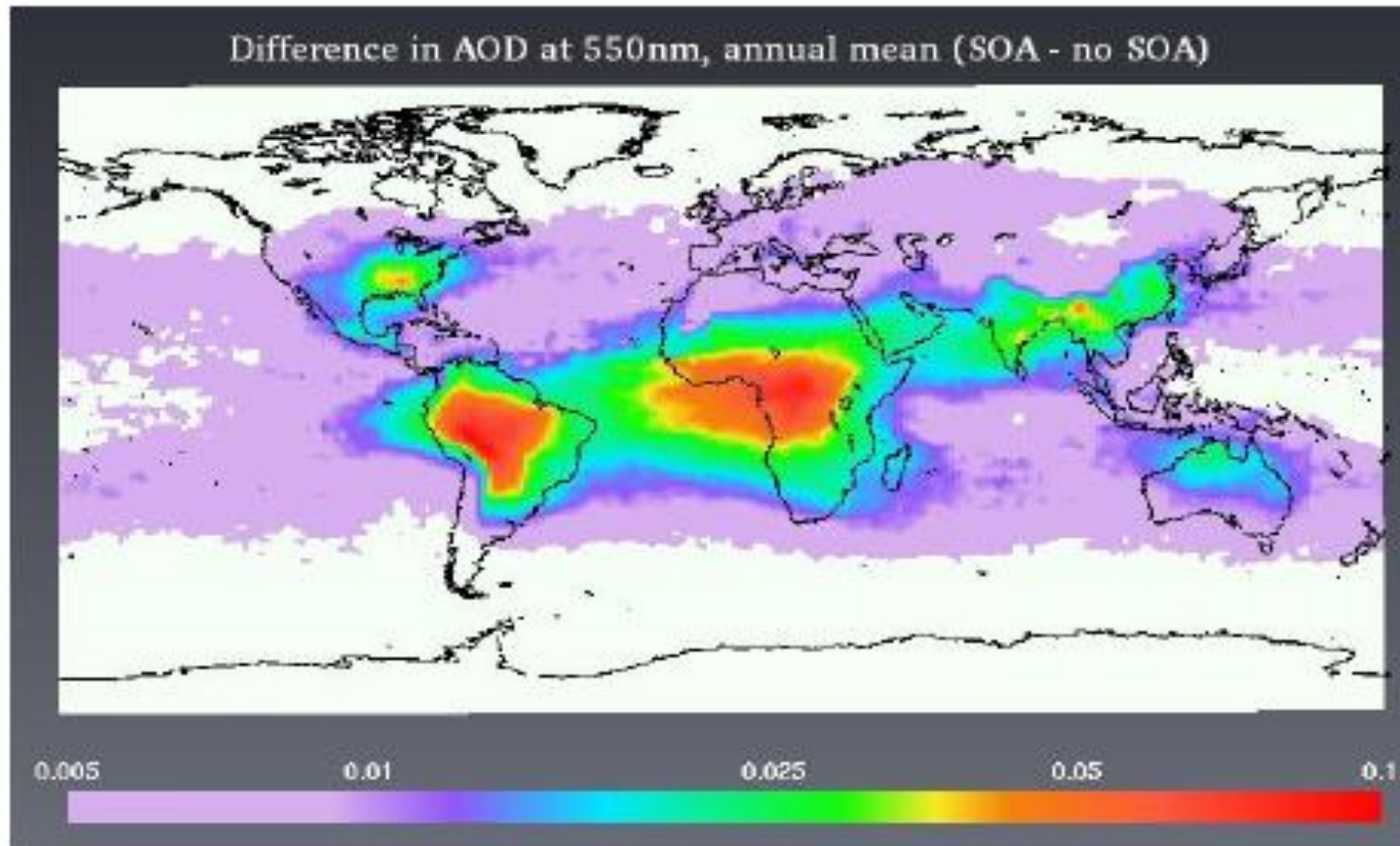


# Secondary Organic Aerosol in Global Modeling

## Issues and Approaches



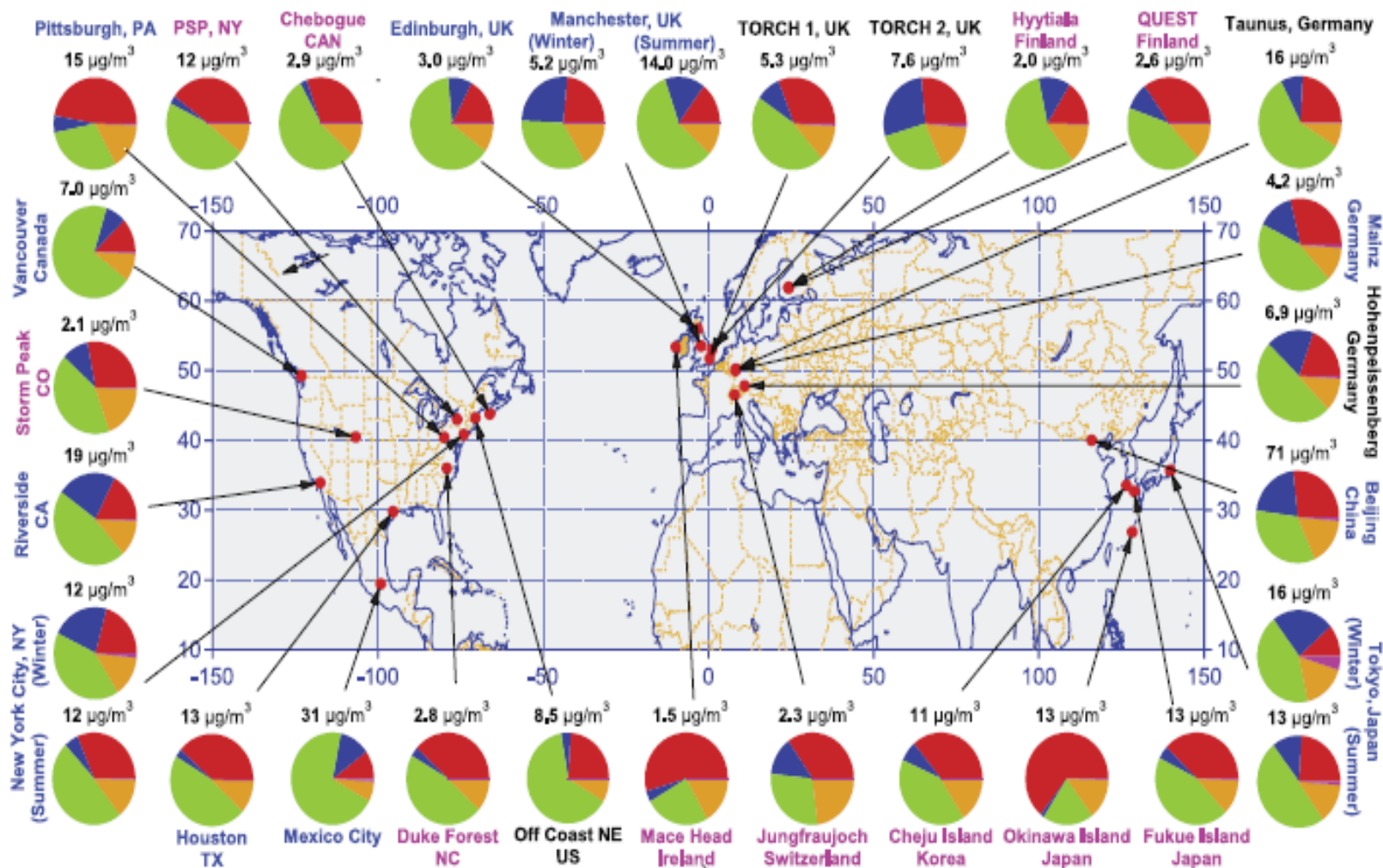
# Topics

- 1. The necessity of dealing with SOA in GCM's.
- 2. Important aspects of the chemistry of SOA formation that need to be dealt with in models (one way or another).
- 3. Some approaches to incorporating these aspects into current models, and their impact.
- (4. What next?)

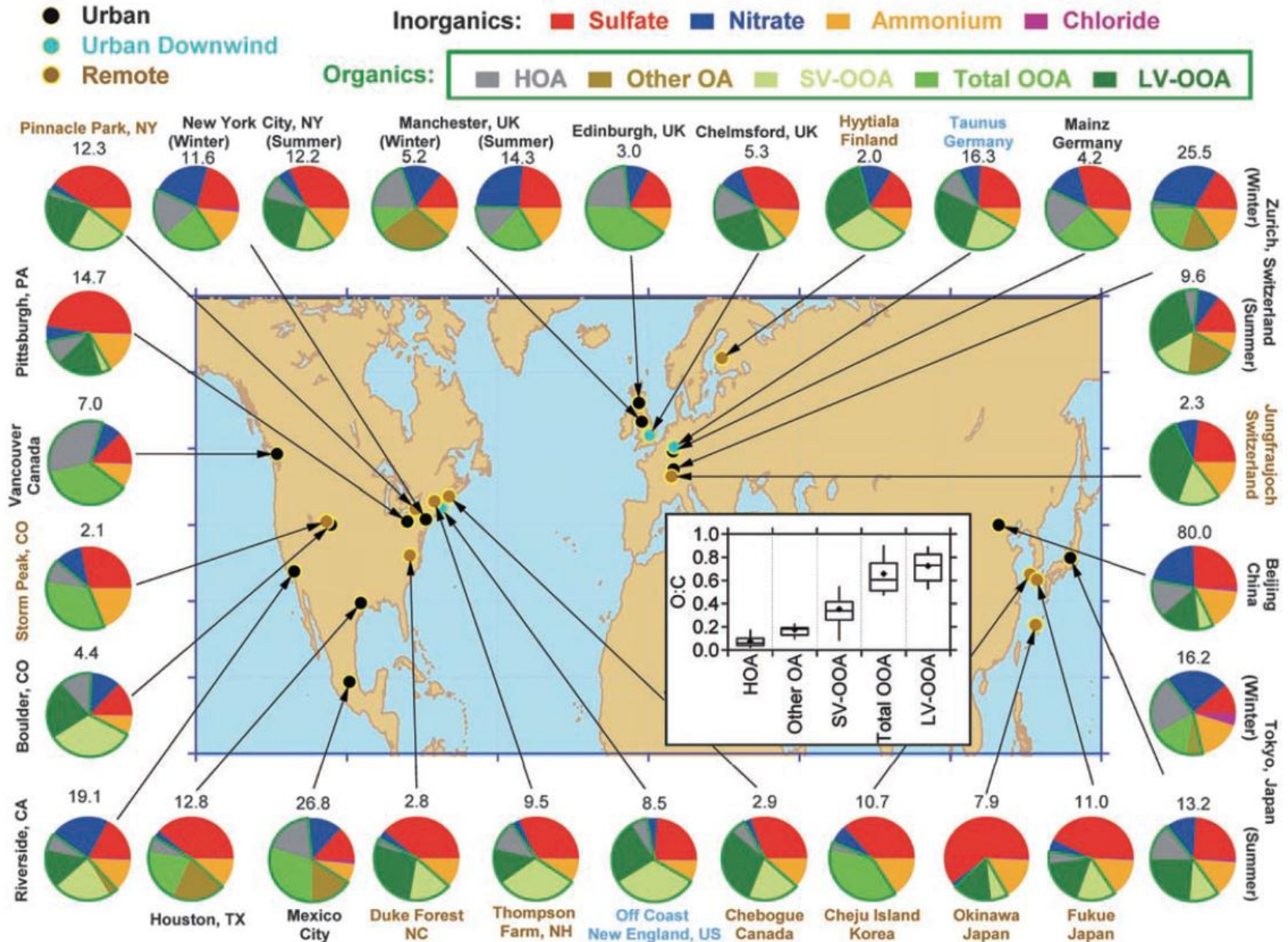
# 1. Must we deal with SOA?

- (Note: Secondary Organic Aerosol is aerosol created in the atmosphere; Primary Organic Aerosol is emitted into it)

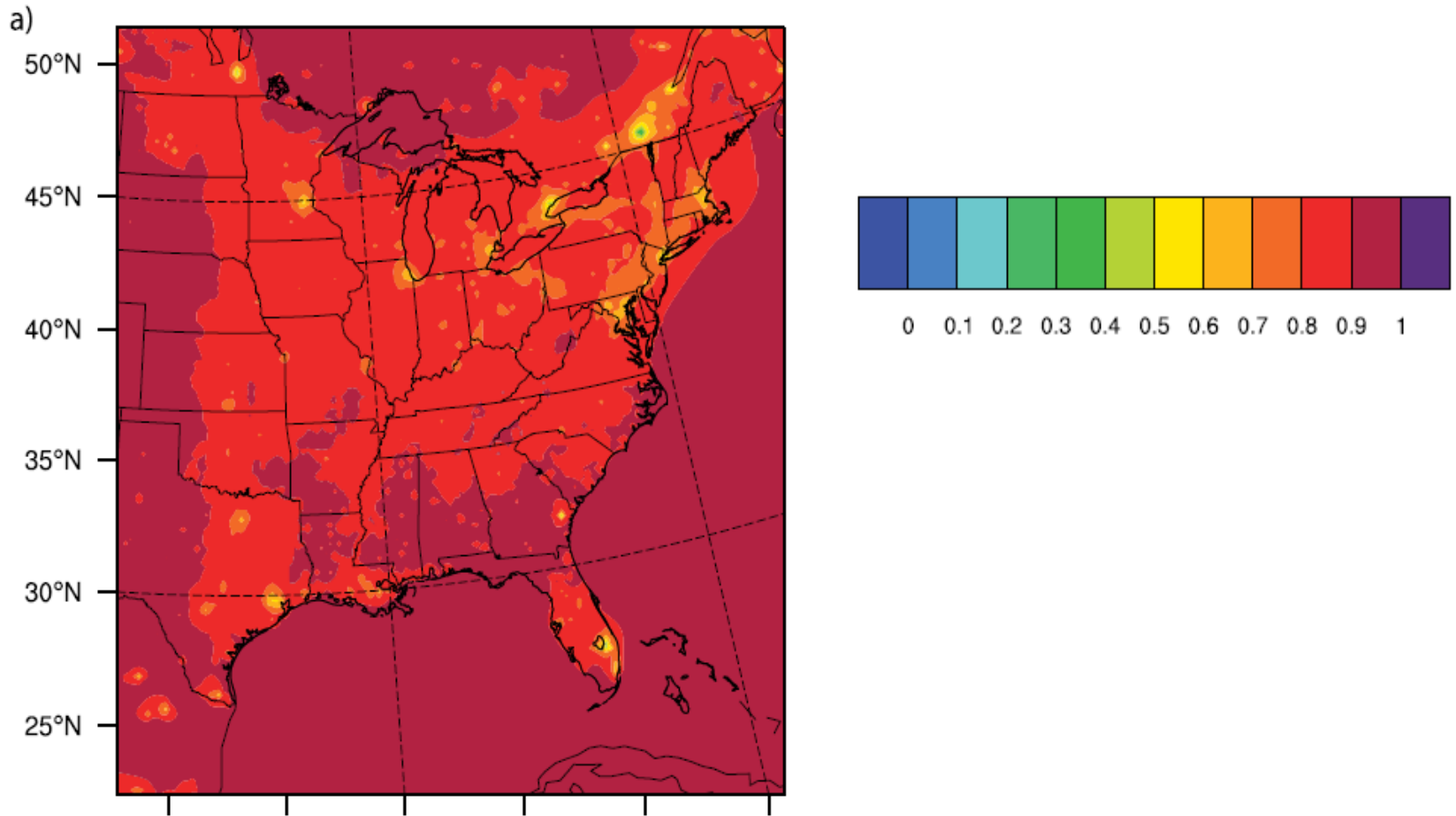
# Global Aerosol (PM2.5) composition (Zhang et al, 2007)



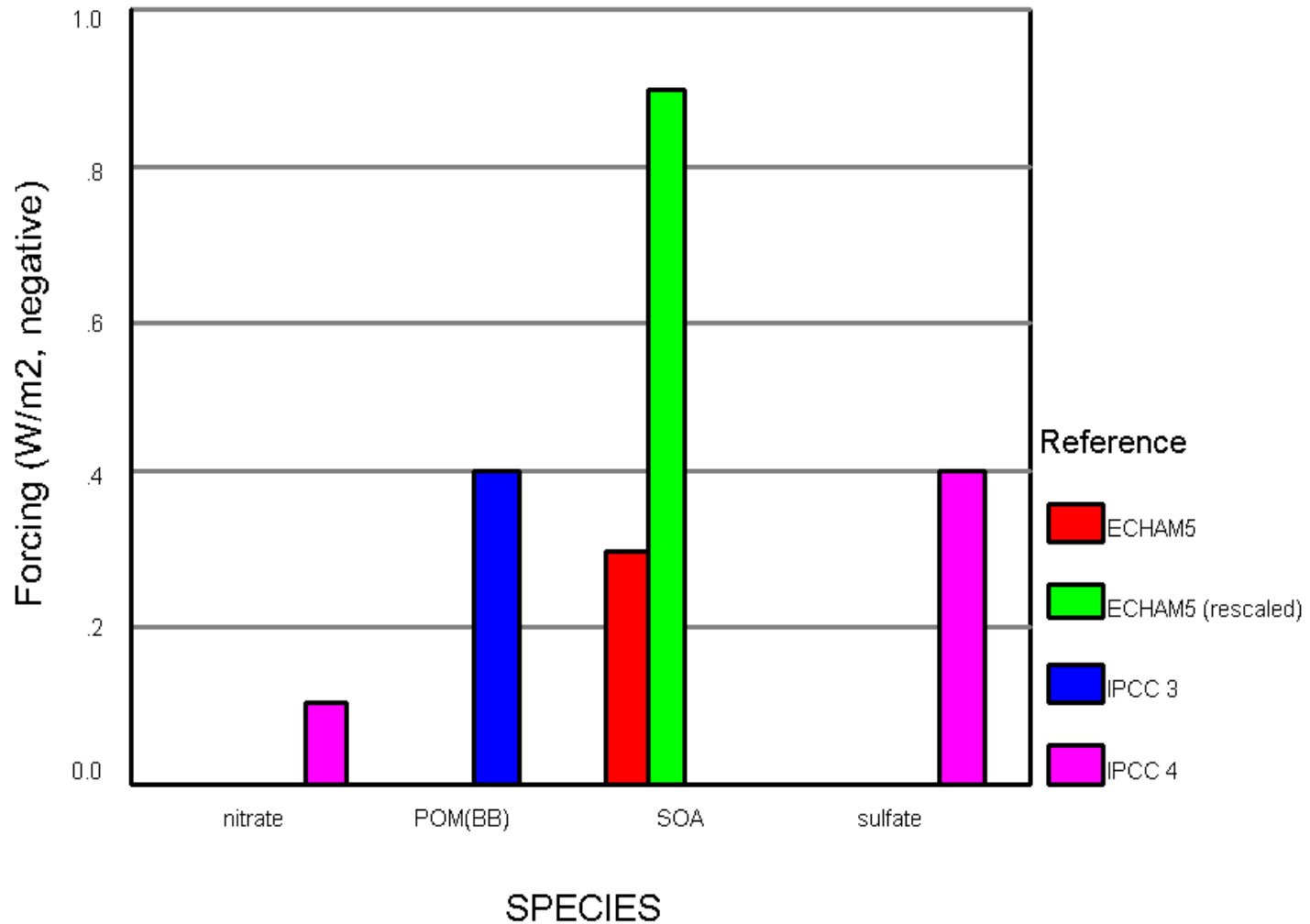
# More OA speciation (Jimenez et al, 2009)



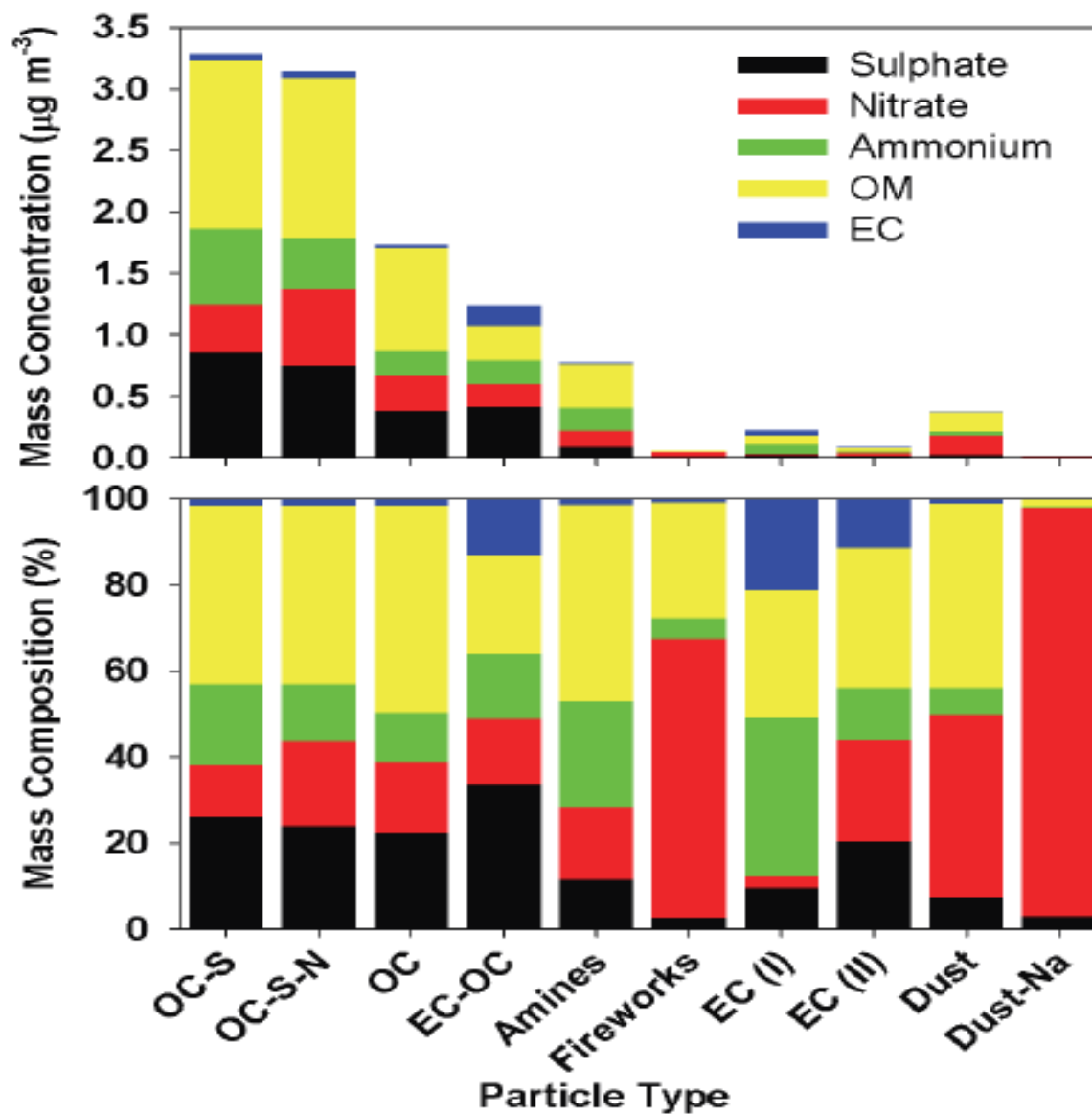
# Fraction of OA that is SOA (WRF-Chem model; Ahmadov et al, 2012)



# Comparison of direct forcing estimates for different species



Mass contribution (top) and % contribution (bottom) to the 10 particle types found (Jeong et al, 2011)





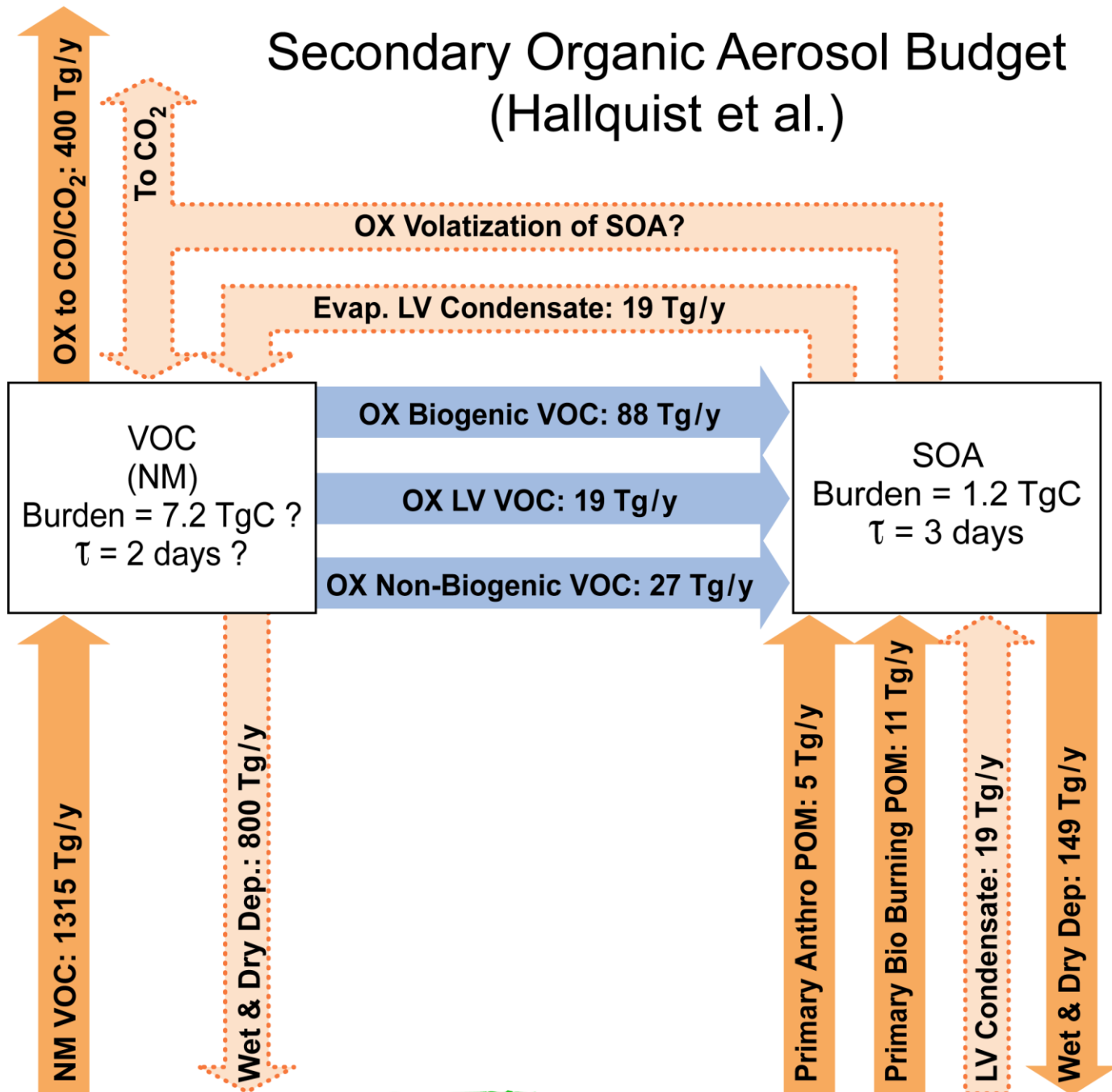
Can we use this information to estimate  
global SOA?

We need something independent of  
the models themselves: Top Down  
Estimate

# Fundamental assumptions for top-down SOA/OA budget estimates

- Most particles in troposphere are internal mixtures of sulfate and organics.
- The OC to S ratio in the internally mixed particles is 3:2 on average.
- This OC/S ratio can be applied to flux estimates, in particular the deposition flux of POC, which can then be estimated from the relatively well-known S flux.

# Secondary Organic Aerosol Budget (Hallquist et al.)

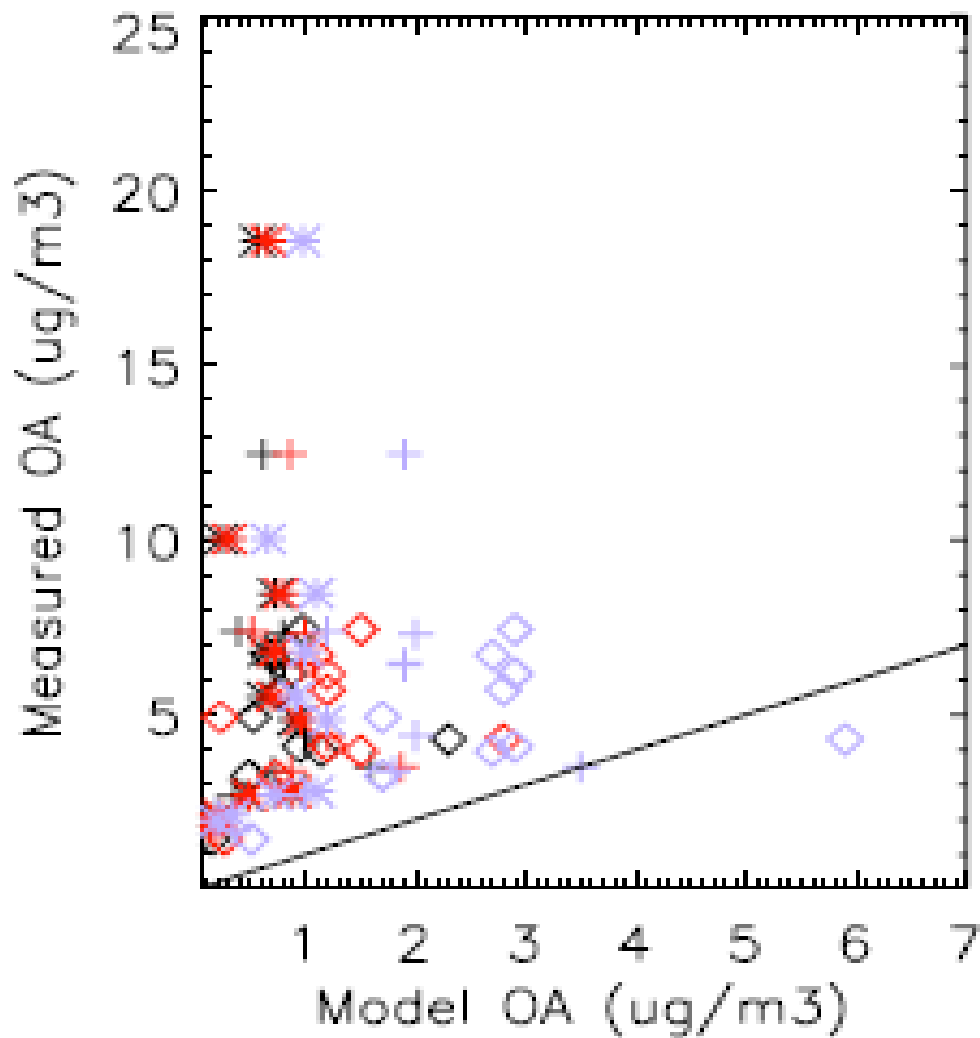


NOTE:  
Oxidants (OX)  
O<sub>3</sub>  
OH  
NO<sub>3</sub>

## 2. Important aspects of SOA chemistry

(That could potentially improve  
GCM OA predictions)

Typical OA underprediction in GCM's  
(from Hoyle et al, 2007)



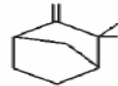
# Selected VOC's from plants

(Do we have all the species necessary?)

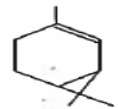
Isoprene



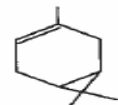
Camphene



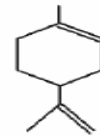
2-Carene



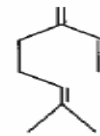
$\Delta^3$ -Carene



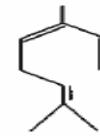
*d*-Limonene



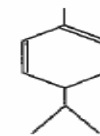
Myrcene



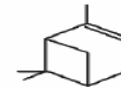
Ocimene



$\alpha$ -Phellandrene



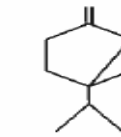
$\alpha$ -Pinene



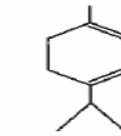
$\beta$ -Pinene



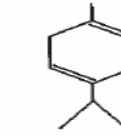
Sabinene



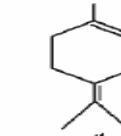
$\alpha$ -Terpinene



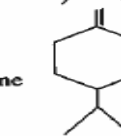
$\gamma$ -Terpinene



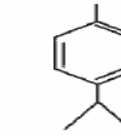
Terpinolene



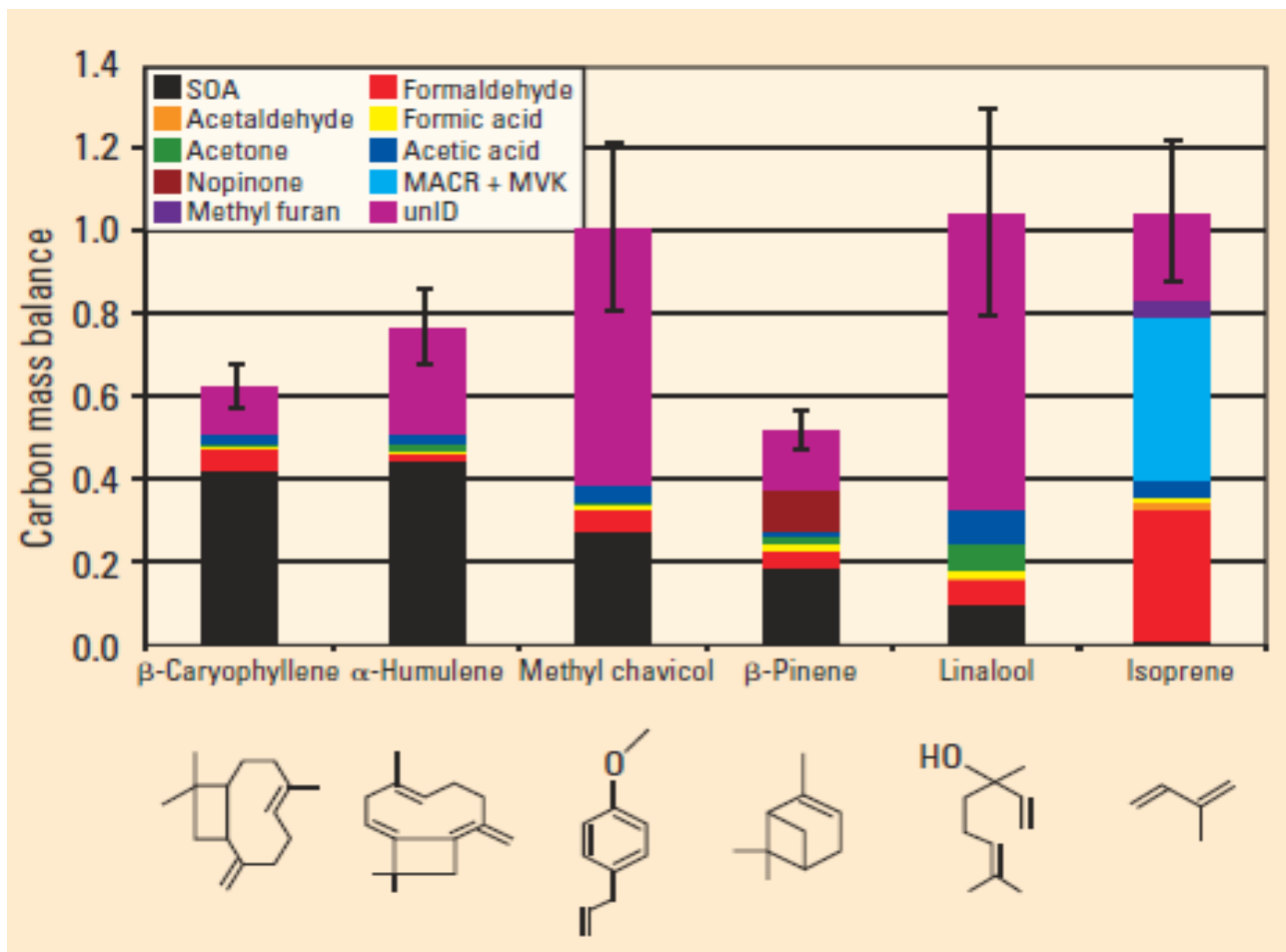
$\beta$ -Phellandrene



*p*-Cymene

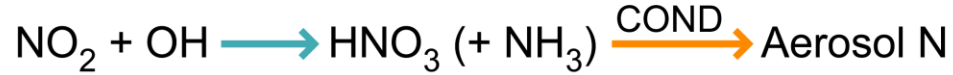


# Carbon mass balance for photochemical oxidation of six different terpinoid compounds

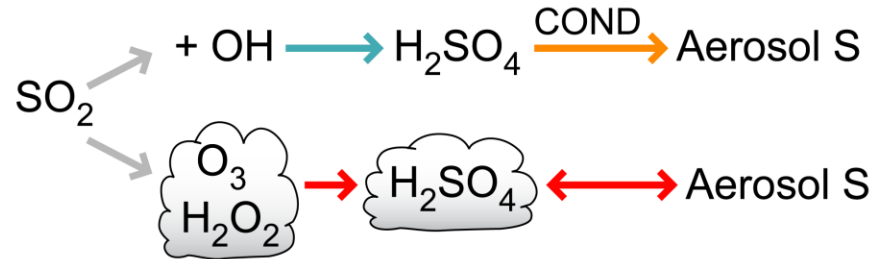


# Mass Flow for N S and C Budgets

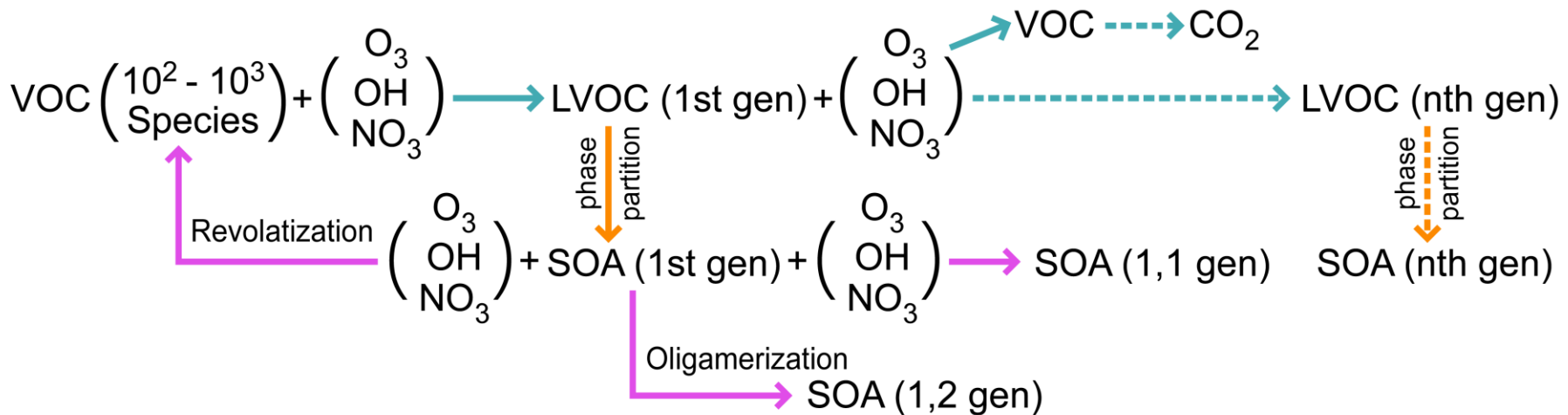
**N**



**S**



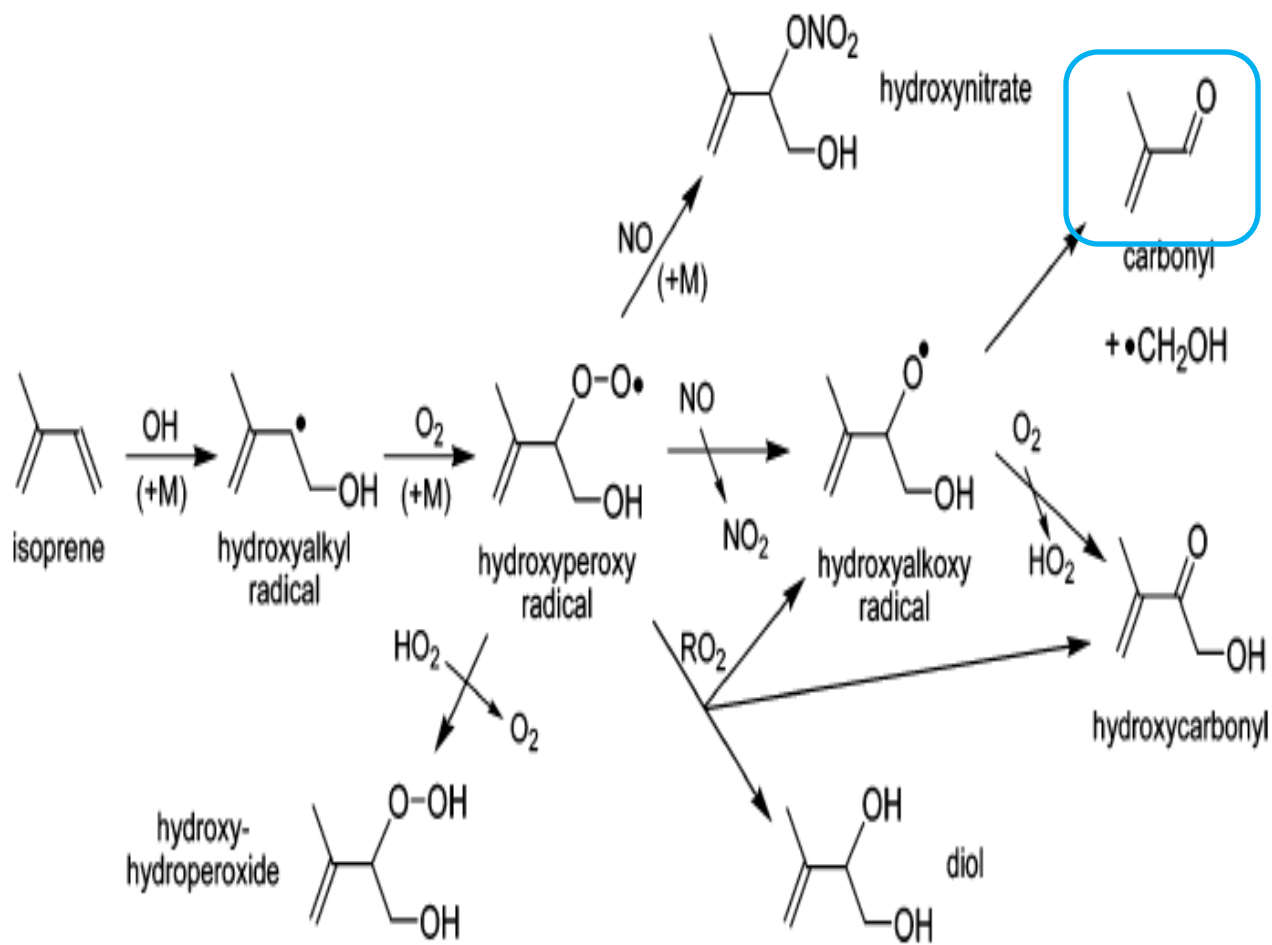
**C**





# Isoprene oxidation mechanism (from Kroll et al 2006)

(Multiple products, multiple generations)



Volatility changes due to oxidation  
(Do we have the right product volatility?)

Changes to vapor pressure of an organic compound upon addition of common functional groups, based upon group-contribution method predictions of Pankow and Asher (2007)

Functional group	Structure	Change in vapor pressure (298 K) <sup>a</sup>
Ketone	-C(O)-	0.10
Aldehyde	-C(O)H	0.085
Hydroxyl	-OH	$5.7 \times 10^{-3}$
Hydroperoxyl	-OOH	$2.5 \times 10^{-3}$
Nitrate	-ONO <sub>2</sub>	$6.8 \times 10^{-3}$
Carboxylic acid	-C(O)OH	$3.1 \times 10^{-4}$
Peroxyacid	-C(O)OOH	$3.2 \times 10^{-3}$
Acyl peroxyxynitrate	-C(O)OONO <sub>2</sub>	$2.7 \times 10^{-3}$
Extra carbon <sup>b</sup>	-CH <sub>2</sub> -, etc.	0.35 <sup>b</sup>

<sup>a</sup>Multiplicative factor.

<sup>b</sup>For comparison between changes in polarity (by addition of a functional group) and changes to size of the carbon skeleton. Vapor pressure also depends on carbon skeleton structure; see Pankow and Asher (2007).

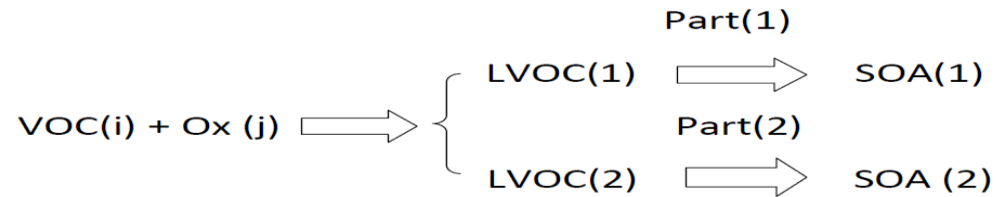
# Parameterizations of SOA production

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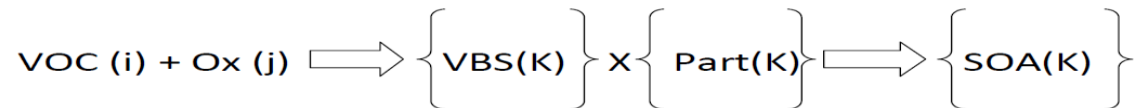
## Constant bulk yield



## Pankow/Odum 2 product equilibrium partitioning

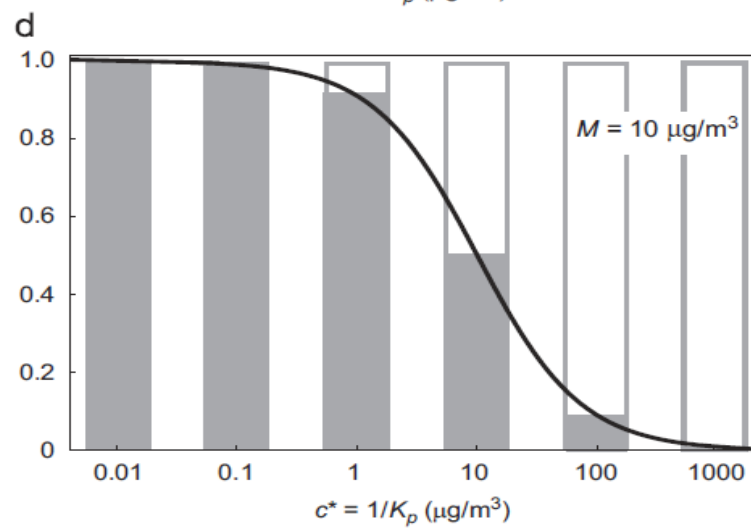
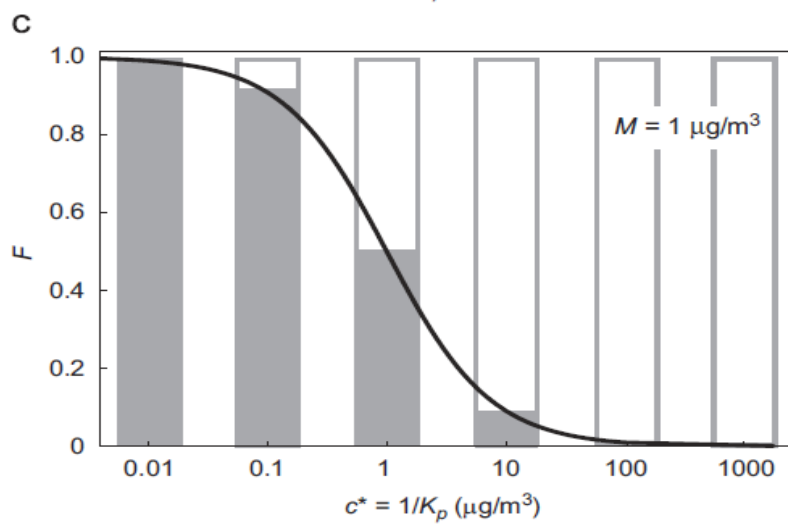
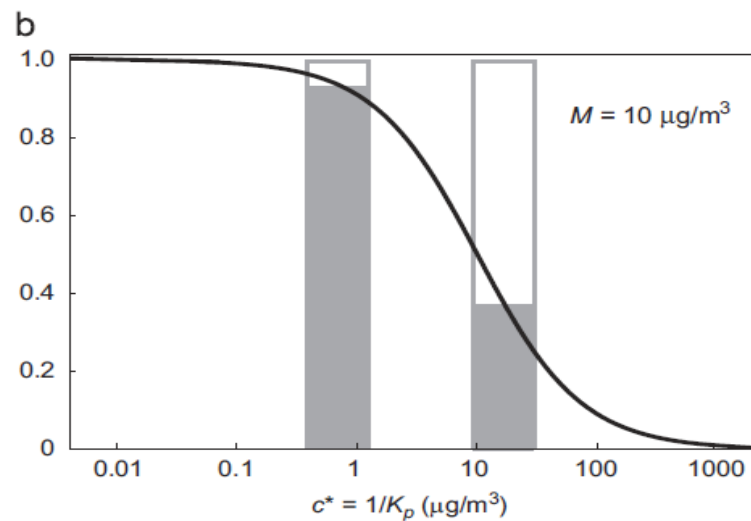
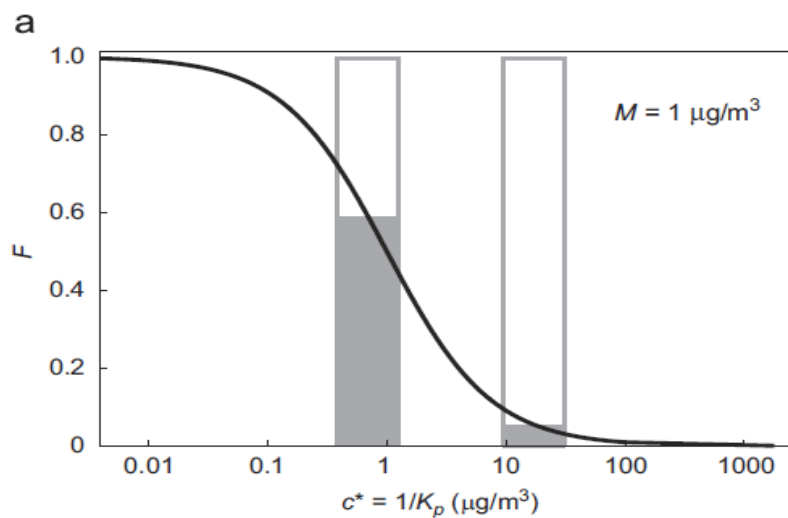


## Volatility Basis Set

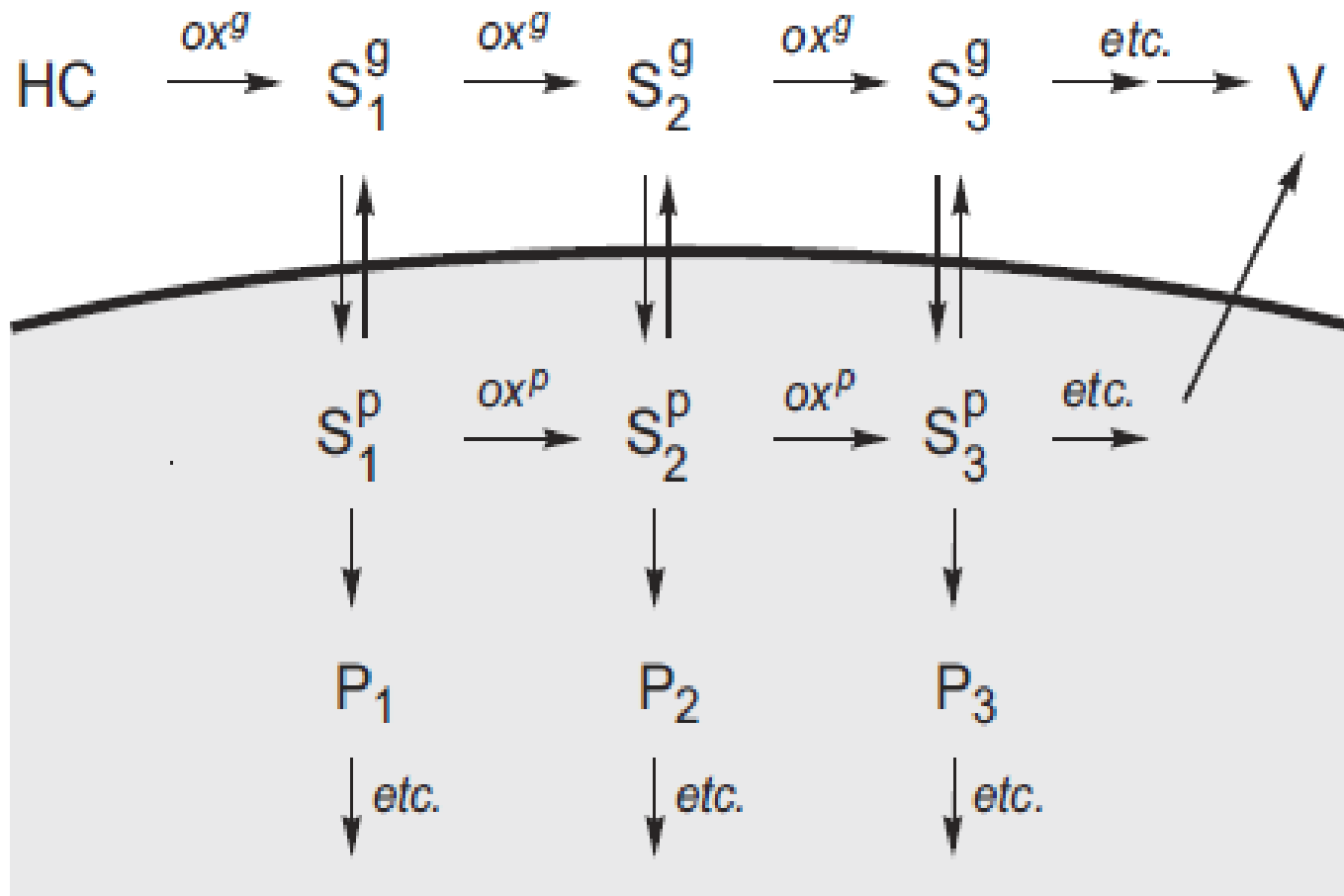


(See next slide for more detail)

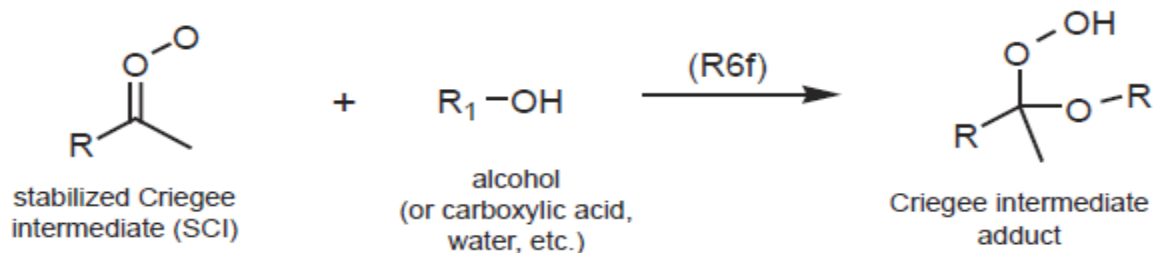
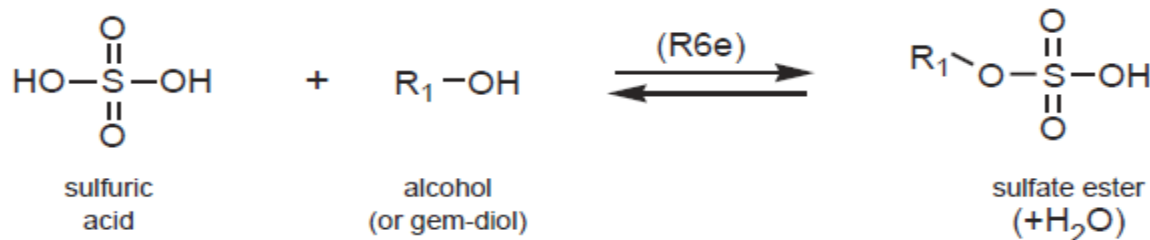
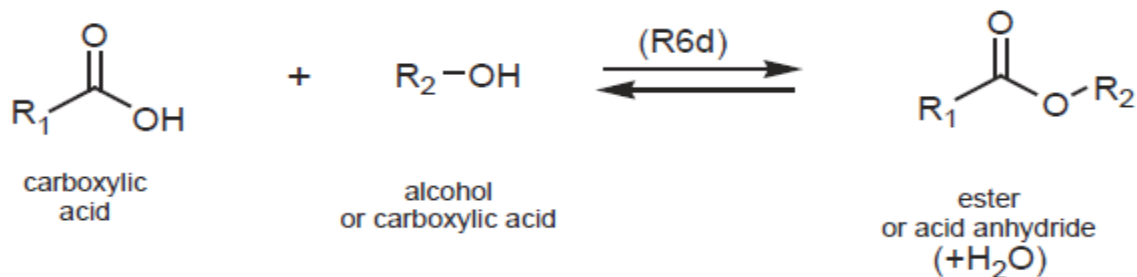
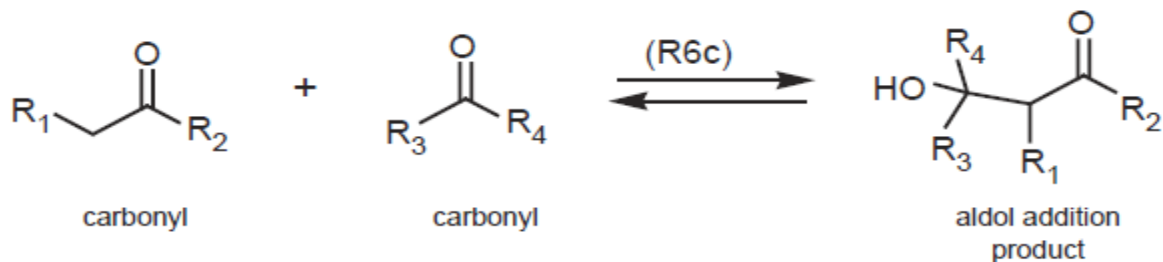
# The Volatility Basis Set approach to SOA yields



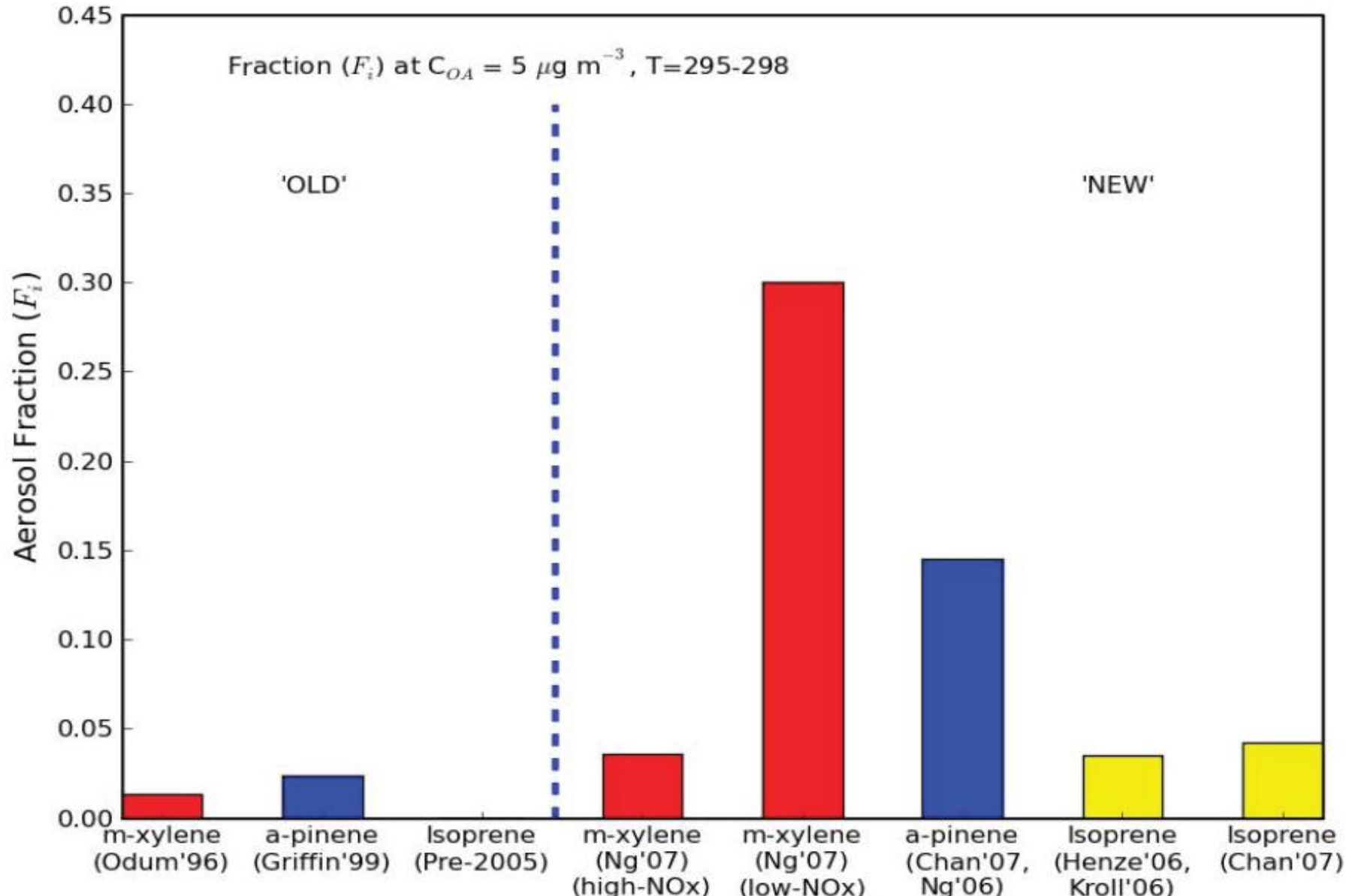
Schematic of multi-generational SOA production  
(Simplifying the MG Issue: but note the condensed phase processes)



Selected condensed phase accretion reactions that reduce volatility  
(The "P" reactions)



# Changes in reaction yields for key species (due to such issues as those just presented)

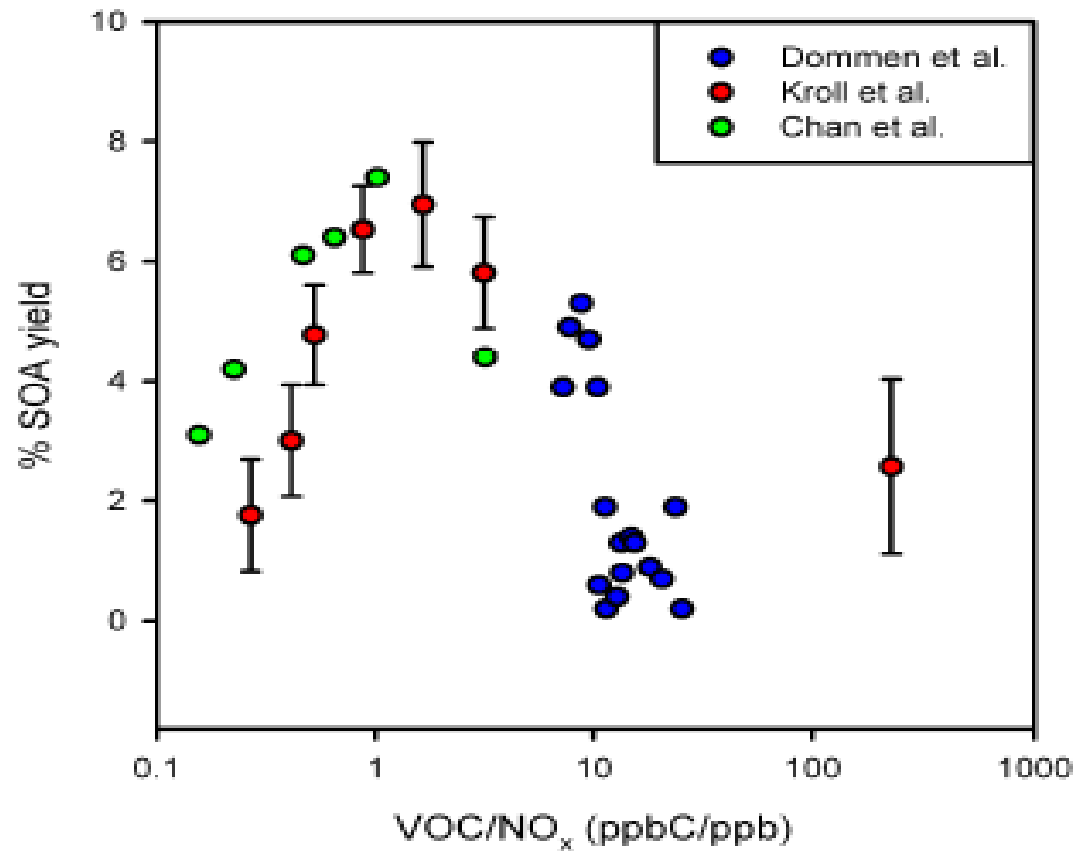


# Some additional complications

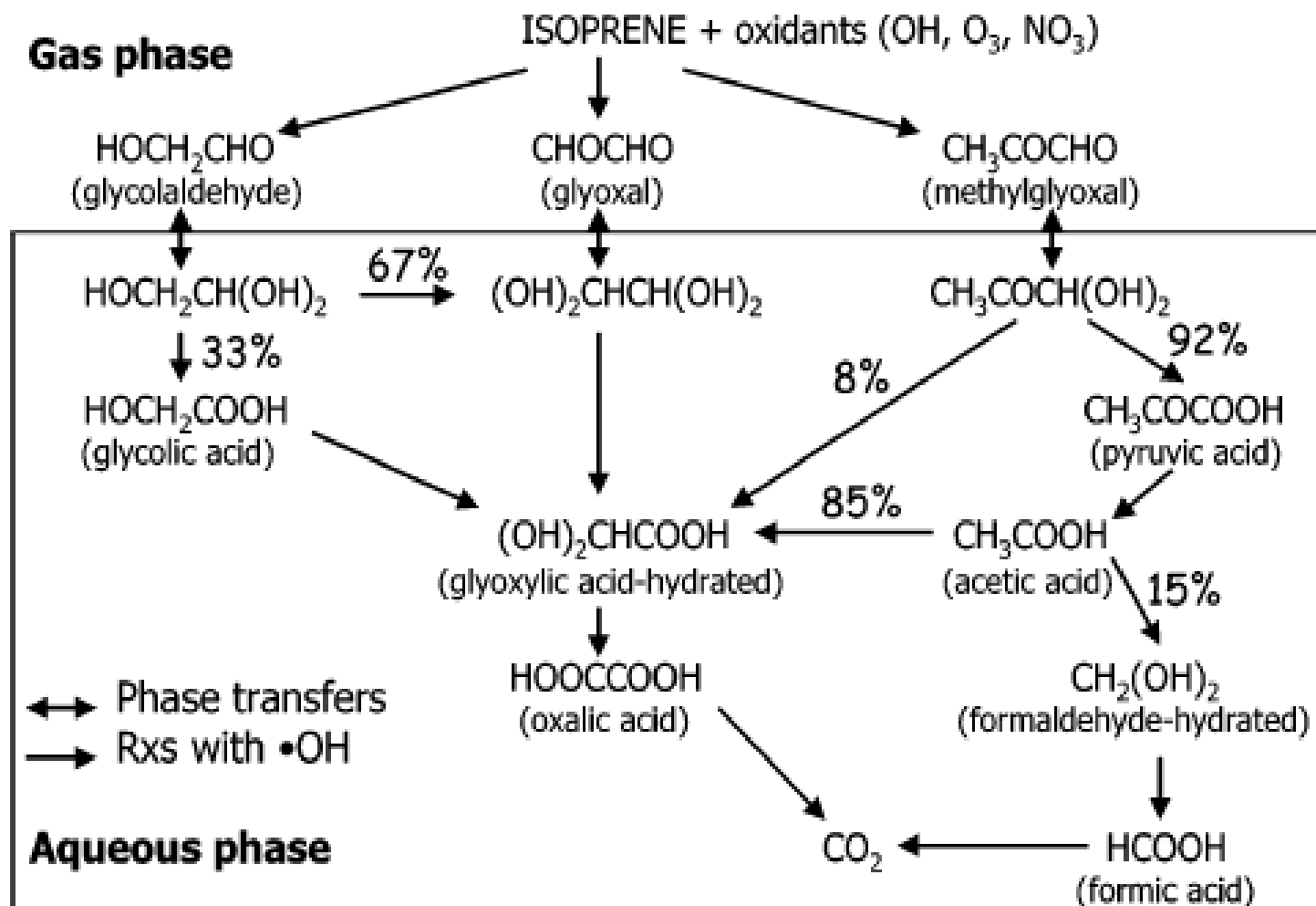
(For which there is at least some support)



# Yield of SOA vs VOC/Nox from various chamber experiments (Hoyle et al, 2011)



Aqueous-phase isoprene chemistry (from Lim et al 2005)  
 (An important “non-Pankowian” process)



# Key aspects of SOA formation impacting GCM predictions

- Oxidation of VOC's to SOA is a “multi-generational” process.
- Aging of SOA can lead to more, or less, volatile SOA species, with a complex overall phase partitioning.
- Condensed phase processes are potentially very important (including possible in-cloud SOA formation, accretion reactions, etc.).
- The yield of SOA from precursors is a function of the **detailed** pre-existing aerosol composition.

### 3. SOA formation in selected current GCM's

What is the impact of incorporating some of the above processes in global models?

# Comparison of selected model SOA mechanisms

Model	SOA Precursors	SOA formation process	Primary SOA source
IMPACT (UMI) Lin et al (2012)	26 precursors, explicit or surrogate, including alkenes, alkanes, terpinoids, aromatics	Modified explicit chemistry of Ito et al (2007), aqueous phase oligomerization as per Fu et al (2008)	Isoprene
PNNL CAM5/MMF (Wang et al, 2011)	Isoprene, hvly alkenes, alkanes, aromatics monoterpenes,	Explicit bulk yields for precursors; Direct reversible condensation of LVOC	Monoterpenes
Oslo CTM2 (Hoyle et al, 2007)	Aromatics, monoterpenes, sesquiterpenes, isoprene, ORVOC	OH, O <sub>3</sub> , NO <sub>3</sub> reacting with 5 terpene classes, isoprene and aromatics; 2 product Odum/Pankow partitioning; hydrophobic aging	Terpenes
STOCHEM CRI v2-R5 (Uttembi et al, 2011)	Isoprene, pinene's, aromatics, cyclic anhydride products	2 gen. oxidation (by O <sub>3</sub> , OH, NO <sub>3</sub> ) with reduced MCM 3.1 reaction set (555 reactions of 195 species); O/P part.	Biogenic (likely isoprene but not specified)
ECHAM5-HAM (O'Donnell et al, 2011)	Isoprene, monoterpenes, aromatics (3)	OH reacting w/ (isoprene or "anthropogenics", O <sub>3</sub> w/ monoterpenes, O/P part.	Isoprene
GEOS-CHEM (Henze et al, 2008)	Aromatics, terpenes, isoprene, alcohols	VAC reactions with RO <sub>x</sub> and No <sub>x</sub> ;  2 P O/P partitioning	Isoprene
GISS GCM II (Farina et al, 2010)	11 different VOC precursor groupings including various terpenes, aromatics, aliphatics, olefins and isoprene	All precursors react with O <sub>3</sub> , OH and NO <sub>3</sub> under high and low NO <sub>x</sub> ; VBS(4); multigenerational oxidation	Terpenes
WRF-CHEM (Regional) (Ahmadov et al, 2012)	11 different VOC precursor classes including alkanes, alkenes, terpenes, aromatics and isoprene	RACM-ESRL chemistry plus updated VOC+OH reactions; VBS(4); multi-generational aging	Biogenic (unspecified)
AeroCom Mean (Textor et al, 2006)	Terpenes	Explicit bulk yields (5%) added to POA	Terpenes

# Comparison of selected model SOA results

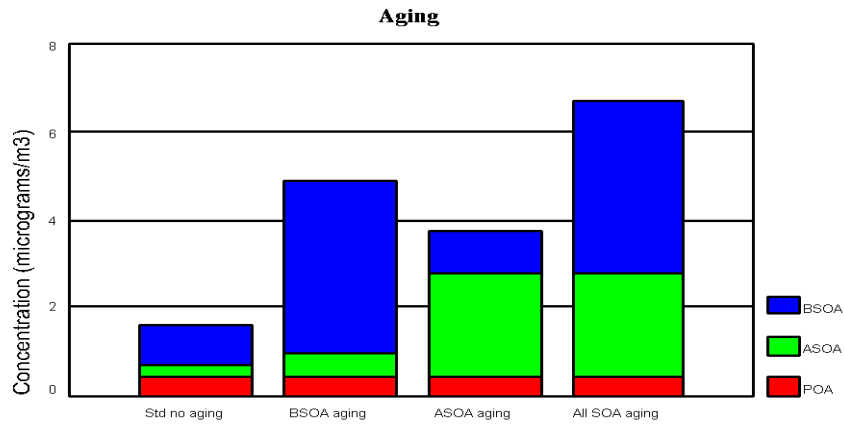
Model	POM burden (Tg)	SOA burden (Tg)	SOA source/sink (Tg/yr)
Top Down ( Hallquist et al, 2009)	2.6	2.4	300 (240)
PNNL CAM5/MMF (Wang et al, 2011)	2.9	1.8	103
Oslo CTM2 (Hoyle et al, 2007)	~1	0.52 <span style="color: red;">SS</span> (0.52-1.78)	55 (55-178)
STOCHEM CRI v2-R5 (Utembi et al, 2011)	1.1	0.23	22.5
ECHAM5-HAM (O'Donnell et al, 2011)	0.99	0.83	27
GEOS-CHEM (Henze et al, 2008)	NA	0.81	30
GISS GCM II (Farina et al, 2010)	NA	0.54-3.3 <span style="color: red;">SS</span>	29-75
WRF-CHEM (Regional) (Ahmadvov et al (12012)	NA	~ 3	NA
IMPACT (UMI) (Lin et al, 2012)	1.97-2.54	1.08-1.65 <span style="color: red;">SS</span>	91-121
AeroCom Mean (Textor et al, 2006)	1.7	~0.3	15

Sensitivity tests with the Oslo CTM2 model showing the impact of model assumptions on SOA production

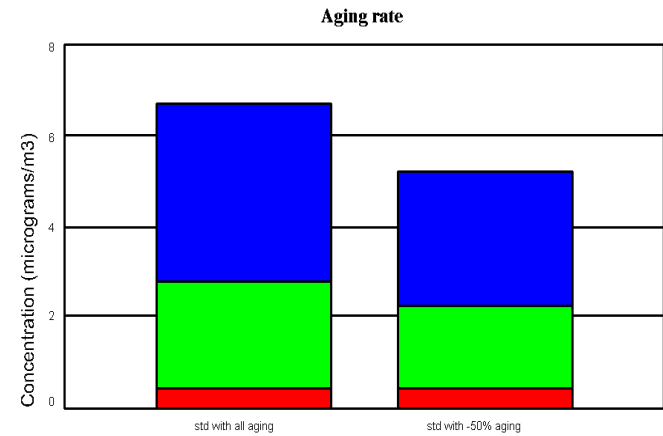
(note model uses Pankow/Odum 2 product oxidation)

Run Description	SOA Production (Tg/yr)	SOA Burden (Tg)
Condensation onto POA (Pankow standard model)	55	0.52
Condensation onto POA and ammonium sulfate	69	0.7
Complete partitioning to aerosol	178	2.1
Condensation onto POA and ammonium sulfate but with aging time decreased to 1.15 days from 5 days	65	0.67

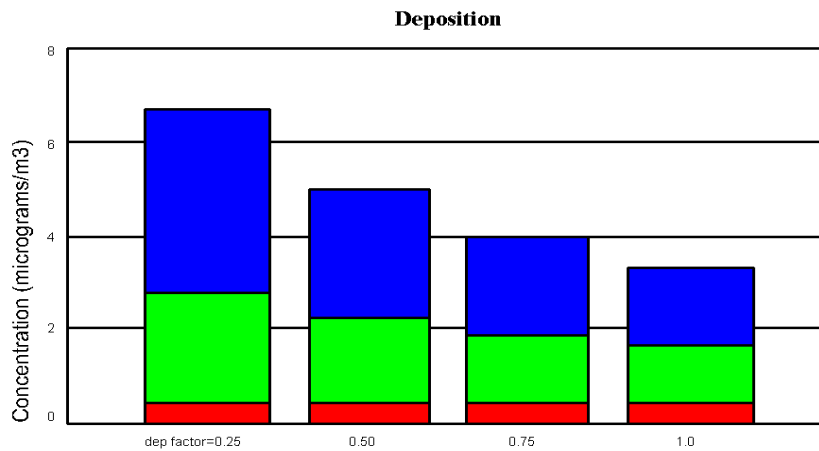
# Impact of various processes in WRF-CHEM



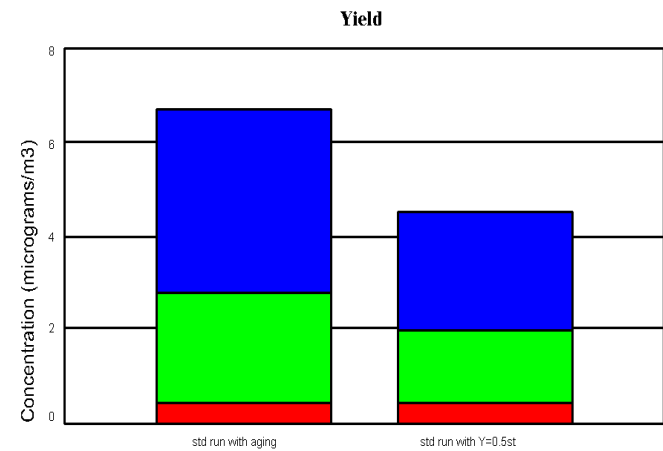
Conditions of runs



Conditions of runs



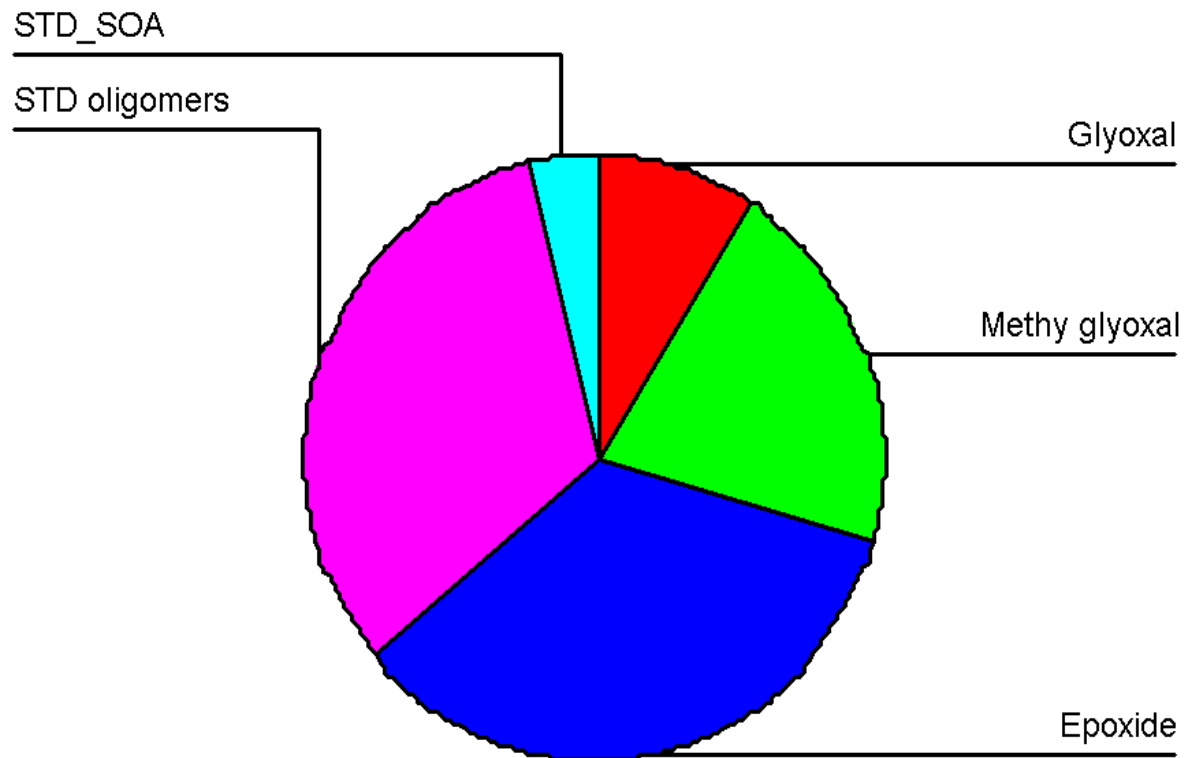
Conditions of runs



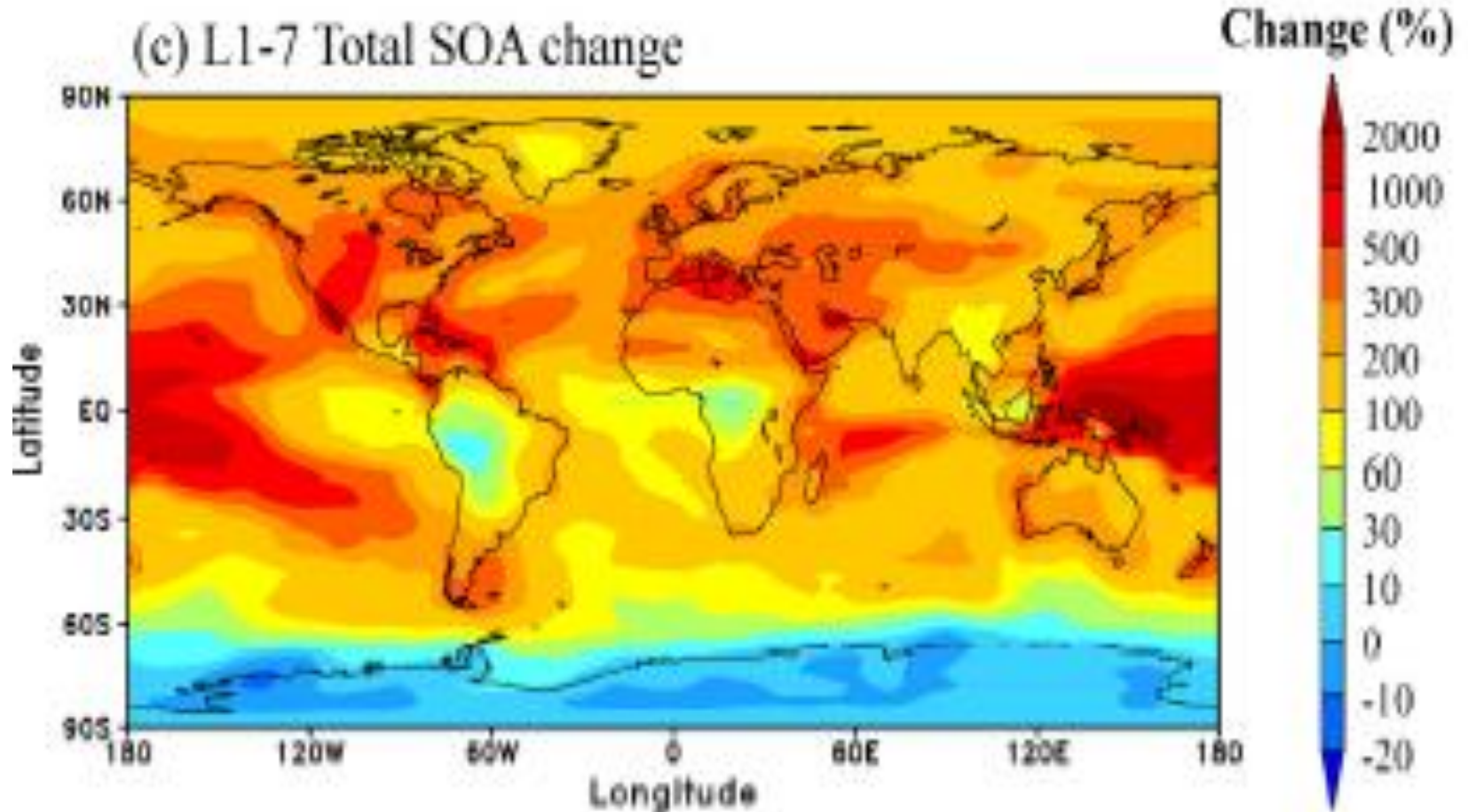
Conditions of runs



# Breakdown of SOA sources in IMPACT



Impact of SOA aging (via SOG and LV-SOG condensation) on SOA mass in GEOS-CHEM  
(from Yu, 2011)



# Conclusions: Part 1

## (Some current action items )

- Multi-generational (MG) nature of SOA formation must be included in models
- Condensed phase SOA processes are difficult to include in models **BUT** should be done (especially for isoprene oxidation products)
- Further extensive expansion of the species and reaction sets included in the models is not the right approach
- Proper phase partitioning of SOA (and SOA precursors) is key issue

## Conclusions: Part 2

### (Future work)

- The coupling of BSOA production with anthropogenic emissions needs to be further quantified
- The possibility of non-equilibrium condensation of SOA should be further explored, as should the isoprene product –condensed phase SOA process
- Simultaneous treatment of aqueous (electrolyte) and organic condensed phase processes should be explored