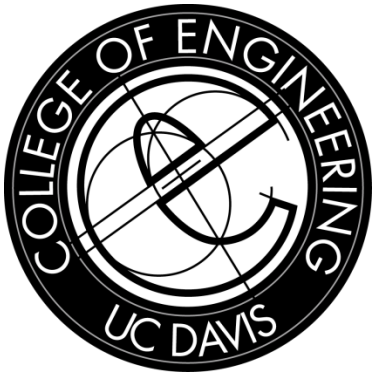
Simulating Secondary Organic Aerosol at Varying Levels of Complexity

Christopher D. Cappa

University of California, Davis

Current ASR Collaborators: John Seinfeld (Caltech), Alma Hodzic, Sasha Madronich, Julia Lee-Taylor (NCAR)



Model Predictions

- Climate Relevant Properties
  - Mass concentrations
- Process Relevant Properties
  - O:C Elemental Composition

Are all the properties and processes under consideration really separable?

O:C ↔ Kappa

Kappa (water) ↔ viscosity

Mass ↔ Number ↔ Kappa ↔ Optical Properties

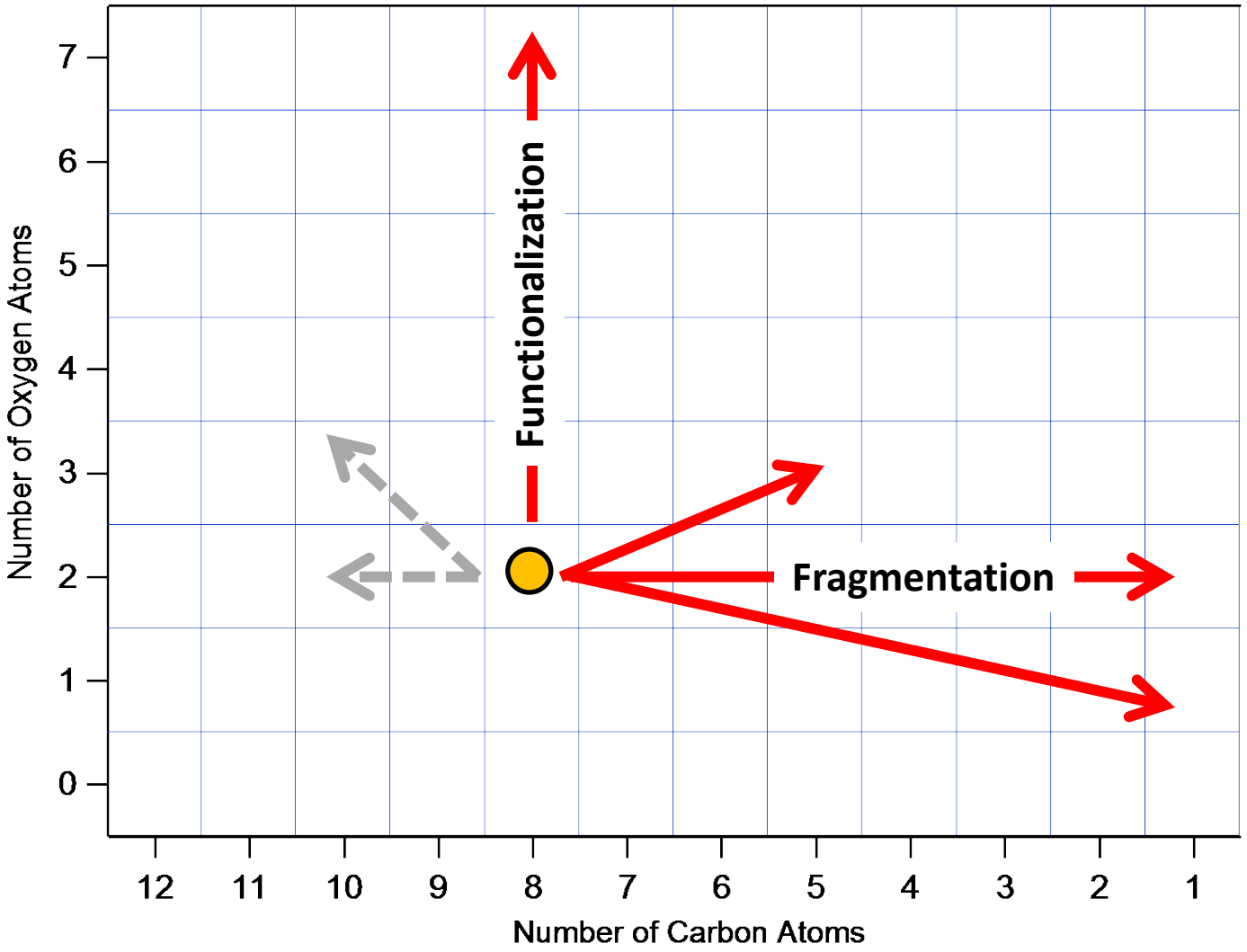
How well can “simple” models be merged to develop robust “complex” models?

- Most SOA models are highly parameterized and link directly back to chamber experiments
- If new processes are added a posteriori (e.g. condensed phase oligomerization reactions, “high viscosity” particles, “ageing” or fragmentation) is the original parameterization still relevant/appropriate?

Contention: There is a need to include “ageing” as part of the fundamental model formulation *and* as part of the fitting process when dealing with photochemical oxidation.

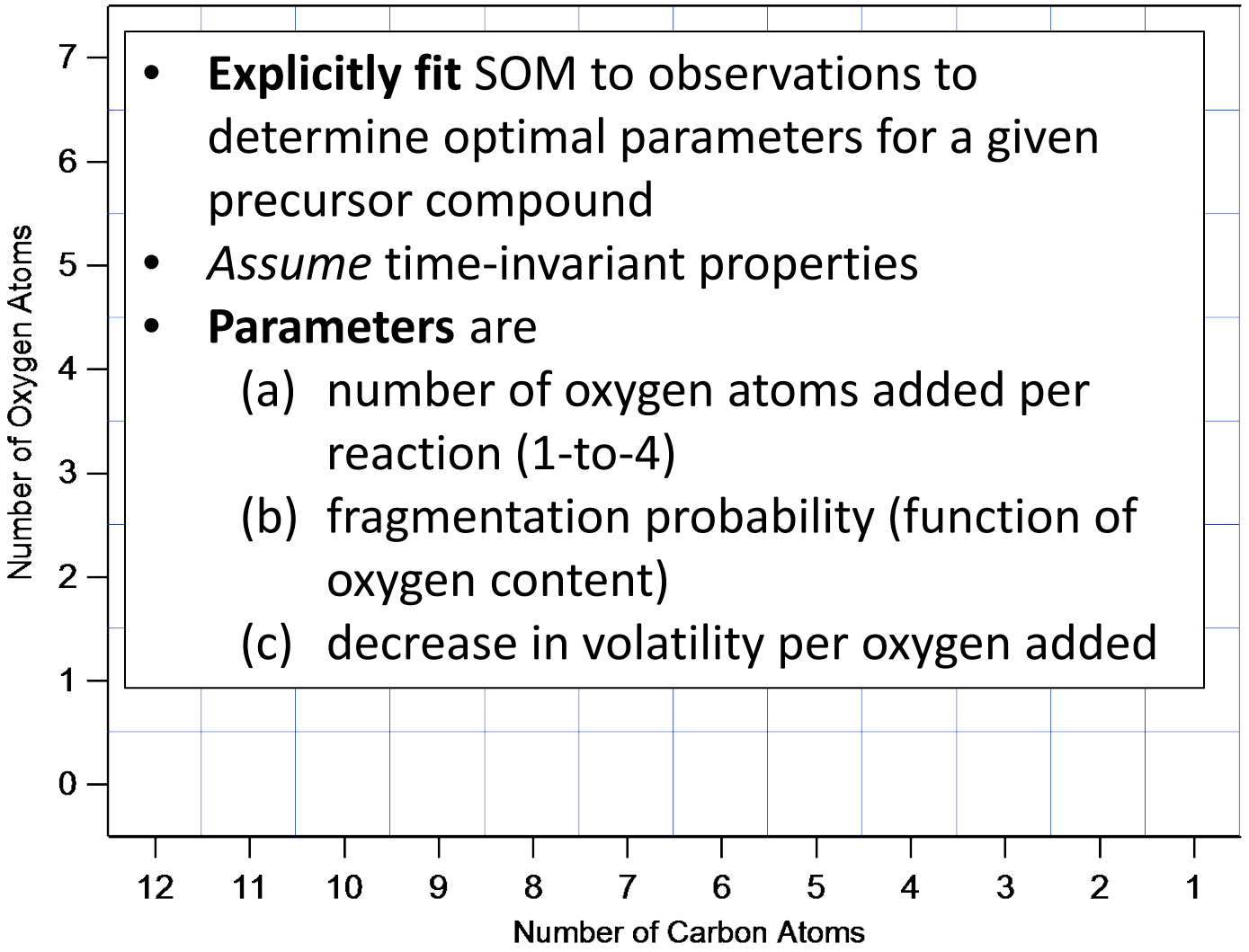
(Really, there is a need to include any processes that might later be considered later during data fitting.)

The Statistical Oxidation Model



[Cappa and Wilson, *ACP*, 2012; Cappa et al., *ACP*, 2013]

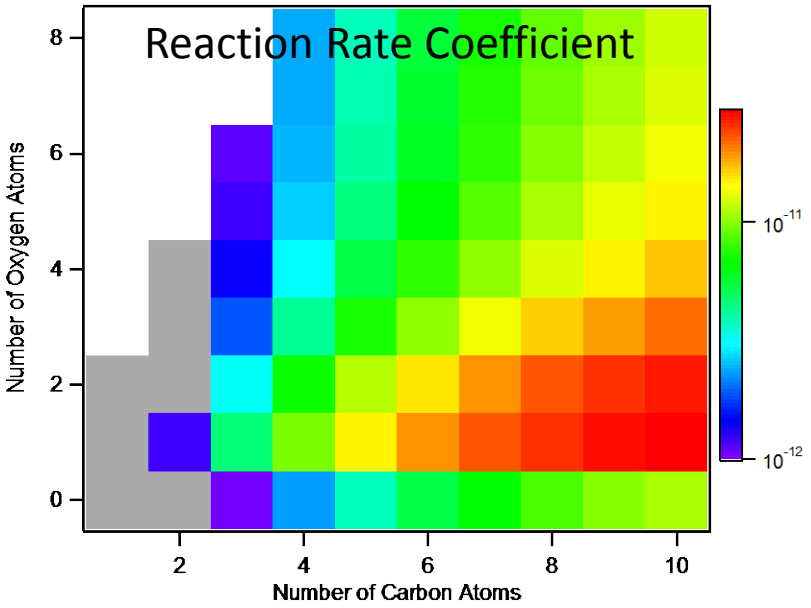
The Statistical Oxidation Model

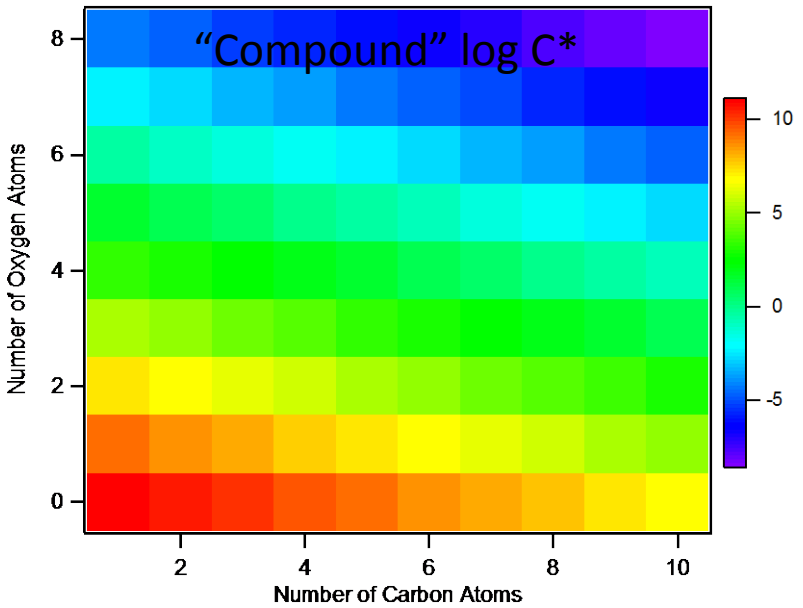


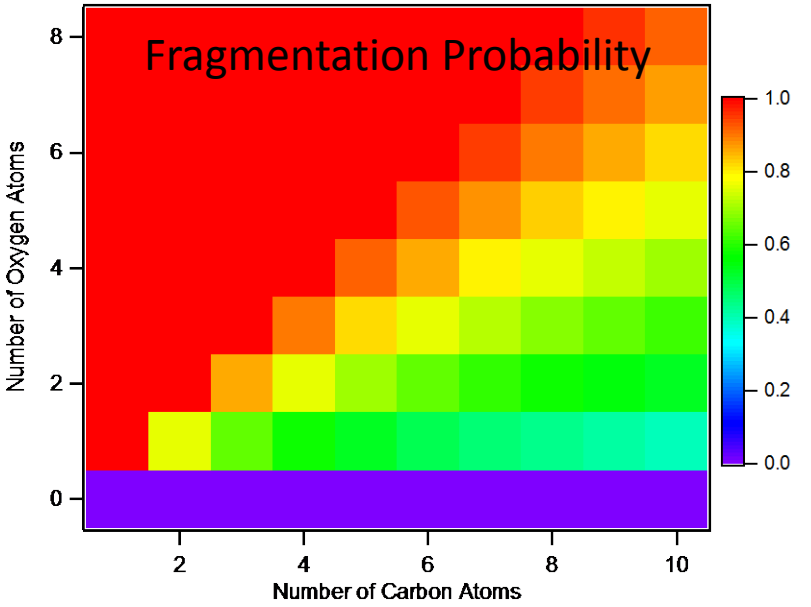
- **Explicitly fit** SOM to observations to determine optimal parameters for a given precursor compound
- *Assume* time-invariant properties
- **Parameters** are
  - (a) number of oxygen atoms added per reaction (1-to-4)
  - (b) fragmentation probability (function of oxygen content)
  - (c) decrease in volatility per oxygen added

[Cappa and Wilson, *ACP*, 2012; Cappa et al., *ACP*, 2013]

The Statistical Oxidation Model







- k_{OH} matrix determined from explicit comparison with GECKO-A [Aumont and co-workers]
- k_{OH} matrix taken as constant
- Fragmentation function as:

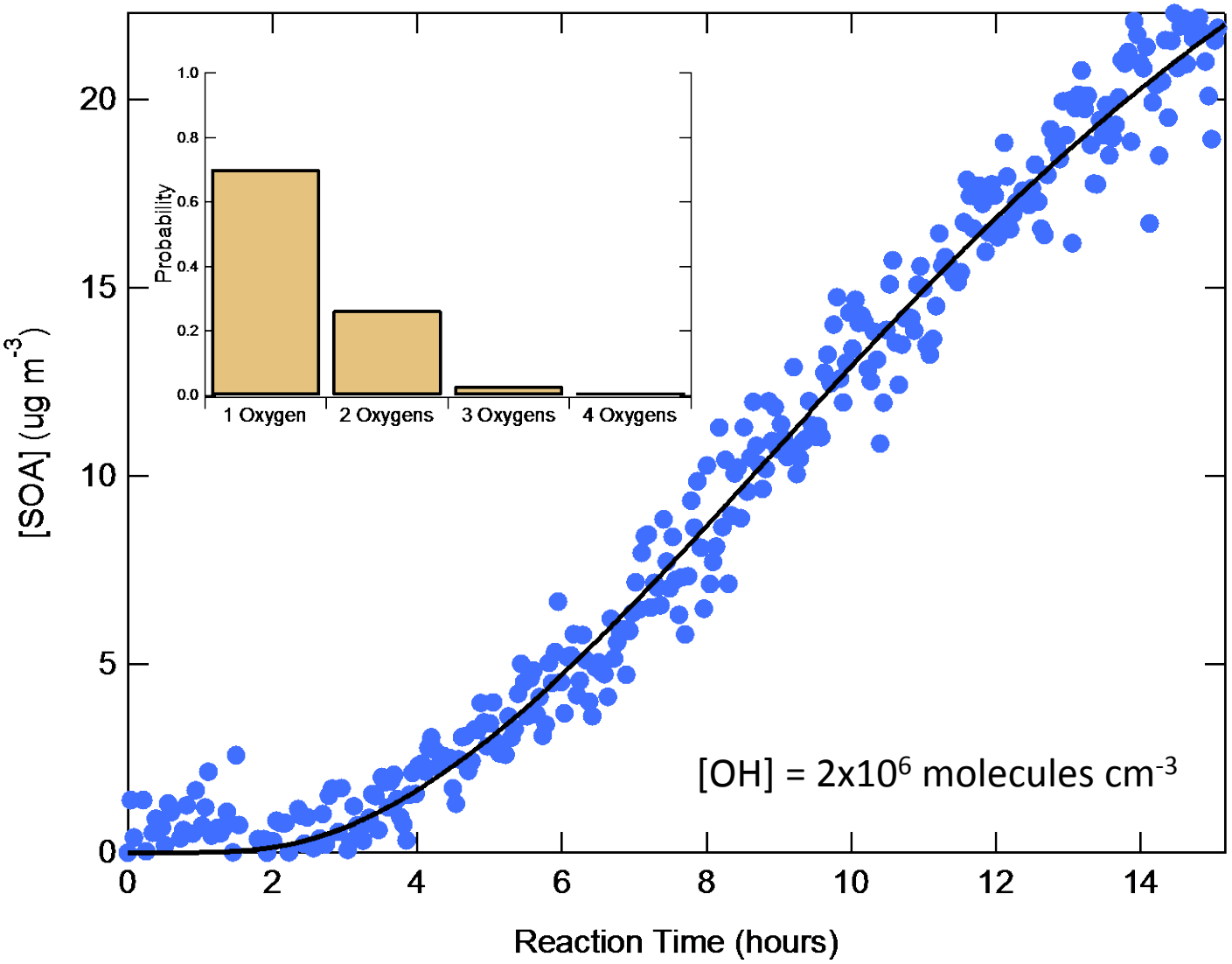
$$P_{frag} = (N_O : N_C)^{m_{frag}} \quad \text{or} \quad c_{frag} \cdot N_O$$

- Saturation concentrations as:

$$\log C^*(N_C, N_O) = \log C^*(N_C, 0) - N_O \cdot \Delta LVP$$

Using the SOM to evaluate the role of multigenerational chemistry and ageing

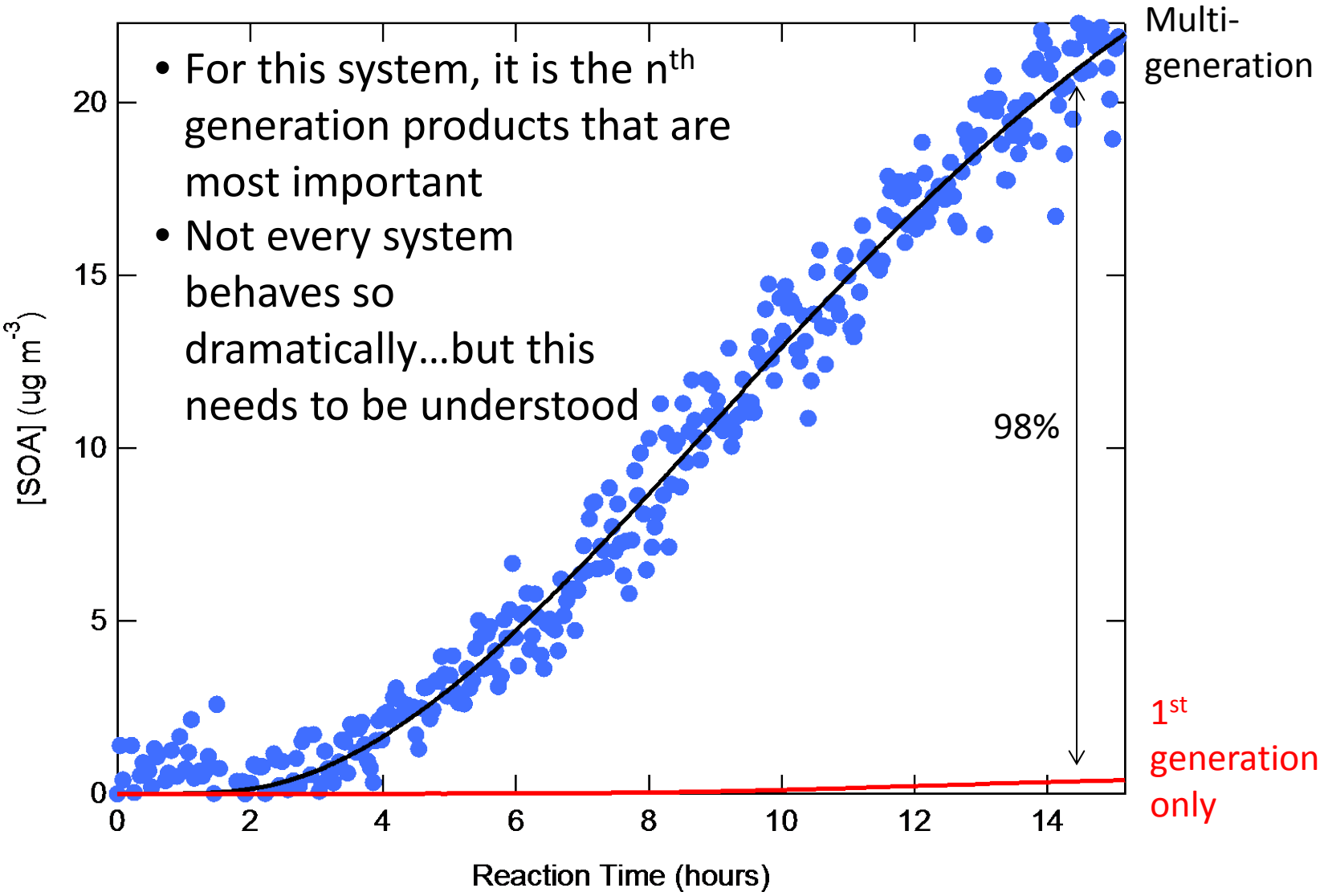
Example: n-dodecane + OH (low-NO_x)



Multi-generation fit

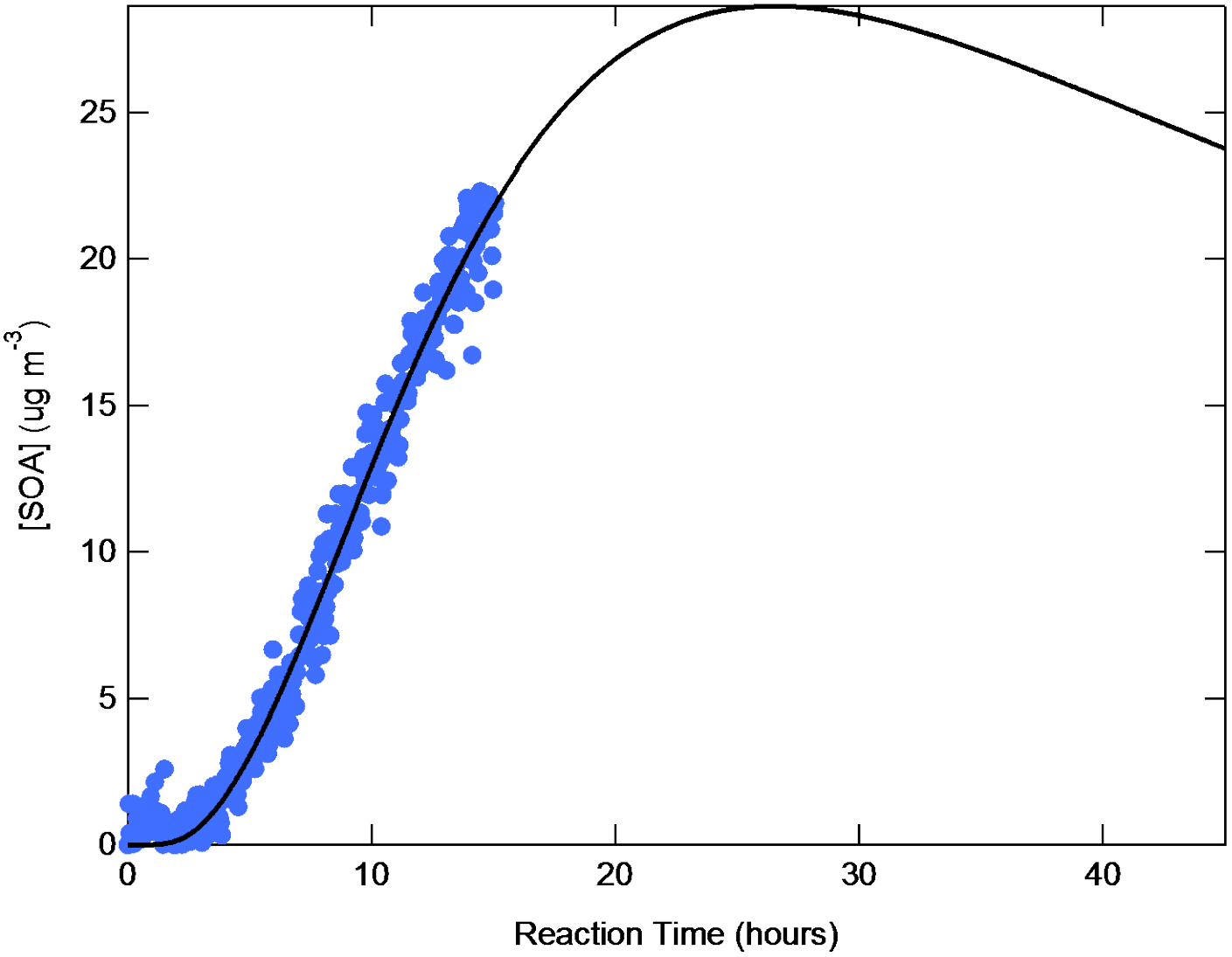
[Cappa et al., ACP, 2013]

Example: n-dodecane + OH (low-NO_x)



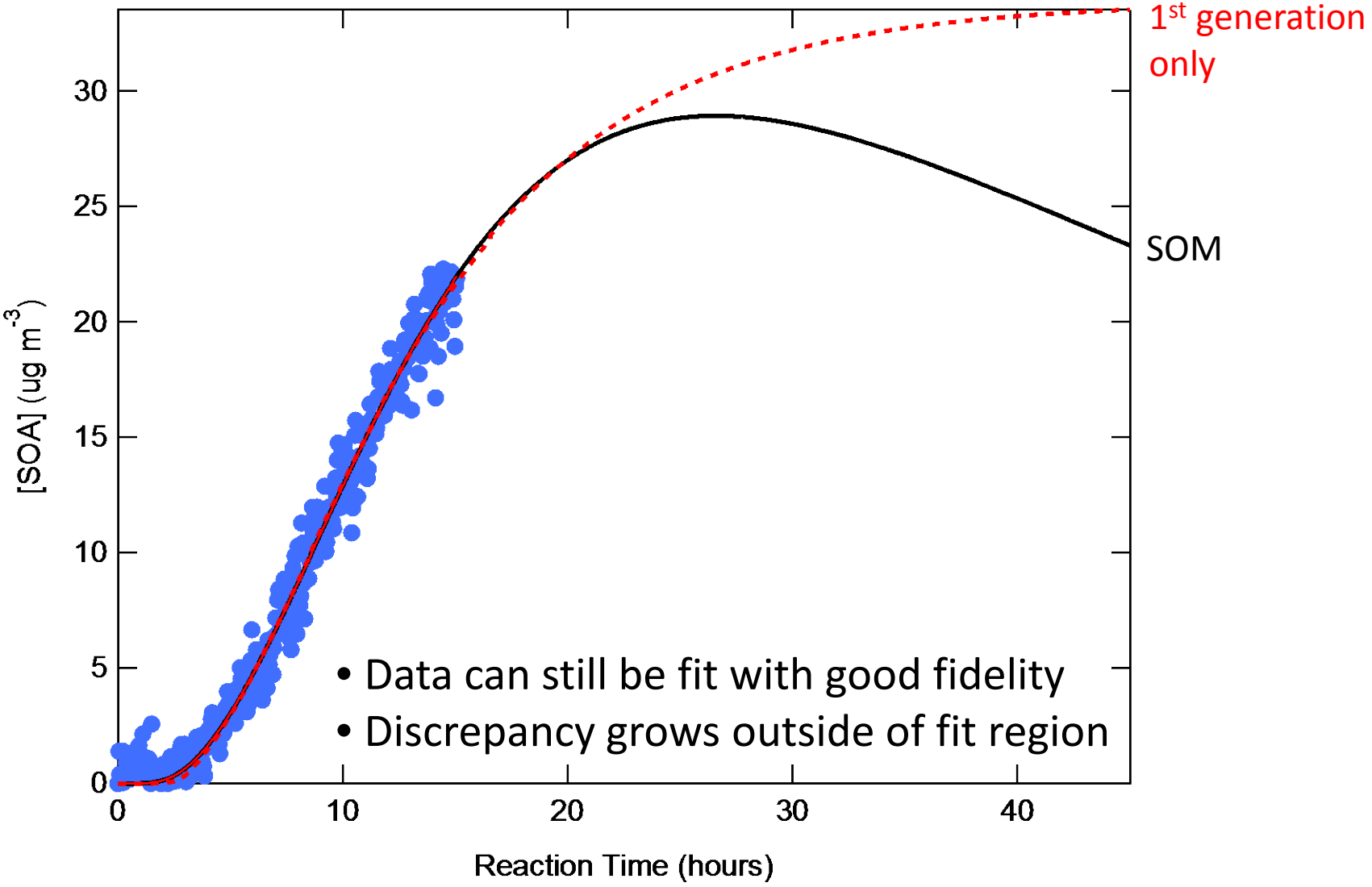
Ageing in multi-generational systems

What if only 1st generation reactions are allowed, but SOM is fit to the observations?

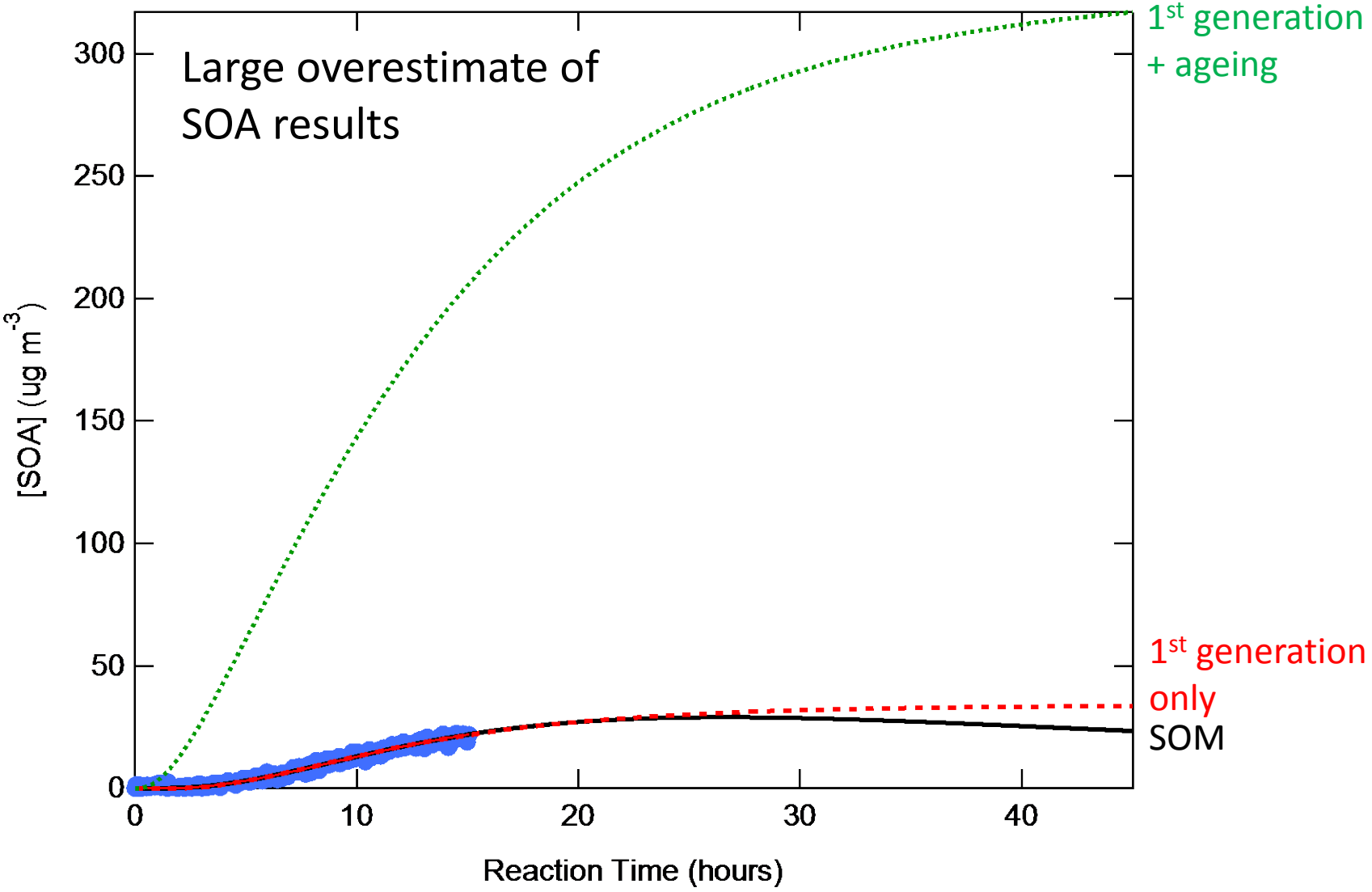


Ageing in multi-generational systems

What if I decided to add "ageing" of 1st generation products?



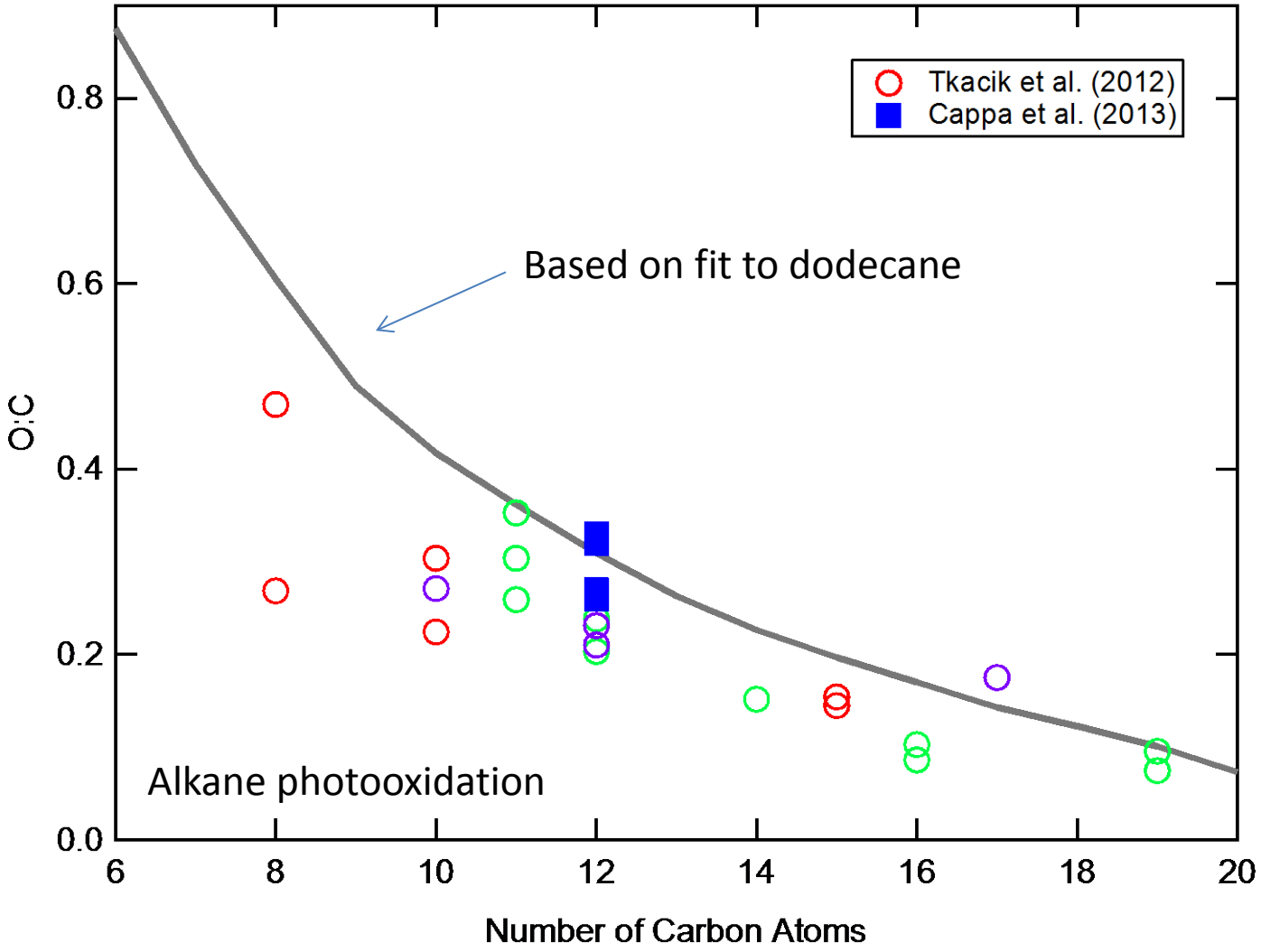
Ageing in multi-generational systems



Using the SOM to predict intensive SOA properties, e.g. O:C

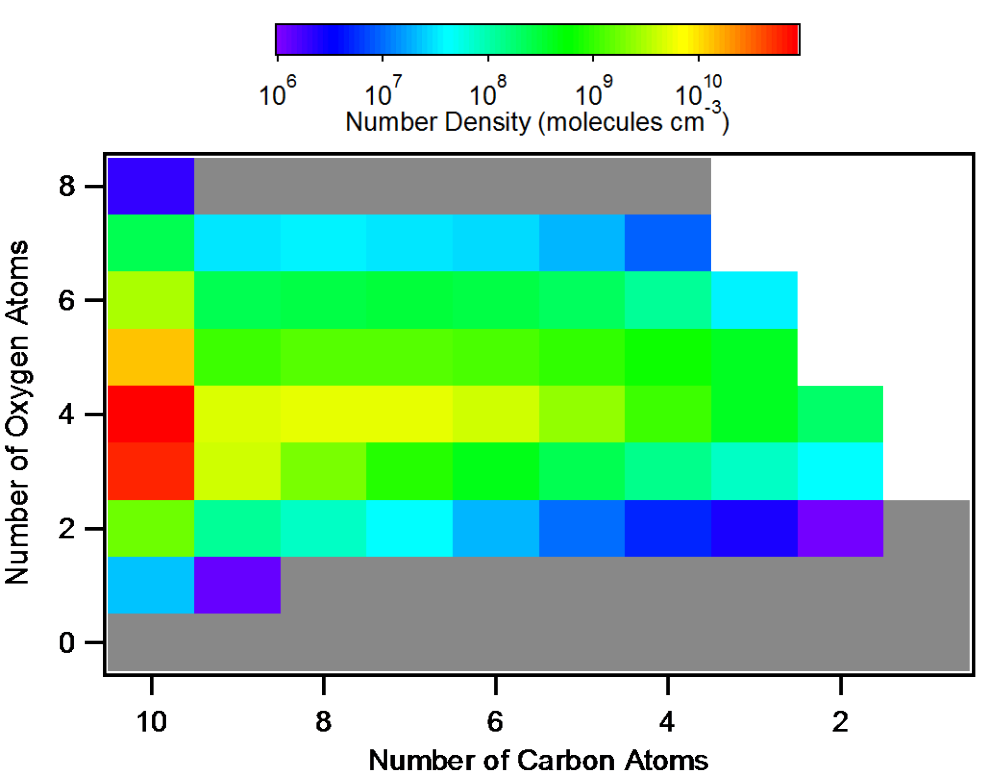
Intensive Properties: Oxygen-to-Carbon Ratio

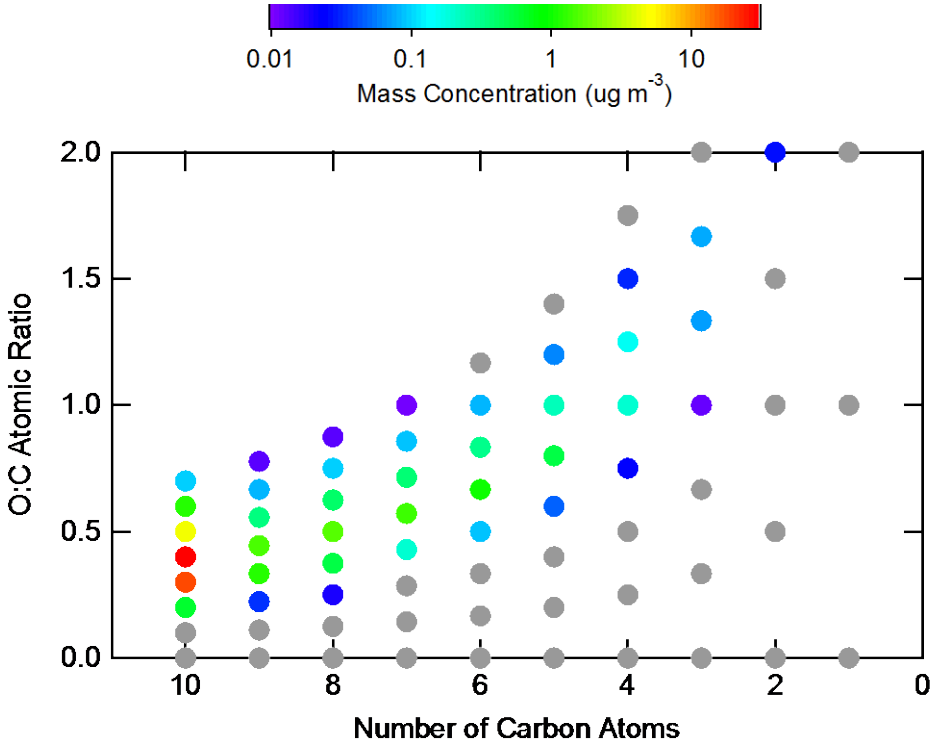
- O:C is an inherent feature of the SOM
- Oxygen addition/content and volatility are intricately linked
- To what extent do condensed phase (oligomerization) rxns affect O:C?



Intensive Properties: Carbon vs. Oxygen

Example from a-Pinene photooxidation (low-NOx)





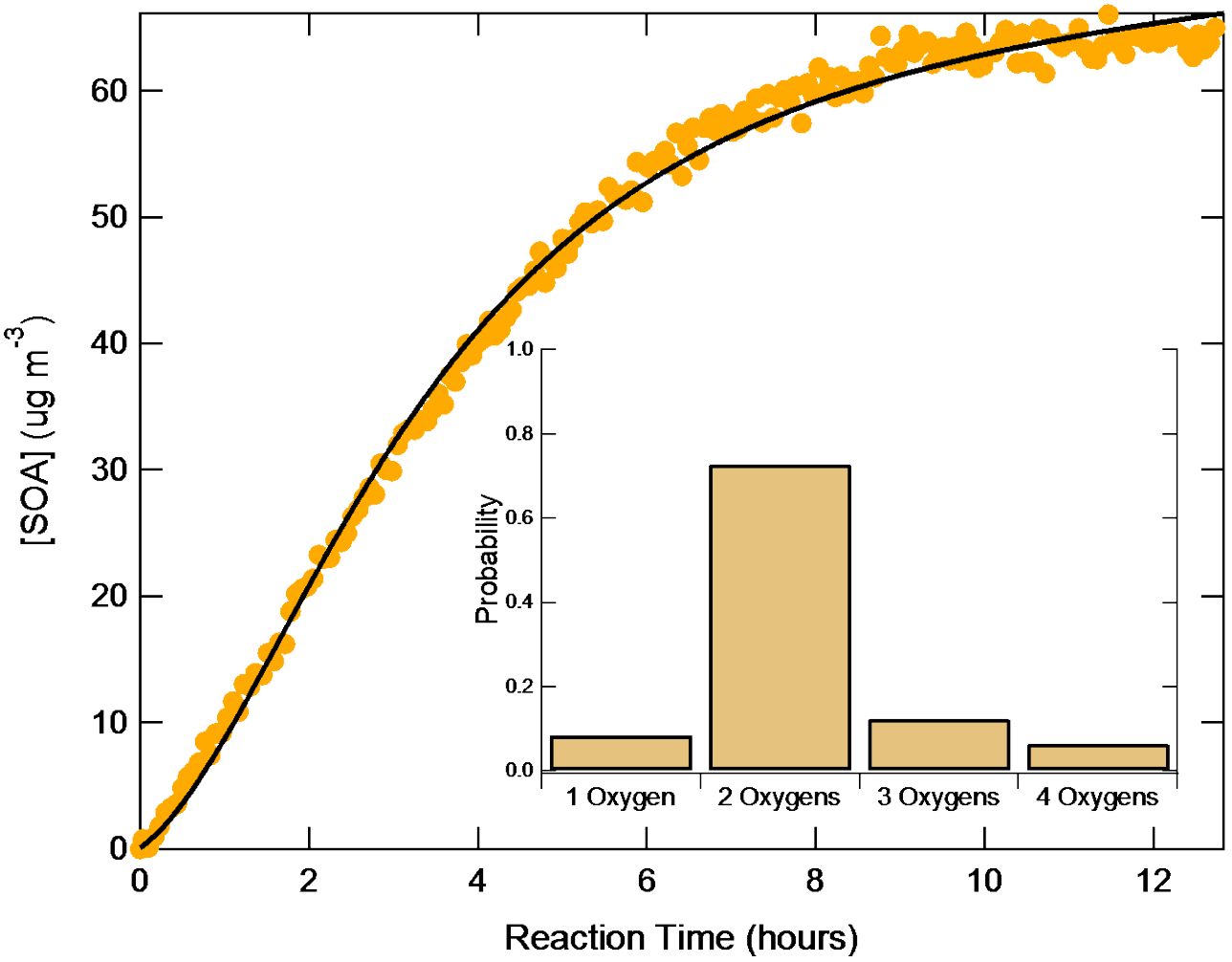
Since SOA models will likely continue to be parameterized based on chamber experiments, there is a clear need to integrate properties and process of interest as part of data fitting process

SOM is currently being developed to allow for use within 3D models (supported by CARB)

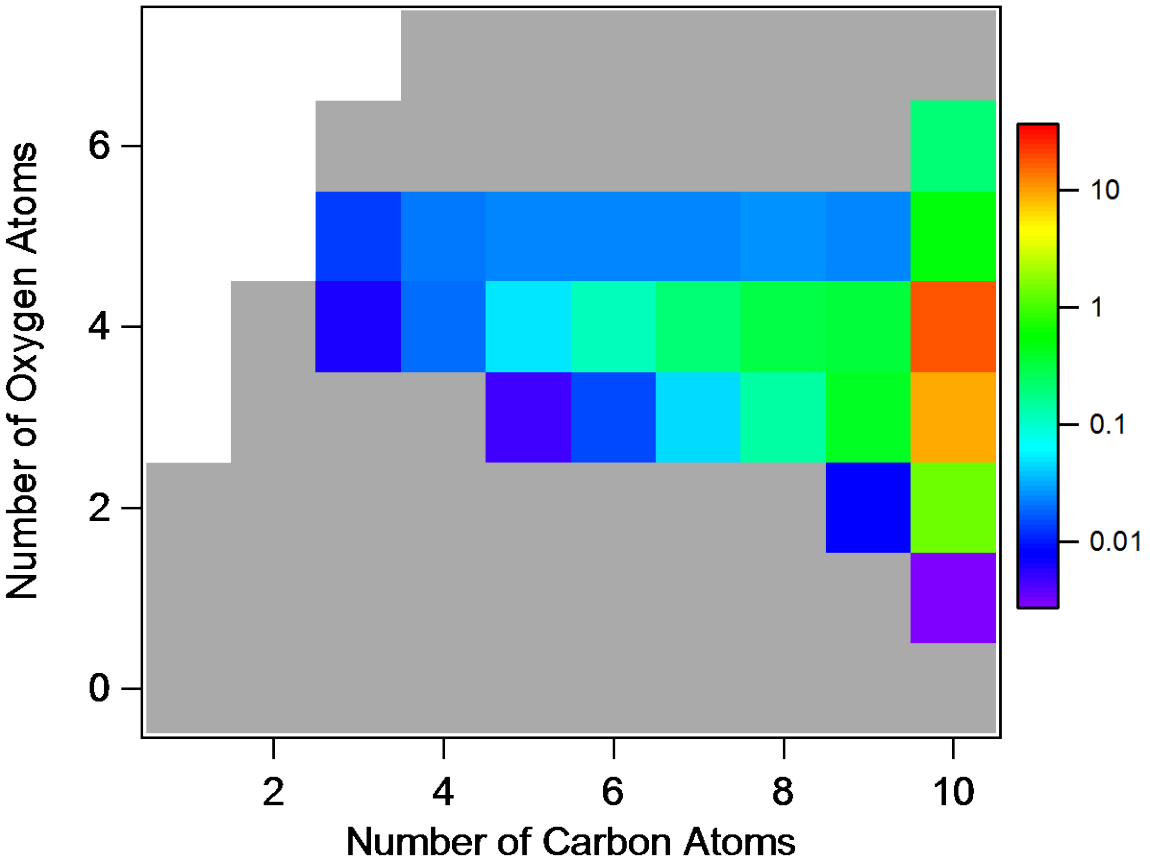
Bonus slides

An Example: α-Pinene + OH (low-NO_x)

Smog chamber observations can be fit with good fidelity



Multi-generational Oxidation



- On average, 2 oxygen atoms are added per reaction with OH
- Predominant species in SOA has 4 oxygen atoms

How much do 2nd, 3rd, etc. generations contribute?

Multi-generational Oxidation