Aqueous-Phase Chemistry in TM4-ECPL:

SOA Formation via Cloud Processes

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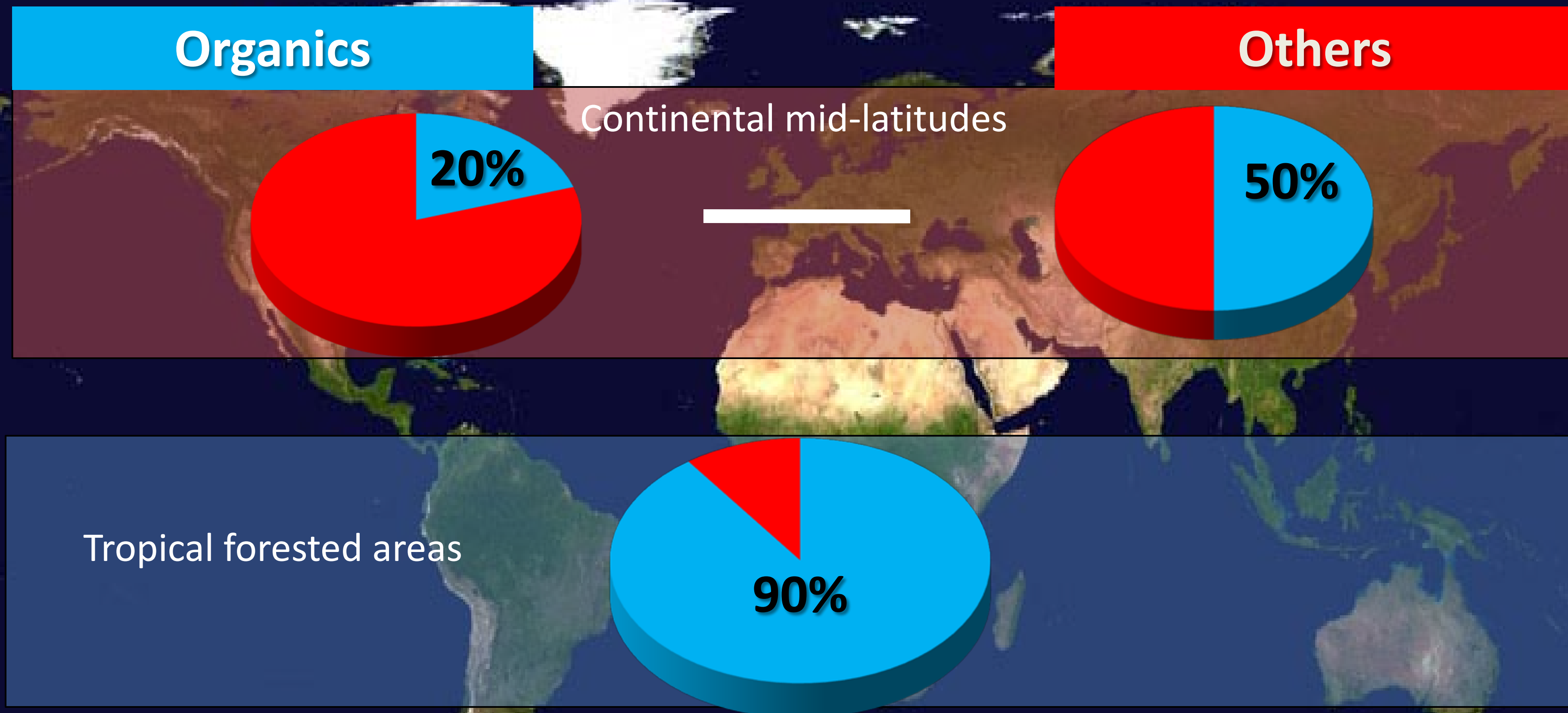
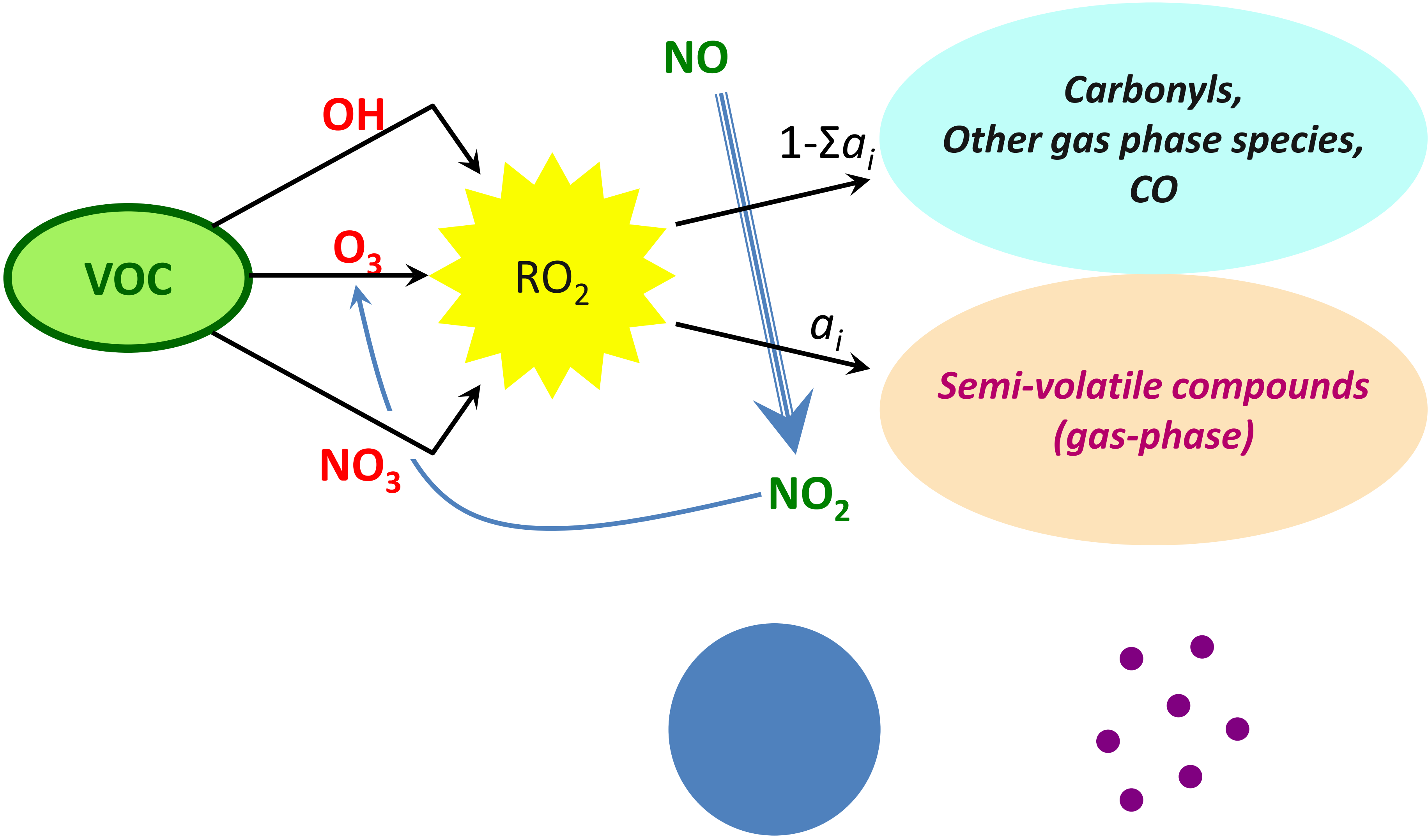
Aerosols in the Atmosphere



SOA is the major component of atmospheric $PM_{2.5}$

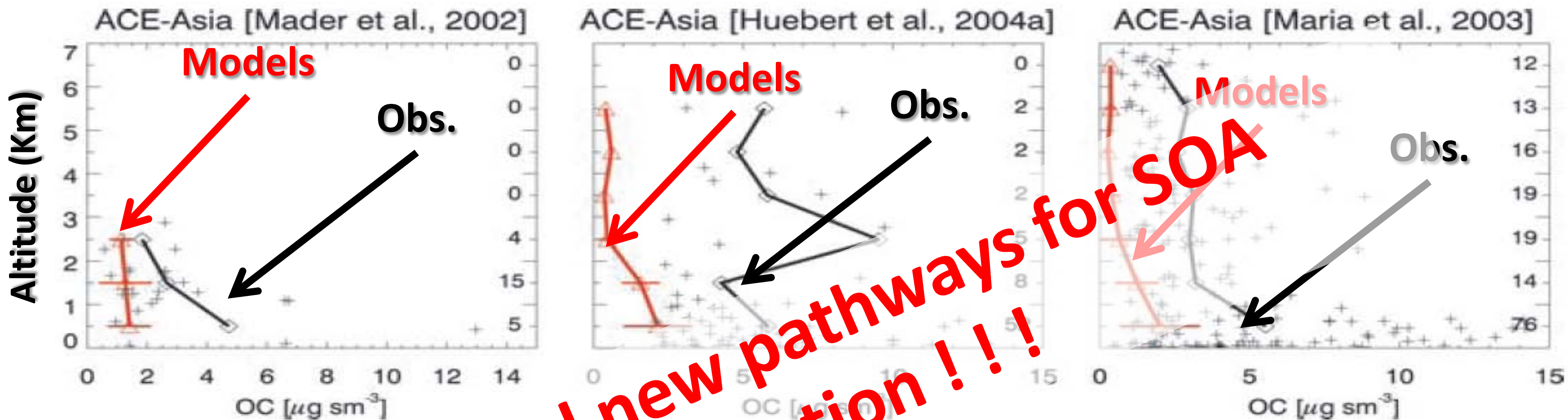
Kanakidou et al., 2005

Partitioning Theory
-The Traditional view of SOA formation-



Traditional view of SOA formation in Models fails to fully explain atmospheric observations

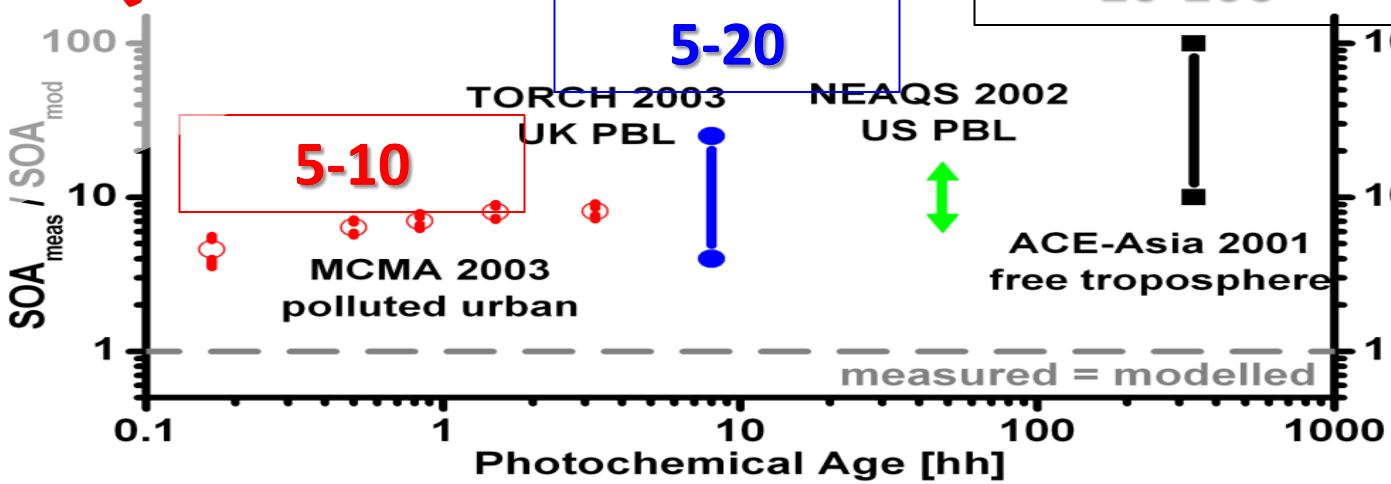
Heald et al., 2005



We need new pathways for SOA Formation ! ! !

Volkamer et al., 2007

Obs.
———
Models



Closing the Gap Between Models and Observations

- Low volatile products can be formed through aqueous reactions in clouds, fogs and wet aerosols *(Blando and Turpin, 2000; Glencser and Varga, 2005; Ervens et al., 2004; Carlton et al., 2006; Volkamer et al., 2007, Lim et al., 2010, Ervens ad Volkamer, 2010)*

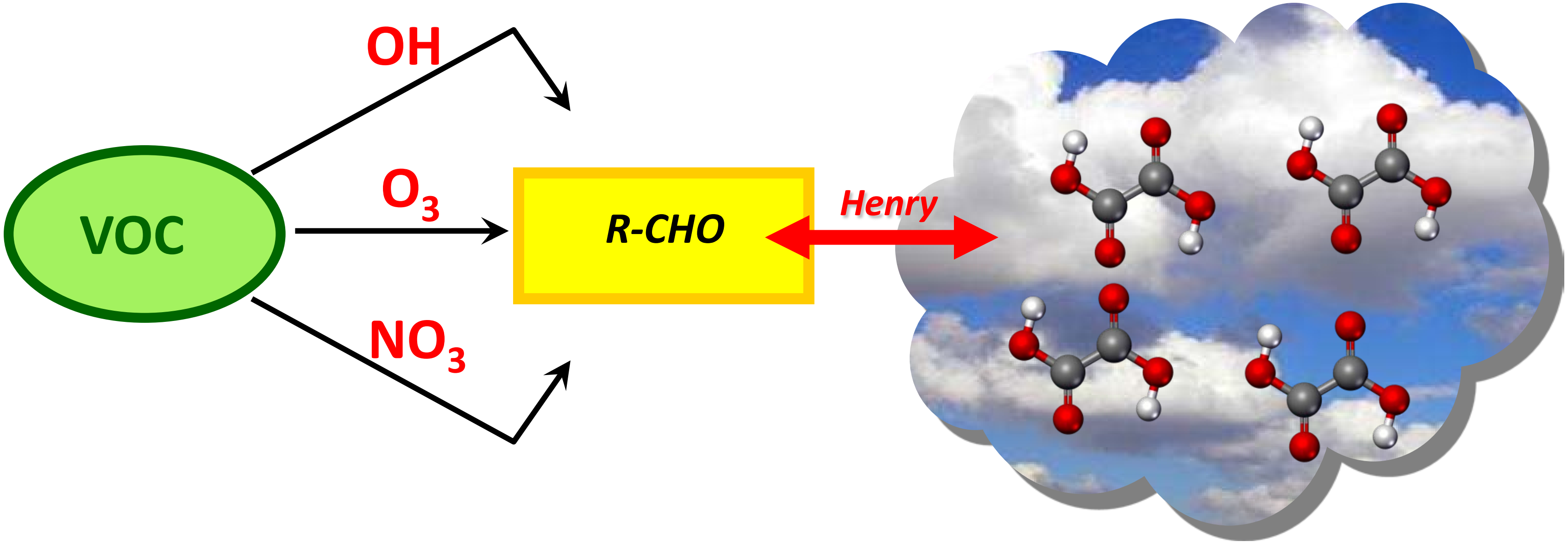
- Water soluble gases react (e.g., via photochemistry, acid catalysis, and with inorganic constituents) in the aqueous phase forming organic acids, oligomers, and organosulfates *(Carlton et al., 2006; Guzman et al., 2006; Perri et al., 2010)*

- Lower volatility products are retained, at least in part, in the particle phase after water evaporation *(Loeffler et al., 2006; El Haddad et al., 2009)*

- SOA formed through atmospheric aqueous chemistry is a strong candidate for closing the gap between the measured organic aerosol and atmospheric model predictions in part because it is formed from different precursors

SOA formation through aqueous chemistry

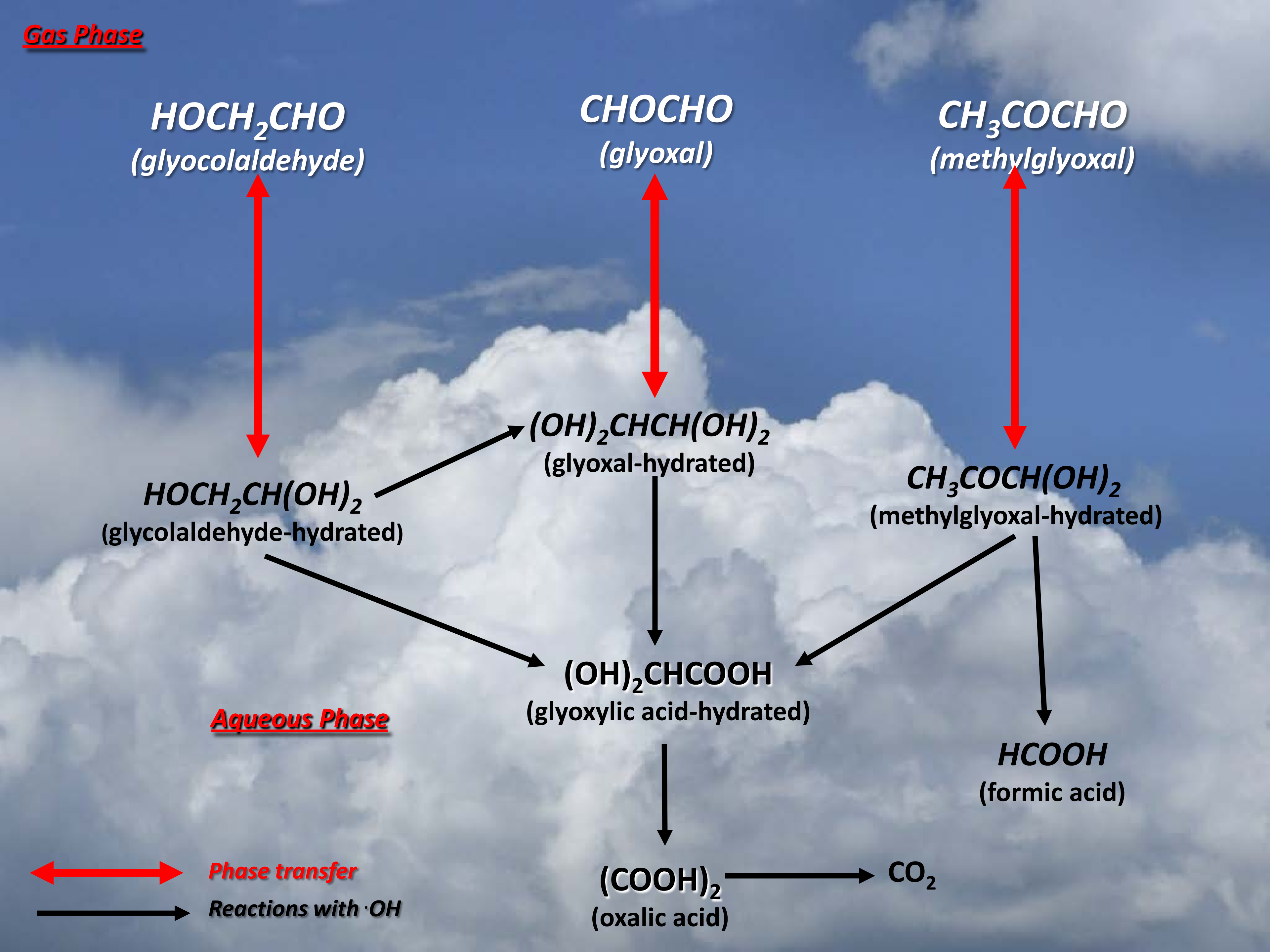
1. VOC photo-oxidation in the gas-phase
2. Production of water-soluble organic compounds in the gas-phase *(e.g. aldehydes)*
3. Phase transfer between the gas and the aqueous phase
4. Production of low volatile compounds in the aqueous-phase *(e.g. oxalic acid)*
5. Upon cloud evaporation new organic particulate matter is formed



Aqueous Phase Chemical Scheme in TM4-ECPL

Reactions		A (mol^{-} lt^{1}s^{-1})	E/R (K)	Ref.
H_2O_2 + hv	→ 2OH			*IUPAC*
$SO_2 + O_3$	→ $SO_4^{=}$			*wetS.f90*
$SO_2 + H_2O_2$	→ $SO_4^{=}$			*wetS.f90*
$OH + H_2O_2$	→ $HO_2 + H_2O$	2.7E7		*Carlton et al., 2007*
$HO_2 + HO_2$	→ $H_2O_2 + O_2$	8.3E5		*Carlton et al., 2007*
$HOCHCH(OH)_2 + OH$	→ $(OH)_2CHCH(OH)_2 + HO_2$	5.0E8		*Lim et al., 2005*
$HOCHCH(OH)_2 + OH$	→ $(OH)_2CHCOOH + HO_2 + HO_2 + H_2O$	1.0E8		*Lim et al., 2005*
$(OH)_2CHCH(OH)_2 + OH$	→ $(OH)_2CHCOOH + HO_2$	1.1E9	1516	*Lim et al., 2005*
$CH_3COCH(OH)_2 + OH$	→ $0.86(OH)_2CHCOOH + 0.14HCOOH$	7.0E8		*Lim et al., 2005*
$(OH)_2CHCOOH + OH$	→ $(COOH)_2 + HO_2 + H_2O$	1.5E8		*Lim et al., 2005*
$(COOH)_2 + 2OH$	→ $2CO_2 + 2H_2O$	4.7E7		*Lim et al., 2005*

The aqueous_phase module


Gas Phase
$HOCH_2CHO$
(glyocolaldehyde)
$CHOCHO$
(glyoxal)
CH_3COCHO
(methylglyoxal)
$(OH)_2CHCH(OH)_2$
(glyoxal-hydrated)
$HOCH_2CH(OH)_2$
(glycolaldehyde-hydrated)
$CH_3COCH(OH)_2$
(methylglyoxal-hydrated)
$(OH)_2CHCOOH$
(glyoxylic acid-hydrated)
Aqueous Phase
$HCOOH$
(formic acid)
$(COOH)_2$
(oxalic acid)
CO_2
Phase transfer
Reactions with ·OH

Solubility of Gases in Cloud Droplets

•Only 9 species are allowed to be partitioned between gas and aqueous phase during a cloud period : **GLY, GLYAL, MGLY, PRV, HCOOH, OXL** and also **H_2O_2, HO_2, OH**

- The equilibrium solubility of gases in water is given by the Henry's law constant

$$H(T) = \frac{[C]}{P_g}$$

or

$$H_{eff}(T) = H(T)\left(1 + \frac{Ki(T)}{[H^+]}\right)$$

•Given the temperature (T), the effective Henry's law coefficient H_{eff} and the liquid water content (LWC), it can be defined **a phase ratio P_x** (Lelieveld and Crutzen, 1991; Dentener, PhD Thesis, 1993)

$$P_x = H_{eff} * R * T * LWC$$

P_x gives the fraction of molecules in a certain, cloud containing volume of air, which resides in the aqueous phase

Solubility of Gases in Cloud Droplets

•The relationship between the chemical concentration of X species in the liquid phase, the gas-phase and the total concentration (X_{tot} molecule cm^{-3}) is calculated using the P_x

$$[X]_{(aq)} = P_x [X]_{(gas)}$$

$$[X]_{(aq)} = \frac{P_x [X]_{total}}{1 + P_x} \qquad [X]_{(gas)} = \frac{[X]_{total}}{1 + P_x}$$

•The conditions of establish this equilibrium are not always fulfilled, and the transfer of species between gas and aqueous phases have to be defined as mass transport, limited by diffusion in the gas phase and across the interface.

Deviations from Henry's Law

Species	Modeled actual ratio : $\frac{C_a}{C_g}$	Equilibrium phase ratio : $K_H RTL$
O_3	$1.072(\pm 0.050) \times 10^{-7}$	1.097×10^{-7}
OH	$4.283(\pm 0.482) \times 10^{-5}$	4.191×10^{-4}
CH_2O	$0.0636(\pm 0.0004)$	0.0636
HCOOH	$1.257(\pm 0.230)$	1.388
HO_2	$0.0665(\pm 0.0144)$	0.3116
H_2O_2	$1.816(\pm 0.012)$	1.807
CH_3OO	$2.478(\pm 0.017) \times 10^{-4}$	2.480×10^{-4}
CH_3OOH	$4.837(\pm 0.028) \times 10^{-3}$	4.821×10^{-3}
NO	$1.681(\pm 0.009) \times 10^{-8}$	1.677×10^{-8}
NO_2	$6.600(\pm 0.035) \times 10^{-8}$	6.583×10^{-8}
HNO_3	$1.367(\pm 3.615) \times 10^{7}$	9.566×10^{7}
NO_3	$3.652(\pm 6.087) \times 10^{-6}$	1.715×10^{-5}
N_2O_5	0.000	7.016×10^{6}

- The modeled phase ratios agree within 1% for CH_2O, H_2O_2, CH_3OO, CH_3OOH, NO, and NO_2, and agree within 20%, for O_3, OH, HCOOH, and HO_2.
- Species that clearly are not in equilibrium are OH, HO_2, HNO_3, and NO_3.

Barth et al., 2003

Exchange between the gas and the aqueous phase

•The rate of change of a chemical species due to mass transfer between gas and liquid phase can be defined as:

$$k_t = \left(\frac{r^2}{3D_g} + \frac{4r}{3\upsilon a} \right)^{-1}$$

Where:

k_t is the transfer coefficient (s^{-1})

r is the droplet radius (cm)

D_g is the gas-phase diffusion coefficient ($cm^2\ s^{-1}$), calculated as

$$D_g = 1.9(MW)^{-\frac{2}{3}}$$

υ is the mean molecular speed ($cm\ s^{-1}$), calculated as

$$\upsilon = \left(\frac{8k_B T N_a}{\pi(MW)} \right)^{-\frac{1}{2}}$$

and α is the mass accommodation coefficient

Some aqueous_phase parameters

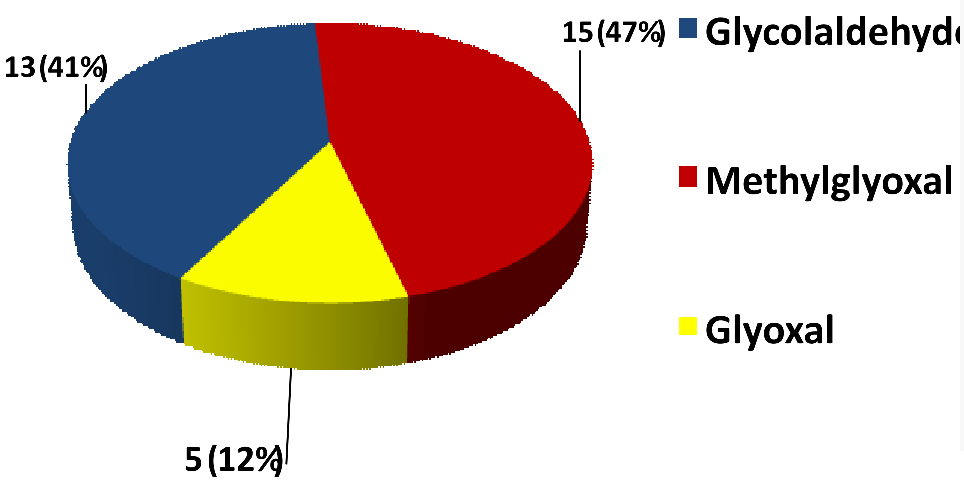
Species	H_K ($M\ atm^{-1}$)	$dlnH_k/d(1/T)$ (K)	*Ref.*	α (298K)	*Ref.*
SO_2	1.2	3200	*Sander, 1999*		
NH_3	76	3400	*Sander, 1999*	0.09	*Lim et al., 2005*
H_2O_2	$8.6 \cdot 10^4$	6500	*Sander, 1999*	0.11	*Lim et al., 2005*
HO_2	$4.0 \cdot 10^3$	5900	*Sander, 1999*	0.01	*Lim et al., 2005*
$SO_4^{=}$	$1.0 \cdot 10^7$				
NH_4^+	$1.0 \cdot 10^7$				
HCOOH	$8.9 \cdot 10^3$	6100	*Sander, 1999*	0.013	*Lim et al., 2005*
$CH_2(OH)CHO$	$4.1 \cdot 10^4$	4600		0.023	*Lim et al., 2005*
CHOCHO	$3.0 \cdot 10^5$		*Sander, 1999*	0.023	*Lim et al., 2005*
CH_3COCHO	$3.2 \cdot 10^4$	7500	*Lim et al., 2005*	0.023	*Lim et al., 2005*
HOC(O)COOH	$9.12 \cdot 10^3$		*Lim et al., 2005*	0.019	*Lim et al., 2005*
$(COOH)_2$	$3.26 \cdot 10^6$		*Lim et al., 2005*	0.019	*Lim et al., 2005*

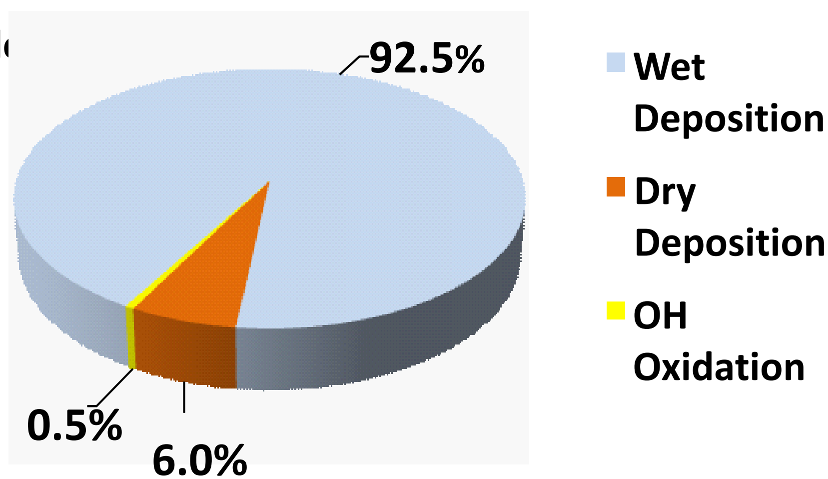
- **Cloud Parameters** as in wetS module: LWC_offset=$1.e^{-10}$ and CC_offset =0.01
- **pH** is calculated in wetS module
- The **radius** of cloud droplets is 5 μm.

Some first OXL results with TM4-ECPL

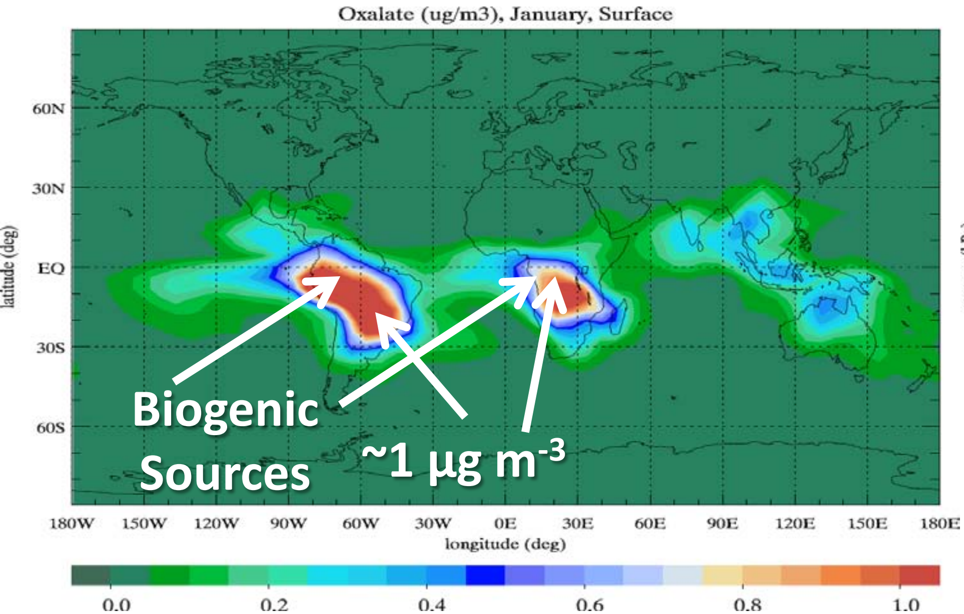
Budget Calculations of Oxalate with TM4-ECPL

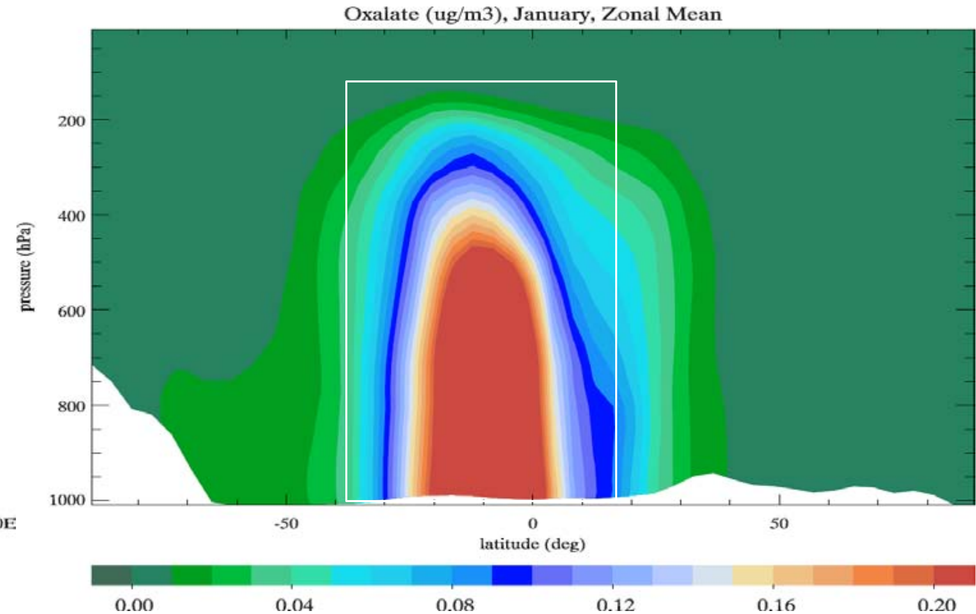
Chemical Production		Sinks			Burden	Mean Global Lifetime
		OH Oxidation	Dry Deposition	Wet Deposition		
33 Tg yr^{-1}		0.1 Tg yr^{-1} (~0.5%)	2 Tg yr^{-1} (~6%)	30 .4 Tg yr^{-1} (~92.5%)	0.5 Tg	5 days
Biogenic VOC	Anthropogenic VOC					
30 Tg yr^{-1} (~91%)	3 Tg yr^{-1} (~9%)					

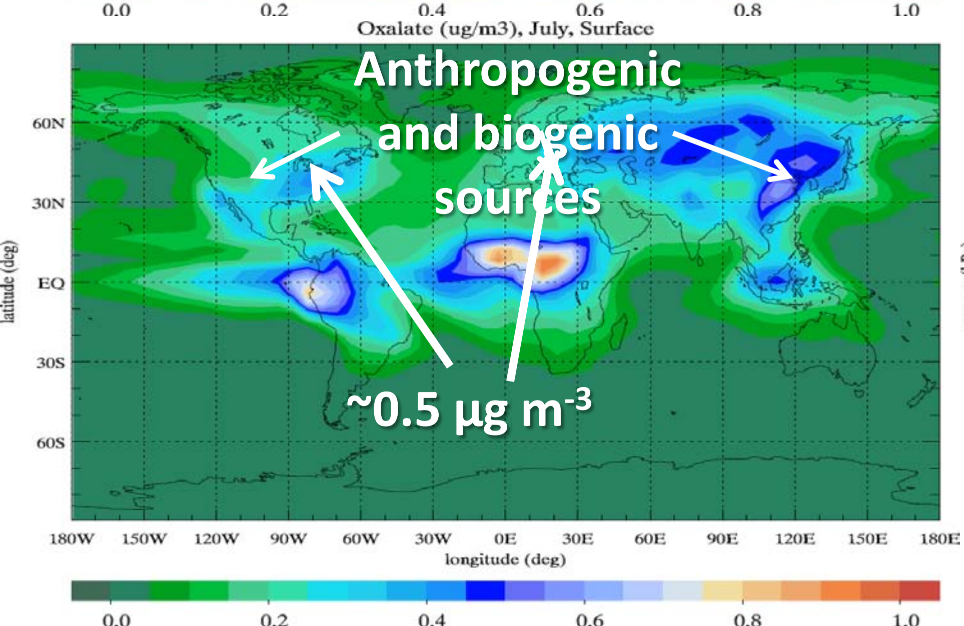


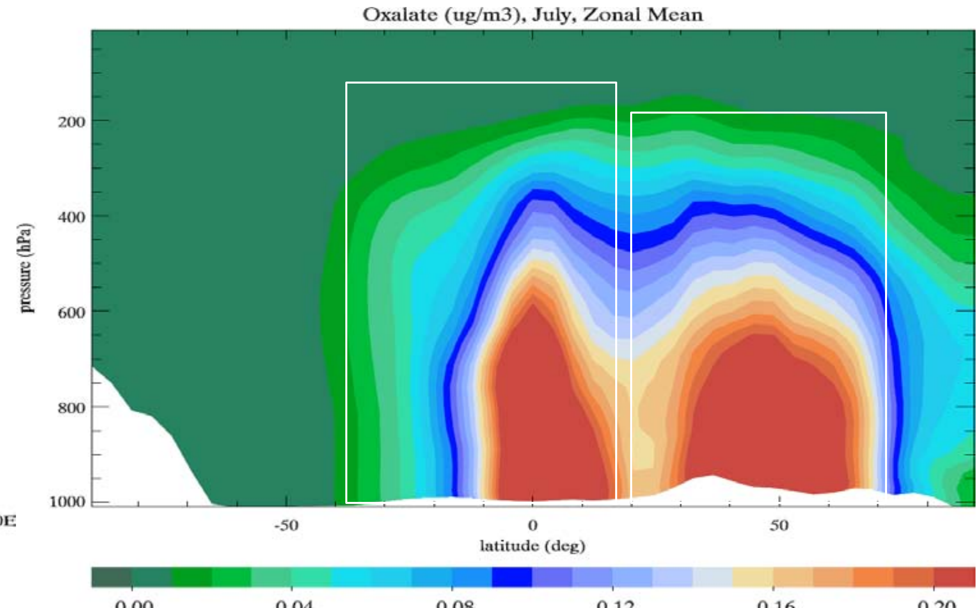


Oxalate Distributions – First Results

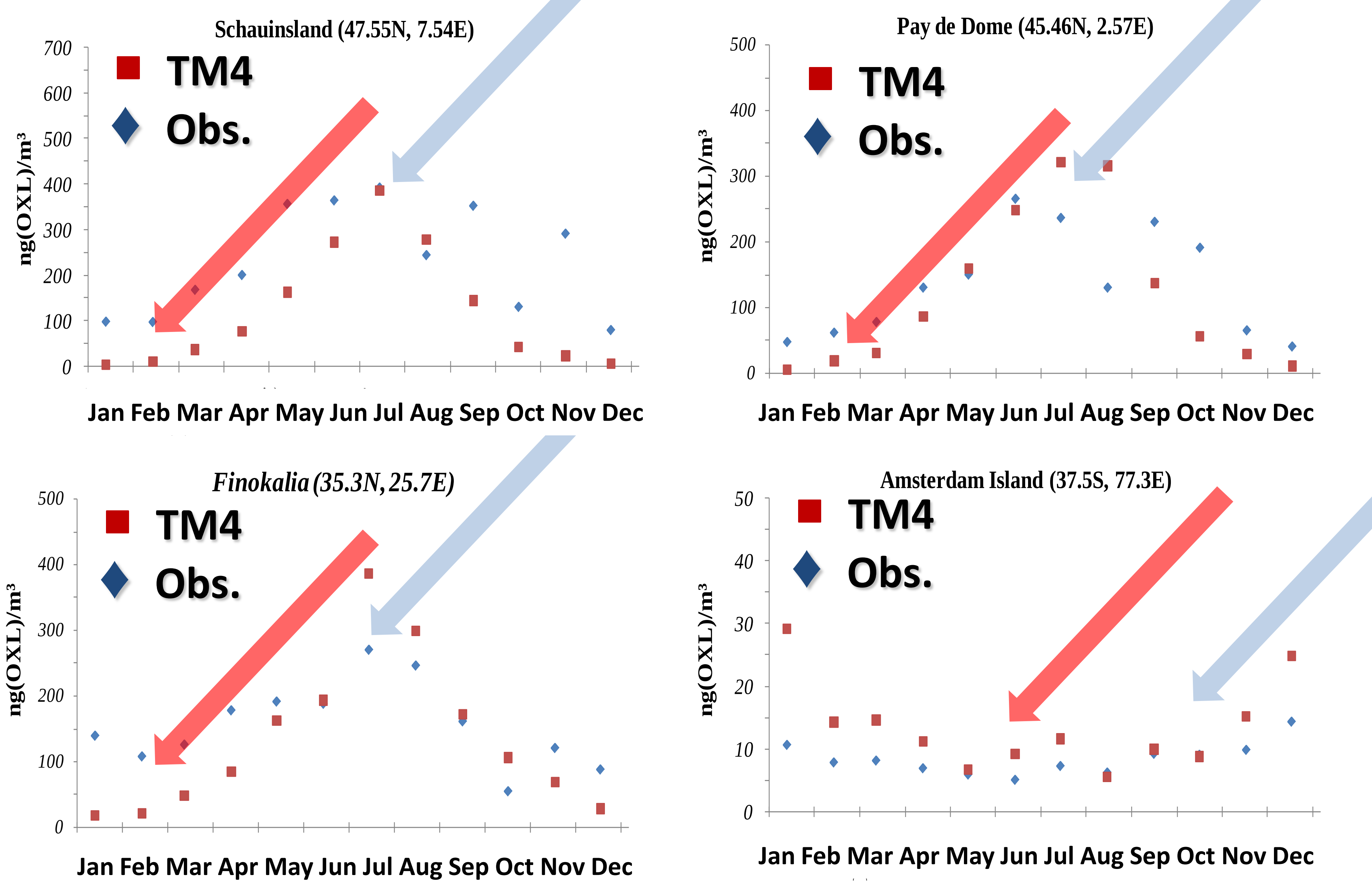








Comparison with Measurements – *First Results*



Future Work . . .

- Some more tests with the EBI solver in the aqueous phase compare to FACSIMILE

- More Validation of OXL results (mainly in C. Africa and the Amazon Basin – extreme VOC emission cases)

- Oxalate production also in particulate water (Ervens and Volkamer, 2010, ACPD)

- Organic mass aqueous phase production through acid catalysis and with inorganic constituents to form organic acids, oligomers and organosulfates (Lim et al., 2010, ACPD)