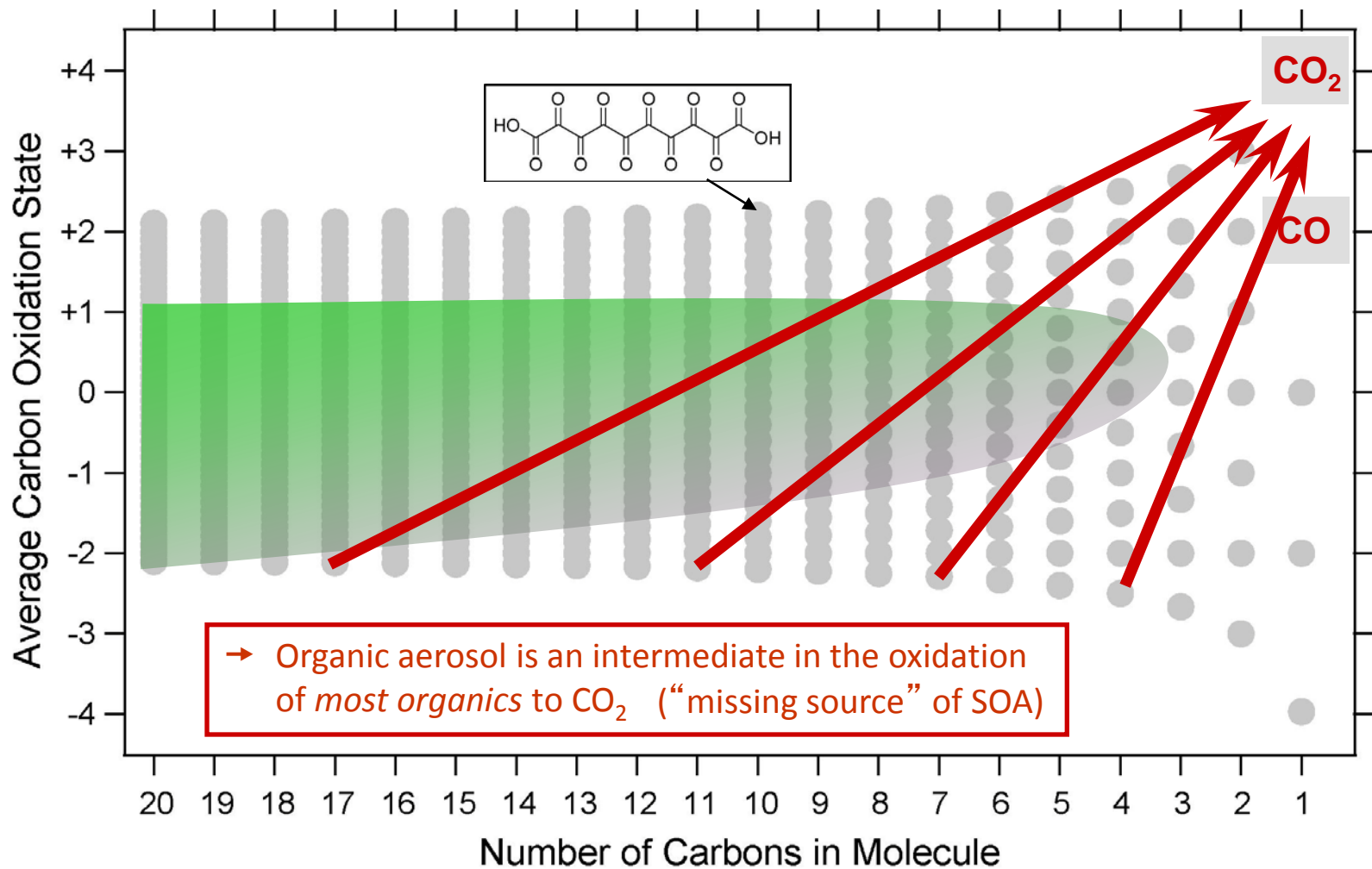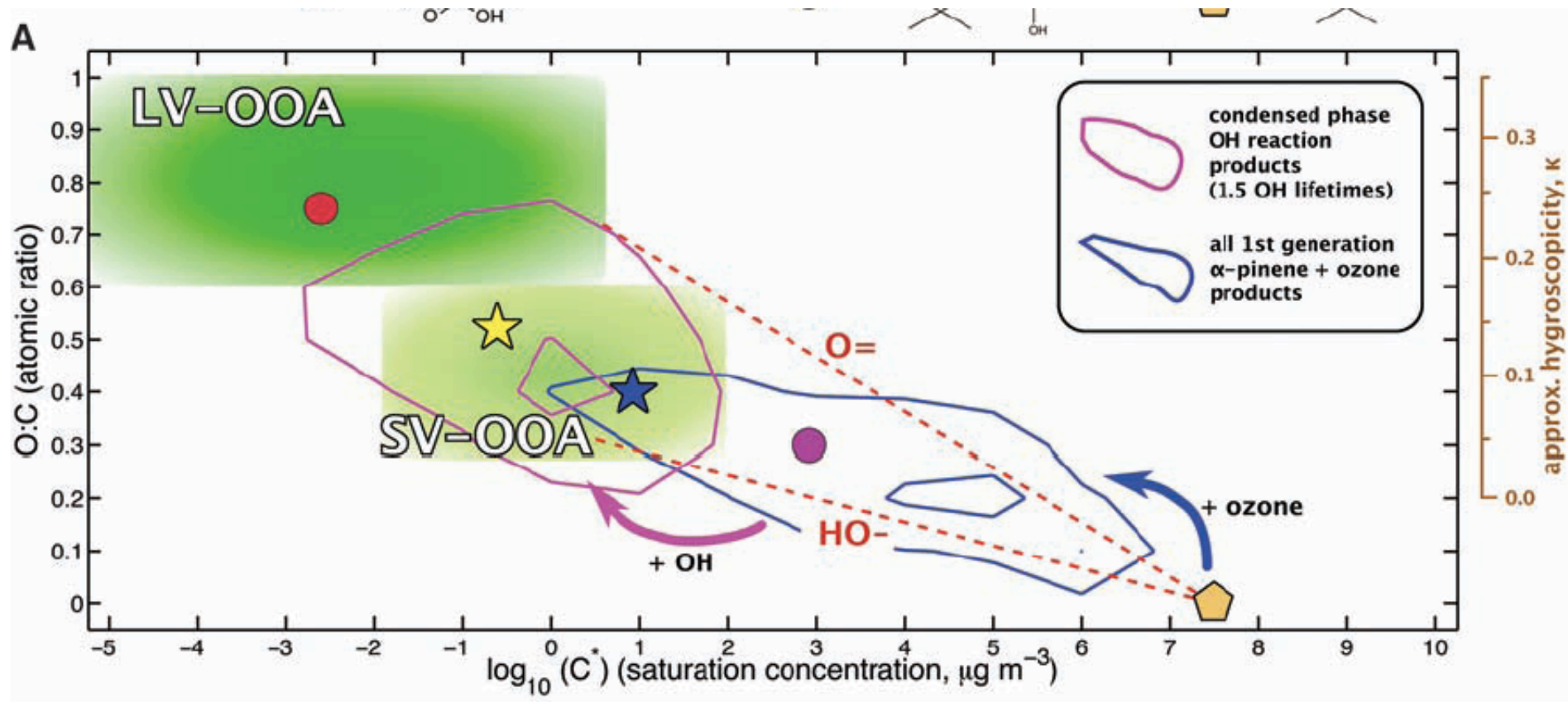# Inclusion of an aqueous phase formation mechanism for organic aerosols in CAM

Joyce E. Penner and Guangxing Lin

Formation of organic aerosol depends on oxidation state of intermediate products

Kroll et al., 2011

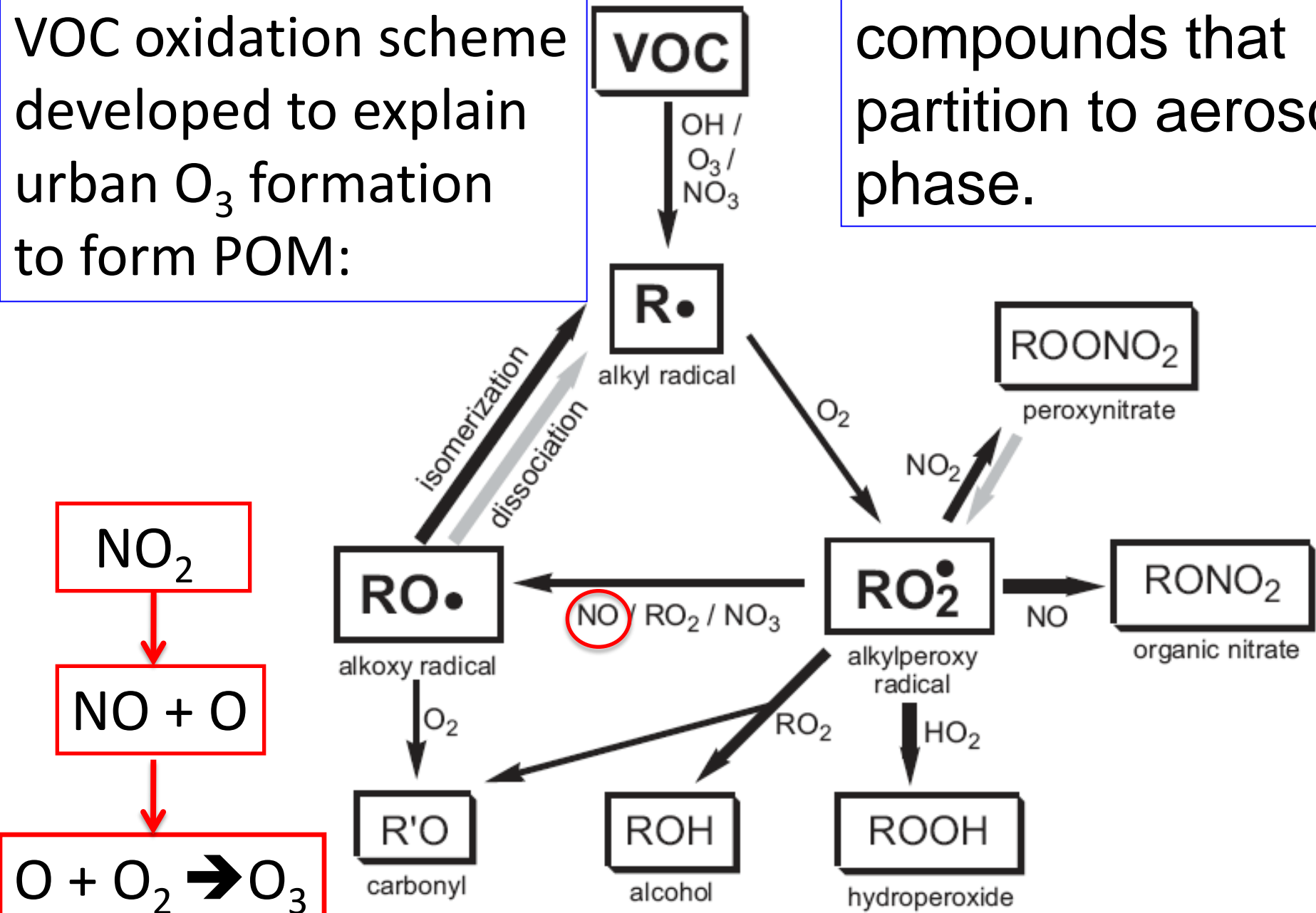# Formation of organic aerosol depends on oxidation state of intermediate products

Jimenez et al. 2009

The U. Michigan model attempts to follow the full oxidation chemistry using 250 chemical compounds

O3	NO2	NO	NO3	N2O5	R4O2	R4N1	DCO3	PIO2
HNO3	HONO	HNO4	OH	HO2	ATO2	ISN1	MAO3	B3O2
H2O2	SO2	HSO4	H2O	CO	ADDT	R3N1	XCO3	ARO2
nmhc	CH4	C2H6	C3H8	ALK4	DCO2	ISNR	HACO	ne_IAP
ALK7	HCHO	ALD2	RCHO	ACET	YCO1	R7N1	PBZN	ne_PINT
MEK	ETHE	PRPE	BUTE	ISOP	PO2	R6N1	IPAN	n_GLYX2
BENZ	TOLU	XYLE	MCO3	PAN	MRO2	R5N1	ETP	n_IEPOX
nco3	PPN	MO2	ETO2	ro2	IEPXO2	INO2	MAP	ne_ZPAN
rno2	ino3	rno3	npan	MPAN	R7O2	MVN2	ADBP	ne_MRP
PRPN	GLYC	IALD	HAC	GLYX1	KO2	MAN2	PHP	n_MGLY3
MGLY1	A-DI	PHEN	CRES	DMP	ADDX	PIN2	RA3P	IEPOX
POXY	DIAL	ADAL	MDAL	ACHO	DCO1	PIN2	EP	ne_ZAP
MVK	MACR	IPRD	HACN	RIP	ZCO2	A3N2	ARP	ne_LIP
crig	ACO2	ACTA	RCOH	ROH	RIO2	R4N2	DAP	n_MGLY2
MOH	EOH	DMS	H2	MP	IPO2	R7N2	RB3P	GLYX2
rooh	APIN	LIMO	AHO2	rmoh	R7O1	RCO3	PP	ne_YPAN
PIP	MNO3	NITP	ISNP	INPN	BUO2	YCO3	ADTP	ne_ISNP
PRN2	ISNT	PINT	AD2P	APAN	ADD2	AO2	BUP	ne_VRP
DPAN	GPAN	XAP	ZAP	AP	XCO2	ZCO3	R4P	MGLY3
XPAN	YAP	YPAN	ZPAN	IAP	ZCO1	GCO3	RP	ne_YAP
LIP	MRP	VRP	ev_A-DI	n_GLYX1	RIO1	BCO3	ADXP	ne_INPN
ev_AD2P	ev_AP	ev_APAN	ev_DPAN	ev_GPAN	IAO2	AO0	R7P	ne_PIP
ev_NITP	ev_XAP	ev_XPAN	ev_YAP	ev_YPAN	A3O2	YCO2	GP	MGLY2
ev_ZAP	ev_ZPAN	ev_IAP	ev_INPN	ev_ISNP	ADDB	EO2	BAP	ev_HAC
ev_LIP	ev_MRP	ev_PINT	ev_PIP	ev_VRP	AO1	MAO2	MAOP	CO2
ne_A-DI	n_MGLY1	ne_AD2P	ne_AP	ne_APAN	XCO1	LIO2	CHO2	
ne_DPAN	ne_GPAN	ne_NITP	ne_XAP	ne_XPAN	PHO2	VRO2	CRO2	

We use a standard VOC oxidation scheme developed to explain urban O_3 formation to form POM:

We identify those compounds that partition to aerosol phase.

VOC

OH / O_3 / NO_3

R•
alkyl radical

isomerization

dissociation

O_2

ROONO$_2$
peroxynitrate

NO_2

NO$_2$

NO + O

O + O_2 ➔ O_3

RO•
alkoxy radical

NO / RO_2 / NO_3

$RO_2^{\bullet}$
alkylperoxy radical

NO

RONO$_2$
organic nitrate

O_2

RO_2

HO$_2$

R'O
carbonyl

ROH
alcohol

ROOH
hydroperoxide

Specific compounds that partition to aerosol phase have at least one of the following:

- Partially soluble
- Aromatic acid
- Aromatic with 2 functional groups that are not aldehydes
- Have 12 or more carbon atoms
- Have at least 10 carbon atoms and 2 functional groups
- Have at least 6 carbon atoms and 2 functional groups 1 of which is an acid
- Be tri-functional

In addition, our SOA formation mechanism includes:

- Reaction of oxidation products within aerosol to form non-evaporative compounds with 1-day e-fold: "oligimerization"

- Reaction of methyglyoxal and glyoxal on clouds and sulfate aerosols to form non-evaporative species (Fu et al., 2008)

- Reaction of epoxides from isoprene to form non-evaporative species on sulfate aerosols (i.e. Paulet et al., 2009; Minerath et al., EST, 2009)

- Formation of MSA from oxidation of DMS

- POA: sources from biomass burning, fossil fuel, ocean

Simulation cases

Name of SOA component	description
Simulation A	Traditional isoprene mechanism + epoxide formation
Simulation B	Simulation A + HOx recycling (Peeters et al., 2009)
Simulation C	the same as Simulation B, but with a reduced rate of HOx recycling by a factor of 10

Results: global budget (Simulation C)

Burden	Total production	Anthropogenic production	Biogenic production	Lifetime
1.54 Tg	119.3 Tg/yr	13.7 Tg/yr	105.6 Tg/yr	4.7 days

Five SOA components
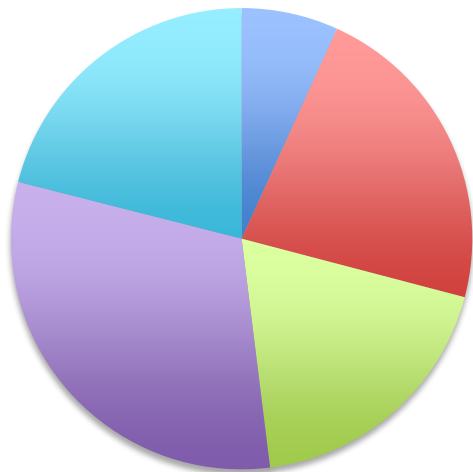
- ■ sv_oSOA
- ■ lv_oSOA
- ■ glyoxal SOA
- ■ methylglyoxal SOA
- ■ epoxide SOA

sv_oSOA and lv_oSOA are formed from gas-particle partitioning;
Glyoxal SOA, methylglyoxal SOA are from uptake of gas glyoxal and methylgloxal by clouds and sulfate;
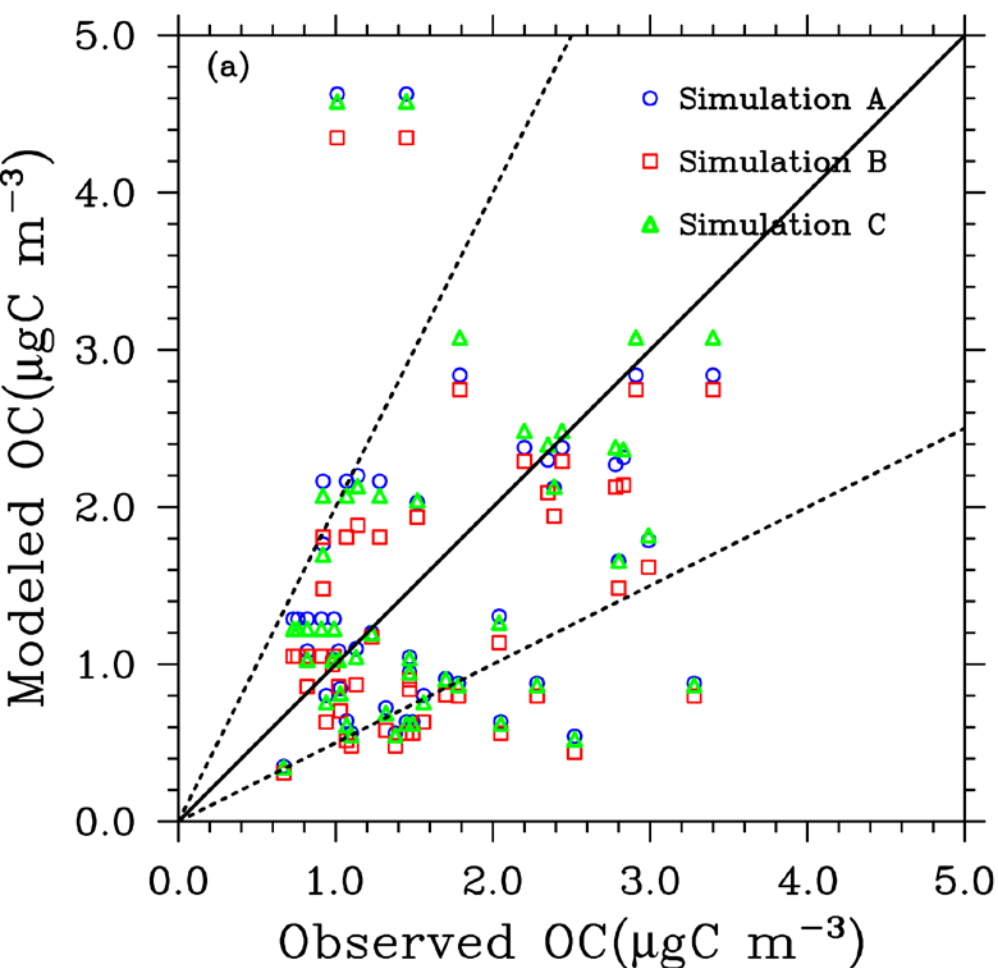Epoxide SOA is from uptake of gas epoxide by sulfate.
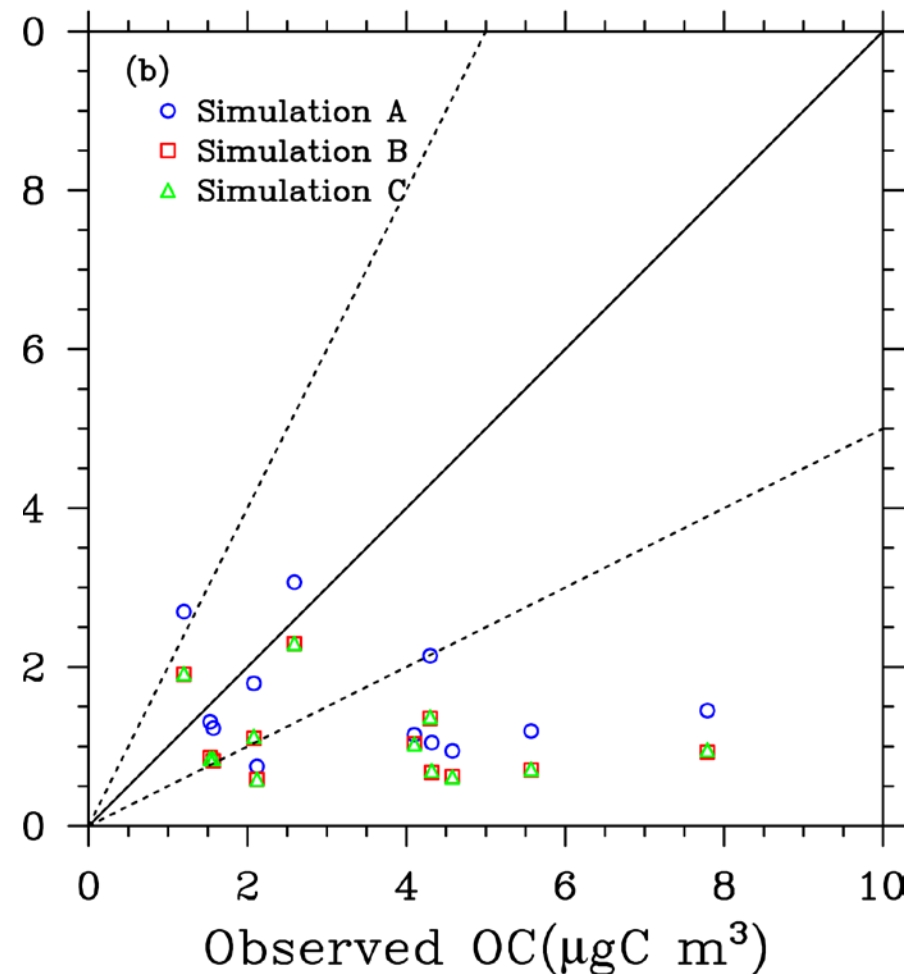
Comparison with top-down estimates
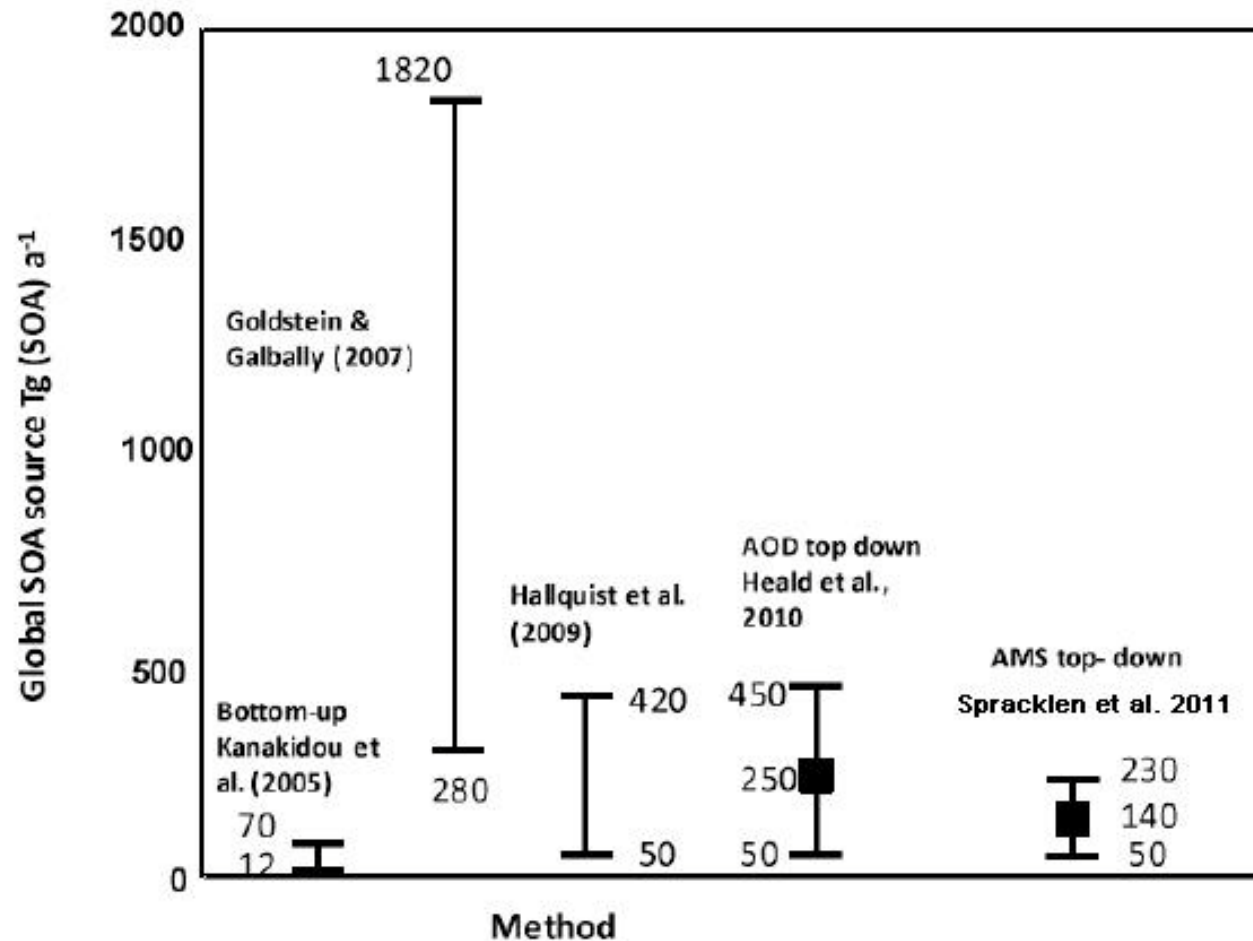
Our estimate:

90 – 120 Tg/yr

Comparison with IMPROVE network

Comparison with EMEP

(a)

○ Simulation A
□ Simulation B
△ Simulation C

(b)

○ Simulation A
□ Simulation B
△ Simulation C

Modeled OC(μgC m^{-3})

Observed OC(μgC m^{-3})

Observed OC(μgC m^{3})

IMPROVE Normalized mean bias:

A	B	C
-5.4%	-15.3%	-5.5%

Comparison of model results in Amazon during wet season:

Run A: no HOx recycling	Observation (ug C/m3)	Total OC	POA	ne_oSOA	ne_MGLY + ne_GLY	ne_IEPOX	Isoprene	
							Obs	mo.
AMMA	1.18	4.78	0.57	0.70	2.08	1.43	6.2	17
AMAZE/Gulardoni	0.7 - 1.7	3.23	0.36	0.31	1.44	1.12	2.0	4.4
Borneo	0.74	1.46	0.25	0.08	0.60	0.53		

Run B: fast HOx recycling	Observation (ug C/m3)	Total OC	POA	ne_oSOA	ne_MGLY+ ne_GLY	ne_IEPOX	Isoprene	
							Obs	mo.
AMMA	1.18	4.12	0.57	0.51	2.53	0.51	6.2	8.4
AMAZE/Gulardoni	0.7 - 1.7	3.45	0.36	0.25	2.44	0.40	2.0	1.9
Borneo	0.74	1.16	0.25	0.06	0.72	0.13		

Ervens et al., 2011
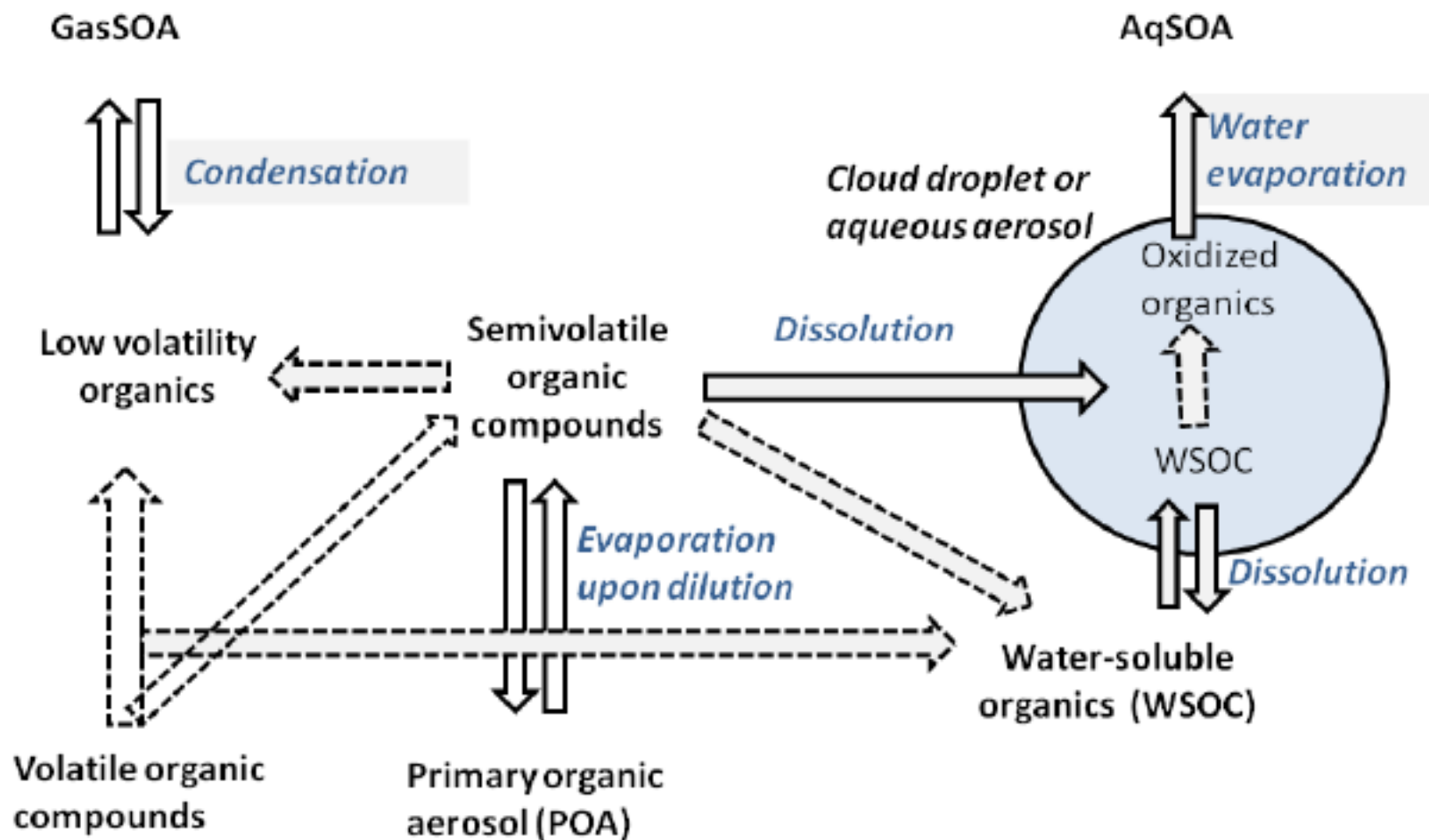
Simulation descriptions (3 simulations)

- Simulation based on Fu et al. (2008) (the same as Simulation C in Lin et al. 2012)
- surface process (Fu et al. 2008,2009)

$$\frac{dC_{aq}}{dt} = \frac{1}{4} \cdot \gamma \cdot A \cdot <v> \cdot C_g$$

- A: sulfate aerosol surface area.
- No detailed chemistry, just a parameterization
- The same uptake parameter γ for the reaction on cloud droplets and aqueous aerosol
- Gas phase glyoxal ➔ glyoxal SOA
- Gas phase methylglyoxal ➔ methyglyoxal SOA

Simulation based on Ervens et al. (2011)

- Multiphase reactions with detailed reactions in cloud water but empirical reaction parameters in aerosol water (Ervens and Volkamer 2010, Ervens et al., 2011)

$$\frac{dC_{aq}}{dt} = R_{aq} + \frac{k_t}{RT} \cdot P_g - \frac{k_t}{HRT} Q \cdot C_{aq}$$

- Different reactions occur in cloud droplets and in aerosol water

- SOA in cloud droplets: organic acids, including glyoxylic acid, oxalic acid, and pyruvic acid.

- SOA in aerosol water: oligomers

Simulation based on Lim et al. (2010)

- Also multiphase reactions, but using detailed reactions in both cloud water and aerosol water (Lim et al., 2010).

- $$\frac{dC_{aq}}{dt} = R_{aq} + \frac{k_t}{RT} \cdot P_g - \frac{k_t}{HRT} Q \cdot C_{aq}$$

- SOA formed in cloud droplets: organic acids
- SOA formed in aerosol water: oligomers

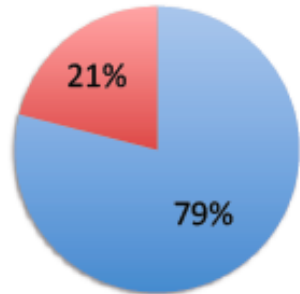# Availability of water in clouds/aerosols
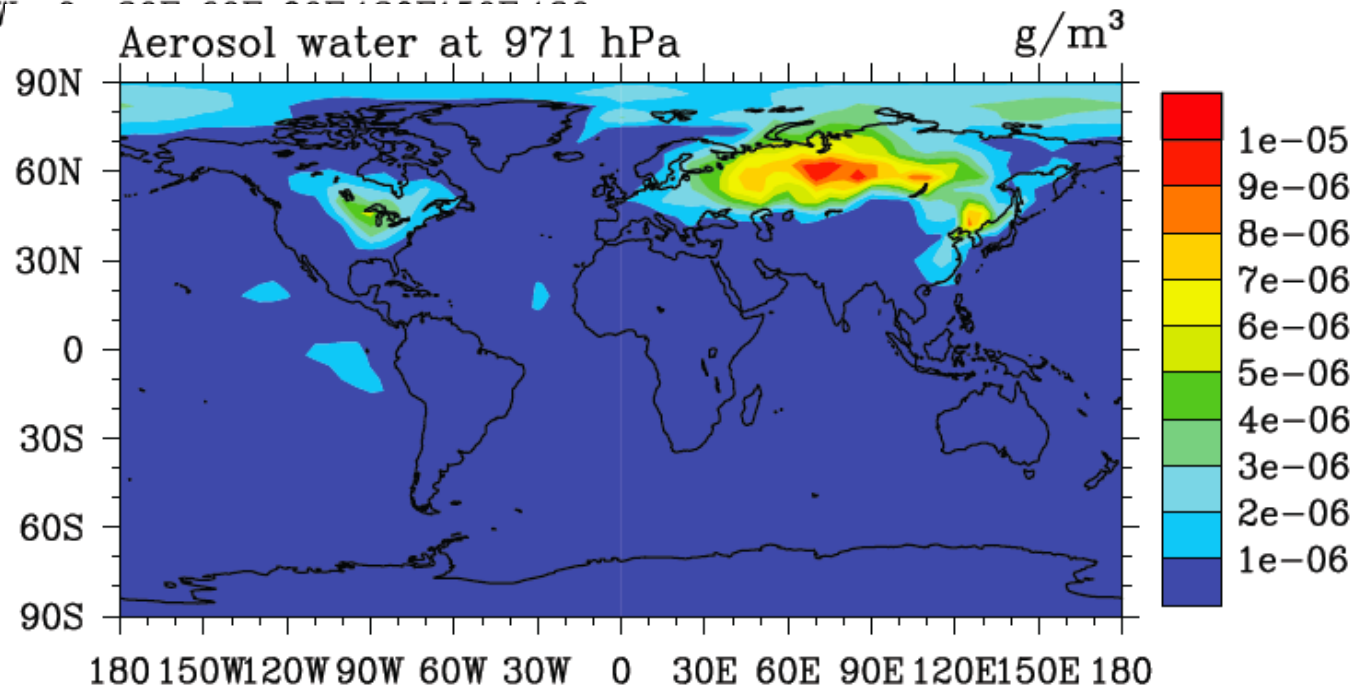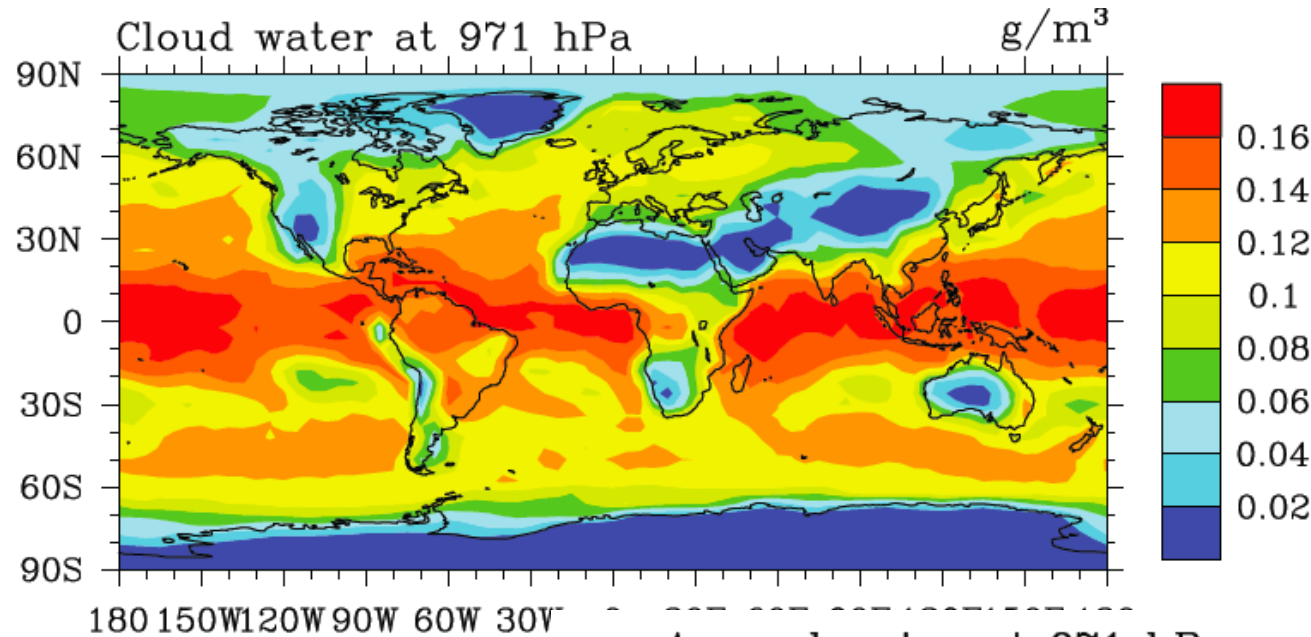
Compare 3 different treatments for SOA formed in aqueous reactions
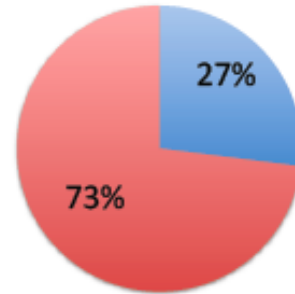

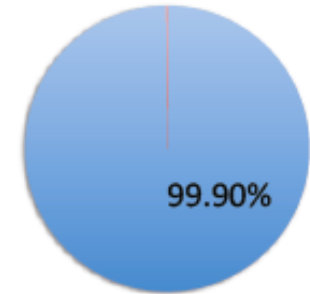**SOA formed in cloud water** versus **SOA formed in aerosol water**

| Simulation Fu	Simulation Ervens	Simulation Lim
21% / 79%	27% / 73%	99.90%

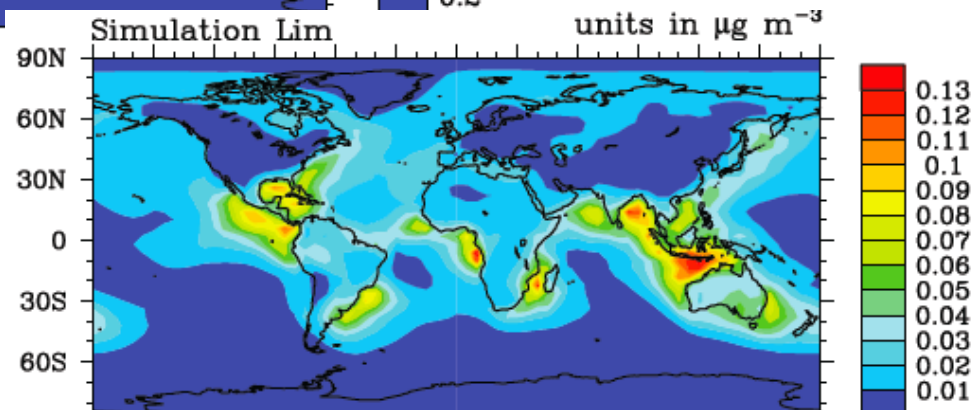Fu et al., JGR 2008

Ervens et al., ACP 2011

Lim et al., ACP 2010

Aqueous SOA formation

Case	Product	Burden (Tg)	Product'n (Tg/ yr)	Destruct'n (Tg/yr)	Net Product'n (Tg/yr)	Deposit'n (Tg/yr)
Fu	glyoxal SOA	0.20	22.6	0.0	22.6	22.6
	M-glyoxal SOA	0.30	36.9	0.0	36.9	36.9
Ervens	Oxalic acid	0.025	6.2	1.7	4.5	4.5
	glyoxal Oligomers	0.054	6.2	0.0	6.2	6.2
	M-glyoxal Oligomers	0.050	6.0	0.0	6.0	6.0
Lim	Oxalic acid	0.023	5.1	1.3	3.8	3.8
	Oligomers	1.8e-4	1.3e-2	1.6e-3	1.1e-2	1.1e-2

Compare surface concentrations

Simulation Fu — units in μg m⁻³

Ervens:

Simulation Ervens — units in μg m⁻³
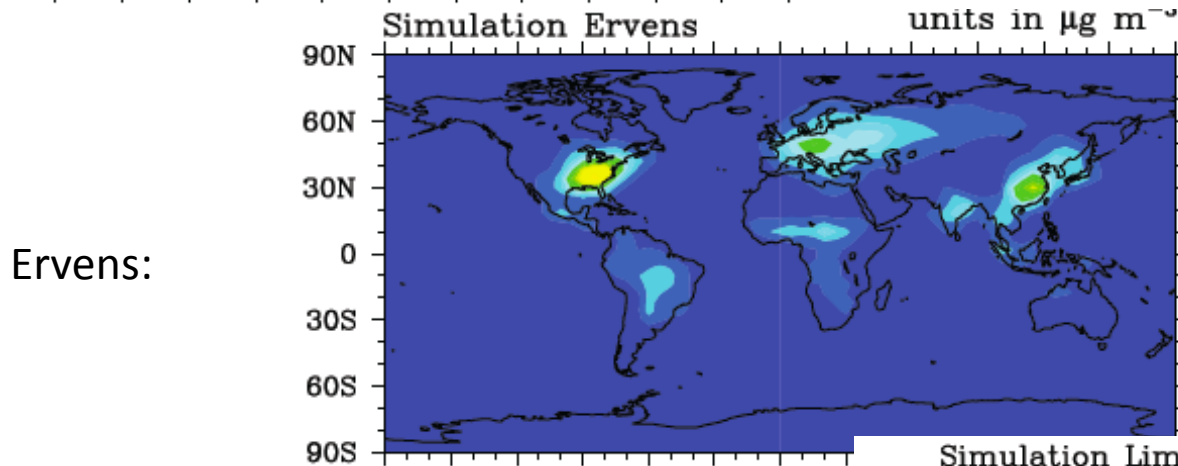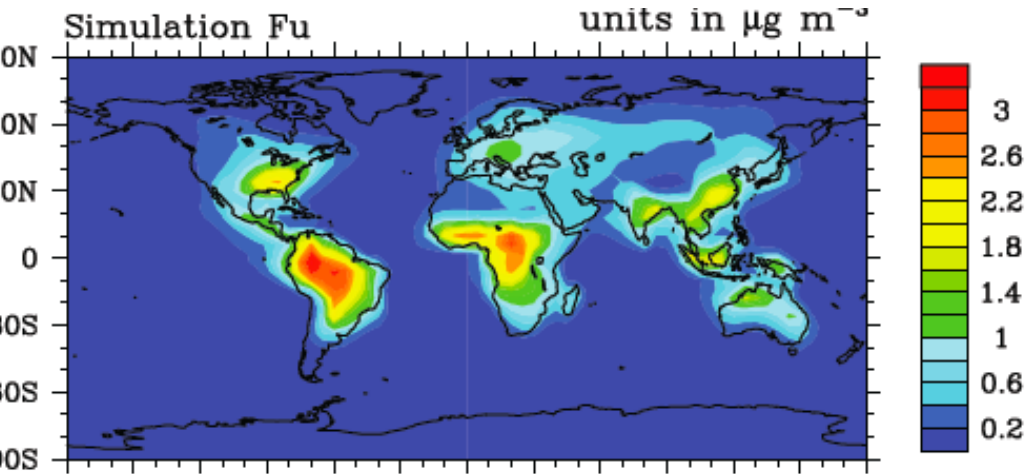
Lim shown with reduced scale:

Simulation Lim — units in μg m⁻³

Comparison with measurements

	Observation (ug C/m3)	Fu	Ervens	Lim
AMMA	1.18	5.59	2.75	1.97
AMAZE/Gulardoni	0.7 - 1.7	4.45	1.56	1.18
Borneo	0.74	1.57	0.76	0.59

Significant improvement in tropical concentrations

Case	IMPROVE network (N=49)		AMS rural measurements (N=17)	
	NMB	R	NMB	R
Fu	1.7%	0.41	20.0%	0.3
Ervens	-11.0%	0.41	-21.0%	0.2
Lim	-34.1%	0.12	-50.0%	0.3

Northern mid-latitude predicted concentrations are not degraded by too much

Conclusion

- These studies require a chemistry model that has enough information represented to be able to add the specific molecular scale processes being studied

- The global SOA production in aqueous phase varies significantly among these three different simulations, but overall, the model with the higher chemical representation (Ervens scheme) is better than the other two.

- The multiphase reaction scheme (Ervens) improves the modeled OA in the tropical regions, but downgrades it somewhat in the Northern Hemisphere.

- Work is beginning to add this scheme to CAM5