Use of the 2-product approximation to simulate the SOA production in global models

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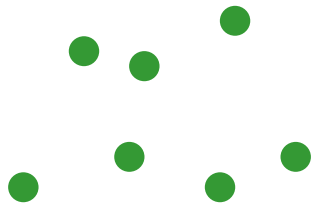
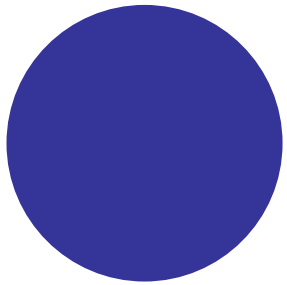
SOA formation

gas-phase
condensable products



T ↑

absorbing
aerosol phase

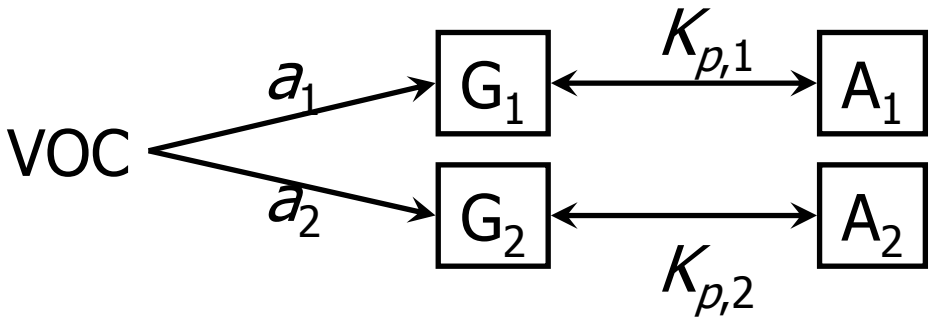


Potential of total evaporation → Upper limit of SOA formation

Potential of total SOA formation → Lower limit of SOA formation

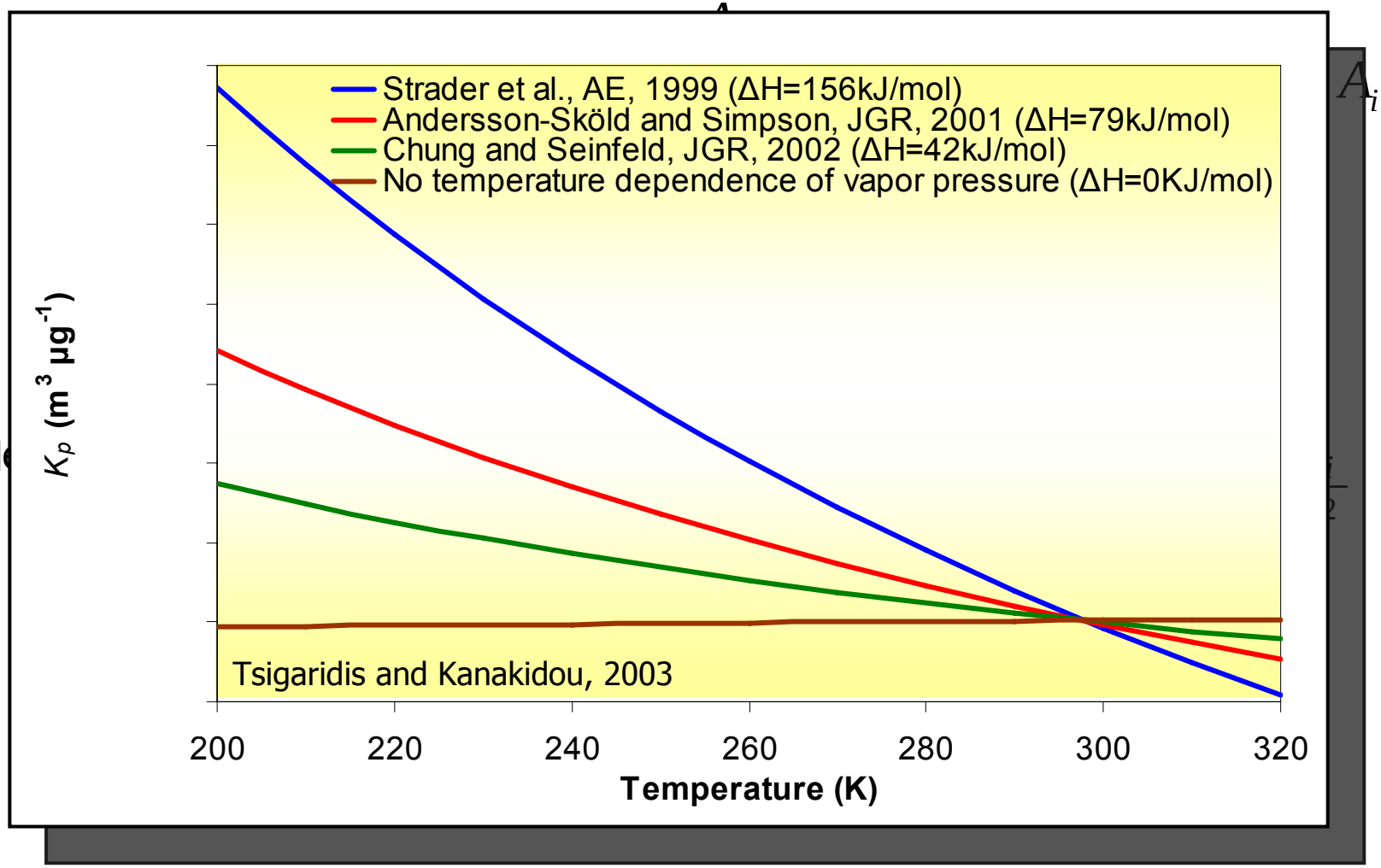
SOA formation – 2 product model

$$G_i = \frac{A_i}{K_{p,i} M_o}$$



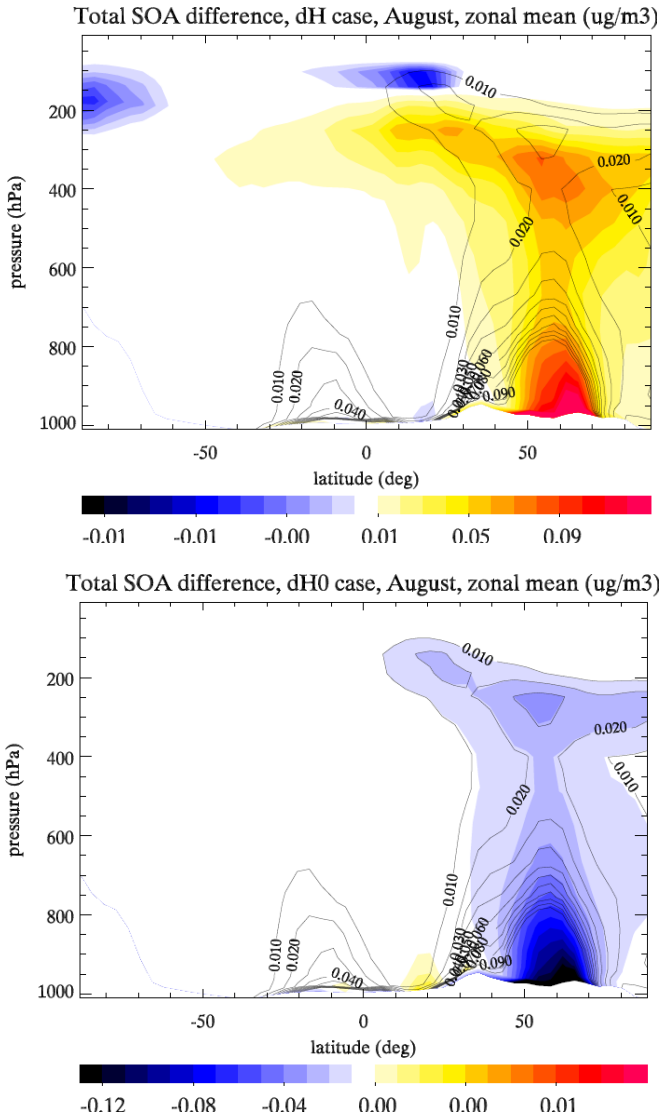
- Ideally, it should keep critical information on:
  - ✓ Total SOA mass production
  - Chemical speciation
  - Physical and chemical properties (volatility/reactivity)
  - Optical properties (absorption/scattering)
  - Hydrophilic/hydrophobic behaviour

Partitioning coefficient



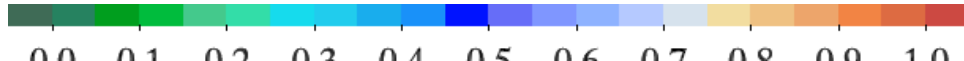
Effect of temperature

Tsigaridis and Kanakidou, 2003



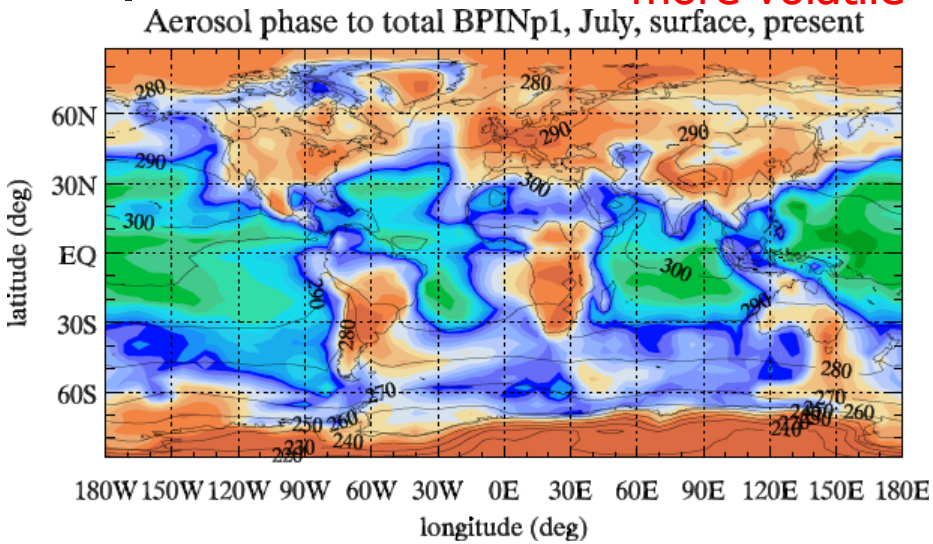
- Doubling the ΔH can lead to both doubling of aerosols and displacement of the maximum to lower altitudes.
- No dependence leads to no aerosols in the upper troposphere.

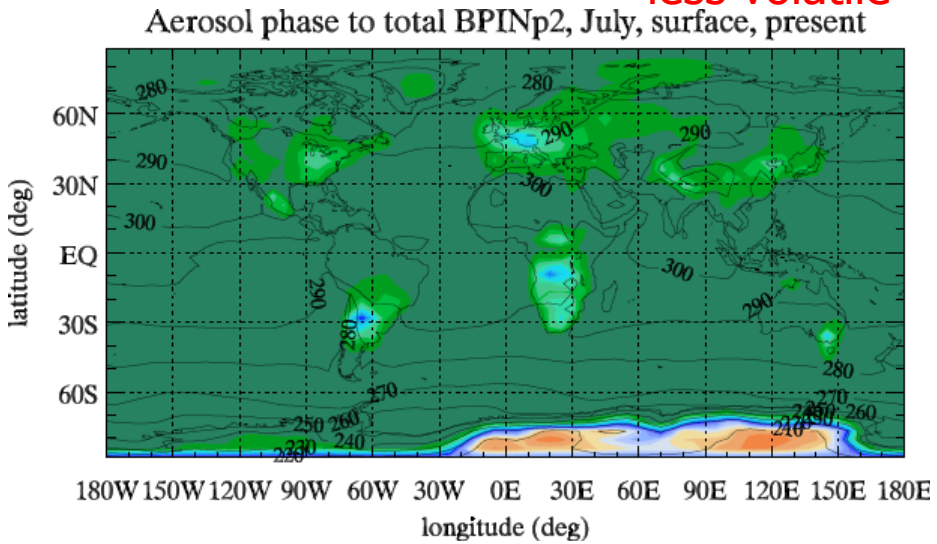
Effect of volatility

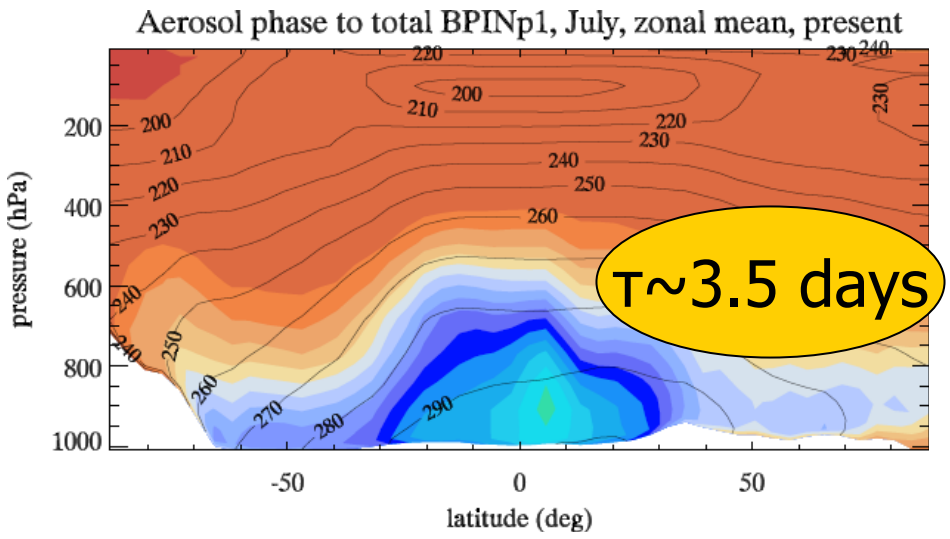


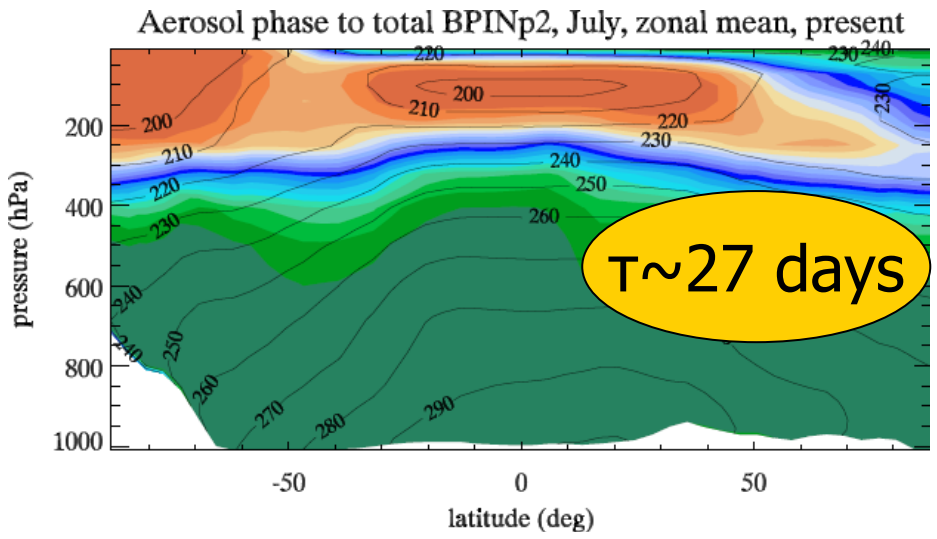
more volatile

less volatile

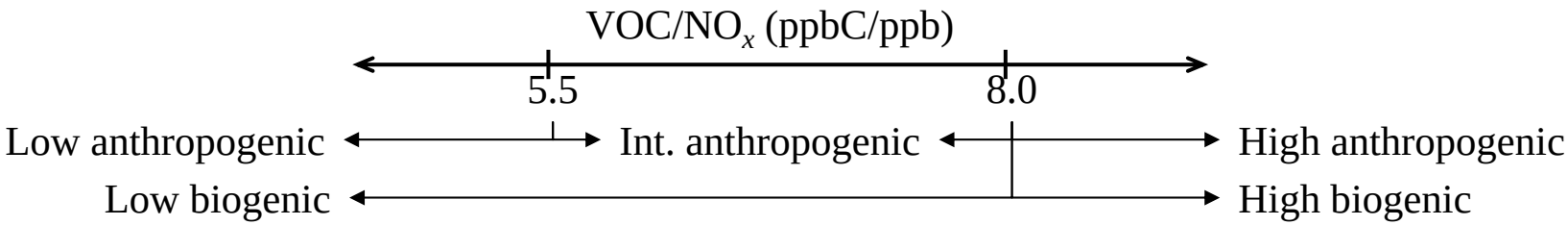






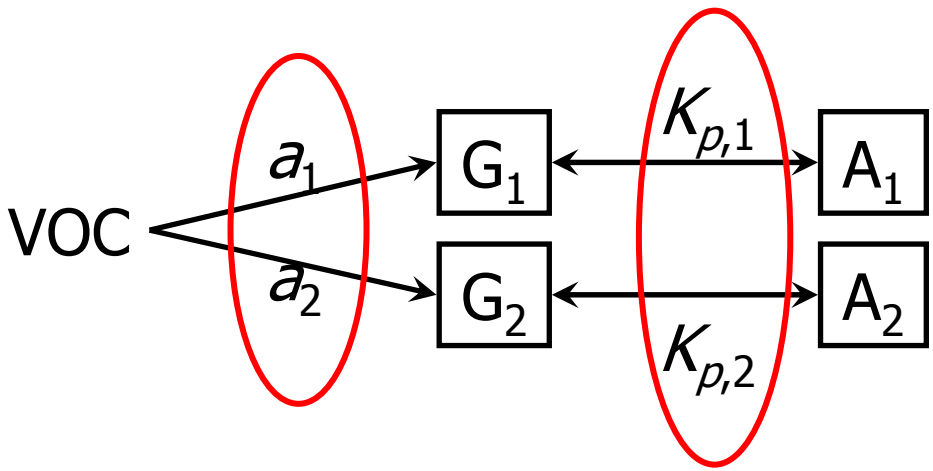


Effect of NO_x levels



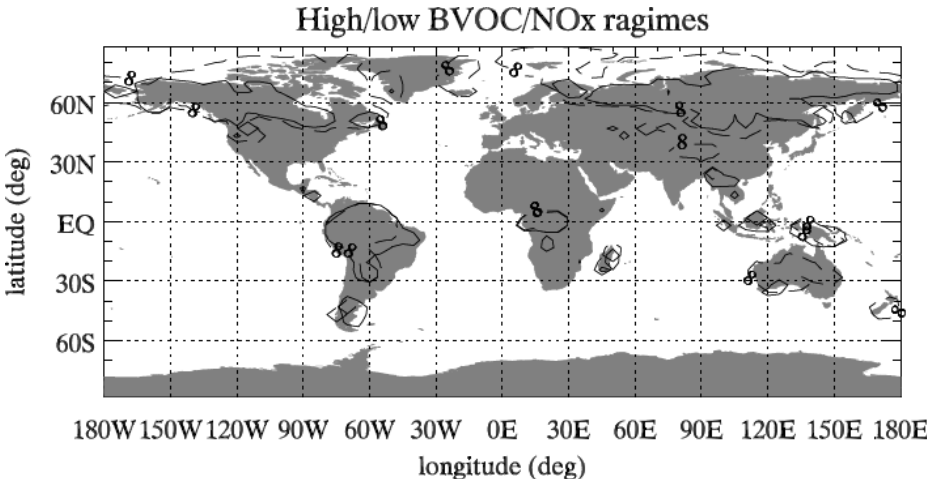
- *a*-pinene: Presto et al., 2005
- xylene: Song et al., 2005

Organic nitrates are more volatile than hydroperoxides

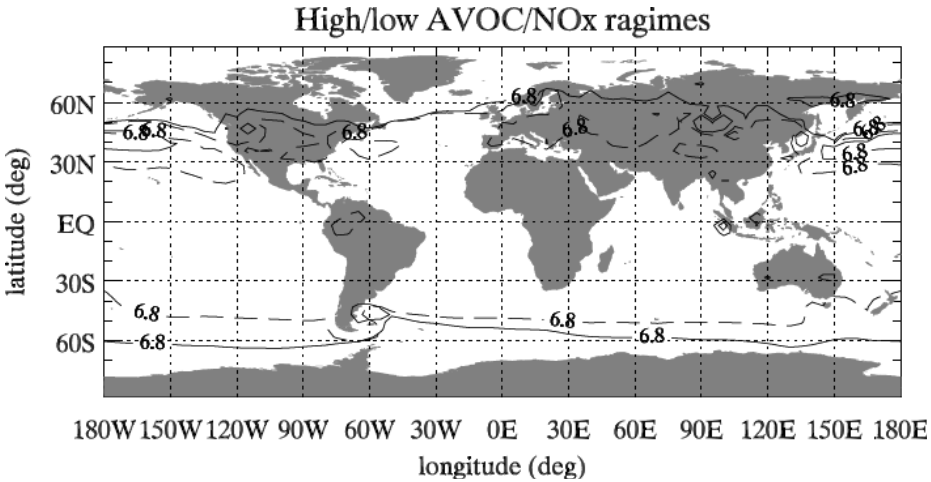


Effect of NO_x levels

a-pin + O_3 → high NOx products
→ low NOx products



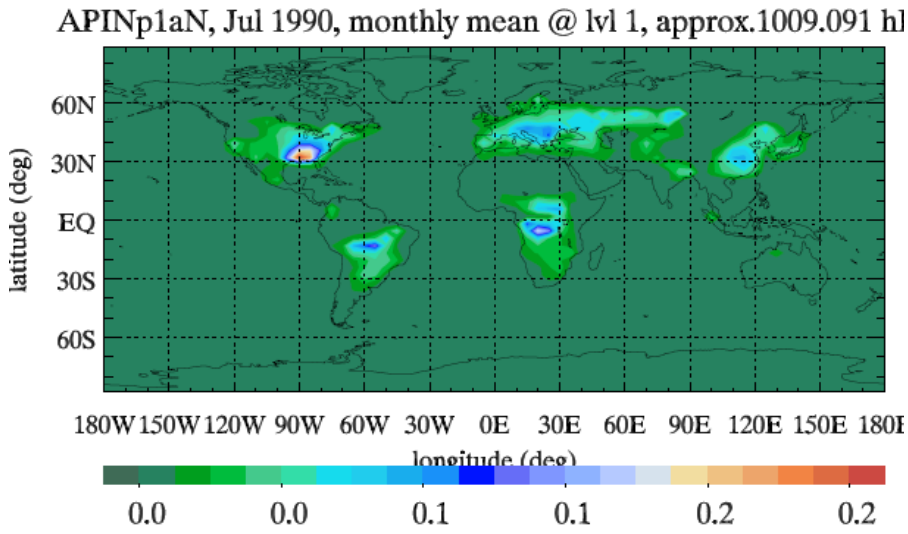
- Biogenics: high VOC/NO_x at forested regions, low outside

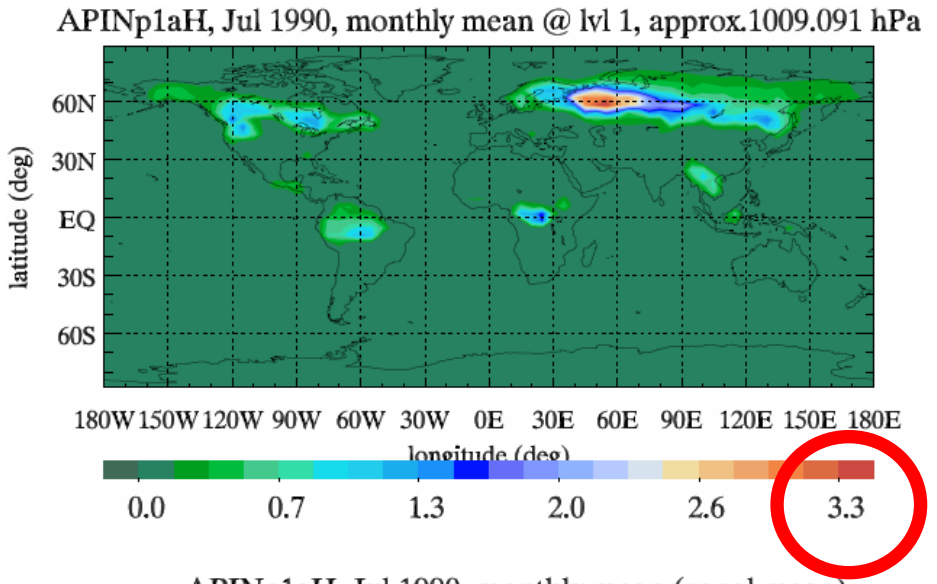


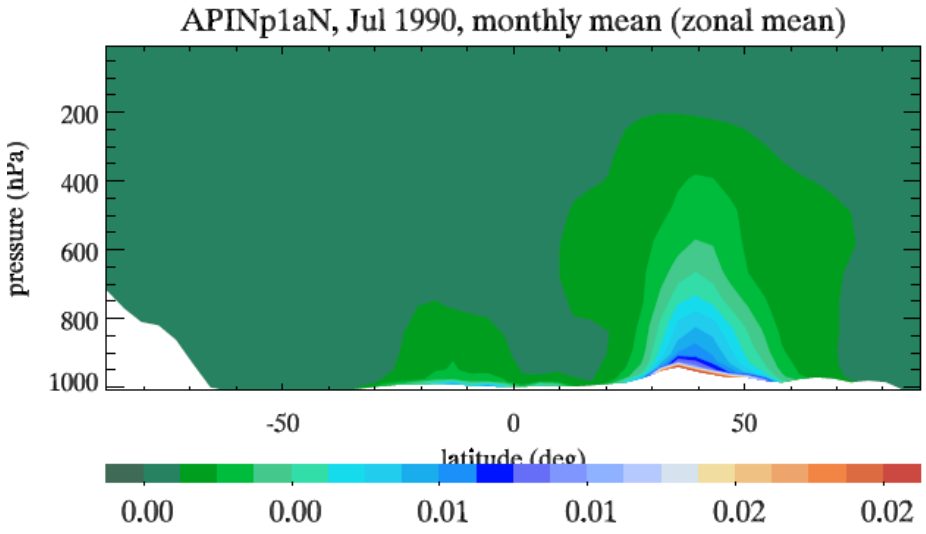
- Anthropogenics: high VOC/NO_x at high latitudes

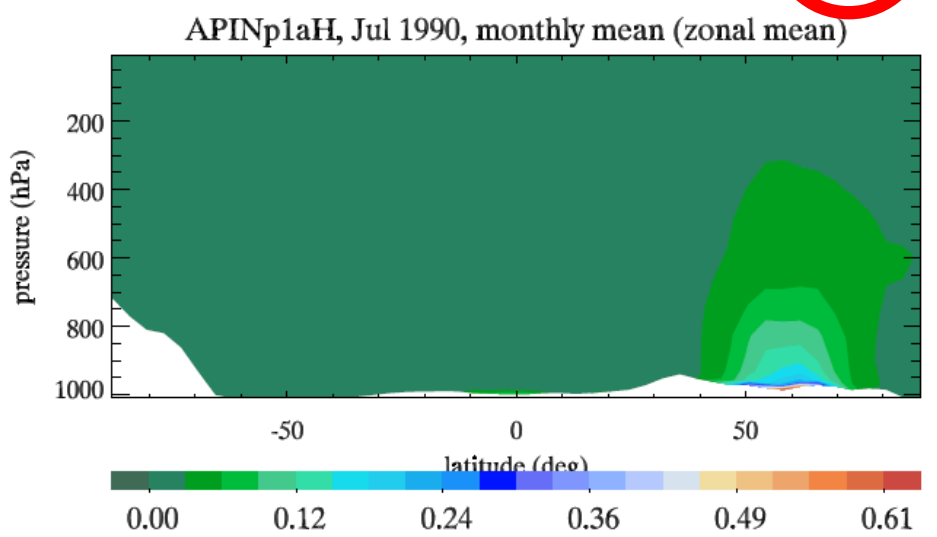
Effect of NO_x levels

a-pin + O_3 → high NOx products
→ low NOx products

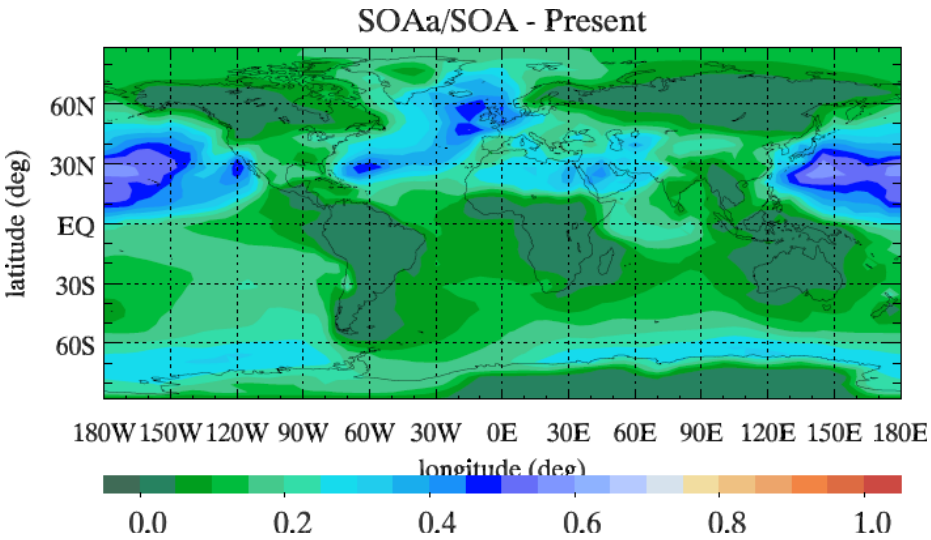


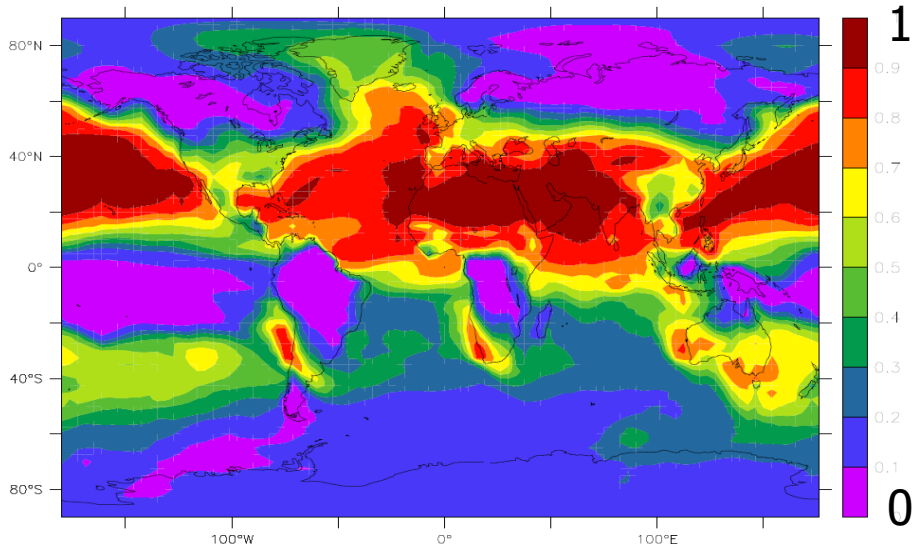






Importance of anthropogenic SOA



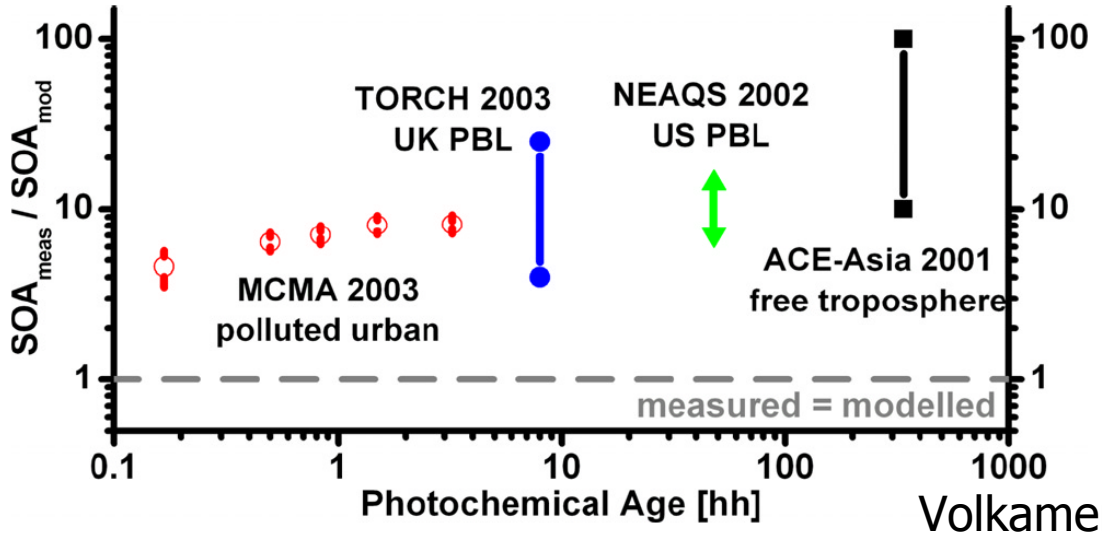


Up: TM3, annual mean

Down: LMDz/INCA, January

- Above forests SOAb dominates on the total SOA mass
- Downwind of industrialized regions SOAa can be more important than SOAb

Where are we now?



Volkamer et al., GRL, 2006

- Vast underestimations of modeled SOA in case studies
- Do we know/consider in the models:
  - All possible pathways?
    - Gas-phase chemistry and gas-to-particle partitioning
    - Multiphase chemistry (cloud processing)
    - Aerosol chemistry (polymer formation and heterogeneous chemistry)
  - All possible precursors?

Open questions

- How fast equilibrium is achieved? Are semi-volatile compounds in equilibrium between the gas and the aerosol-phase at all times?
- How inhibition of evaporation occurs? How important is oligomerization, heterogeneous reactions and oxidation by e.g. acidic particles, cloud processing?
- Quantification of the temperature effect both for the oxidation pathways and for the various products.
- Quantification of the non-carbonaceous aerosols absorbing efficiency of semi-volatile compounds.
- "Clever" lumping

2-product model: future extensions

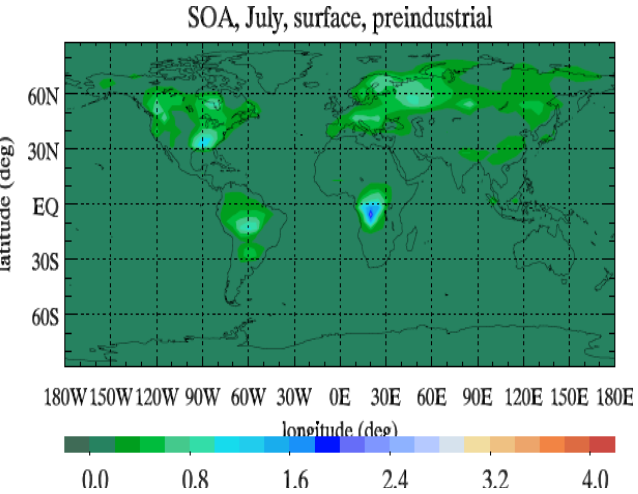
- Oxidation does not occur in one step; how does the SOA production yield changes over time? Why?
  - SOA formation from secondary products.
  - Oligomerization (Pun and Seigneur, 2007?).
  - Which are the building blocks for accretion reactions?
  - SOA ageing. Oxidation of SOA in the aerosol phase increases or decreases the aerosol mass?
  - Effect of water and other important parameters (UV radiation (Presto et al., 2005), others?).
  - Key question: Is gas and aerosol equilibrium achieved? How fast?
- How can we include the second/third/… generation products efficiently for global modeling?
- Can we separate the production yield from various oxidants, or we should treat them simultaneously?
  - OH (daytime), O_3 (24-hours), NO_3 (night) should be treated separately, is this feasible?

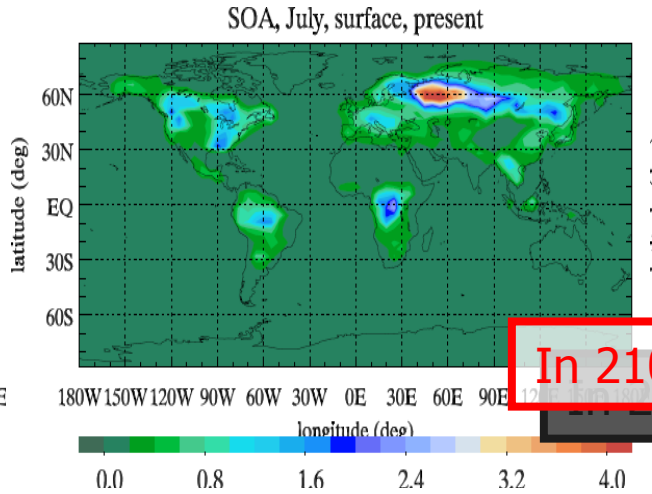
WARNING!

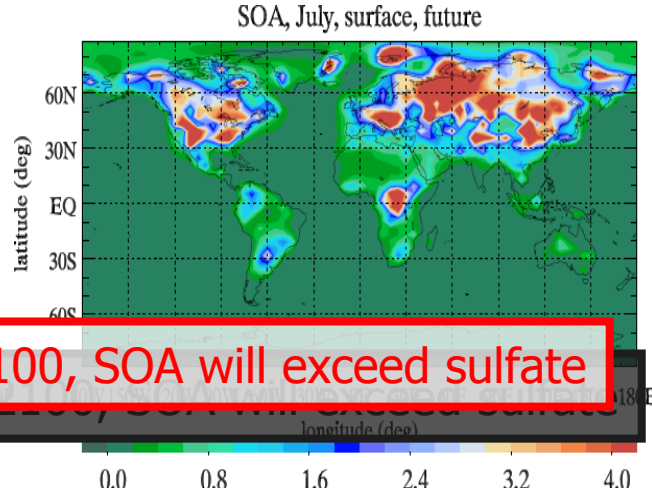
Do we have a concrete definition of SOA?

- Evaporated semivolatiles emitted as POA can condense again; are they SOA or POA?
- Oligomerized POA are still POA?

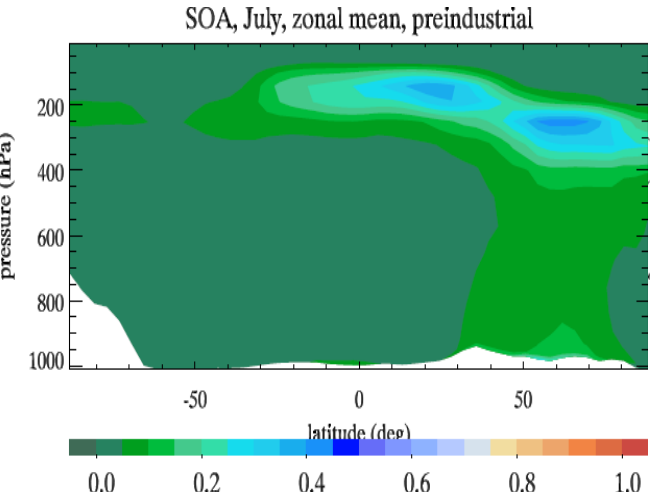
Pre-industrial/present/future importance of SOA

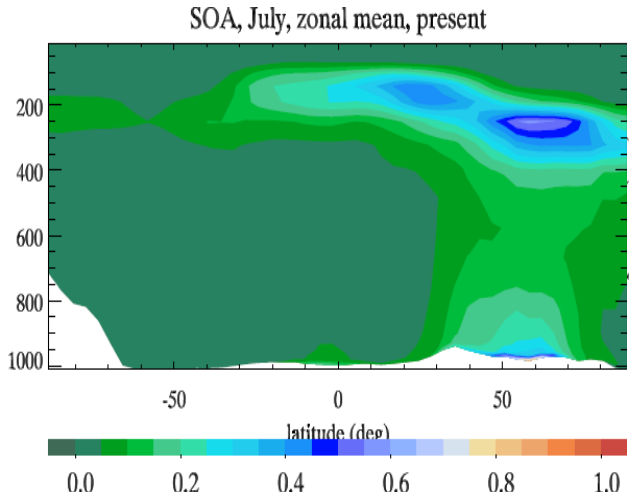


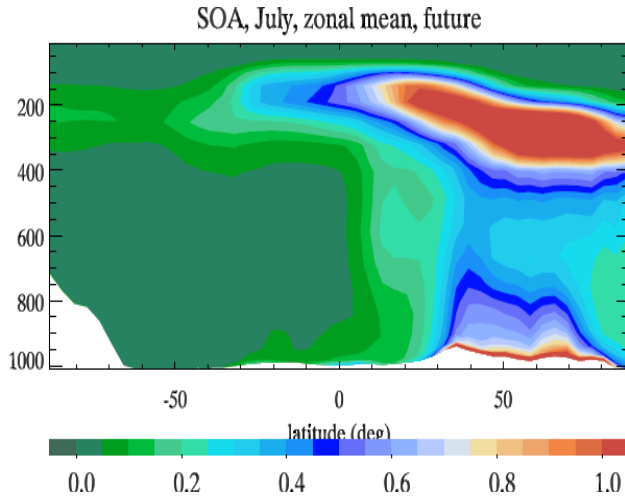




In 2100, SOA will exceed sulfate







SOAb (Tg y^{-1}):	12.8	17.4 (+36%)	51.2 (+294%)
Biog. emiss (Tg y^{-1}):	193	192 (<1%)	390 (+203%)