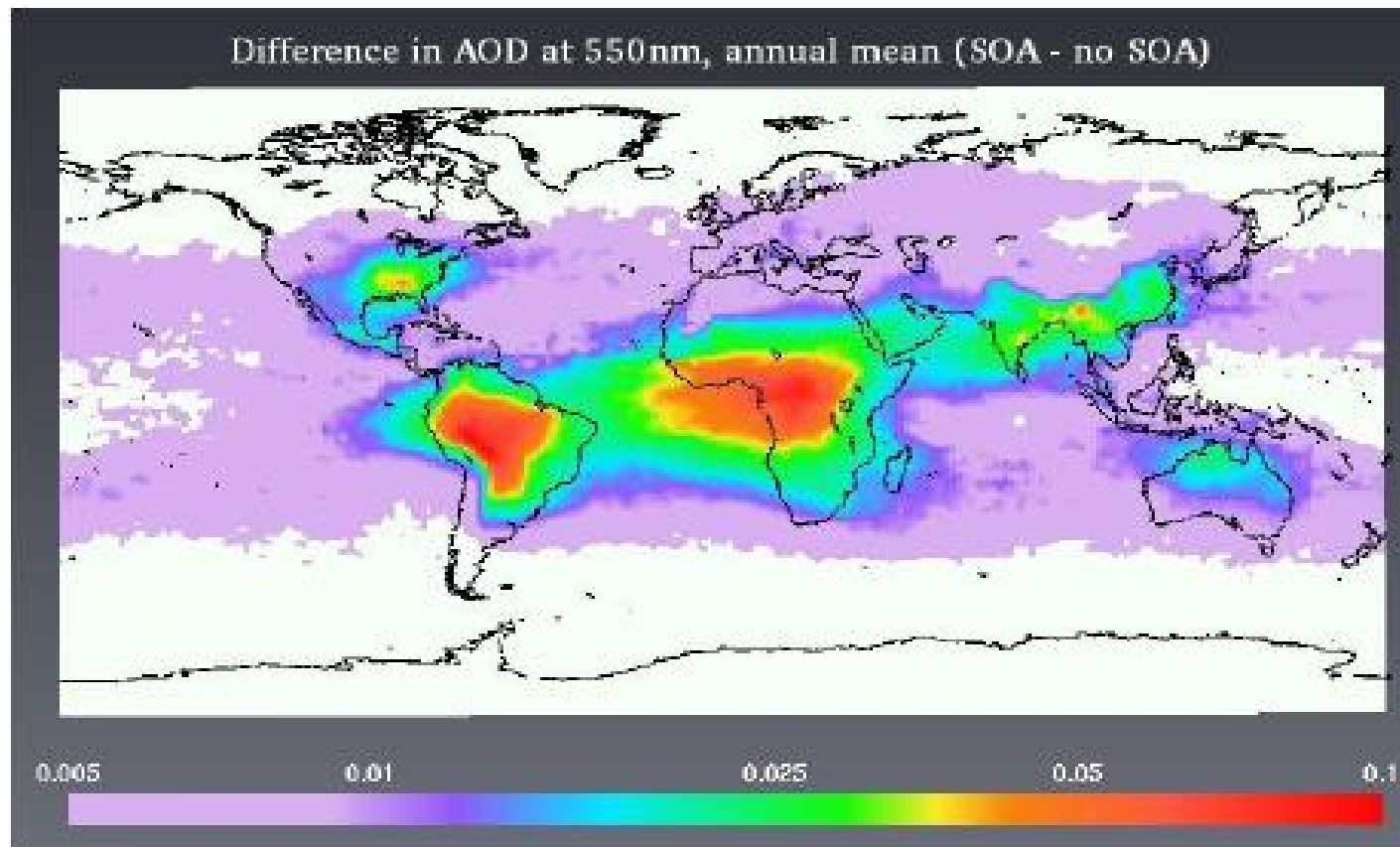


Putting Secondary Organic Aerosol in Global Models (and FRP's)

Issues and Approaches



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(University of Washington)

Walter Sessions
(NRL Monterey)

Outline of Talk

- 1. The necessity of dealing with SOA in GCM's and why it is hard.
- 2. Important aspects of the chemistry of SOA formation that need to be dealt with in models (one way or another).
- 3. Some approaches in current models and how they work.
- 4. What next?

1. Why deal with SOA?

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

Why include any particular aerosol component in GCM's

1. Does it impact direct forcing?

(Mass, Hygroscopicity, SSA)

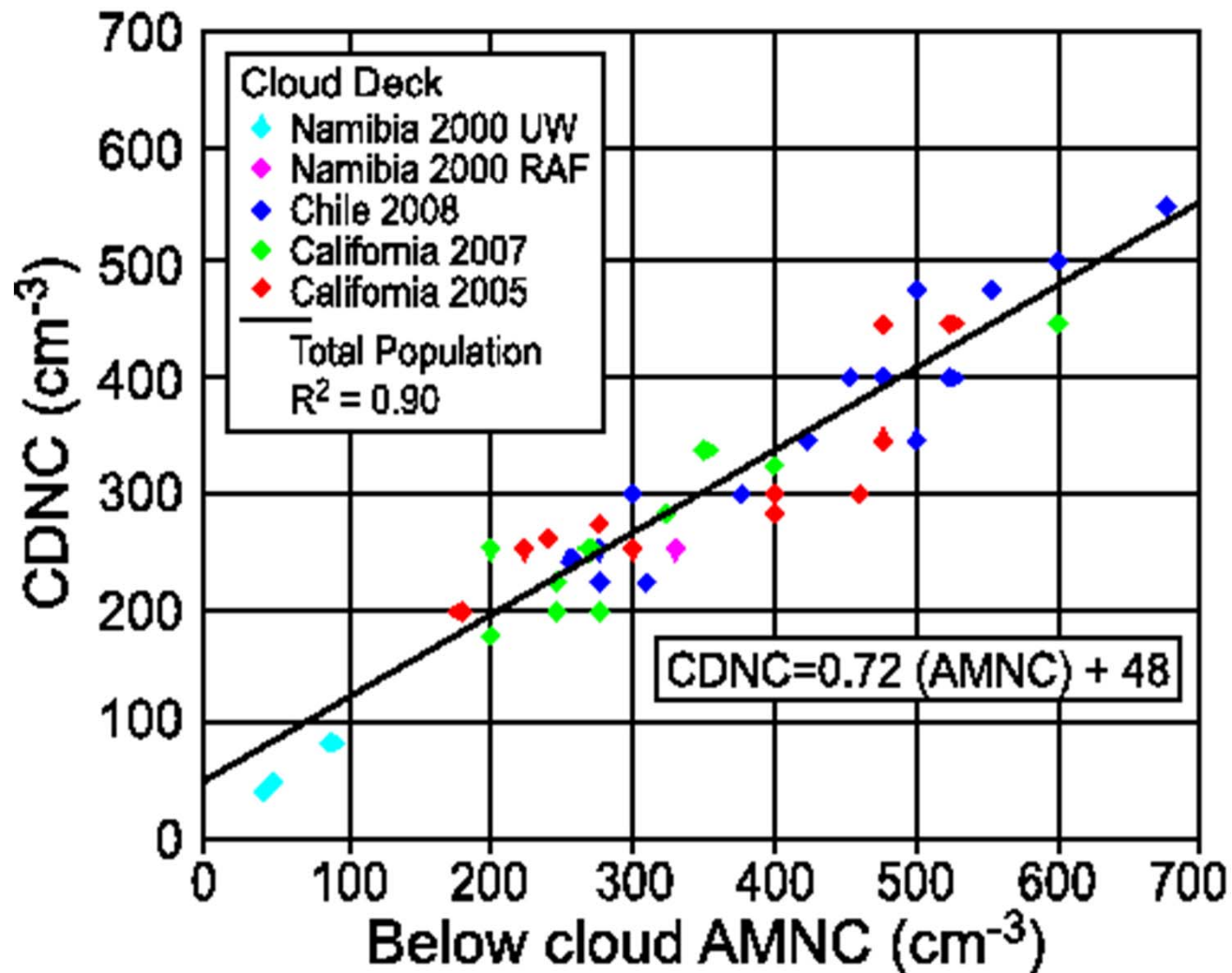
2. Does it impact indirect forcing (1st or 2nd indirect effects)?

(Size Distribution and CCN activity)

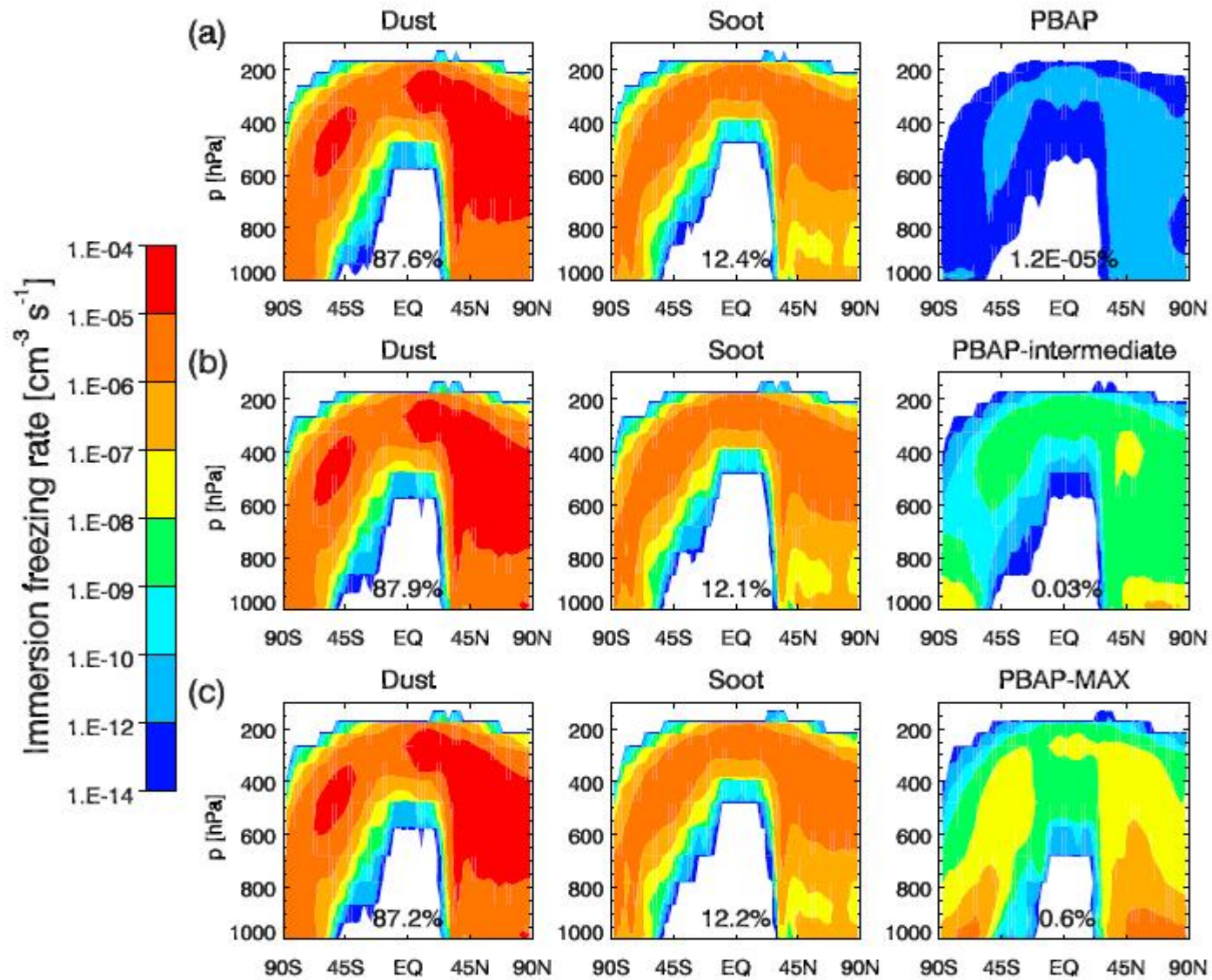
3. Does it impact indirect forcing (cloud glaciation)?

(Ice Nucleation activity)

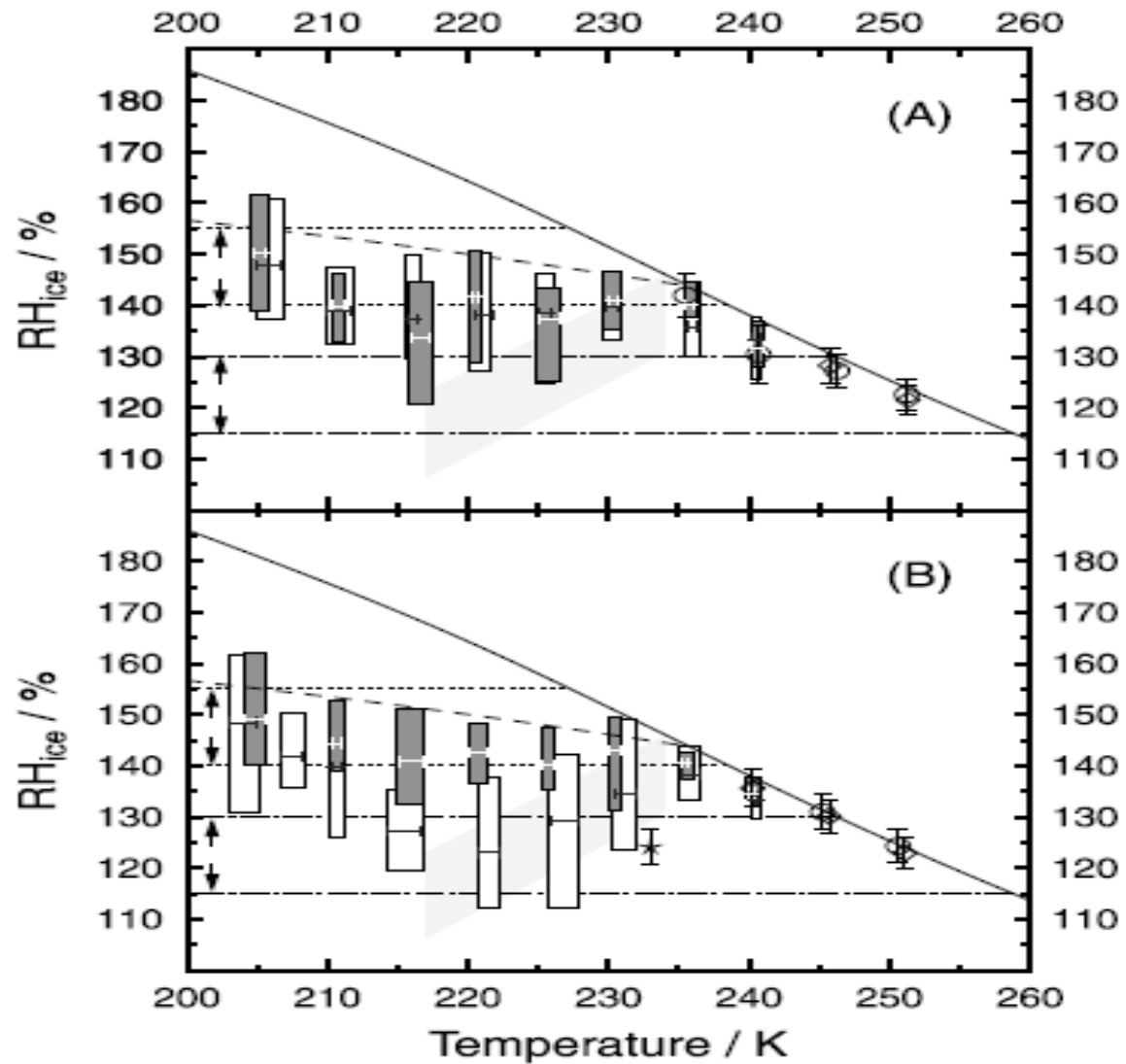
CDNC-AMNC relationship independent of composition
(from Hegg et al, 2012)



Contributions of particle types to the global ice nucleation rate (Hoose et al, 2010)



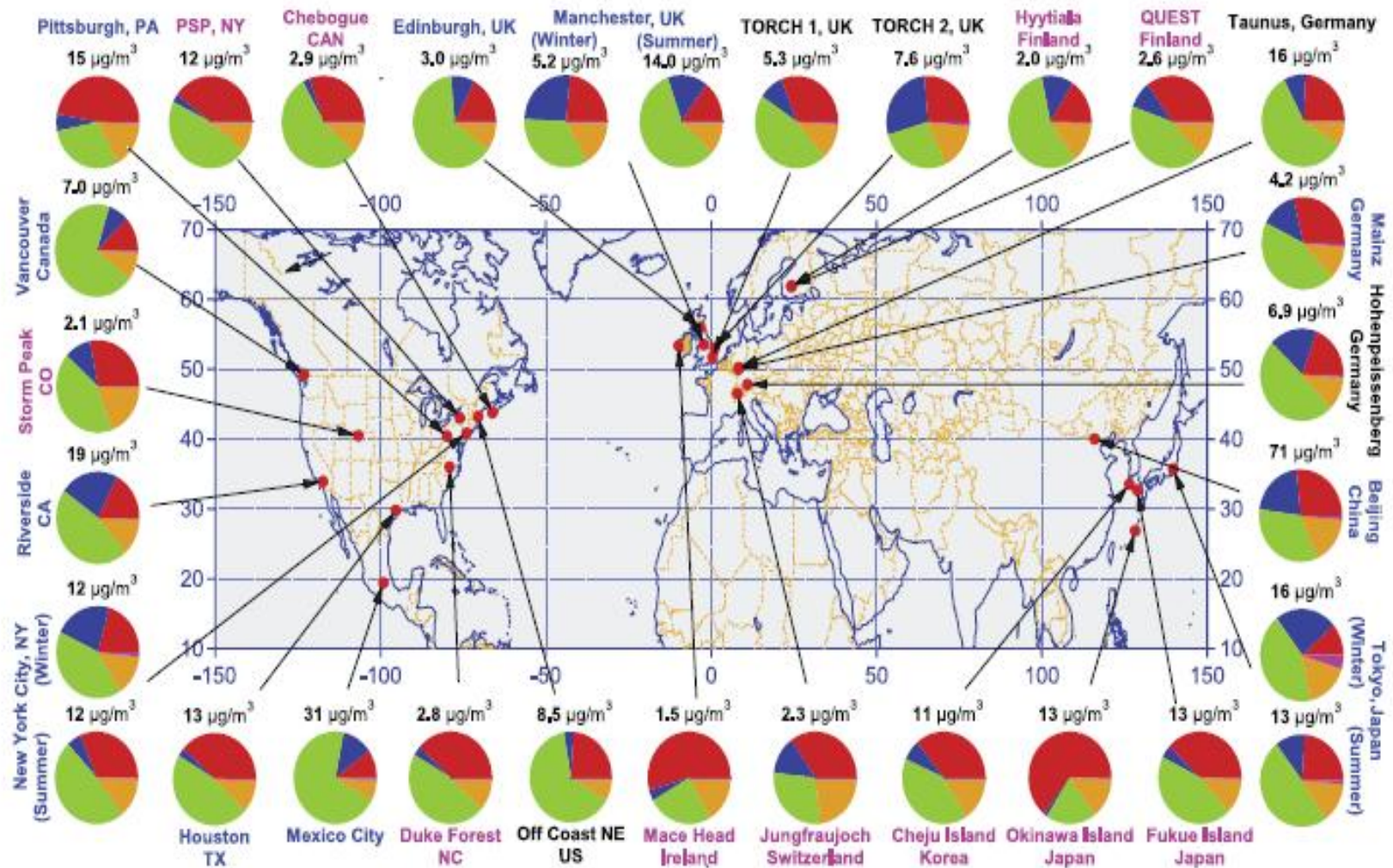
Onset conditions for ice nucleation as a function of T and RH for SRFA (a) and leonardite (b) (from Wang & Knopf, 2011)



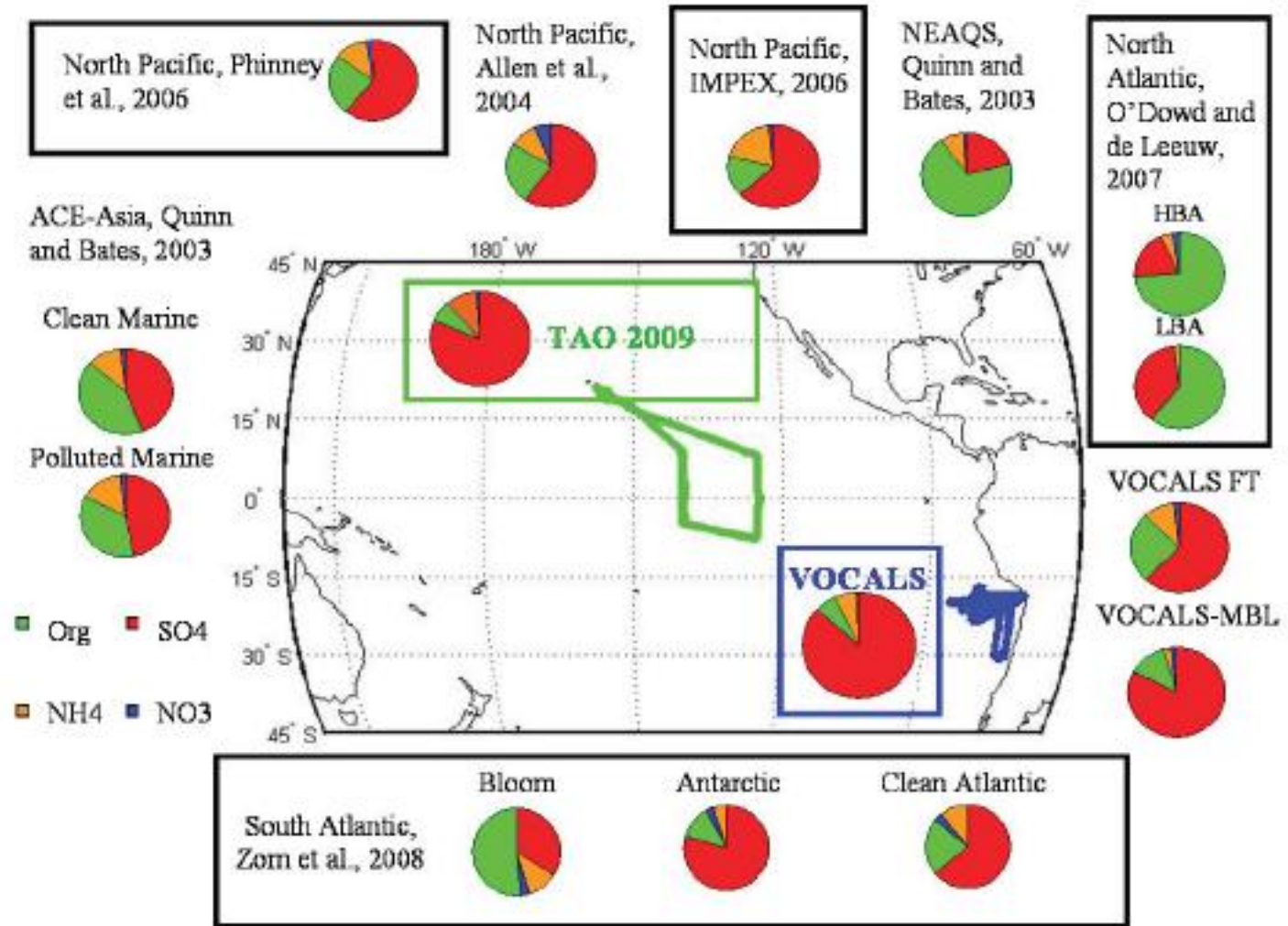
What this suggests is that, while various attributes of OA (or any aerosol) can be quite important for this or that climate issue, the single most important attribute of OA impacting its significance in GCM's is:

MASS

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



MBL (except as noted) aerosol composition (Shank et al 2012)



Summary Aerosol Composition

For sub-micron aerosol (where most of the mass is), the main constituents are:

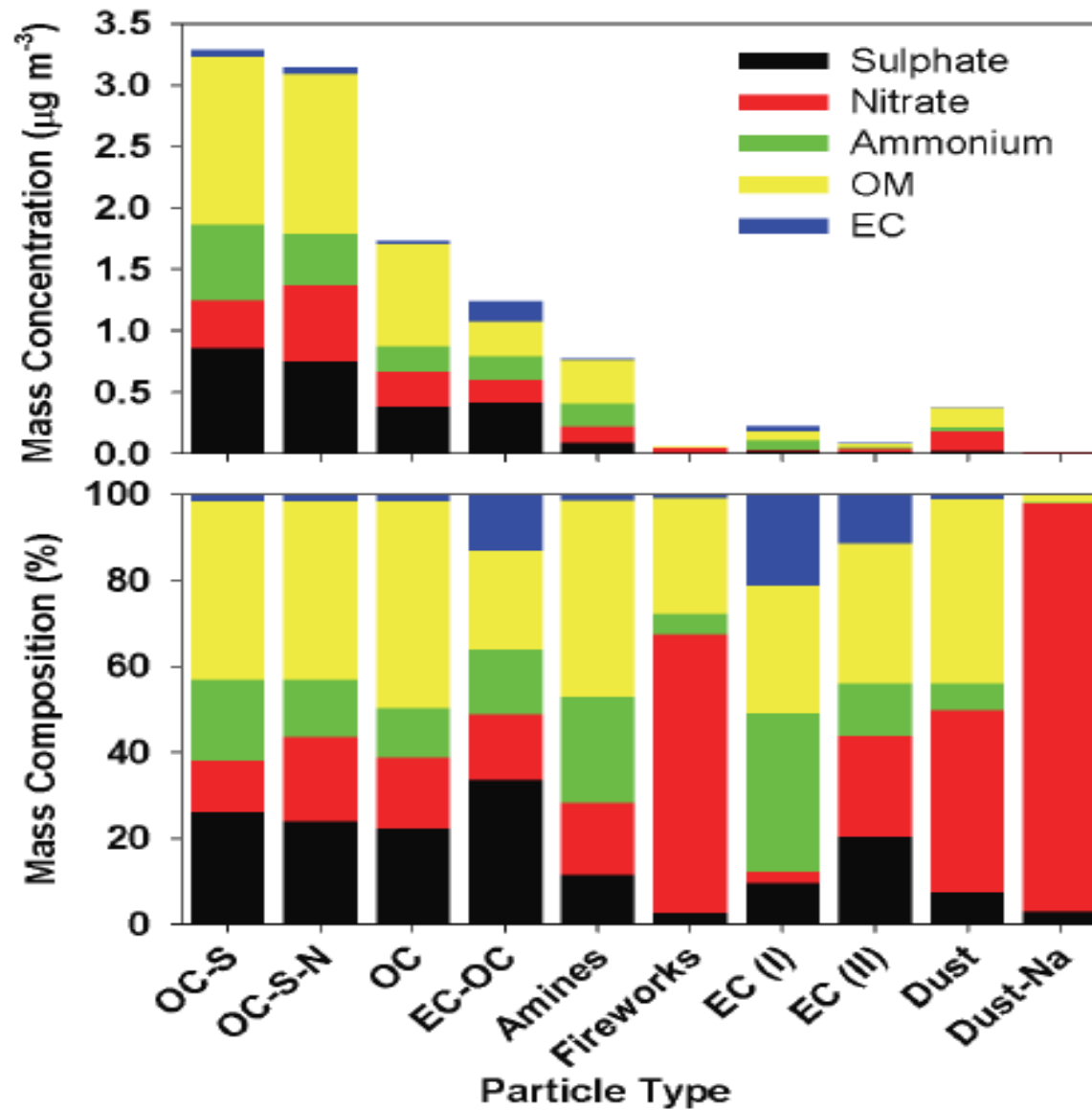
sulfate

nitrate

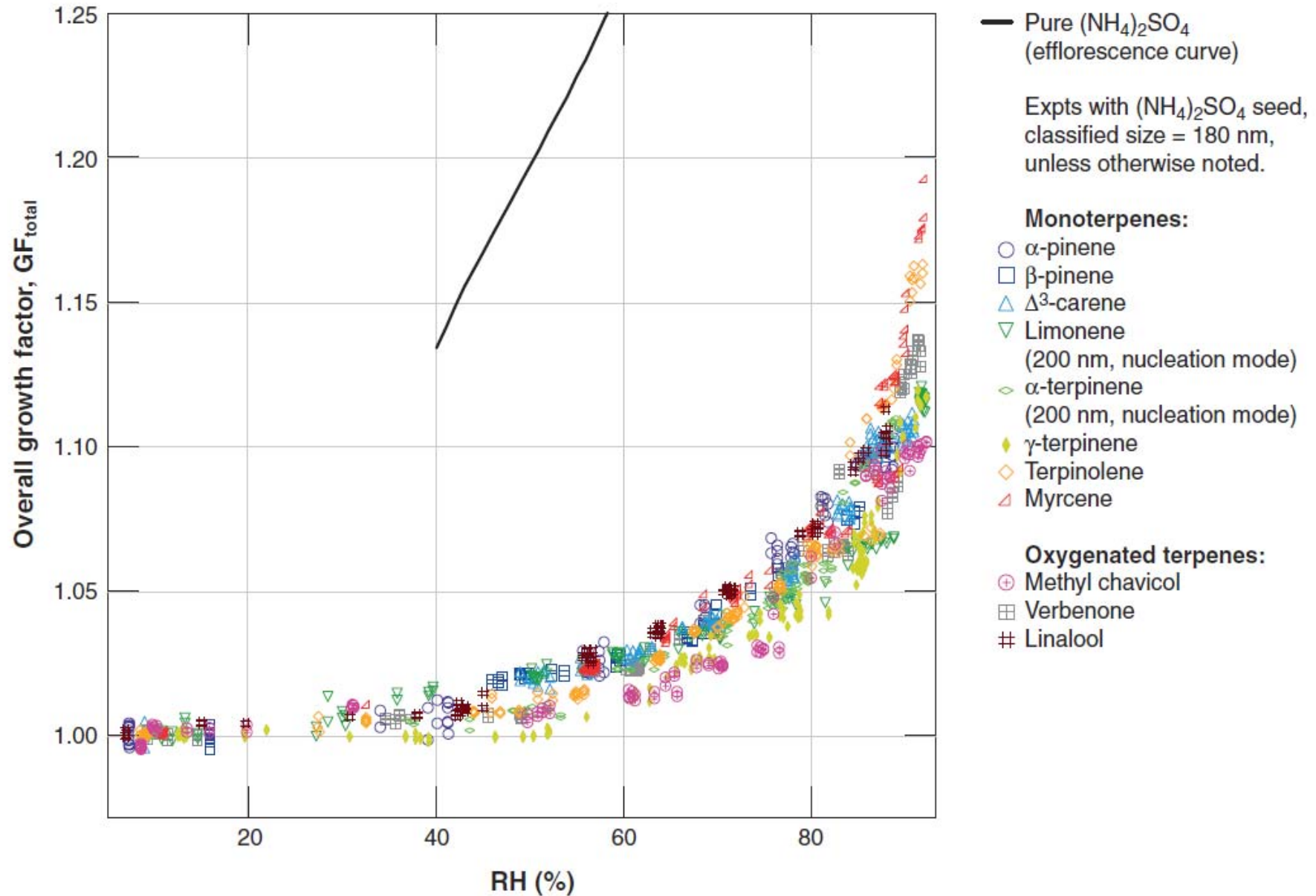
organics

(Note that sulfate and nitrate are in most models)

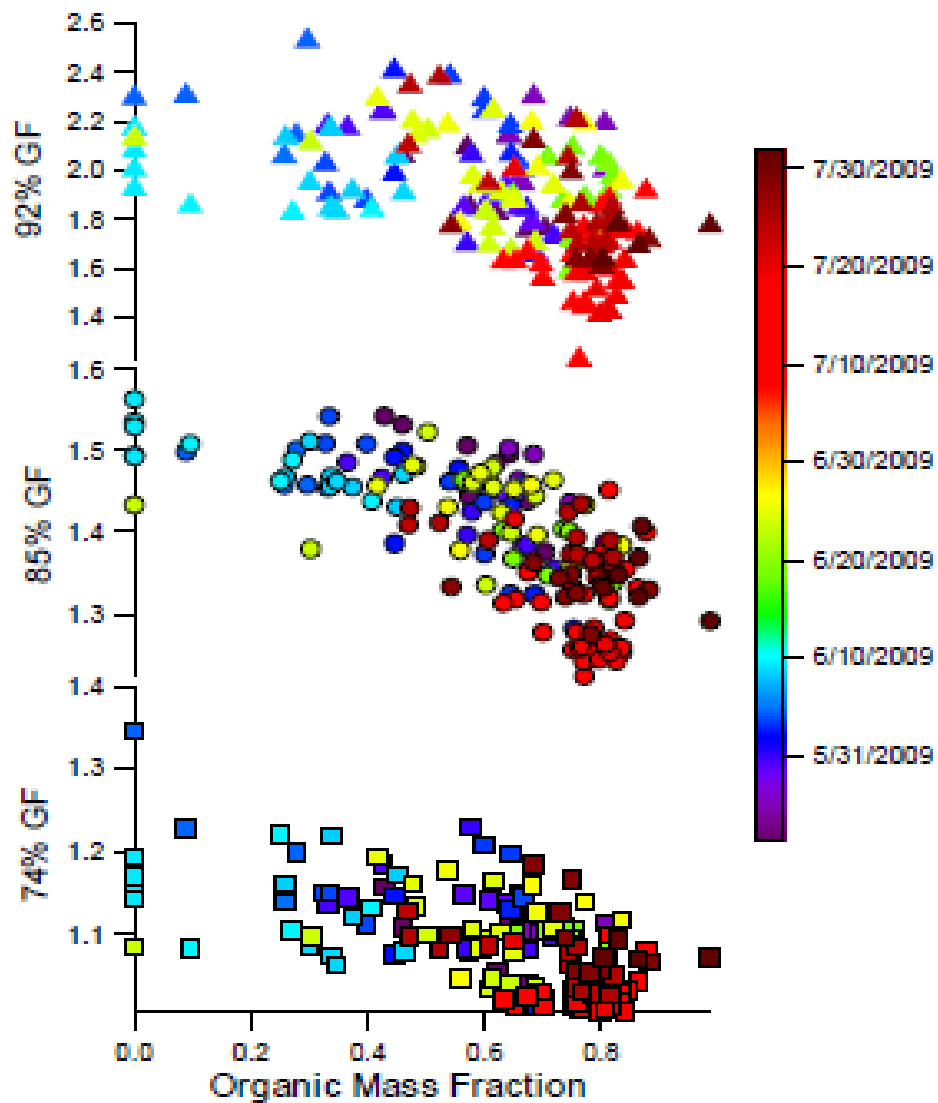
Mass contribution (top) and % contribution (bottom) to the 10 particle types found (Jeong et al, 2011)



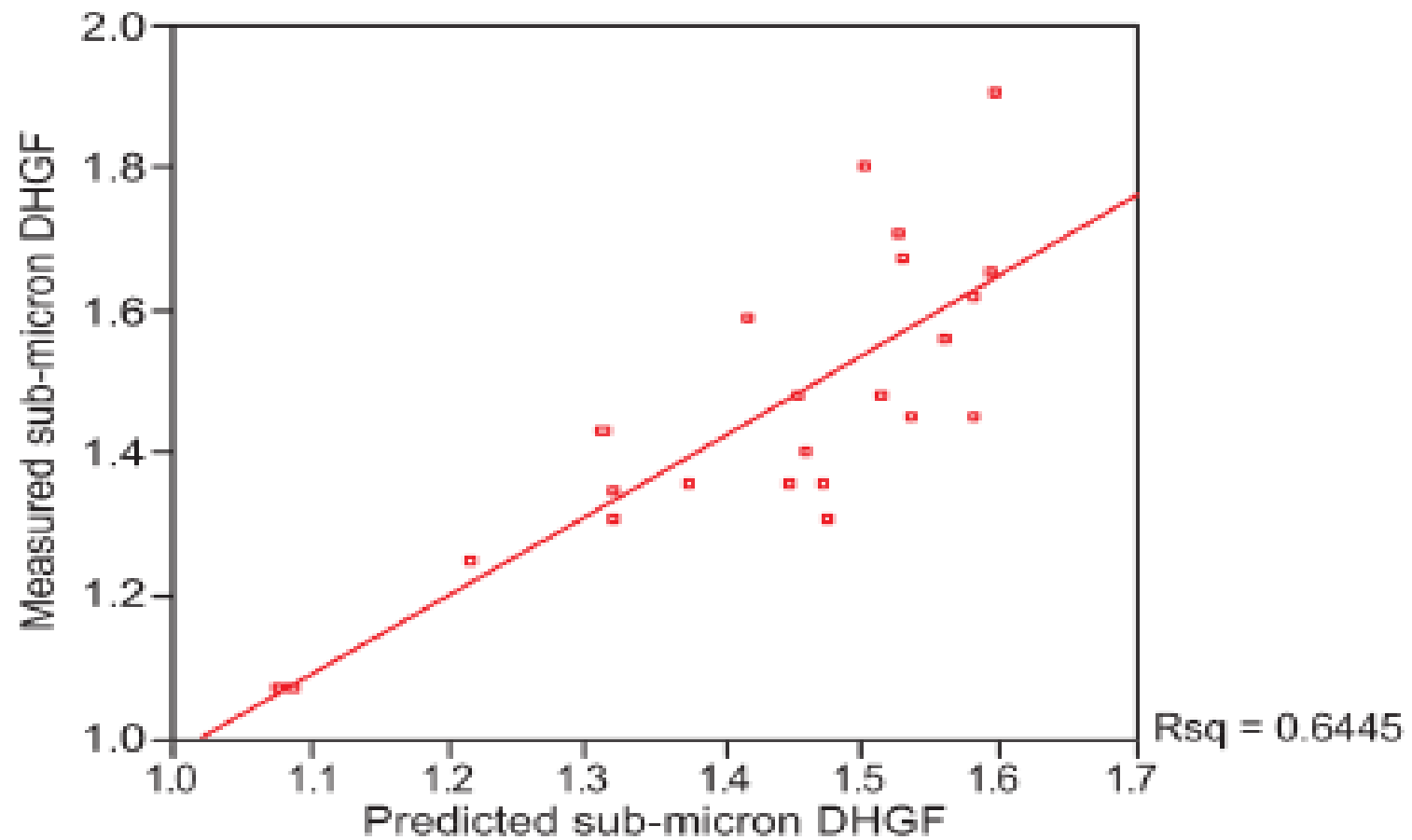
Hygroscopicity of selected SOA (Varutbangkul et al, 2006)



SOA hygroscopic growth factor plotted against OA mass fraction for LA aerosol (From Hersey et al, 2010)



Example of the prognostic skill of the ZSR mixing rule

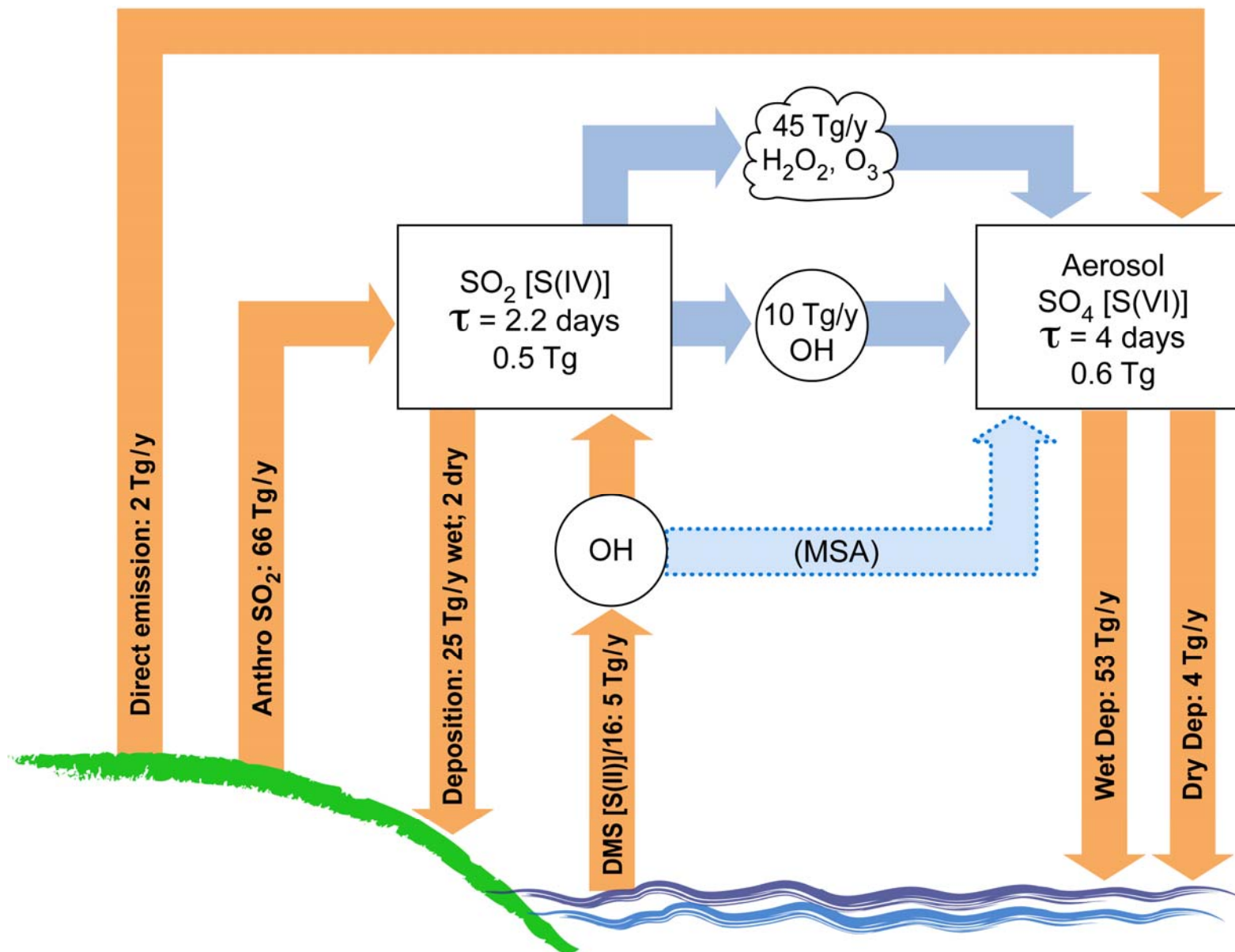


KEY POINT (s)

The sulfate, nitrate and organics in atmospheric aerosol are largely internally mixed.

The sulfate, nitrate and organics in GCM's are largely externally mixed
(They are also inconsistently categorized)

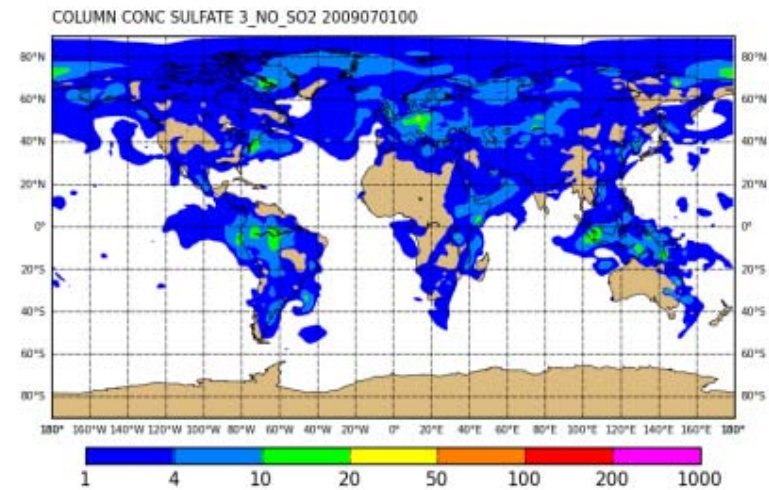
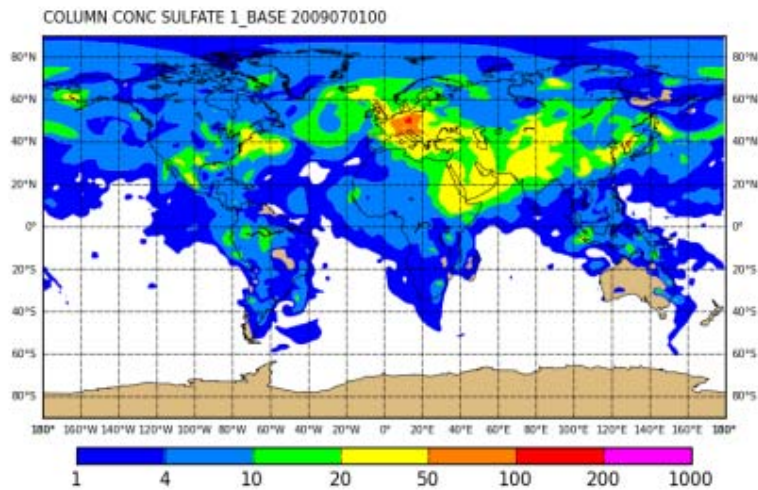
Aerosol Sulfate Budget (Rasch et al. - mostly)



Sulfate column burden from the NAAPS model for July 1st, 2009

Base case, std emissions

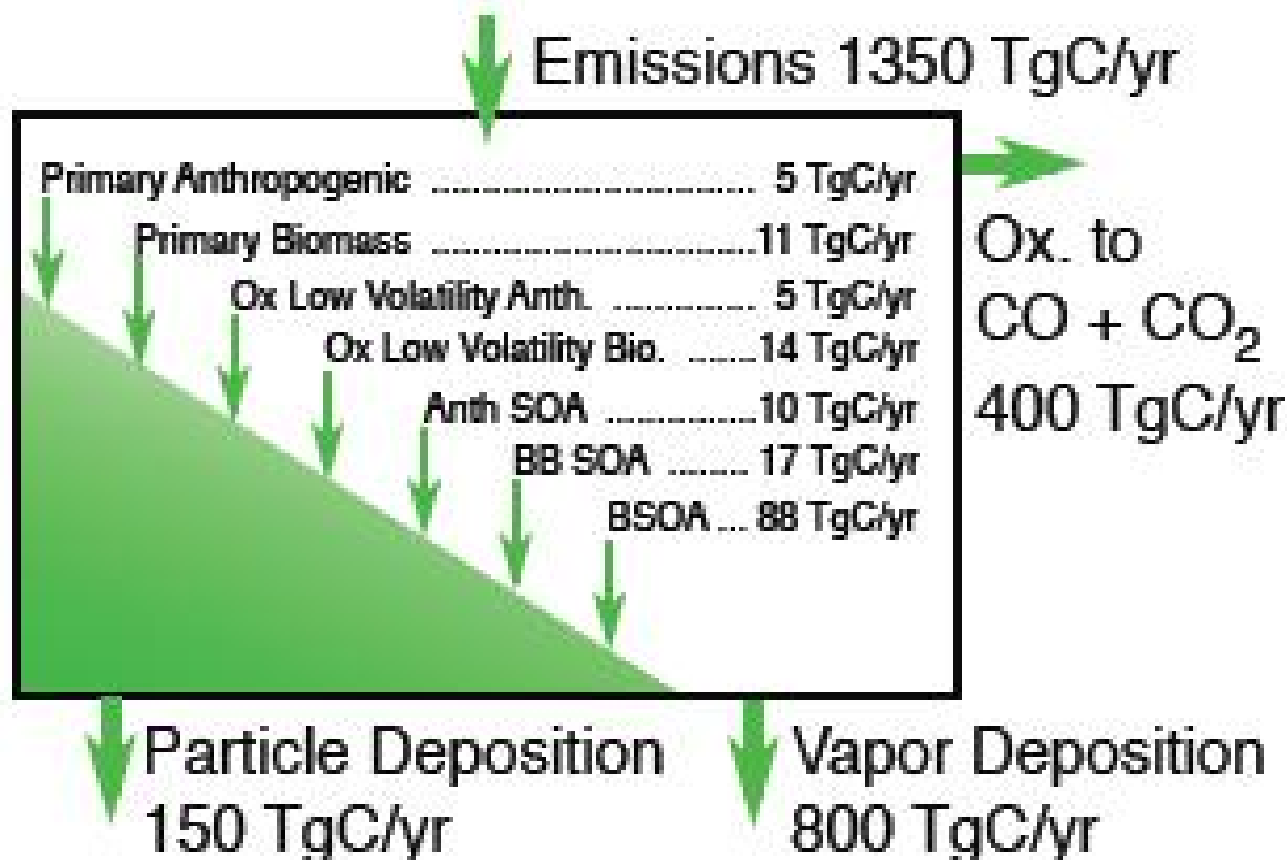
No SO₂ emissions



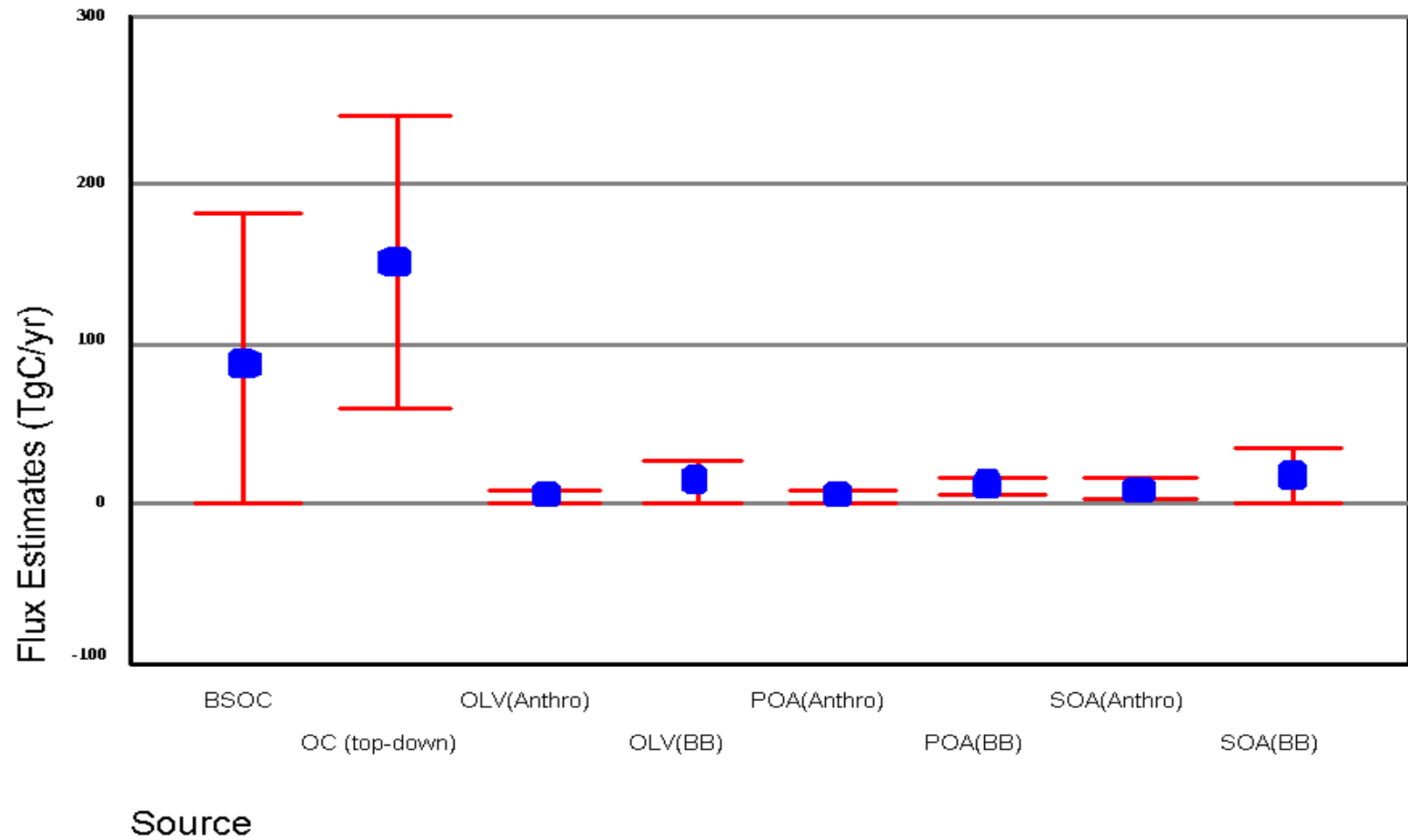
Fundamental assumptions for top-down OA flux estimates

- 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.

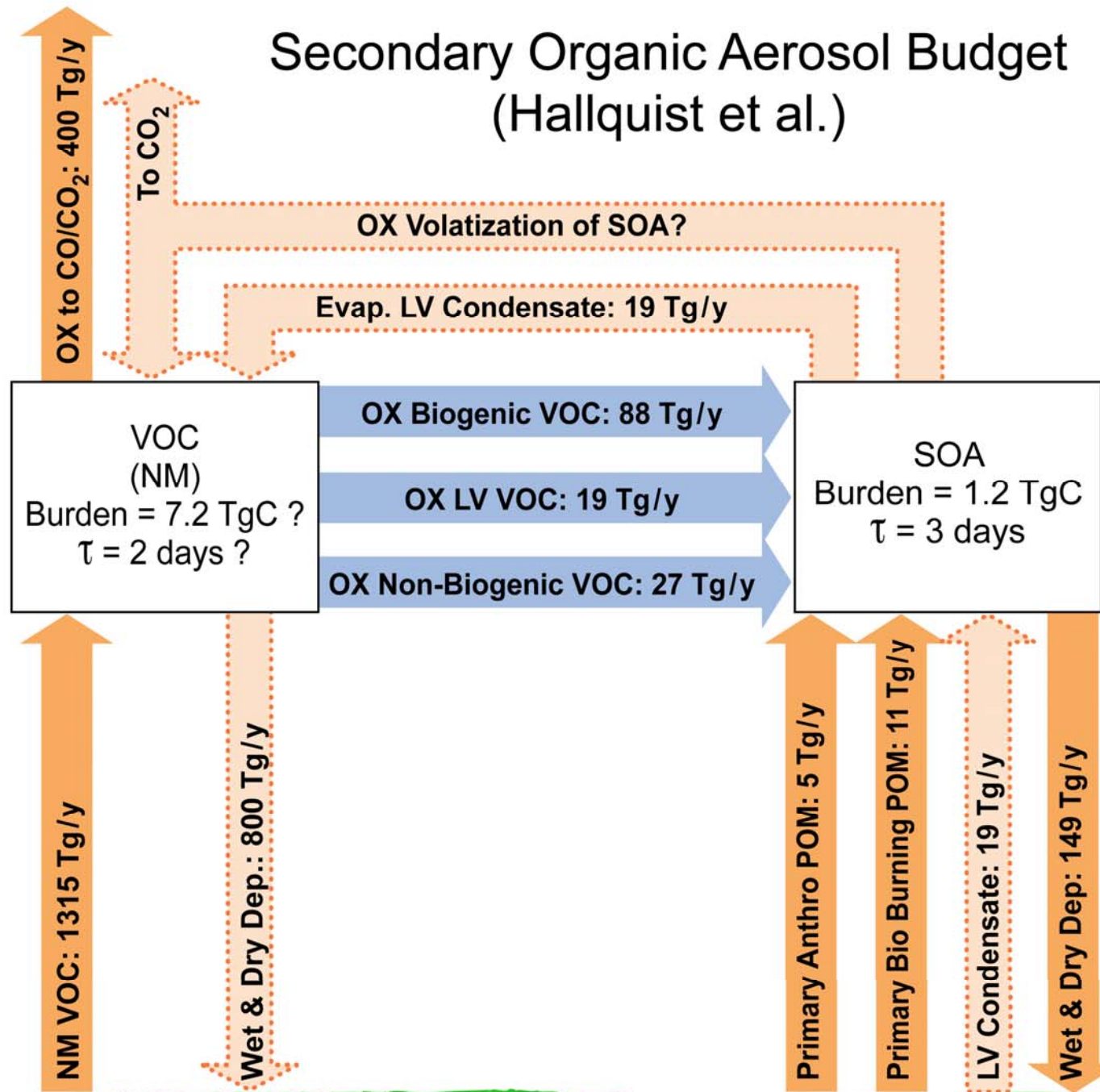
Global Flux estimates for VOC and OA (Hallquist et al, 2009)



Uncertainties in the global SOA budget



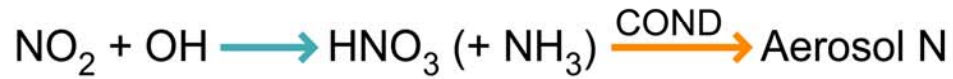
Secondary Organic Aerosol Budget (Hallquist et al.)



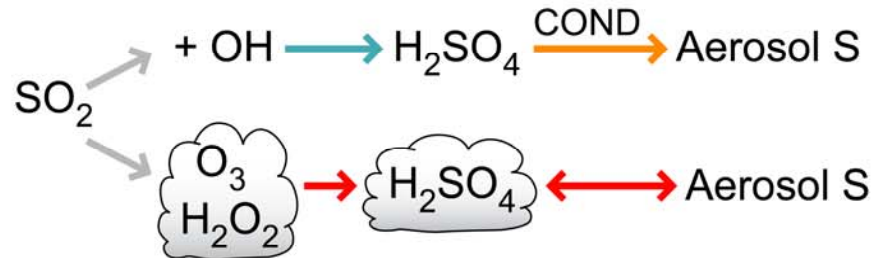
NOTE:
Oxidants (OX)
O₃
OH
NO₃

Mass Flow for N S and C Budgets

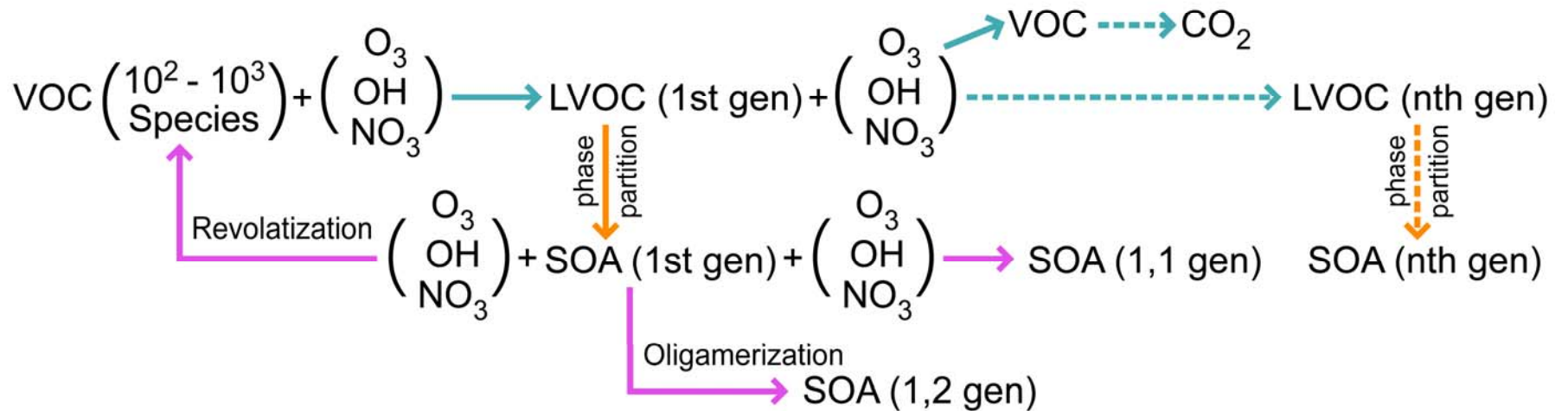
N



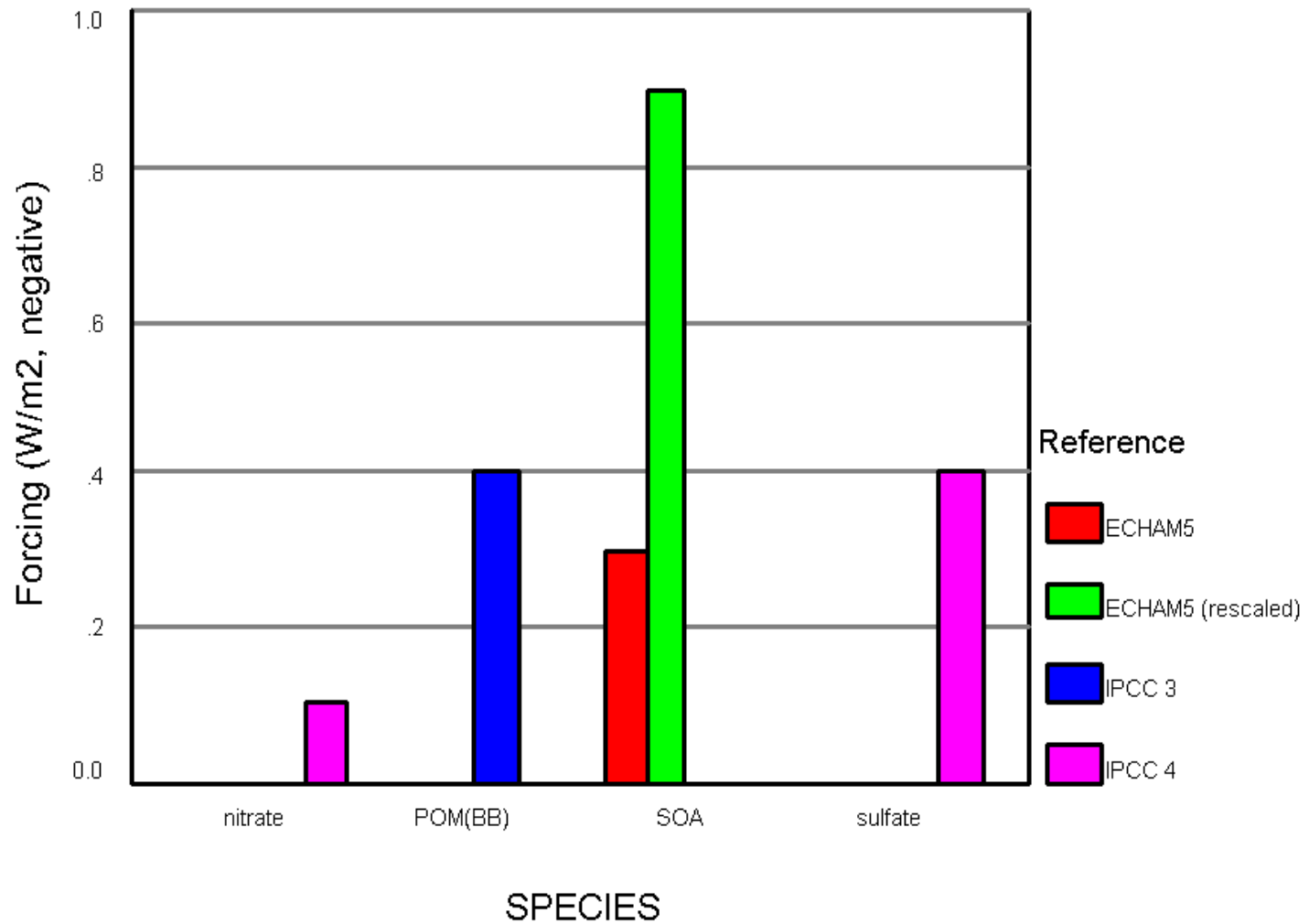
S



C



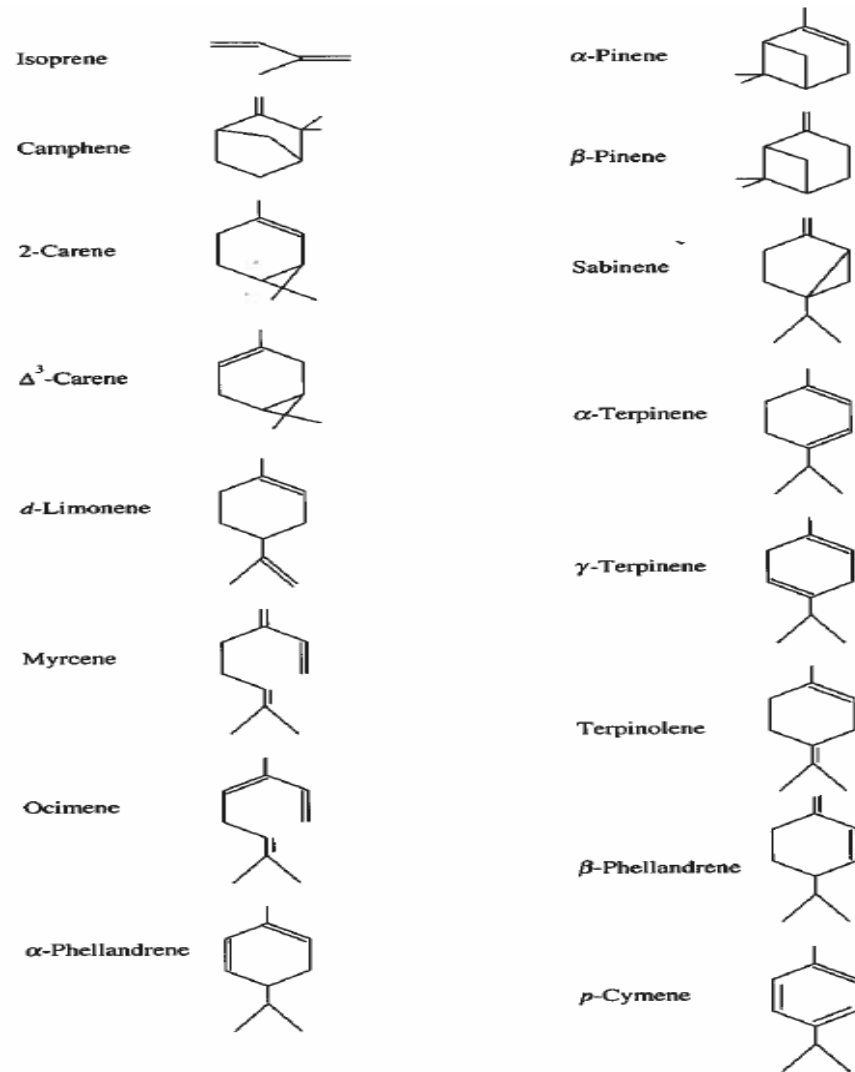
Comparison of direct forcing estimates for different species



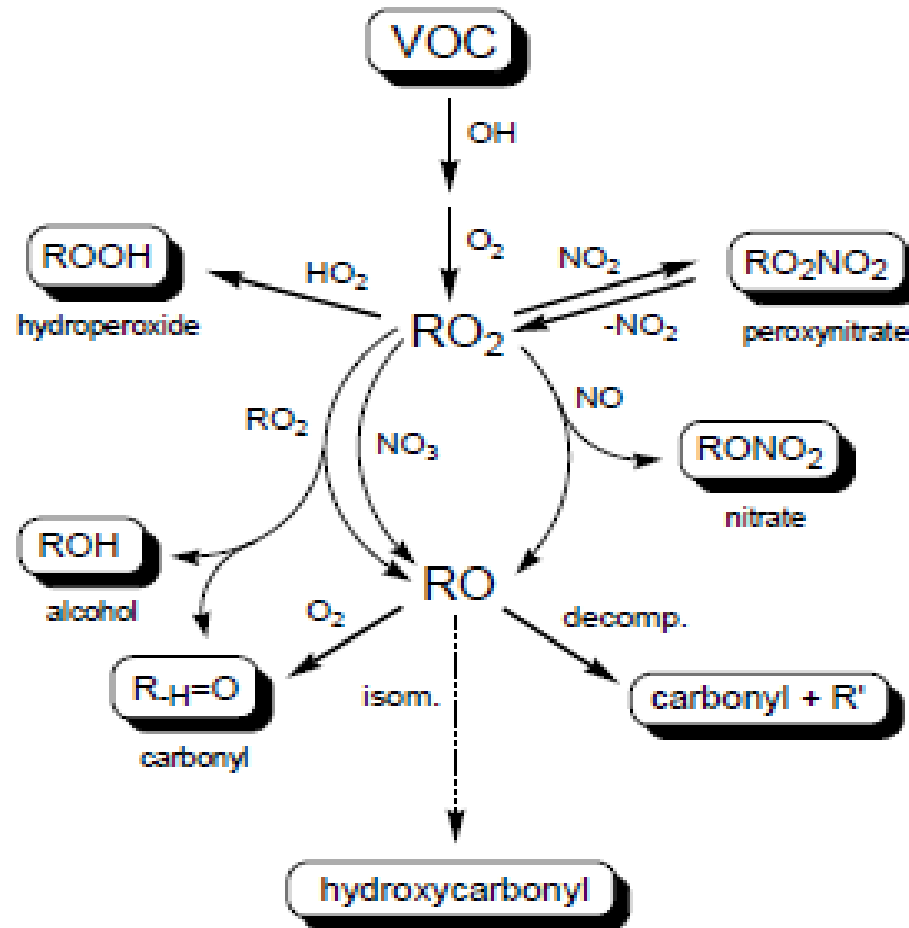
2. Important aspects of SOA chemistry

Selected VOC's from plants

(Do we have all the species necessary?)



Schematic of VOC oxidation (Do we have the proper chemistry?)



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

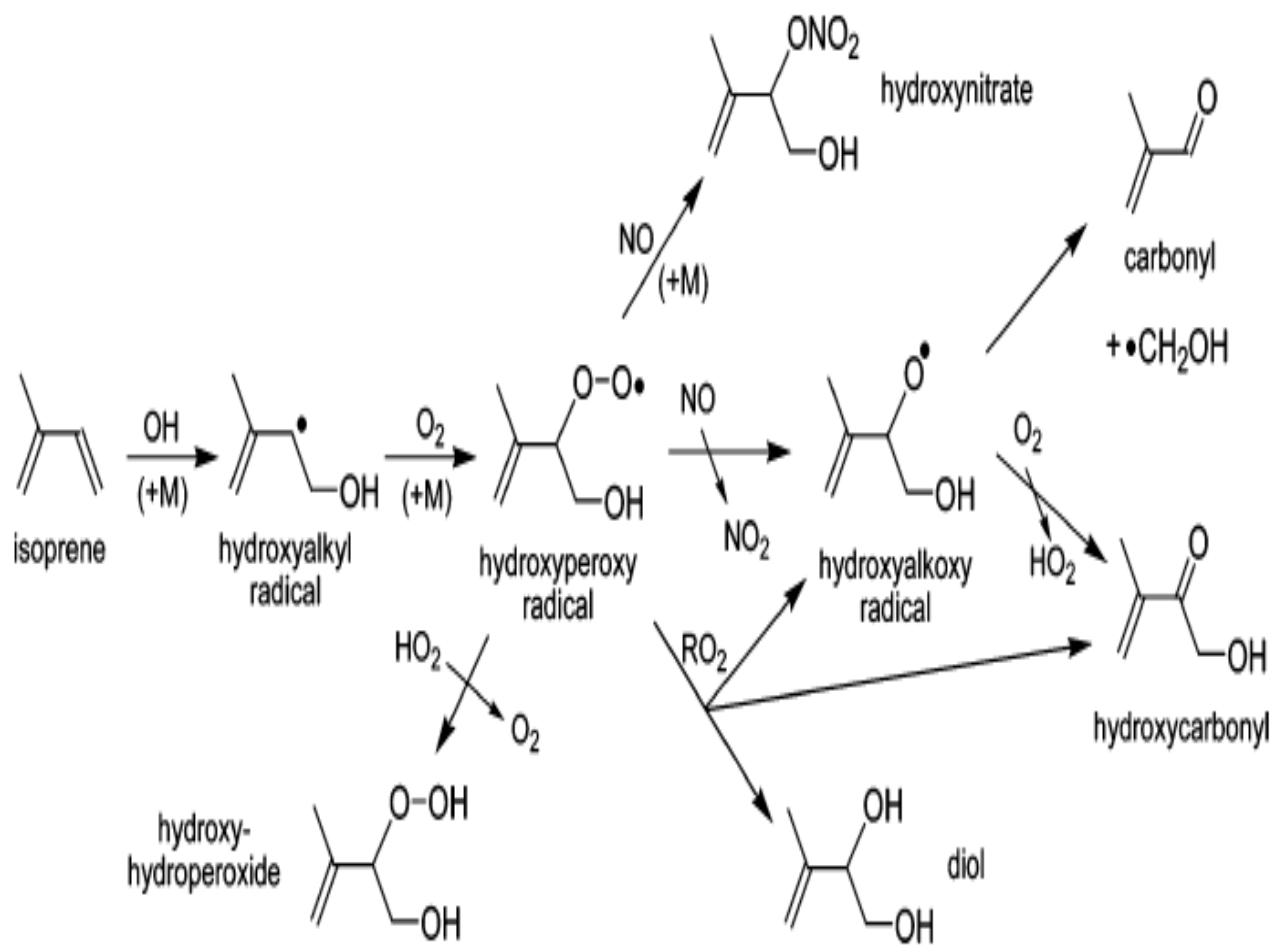
Changes to vapor pressure of an organic compound upon addition of common functional groups, based upon group-contribution method predictions of Pankow and Asher (2007)

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

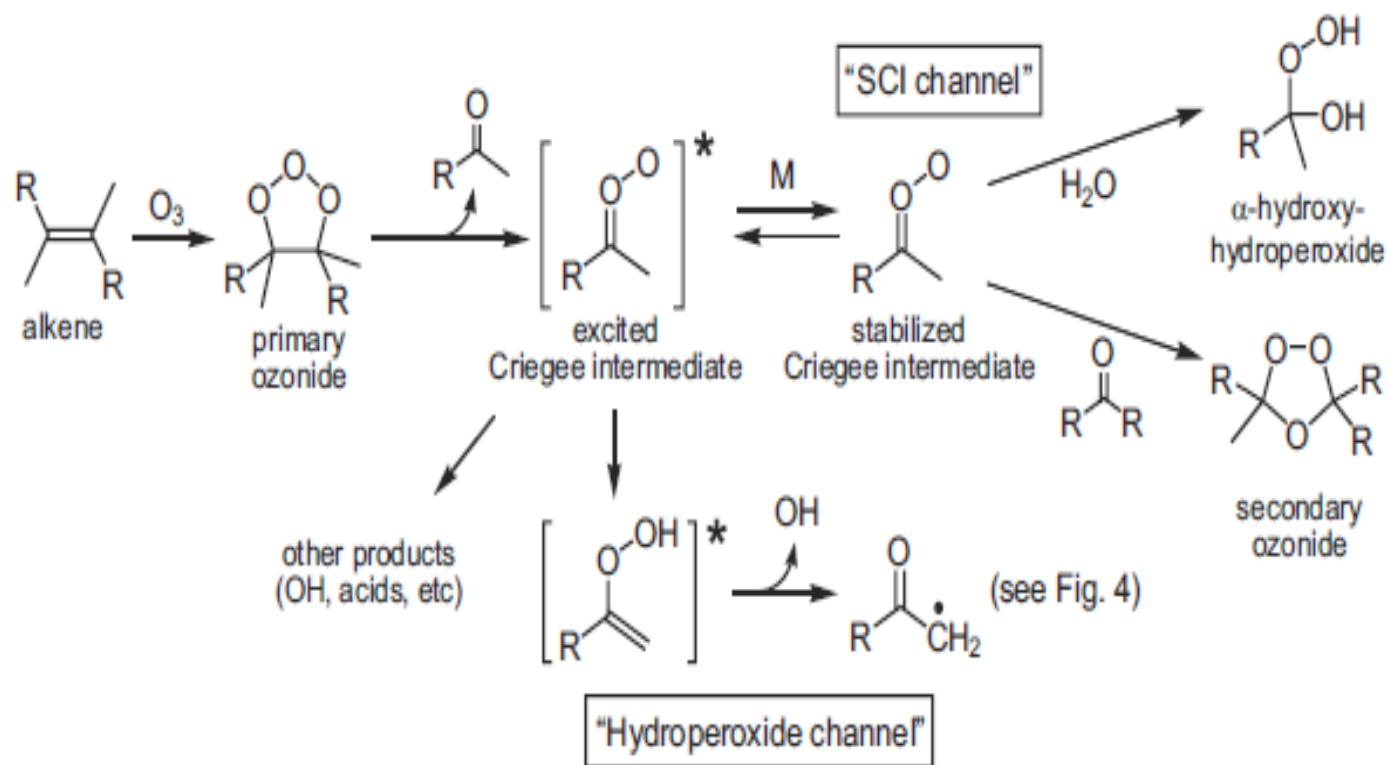
^aMultiplicative factor.

^bFor 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).

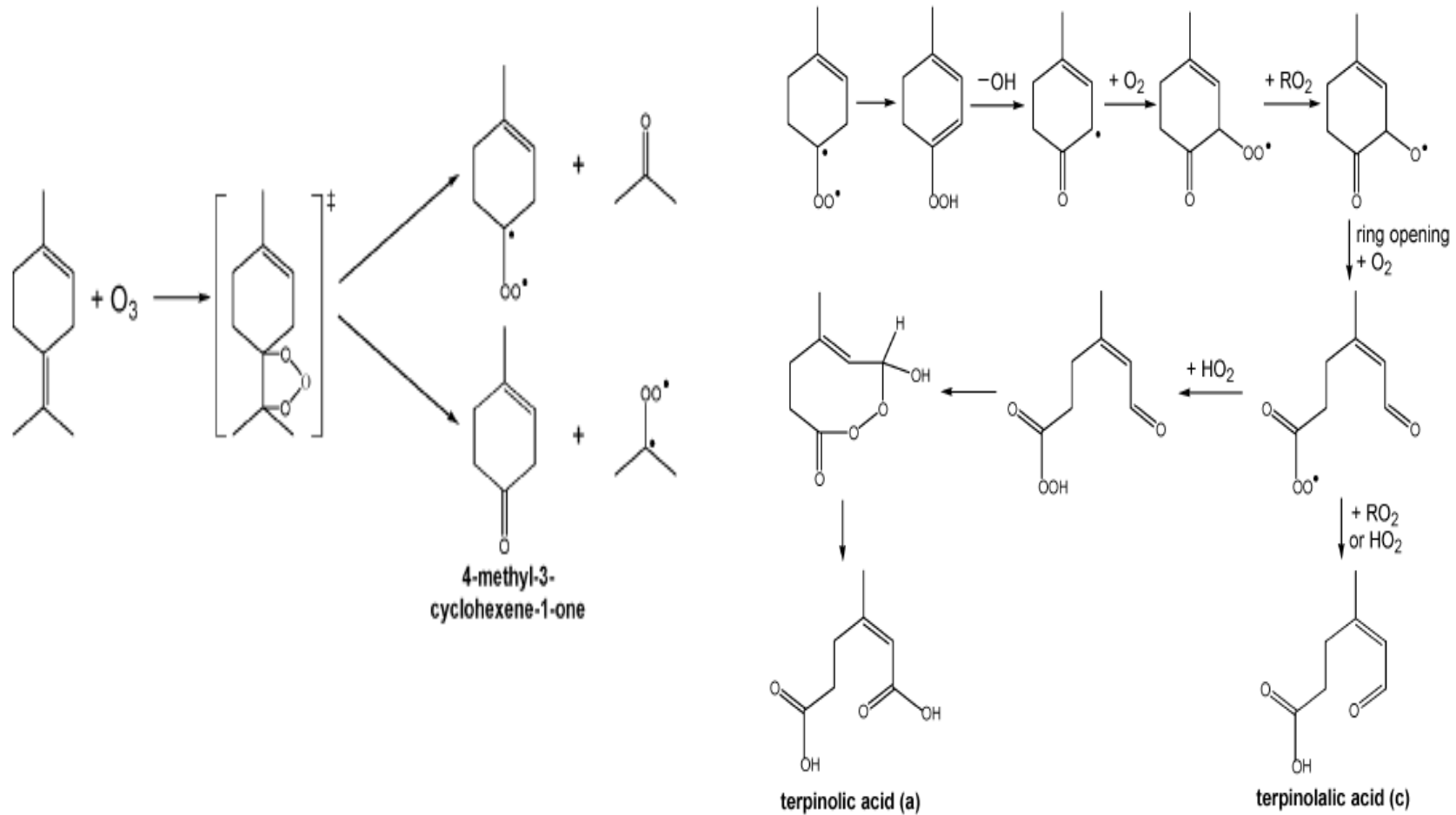
Isoprene oxidation mechanism (from Kroll et al 2006)
(Multiple products, multiple generations)



Simplified schematic of alkene ozonolysis

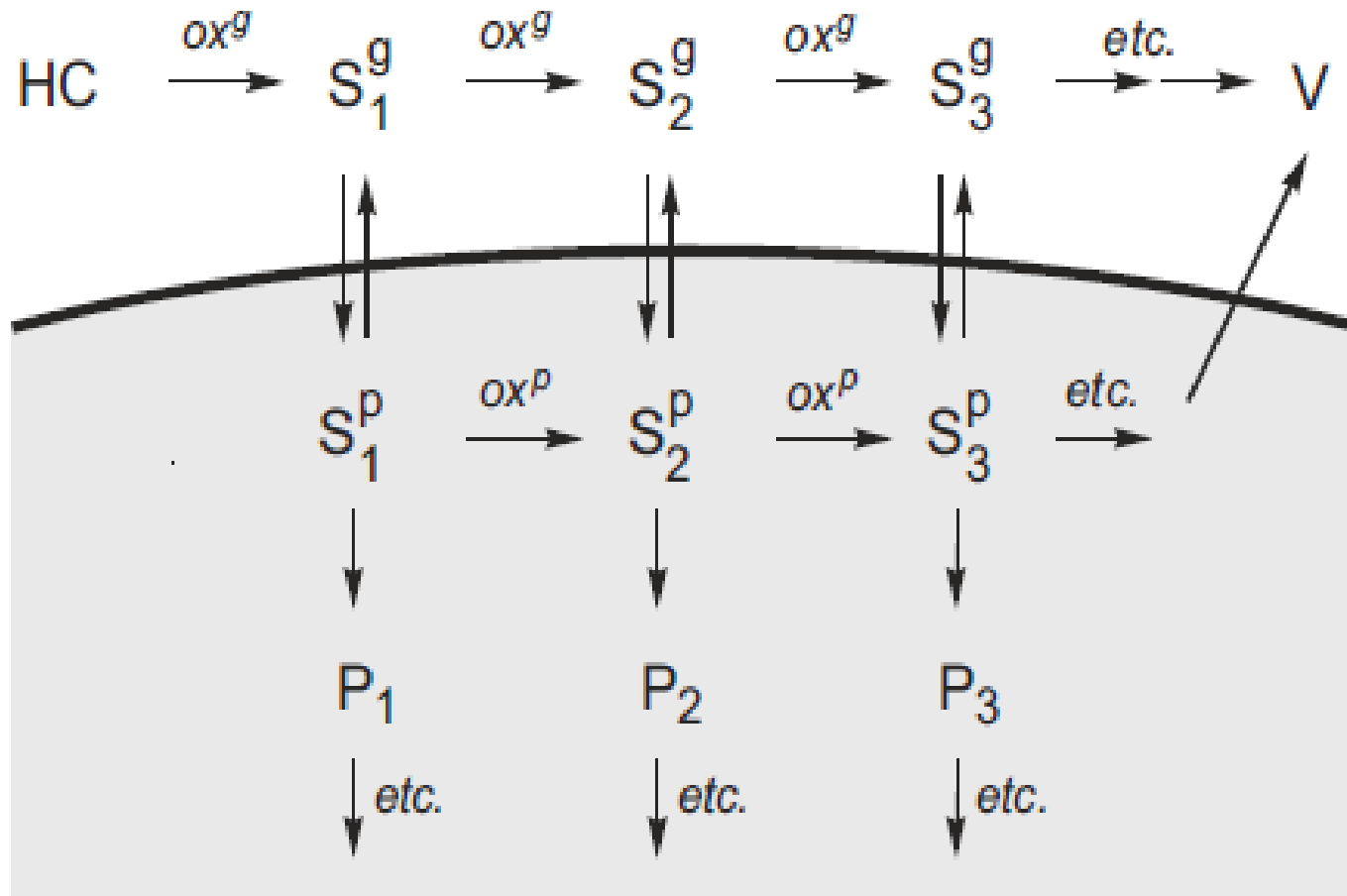


Terpinoline Ozonolysis (Ma & Marston, 2009)

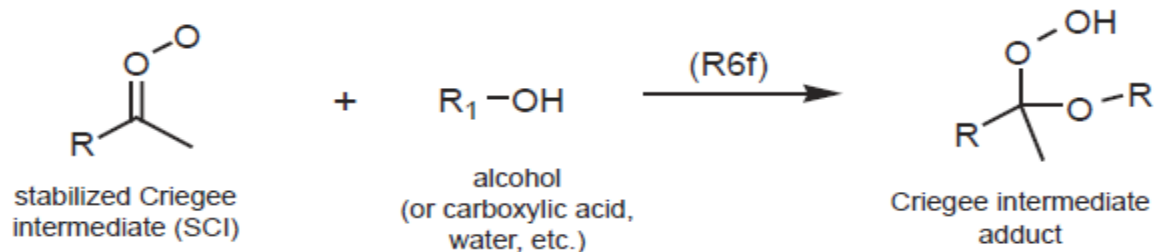
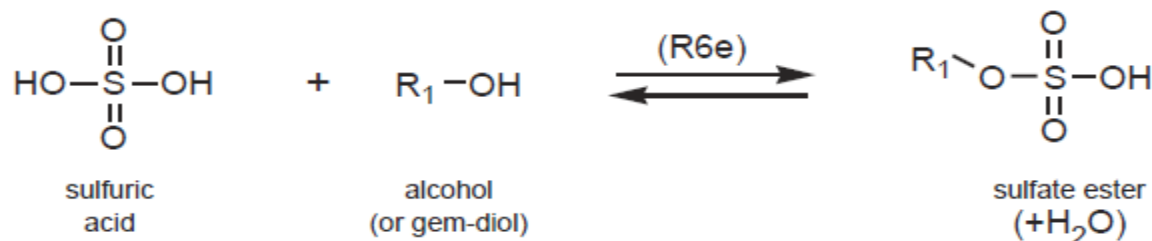
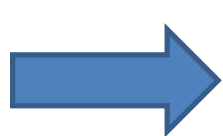
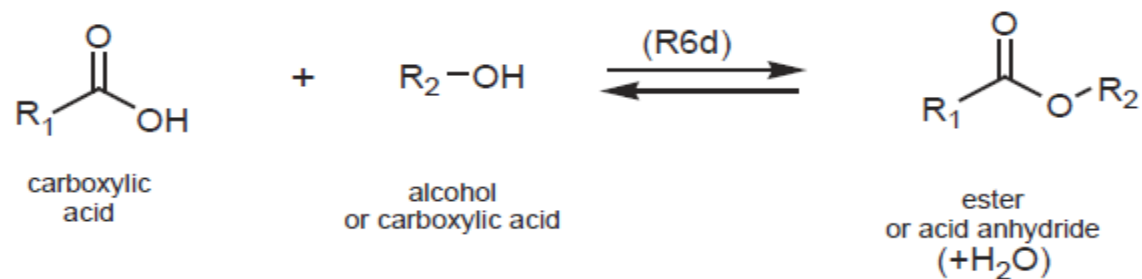
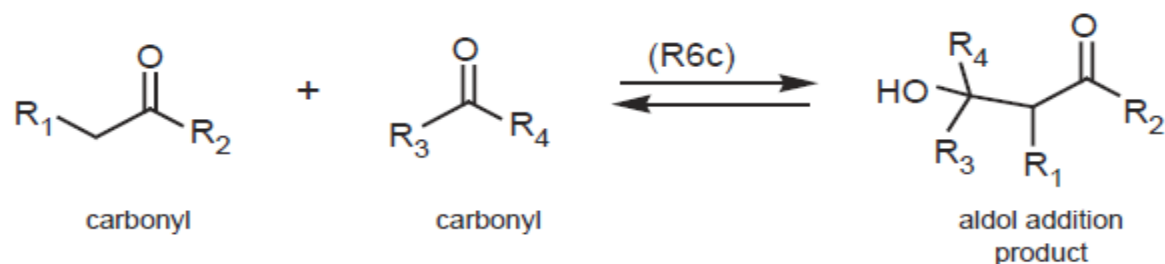


Schematic of multi-generational SOA production

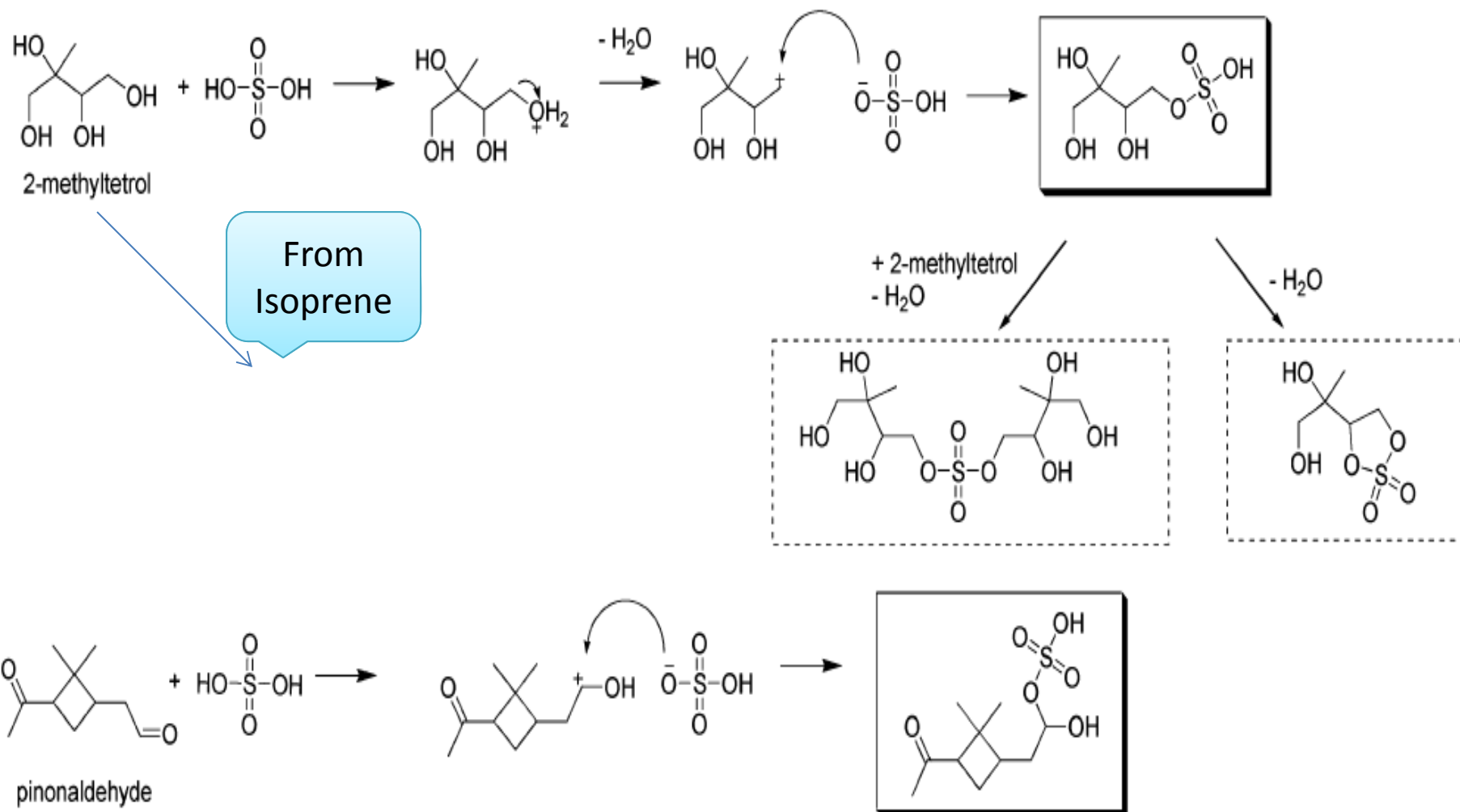
(Simplifying the MG Issue: but note the nature of the condensed phase: it must be organic, i.e. Pankow/Odum partitioning)



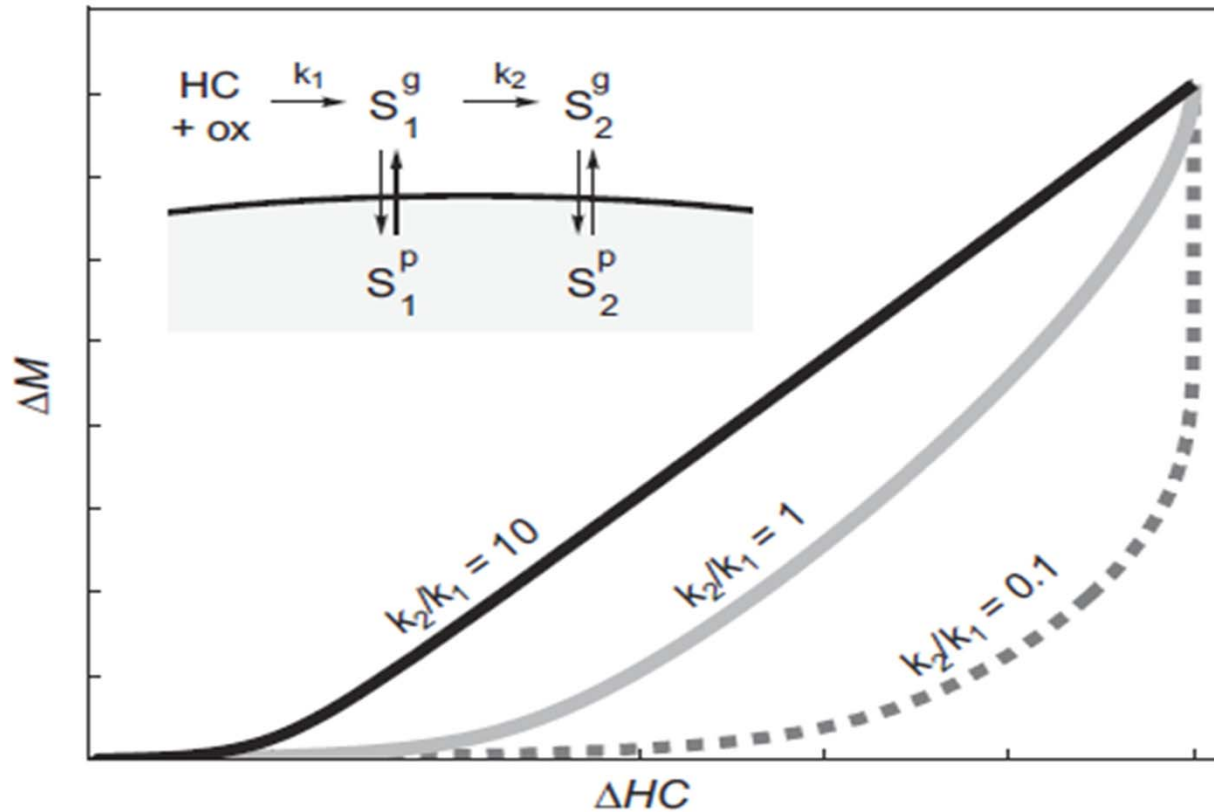
Selected condensed phase accretion reactions that reduce volatility
(The "P" reactions)



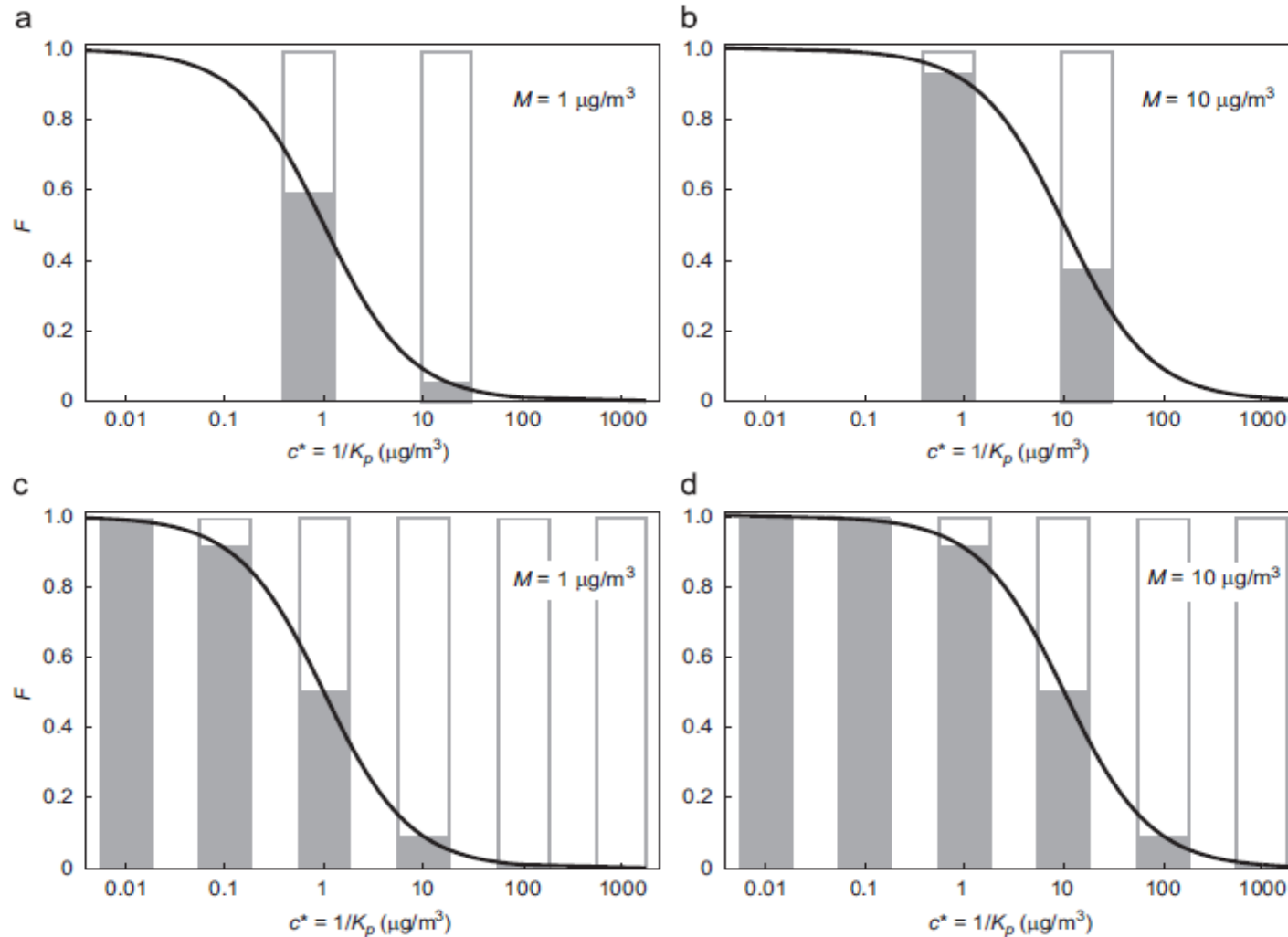
Proposed sulfate esterification reactions (from Surratt et al 2007)



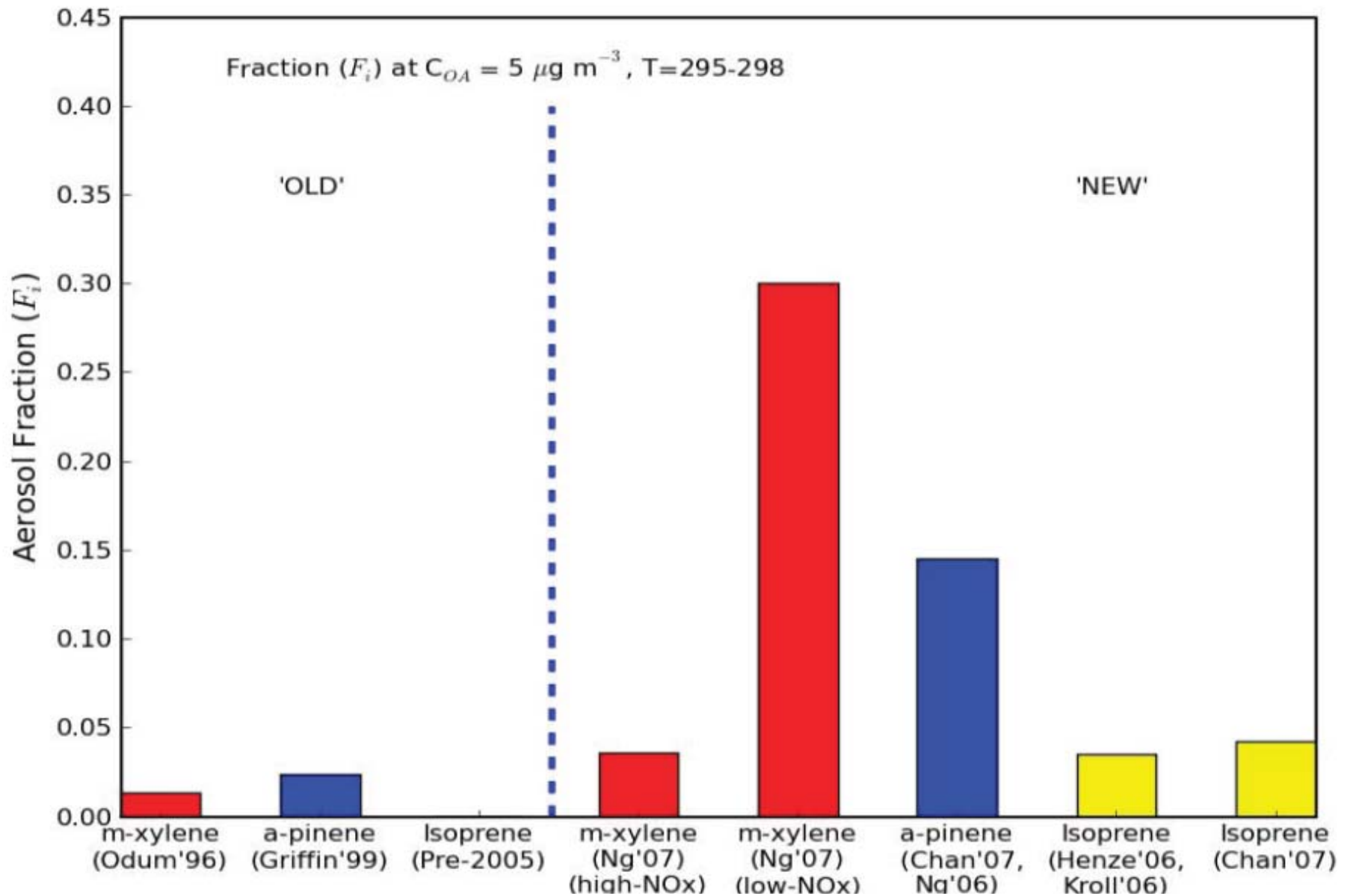
Mass production curves for 2 generation oxidation of an HC where the 2nd generation product is much less volatile than the 1st (Kroll & Seinfeld, 2008)



Comparison of the two product model phase partitioning with that in the VBS



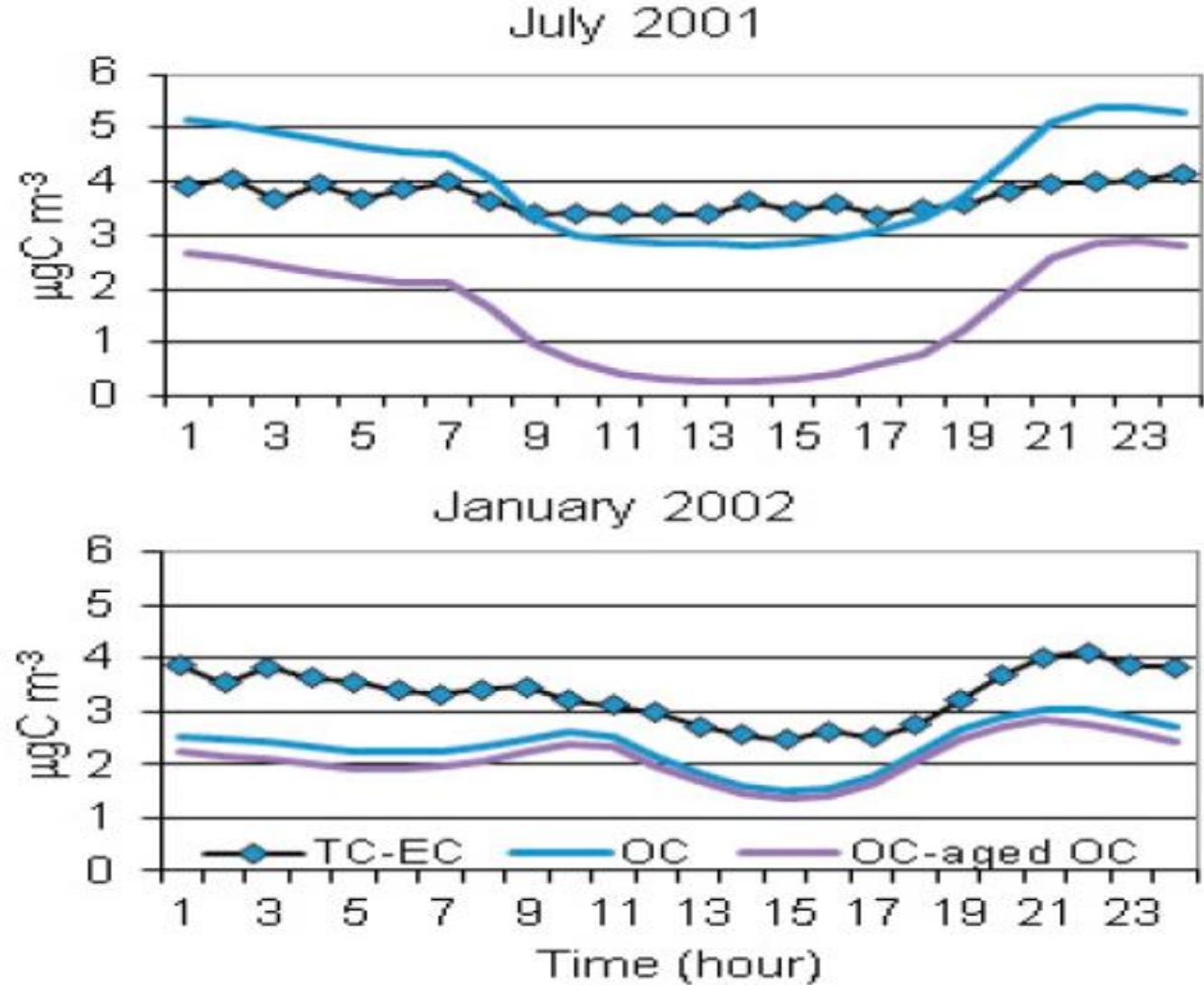
Changes in reaction yields for key species (due to such key aspects)



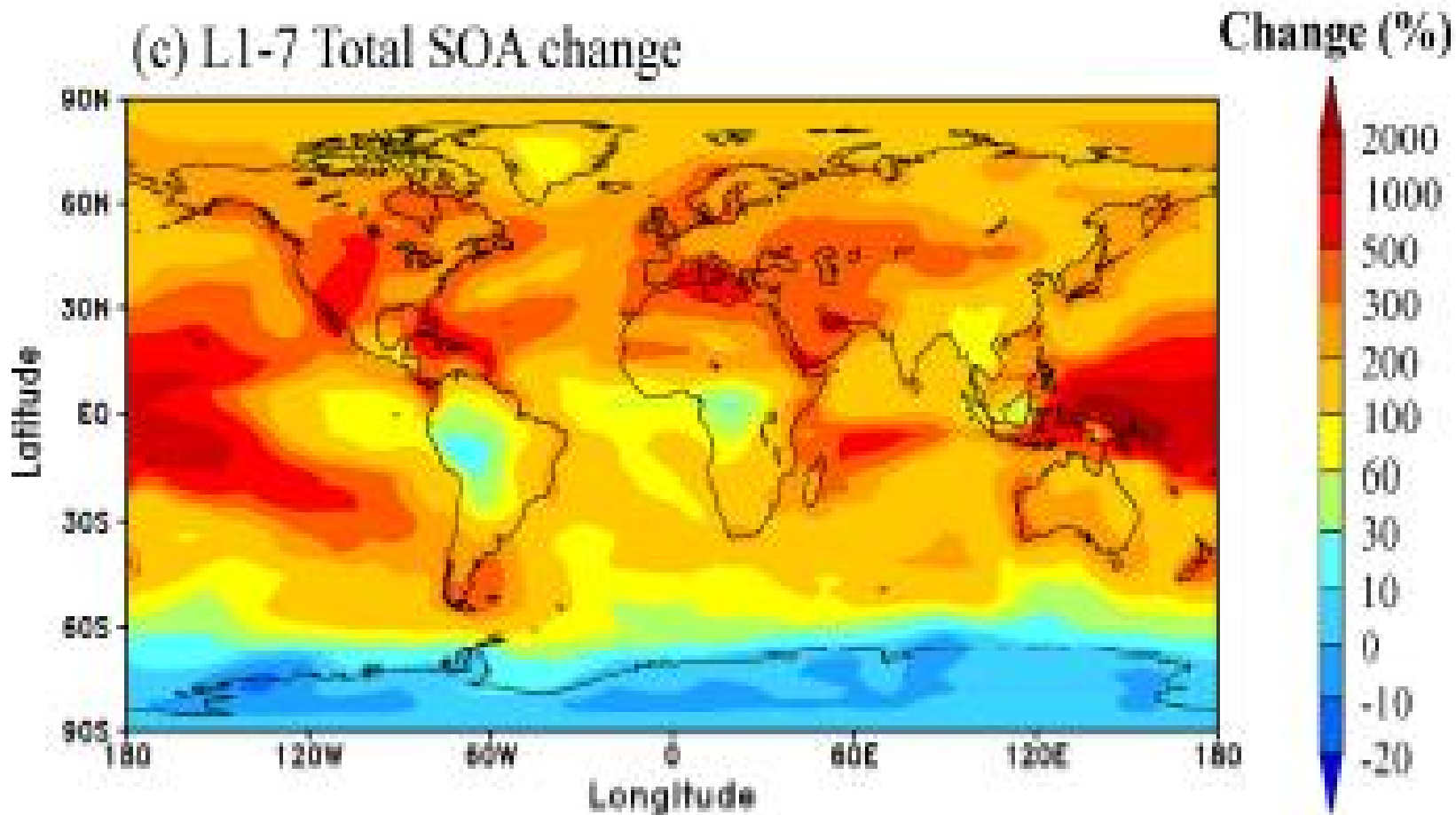
Schematic of the interaction of particle formation and growth with oxidative aging
 (from Yu et al, 2011)



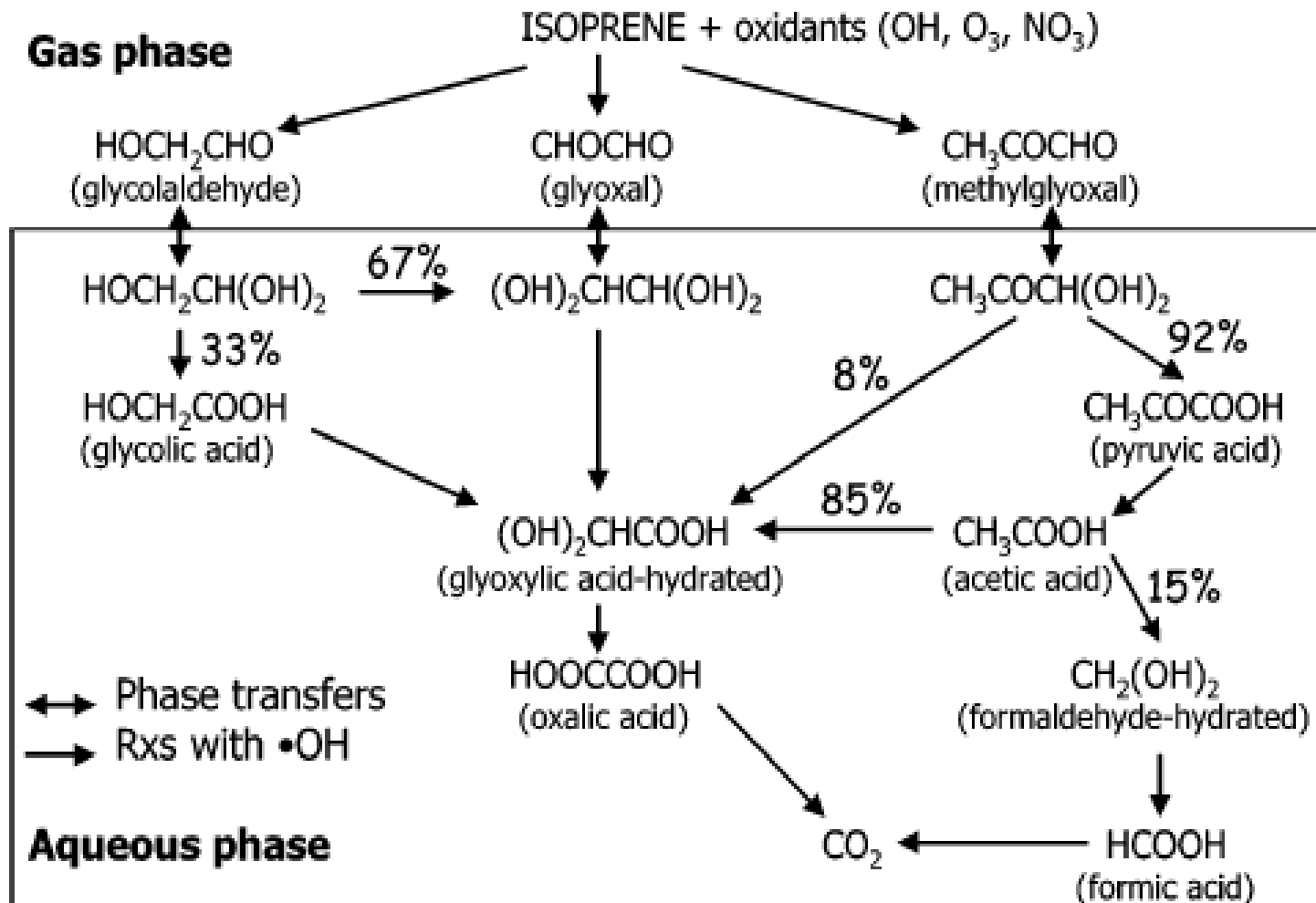
Simulated OA (monthly avg.'s) at four SEARCH sites using CMAQ



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

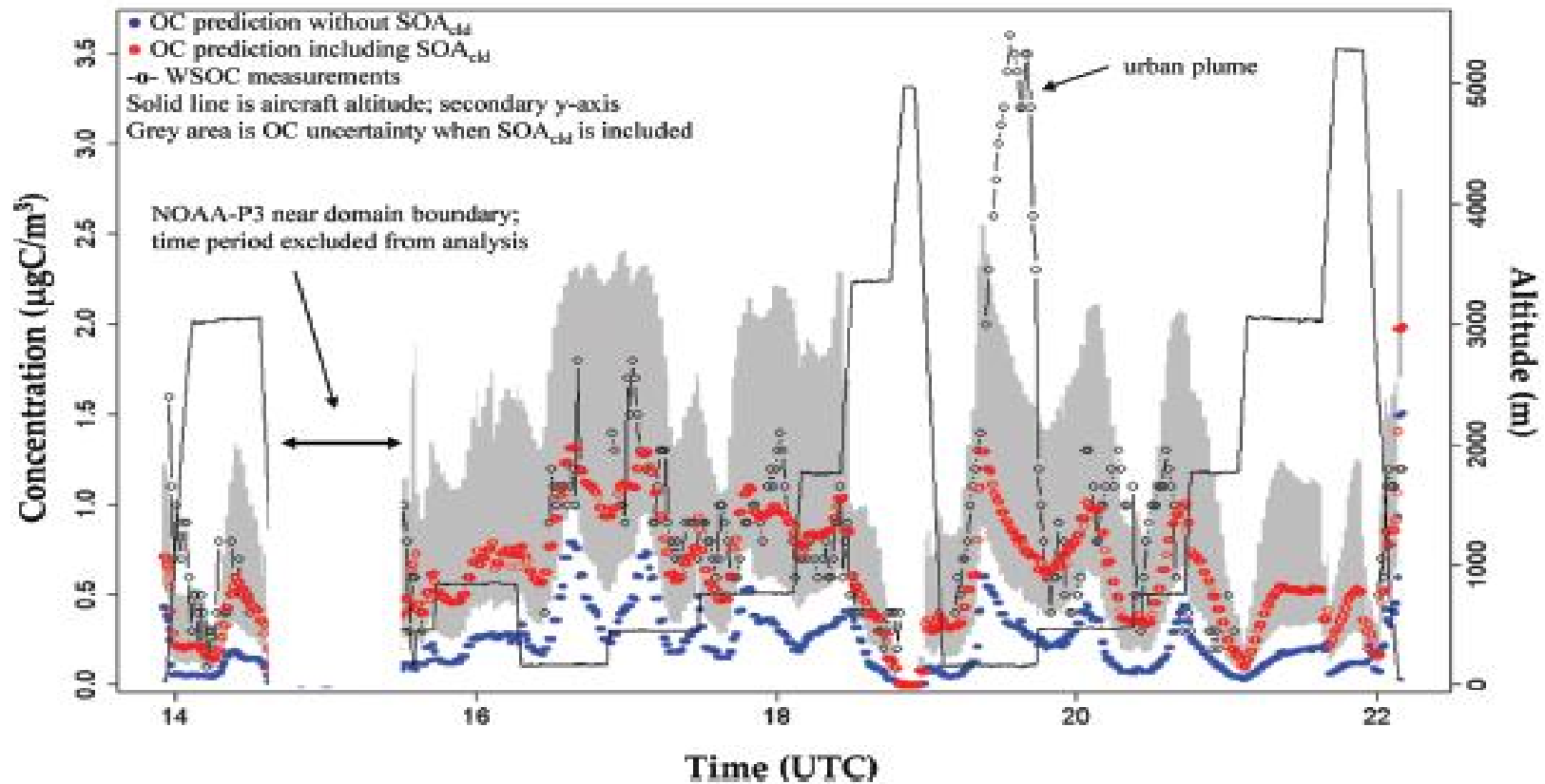


In-cloud isoprene chemistry (from Lim et al 2005)
 (An important “non-Pankowian” process)

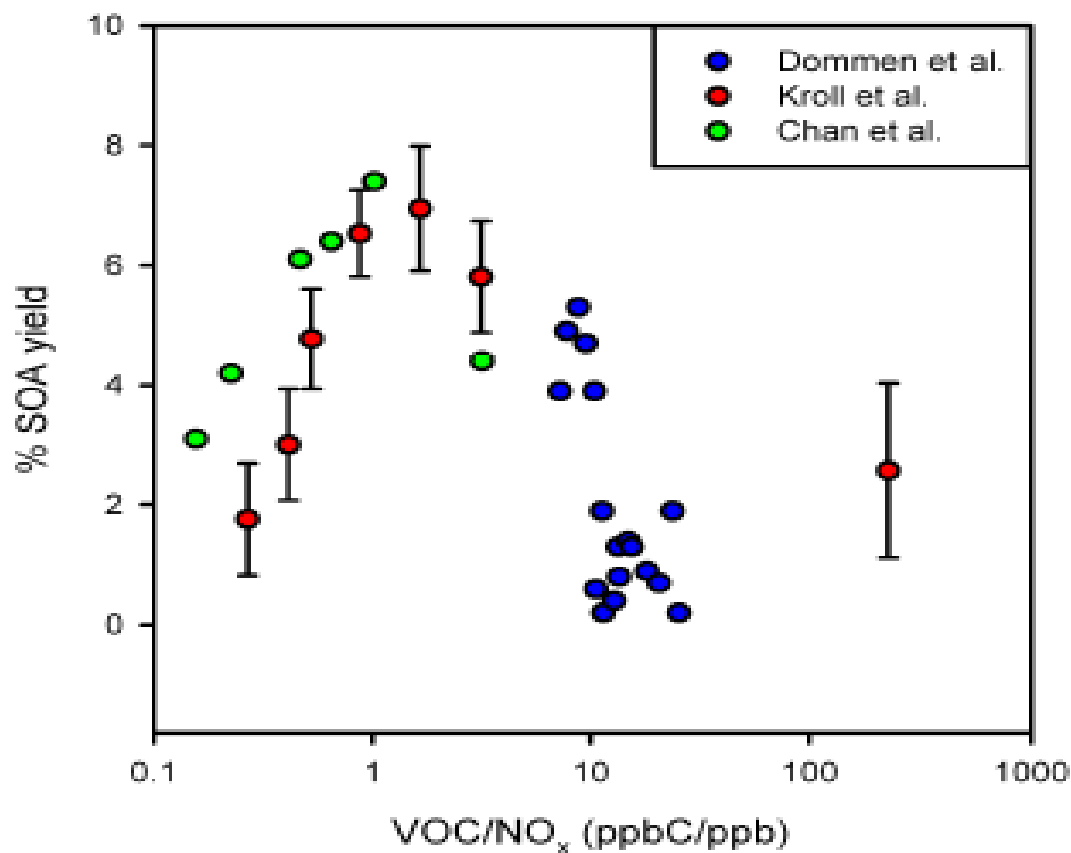


Impact of condensed phase SOA production in the CMAQ model

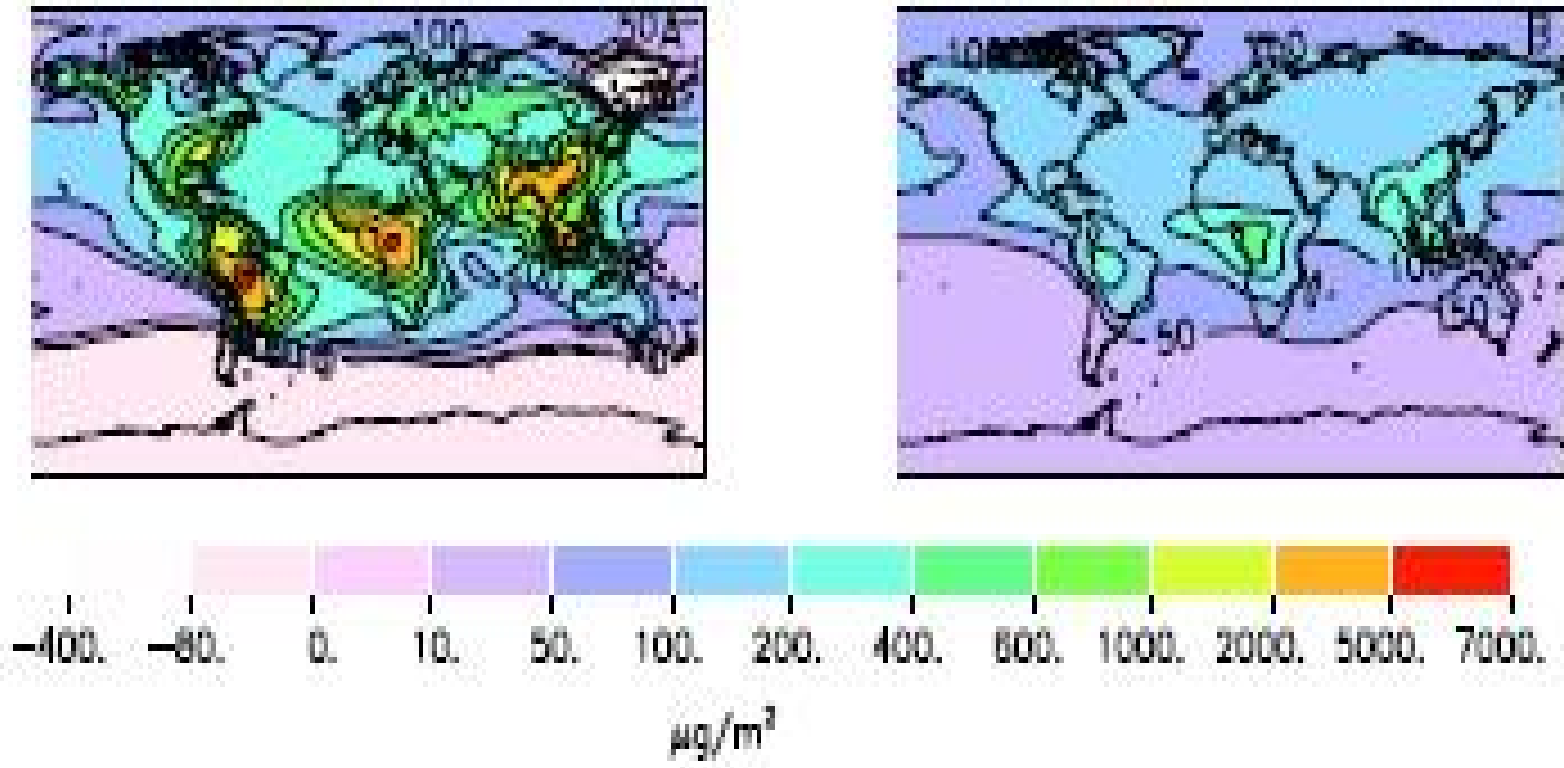
(from Carlton et al, 2008)



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



Total column SOA increase from preindustrial times.
Left panel shows total SOA while right shows only SOA formed directly from anthropogenic emissions



Key aspects of SOA formation impacting GCM predictions

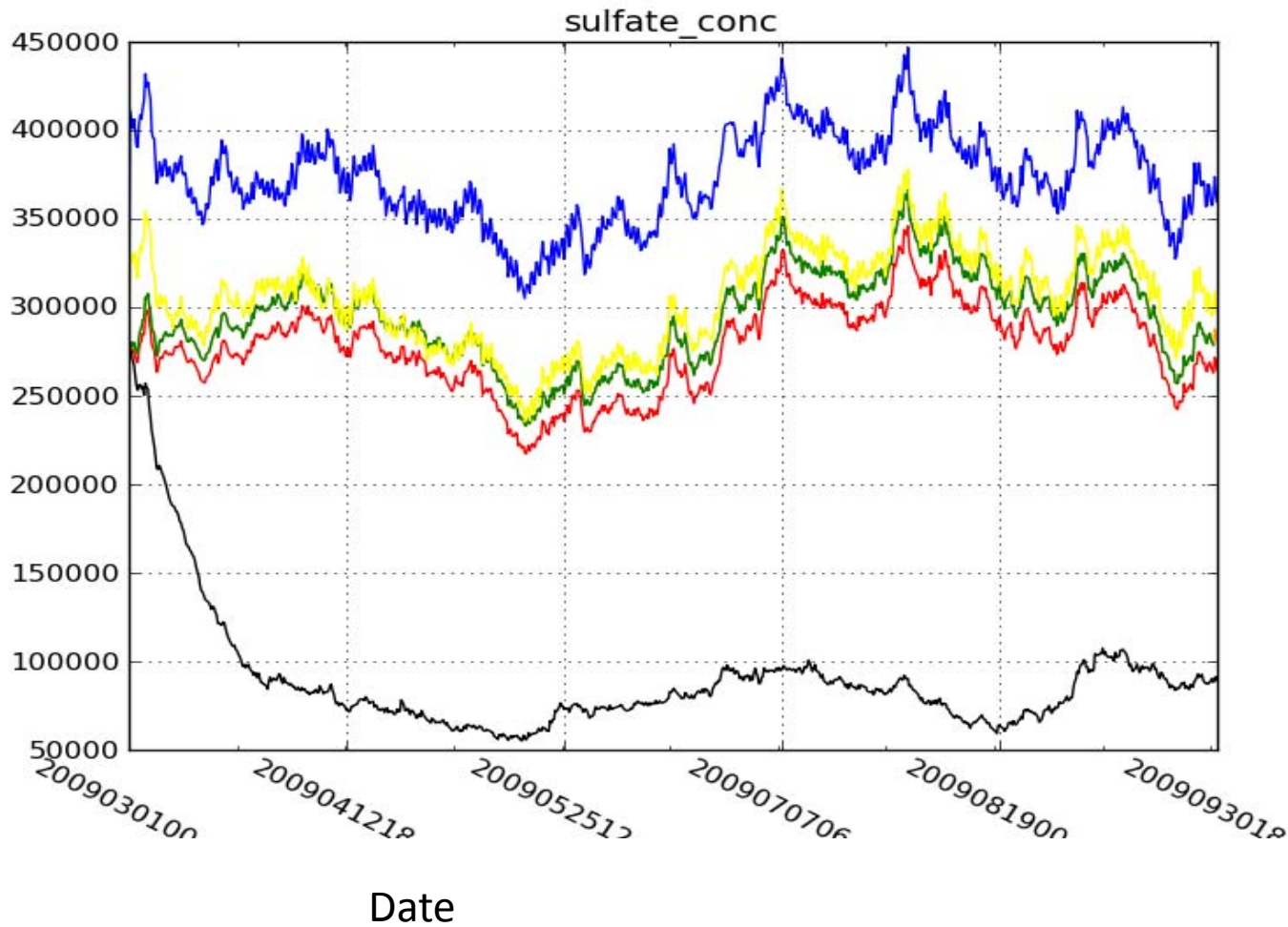
- Oxidation of VOC's to SOA is a “multi-generational” process.
- Aging of SOA can lead to more, or less, volatile SOA species.
- Condensed phase processes are very important (including possible in-cloud SOA formation).
- The yield of SOA from precursors is a function of the pre-existing aerosol composition.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

SOA formation in selected current GCM's

What mechanisms are employed?

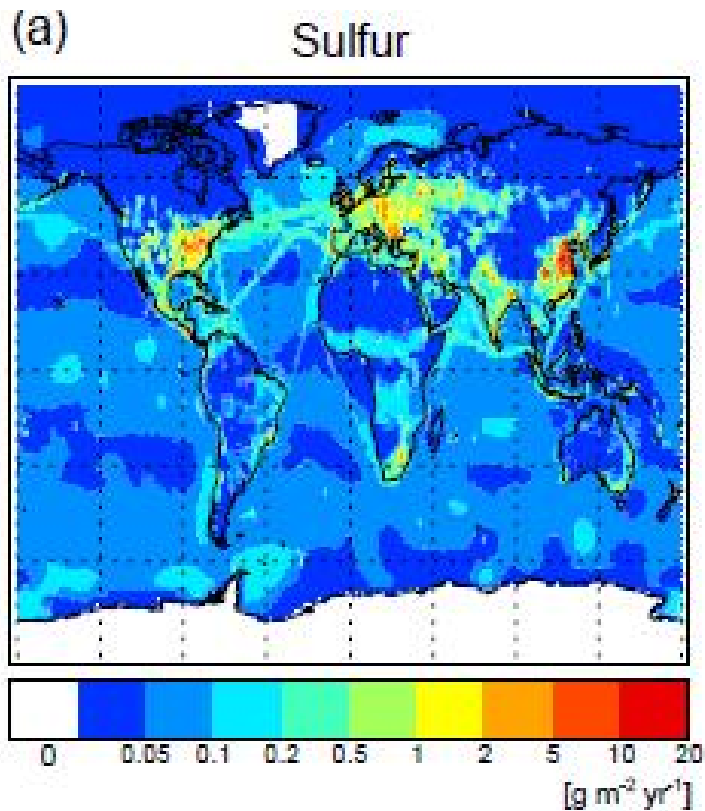
What results are obtained

“Sulfate” (sulfate + OA as 2X sulfate) from the NAAPS model for an ~ 6 month period in 2009

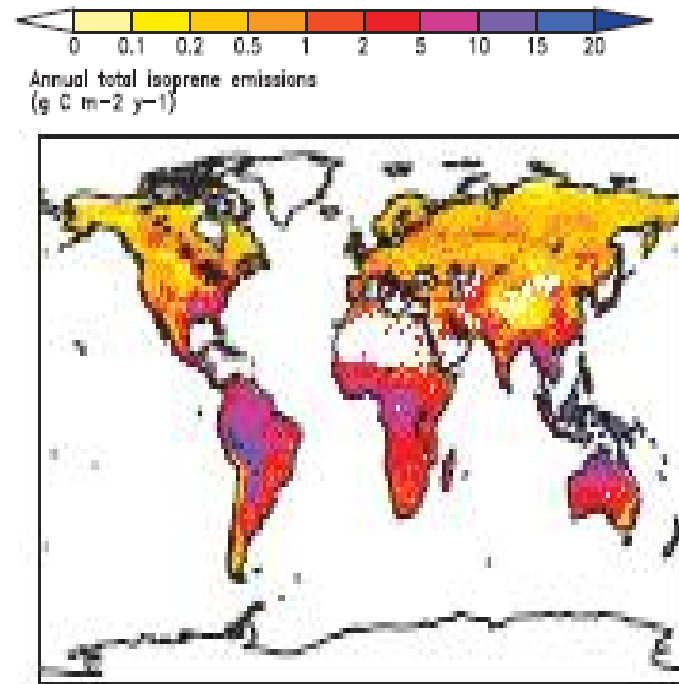


Geographic emission patterns for sulfur and organic aerosol precursors

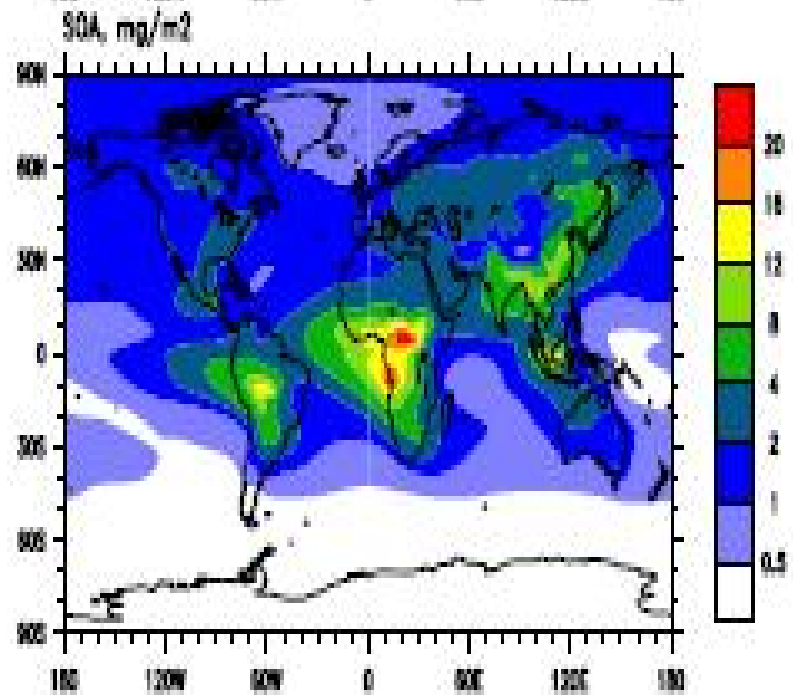
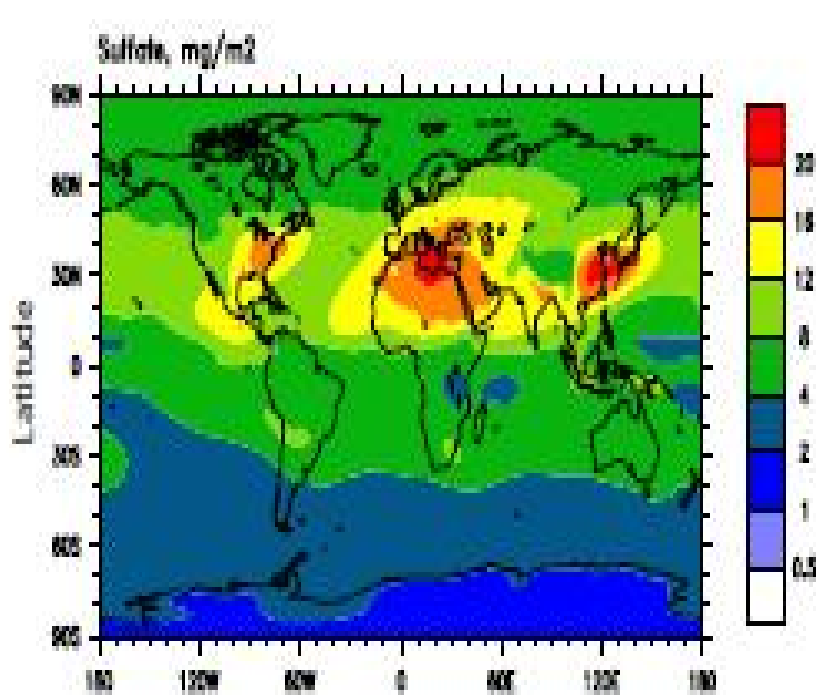
Sulfur emissions (primarily SO₂)



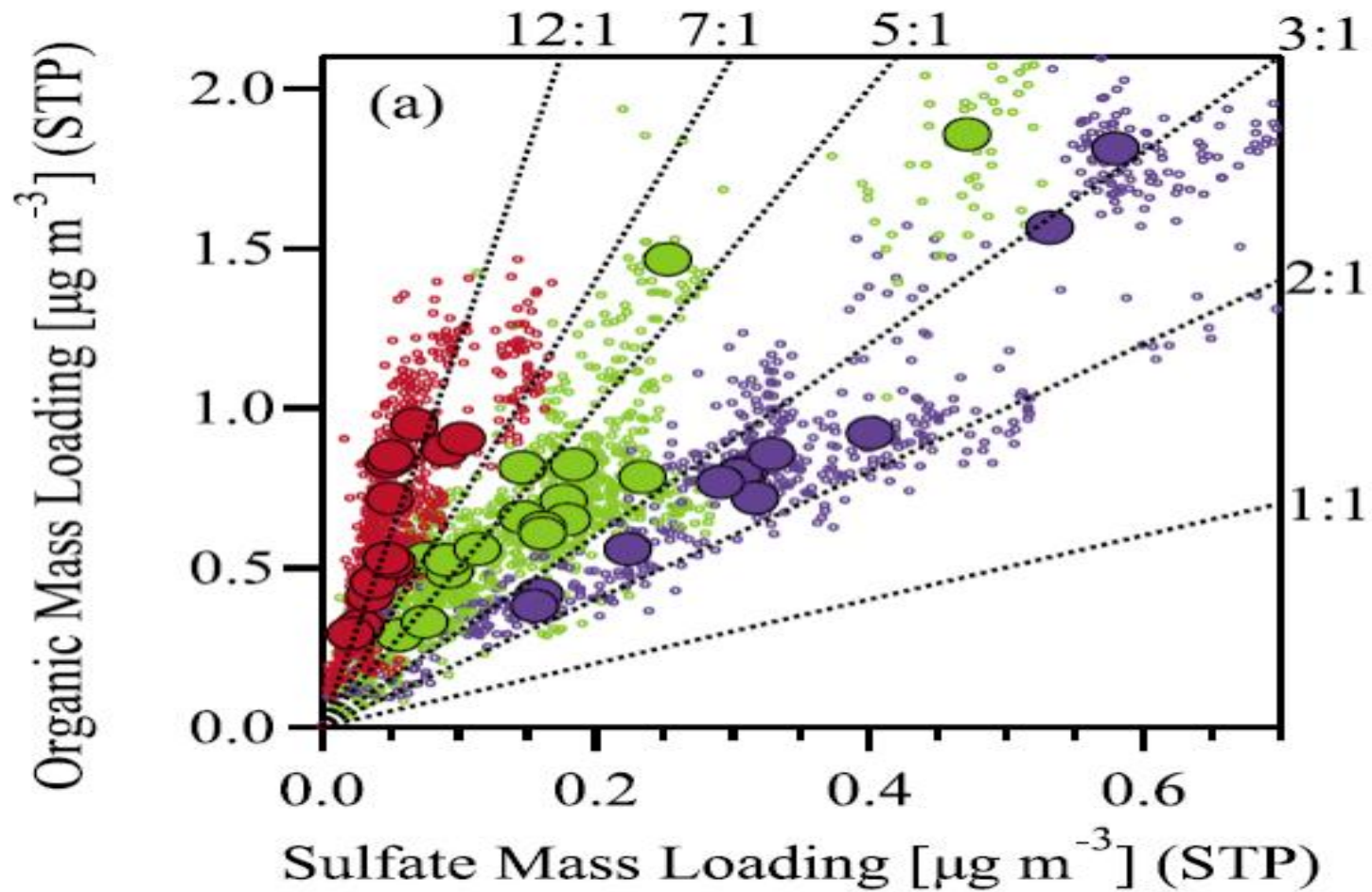
Isoprene emissions



Geographic distribution of secondary Sulfate and SOA



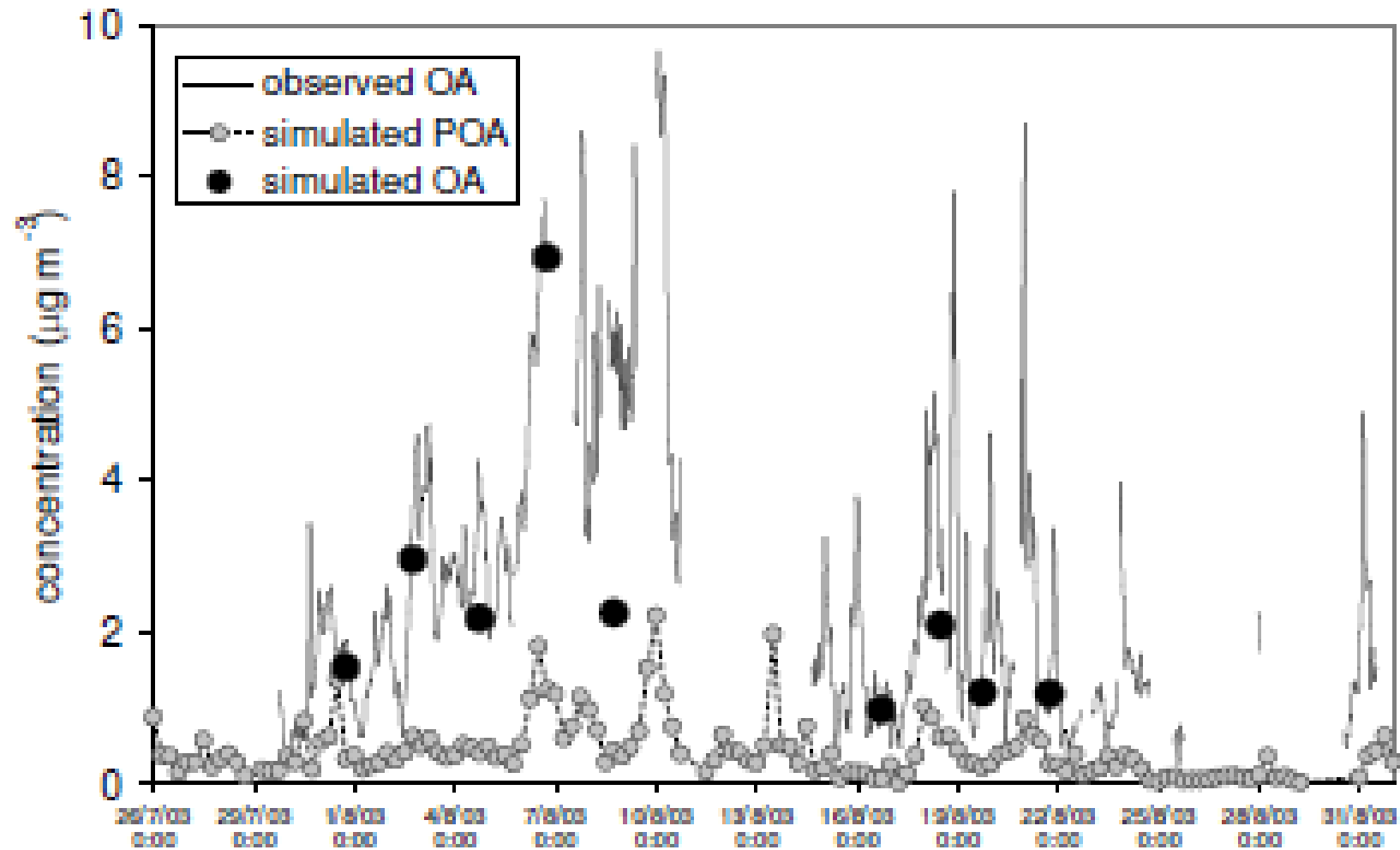
Organic – sulfate aerosol mass relationship in Amazonia



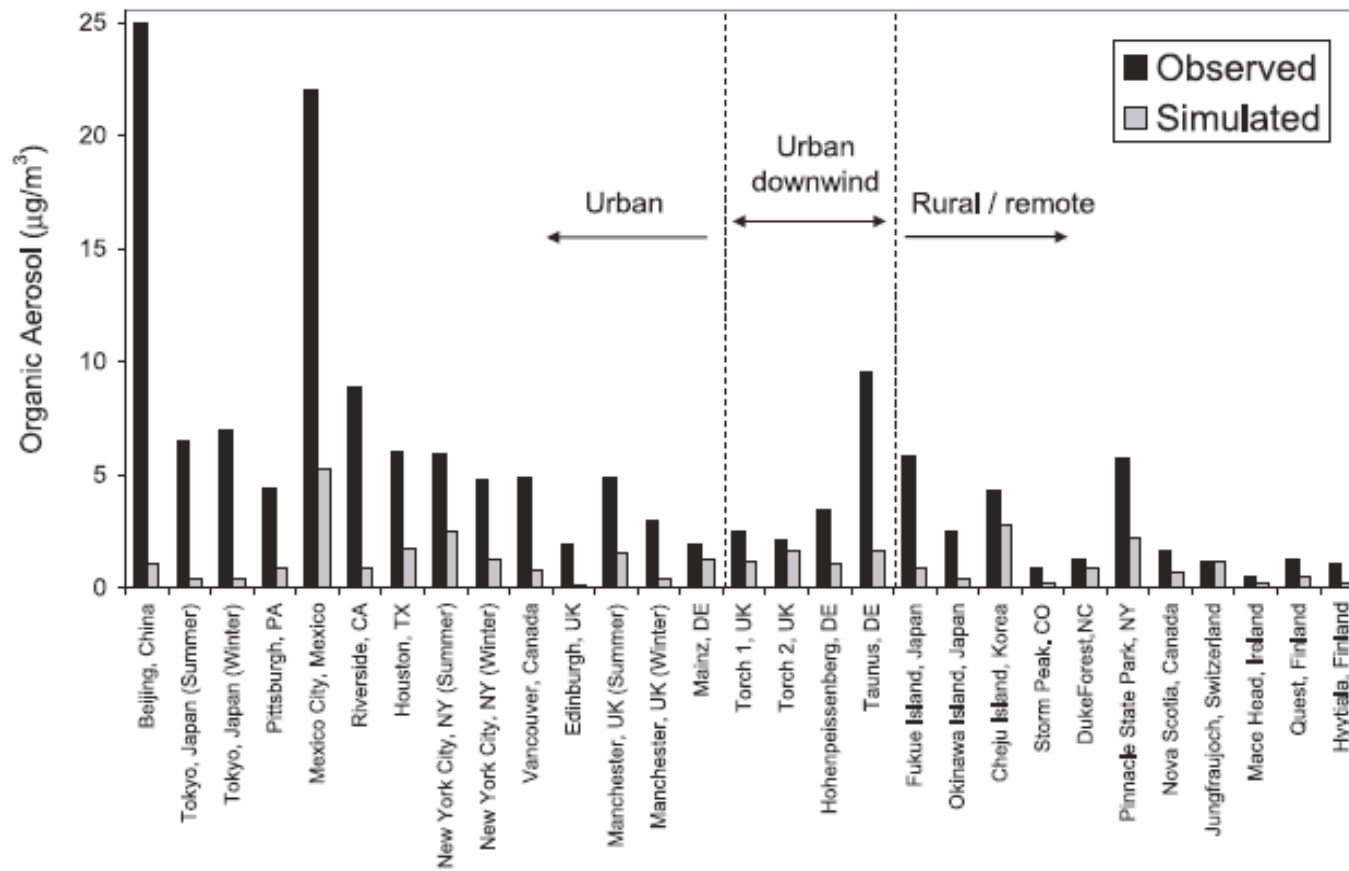
SOA chemical mechanisms in selected GCM's (from Emmerson & Evans, 2009)

	Reactions	No. of Species	Model Chemistry Includes...	Notes
MCM	13 500 766 (M) 6502 (T)	5600 248 (M) 2241 (T)	135 VOCs including 22 alkanes $\leq C_{12}$, 16 alkenes $\leq C_6$, 6 aldehydes, 18 aromatics, isoprene, α - and β -pinene	The benchmark scheme
CRI-reduced	555	196	23 VOCs including alkanes $\leq C_4$, alkenes $\leq C_4$ 9 oxygenated compounds, benzene, toluene, o-xylene, isoprene, α - and β -pinene	4% of the size of the MCM
GEOSito	490	179	alkanes $\leq C_8$, alkenes $\leq C_4$, 11 oxygenated compounds, benzene, toluene, m-xylene, isoprene, α - and β -pinene	Ito et al. (2007) extended GEOS-CHEM mechanism
GEOS-CHEM	273	93	alkanes $\leq C_3$, alkenes $\leq C_4$, 9 oxygenated compounds, isoprene	
MOZART-2	158	63	alkanes $\leq C_4$, alkenes $\leq C_3$, acetylene, acetaldehyde, acetone, methanol, isoprene and lumped monoterpenes	
TOMCAT	152	58	Ethane, propane, acetylene, acetaldehyde, acetone, methanol and isoprene	Includes Mainz Isoprene Mechanism; Pöschl et al. (2000)
CBM-IV	85	47	Ethene, isoprene, lumped parafins, olefins, aldehydes and aromatics	

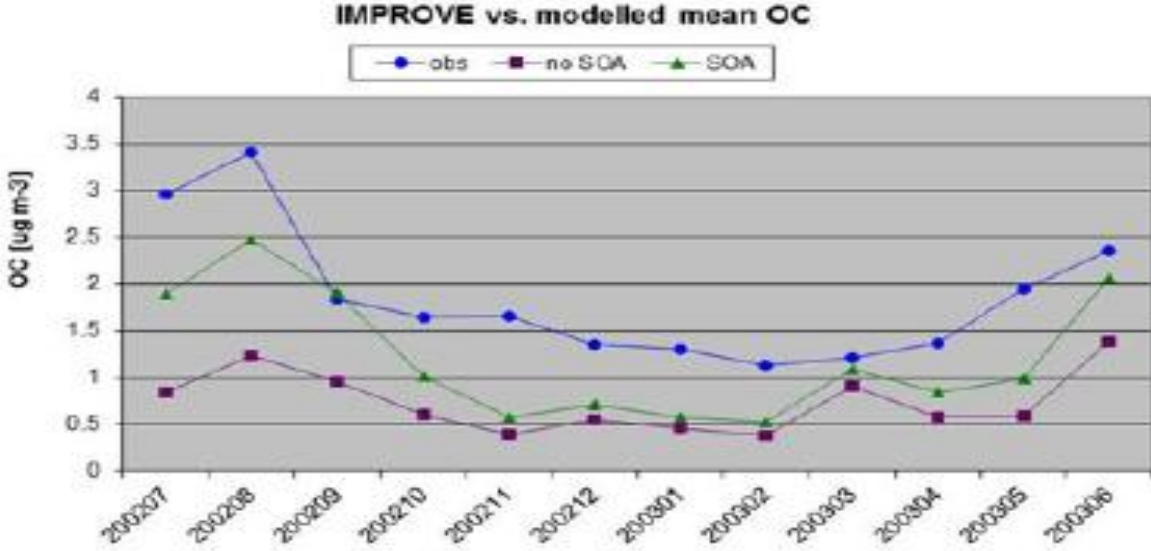
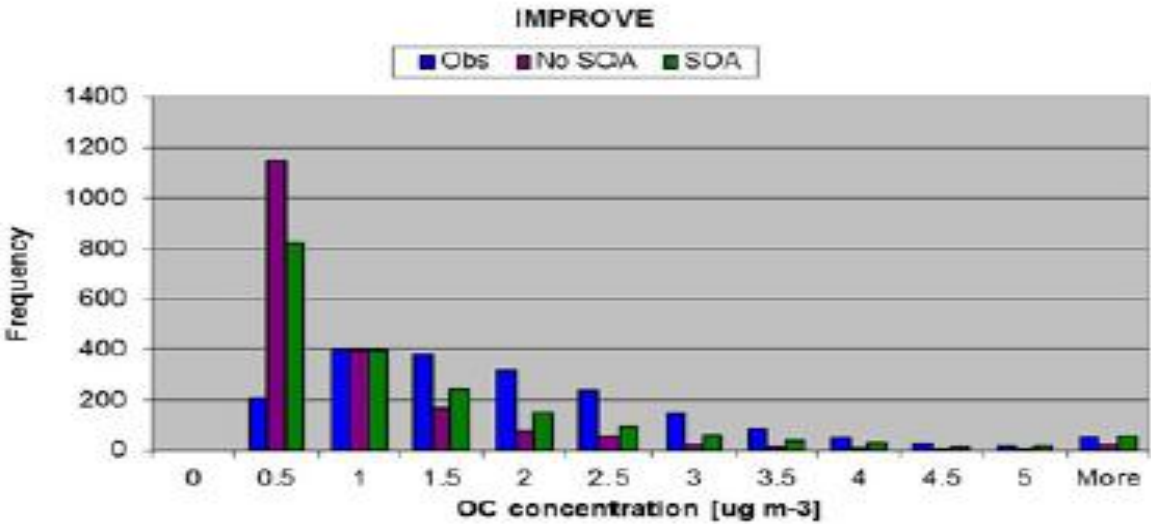
From Johnson et al 2006 TORCH MCM model
(After increasing all partition coefficients uniformly by a factor of 500)



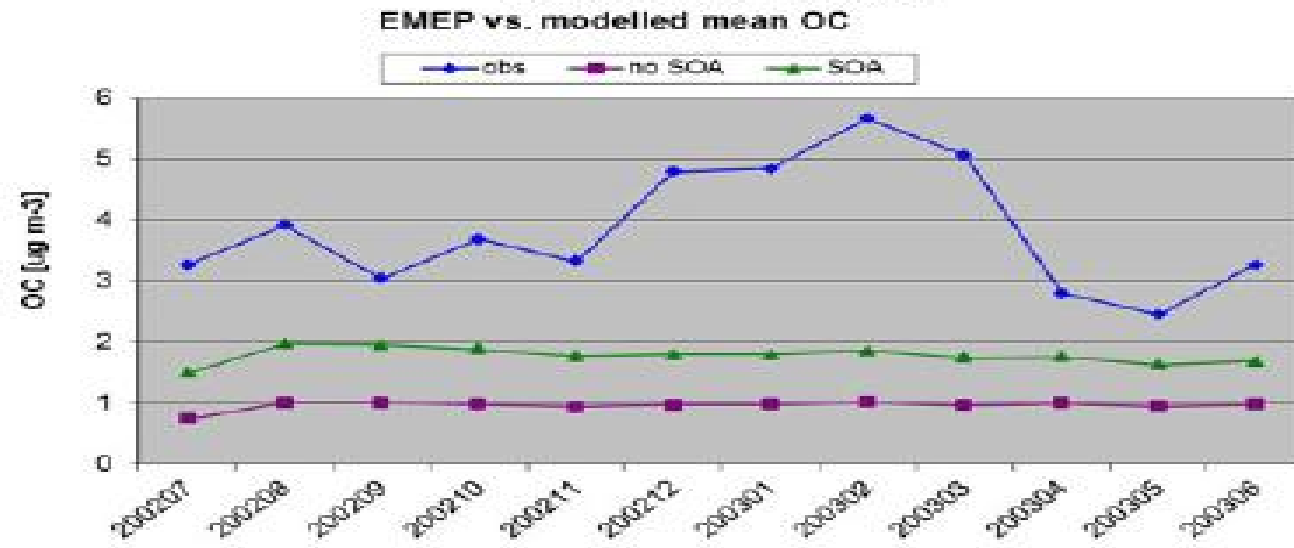
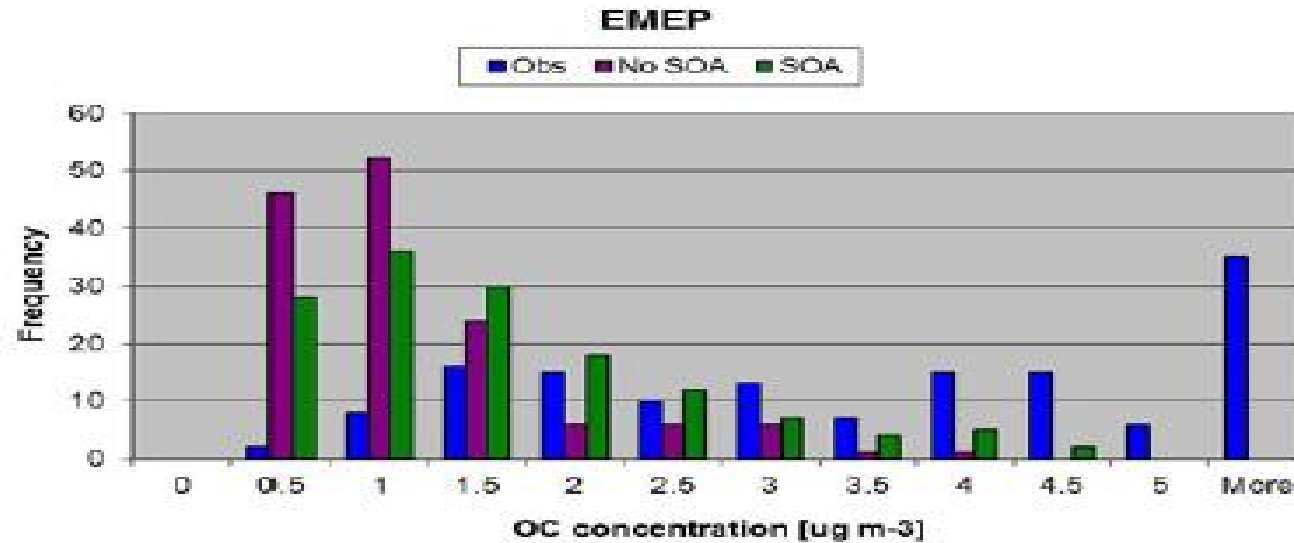
From Utembe et al 2011 CRI v2_R5



IMPROVE observations and modeled OC mass (from O'Donnell et al, 2011)



EMEP observations and modeled OC mass (from O'Donnell et al, 2011)



Comparison of selected model SOA mechanisms

Model	SOA Precursors	SOA formation process	Primary SOA source
Top Down (based on Hallquist et al, 2009)	NA	NA	isoprene
PNNL CAM5/MMF (Wang et al, 2011)	isoprene monoterpenes aromatics	Explicit bulk yields added to POA. Direct reversible condensation of SOA	monoterpenes
Oslo CTM2 (Hoyle et al, 2007)	toluene, m-xylene, other aromatics, monoterpenes, sesquiterpenes, isoprene, ORVOC	OH + isoprene, (OH, O ₃ , NO ₃) + 5 terpene classes, OH + aromatics; 2 product approach; explicit partitioning into POA; hydrophobic aging	terpenes
STOCHEM CRI v2-R5 (Utembi et al 2011)	Isoprene, pinene's, benzene, toluene, Cyclic anhydride products	2 generation oxidation by (OH, O ₃ , NO ₃) coupled to reduced MCM 3.1 reaction set (555 reactions of 196 species). Pankow partitioning	biogenic (likely isoprene but not specified)
ECHAM5-HAM (O'Donnell et al, 2011)	isoprene, monoterpenes, xylene, toluene, benzene	OH+isoprene, OH+ anthropogenics, O ₃ +monoterpenes; 2 product approach; Partitioning only into POA	isoprene
GEOS-CHEM (Henze et al, 2008)	toluene, m-xylene, benzene, terpenes, isoprene, alcohols	Various reactions of VAC with RO _x and NO _x	isoprene
AeroCom Mean (Textor et al, 2006)	terpenes	Explicit bulk yield (5%) added to POA	terpenes

Comparison of selected model SOA results

Model	POM burden (Tg)	SOA burden (Tg)	SOA source/sink (Tg)	
Top Down (based on 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 (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	
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

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

Conclusions (Part 1)

(Some big problems)

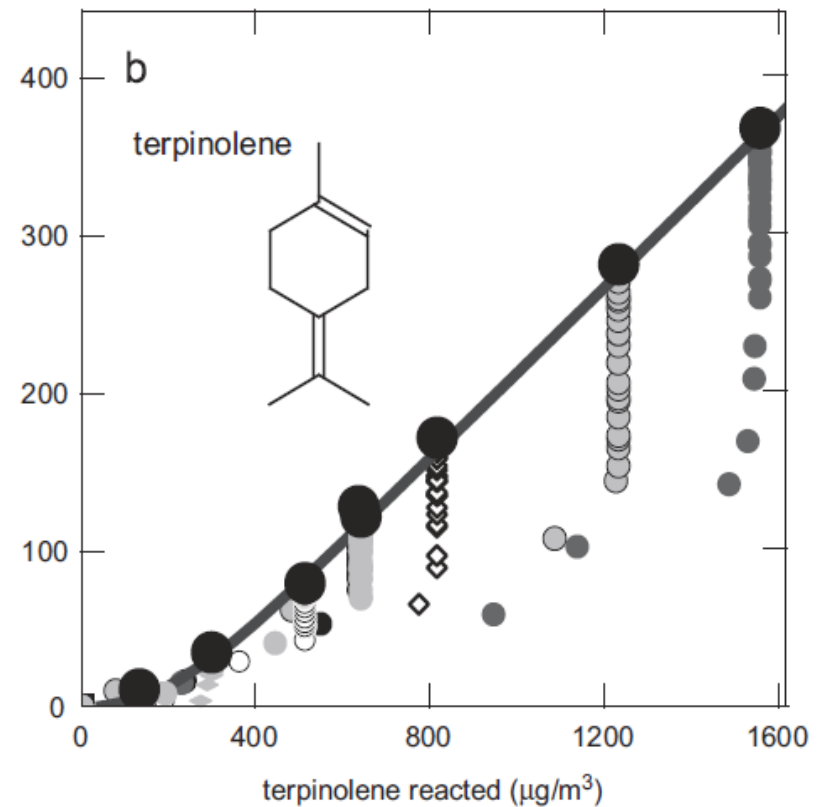
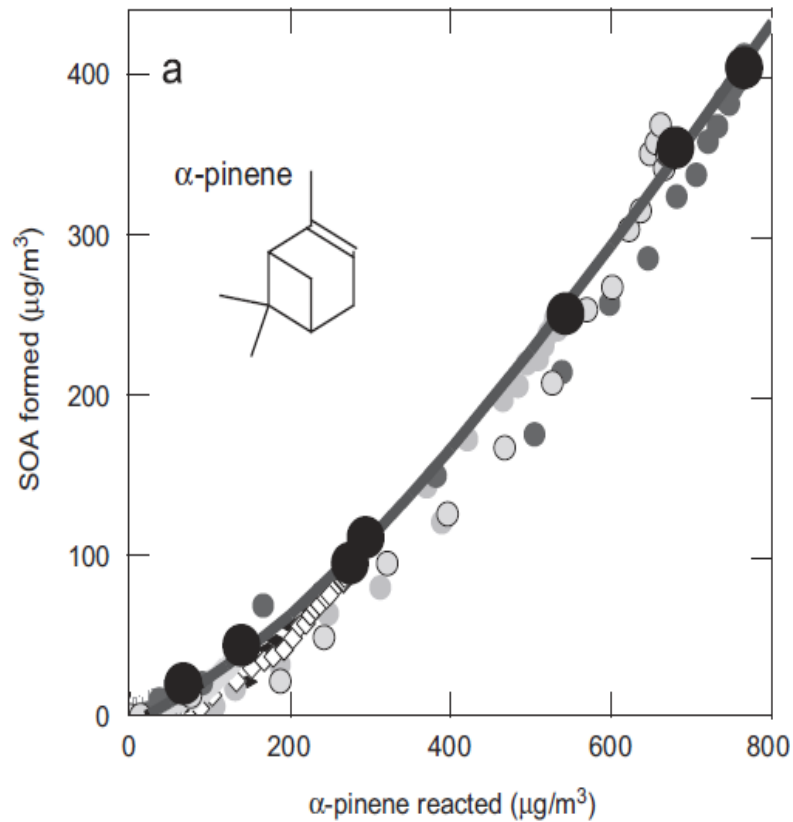
- Multi-generational nature of SOA formation, together with not yet well understood condensed phase processes, make SOA difficult to include in models
- Expansion of the species and reaction sets included in the models is not the right approach
- Proper phase partitioning of SOA is key

Conclusions (Part 2)

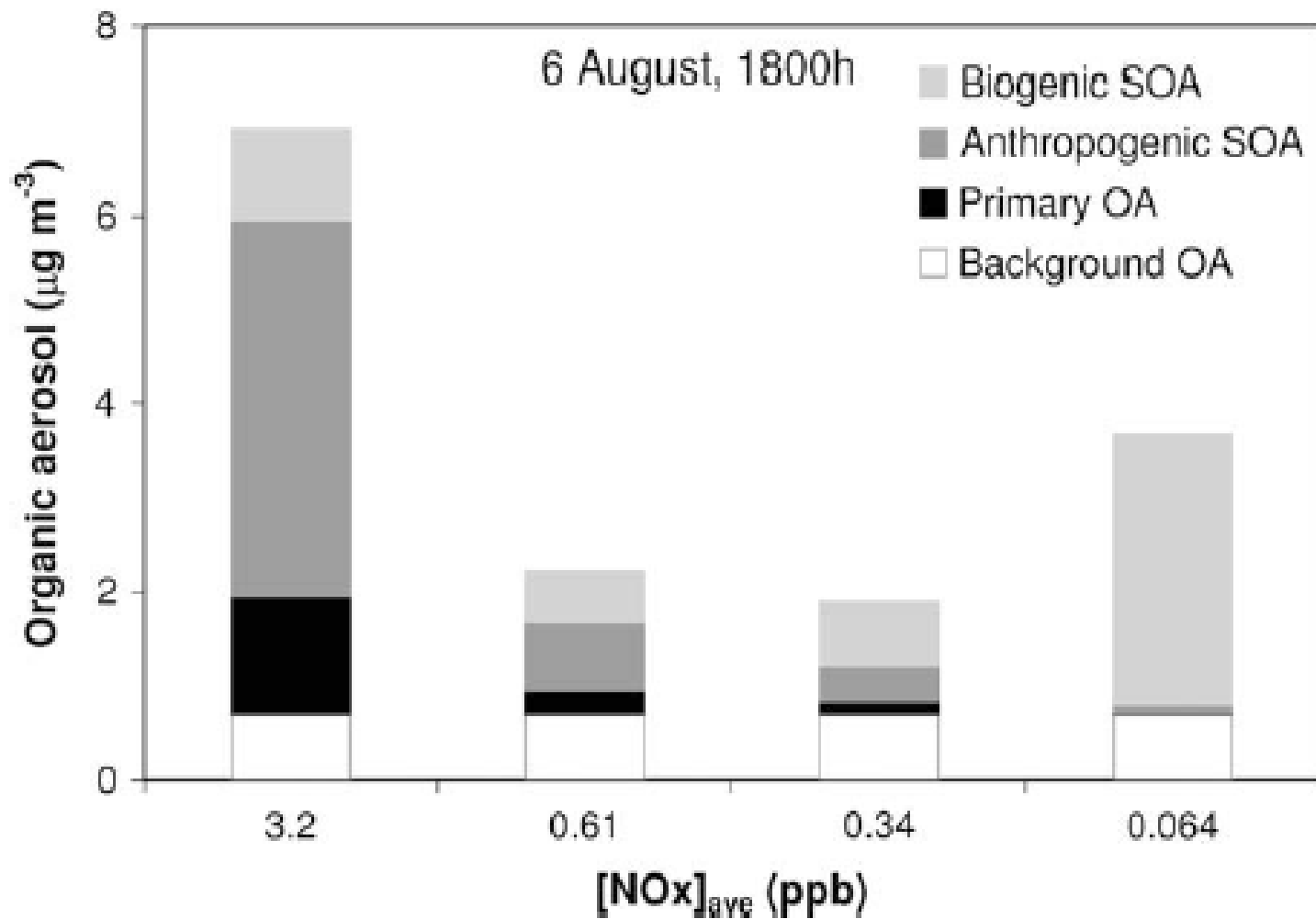
- Top down flux estimates can help constrain budgets but are not in themselves the solution
- Implementation of the VBS approach to partitioning may help
- The coupling of BSOA production with anthropogenic emissions needs to be further quantified (not yet ready for model inclusion)
- FRP's are really complicated

EXTRAS

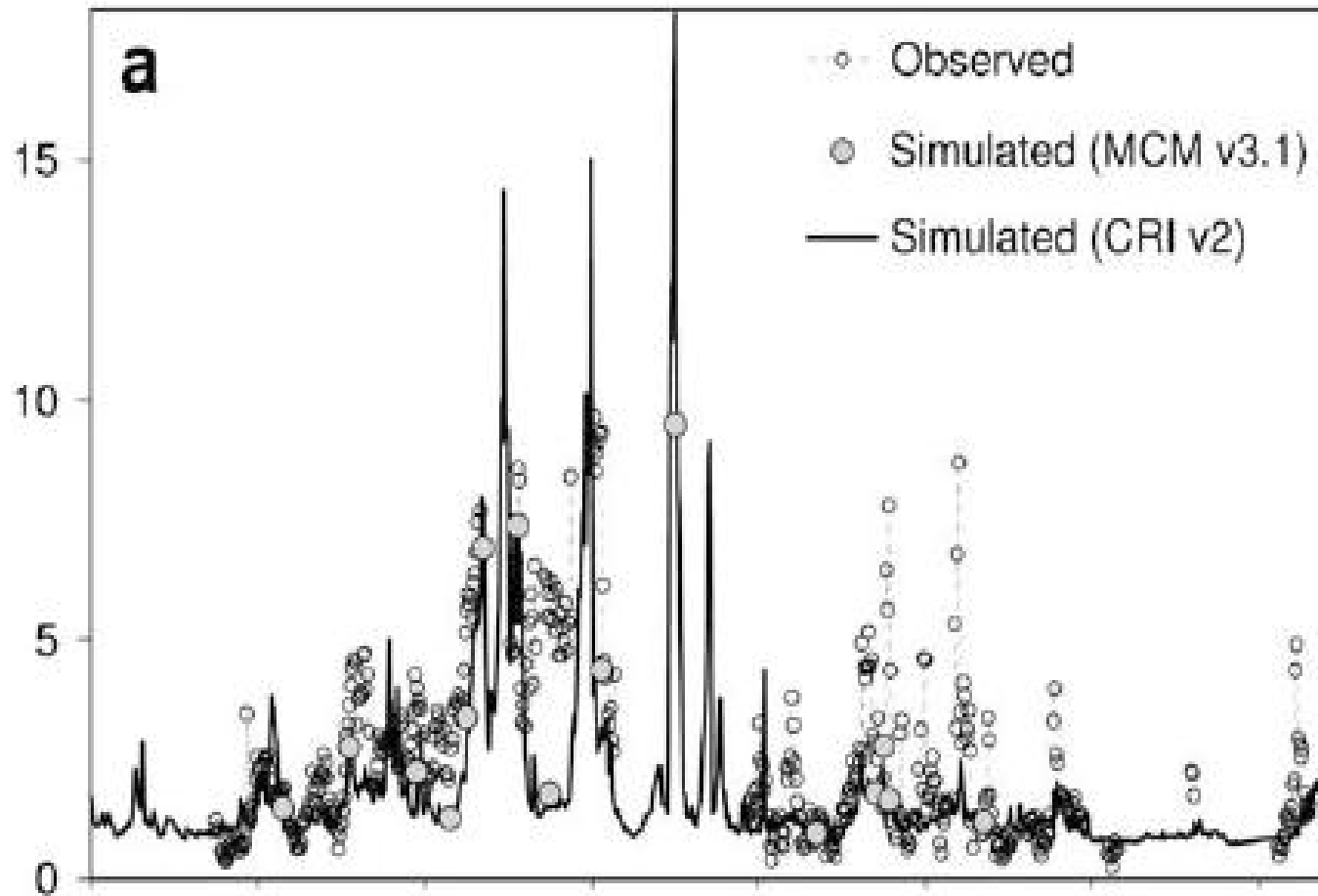
Contrasting examples of mass production curves for oxidation reactions with differing 1st and 2nd generation reaction rates

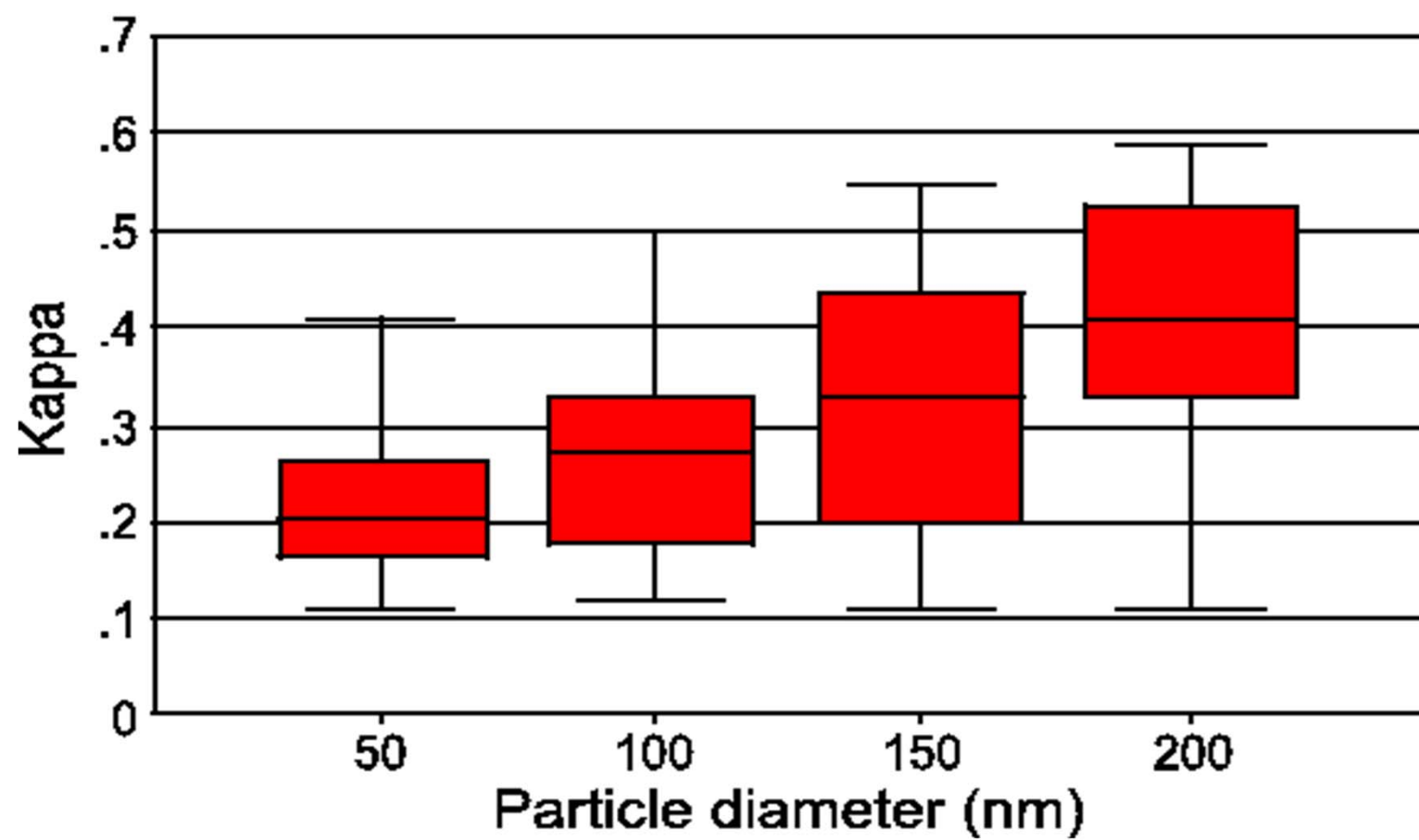


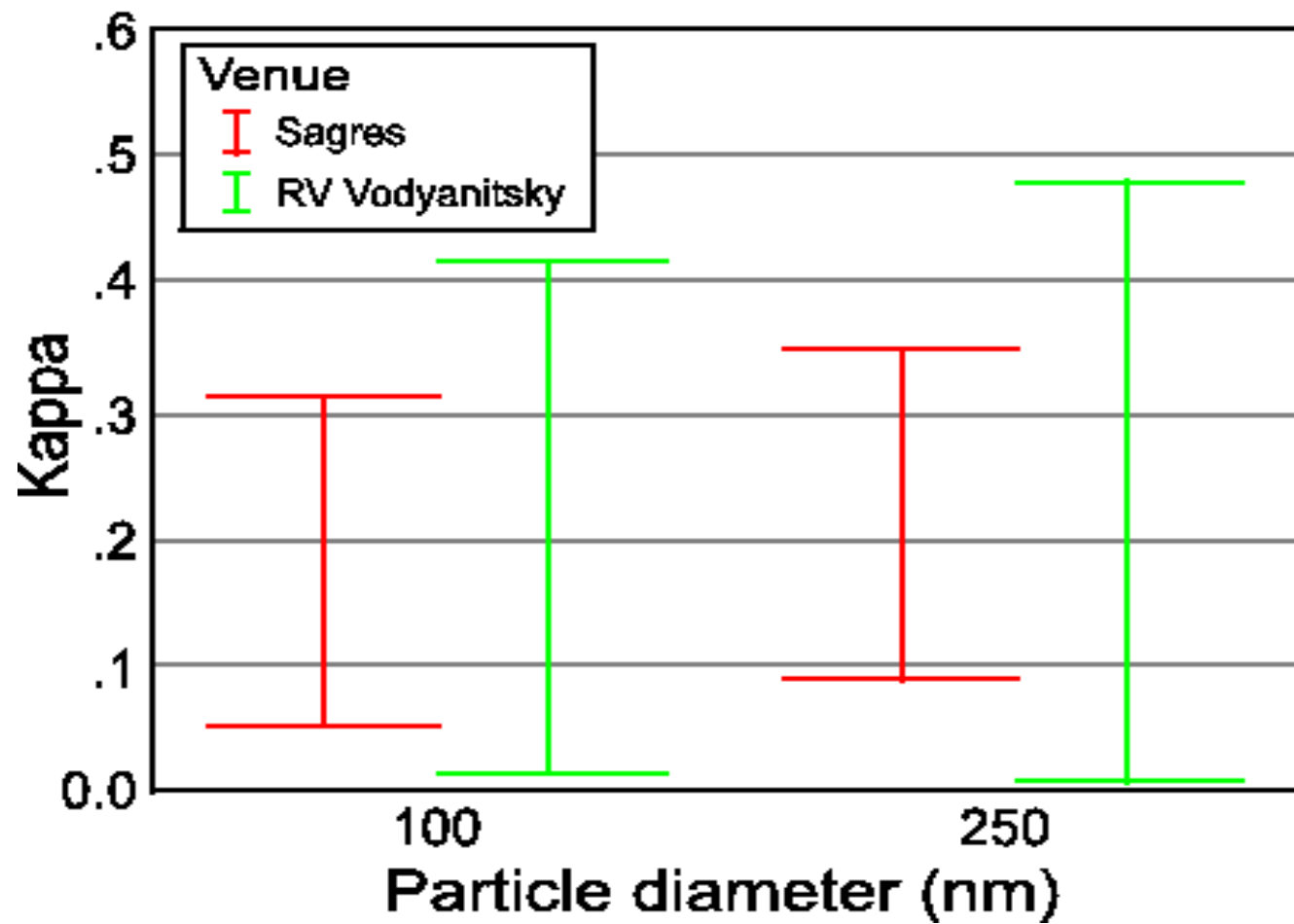
From Utembe et al 2009 impact of pollution on OA mix

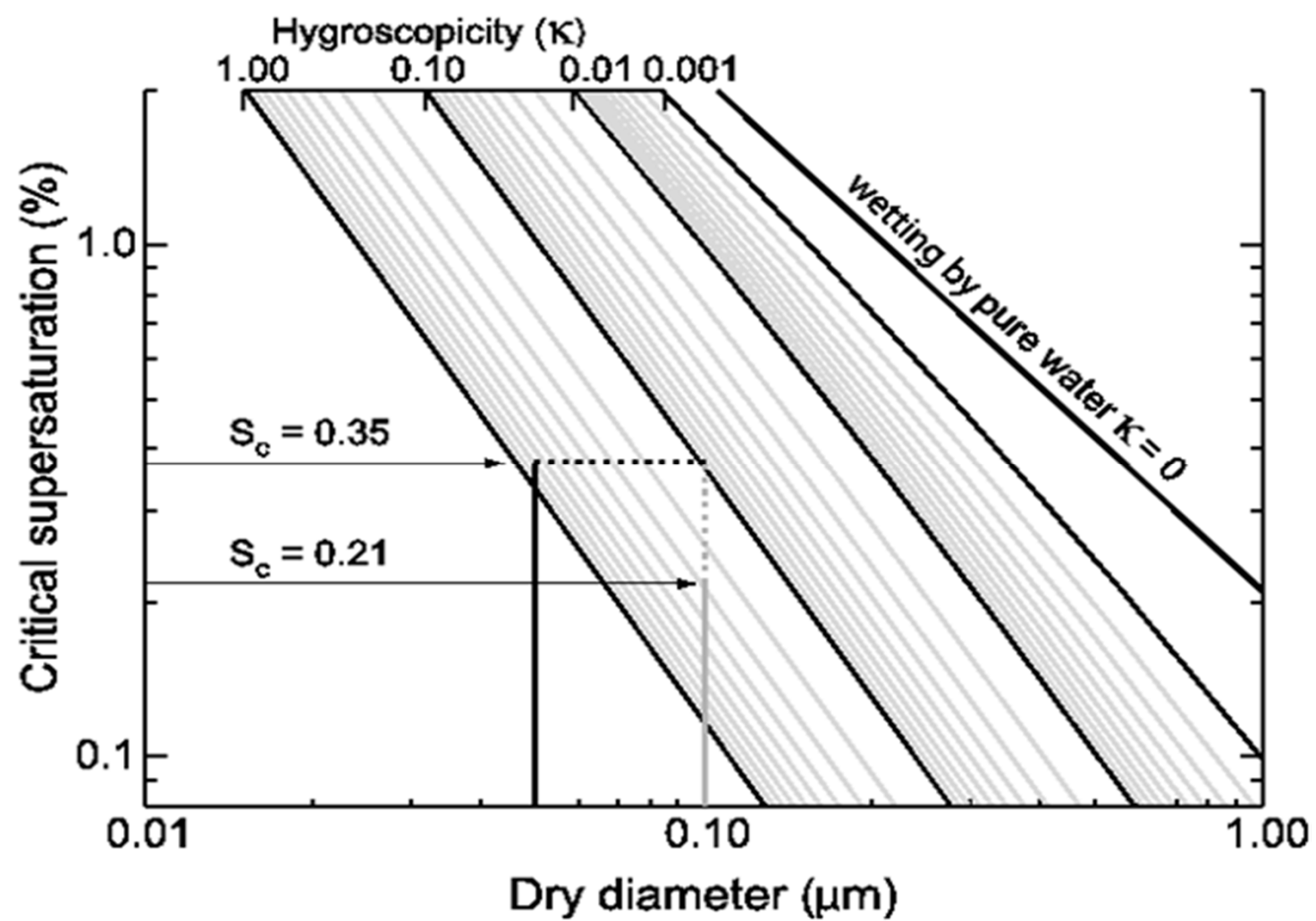


From Utembe et al 2009; OA conc. ($\mu\text{g}/\text{m}^3$ vs time)

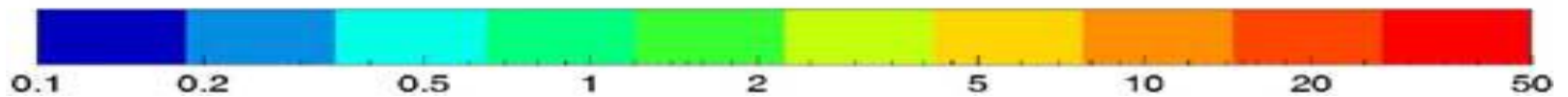
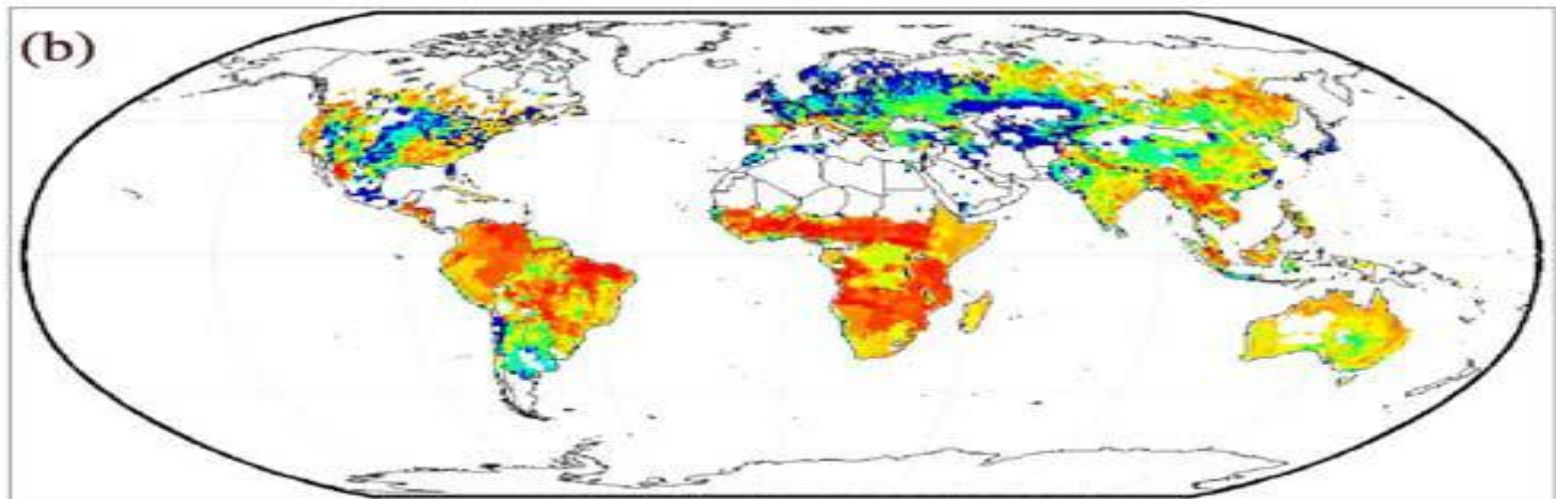
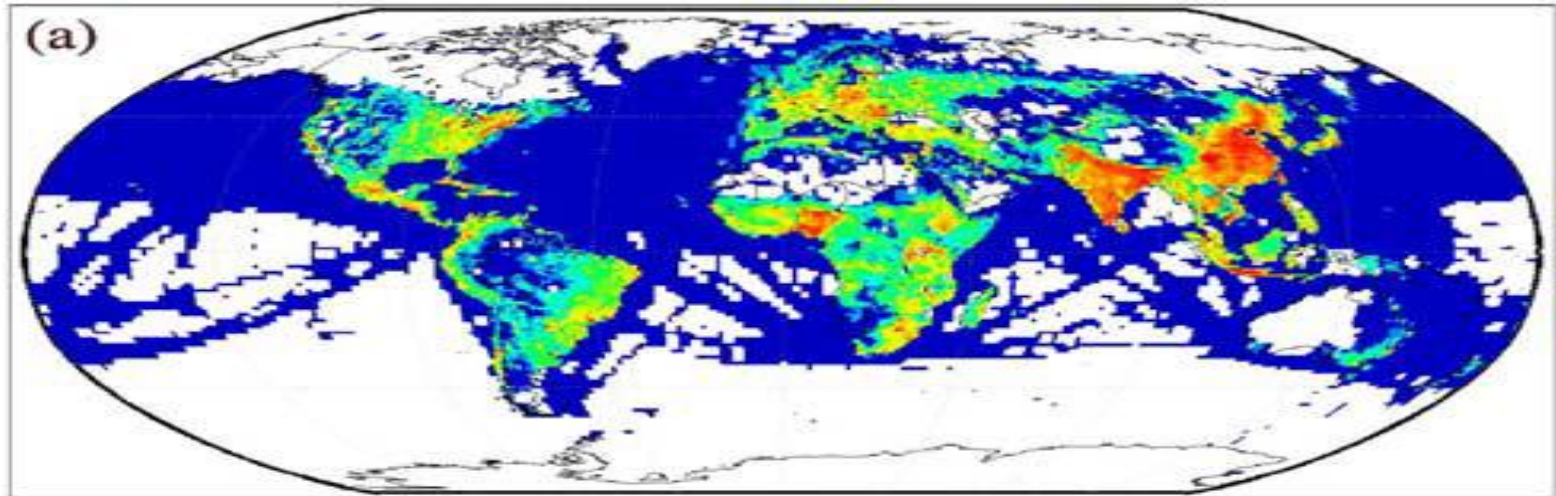




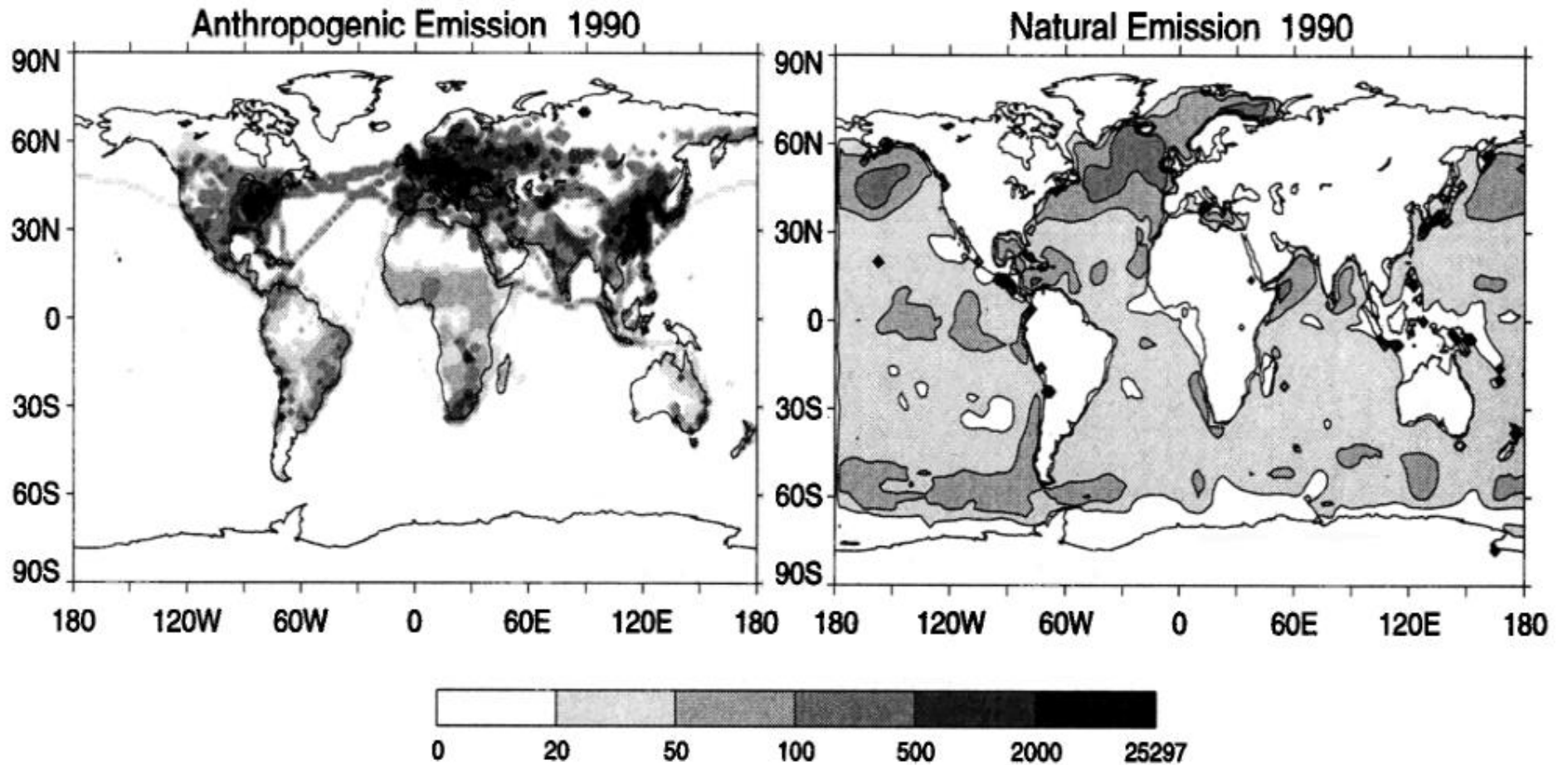




Primary Organic Aerosol emissions (a=contained, b=open)



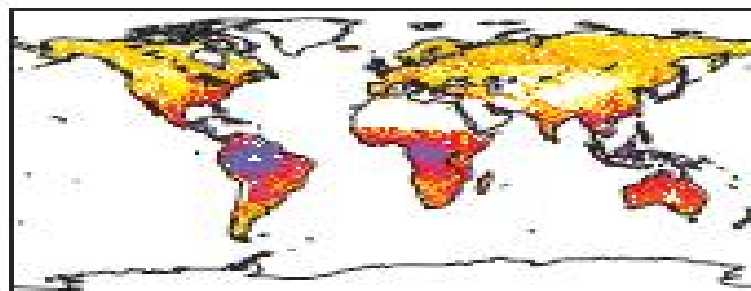
Annual Emissions ($\text{mg S m}^{-2} \text{ yr}^{-1}$ of sulfate precursors)
(Chin et al, 2000)



Average annual mean isoprene emissions from three different emission models



MEGAN



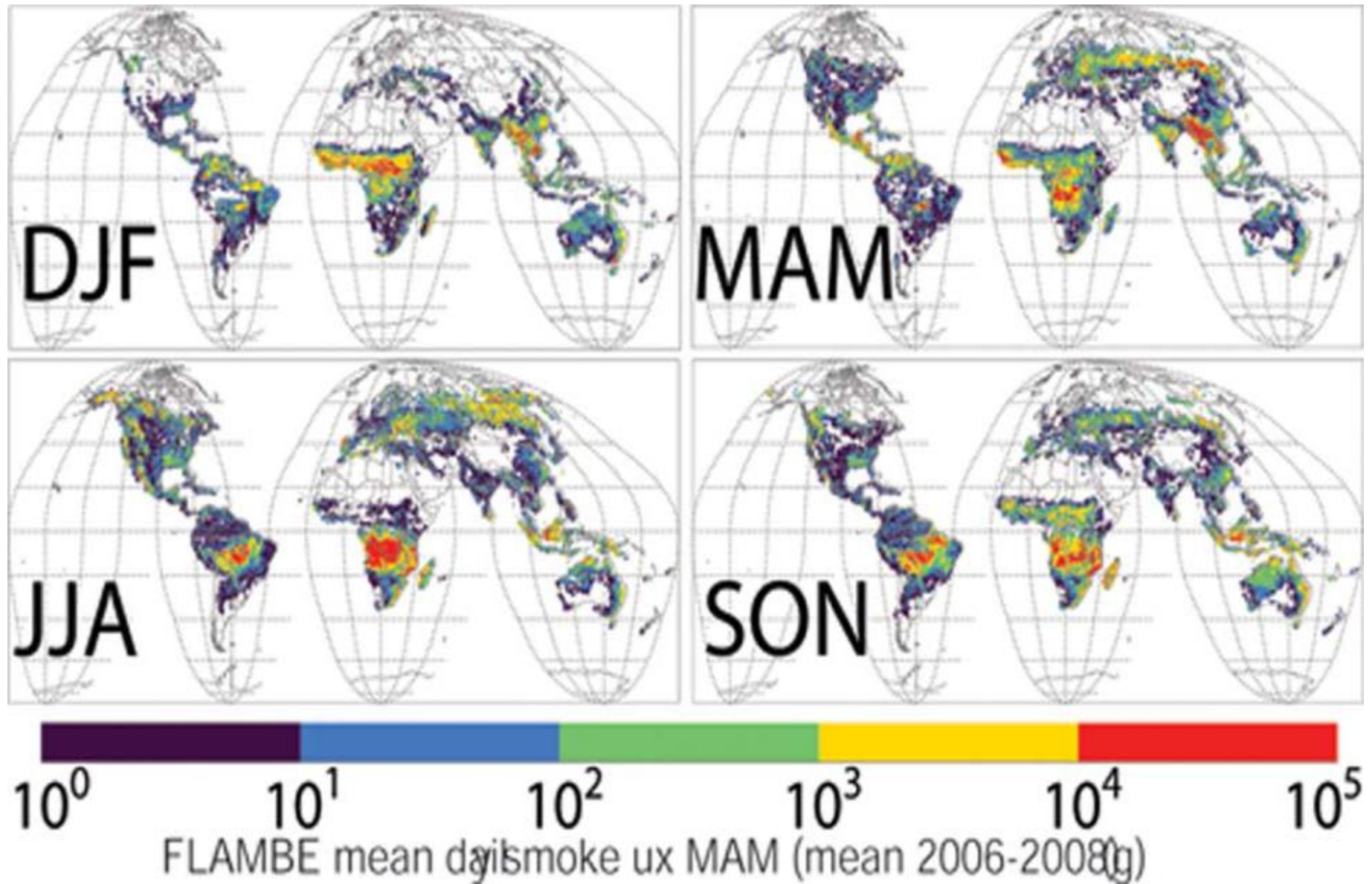
BVOCEN



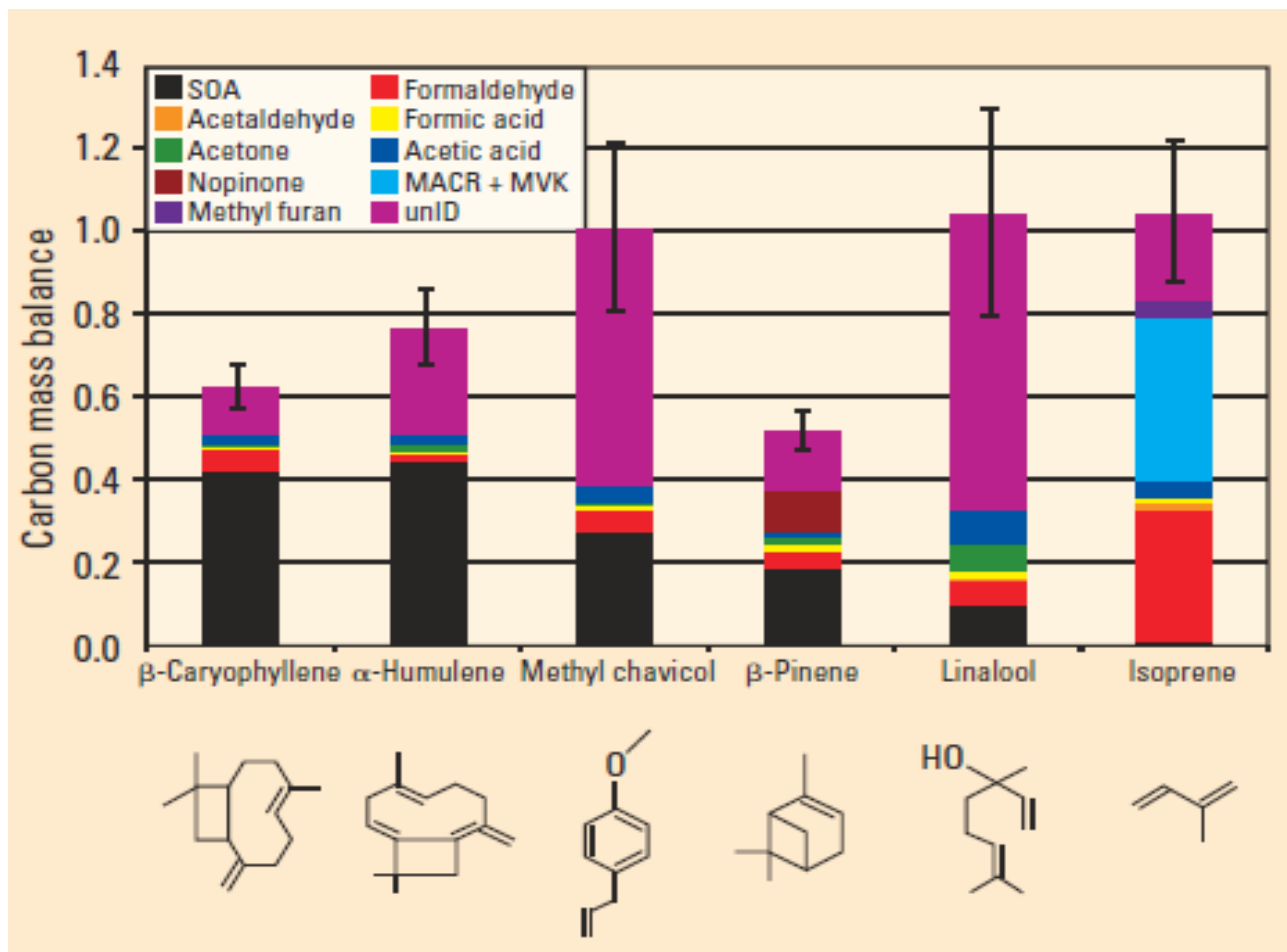
LPJ-GUESS



Smoke emissions from biomass burning



Carbon mass balance for photochemical oxidation of six different terpinoid compounds



Isoprene oxidation leading to Methyltetrols

