Organics in the global troposphere: Recent advances and future plans at ECPL

Environmental Chemical Processes Laboratory (ECPL)
Department of Chemistry
University of Crete, Heraklion, Greece

Maria Kanakidou mariak@chemistry.uoc.gr

Stelios Myriokefalitakis → PhD defense on June

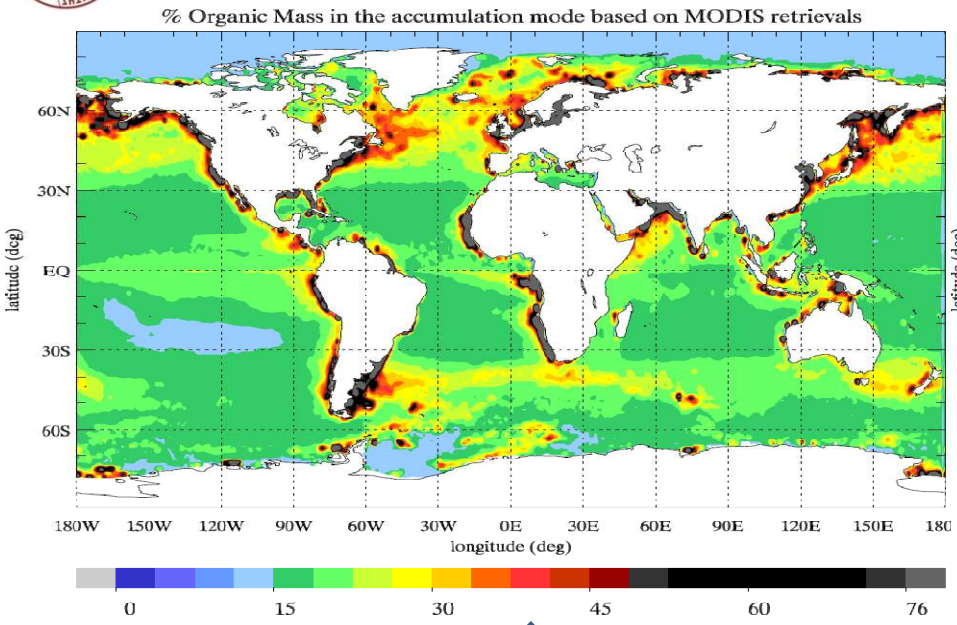
Nikos Daskalakis → *AEROCOM OA exercise*

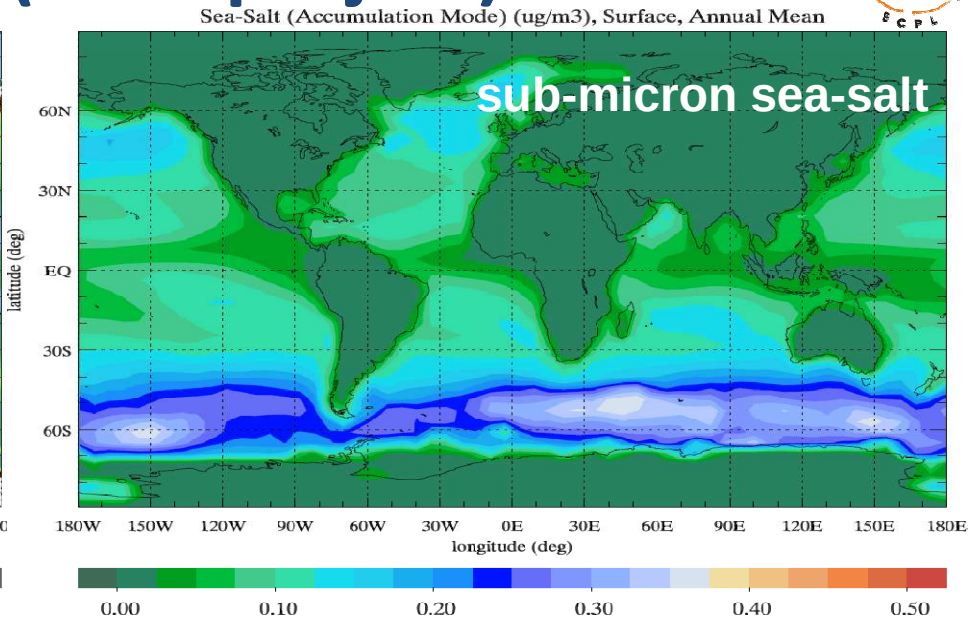
Kostas Tsigaridis NASA-GISS / lumping/simplifying SOA

Improving OA parameterisations in TM4

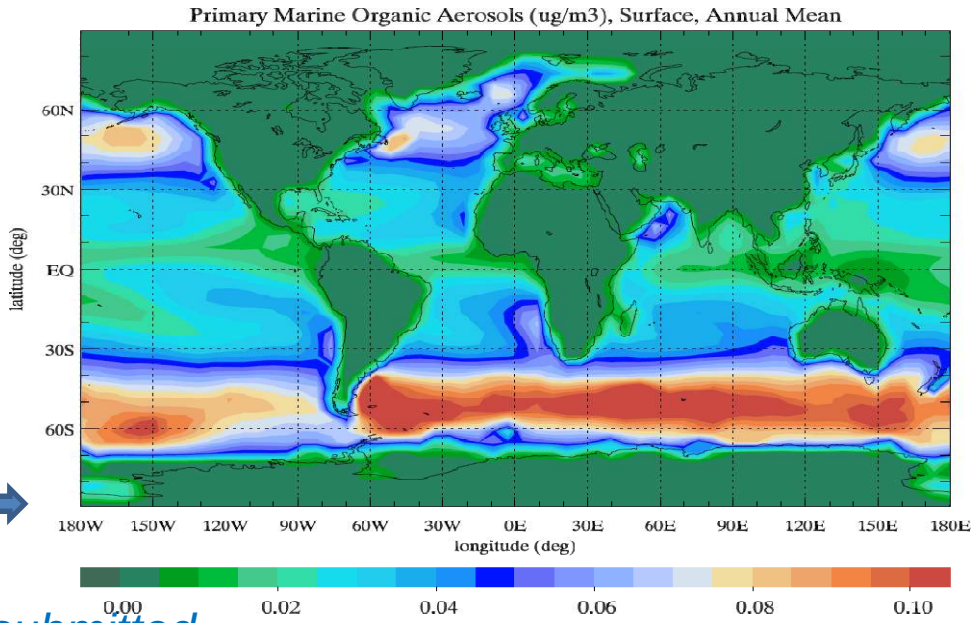
1. CB4→ explicit chemistry (oxidant fields) *Myriokefalitakis et al., ACP, 2008*
2. POA from the oceans (*Vignati et al., 2009 to be submitted*)
3. SOA from oceanic isoprene + monoterpenes (*Myriokefalitakis et al., to be submitted*)
4. SOA ageing by reactions with OH in gas phase (as by *Tsigaridis & Kanakidou, ACP, 2003* now in TM4)
5. SOA from multiphase reactions
   - Ervens et al GRL 2008 simple parameterization
   - Explicit scheme for glyoxal /oxalic acid
6. Impact of heterogeneous chemistry

Marine POA (MAP project)





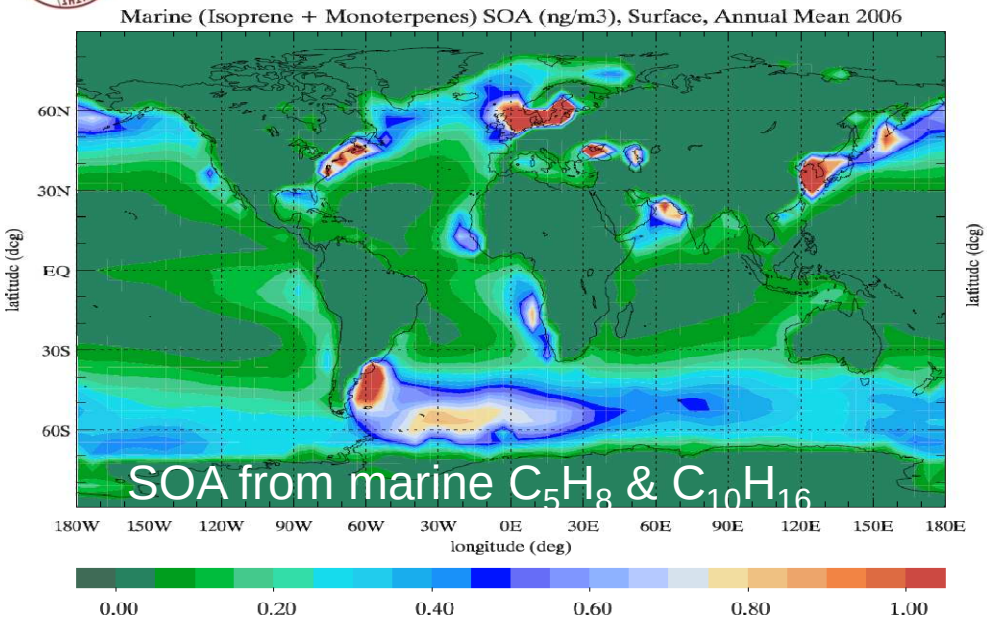
% OA in sub-micron sea-salt aerosol

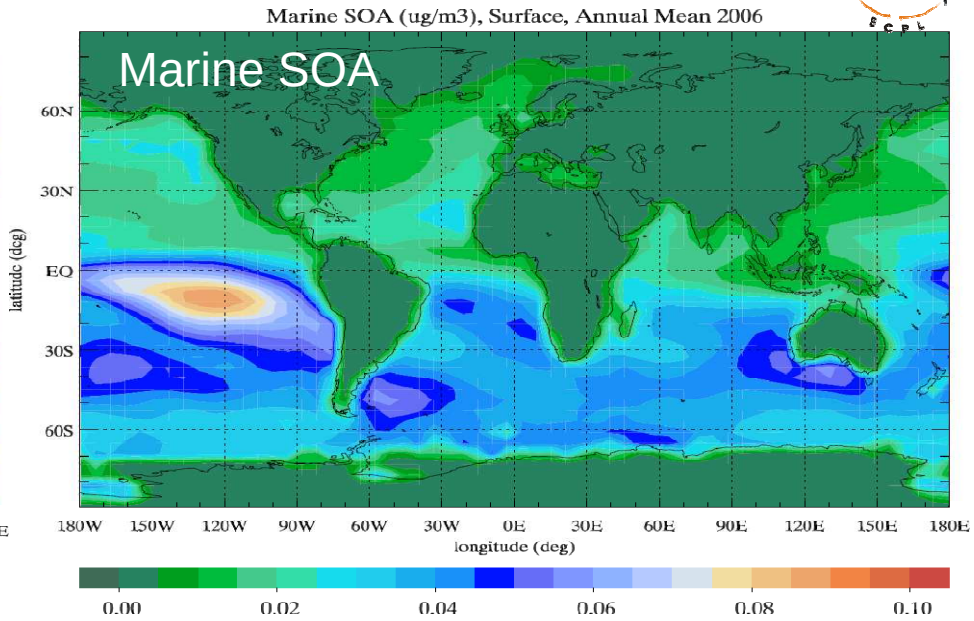


Marine POA in the accumulation mode

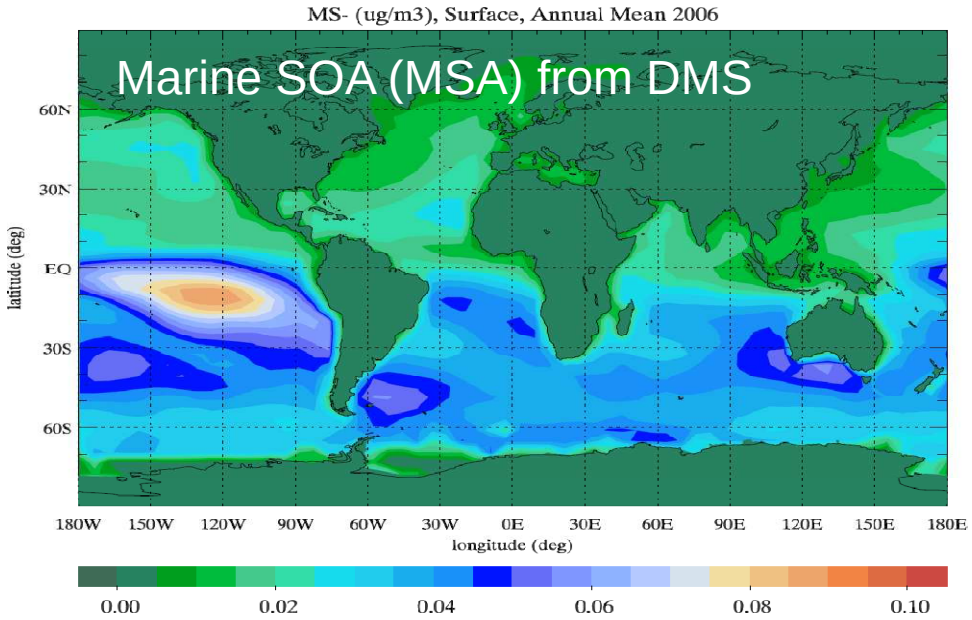
Vignati et al., 2009 to be submitted

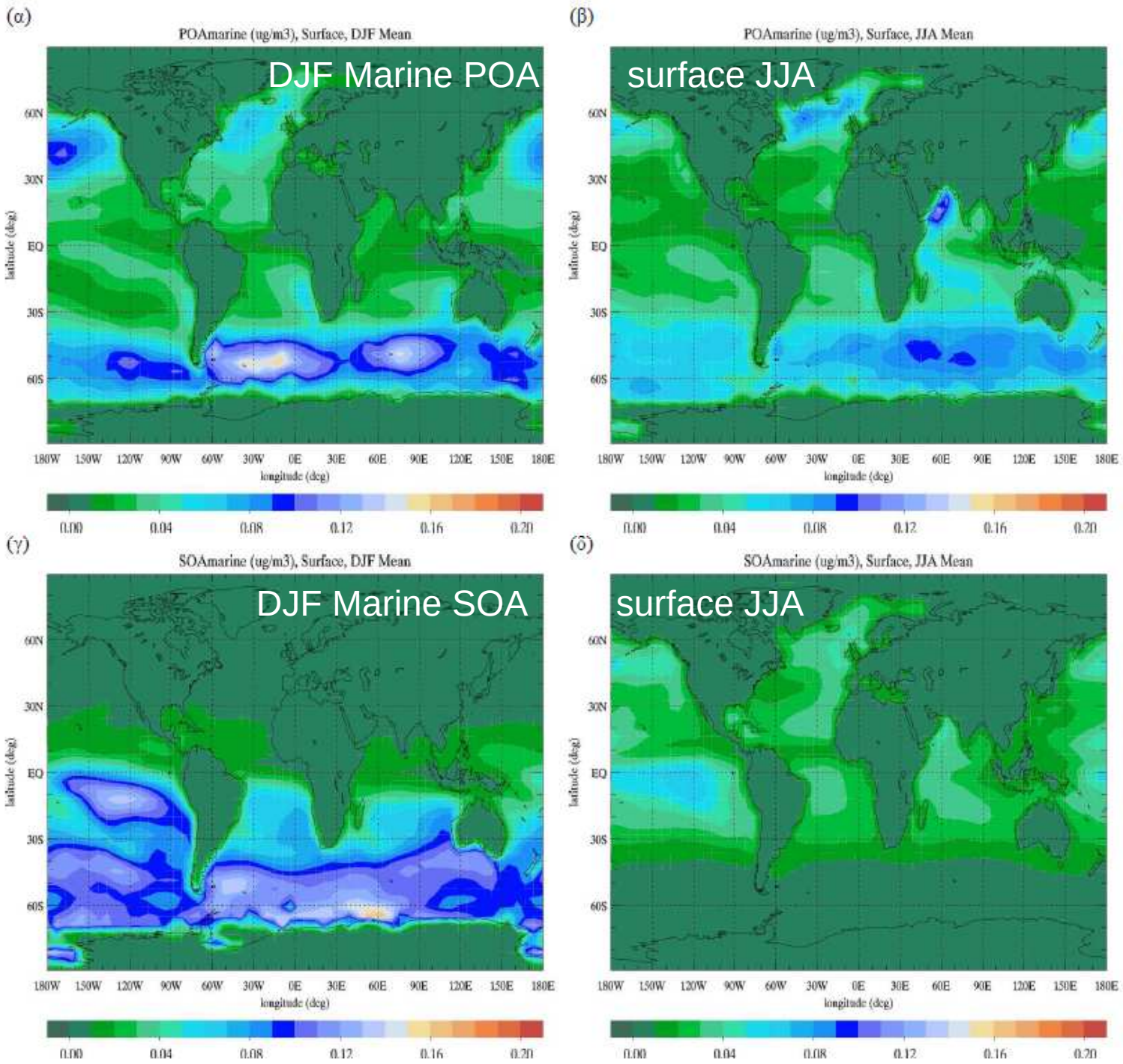
Marine SOA





Myriokefalitakis et al to be submitted 2009



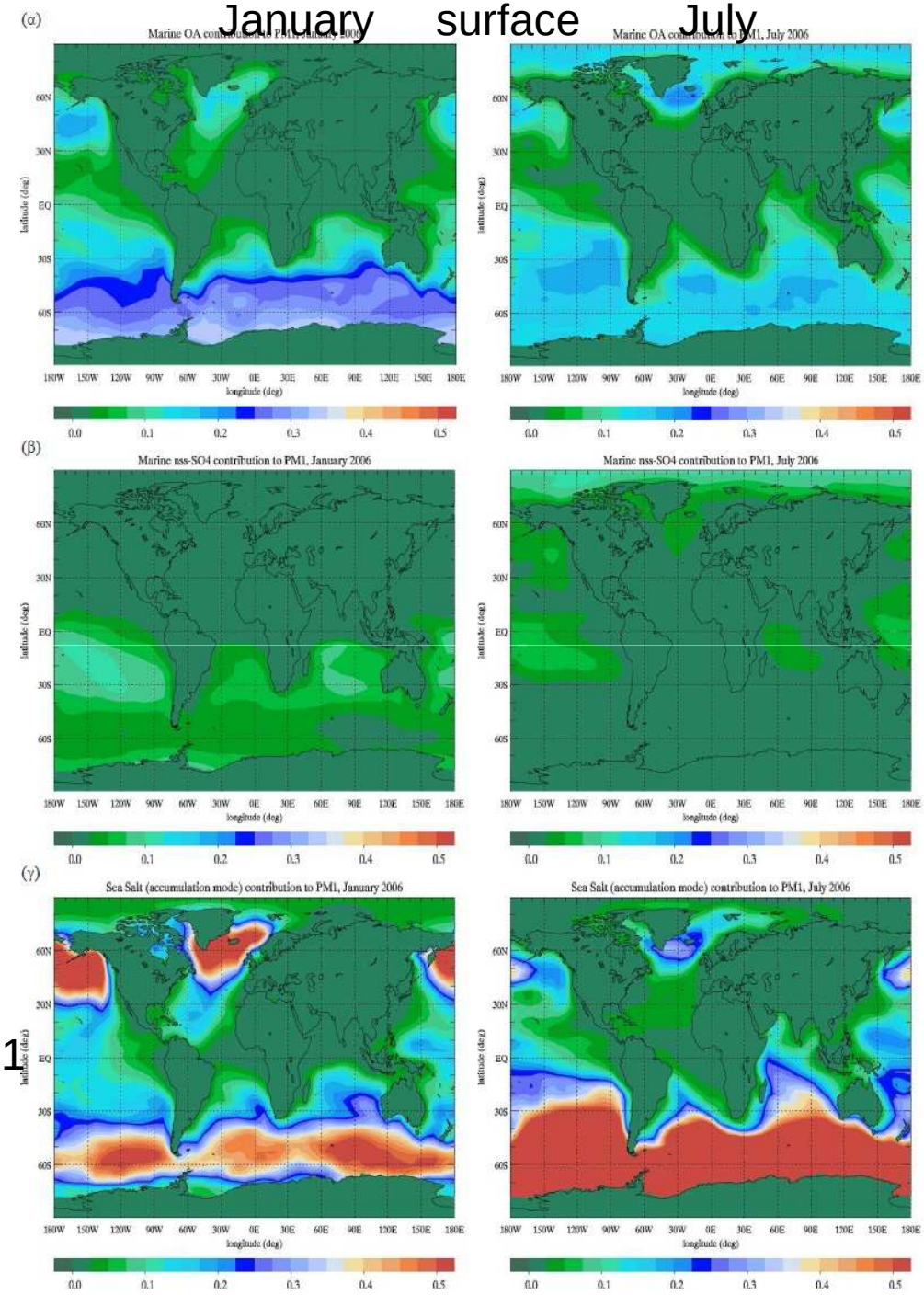

(α)
POAmarine (ug/m3), Surface, DJF Mean
DJF Marine POA
(β)
POAmarine (ug/m3), Surface, JJA Mean
surface JJA
(γ)
SOAmarine (ug/m3), Surface, DJF Mean
DJF Marine SOA
(δ)
SOAmarine (ug/m3), Surface, JJA Mean
surface JJA
60N
30N
EQ
30S
60S
latitude (deg)
180W 150W 120W 90W 60W 30W 0E 30E 60E 90E 120E 150E 180E
longitude (deg)
0.00 0.04 0.08 0.12 0.16 0.20

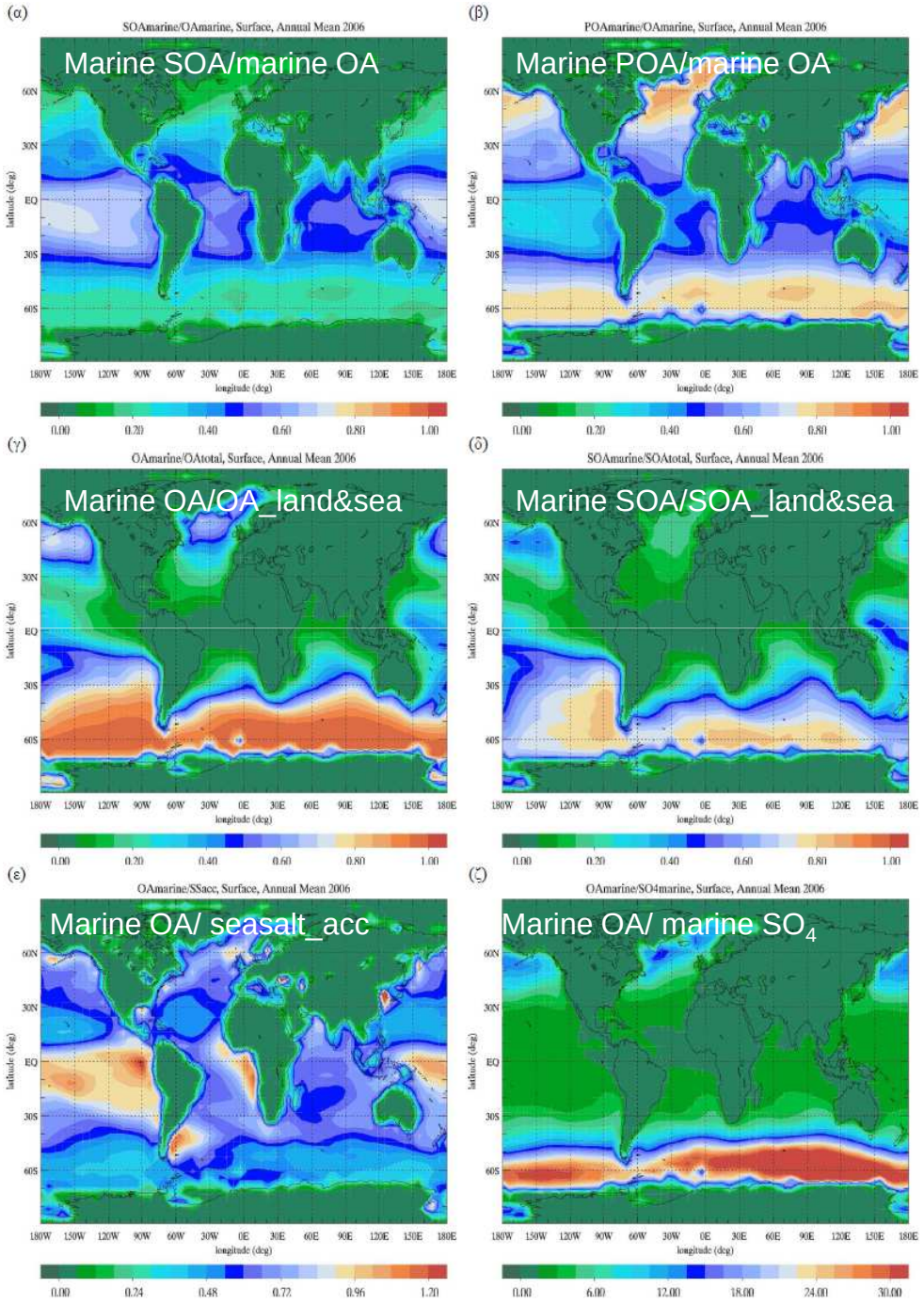
January surface July

Marine OA/marine PM1

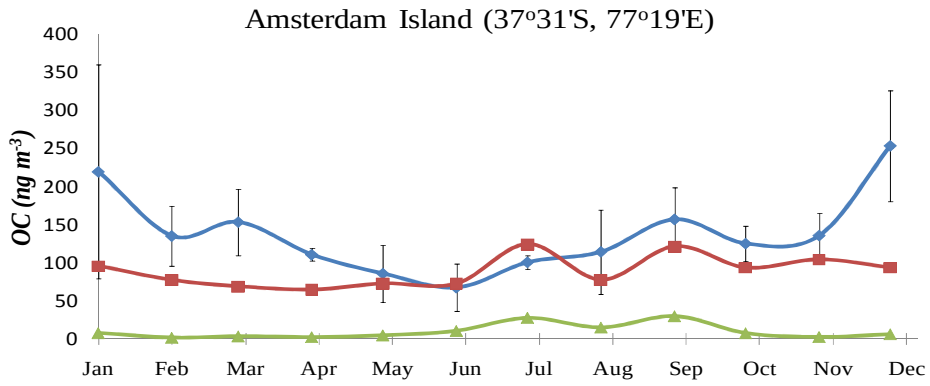
Marine $SO_4^=$/marine PM1

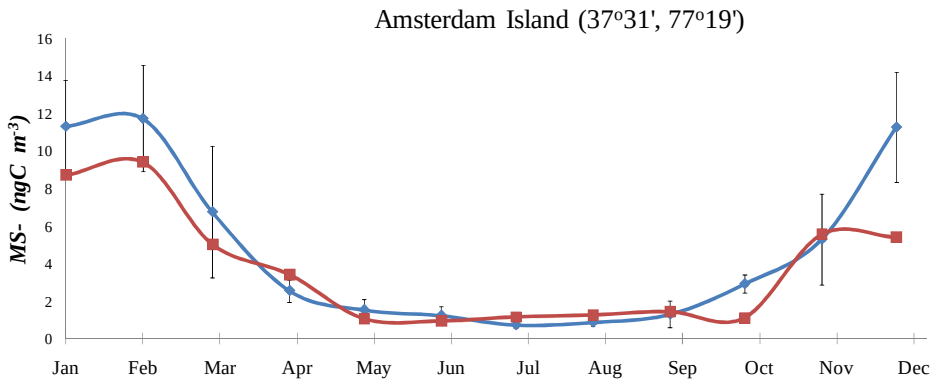
Sea-salt accum./marine PM1

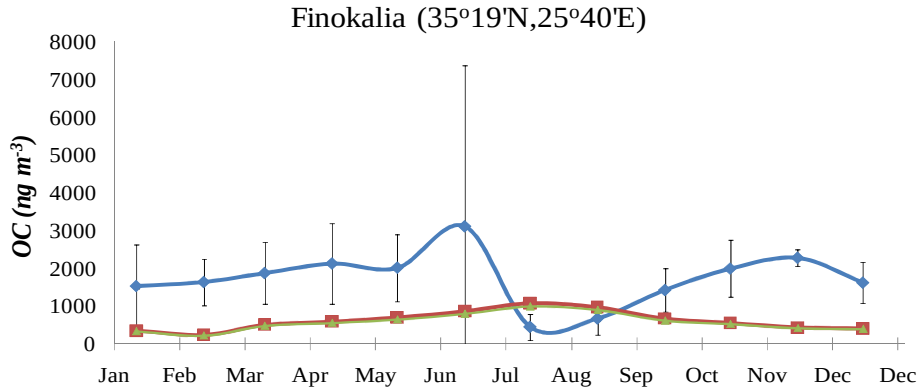


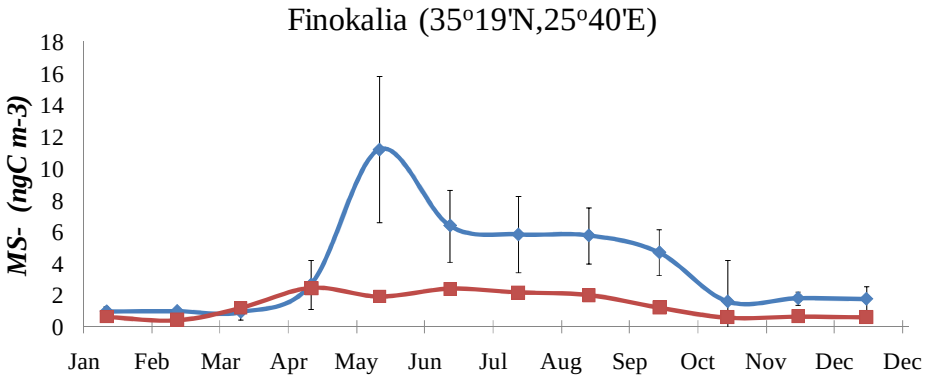

(α)
SOAmarine/OAmarine, Surface, Annual Mean 2006
Marine SOA/marine OA
(β)
POAmarine/OAmarine, Surface, Annual Mean 2006
Marine POA/marine OA
(γ)
OAmarine/OAtotal, Surface, Annual Mean 2006
Marine OA/OA_land&sea
(δ)
SOAmarine/SOAtotal, Surface, Annual Mean 2006
Marine SOA/SOA_land&sea
(ε)
OAmarine/SSacc, Surface, Annual Mean 2006
Marine OA/ seasalt_acc
(ζ)
OAmarine/SO4marine, Surface, Annual Mean 2006
Marine OA/ marine SO4
latitude (deg)
longitude (deg)

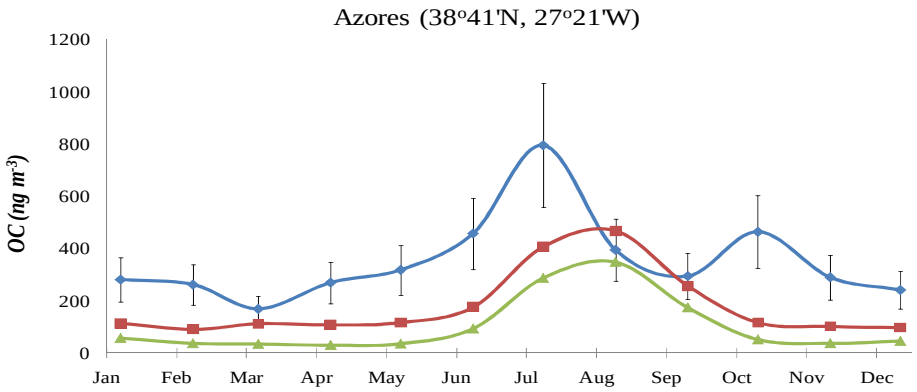
Marine OA model vs observations

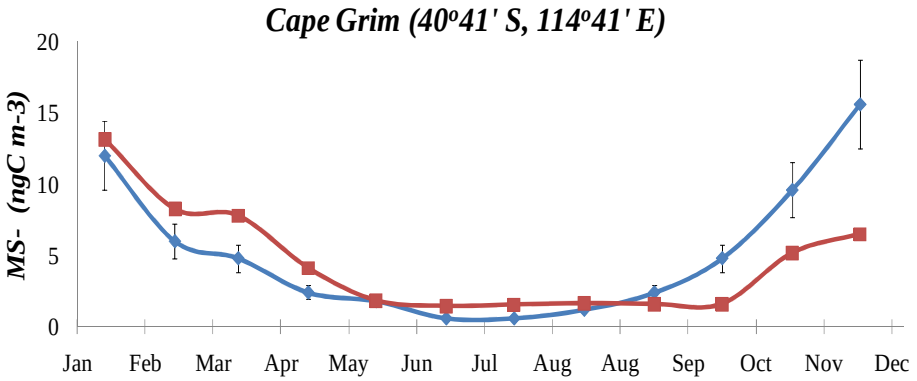


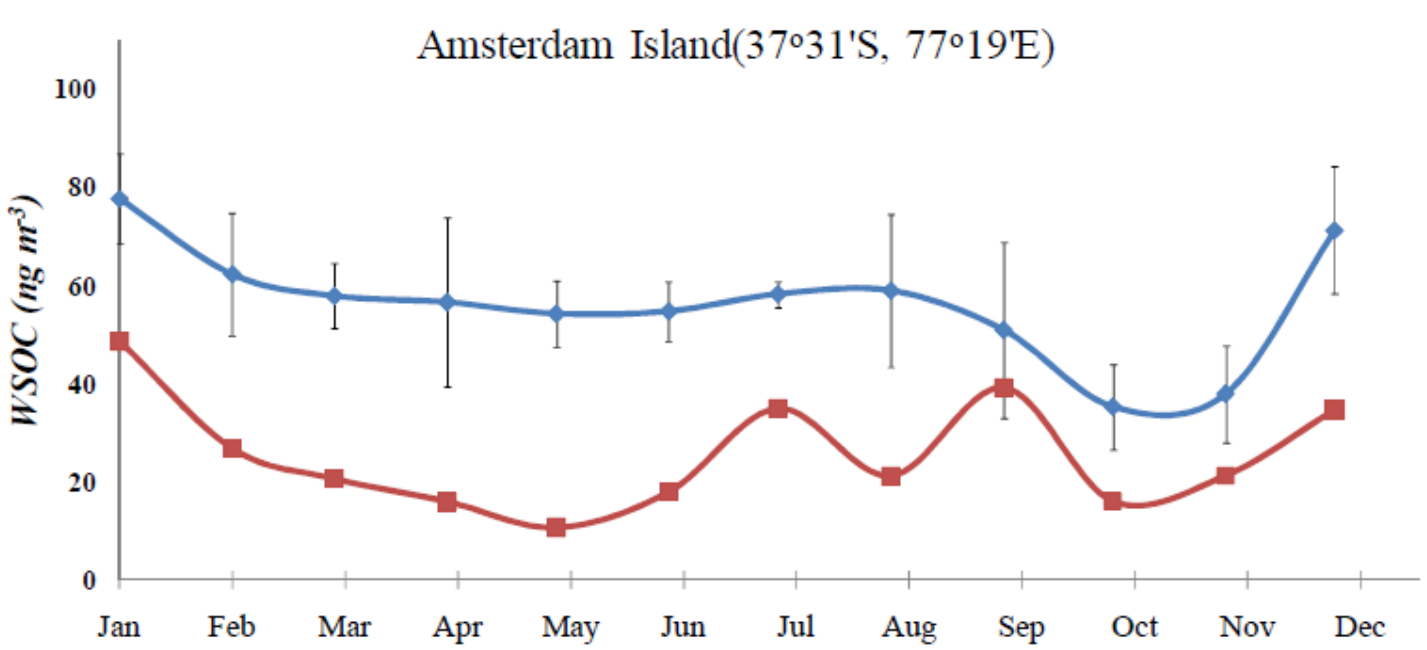


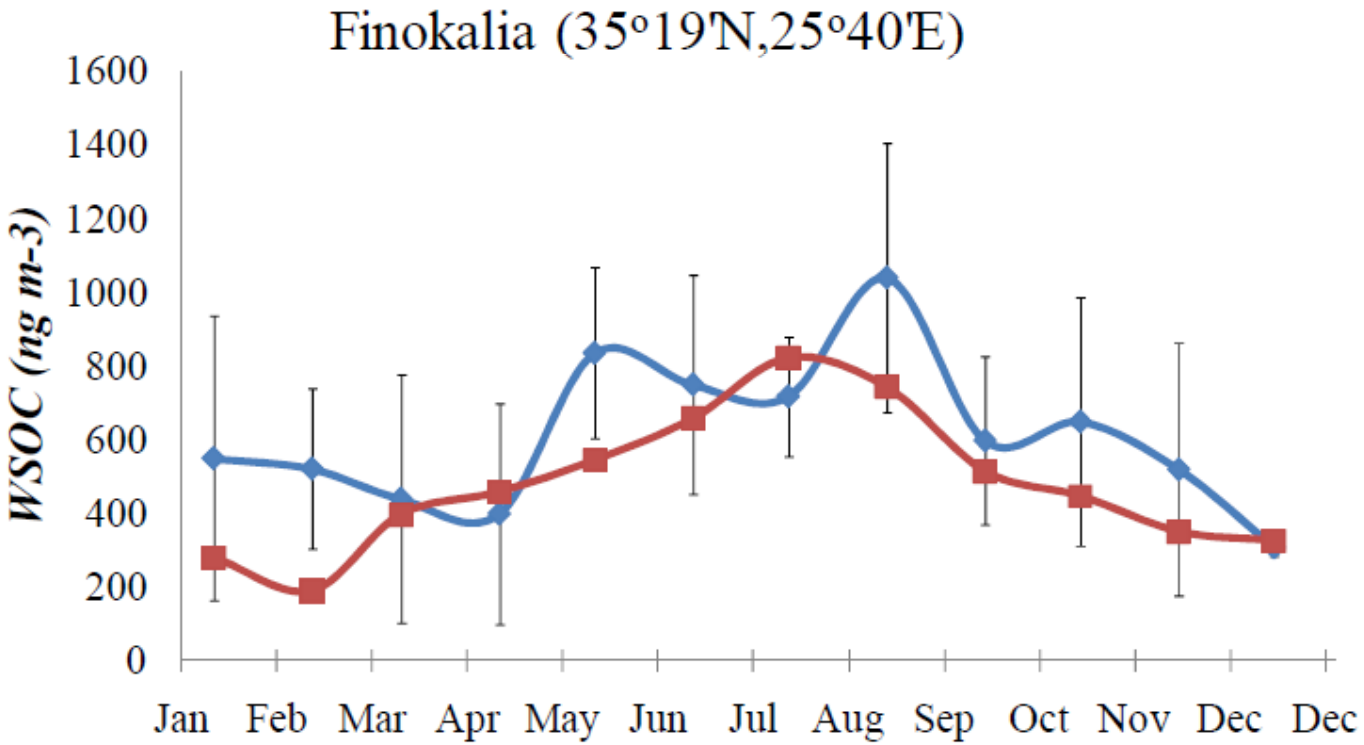


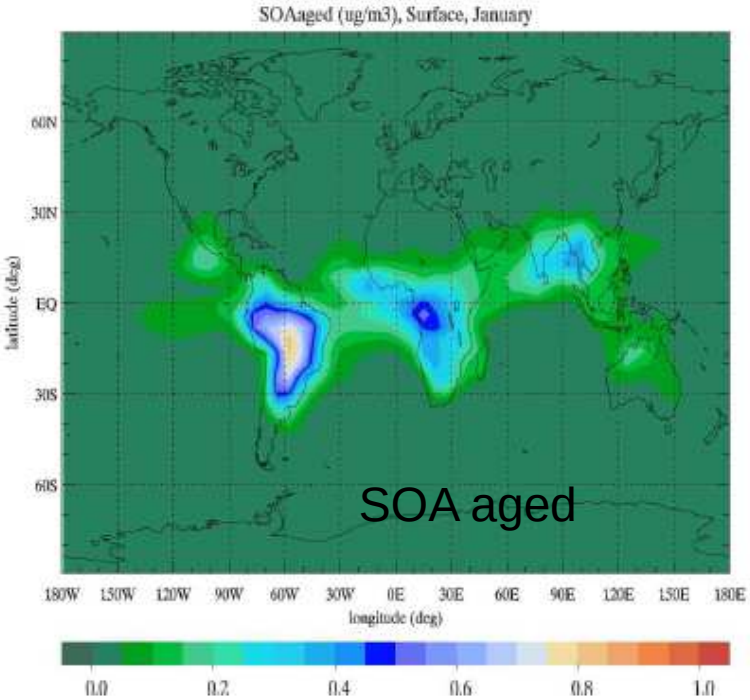


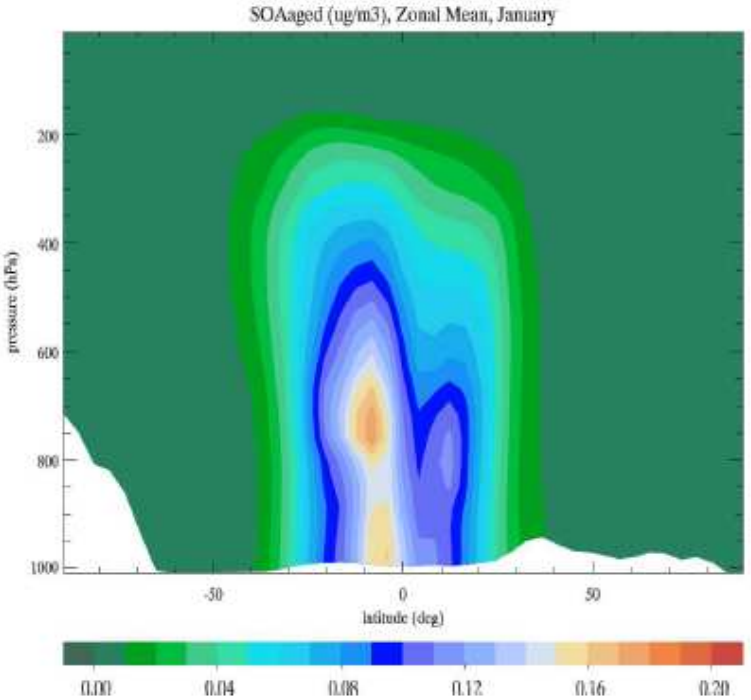


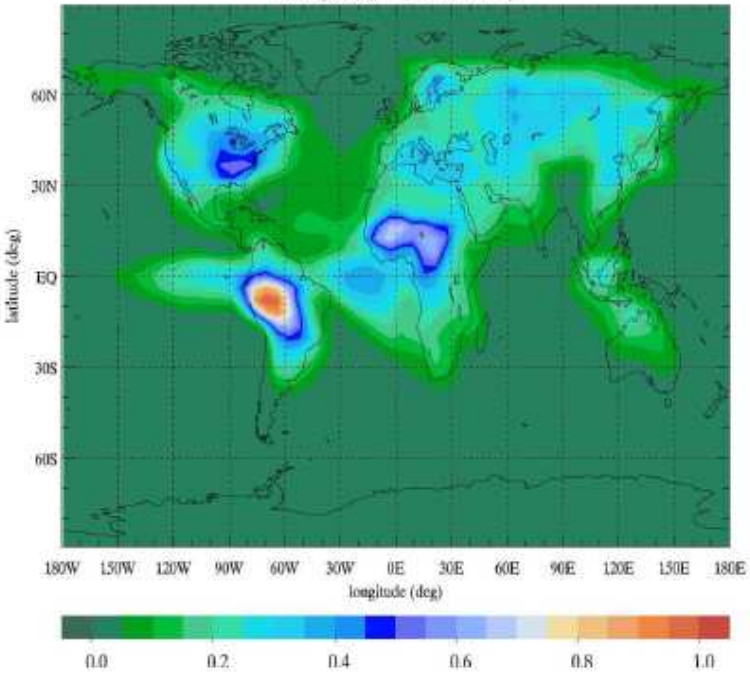


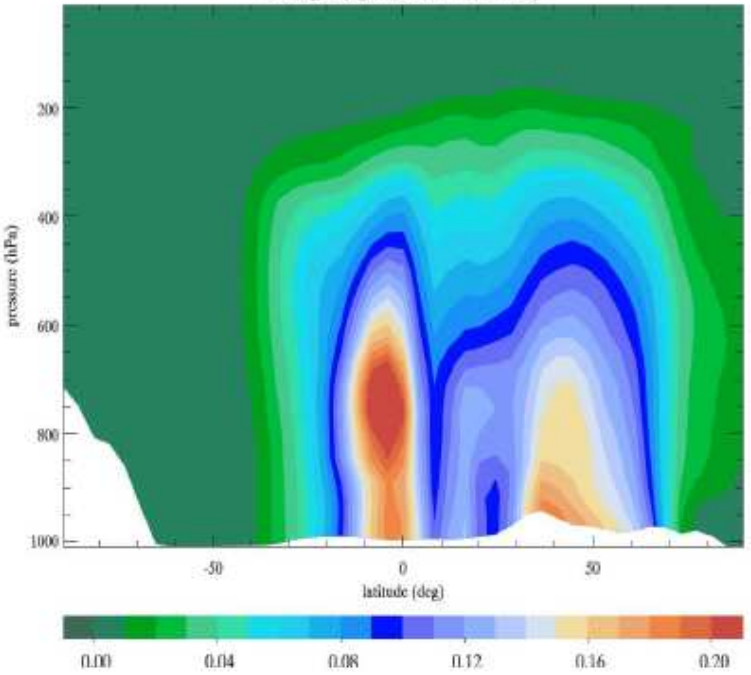

Amsterdam Island(37°31'S, 77°19'E)
WSOC (ng m-3)
100
80
60
40
20
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec


Finokalia (35°19'N,25°40'E)
WSOC (ng m-3)
1600
1400
1200
1000
800
600
400
200
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Dec


SOAaged (ug/m3), Surface, January
SOA aged
60N
30N
EQ
30S
60S
latitude (deg)
180W 150W 120W 90W 60W 30W 0E 30E 60E 90E 120E 150E 180E
longitude (deg)
0.0 0.2 0.4 0.6 0.8 1.0

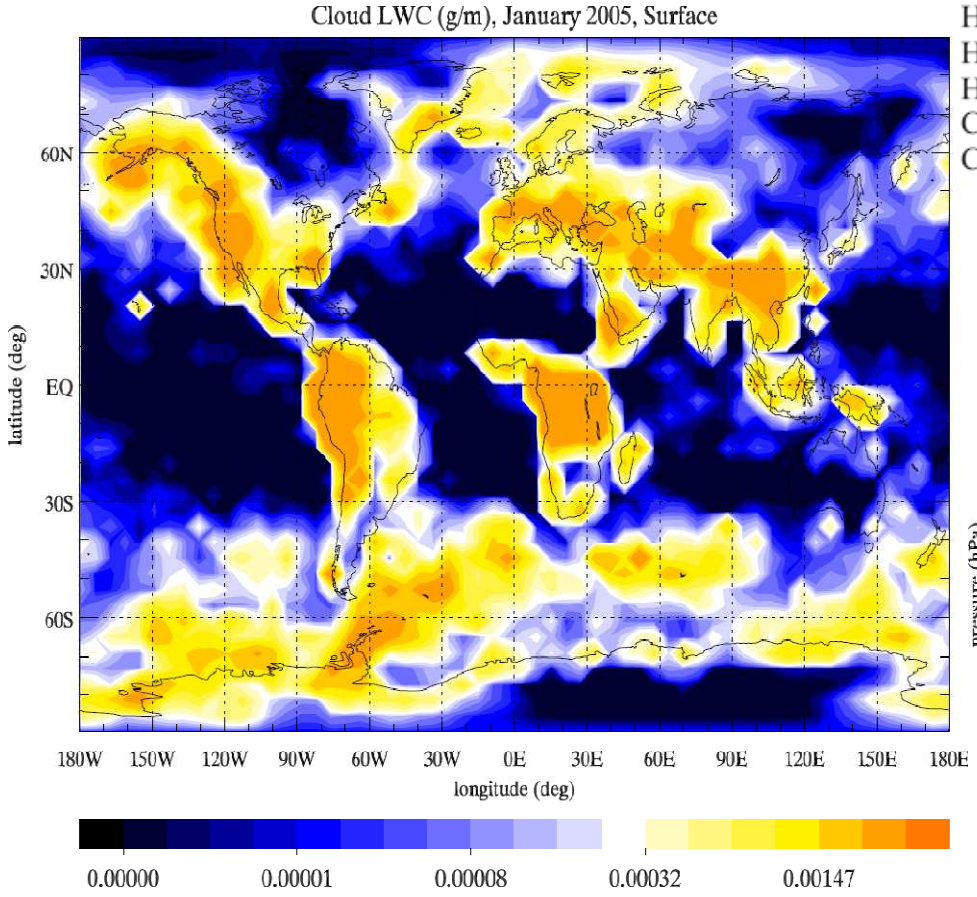

SOAaged (ug/m3), Zonal Mean, January
200
400
600
800
1000
pressure (hPa)
-50 0 50
latitude (deg)
0.00 0.04 0.08 0.12 0.16 0.20

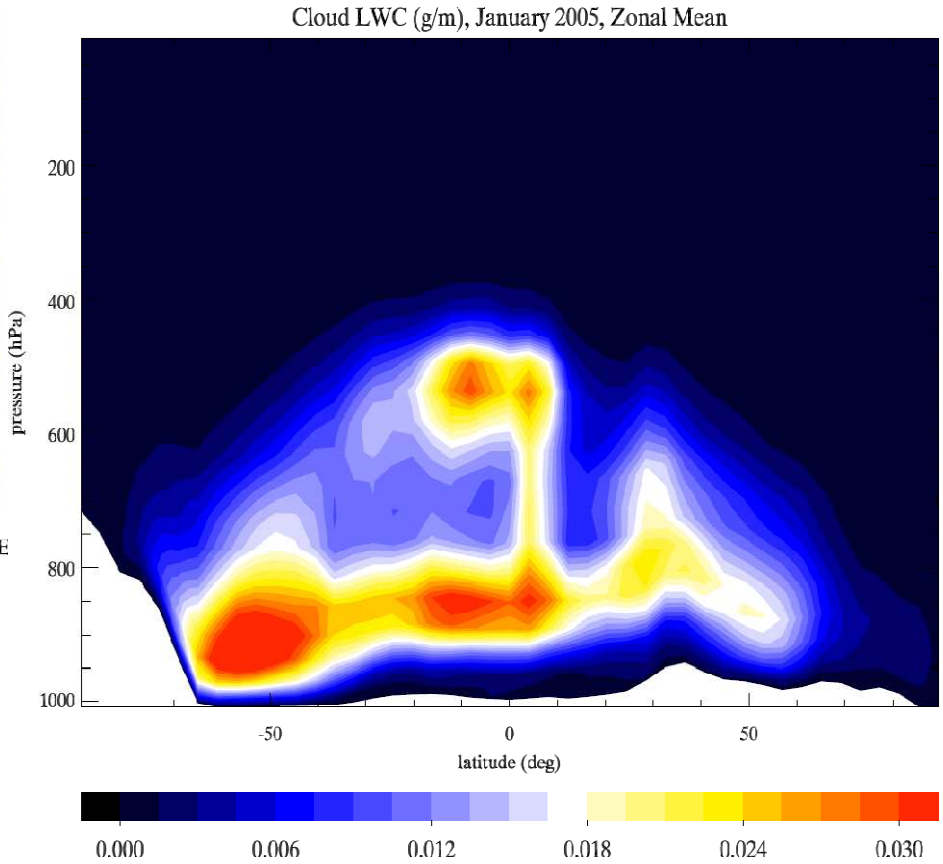

SOAaged (ug/m3), Surface, July
60N
30N
EQ
30S
60S
latitude (deg)
180W 150W 120W 90W 60W 30W 0E 30E 60E 90E 120E 150E 180E
longitude (deg)
0.0 0.2 0.4 0.6 0.8 1.0


SOAaged (ug/m3), Zonal Mean, July
200
400
600
800
1000
pressure (hPa)
-50 0 50
latitude (deg)
0.00 0.04 0.08 0.12 0.16 0.20

Aqueous phase chemistry – where ?

Species	$\frac{C_a}{C_g}$	$K_H RTL$
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}





Partitioning

Partitioning gas to particle

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

Partitioning gas to liquid phase

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

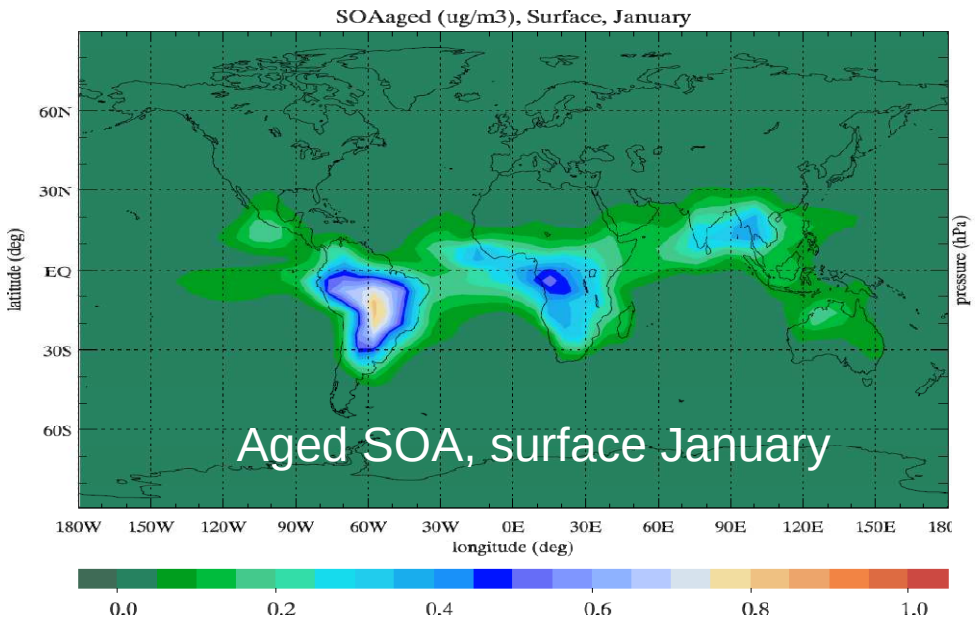
$$H_{eff}(T) = H(T)\left(1 + \frac{Ki(T)}{[H^+]}\right)$$

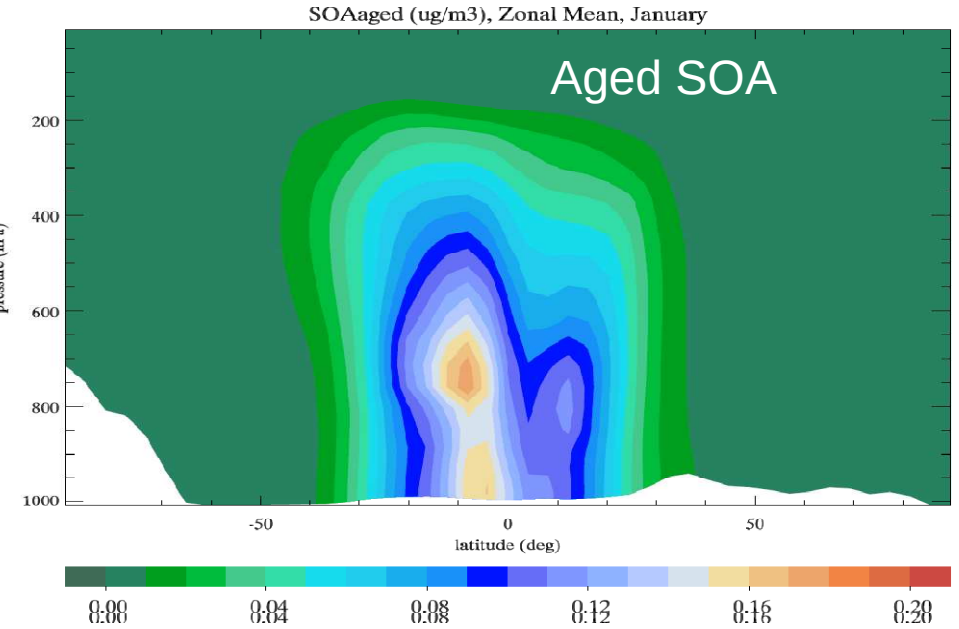
$$P_x = H_K L$$

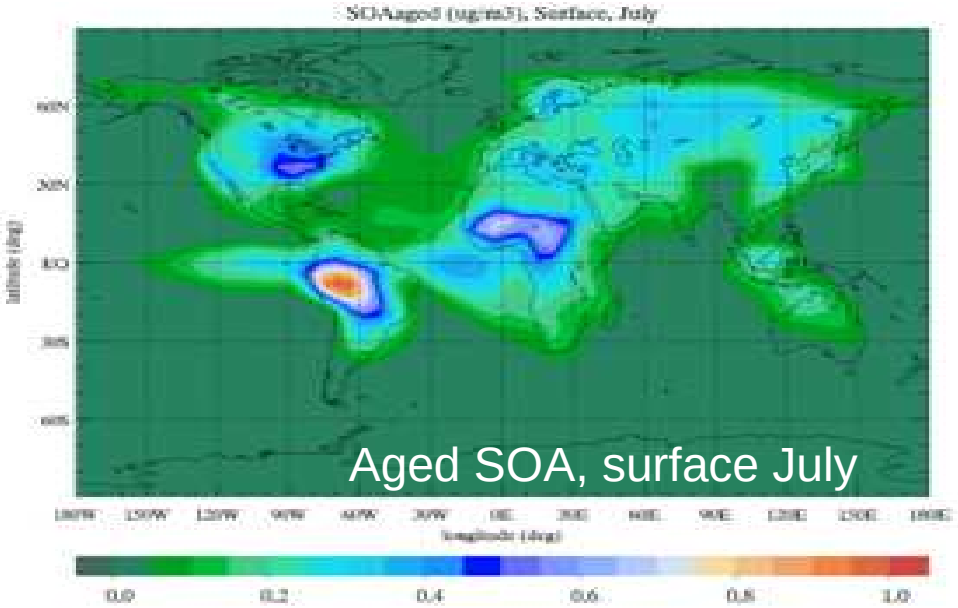
Aqueous phase chemistry in TM4 -reactions

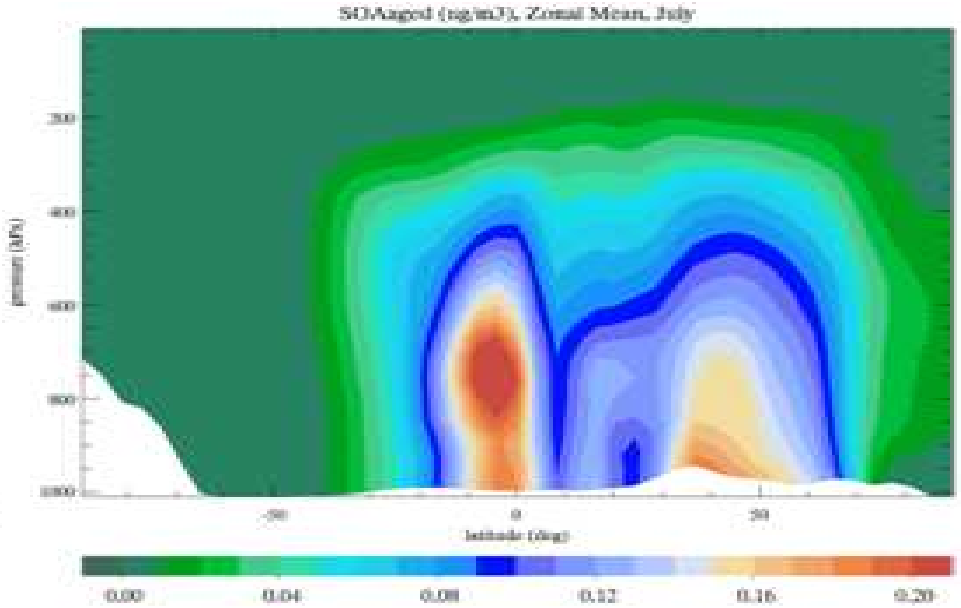
Reactions			A	E/R	Ref
			$(mol \cdot lt^{1}s^{-1})$	(K)	
$H_2O_2 + h\nu$	→	$2OH$			IUPAC
$SO_2 + O_3$	→	$SO_4^{=}$			Dentener (1993)
$SO_2 + H_2O_2$	→	$SO_4^{=}$			Dentener (1993)
$OH + H_2O_{2-}$	→	$HO_2 + H_2O$	2.7E7		Carlton et al. (2007)
$HO_2 + HO_2$	→	$H_2O_2 + O_2$	8.3E5		Carlton et al. (2007)
$HOCHCH(OH)_2 + OH$	→	$(OH)_2CHCH(OH)_2 + HO_2$	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)

Oxalic acid simulations







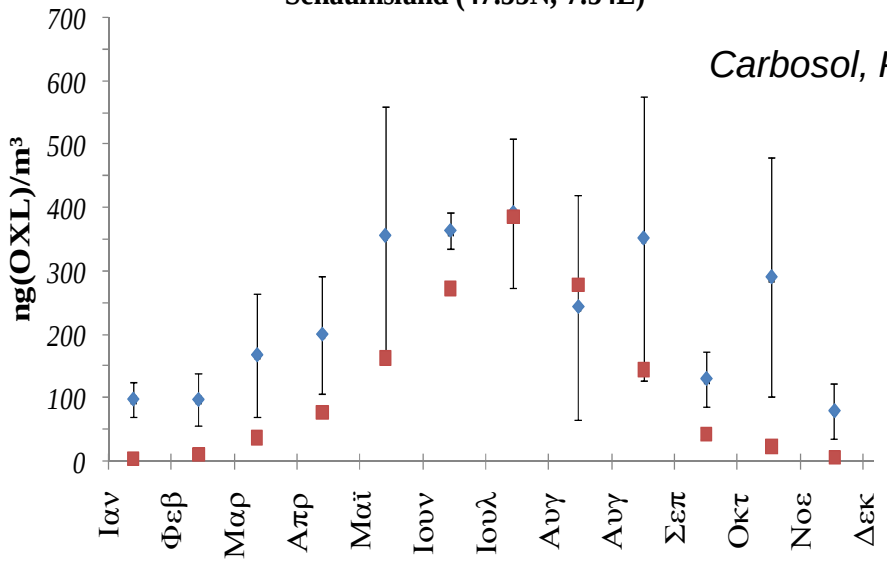


Oxalic acid simulations vs measurements

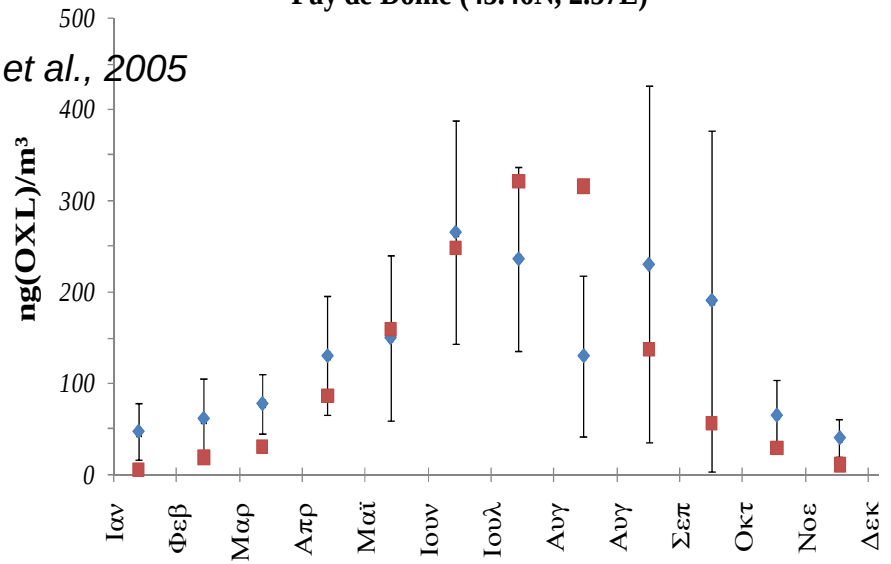
Myriokefalitakis PhD thesis 2009

Carbosol, Pio et al., 2005

Schauinsland (47.55N, 7.54E)

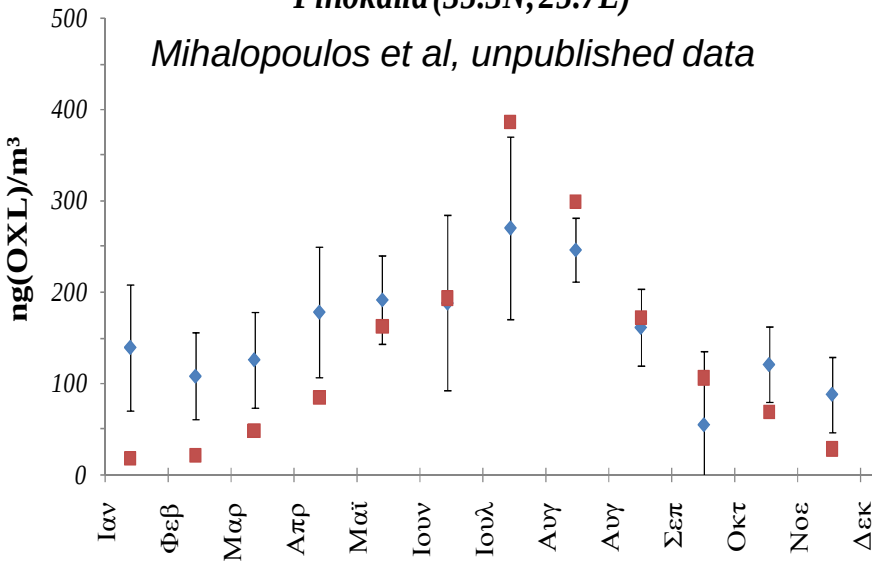


Pay de Dome (45.46N, 2.57E)



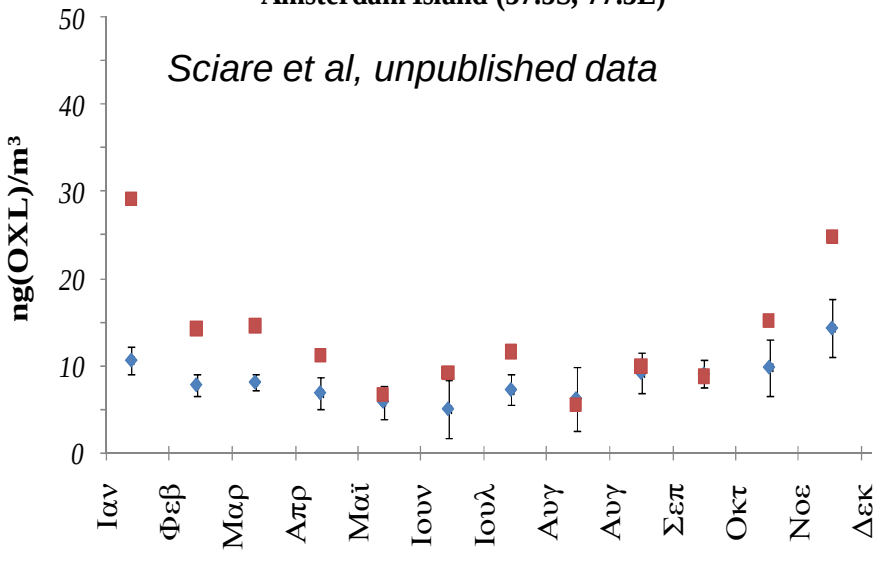
Finokalia (35.3N, 25.7E)

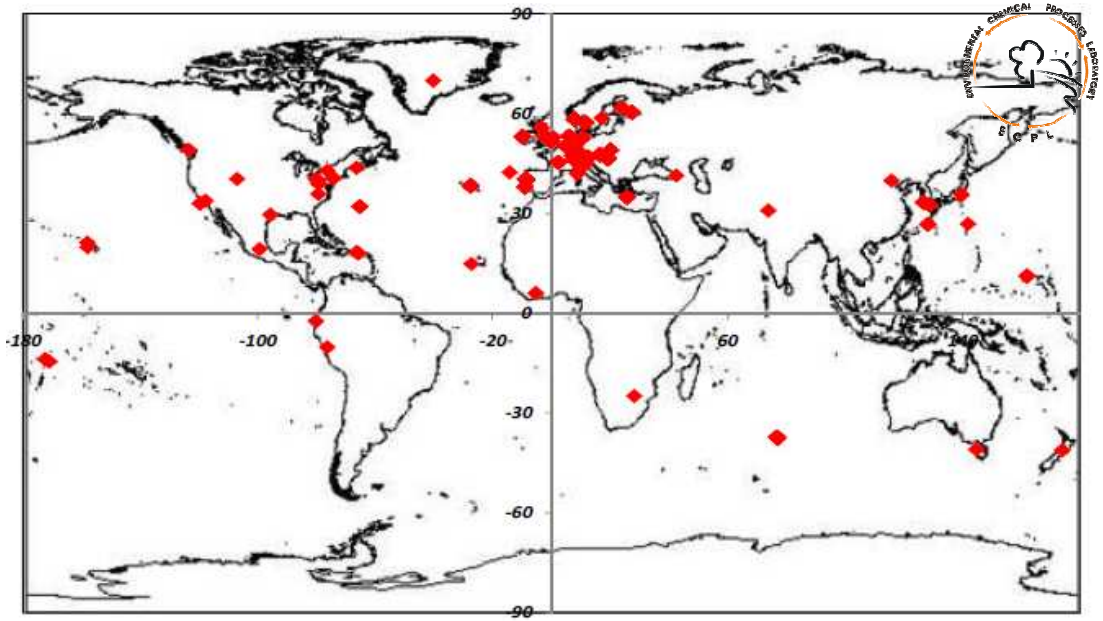
Mihalopoulos et al, unpublished data



Amsterdam Island (37.5S, 77.3E)

Sciare et al, unpublished data





- earlier model version

X this work

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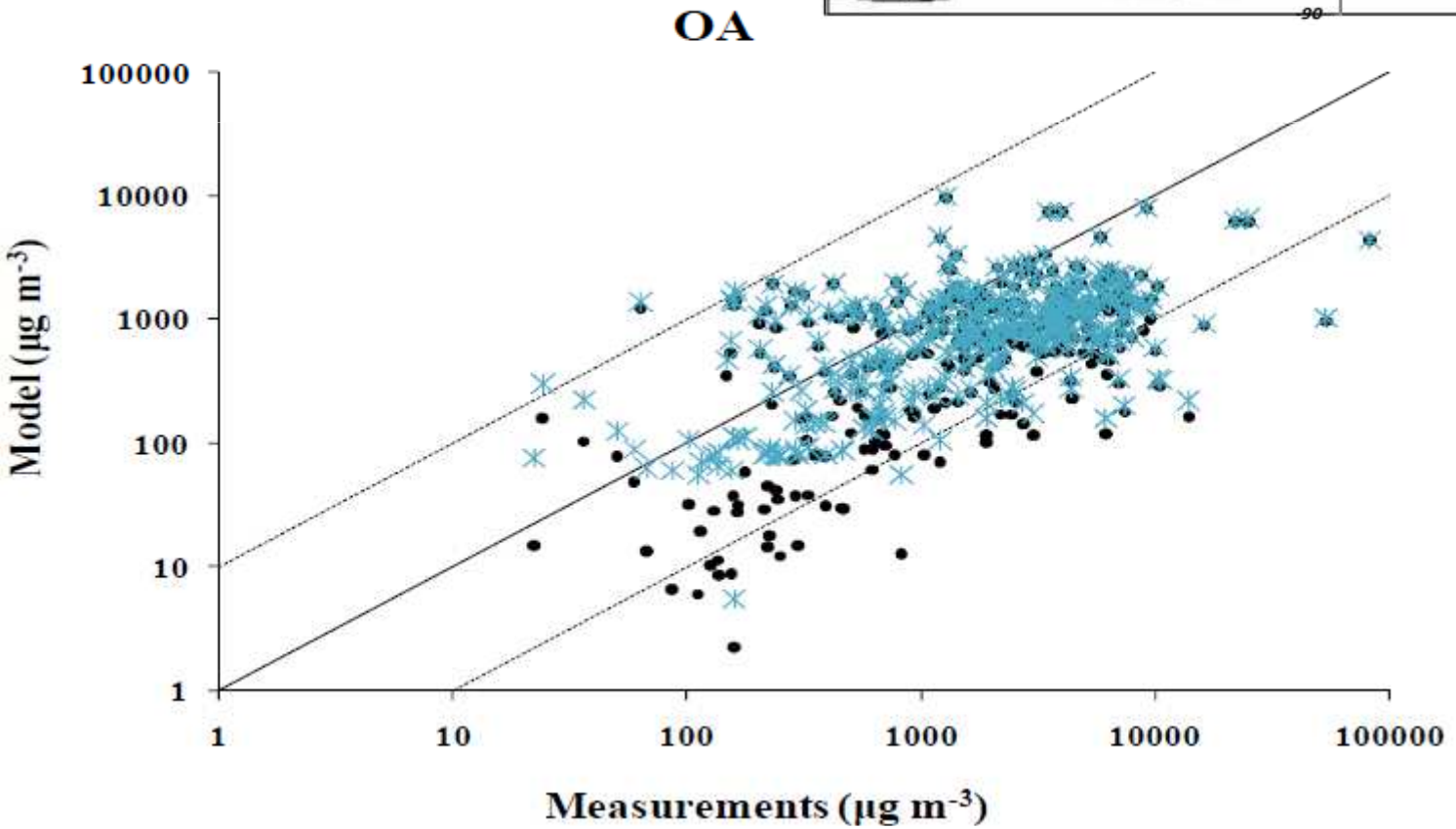
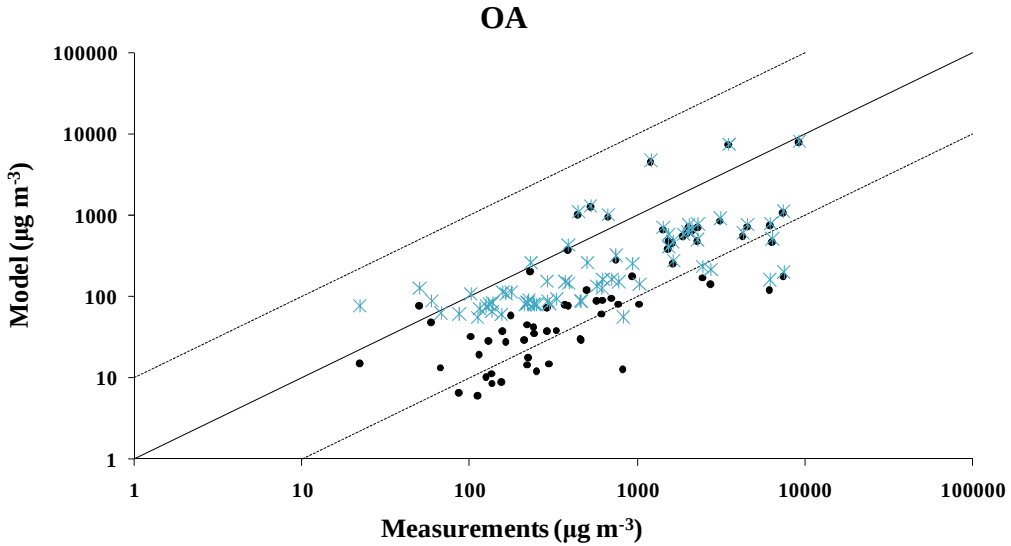
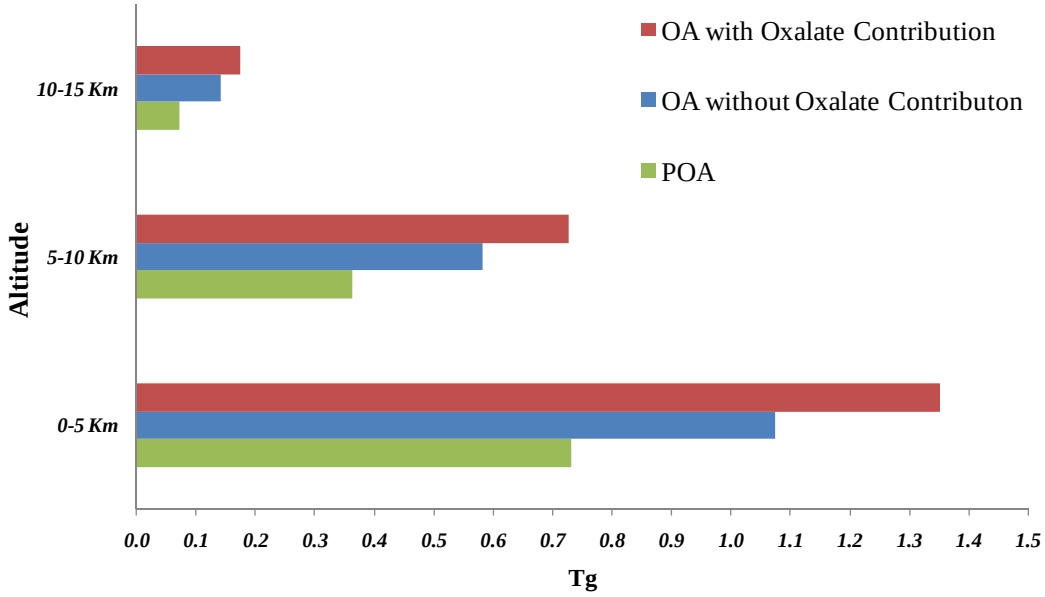


OA – simulations vs measurements



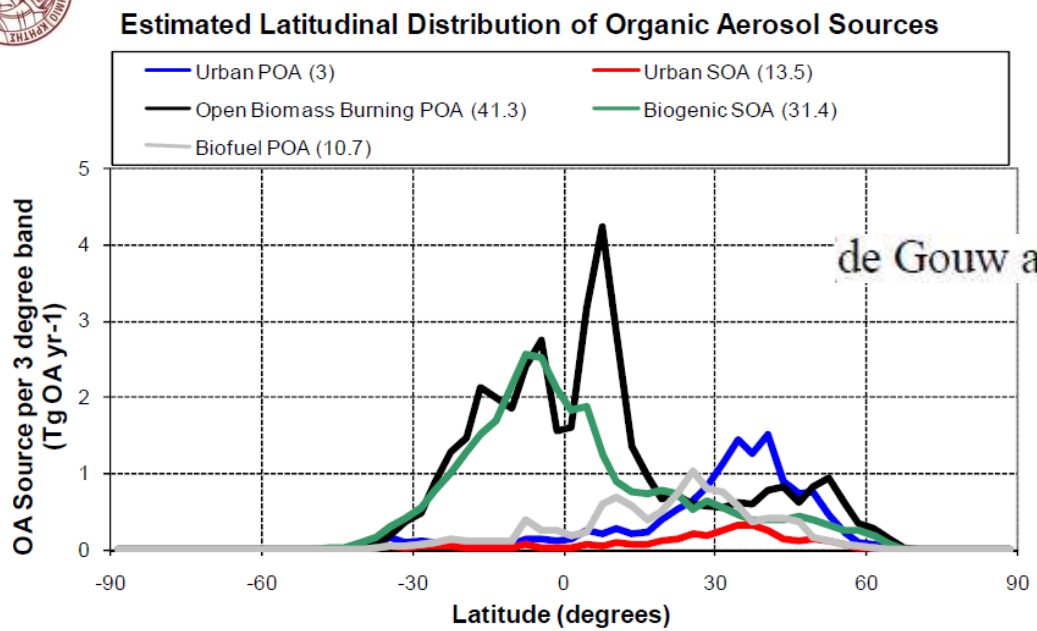
Myriokefalitakis PhD thesis 2009



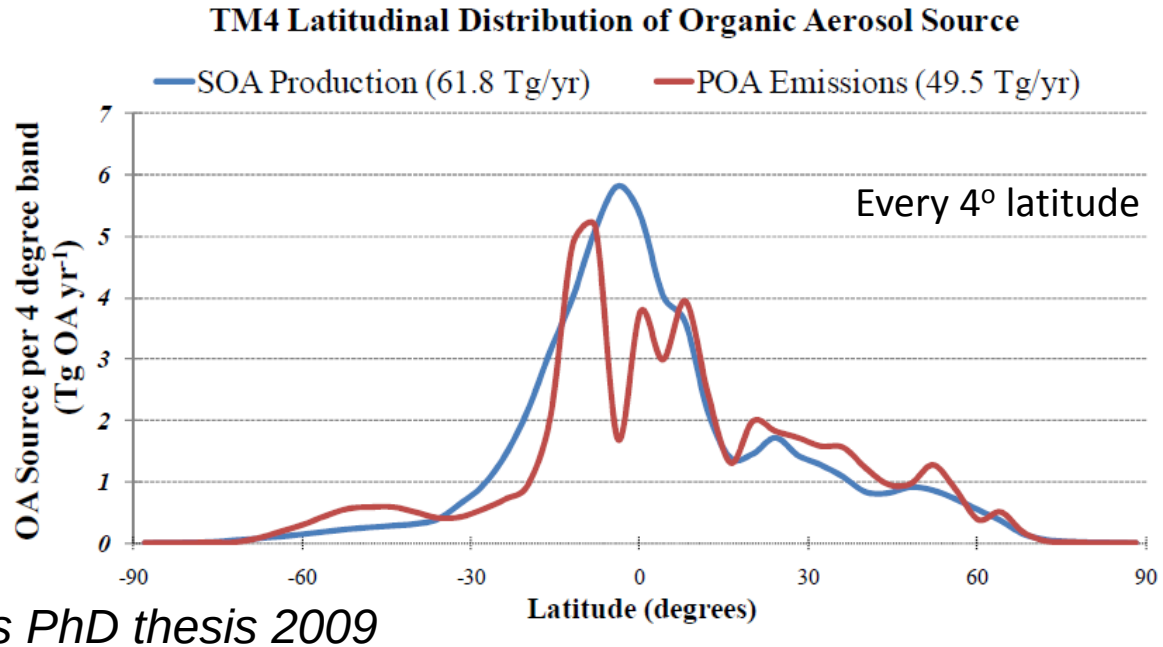
OA budget

OA	*sources* *(Tg yr^{-1})*	*production* *(Tg yr^{-1})*	*burden* *(Tg)*	*lifetime* *(days)*
SOAi		7.4	0.20	8.5
SOAt		4.5	0.10	8.3
SOAa		0.6	0.01	8.1
SOAaged		11.4	0.28	8.1
Oxalate		32.5	0.46	5.1
MS^-		3.9	0.05	4.3
Amine Salts		1.1	0.01	5.0
SOA		**61.8**	**1.10**	**7.1**
POA(land)	42.6	5.1	1.12	8.6
POA(ocean)	6.9		0.06	3.0
POA	**49.5**		**1.18**	**7.7**

117 Tg yr^{-1}



de Gouw and Jimenez, 2009



Myriokefalitakis PhD thesis 2009

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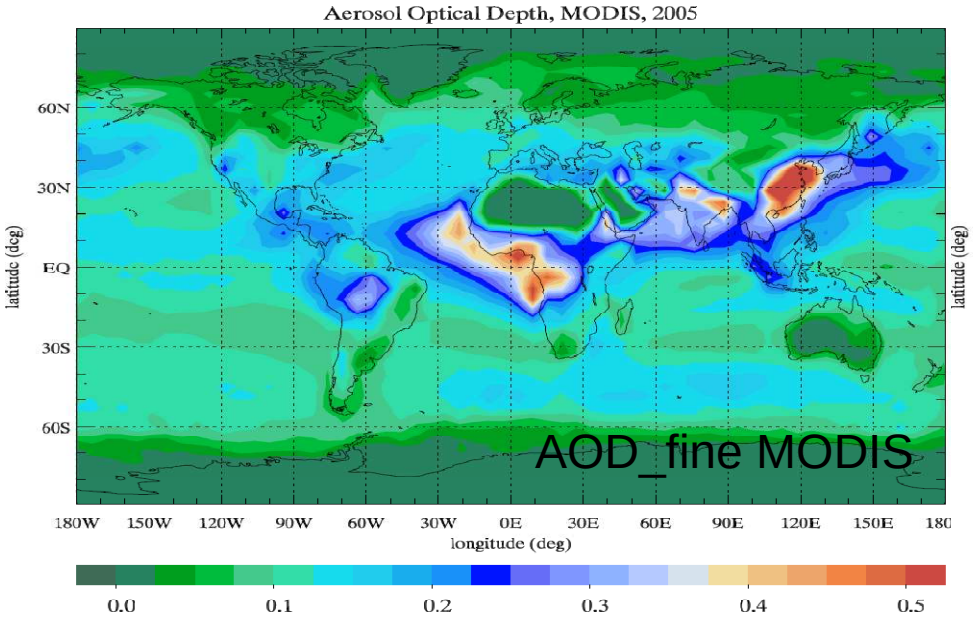

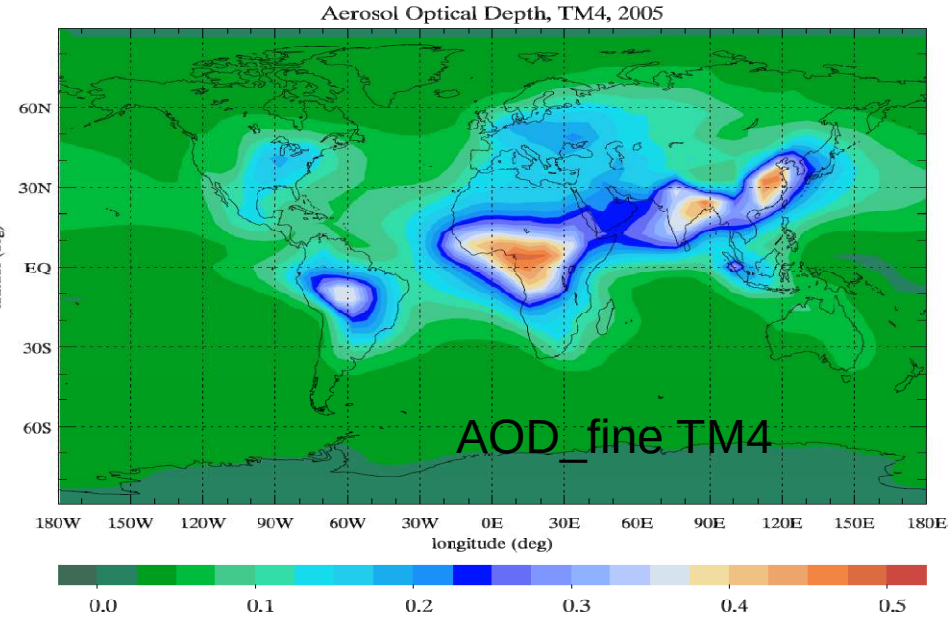

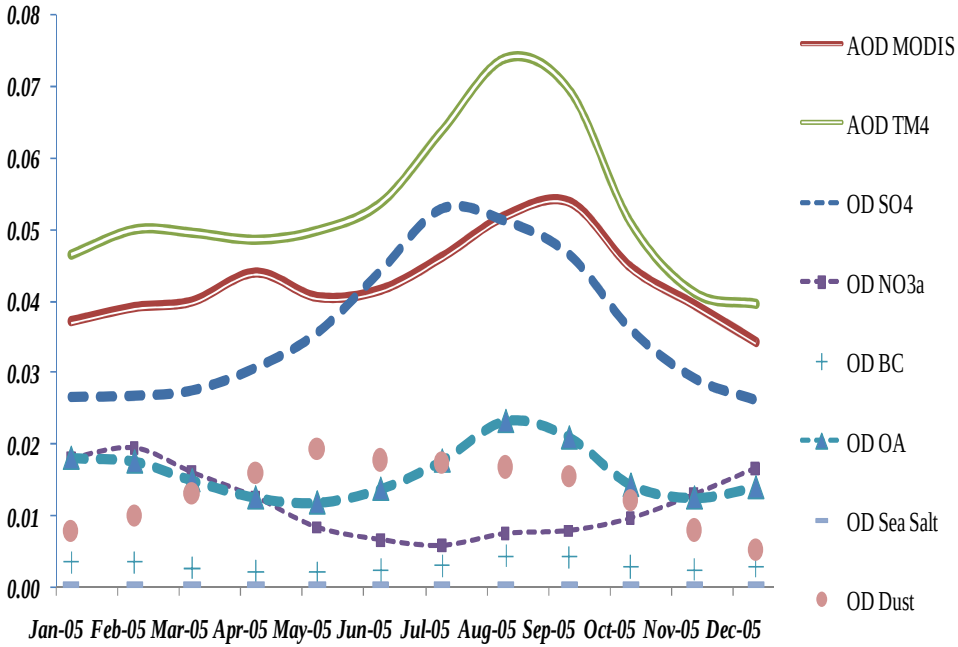

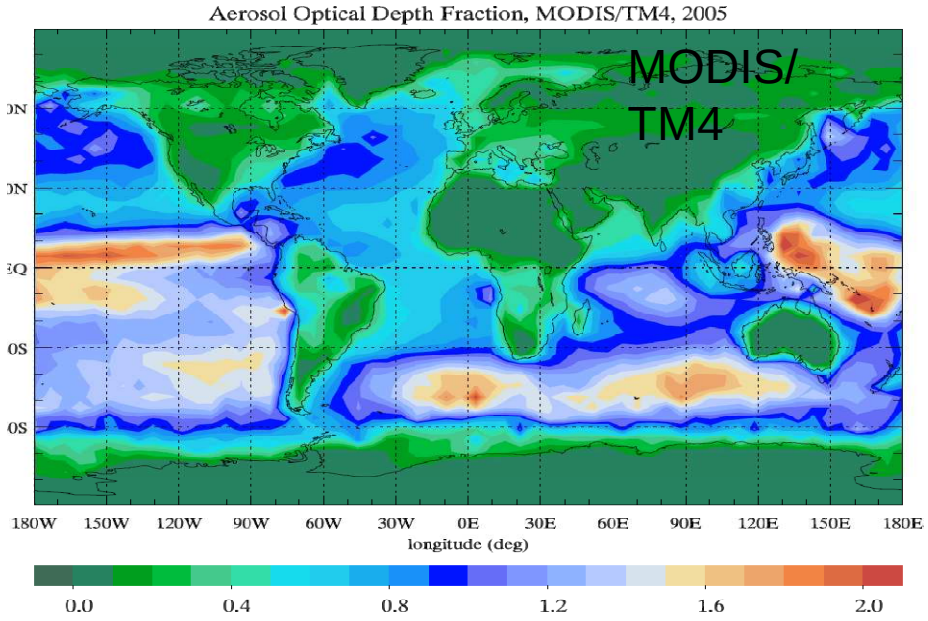

Impact of heterogeneous reactions on accumulation aerosol

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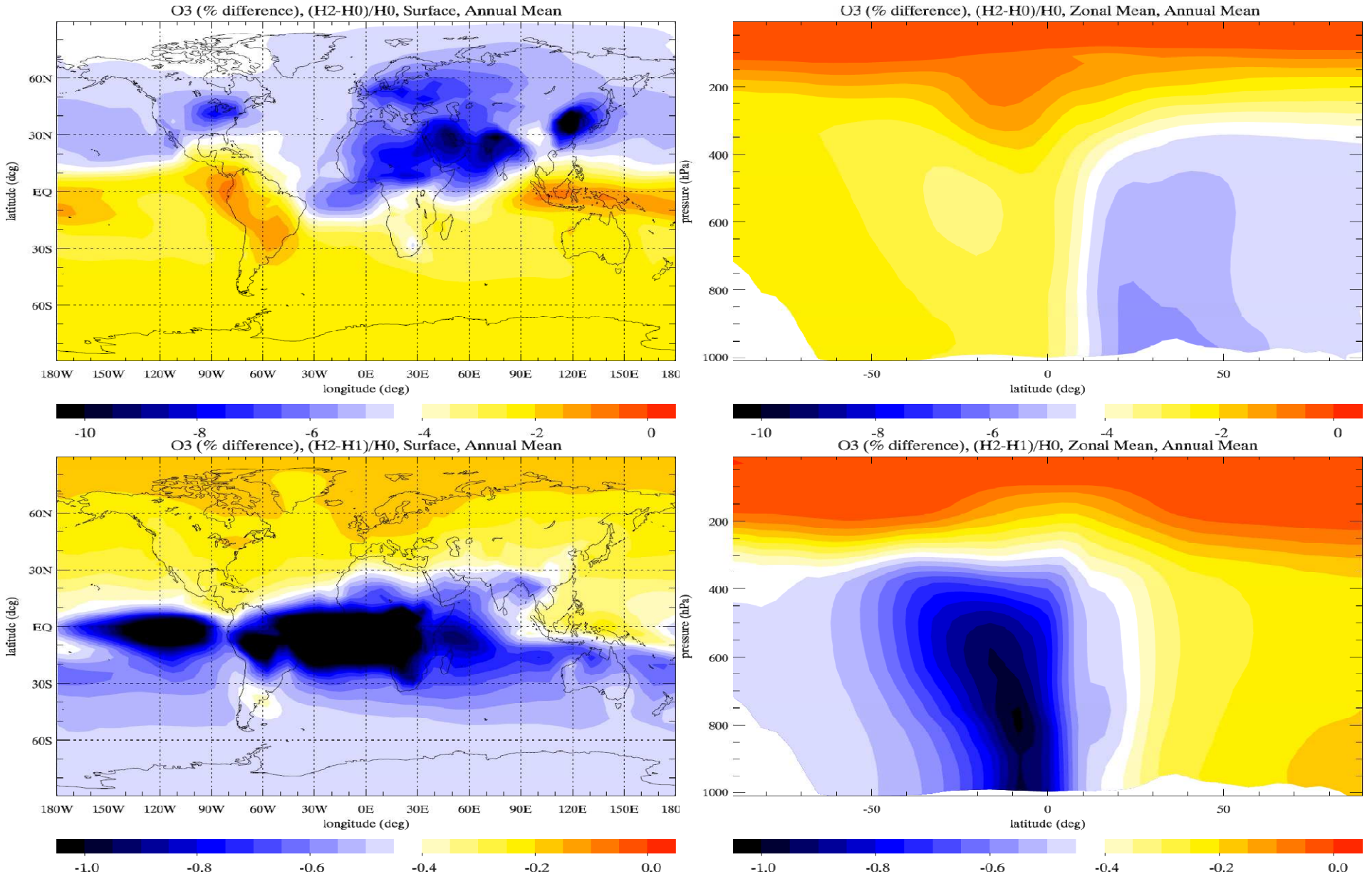

Next steps:

- OA improvements
  - POA semi-volatile & aging by reaction with OH
  - Primary biogenics
  - Further improvement of aqueous phase chemistry
  - SOA dependence on volatility

- OA AEROCOM

- Elements carried by OA

- Coupling gases and aerosols

Impact on Js & heterogeneous chemistry → improve oxidants

- Oxidant inter-annual simulations – past & future

- Couple with biogenic emissions module.