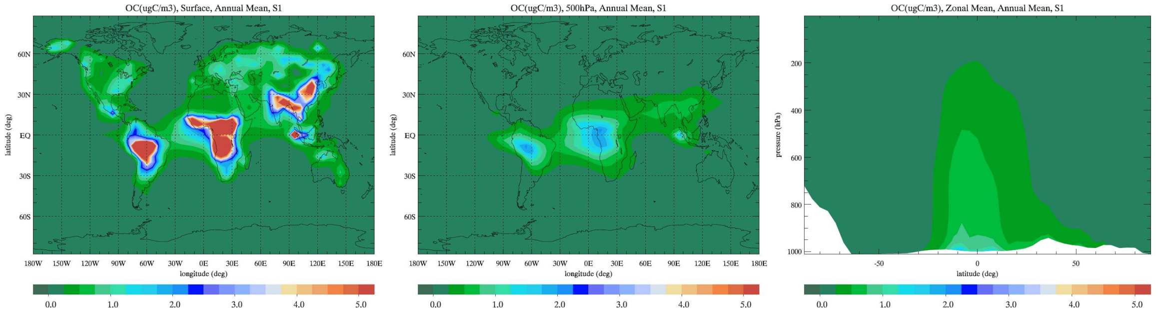
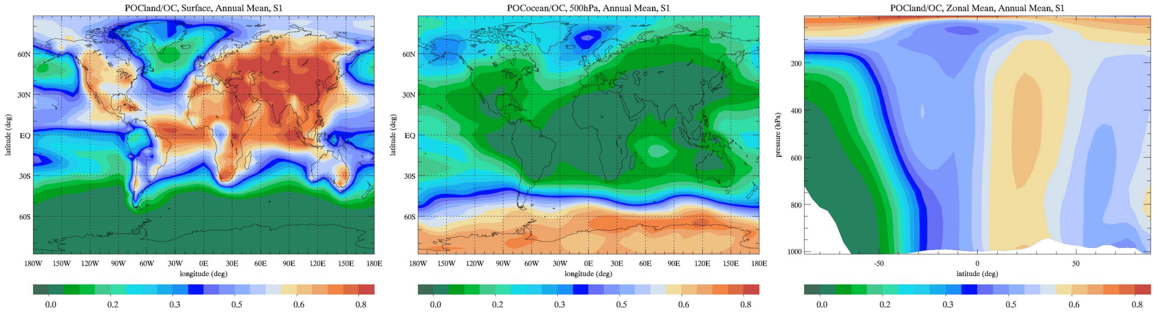
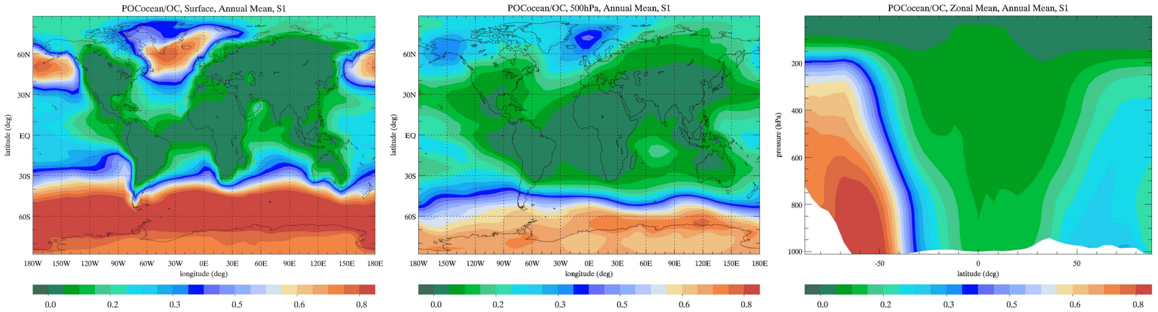
a) OC in ug/m3



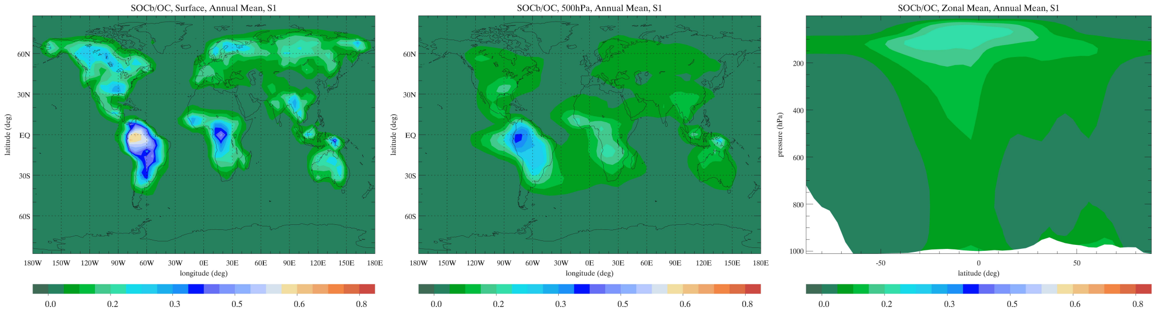
b) POClan/OC



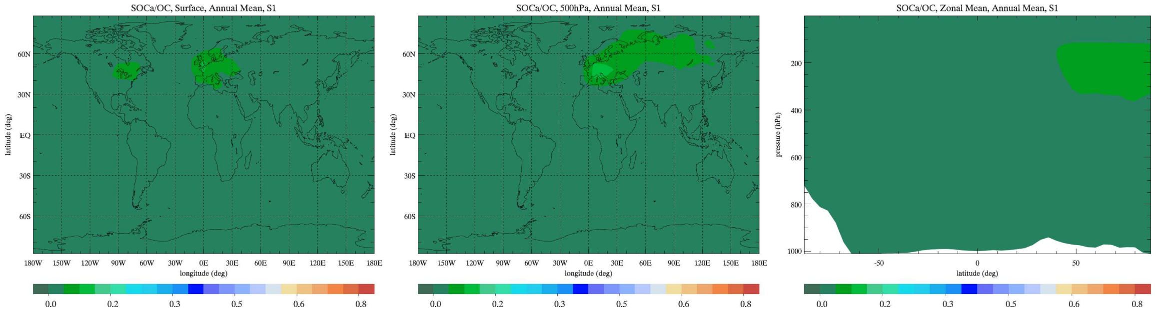
c) POCocean/OC



d) SOCb/OC



e) SOCa/OC



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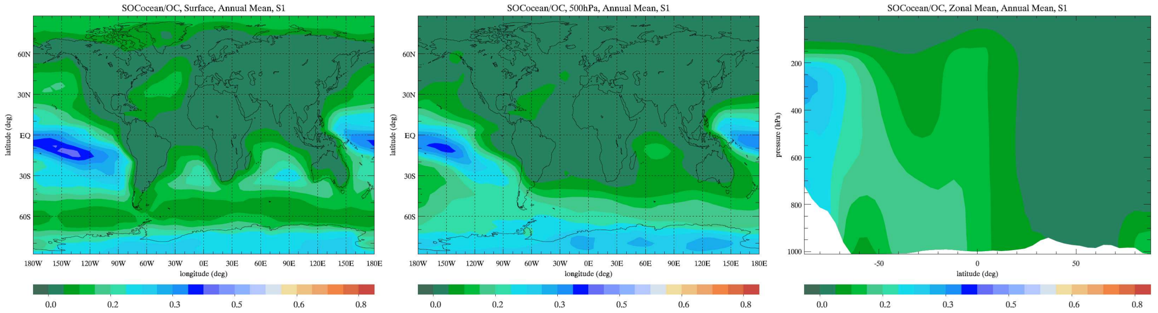
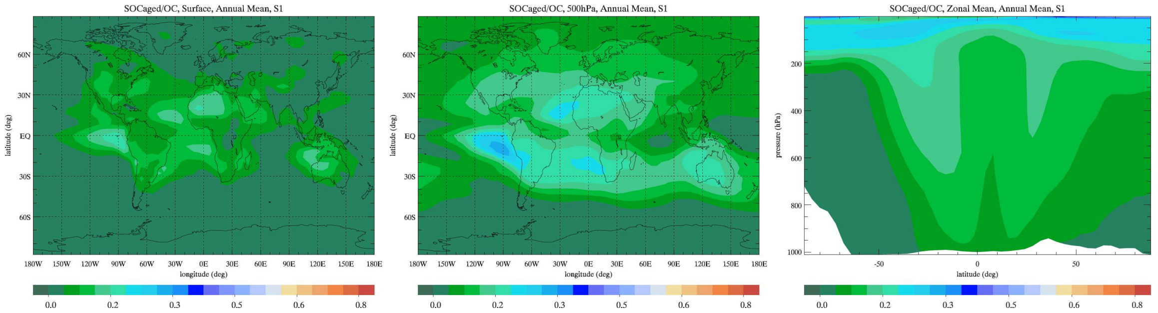
f) SOCocean/OC



g) SOCaged/OC



h) OCoxl/OC

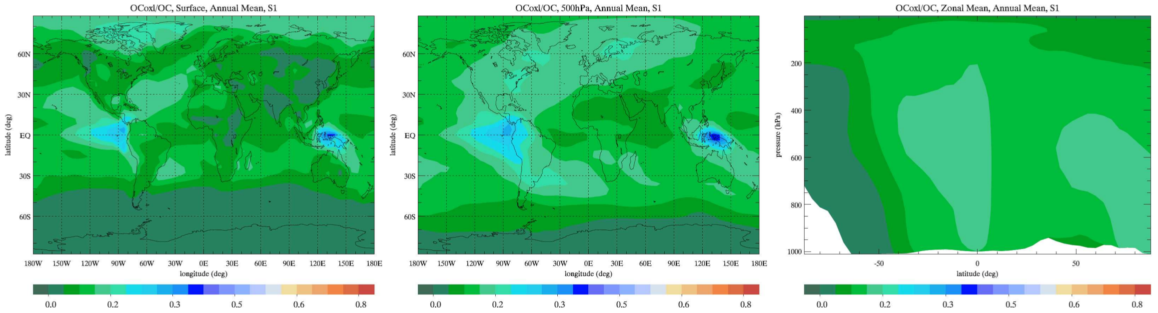


Figure S1. a) Annual mean OC (μC m^{-3}) and annual mean contributions to total OC (carbon mass ratio) of b) Primary OC from land –POCland, c) Primary OC from oceans – POCocean, d) Secondary OC from precursors of biogenic origin – SOCb, e) Secondary OC from precursors of anthropogenic origin – SOCa, f) Secondary OC from precursors of oceanic origin – SOCocean, g) Aged Secondary OC – SOCaged and h) OXL expressed in carbon mass – OCoxl, as calculated by the model for S1 Simulation; for surface (left), 500 hPa (middle), and zonal mean (right).

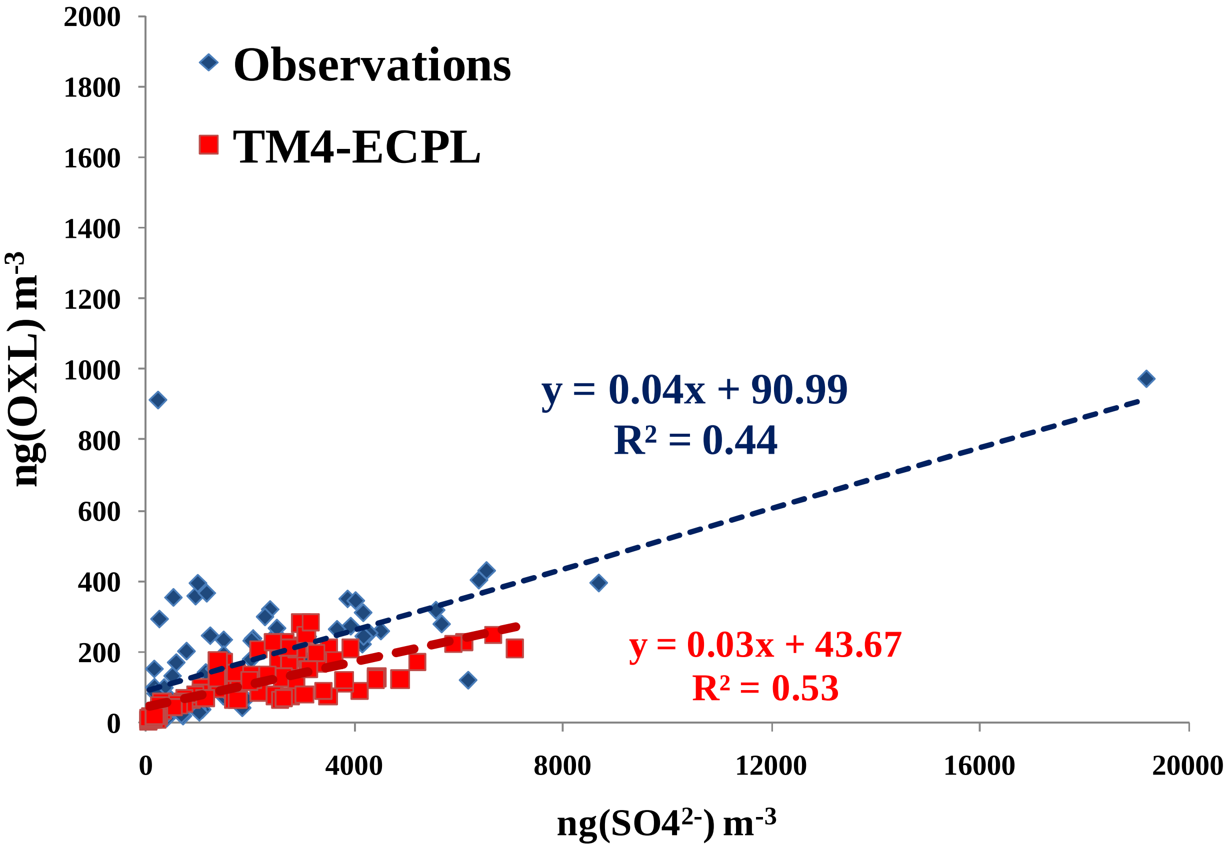


Figure S2. OXL (ng-OXL m $^{-3}$) as a function of SO_4^{2-} (ng-SO_4^{2-} m^{-3}) mass concentrations from observations (red squares) and as calculated by the model (blue diamonds), based on monthly mean values. Observations are taken from Crahan et al., 2004, Fosco and Schmeling, 1988; Biswas et al., 2008; Saarnio et al. 2010; Legrand et al., 2007; Koulouri et al., 2008; Sciare J., unpublished data.

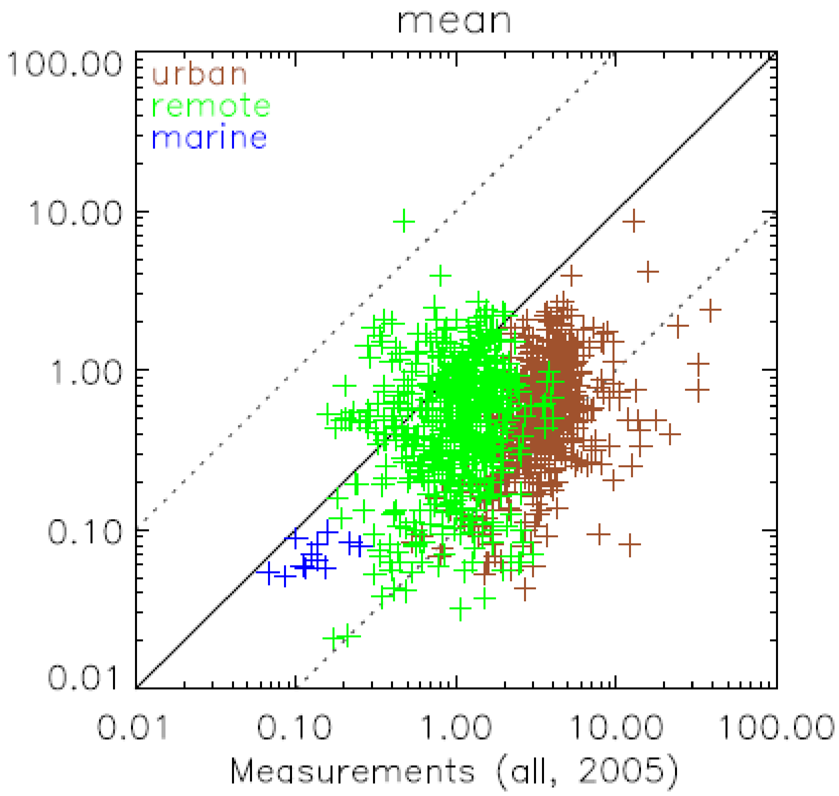
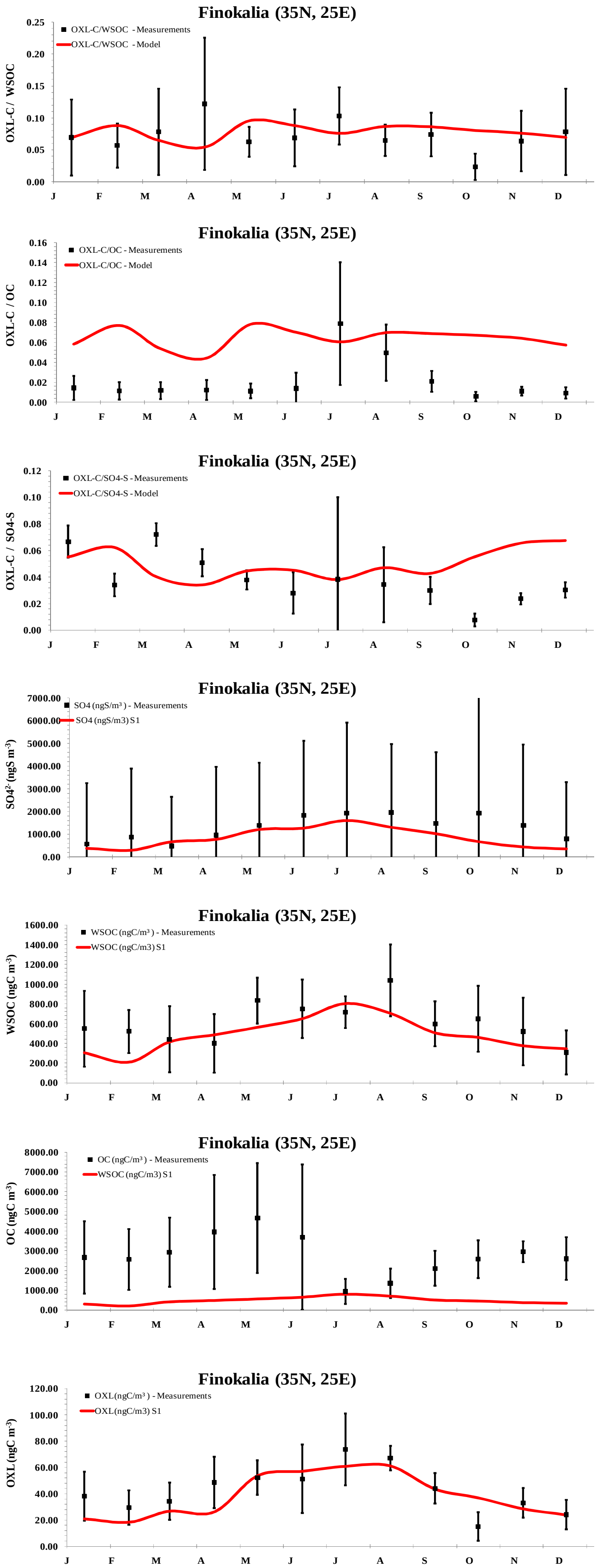
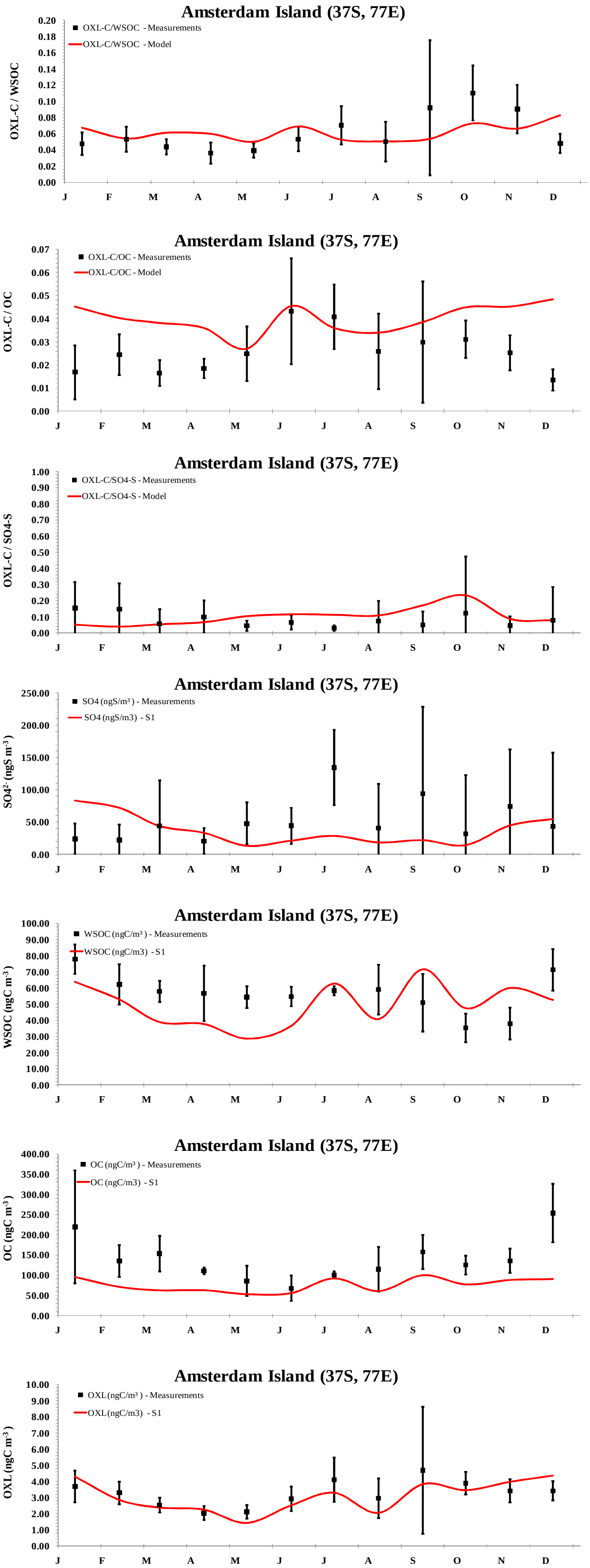


Figure S3. Comparison of OC computed by TM4-ECPL for 2005 (y-axis) with PM2.5 observations (x-axis) in ug-C/m3 from Bahadur et al. (2009), Sciare et al (2009) and Koulouri et al (2008).



a)



b)

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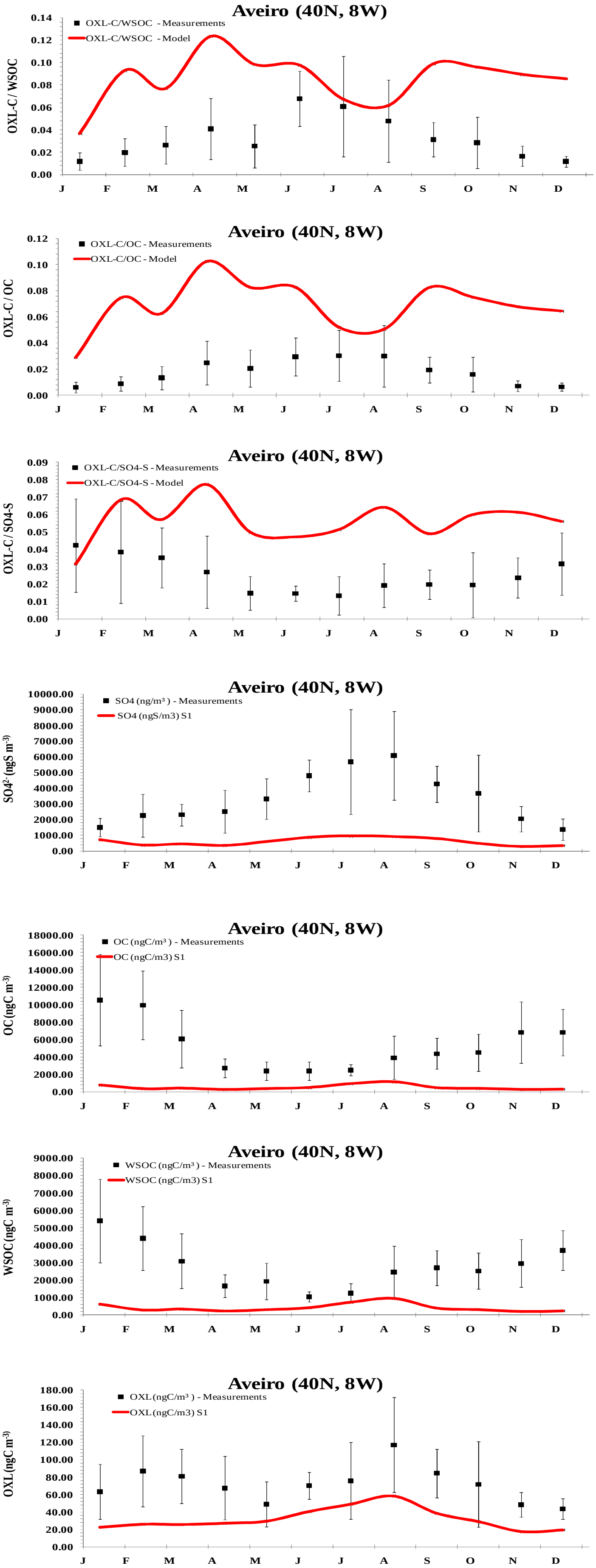
Aveiro (40N, 8W)
OXL-C/WSOC - Measurements
OXL-C/WSOC - Model
OXL-C/ WSOC
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14
Aveiro (40N, 8W)
OXL-C/OC - Measurements
OXL-C/OC - Model
OXL-C/ OC
0.00 0.02 0.04 0.06 0.08 0.10 0.12
Aveiro (40N, 8W)
OXL-C/SO4-S - Measurements
OXL-C/SO4-S - Model
OXL-C/ SO4-S
0.00 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09
Aveiro (40N, 8W)
SO4 (ng/m³) - Measurements
SO4 (ngS/m3) S1
SO4²⁻ (ngS m⁻³)
0.00 1000.00 2000.00 3000.00 4000.00 5000.00 6000.00 7000.00 8000.00 9000.00 10000.00
Aveiro (40N, 8W)
OC (ngC/m³) - Measurements
OC (ngC/m3) S1
OC(ngC m⁻³)
0.00 2000.00 4000.00 6000.00 8000.00 10000.00 12000.00 14000.00 16000.00 18000.00
Aveiro (40N, 8W)
WSOC (ngC/m³) - Measurements
WSOC (ngC/m3) S1
WSOC(ngC m⁻³)
0.00 1000.00 2000.00 3000.00 4000.00 5000.00 6000.00 7000.00 8000.00 9000.00
Aveiro (40N, 8W)
OXL (ngC/m³) - Measurements
OXL (ngC/m3) S1
OXL(ngC m⁻³)
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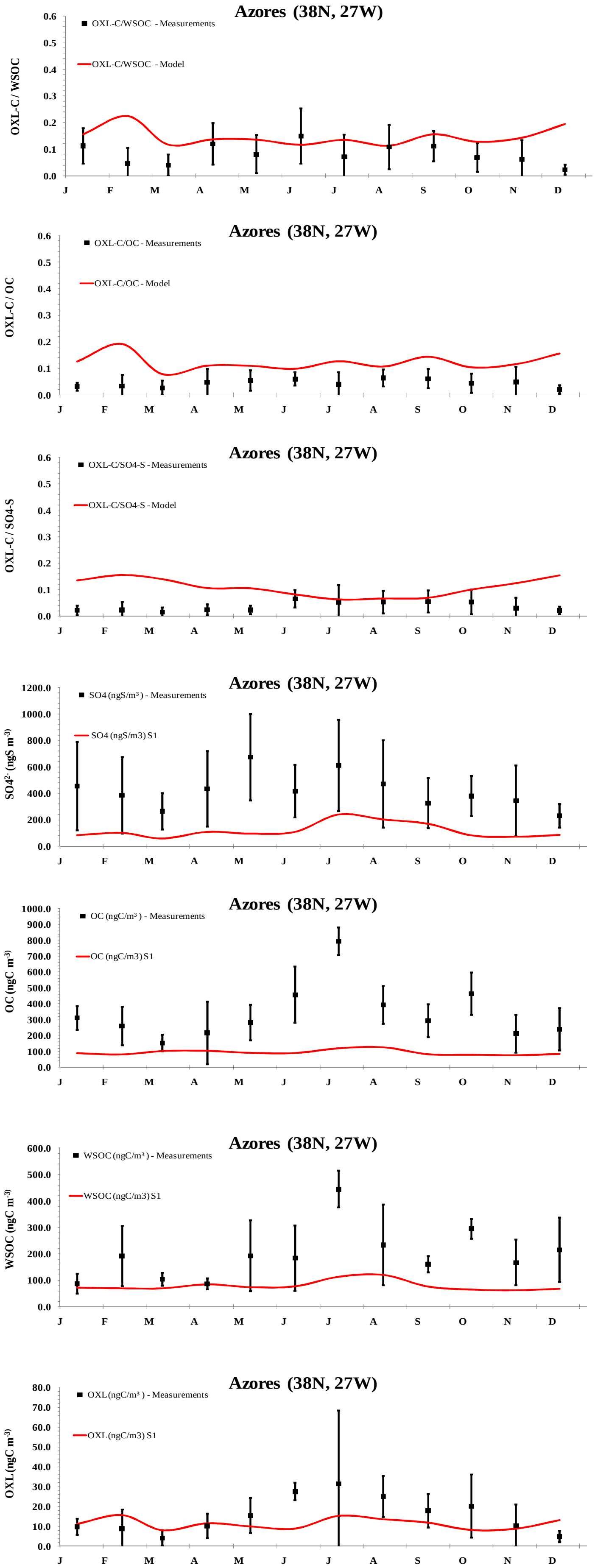
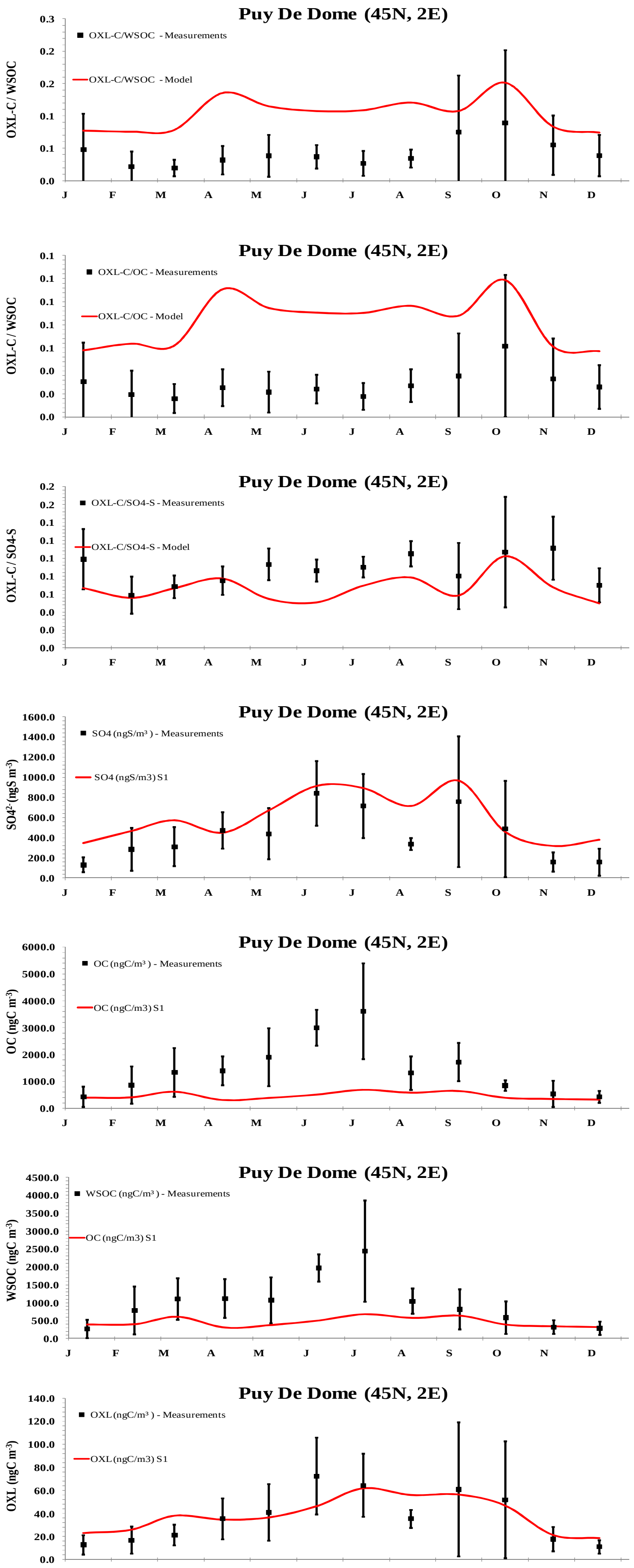
J F M A M J J A S O N D

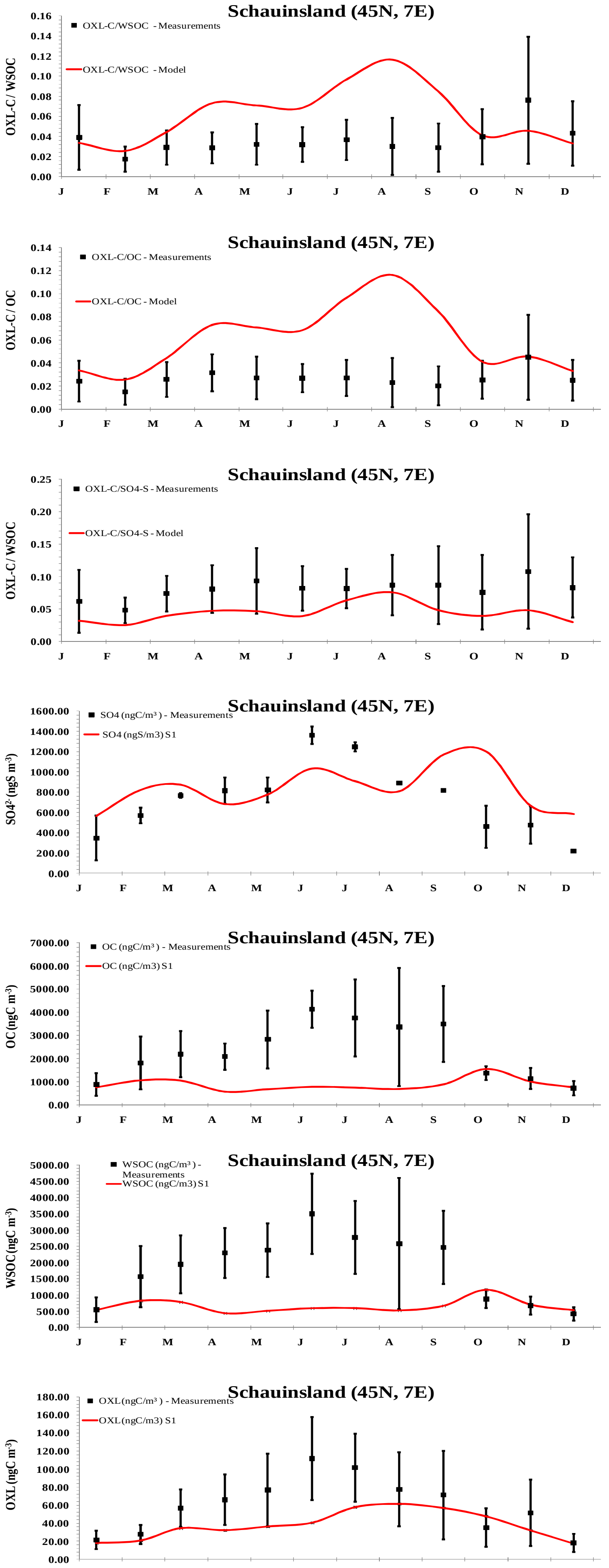
c)


Azores (38N, 27W)
OXL-C/WSOC - Measurements
OXL-C/WSOC - Model
OXL-C/ WSOC
0.0 0.1 0.2 0.3 0.4 0.5 0.6
Azores (38N, 27W)
OXL-C/OC - Measurements
OXL-C/OC - Model
OXL-C/ OC
0.0 0.1 0.2 0.3 0.4 0.5 0.6
Azores (38N, 27W)
OXL-C/SO4-S - Measurements
OXL-C/SO4-S - Model
OXL-C/ SO4-S
0.0 0.1 0.2 0.3 0.4 0.5 0.6
Azores (38N, 27W)
SO4 (ngS/m³) - Measurements
SO4 (ngS/m3) S1
SO4²⁻ (ngS m⁻³)
0.0 200.0 400.0 600.0 800.0 1000.0 1200.0
Azores (38N, 27W)
OC (ngC/m³) - Measurements
OC (ngC/m3) S1
OC (ngC m⁻³)
0.0 100.0 200.0 300.0 400.0 500.0 600.0 700.0 800.0 900.0 1000.0
Azores (38N, 27W)
WSOC (ngC/m³) - Measurements
WSOC (ngC/m3) S1
WSOC (ngC m⁻³)
0.0 100.0 200.0 300.0 400.0 500.0 600.0
Azores (38N, 27W)
OXL (ngC/m³) - Measurements
OXL (ngC/m3) S1
OXL (ngC m⁻³)
0.0 10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0
J F M A M J J A S O N D

d)



e)



f)

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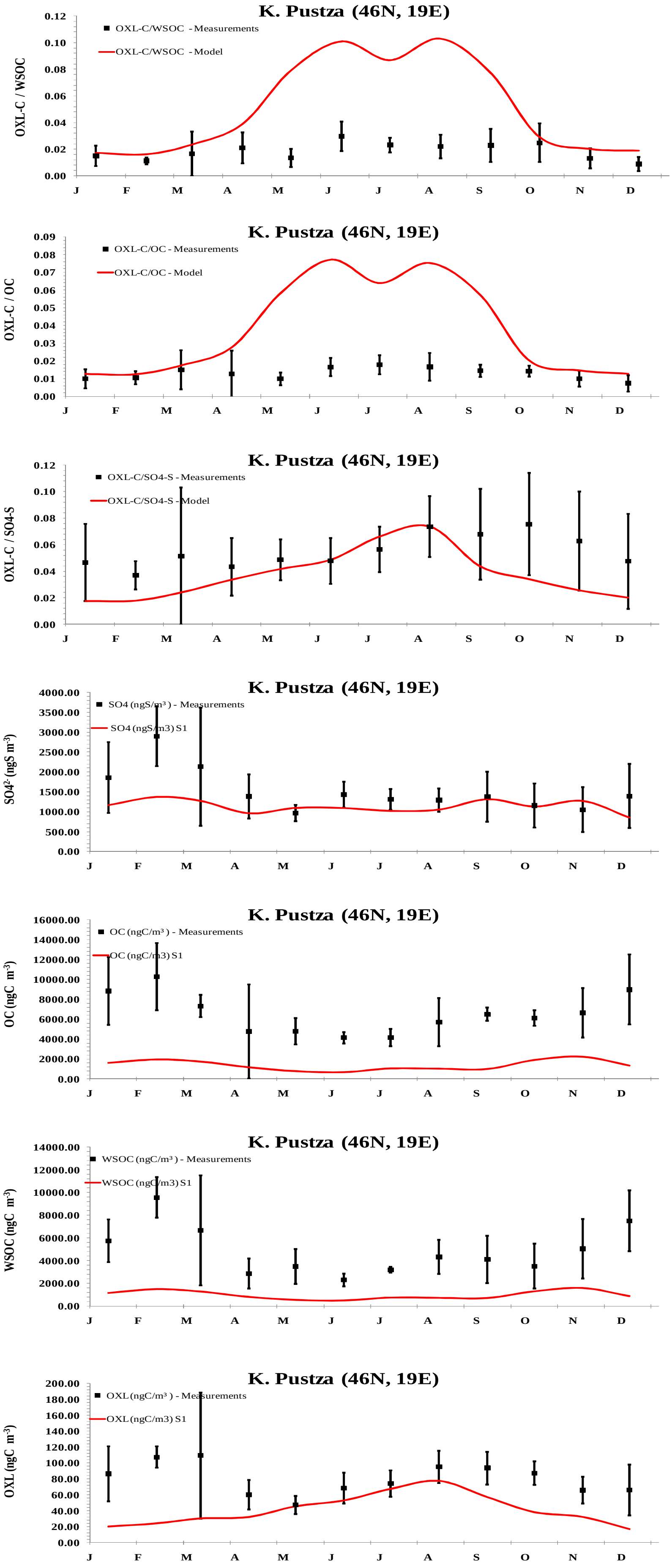
K. Pustza (46N, 19E)
OXL-C/WSOC - Measurements
OXL-C/WSOC - Model
OXL-C / WSOC
0.12
0.10
0.08
0.06
0.04
0.02
0.00
J F M A M J J A S O N D
K. Pustza (46N, 19E)
OXL-C/OC - Measurements
OXL-C/OC - Model
OXL-C / OC
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
J F M A M J J A S O N D
K. Pustza (46N, 19E)
OXL-C/SO4-S - Measurements
OXL-C/SO4-S - Model
OXL-C / SO4-S
0.12
0.10
0.08
0.06
0.04
0.02
0.00
J F M A M J J A S O N D
K. Pustza (46N, 19E)
SO4 (ngS/m³) - Measurements
SO4 (ngS/m3) S1
SO4²⁻ (ngS m⁻³)
4000.00
3500.00
3000.00
2500.00
2000.00
1500.00
1000.00
500.00
0.00
J F M A M J J A S O N D
K. Pustza (46N, 19E)
OC (ngC/m³) - Measurements
OC (ngC/m3) S1
OC (ngC m⁻³)
16000.00
14000.00
12000.00
10000.00
8000.00
6000.00
4000.00
2000.00
0.00
J F M A M J J A S O N D
K. Pustza (46N, 19E)
WSOC (ngC/m³) - Measurements
WSOC (ngC/m3) S1
WSOC (ngC m⁻³)
14000.00
12000.00
10000.00
8000.00
6000.00
4000.00
2000.00
0.00
J F M A M J J A S O N D
K. Pustza (46N, 19E)
OXL (ngC/m³) - Measurements
OXL (ngC/m3) S1
OXL (ngC m⁻³)
200.00
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
J F M A M J J A S O N D

g)

Figure S4. Comparison between model results (S1) (red line) and observations (black squares) of OXL fraction to water soluble organics (OXL/WSOC), to total OC (OXL/OC), to sulfate (OXL/SO_4^{-2}) and concentrations of SO_4^{-2}, OC, WSOC and OXL (from top to bottom) for the following locations: a) Finokalia, b) Amsterdam Island, c) Aveiro, d) Azores, e) Puy de Dome, f) Schauinsland and h) K-Pustza. All values of organics are expressed in ngC m^{-3}. SO_4^{-2} is expressed in ngS m^{-3}.

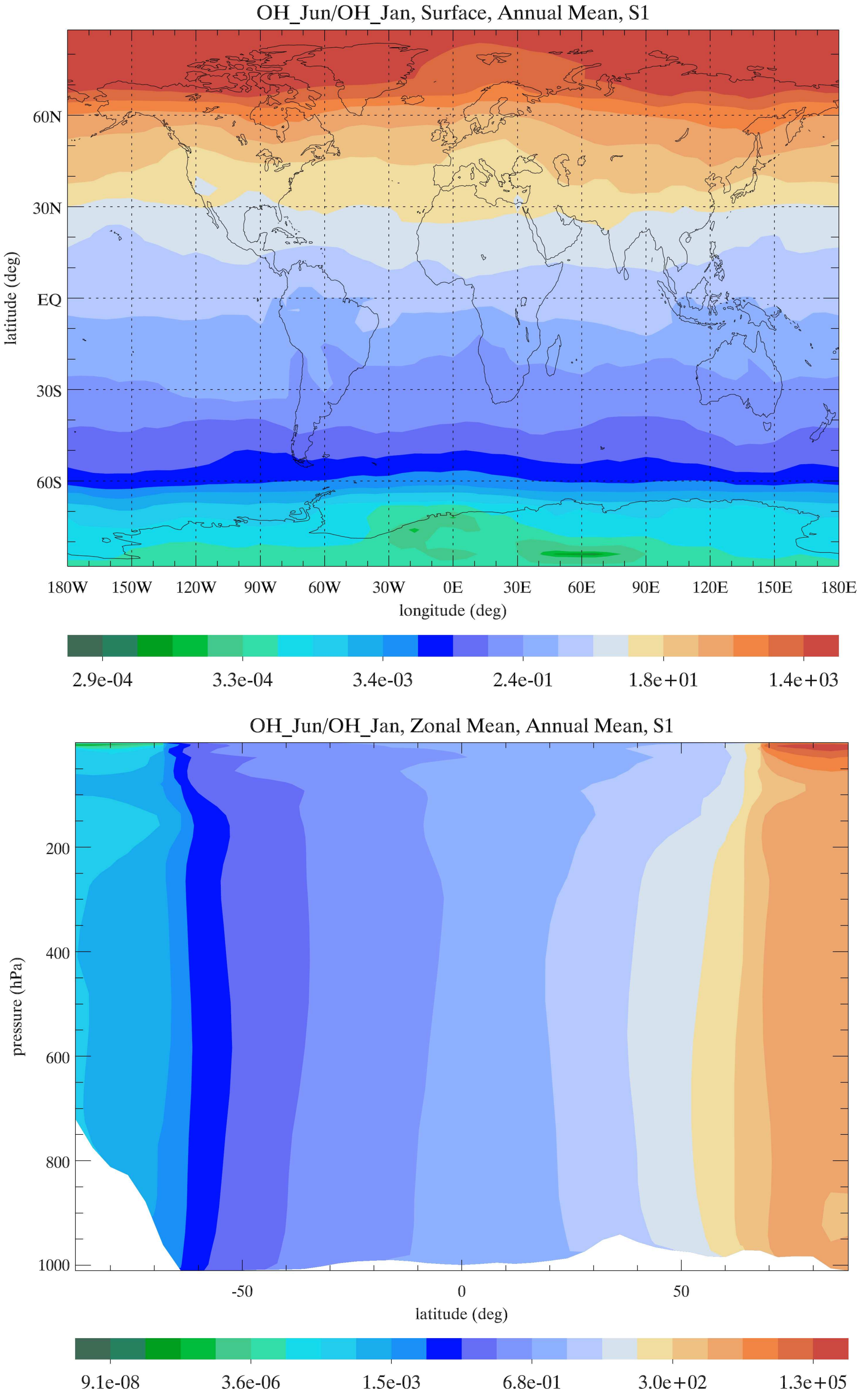

Figure S5: Ratio of OH total concentrations in June to those in January: Top: surface, Bottom: zonal mean.

Table 1. The aqueous phase chemical mechanism and corresponding rate constants used in TM4-ECPL. Units for the photolysis frequencies are s^{-1}, and for the second order aqueous reactions are expressed in L mol^{-1} s^{-1}. Reaction rates are taken from Lim et al. (2005), unless referred differently. Reactions rates are calculated as follows:

$$k = k_{298} \exp\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right]$$

	Aqueous Phase Reactions			K_{298}	E/R
1	$O_3 + hv\ (+ H_2O)$	→	$H_2O_2 + O_2$	[a]	
2	$H_2O_2 + hv$	→	2OH	[a]	
3	$NO_3^- + hv\ (+ H^+)$	→	$NO_2 + OH$	[a]	
4	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	$9.7\ 10^{5}$	2500
5	$HO_2 + O_2^-\ (+ H^+)$	→	$H_2O_2 + O_2$	$1.0\ 10^{8}$	900
6	$O_3 + O_2^-\ (+ H^+)$	→	$OH + 2O_2$	$1.5\ 10^{9}$	
7	$O_3 + OH$	→	$HO_2 + O_2$	$1.1\ 10^{8}$	
8	$HO_2 + OH$	→	$O_2 + H_2O$	$7.1\ 10^{9}$	
9	$OH + OH$	→	H_2O_2	$5.5\ 10^{9}$	
10	$H_2O_2 + OH$	→	$HO_2 + H_2O$	$2.7\ 10^{7}$	
11	$NO_3 + OH^-$	→	$NO_3^- + OH$	$9.4\ 10^{7}$	2700
12	$S(IV) + H_2O_2$	→	SO_4^{2-}	[b]	
13	$S(IV) + O_3$	→	SO_4^{2-}	[c]	
14	$CH_2(OH)_2 + OH\ (+ O_2)$	→	$HCOOH + HO_2 + H_2O$	$1.1\ 10^{9}$	1020
15	$CH_2(OH)_2 + NO_3\ (+ O_2)$	→	$HCOOH + HO_2 + NO_3^- + H^+$	$1.0\ 10^{6}$	4400
16	$GLYAL + OH\ (+ O_2)$	→	$GLY + HO_2$	$1.0\ 10^{9}$	1564 [d]
17	$GLYAL + OH\ (+ O_2)$	→	$GLX + HO_2 + H_2O$	$5.0\ 10^{8}$	1564 [d]
18	$GLYAL + NO_3\ (+ O_2)$	→	$GLX^- + NO_3^- + H^+$	$1.1\ 10^{7}$ [e]	
19	$GLYAL + NO_3\ (+ O_2)$	→	$GLY + NO_3^- + H^+$	$5.5\ 10^{6}$ [g]	
20	$GLY + OH\ (+ O_2)$	→	$GLX + HO_2$	$1.1\ 10^{9}$	1564 [g]
21	$GLY + OH$	→	0.03GLX + 0.97OXL	$3.1\ 10^{9}$ [h]	
22	$GLY + NO_3\ (+ O_2)$	→	$GLX + HO_2 + NO_3^- + H^+$	$6.3\ 10^{7}$ [f]	
23	GLY + *hv*/OH (*only in aerosol water*)	→	0.2OXL + 0.8*OLIGOMERIC-SOA*	[i]	
24	$GLY + NH_4^+$ *(only in aerosol water)*	→	*OLIGOMERIC-SOA*	$1.3\ 10^{-7}$ (*pH = 2*) [j] $2.4\cdot 10^{-4}$ (*pH = 5*) [j] 0.43 (*pH = 7*) [j]	
25	$MGLY + OH\ (+ O_2)$	→	$0.92PRV + 0.08GLX + HO_2 + H_2O$	$1.1\ 10^{9}$ [k]	1600
26	$MGLY + NO_3\ (+ O_2)$	→	$0.92PRV + 0.08GLX + NO_3^- + H^+$	$6.3\ 10^{7}$ [e]	
27	$HCOOH + OH\ (+ O_2)$	→	$CO_2 + HO_2 + H_2O$	$1.2\ 10^{8}$	990
28	$HCOO^- + OH\ (+ O_2)$	→	$CO_2 + H_2O\ (+ O_2^-)$	$3.1\ 10^{9}$	1240
29	$HCOOH + NO_3\ (+ O_2)$	→	$CO_2 + NO_3^- + 2H^+\ (+ O_2^-)$	$3.8\ 10^{5}$	3400
30	$HCOO^- + NO_3\ (+ O_2)$	→	$CO_2 + NO_3^- + H^+\ (+ O_2^-)$	$5.1\ 10^{7}$	2200

31	$CH_3COOH + OH\ (+ O_2)$	→	$0.85GLX + 0.15CH_2(OH)_2$	$1.5\ 10^{7}$	1330
32	$CH_3COO^- + OH\ (+ O_2)$	→	$0.85GLX^- + 0.15CH_2(OH)_2$	$1.9\ 10^{9}$	1800
33	$CH_3COOH + NO_3\ (+ O_2)$	→	$0.85GLX + 0.15CH_2(OH)_2 + NO_3^- + H^+$	$1.4\ 10^{4}$ [e]	3800
34	$CH_3COO^- + NO_3\ (+ O_2)$	→	$0.85GLX^- + 0.15CH_2(OH)_2 + NO_3^- + H^+$	$2.9\ 10^{6}$ [e]	3800
35	$PRV + OH\ (+ O_2)$	→	$CH_3COOH + HO_2 + CO_2$	$1.2\ 10^{8}$	2766
36	$PRV^- + OH$	→	$CH_3COO^- + HO_2 + CO_2$	$7.0\ 10^{8}$	2285
37	$PRV + NO_3\ (+ O_2)$	→	$CH_3COOH + CO_2 + HO_2 + NO_3^- + H^+$	$4.8\ 10^{6}$ [e]	
38	$PRV^- + NO_3$	→	$CH_3COO^- + CO_2 + NO_3^- + H^+$	$1.9\ 10^{8}$ [e]	
39	$GLX + OH\ (+ O_2)$	→	$OXL + HO_2 + H_2O$	$3.6\ 10^{8}$ [g]	962 [g]
40	$GLX^- + OH$	→	$OXL^- + HO_2 + H_2O$	$2.8\ 10^{9}$ [g]	4330 [g]
41	$GLX + NO_3\ (+ O_2)$	→	$OXL + HO_2 + NO_3^- + H^+$	$3.0\ 10^{6}$ [m]	
42	$GLX^- + NO_3$	→	$OXL^- + NO_3^- + H^+$	$1.1\ 10^{8}$ [m]	
43	$OXL + 2OH$	→	$2CO_2 + 2H_2O$	$1.4\ 10^{6}$	2766 [n]
44	$OXL^- + OH\ (+ O_2)$	→	$2CO_2 + 2H_2O\ (+ O_2^-)$	$1.9\ 10^{8}$ [g]	2766 [g]
45	$OXL^{2-} + OH\ (+ O_2)$	→	$2CO_2 + OH^-\ (+ O_2^-)$	$1.6\ 10^{8}$ [g]	4330 [g]
46	$OXL + 2NO_3$	→	$2CO_2 + 2NO_3^- + 2H^+$	$6.8\ 10^{7}$ [o]	
47	$OXL^- + NO_3\ (+ O_2)$	→	$2CO_2 + NO_3^- + H^+\ (+ O_2^-)$	$6.8\ 10^{7}$ [l]	
48	$OXL^{2-} + NO_3\ (+ O_2)$	→	$2CO_2 + NO_3^-\ (+ O_2^-)$	$2.2\ 10^{8}$ [l]	

[a] *using the gas-phase photolysis rates (Myriokefalitakis et al. (2008) supplementary material.), increased by a factor of 1.5 as recommended by Barth et al. (2003)*

[b] *Seinfeld and Pandis (1998);* $K = \dfrac{7.5\times10^{7}\, e^{-4430\left(\frac{1}{T}-\frac{1}{298}\right)}\left[H^+\right]}{1+13\left[H^+\right]}$

[c] *Seinfeld and Pandis (1998);* $K_1 = 2.4\ 10^{4}$, $K_2 = 3.7\ 10^{5\ e-530(1/T - 1/298)}$, $K_3 = 1.5\ 10^{9}\ e^{-5280(1/T - 1/298)}$

[d] *as for GLY + OH*

[e] *Herrmann et al. (2005)*

[f] *as for MGLY +* NO_3

[g] *Herrmann (2003)*

[h] *lumped reactions based on Carlton et al. (2007)*

[i] *photochemical lumped reaction in aerosol water content based on Ervens and Volkamer (2010) with rate of* $4s^{-1}$ *scaled on the photolysis frequencies of* H_2O_2

[j] *Noziere et al. (2009)*

[k] *Ervens et al. (2004)*

[l] *Herrmann et al. (2000)*

[m] *as for glycolic acid from Herrmann et al. (2005)*

[n] *as for* $OXL^- + OH$

[o] *as for* $OXL^- + NO_3$

Table 2. Outline of simulations performed in this study.

Simulation	**Description**
S1	In-cloud OXL formation taking into account the effect of the ionic strength of cloud droplets on GLYAL, GLY and MGLY.
S1.1	As S1, neglecting the effect of the ionic strength of cloud droplets on GLYAL, GLY and MGLY.
S1.1.1	As S1, neglecting the effect of the ionic strength of cloud droplets on GLYAL and MGLY.
S1.1.2	As S1, neglecting the effect of the ionic strength of cloud droplets on MGLY.
S1.2	As S1, omitting the temperature dependence of Henry constants.
S1.3	As S1, assuming constant pH values of 4.5 for cloud droplets.
S1.4	As S1, assuming a constant droplet radius of 5 μm.
S1.5	As S1, assuming a Henry law constant of OH radicals of 9 10^3 mol L^{-1} atm^{-1}
S2	As S1, also taking into account potential primary sources of OXL.
S3	As S2, also taking into account the potential chemical formation of OXL into aerosol water.
S4	As S3, also taking into account GLY concentrations over oceans.

Table 3. Global OXL budget analysis

	Atmospheric Burden (Tg)	**Primary Source (Tg yr^{-1})**	**Cloud Chemical Production (Tg yr^{-1})**	**Cloud Chemical Destruction (Tg yr^{-1})**	**Particulate Chemical Production (Tg yr^{-1})**	**Net Chemical Production (Tg yr^{-1})**	**Dry Deposition (Tg yr^{-1})**	**Wet Deposition (Tg yr^{-1})**
S1	0.30	-	31.8	10.6	-	21.2	1.3	19.9
S1.1	0.19	-	21.2	8.0	-	13.2	0.8	12.4
S1.1.1	0.20	-	21.9	8.2	-	13.7	0.8	12.9
S1.1.2	0.30	-	31.9	11.0	-	20.9	1.3	19.6
S1.2	0.31	-	35.5	13.7	-	21.8	1.3	20.5
S1.3	0.29	-	34.4	14.2	-	20.2	1.3	18.9
S1.4	0.30	-	32.4	11.1	-	21.3	1.3	20.0
S1.5	0.26	-	37.2	18.8	-	18.4	1.1	17.3
S2	0.31	0.1	31.8	10.6	-	21.2	1.3	19.9
S3	0.33	0.1	35.0	14.2	1.5	22.3	1.4	20.9
S4	0.34	0.1	36.8	14.9	1.8	23.7	1.5	22.2