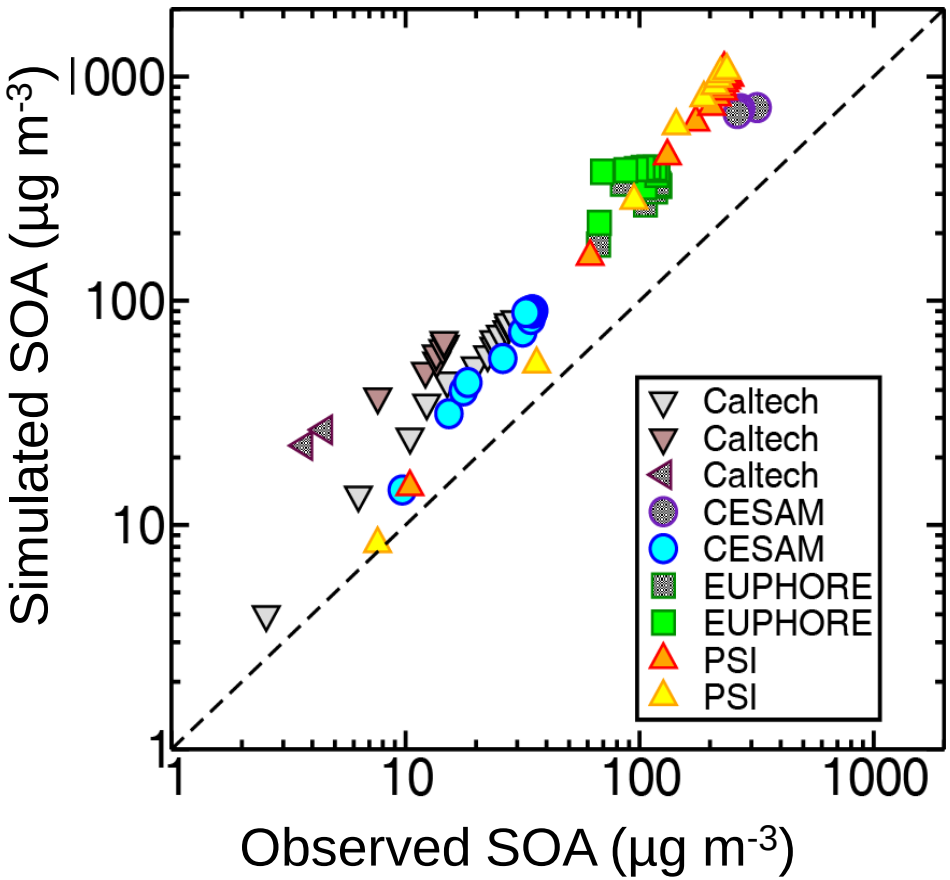


Henry's Law solubility coefficients

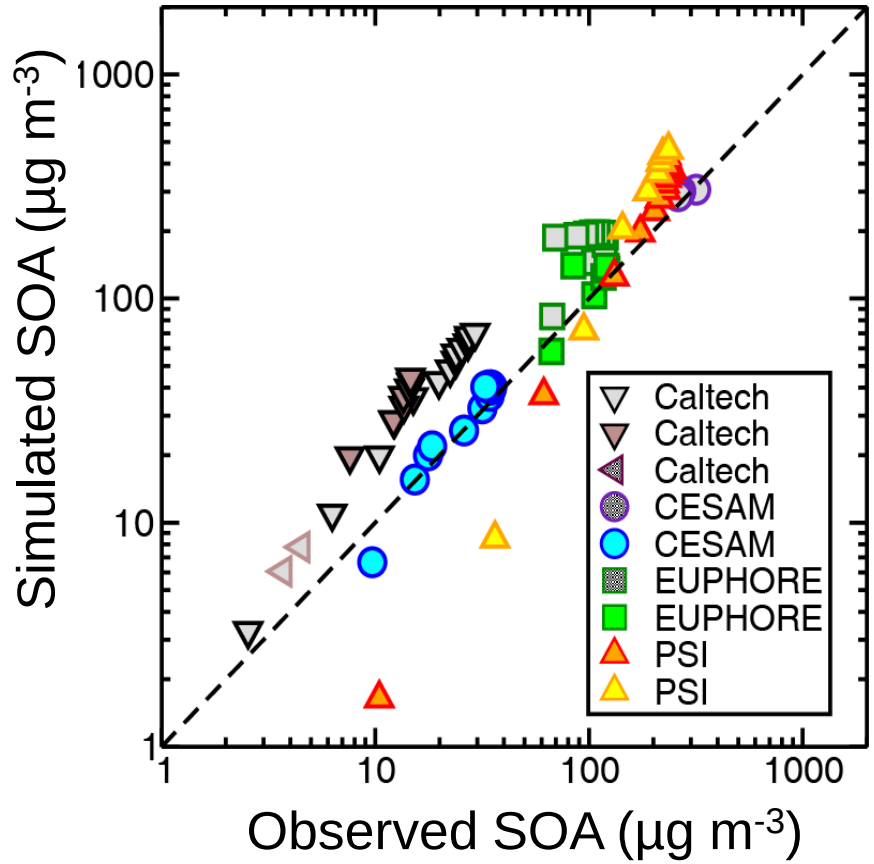


GECKO-A vs chamber observation – α-pinene oxidation

Vapor pressure estimation method: Myrdal & Yalkowsky (1997)



Vapor pressure estimation method: Nannoolal et al. (2008)

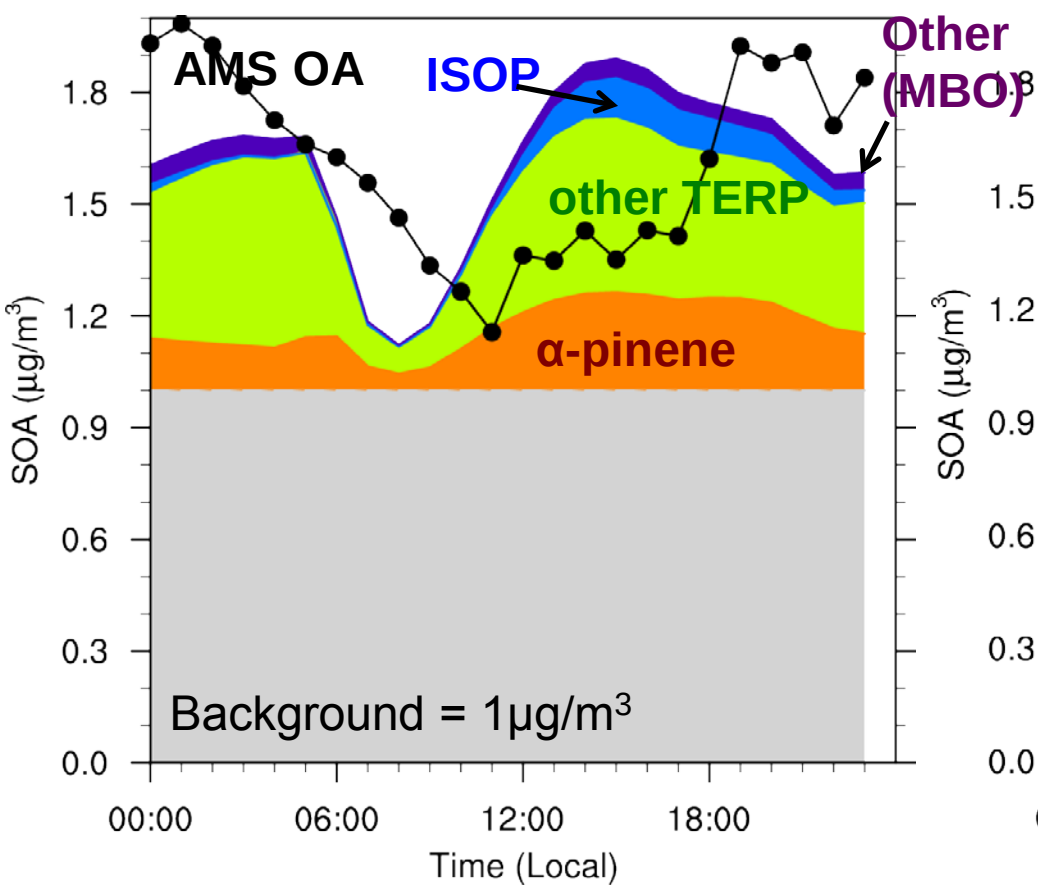


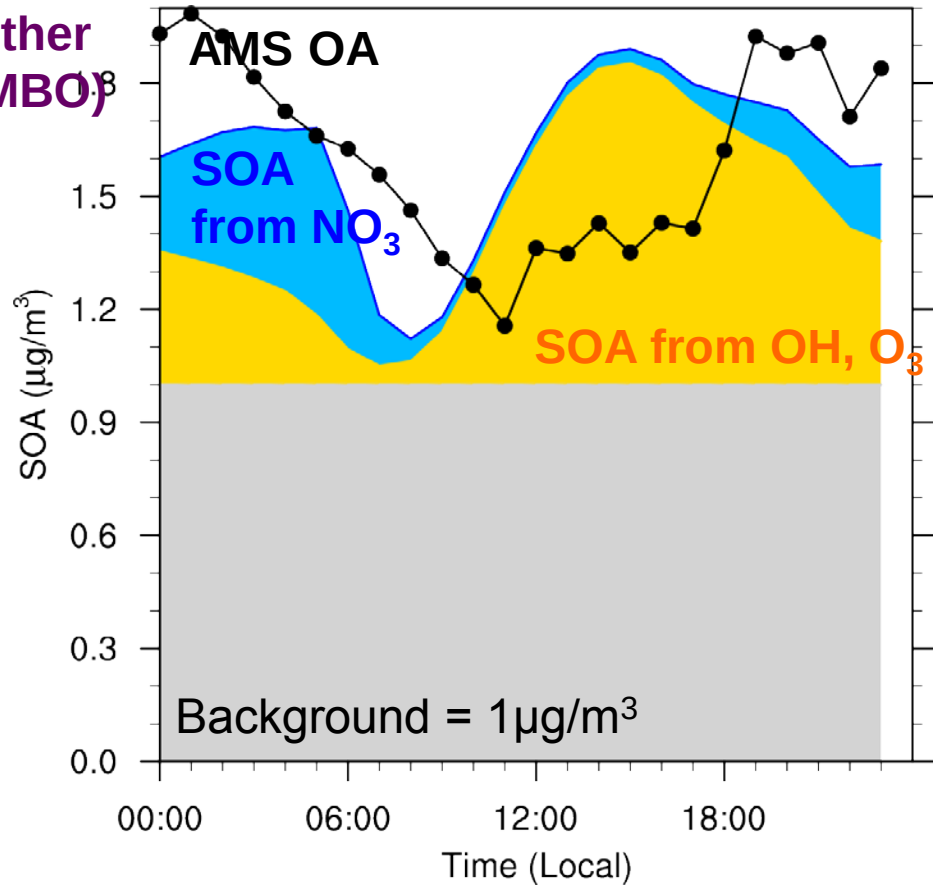
Valorso, PhD thesis, 2011

GECKO-A: SOA concentrations at Manitou Forest

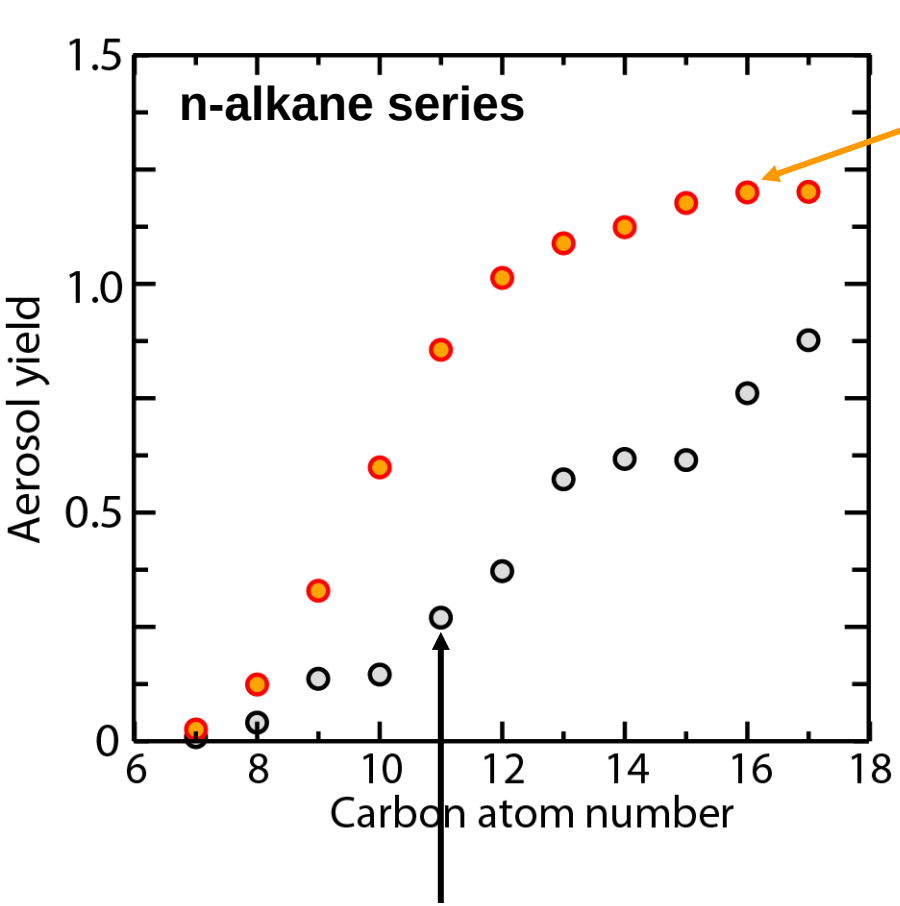
Eulerian simulation (emissions are continuously added to the box model)

- Precursor contribution to SOA formation
- SOA from OH, O_3 vs. NO_3 oxidation





Evaluation of GECKO-A using chamber data – alkane series



SIMULATION WITHOUT WALL LOSS

Experimental SOA Yields

[Source : Lim and Ziemann, EST, 2009]

Experimental conditions :

[alkane] ≈ 1ppm; [CH_3ONO] ≈ 10 ppm
[NO] ≈ 10 ppm ; RH = 0.5 %

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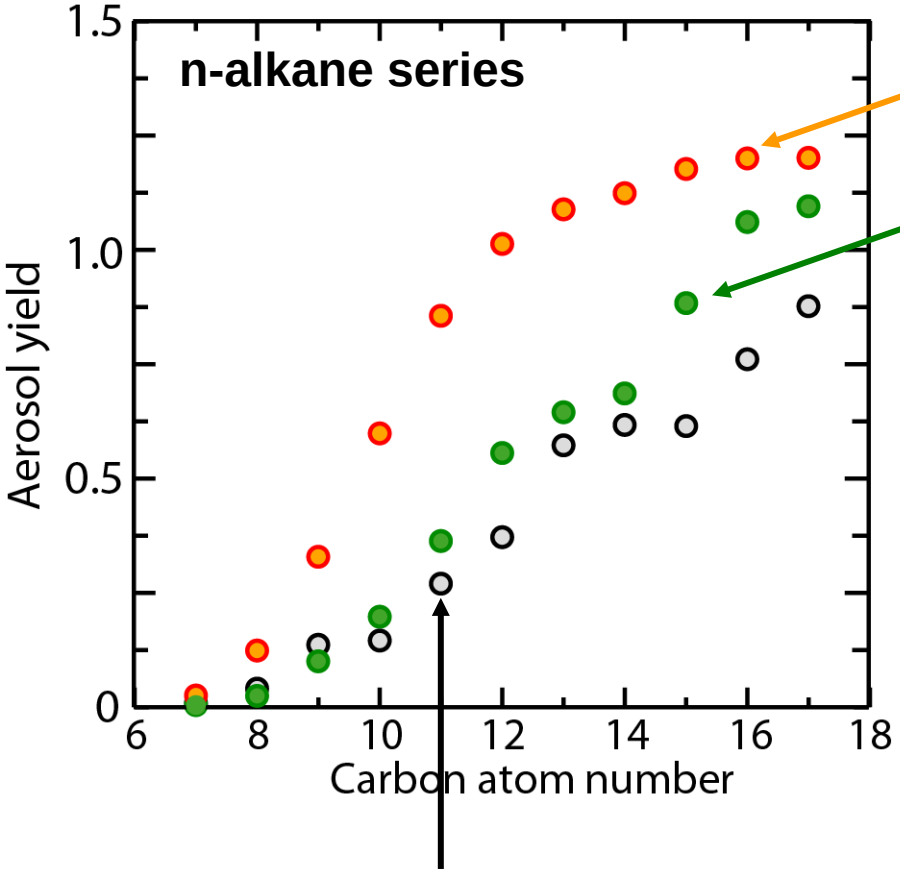

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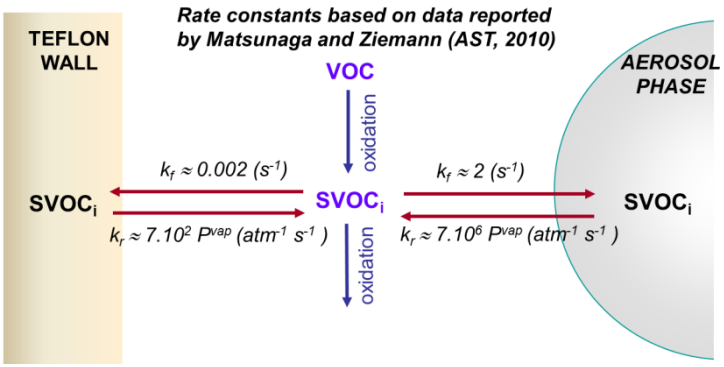
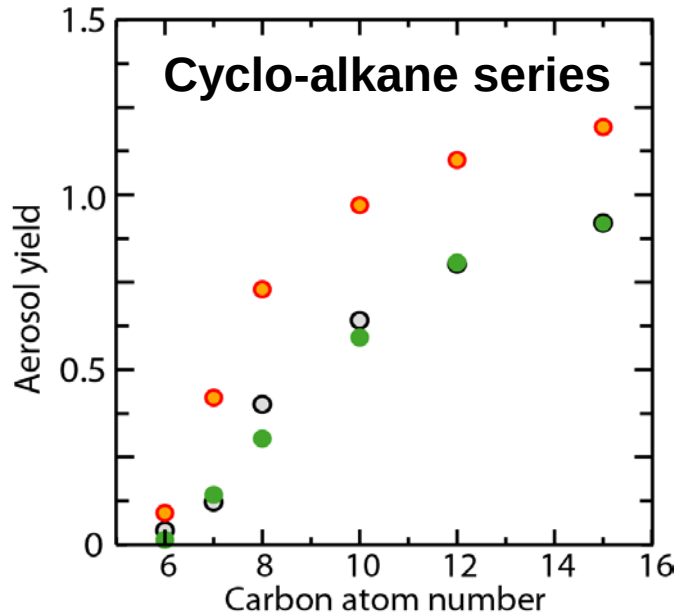
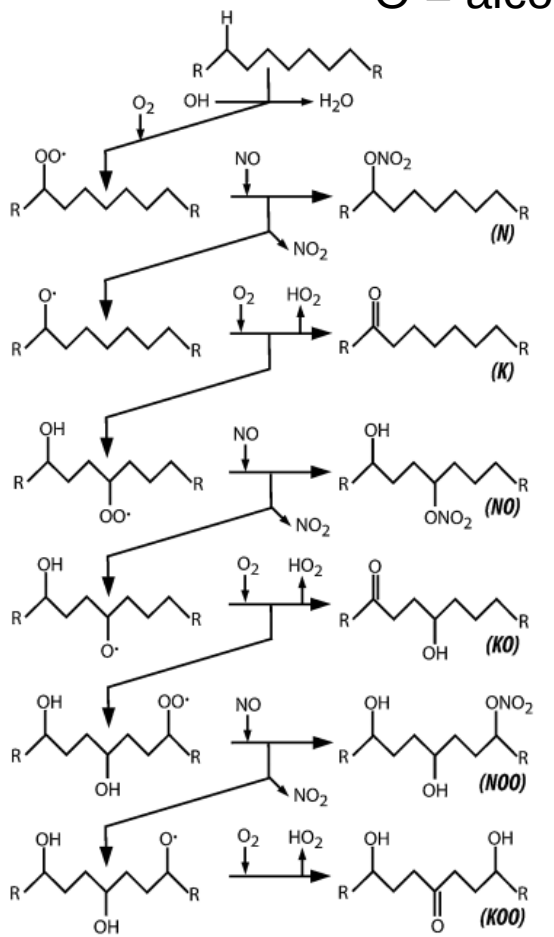


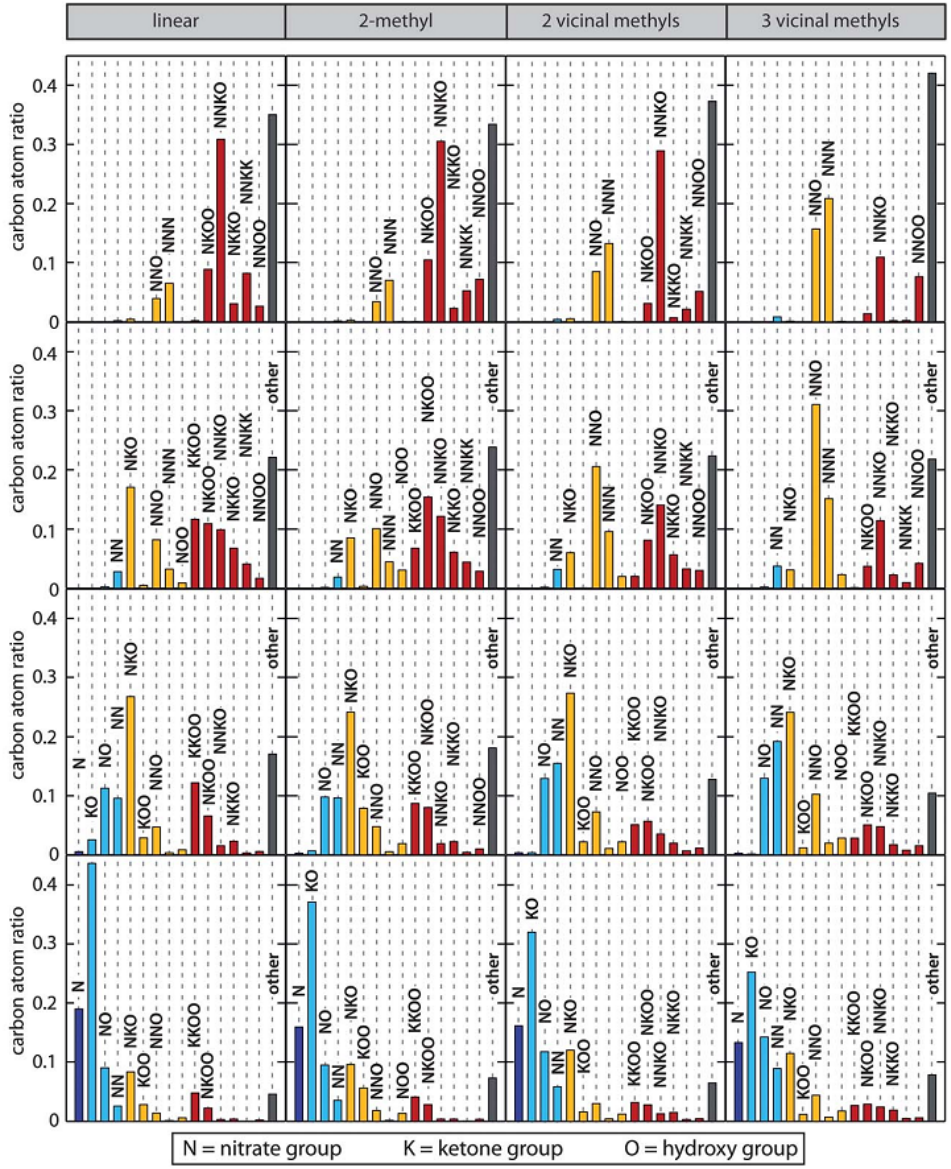


SOA Composition

Functionalization pathways

K = ketone
N = nitrate
O = alcohol





C-10

C-14

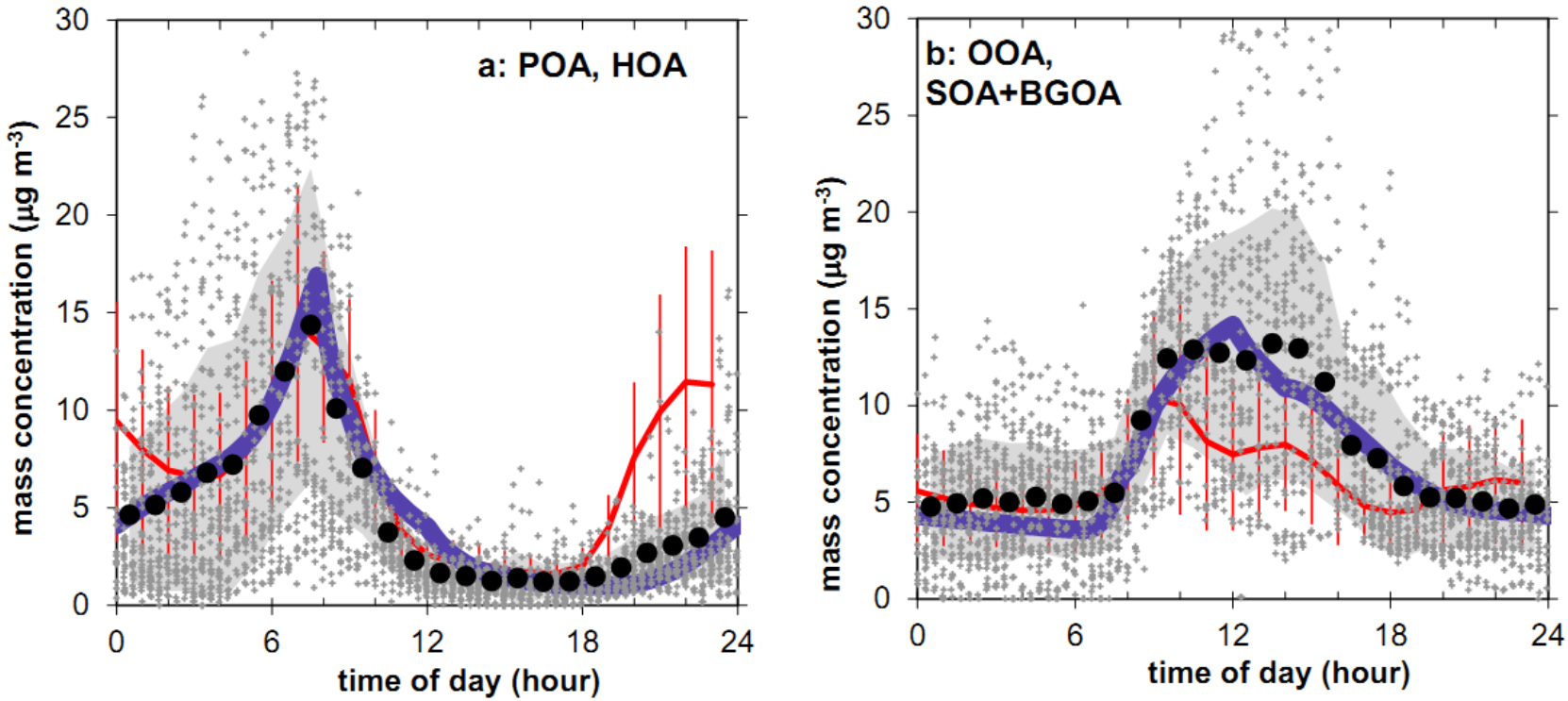
C-18

C-22

KO = 0.58 (0.55), N = 0.28 (0.30) NO = 0.10 (0.15) GECKO-A (Ziemann)

Model-Measurement Comparisons

Mexico City, March 2006

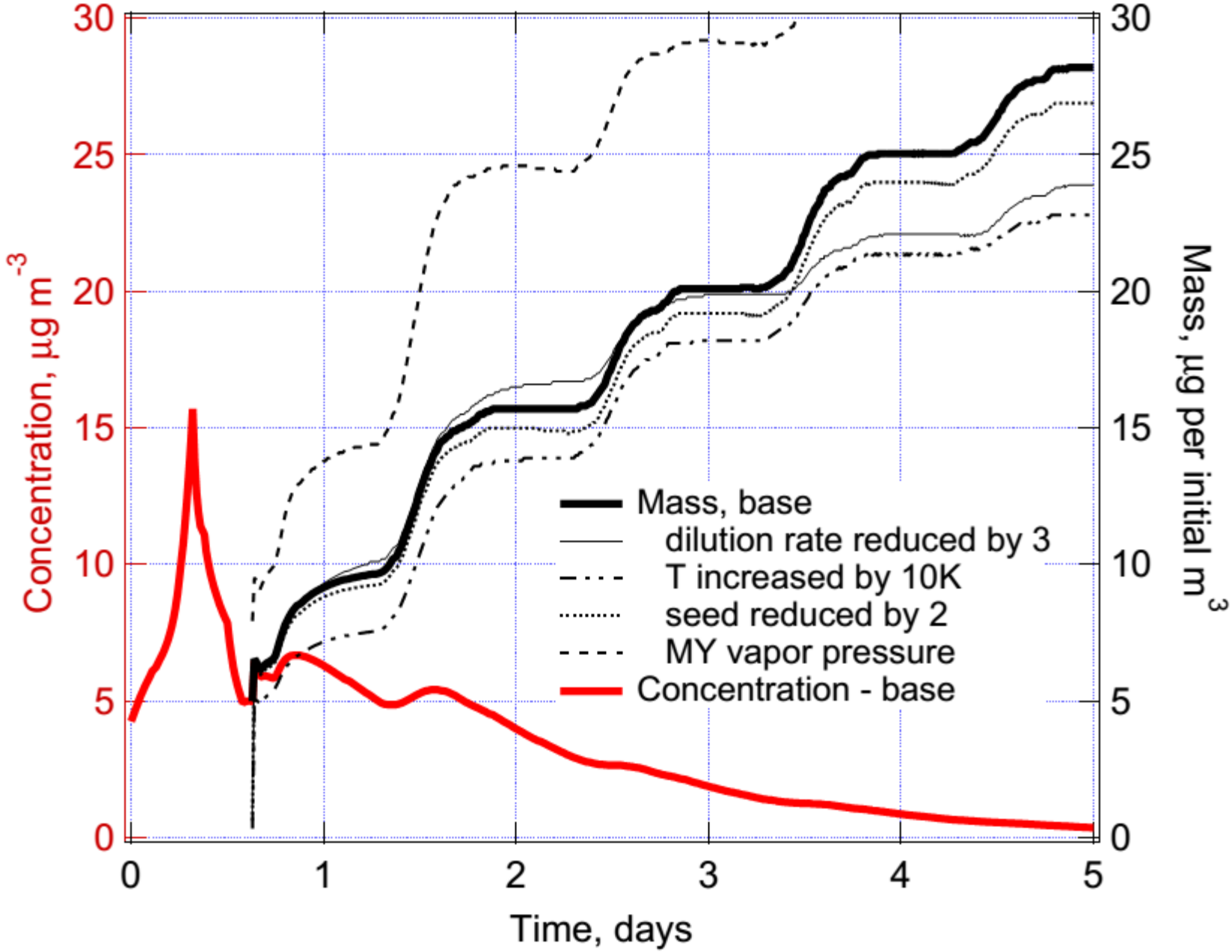


Measurements

GECKO-A box model, explicit chemistry

3-dimensional regional model, VBS aerosol chemistry

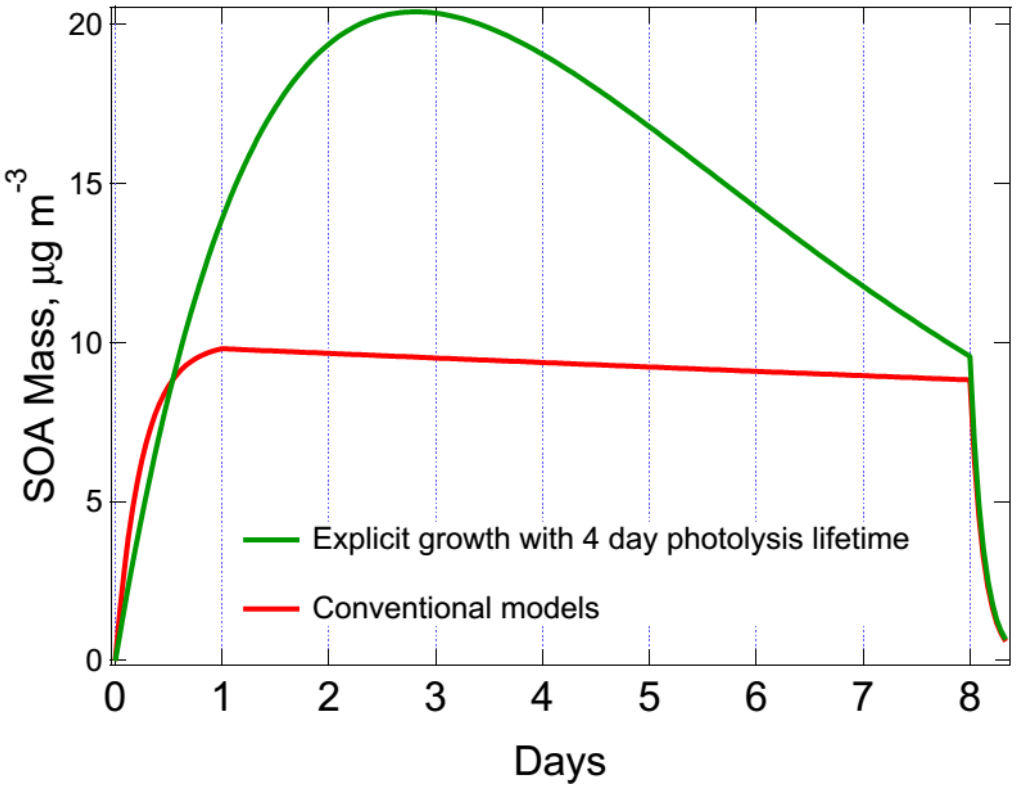
Lee-Taylor et al., ACP 2011


Concentration, µg m-3
Mass, µg per initial m3
Time, days
Mass, base
dilution rate reduced by 3
T increased by 10K
seed reduced by 2
MY vapor pressure
Concentration - base
0
5
10
15
20
25
30
0
1
2
3
4
5

A new picture for organic aerosol evolution?

New:

- Rapid initial growth
- Ongoing regional growth
- Loss by hν, O_3, OH
- Only a fraction of carbon is rained out



Conventional:

- Rapid initial growth
- No regional growth
- Majority of carbon removed by wet deposition

Summary

Evaluations with smog chamber data

- good/very good agreement (after model refinement)
- significant wall losses
- ...more studies needed

Evaluations with field data

- fair/good agreement
- complex mixtures of precursors & seeds
- ...more studies needed

Composition

- organic nitrates too high? organic acids too low?
- probably in-particle chemistry

Regional growth

- strong and long-lasting
- need faster removal to balance budget?
- fairly fundamental revision, if true.

Parameterizations (fitting to GECKO-A results)

- underway: VBS, SOM
- Test new growth & removal in WRF-Chem

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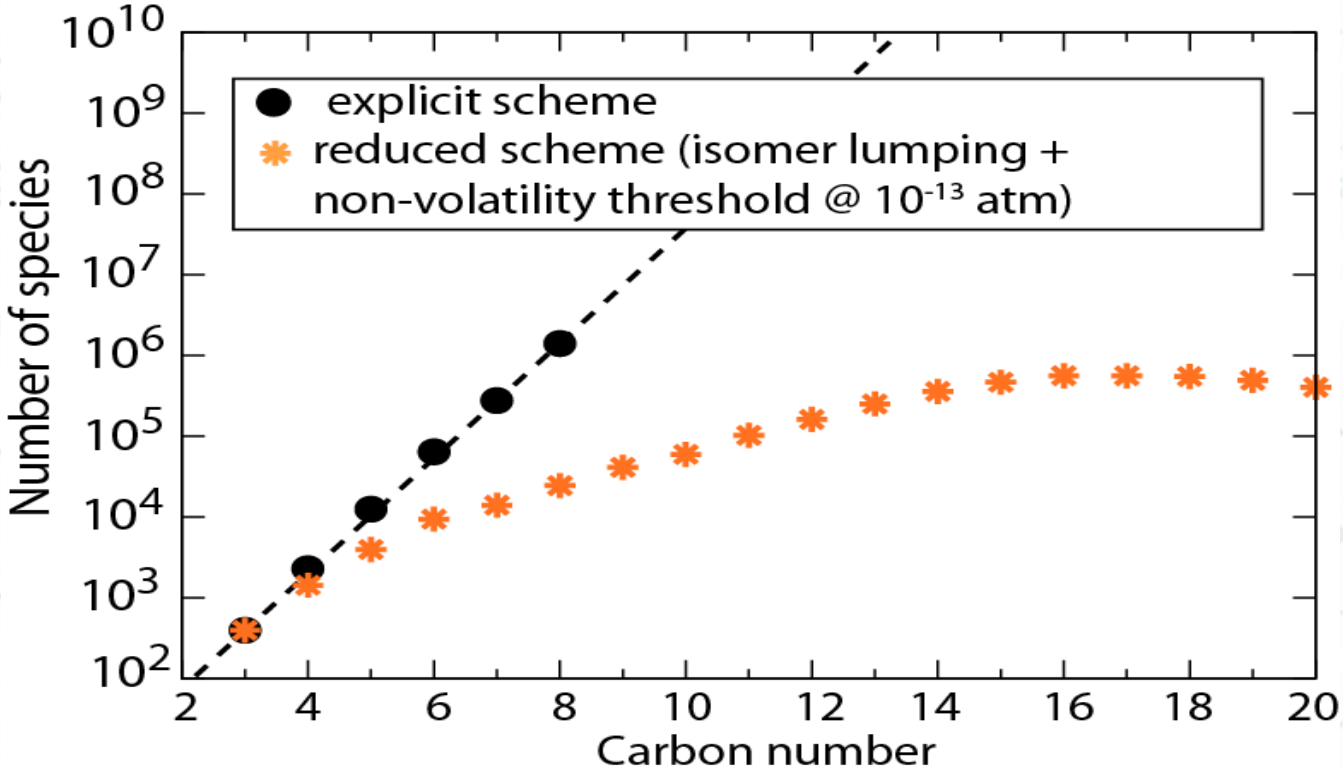
DOE/ASR
growing list of collaborators...



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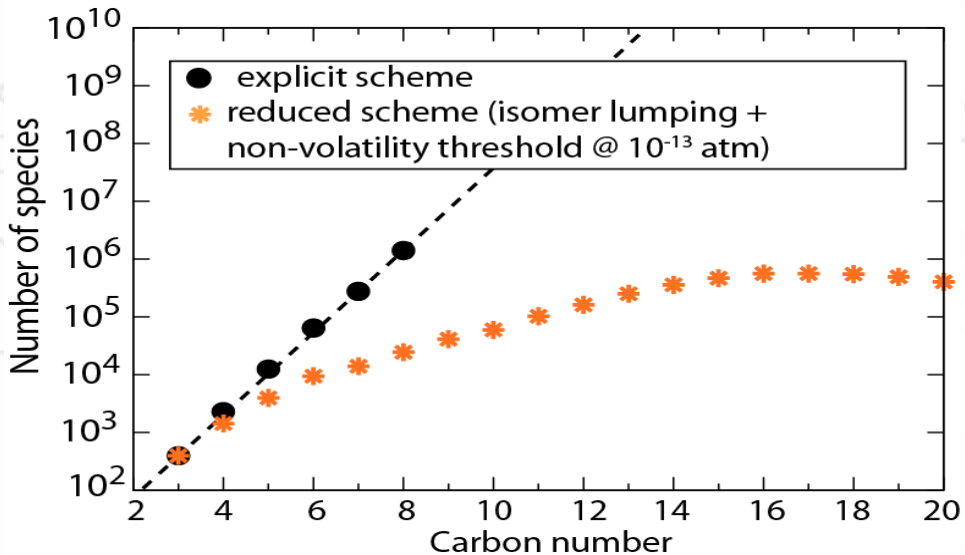

GECKO-A

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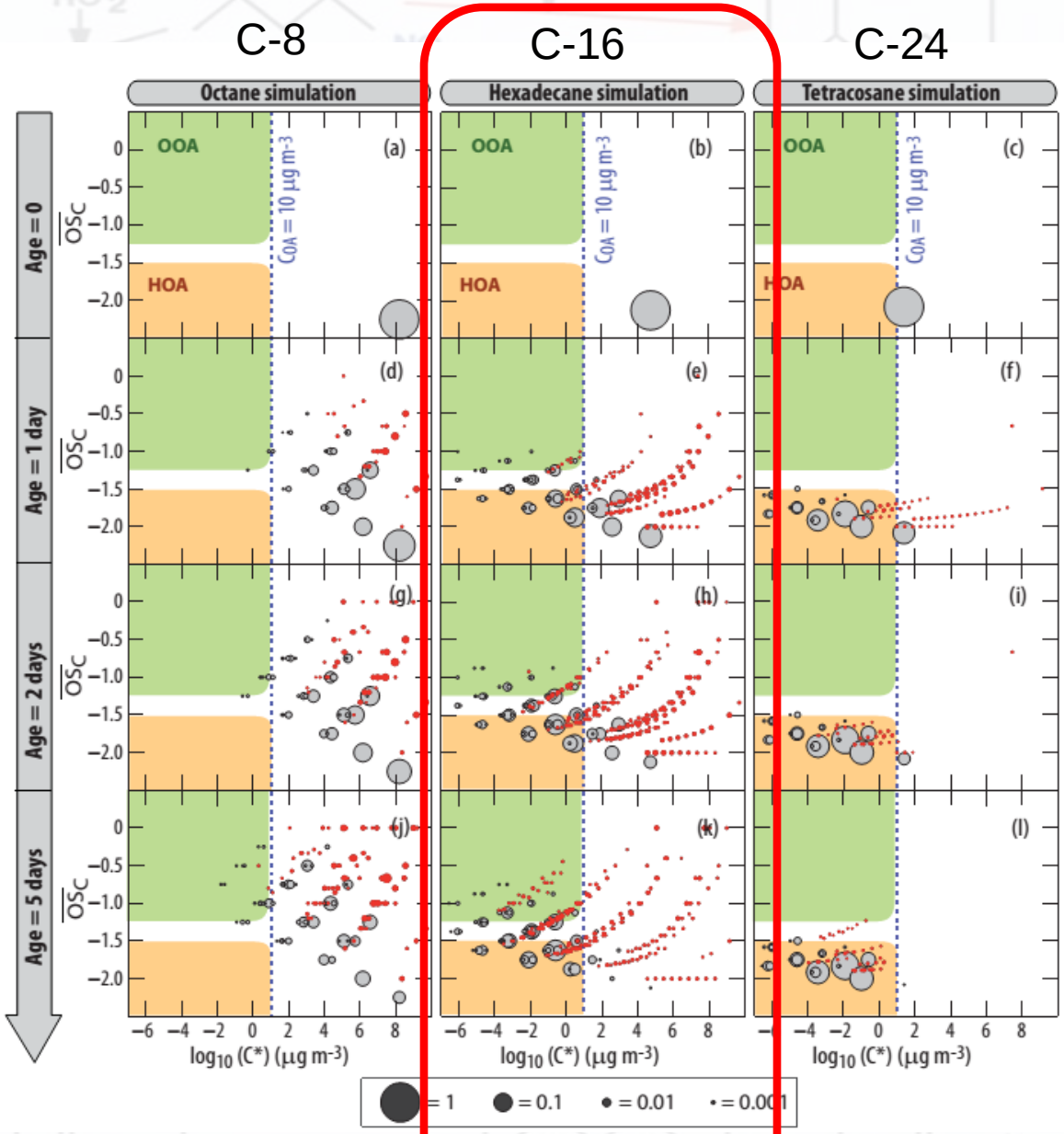
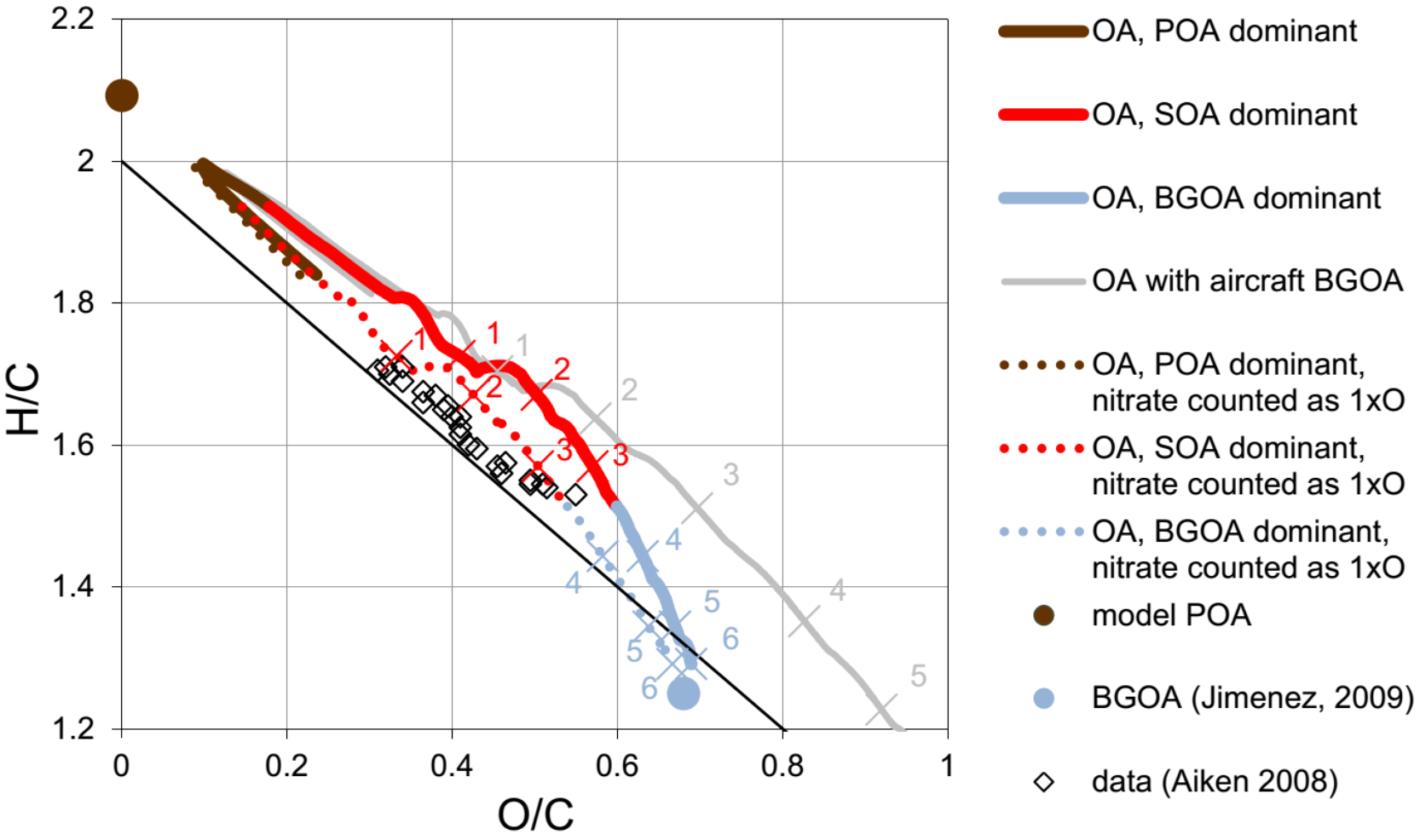
(at high NOx)




2.2
2
1.8
1.6
1.4
1.2
H/C
0
0.2
0.4
0.6
0.8
1
O/C
1
2
3
4
5
6
OA, POA dominant
OA, SOA dominant
OA, BGOA dominant
OA with aircraft BGOA
OA, POA dominant, nitrate counted as 1xO
OA, SOA dominant, nitrate counted as 1xO
OA, BGOA dominant, nitrate counted as 1xO
model POA
BGOA (Jimenez, 2009)
data (Aiken 2008)

Atmos. Chem. Phys., 11, 6895–6910, 2011

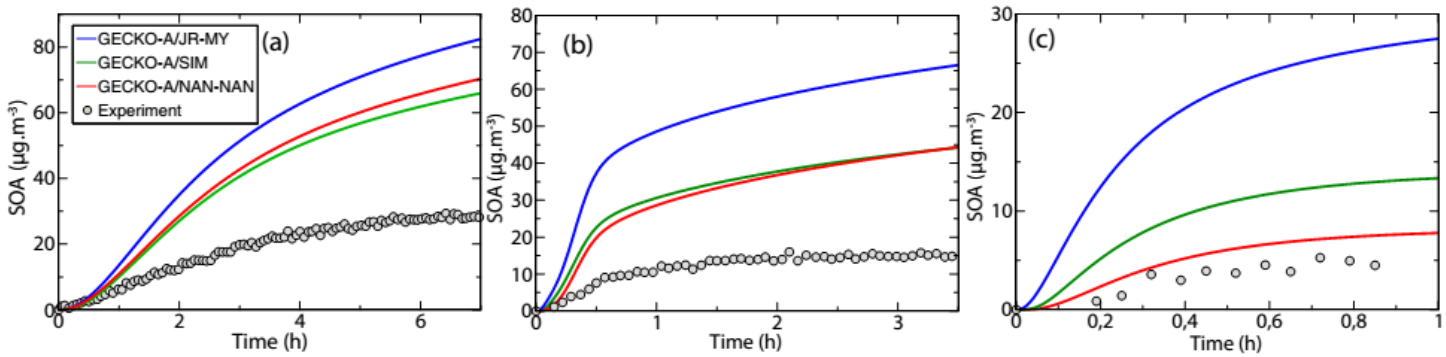


Fig. 5. Time evolution of SOA during α-pinene photo oxidation for **(a)** the low-, **(b)** intermediate- and **(c)** high-NO_x experiments. Dots and lines represent, respectively, measurements and values modelled using the various P^{vap} methods.

Caltech smog chamber, Ng et al.

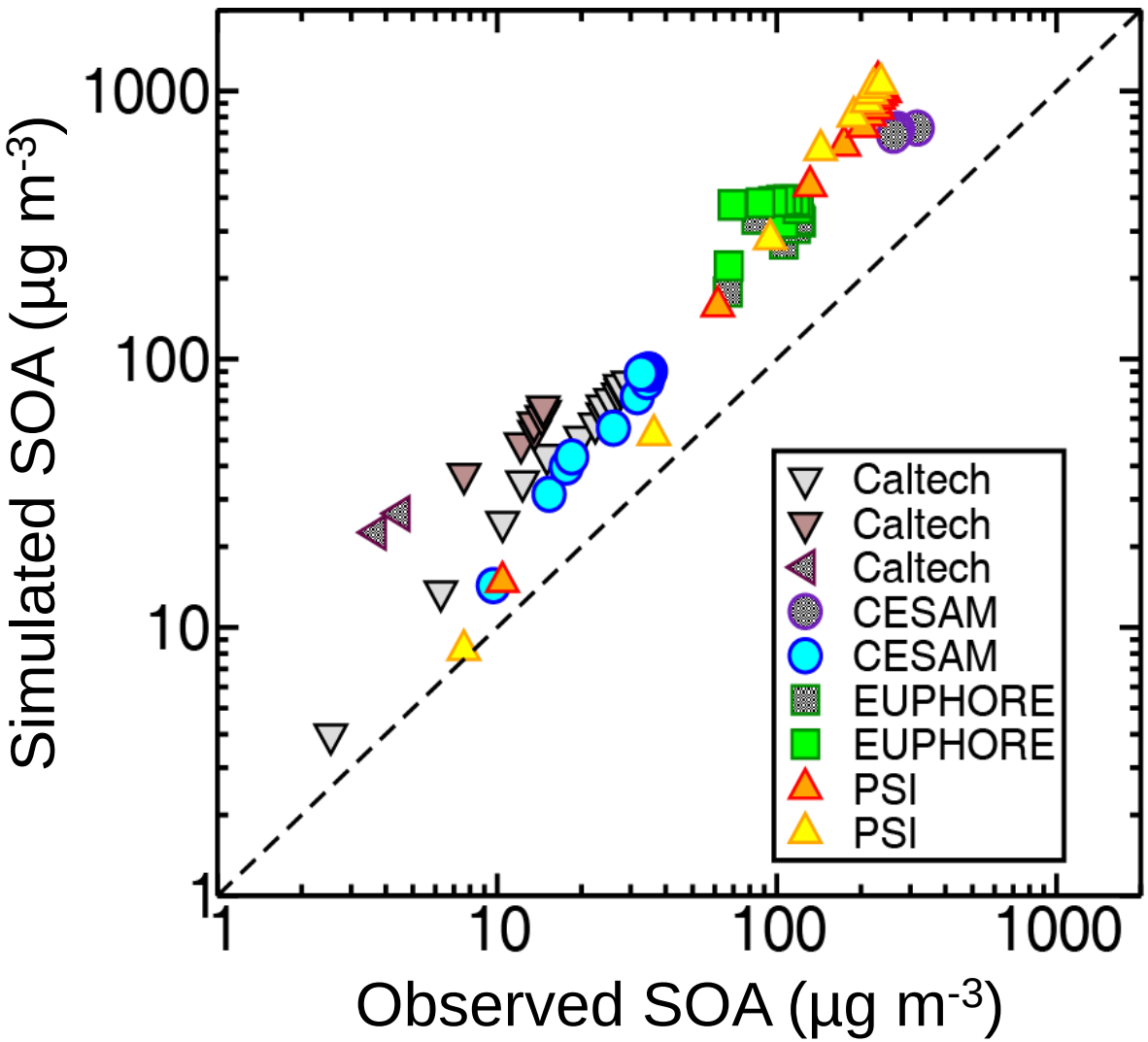
Alpha-pinene oxidation : selected chamber data

	$[\alpha\text{-pinène}]_0$ (ppb)	$[NO]_0$ (ppb)	$[NO_2]_0$ (ppb)	$[O_3]_0$ (ppb)	Relative humidity (%)	Temperature (K)	Irradiation
CALTECH (USA)							
Experience 1	13,8	-	-	4	5,4	298	Black light
Experience 2	13,1	198	-	-	6,3	296	Black light
Experience 3	12,6	475	463	-	3,3	299	Black light
CESAM (Créteil)							
Experience 1	205	-	-	1200	0	295	-
Experience 2	34 (+27)	-	-	165	0	295	-
EUPHORE (Spain)							
Experience 1	109	-	-	190	1	284	-
Experience 2	106	-	-	190	1	289	-
PSI (Switzerland)							
Experience 1	277	50	52,4	0,35	50	293	Solar spectrum
Experience 2	265,28	65,6	56	0,5	60	293	Solar spectrum

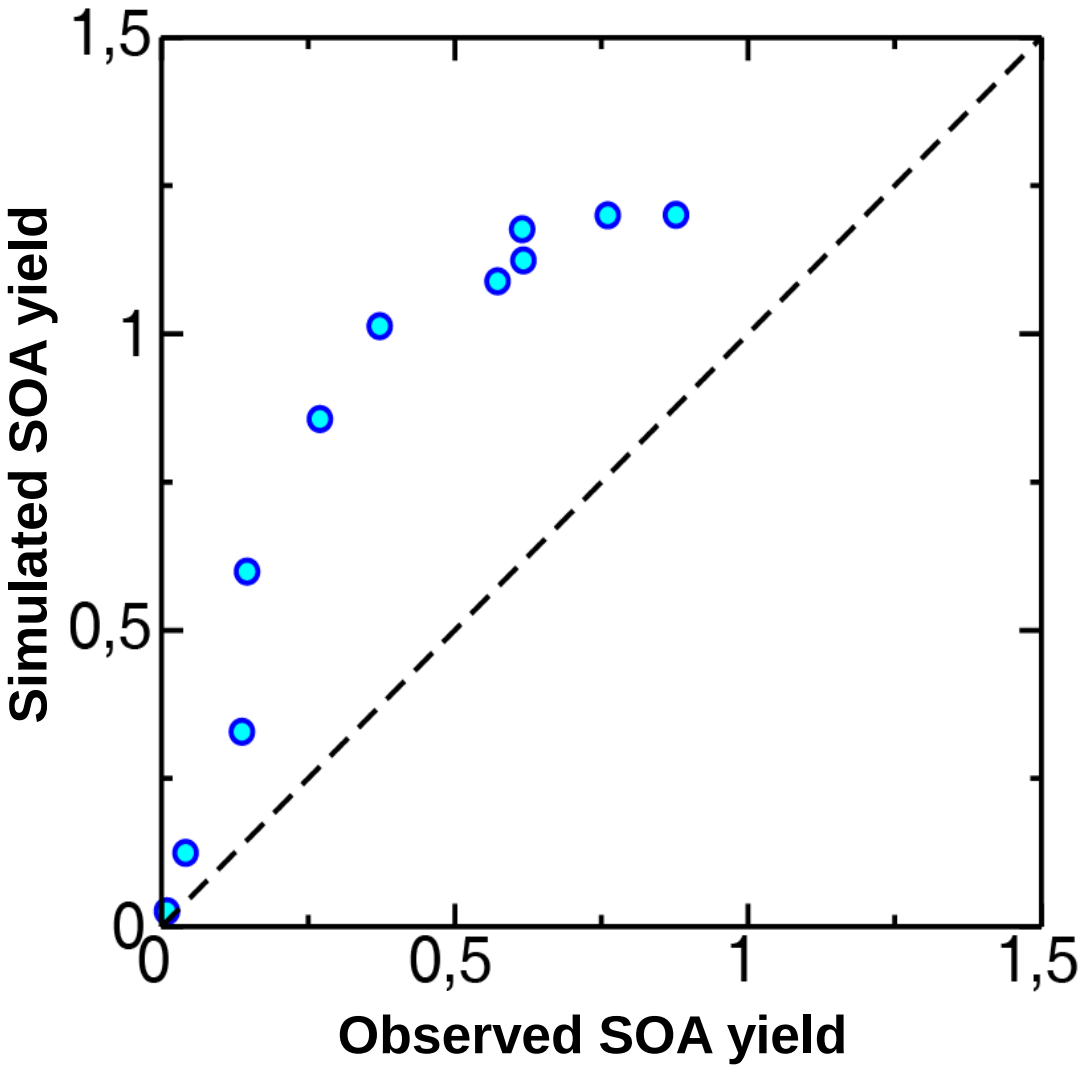
12,6 – 277 ppb **0 - 938 ppb** **0 - 1200 ppb** **0 - 60 %** **284 - 299 K**

GECKO-A vs chamber observation – α-pinene oxidation

Vapor pressure estimation method :
Myrdal & Yalkowsky (1997)



GECKO-A vs chamber observation – aliphatic compounds



Experiences :

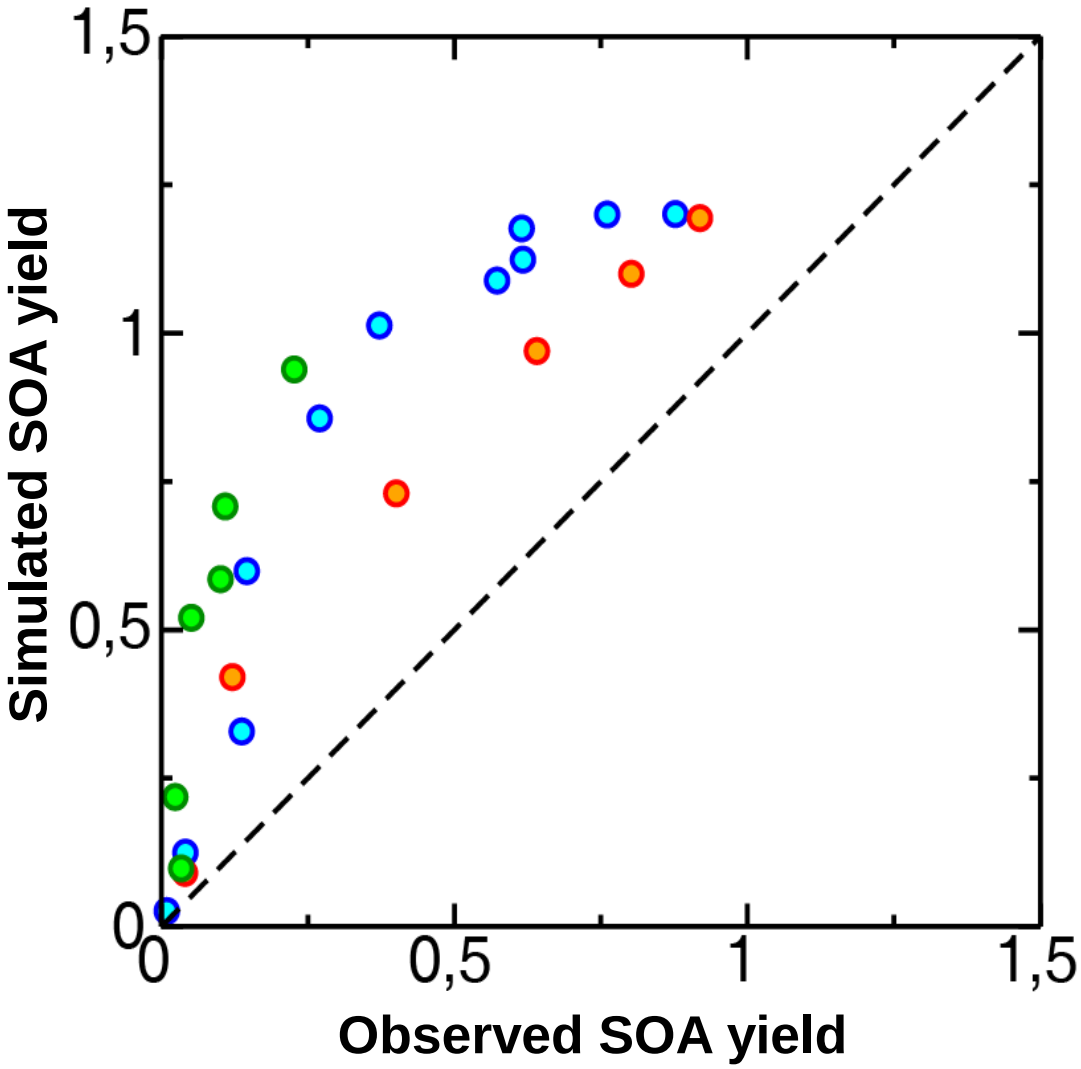
(a) Lim et Ziemann, 2009

(b) Presto et al., 2008

(c) Chacon-Madrid et Donahue, 2011

Linear alkanes (a)

GECKO-A vs chamber observation – aliphatic compounds



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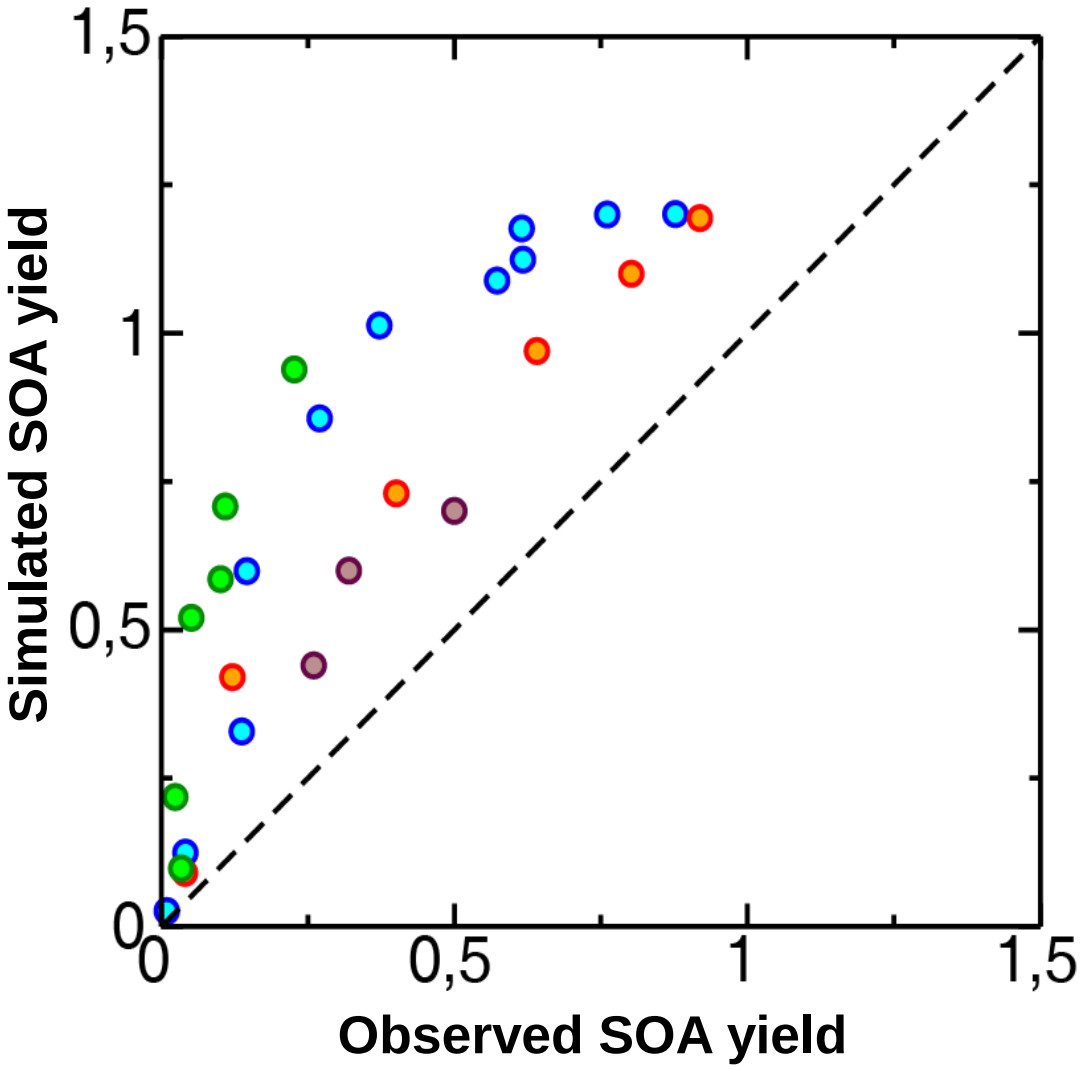
- **Linear alkanes (a)**
- **Cyclic alkanes (a)**
- **Branched alkanes (a)**

GECKO-A vs chamber observation – aliphatic compounds



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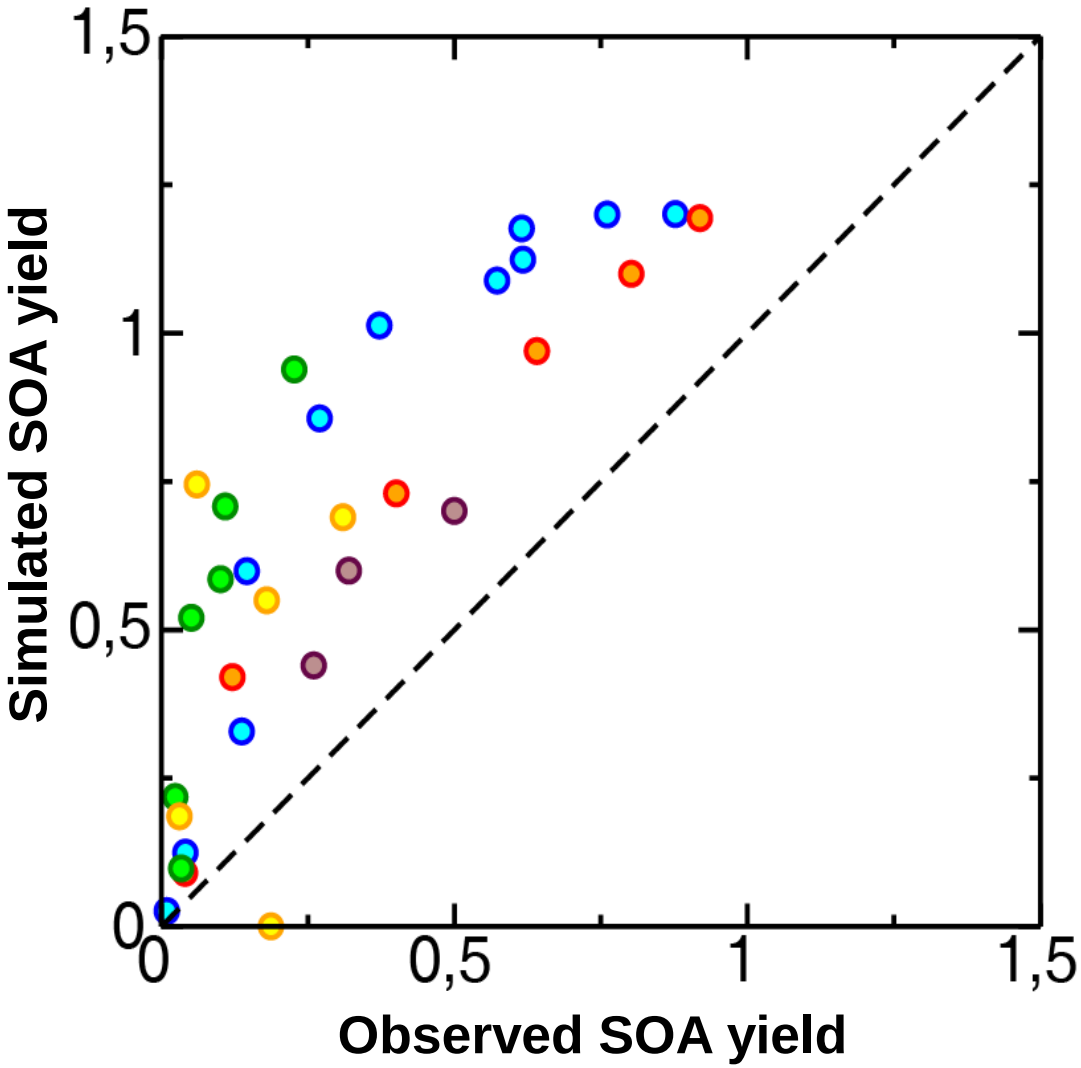
- Linear alkanes (a)
- Cyclic alkanes (a)
- Branched alkanes (a)
- Linear alkanes (b)

GECKO-A vs chamber observation – aliphatic compounds



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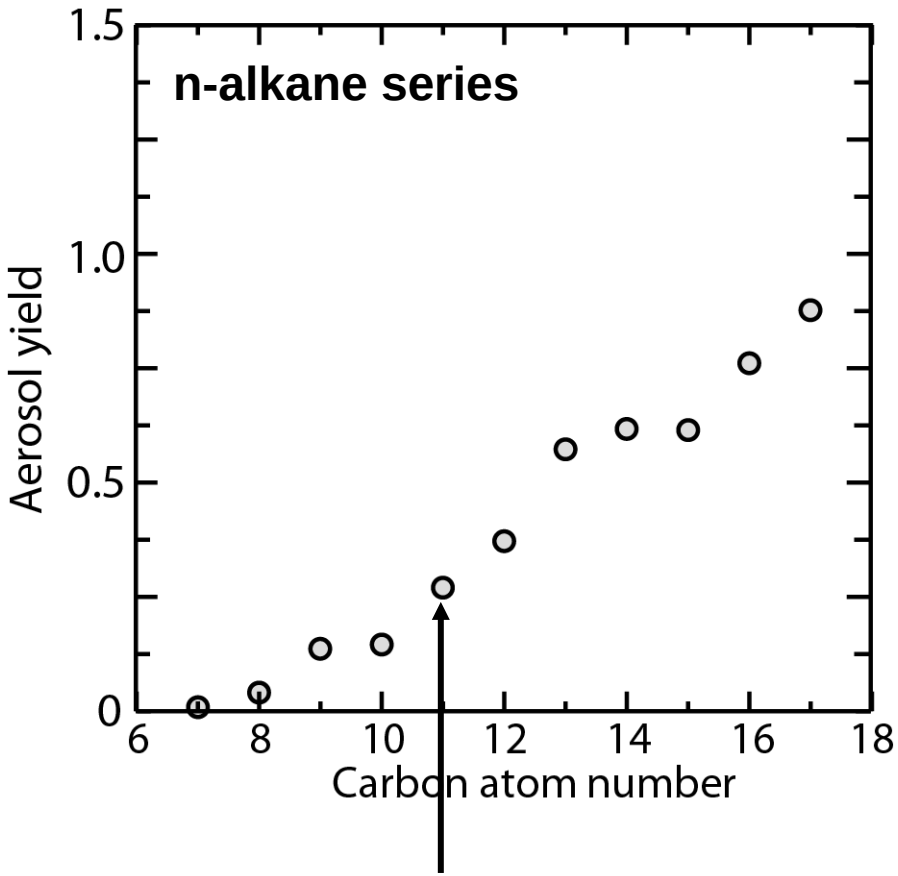
- **Linear alkanes (a)**
- **Cyclic alkanes (a)**
- **Branched alkanes (a)**
- **Linear alkanes (b)**
- **Oxygenated VOC (c)**

Evaluation of GECKO-A using chamber data – alkane series



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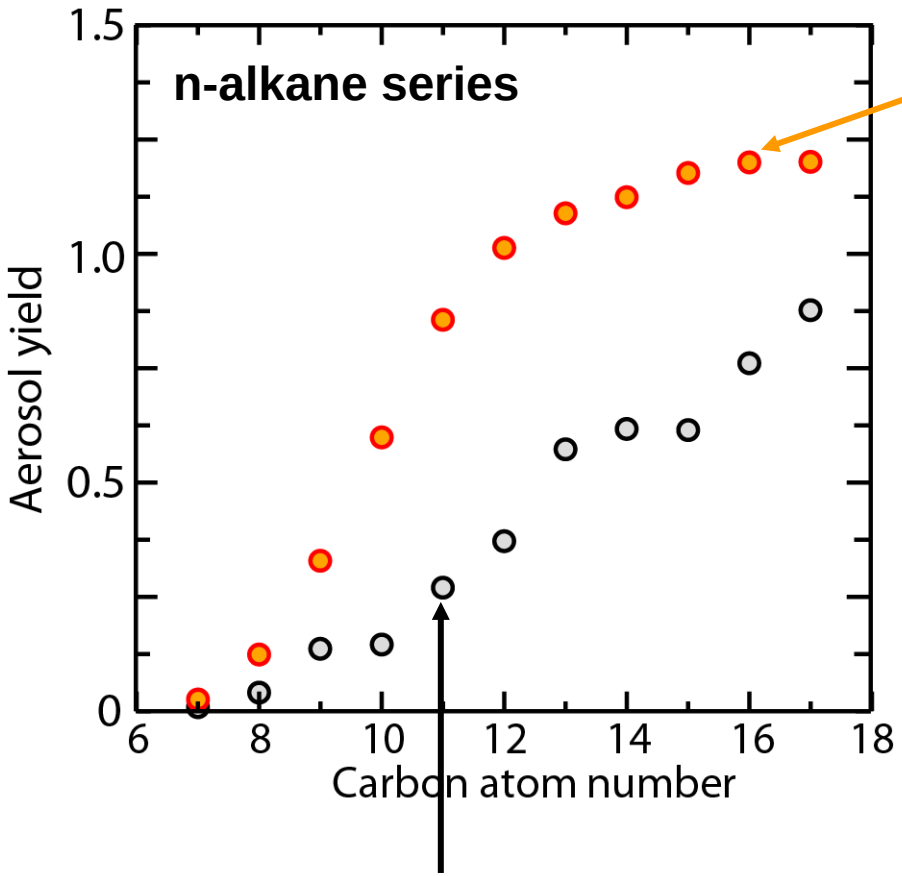

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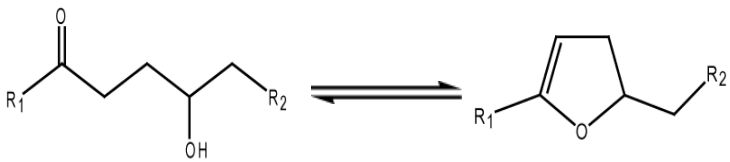
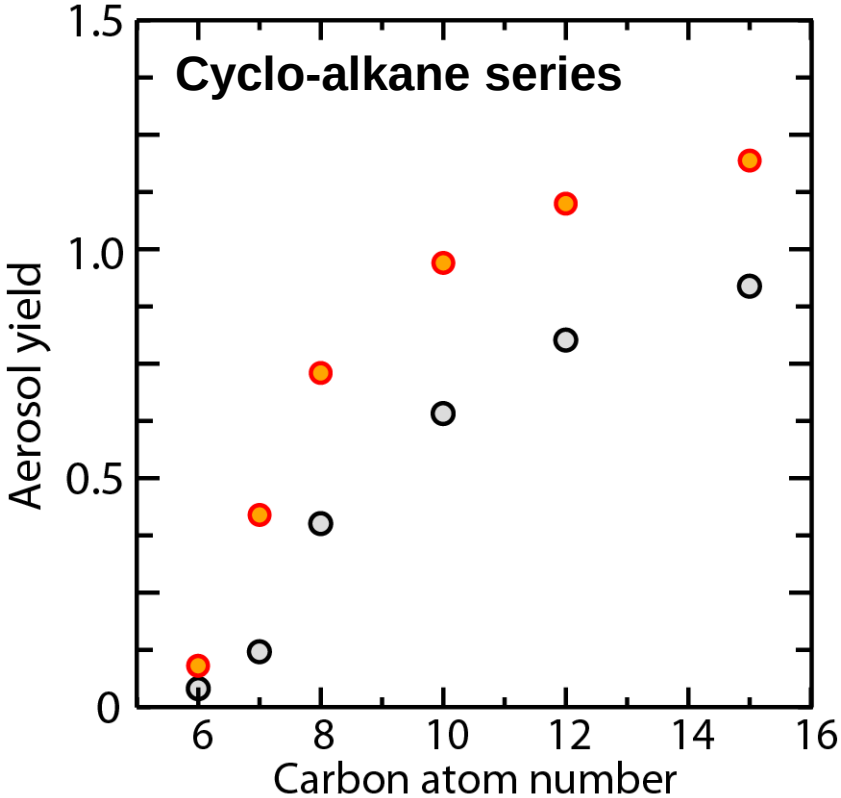
SOA yields simulated with GECKO-A

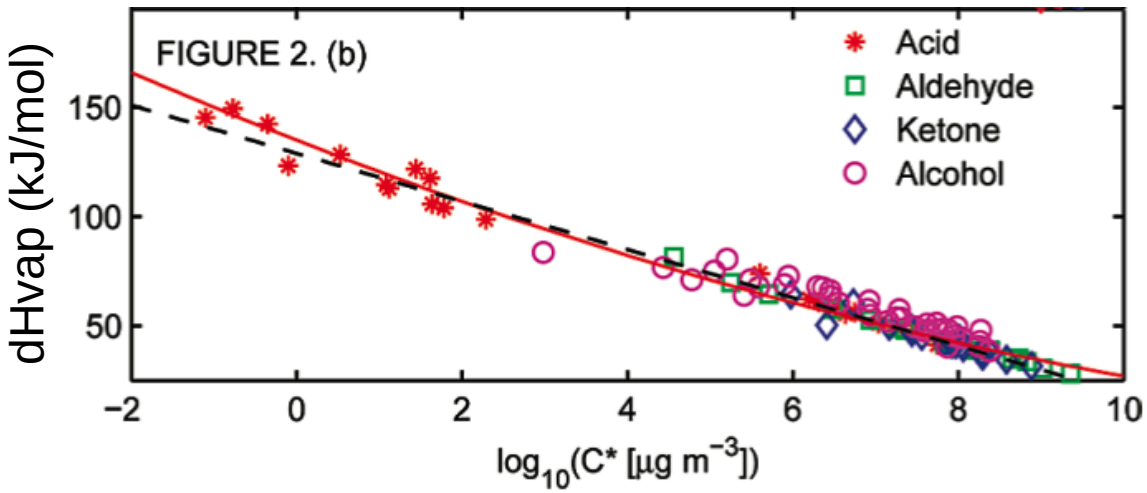
Scheme generated assuming that 1-4 hydroxycarbonyls are converted into dihydrofuran with 100% yields.



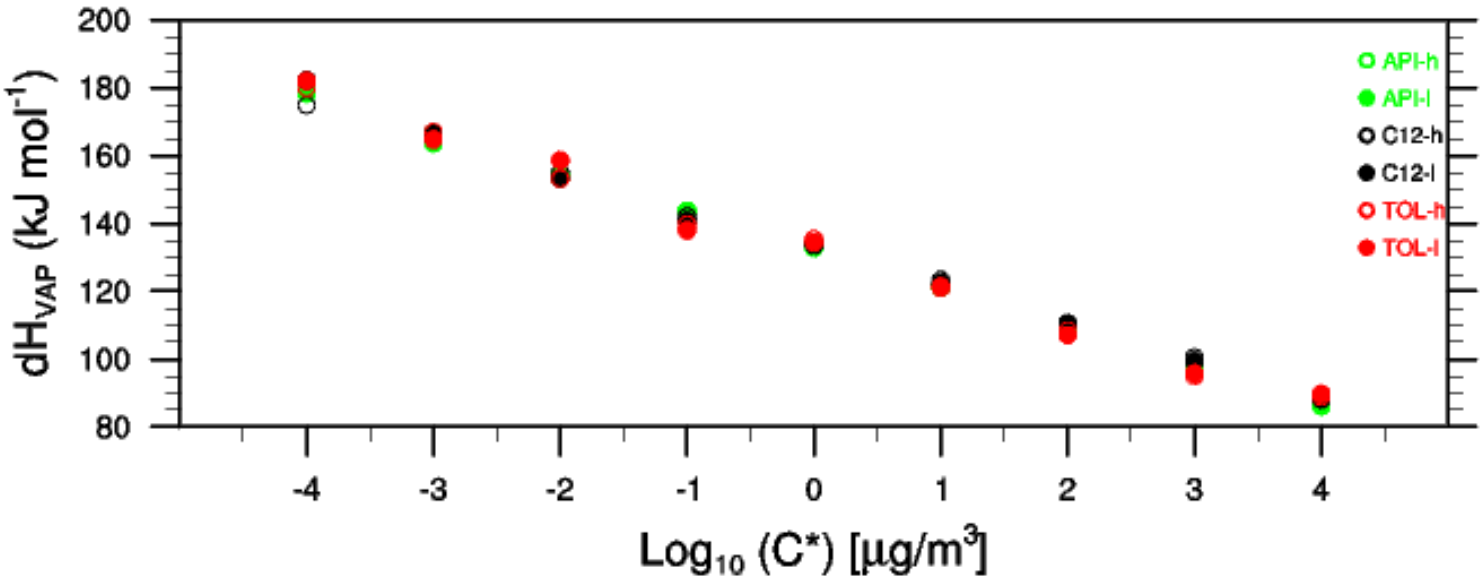


Enthalpy of vaporization for VBS

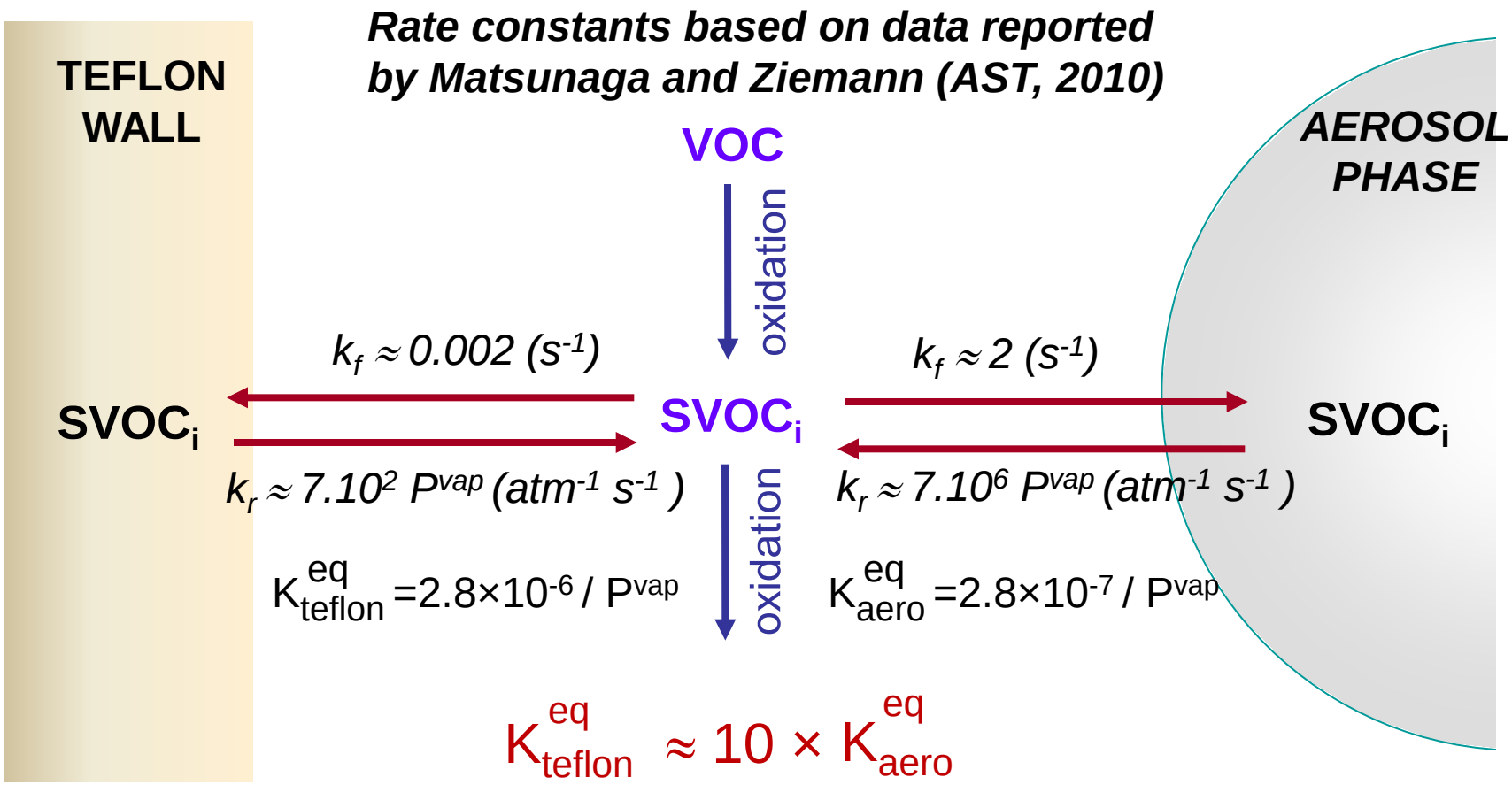
- **Epstein et al., 2010**



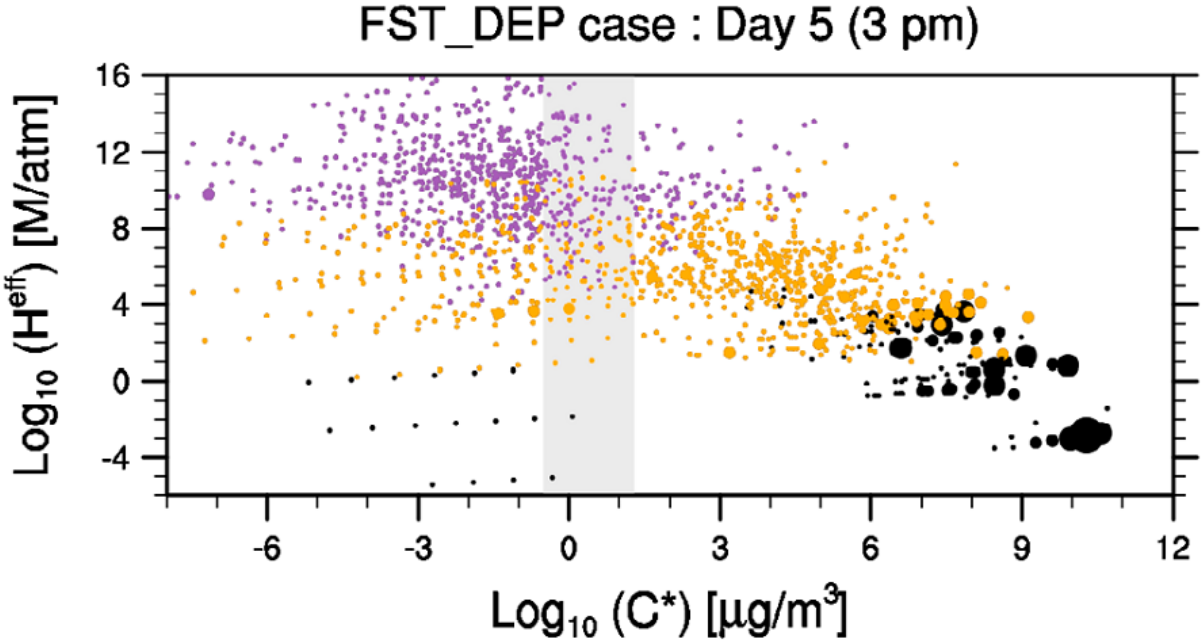
- **GECKO-A**

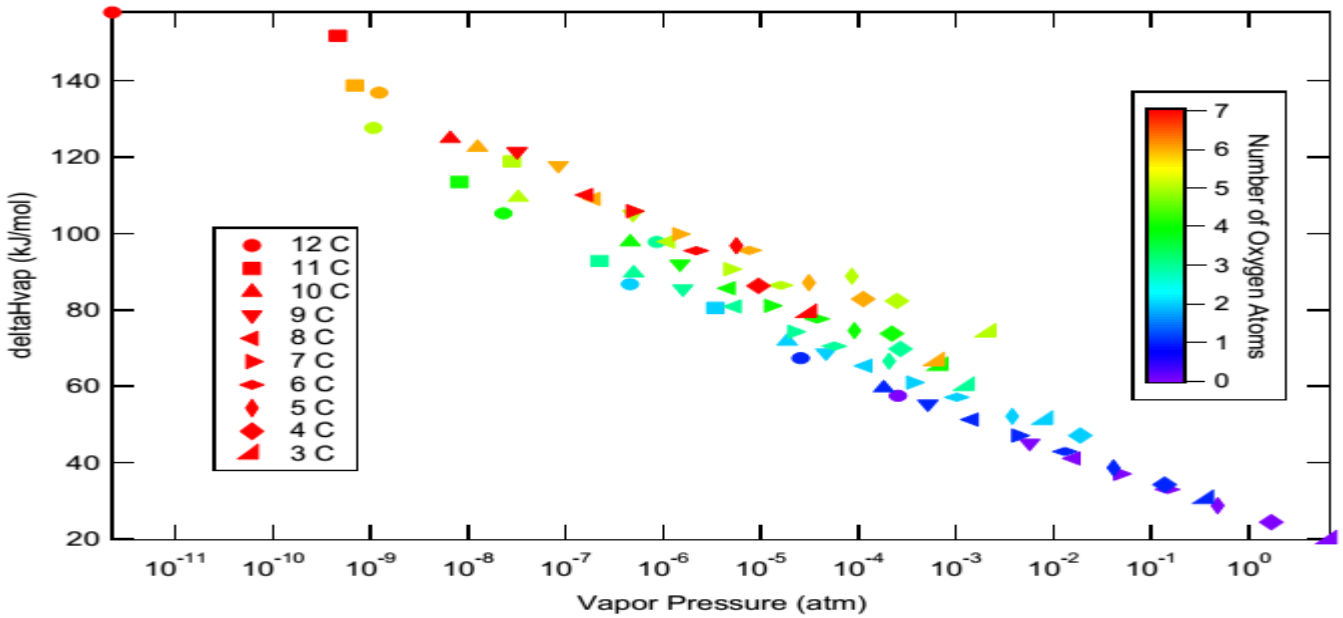


Wall loss of organic compounds



Kinetic control favors partitioning into the aerosol phase, thermodynamic control favors partitioning into the teflon wall.


FST_DEP case : Day 5 (3 pm)
Log10 (H^eff) [M/atm]
Log10 (C*) [µg/m3]
16
12
8
4
0
-4
-6
-3
0
3
6
9
12


deltaHvap (kJ/mol)
Vapor Pressure (atm)
12 C
11 C
10 C
9 C
8 C
7 C
6 C
5 C
4 C
3 C
Number of Oxygen Atoms
140
120
100
80
60
40
20
10-11
10-10
10-9
10-8
10-7
10-6
10-5
10-4
10-3
10-2
10-1
100

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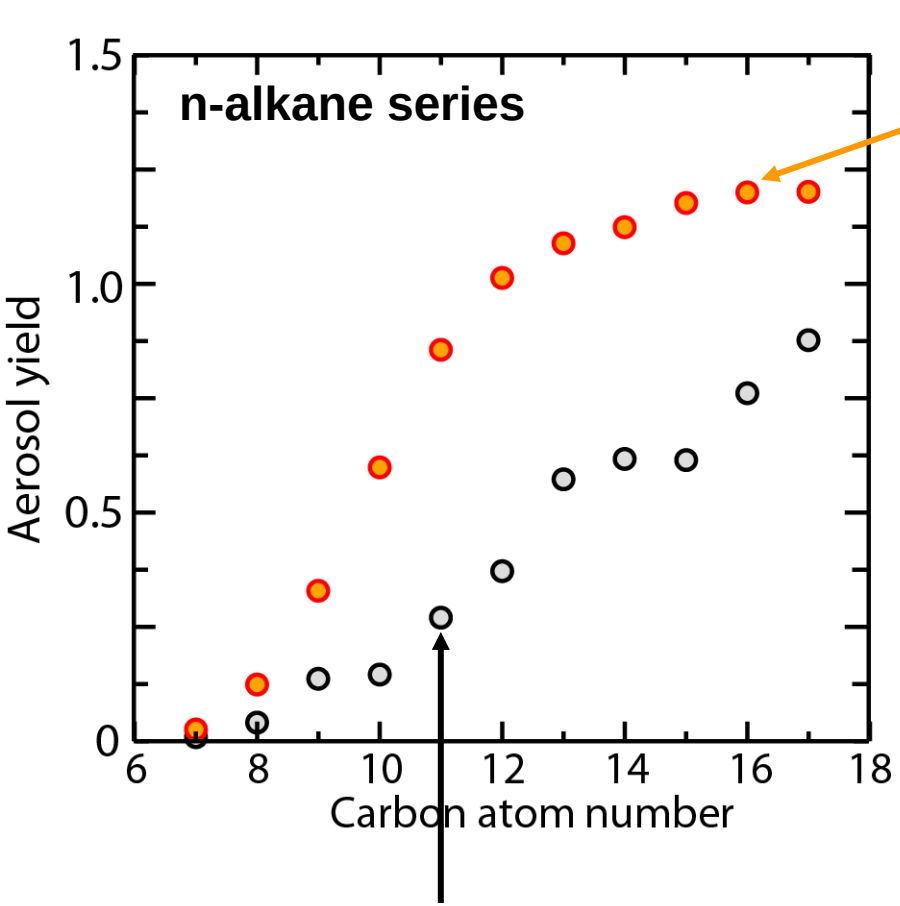

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Title slide: gecko-a

- acknowledgements
- julia, bernard and group, alma, doe/asr, growing list of collaborators

overview of gecko-a

- history, ncar mm
- gas phase, comparisons to MCM, SAPRC99 (Aumont et al. 2005)
- Mechanism growth curves, use schemes as wallpaper

SOA yields from smog chambers

- alpha pinene
- alkanes, with and without wall effects

field simulations

- MILAGRO
  - urban POA and SOA mass
  - composition: typical molecules
  - issues: acids, nitrates
  - Regional growth
- BEACHON

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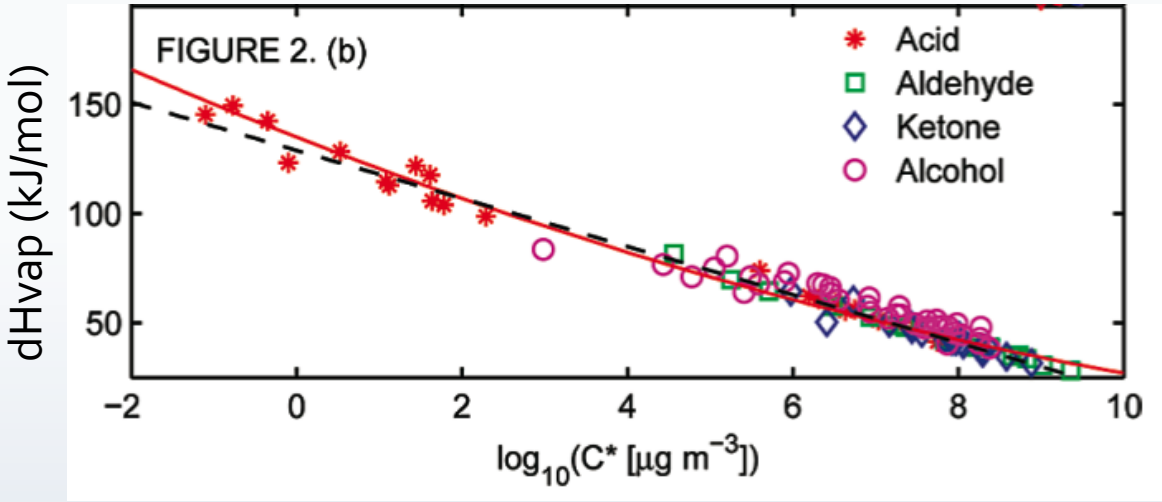

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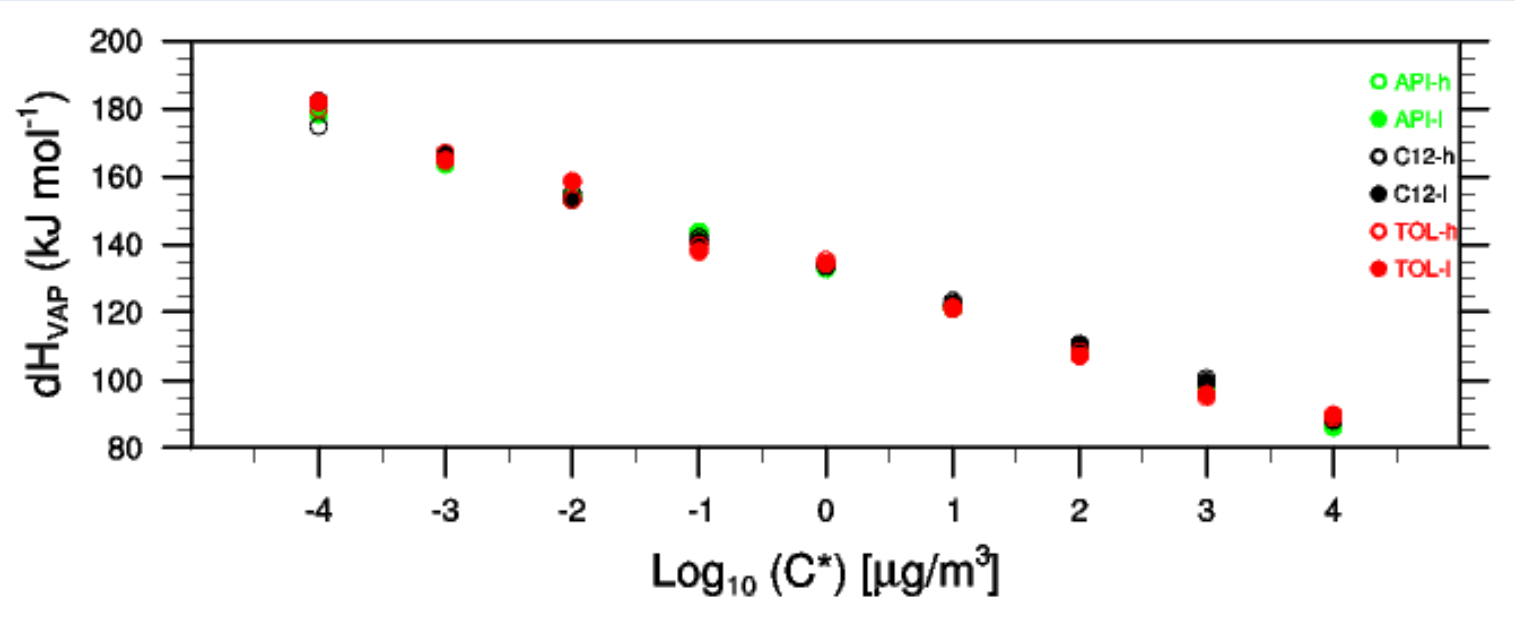


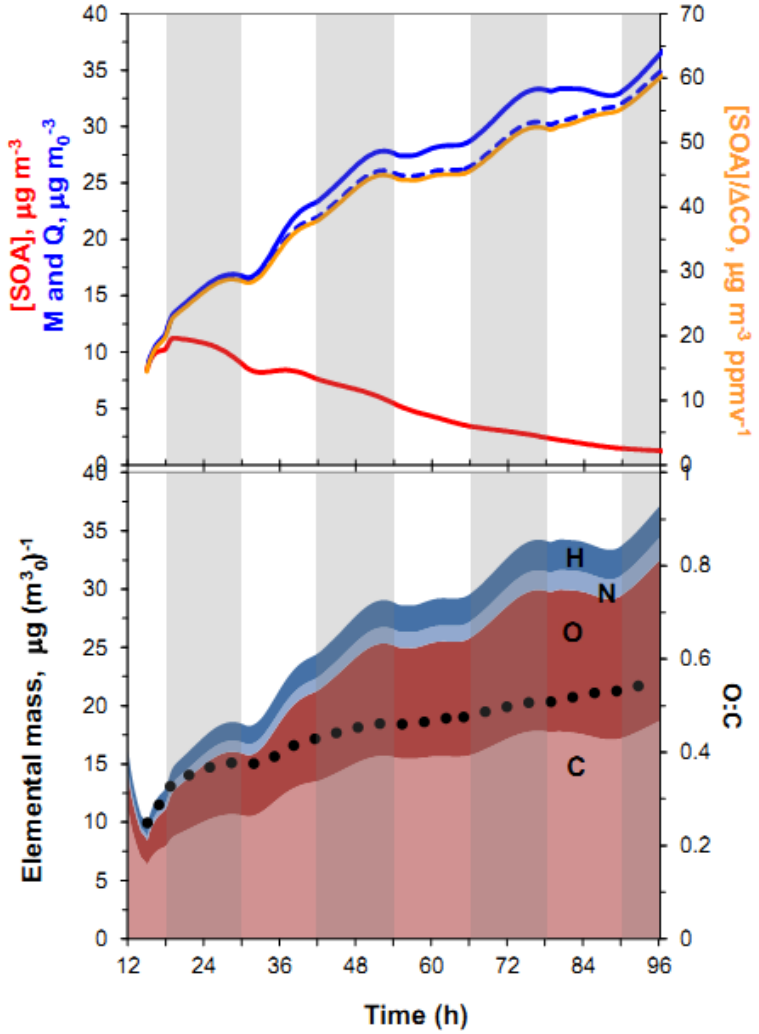
Growth of Organic Aerosols Downwind of a Megacity

Concentration decreases with dilution

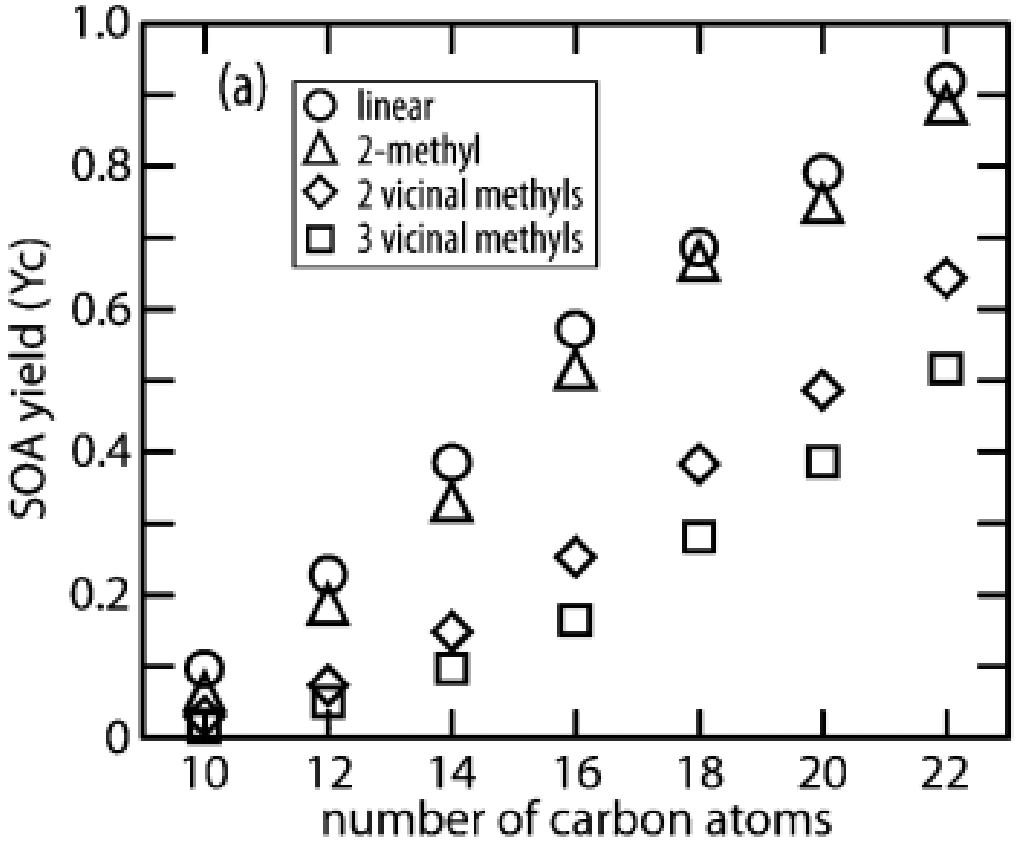
Plume-integrated mass increases despite dilution/evaporation

Most new mass in C and O atoms → continuing oxidation of the gas phase

Important implication for regional radiative forcing and global climate.



Lee-Taylor et al., APCD 2011


(a)
linear
2-methyl
2 vicinal methyls
3 vicinal methyls
SOA yield (Yc)
1.0
0.8
0.6
0.4
0.2
0
10
12
14
16
18
20
22
number of carbon atoms