TM-meeting, 30-31 May 2011, ISPRA

TM4-ECPL modeling activities

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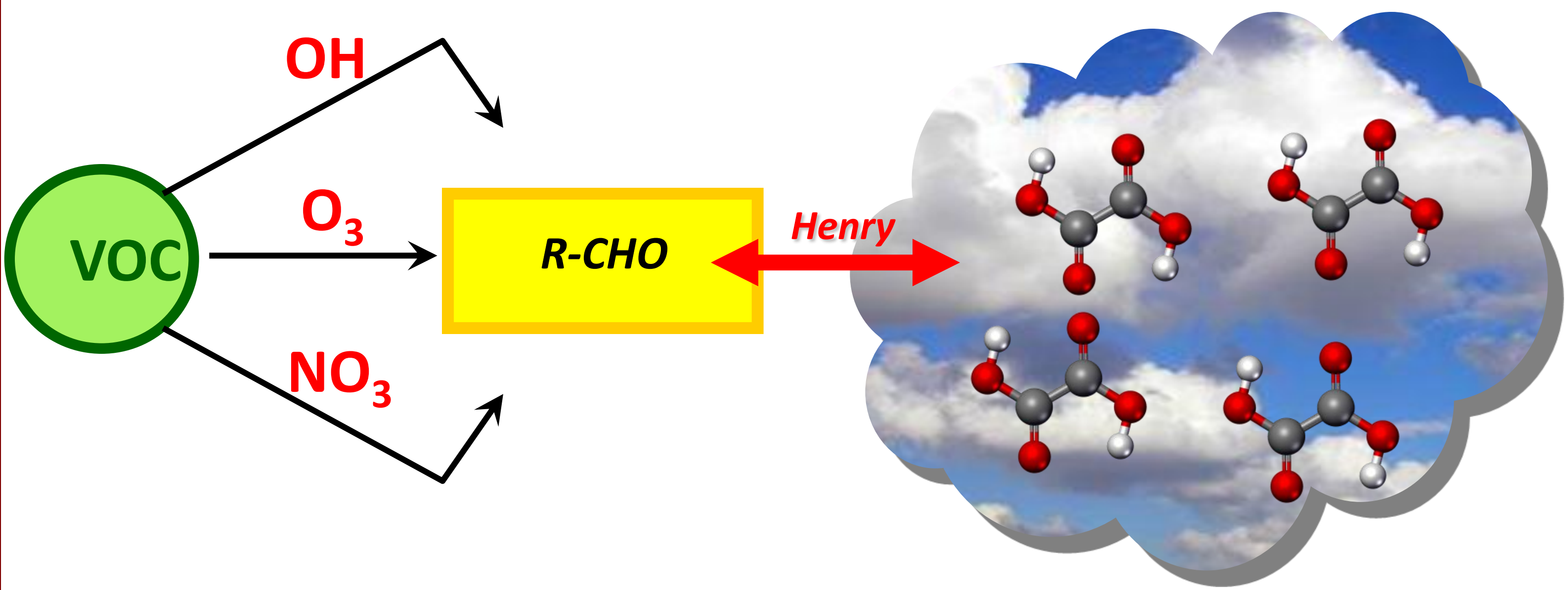
Kostas Tsigaridis
NASA,GISS & Uni Columbia, NY

1. **Multiphase chemistry (Stelios)**
2. Interannual model evaluation & AEROCOM (Nikos)
3. Other ongoing and future activities (Maria)

SOA formation via aqueous-phase chemistry in TM4-ECPL

1. VOC photo-oxidation in the gas-phase
2. Production of water-soluble organic compounds in the gas-phase *(e.g. aldehydes, organic acids)*
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 <u>new organic particulate matter</u> is formed



Myriokefalitakis et al, ACPD, 11,485,2011

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The Revised Aqueous-Phase Chemical Scheme in TM4-ECPL

1. NO_3 Aqueous-phase Oxidation of Aldehydes and Organic Acids
2. Lower Henry Constant of OH radicals ($9\ 10^{3}$ mol lt^{-1} atm^{-1} -> 30 mol lt^{-1} atm^{-1})
3. Different cloud droplet radius over land (5 μm) and over oceans (10 μm)
4. Simultaneously S(IV) and Organic molecules aqueous-phase oxidation using EBI solver

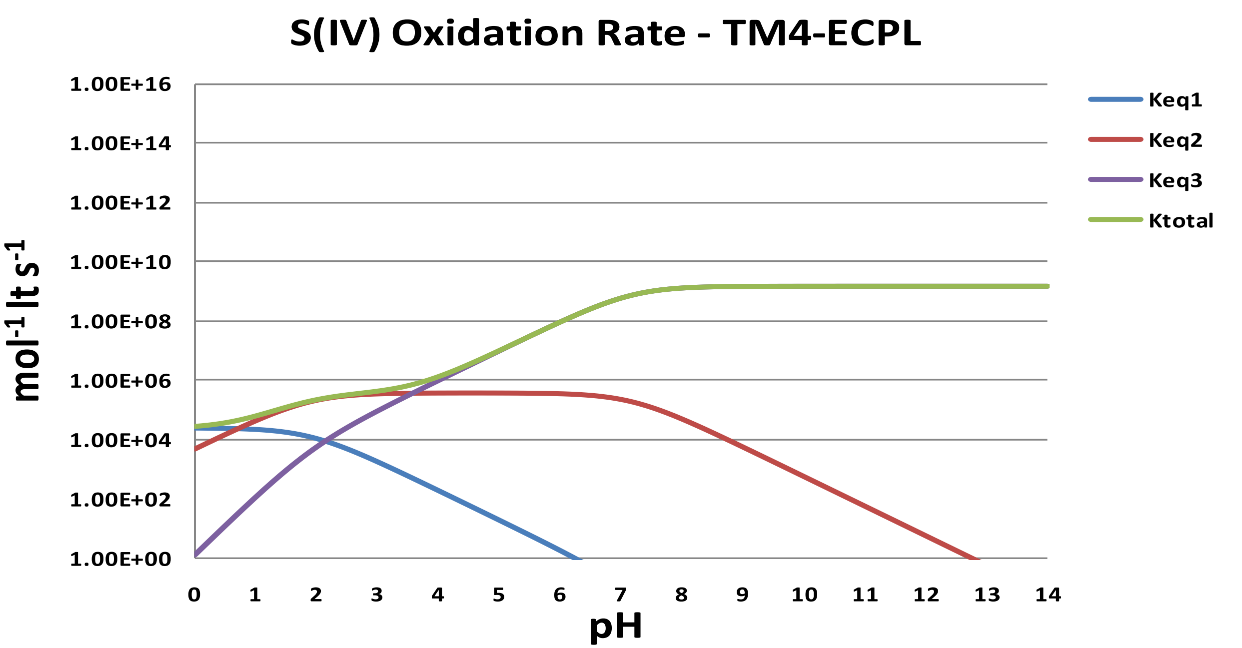
pH Dependence of S(IV) oxidation by ozone

•TM4-ECPL does not take into account the different forms of the sulfuric acid ($SO_2.H_2O$, HSO_3^-, SO_3^{-2}). , in order to take into account the different forms and reaction rates, we use the mole fraction (ξ) of each acid as a function of pH. The total mass of S(IV) is calculated as S(IV)=$SO_2.H_2O$ + HSO_3^- + SO_3^{2-}.

$$\xi_{SO_2.H_2O} = \frac{[SO_2 \cdot H_2O]}{[S(IV)]} = \left(1 + \frac{Keq_1}{[H^+]} + \frac{Keq_1 Keq_2}{[H^+]^2}\right)^{-1} \quad \xi_{HSO_3^-} = \frac{[HSO_3^-]}{[S(IV)]} = \left(1 + \frac{[H^+]}{Keq_1} + \frac{Keq_2}{[H^+]}\right)^{-1} \quad \xi_{SO_3^{2-}} = \frac{[SO_3^{2-}]}{[S(IV)]} = \left(1 + \frac{[H^+]}{Keq_2} + \frac{[H^+]^2}{Keq_1 Keq_2}\right)^{-1}$$

•For 25°C, the oxidation of $SO_2.H_2O$, HSO_3^-, SO_3^{-2} accounts a rate of Keq_1= 2.4 10^4 mol^{-1} lt s^{-1}, Keq_2= 3.7 10^5 mol^{-1} lt s^{-1} and Keq_3= 1.5 10^9 mol^{-1}lt s^{-1} proportionally (Seinfeld and Pandis,1998).

•Ktotal(SIV)=Keq1*$\xi_{SO2.H2O}$ + Keq2*ξ_{HSO3-} + Keq_3*$\xi_{SO3=}$



Inorganic Aqueous-Phase Chemistry

	Aqueous Phase Reactions		
1	$O_3 + h\nu\ (+ H_2O)$	→	$H_2O_2 + O_2$
2	$H_2O_2 + h\nu$	→	2OH
3	$NO_3^- + h\nu\ (+ H^+)$	→	$NO_2 + OH$
4	$HO_2 + HO_2$	→	$H_2O_2 + O_2$
5	$HO_2 + O_2^-\ (+ H^+)$	→	$H_2O_2 + O_2$
6	$O_3 + O_2^-\ (+ H^+)$	→	$OH + 2O_2$
7	$O_3 + OH$	→	$HO_2 + O_2$
8	$HO_2 + OH$	→	$O_2 + H_2O$
9	OH + OH	→	H_2O_2
10	$H_2O_{2-} + OH$	→	$HO_2 + H_2O$
11	$NO_3 + HO^-$	→	$NO_3^- + OH$
12	$S(IV) + H_2O_2$	→	SO_4^{2-}
13	$S(IV) + O_3$	→	SO_4^{2-}

SO_4^{2-} -validation in TM4-ECPL

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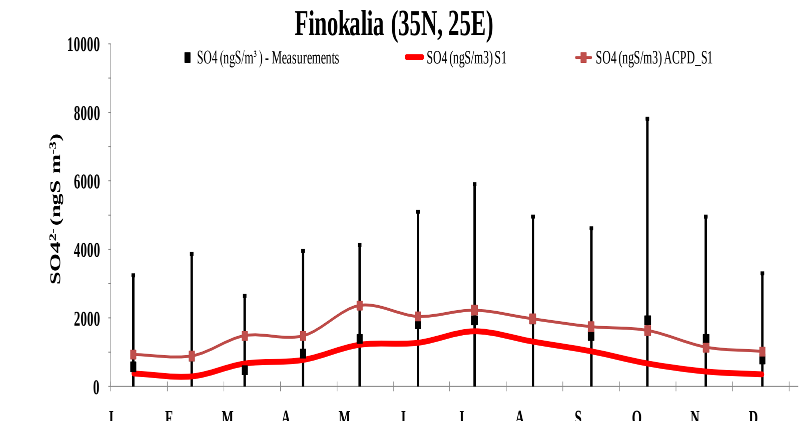
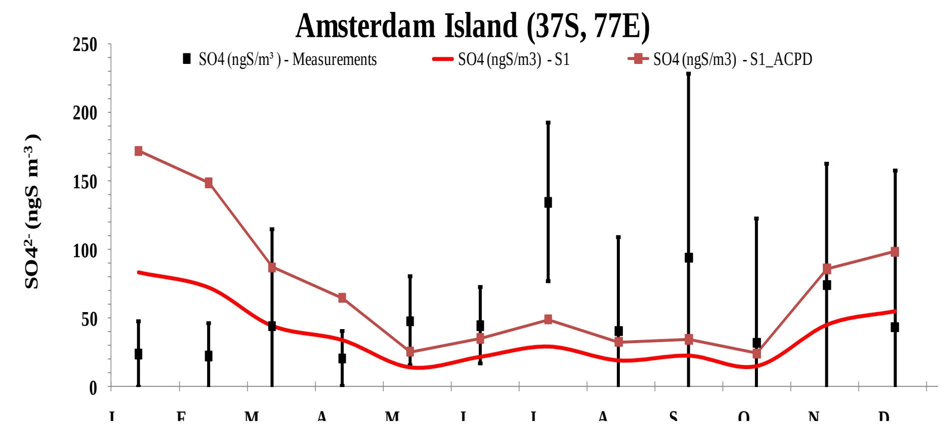
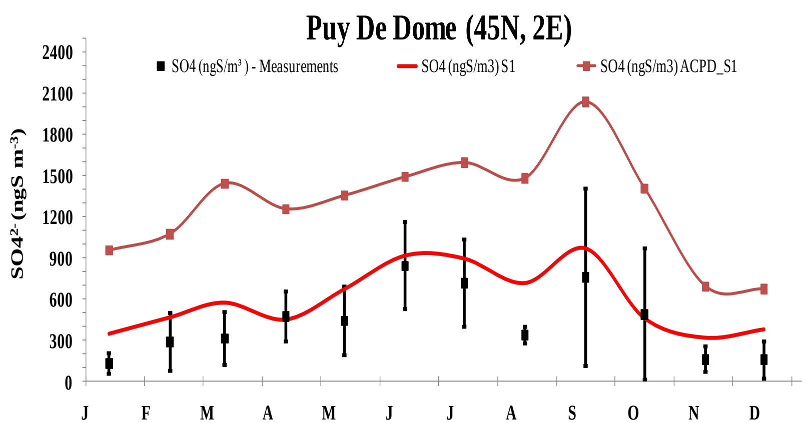
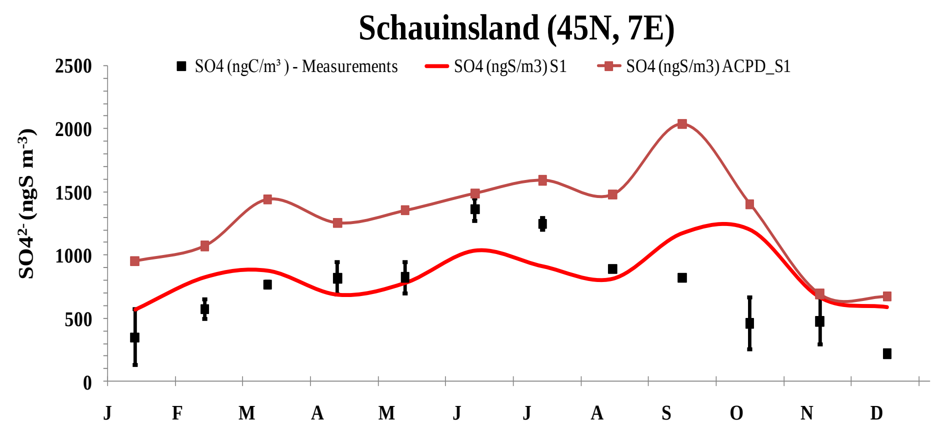
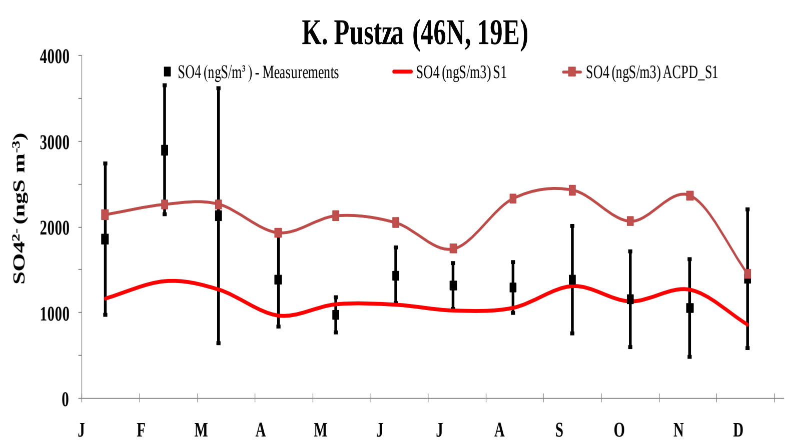
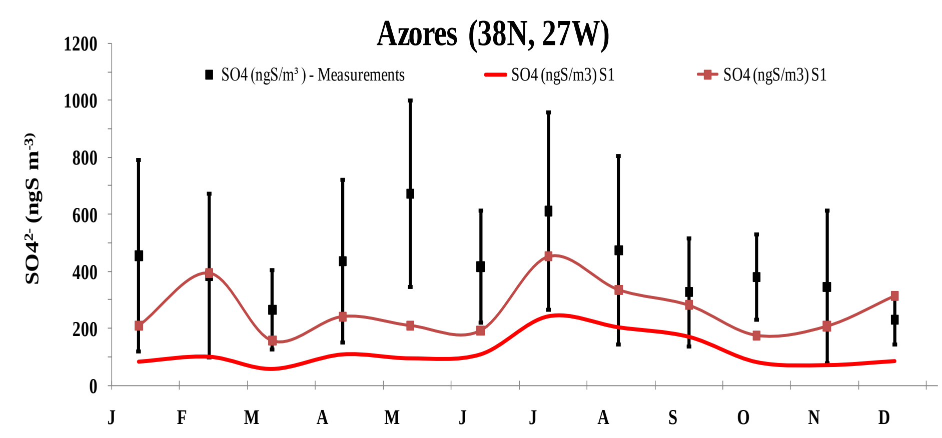












Organic Aqueous-Phase Chemical Scheme – Aldehydes (C1-C3)

Aqueous Phase Reactions

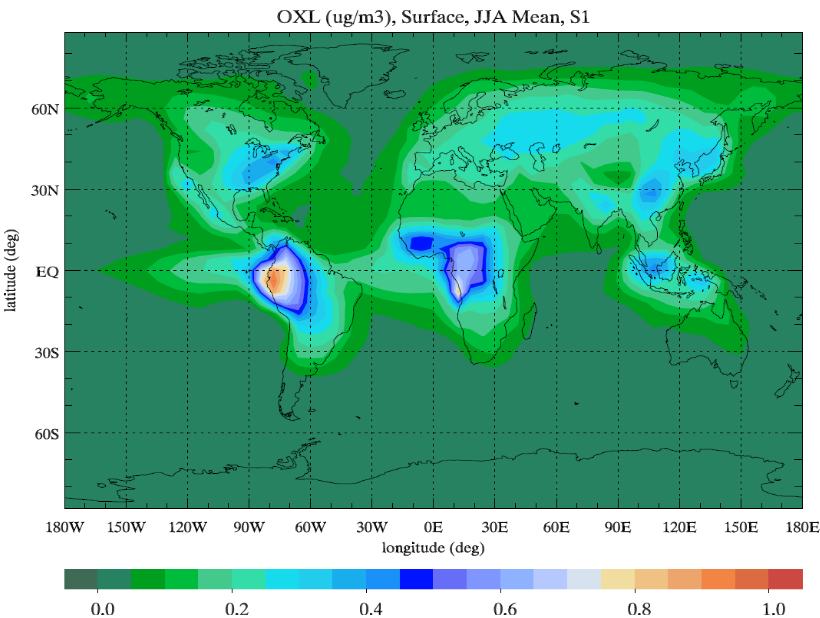
14	$CH_2(OH)_2$ + OH (+ O_2)	→	HCOOH + HO_2 + H_2O
15	$CH_2(OH)_2$ + NO_3 (+ O_2)	→	HCOOH + HO_2 + NO_3^- + H^+
16	GLYAL + OH (+ O_2)	→	GLY + HO_2
17	GLYAL + 2 OH (+ 2 O_2)	→	GLX + 2HO_2 + 2 H_2O
18	GLYAL + NO_3 (+ O_2)	→	GLX + HO_2 + NO_3^- + H^+
19	GLYAL + 2 NO_3 (+ O_2)	→	GLY + 2 NO_3^- + 2 H^+ + H_2O
20	GLY + OH (+ O_2)	→	GLX + HO_2+ H_2O
21	GLY + OH	→	0.03GLX + 0.97OXL+ H_2O
22	GLY + NO_3 (+ O_2)	→	GLX + HO_2 + NO_3^- + H^+
23	GLY + *hv*/OH *(only in aerosol water)*	→	0.2OXL + 0.8*OLIGOMERIC-SOA*
24	GLY + NH_4^+ *(only in aerosol water)*	→	*OLIGOMERIC-SOA*
25	MGLY + OH (+ O_2)	→	0.92PRV + 0.08GLX + HO_2 + H_2O
26	MGLY + NO_3 (+ O_2)	→	0.92PRV + 0.08GLX + HO_2+ NO_3^- + H^+

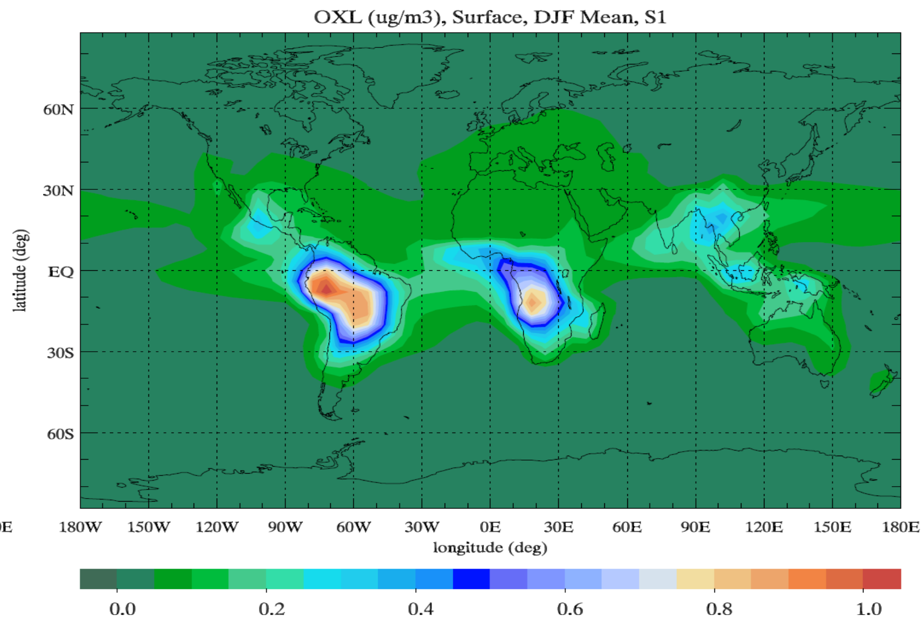
Organic Aqueous-Phase Chemical Scheme – Organic Acids

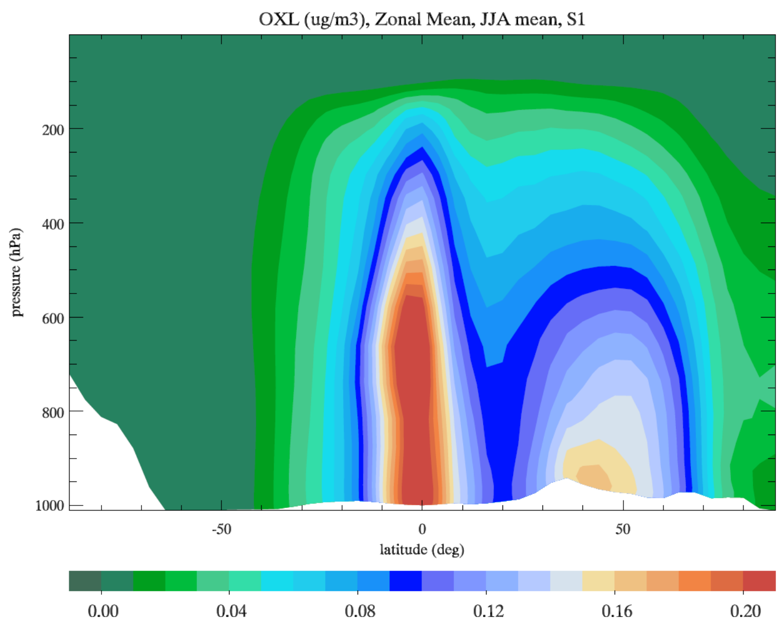
Aqueous Phase Reactions

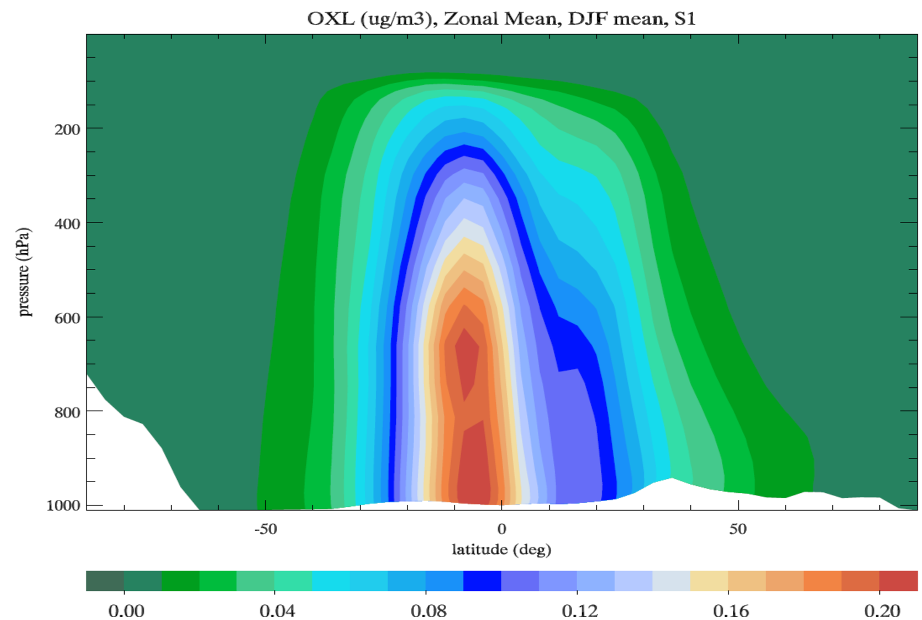
$HCOOH + OH\ (+ O_2)$	→	$CO_2 + HO_2 + H_2O$
$HCOO^- + OH\ (+ O_2)$	→	$CO_2 + H_2O\ (+ O_2^-)$
$HCOOH + NO_3\ (+ O_2)$	→	$CO_2 + NO_3^- + 2H^+\ (+ O_2^-)$
$HCOO^- + NO_3\ (+ O_2)$	→	$CO_2 + NO_3^- + H^+\ (+ O_2^-)$
$CH_3COOH + OH\ (+ O_2)$	→	$0.85GLX + 0.15CH_2(OH)_2$
$CH_3COO^- + OH\ (+ O_2)$	→	$0.85GLX^- + 0.15CH_2(OH)_2$
$CH_3COOH + NO_3\ (+ O_2)$	→	$0.85GLX + 0.15CH_2(OH)_2 + NO_3^- + H^+$
$CH_3COO^- + NO_3\ (+ O_2)$	→	$0.85GLX^- + 0.15CH_2(OH)_2 + NO_3^- + H^+$
$PRV + OH\ (+ O_2)$	→	$CH_3COOH + HO_2 + CO_2$
$PRV^- + OH$	→	$CH_3COO^- + HO_2 + CO_2$
$PRV + NO_3\ (+ O_2 + H_2O)$	→	$CH_3COOH + CO_2 + HO_2 + NO_3^- + H^+$
$PRV^- + NO_3\ (+ O_2 + H_2O)$	→	$CH_3COO^- + CO_2 + HO_2 + NO_3^- + H^+$
$GLX + OH\ (+ O_2)$	→	$OXL + HO_2 + H_2O$
$GLX^- + OH\ (+O_2)$	→	$OXL^- + HO_2 + H_2O$
$GLX + NO_3\ (+ O_2)$	→	$OXL + HO_2 + NO_3^- + H^+$
$GLX^- + NO_3\ (+ O_2)$	→	$OXL^- + + HO_2 + NO3^- + H^+$
$OXL + 2OH$	→	$2CO_2 + 2H_2O$
$OXL^- + OH\ (+ O_2)$	→	$2CO_2 + H_2O\ (+ O_2^-)$
$OXL^{2-} + OH\ (+ O_2)$	→	$2CO_2 + HO^-\ (+ O_2^-)$
$OXL + 2NO_3$	→	$2CO_2 + 2NO_3^- + 2H^+$
$OXL^- + NO_3\ (+ O_2)$	→	$2CO_2 + NO_3^- + H^+\ (+ O_2^-)$
$OXL^{2-} + NO_3\ (+ O_2)$	→	$2CO_2 + NO_3^-\ (+ O_2^-)$

OXL Calculated Distributions

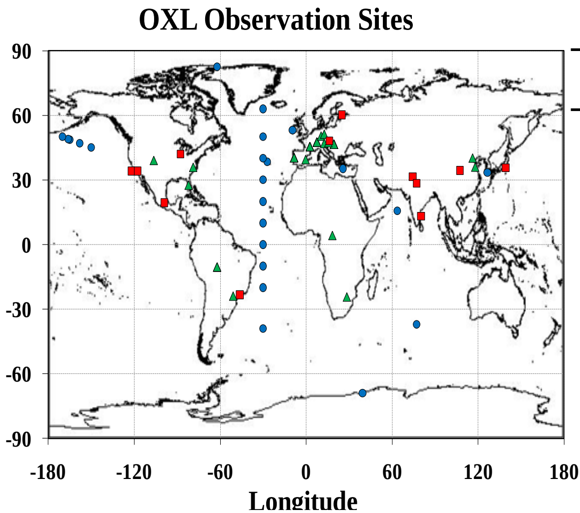




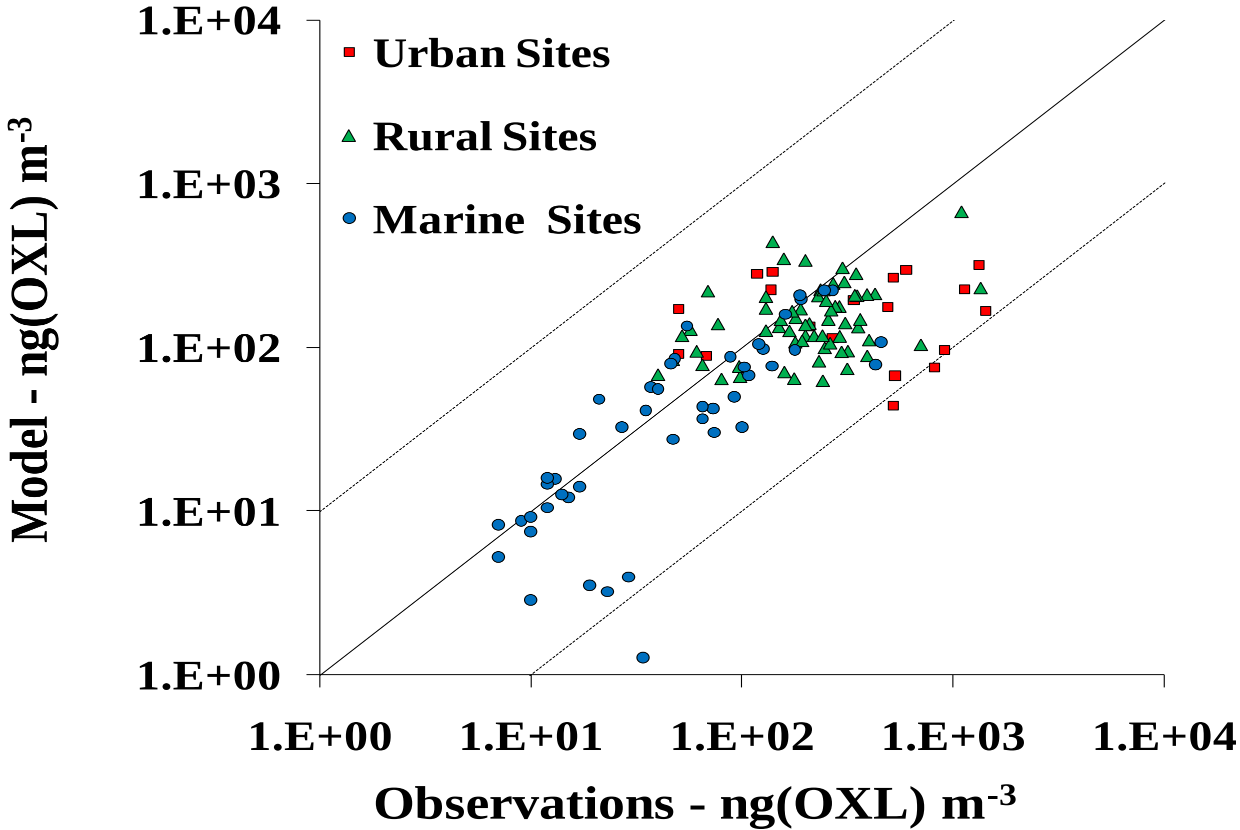




Global OXL Validations



	Sites	Simulation	Slope	r^2	N	a	F-value
Global	*Urban*	*S1*	*0.64±1.19*	*-0.04*	*19*	*0.05*	*0.290*
	Rural	*S1*	*0.92±0.24*	*0.18*	*64*	*0.05*	*14.842*
	Marine	*S1*	*1.13±0.17*	*0.46*	*50*	*0.05*	*42.653*
	Rural + Marine	S1	1.16±0.14	0.36	114	0.05	65.598
	All Observations	**S1**	**1.29±0.20**	**0.23**	**133**	**0.05**	**41.346**



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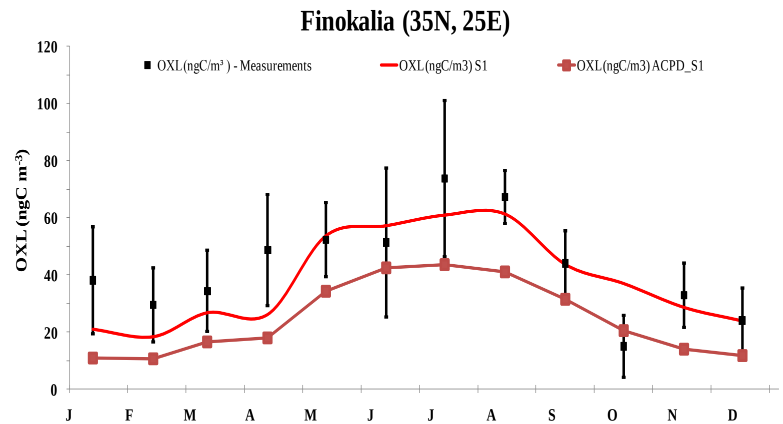
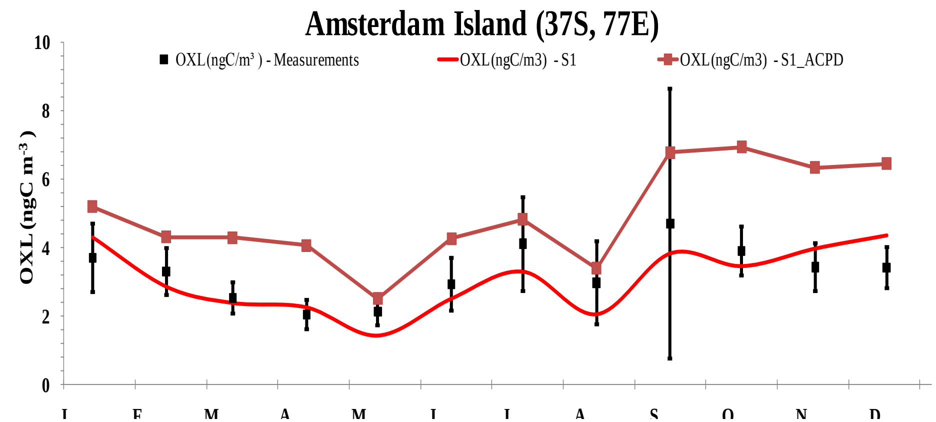
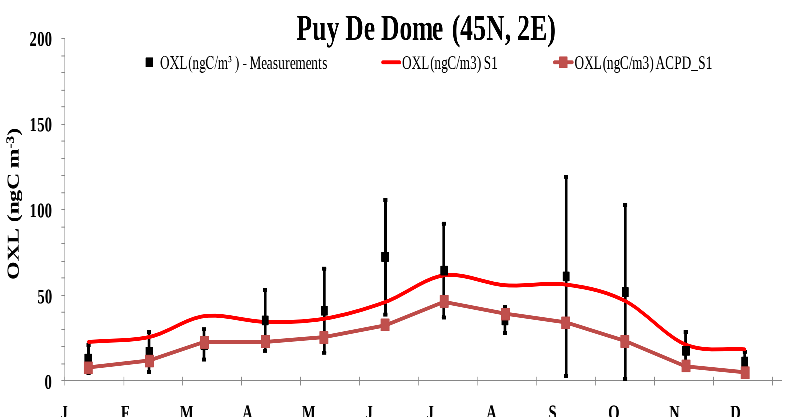
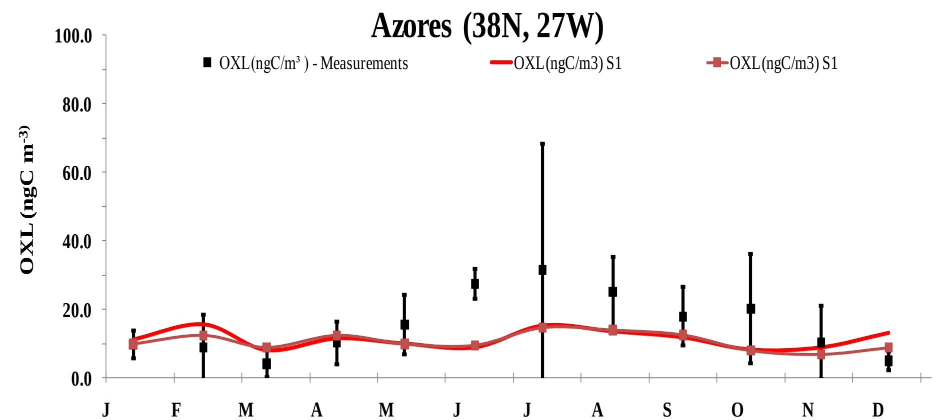
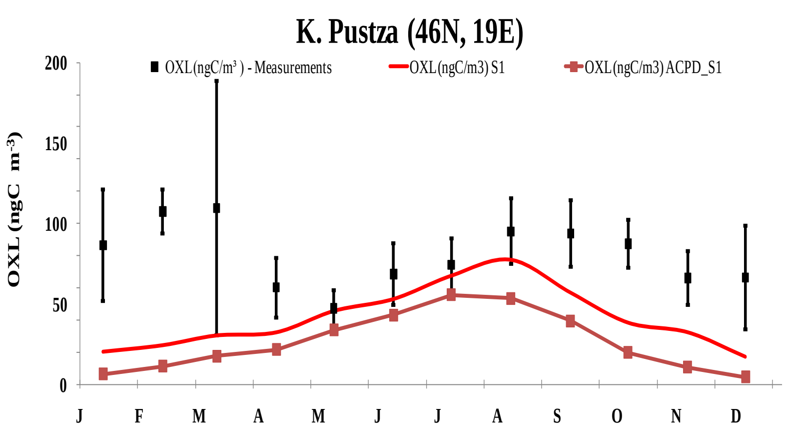
OXL Validations – OLD(ACPD) Vs. Revised Simulations

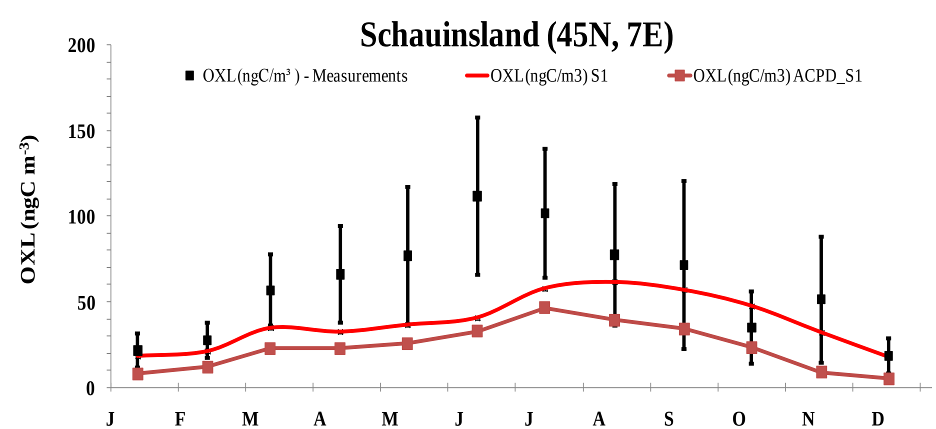












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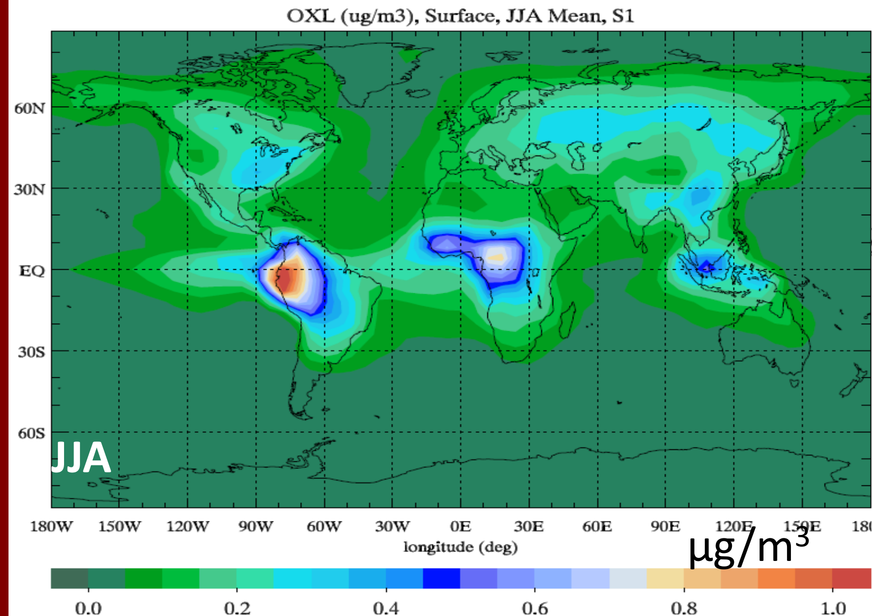
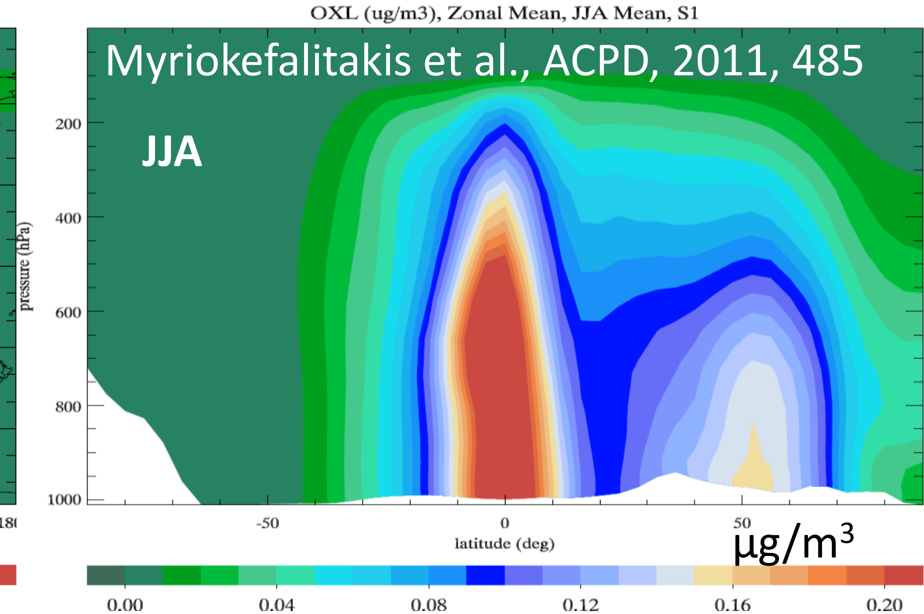
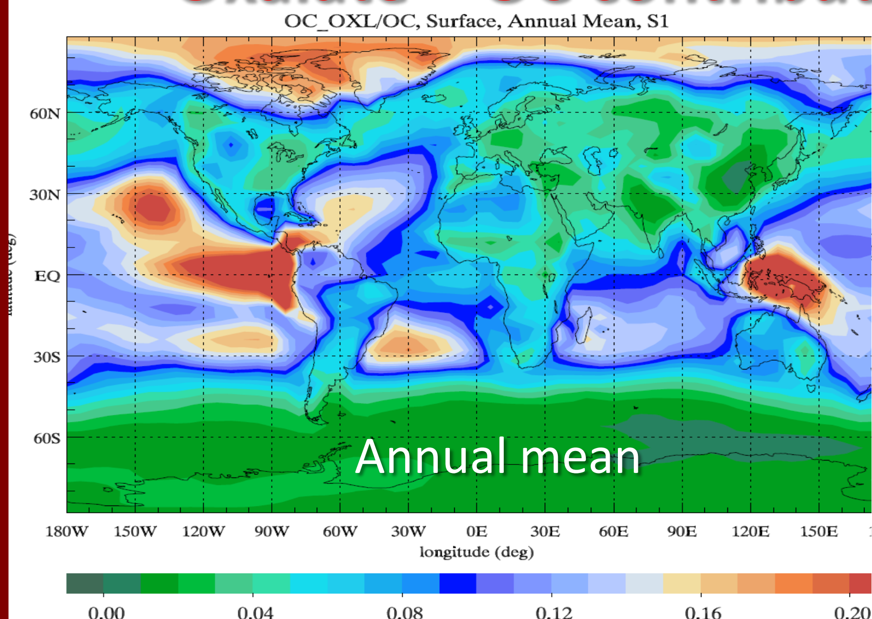
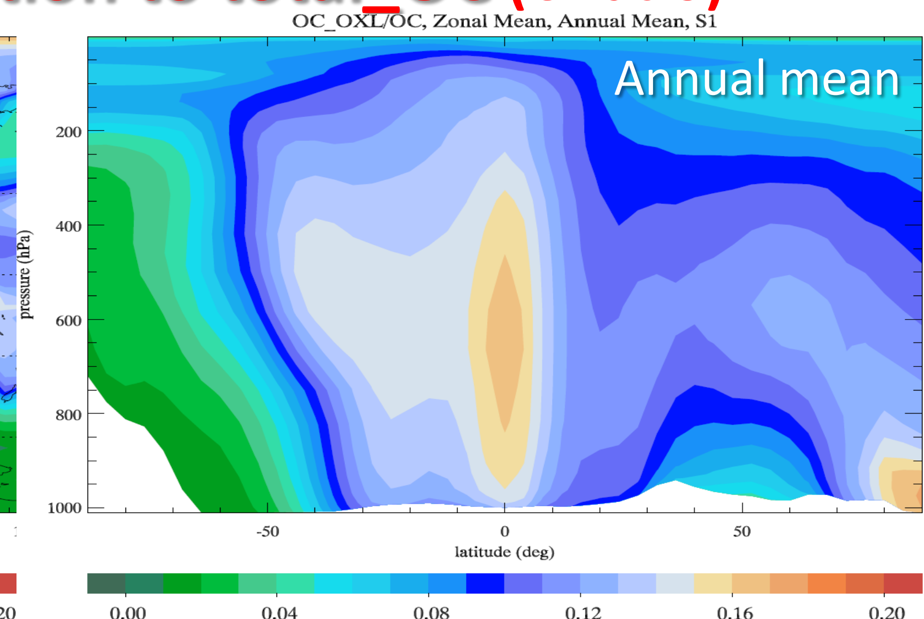
Global Oxalate Distributions





Oxalate – OC contribution to total_OC (C-ratio)





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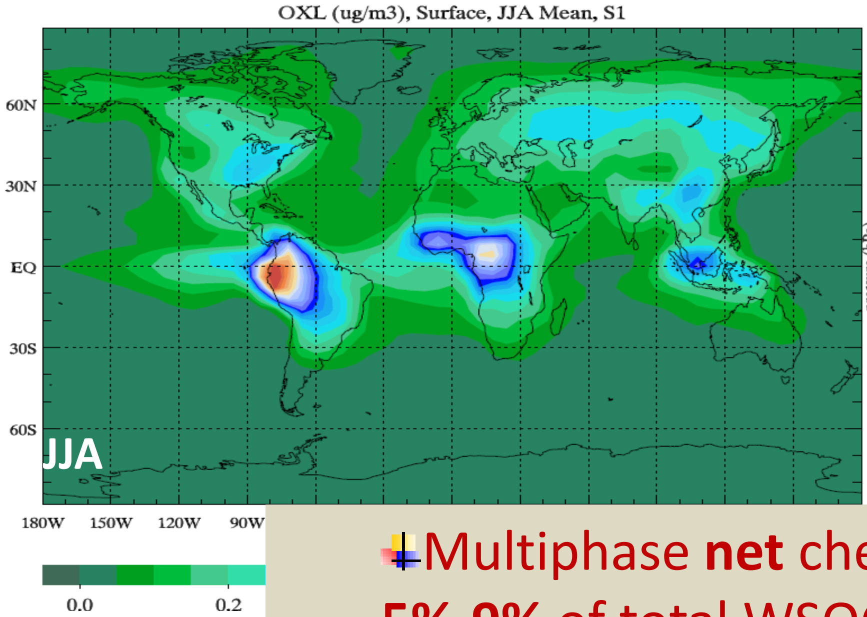
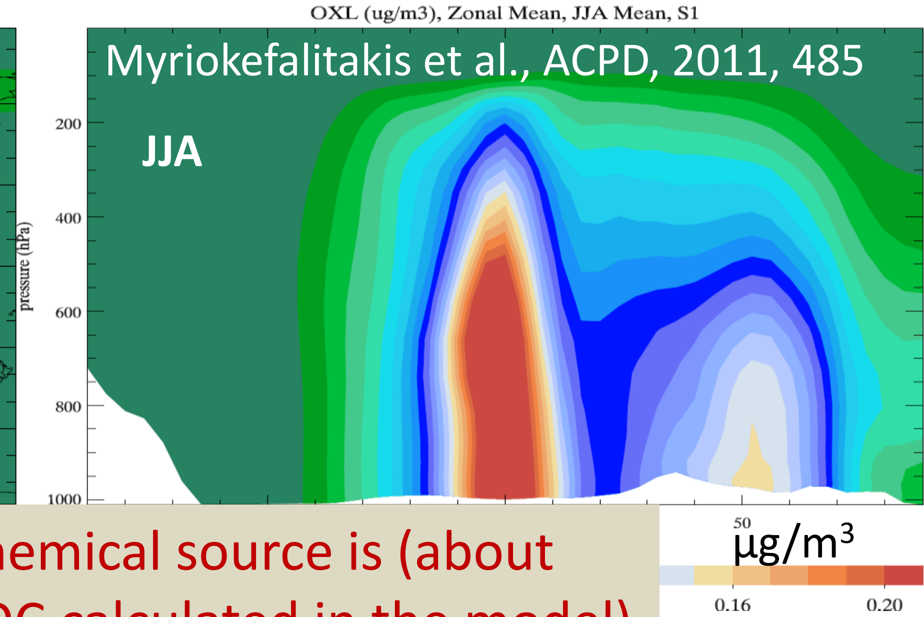
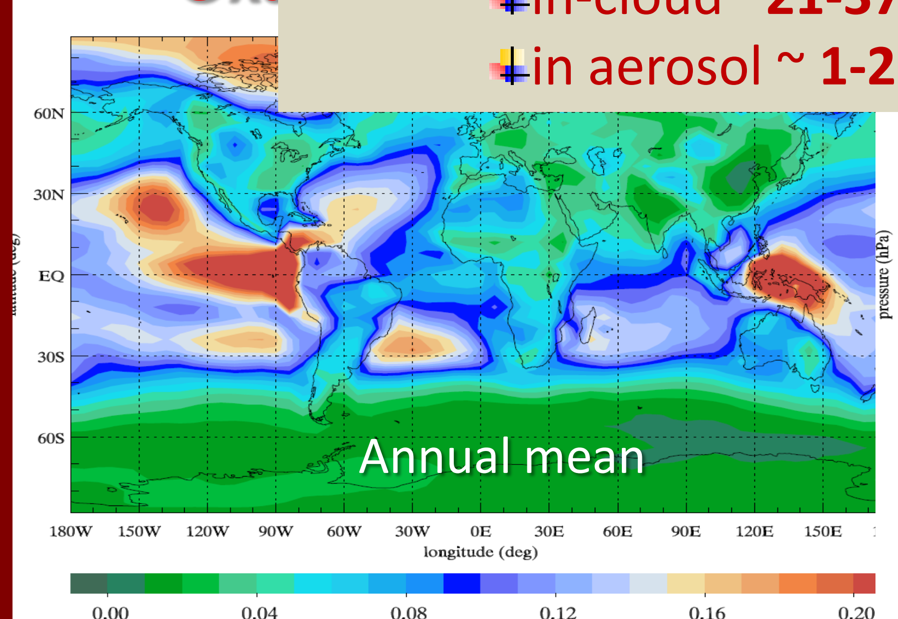
Global Oxalate Distributions

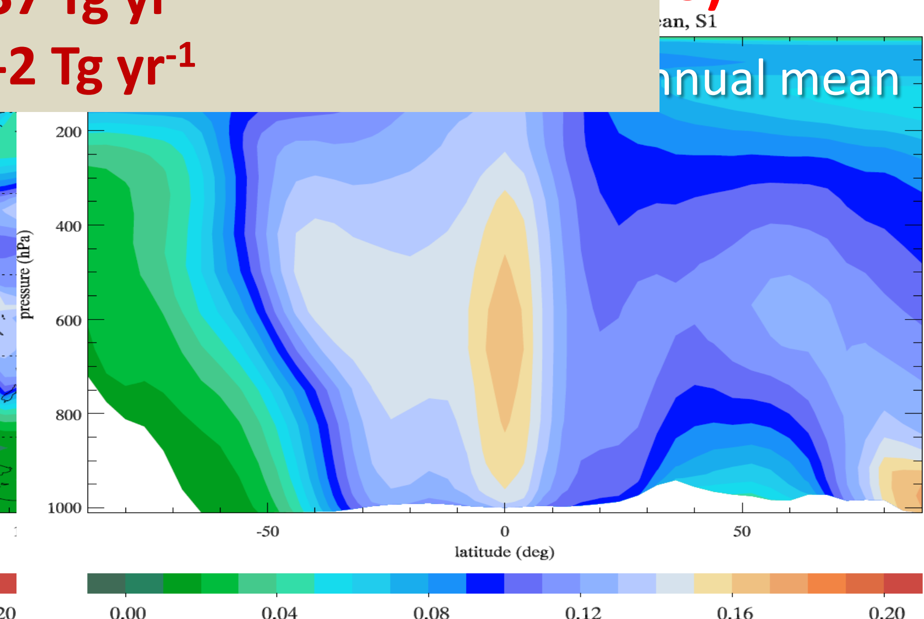




- Multiphase **net** chemical source is (about **5%-9%** of total WSOC calculated in the model)
  - in-cloud ~**21-37 Tg yr^{-1}**
  - in aerosol ~ **1-2 Tg yr^{-1}**

Oxa… io)





1. Multiphase chemistry (Stelios)
2. **Interannual model evaluation & AEROCOM (Nikos)**
3. Other ongoing and future activities (Maria)

Changes in TM4ECPL

anthropogenic emissions updated **to CIRCE database (2000 – 2010)**
Interannual 2000 – 2005, 2010 (projection), 2006-2009 interpolated
0.1x0.1 ascii files → 1x1 hdf files

•*land emissions (2d)*
BC, CO, NH_3, NOx, OC, SO_2, NMVOC
•*ship emissions (2d)*
BC, CO, NOx, OC, SO_2, NMVOC
•*aircraft emissions (3d)*
BC, CO, NOx, OC, SO_2 , NMVOC
All 3 categories with speciated NMVOC
speciation based on POET NMVOC speciation
species:acetone, butane, butene, C_2H_2 , C_2H_5OH, C_2H_6, C_3H_6, C_3H_8, CH_2O, CH_3CHO, CH_3OH, MEK, toluene, benzene, xylene

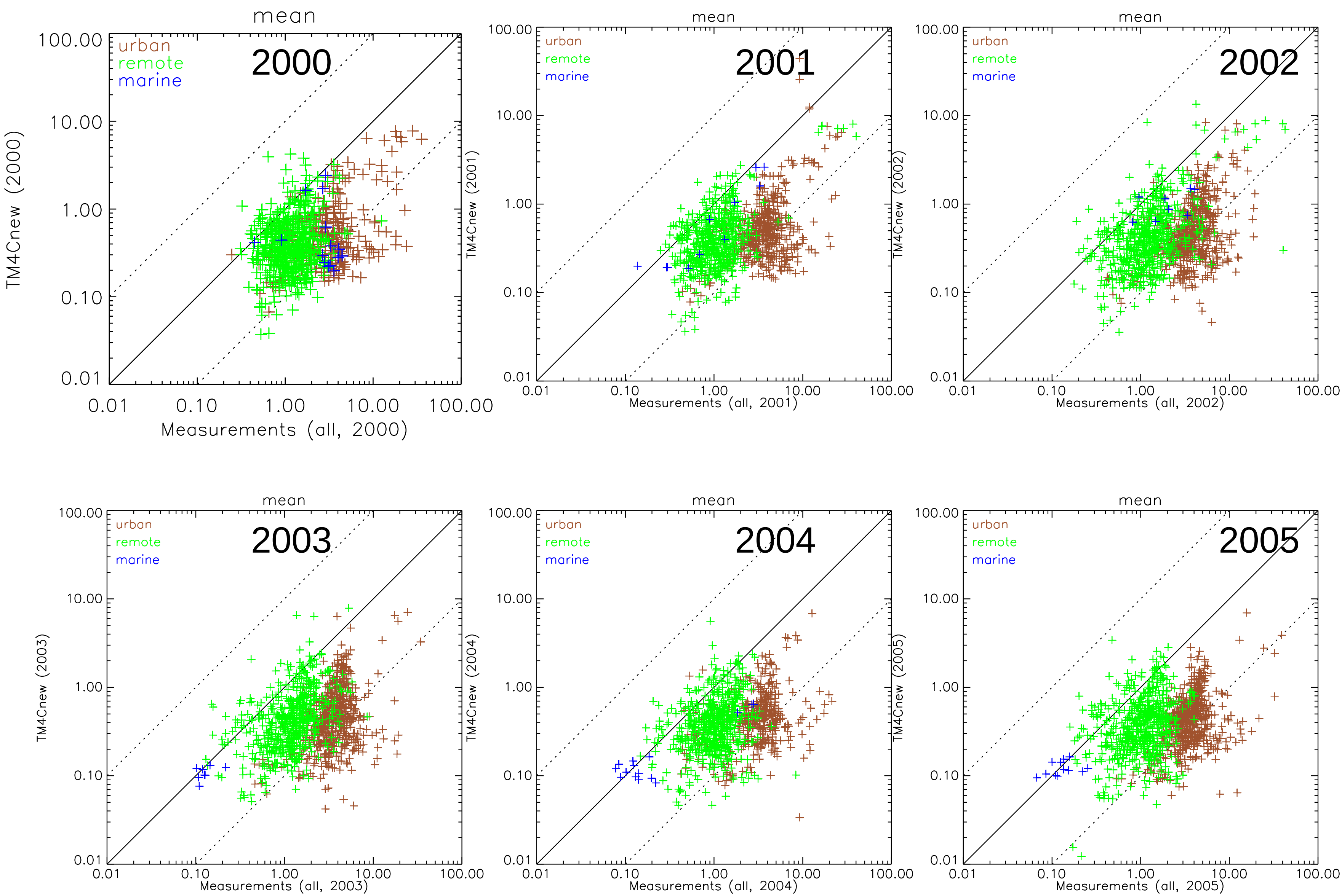
Global Fire Emission Database v2 (1998 – 2008)
Gridded 1x1 netcdf files used, already speciated nmvocs (van der Werf)
Vertical elevation of Biomass Burning emissions based on Dentener et al, 2006

AEROCOM runs re-done
Interannual 6x4 (2000-2007)
2006 3x2

Model evaluation

updated version (CIRCE anthropogenic, GFED v2, ERA meteorology,

Organic Carbon (comparison at all available stations) (ug/m3)



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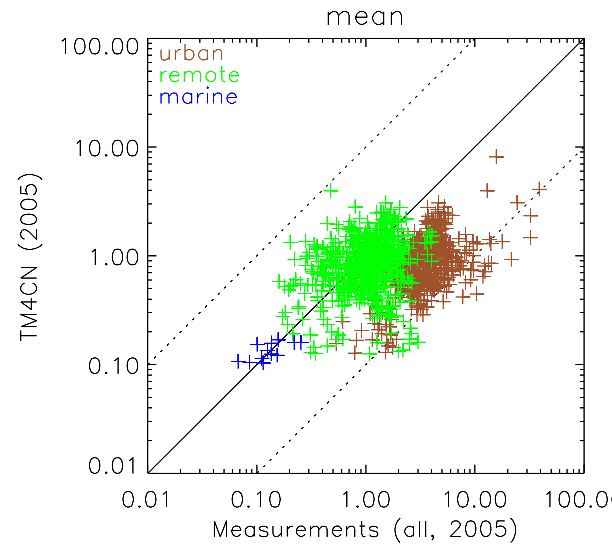
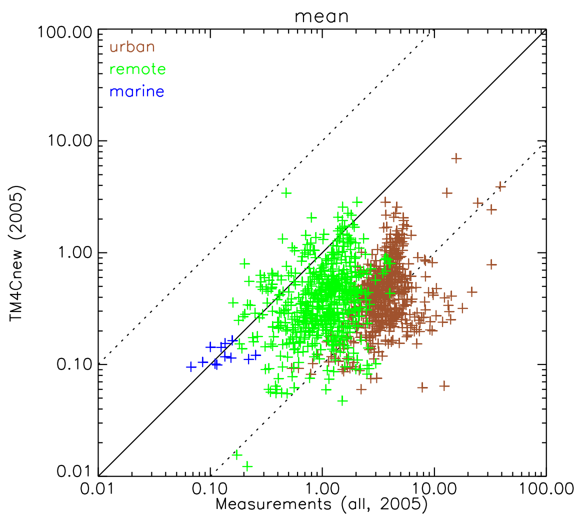
Organic Carbon -evaluation

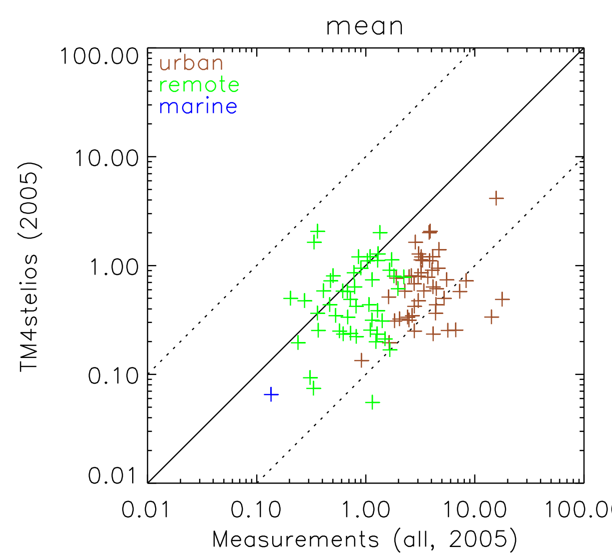
Model evaluation after the changes
- CIRCE anthropogenic
- Poet biogenic
- GFED v2
- operational meteo data





Model evaluation after the changes
- CIRCE anthropogenic
- Poet biogenic
- GFED v2
- ERA meteo data

Model evaluation before the changes
- POET anthropogenic
- Poet biogenic
- GFED v2 CO and BC
- operational meteo data



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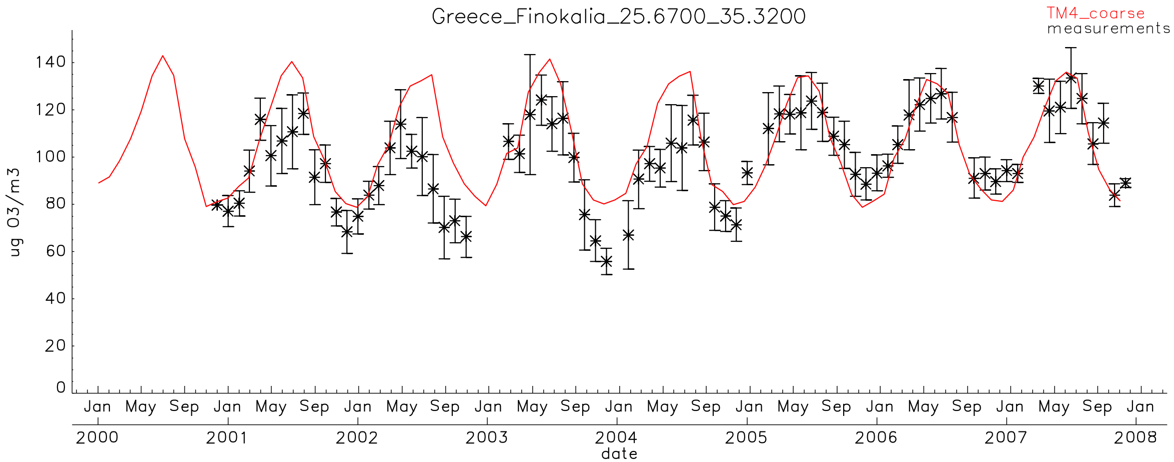
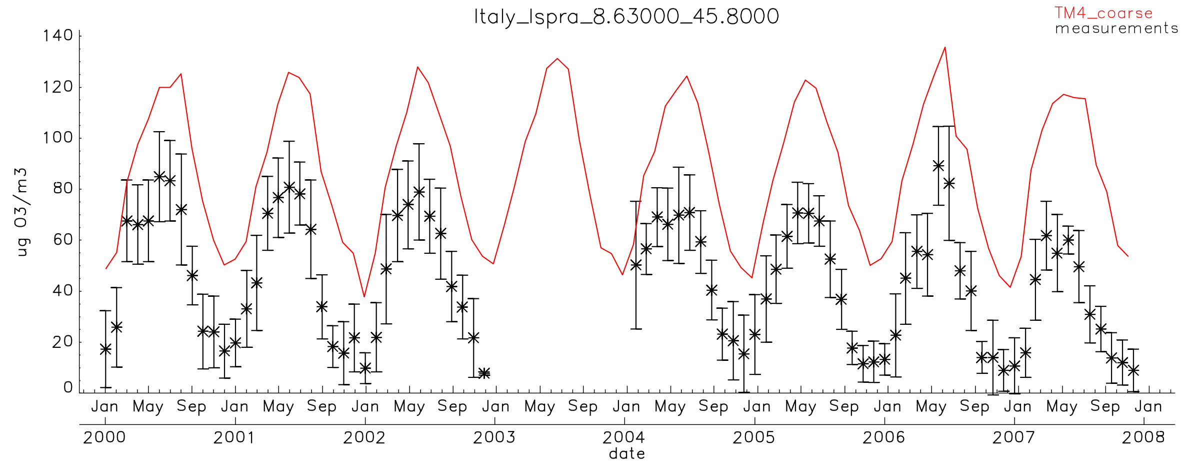
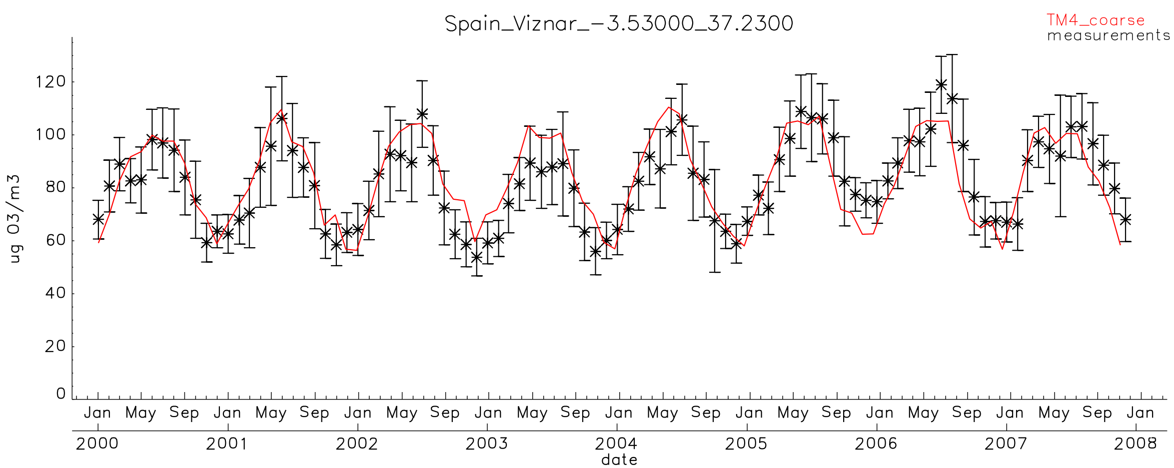


Greece
Finokalia

Italy
Ispra





Spain
Viznar

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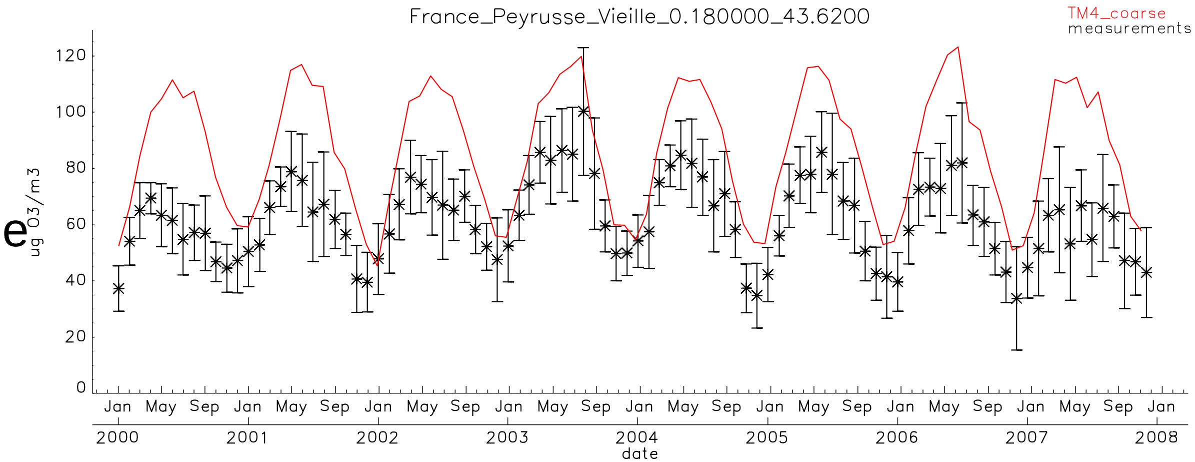
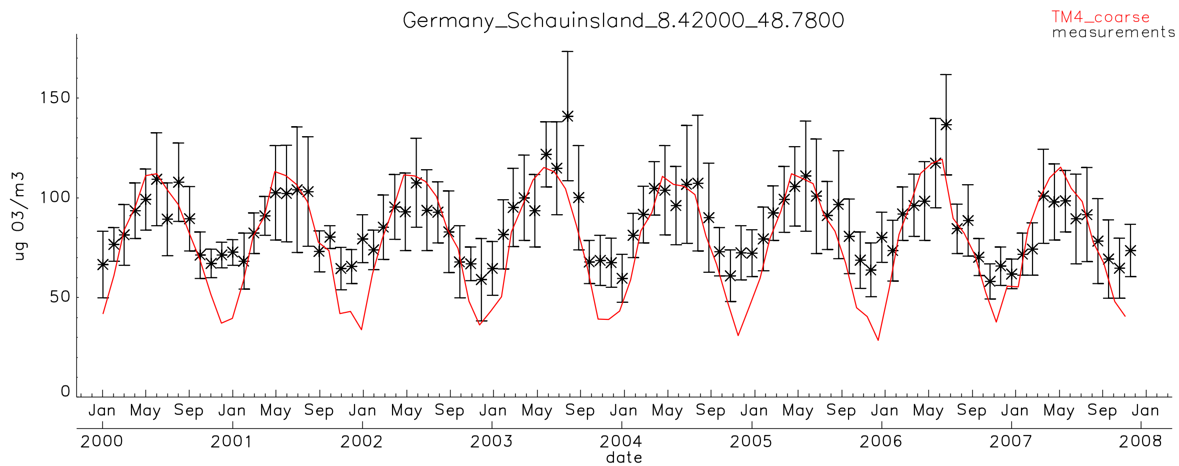
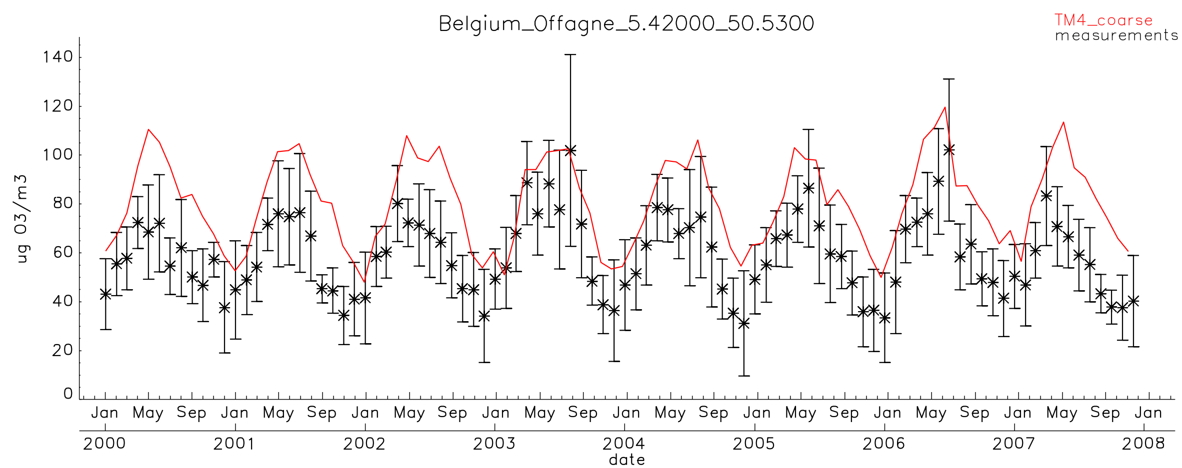
France
Peyrusse Vieille



Germany
Schauinsland



Belgium
Offagne



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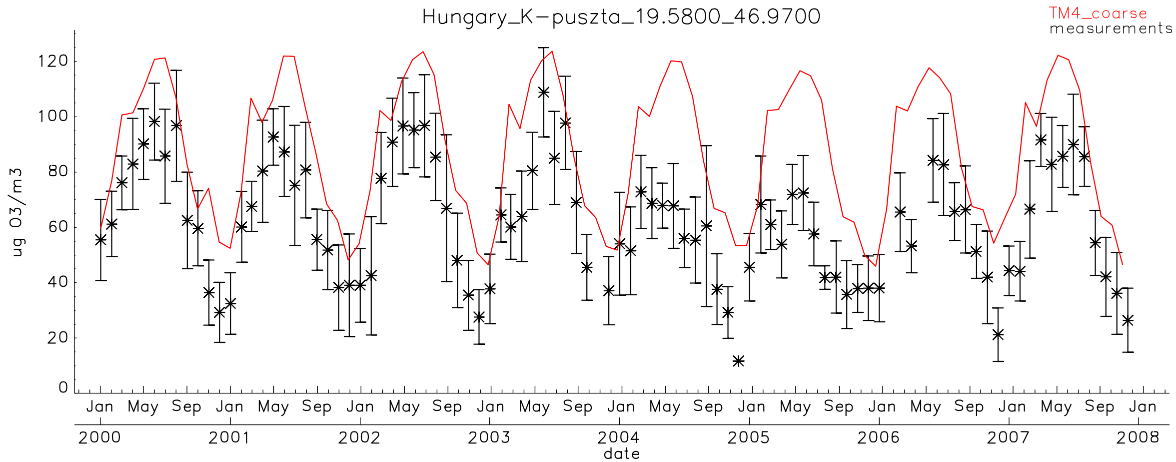
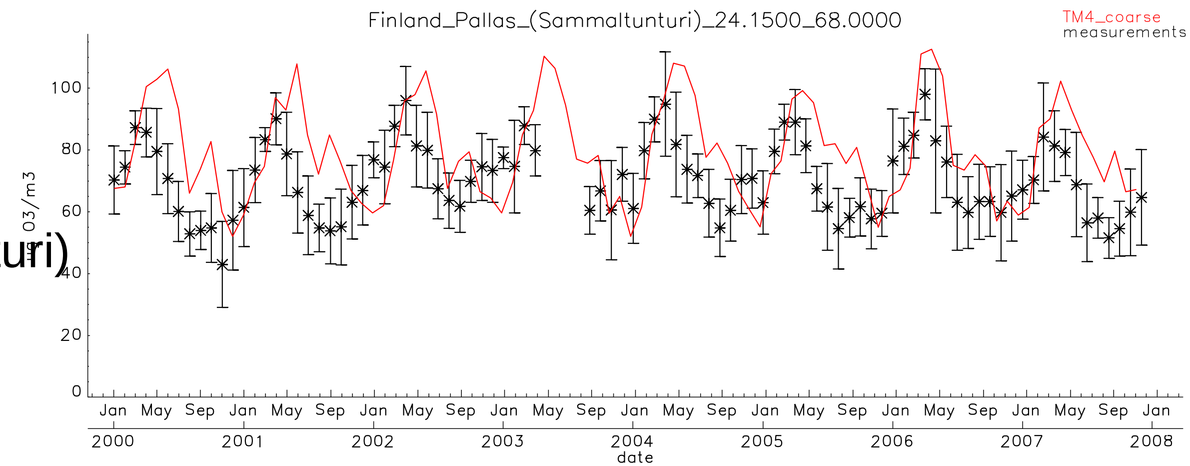
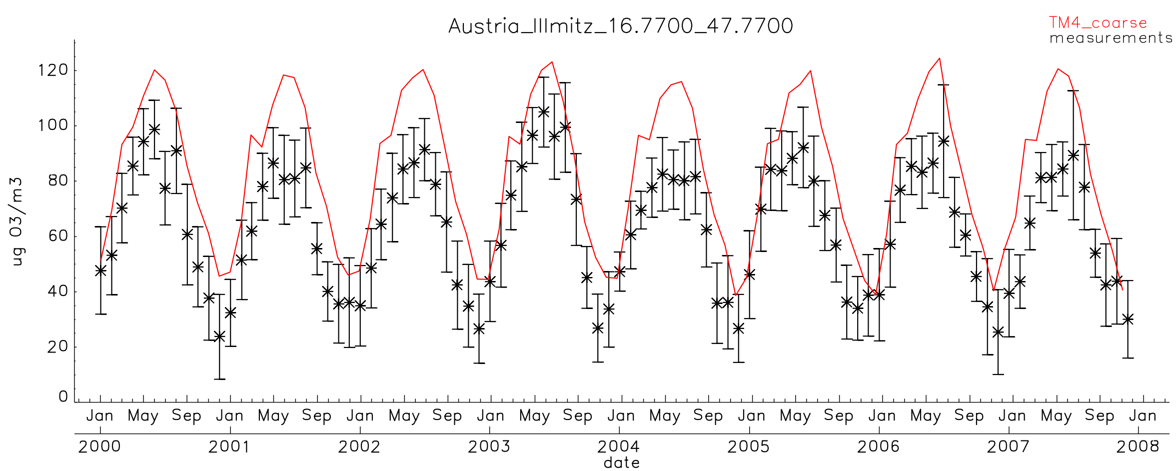


Hungary
K-puszta



Finland
Pallas (Sammaltunturi)



Austria
Illmitz

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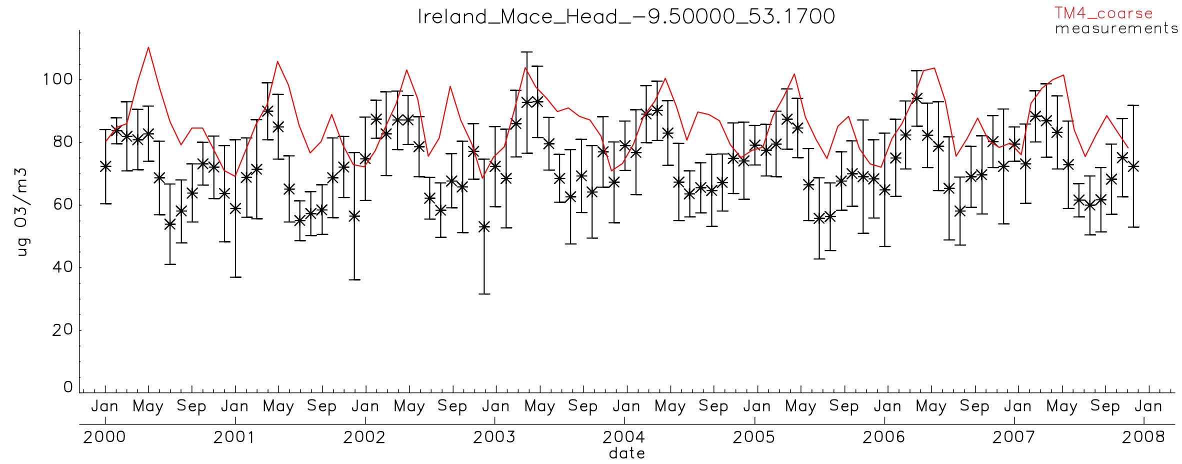
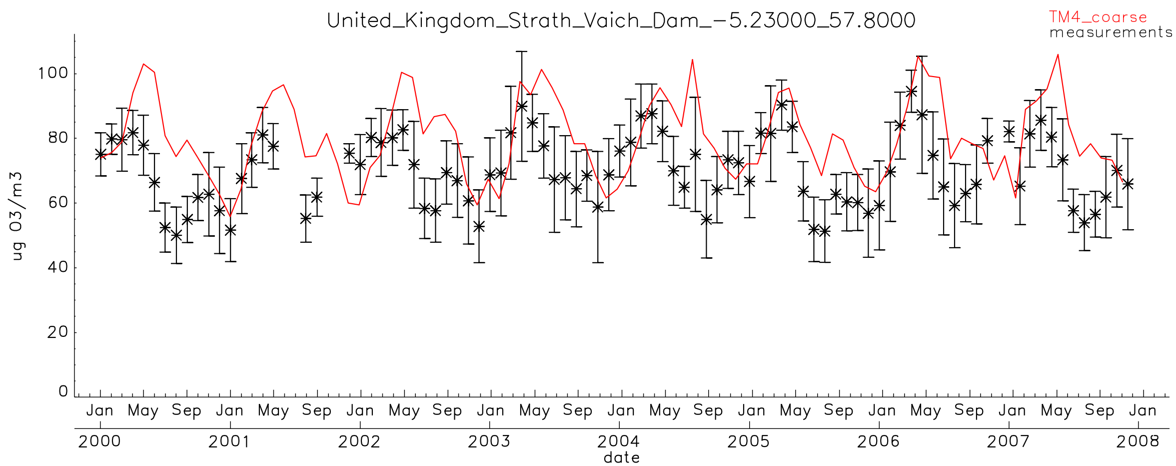
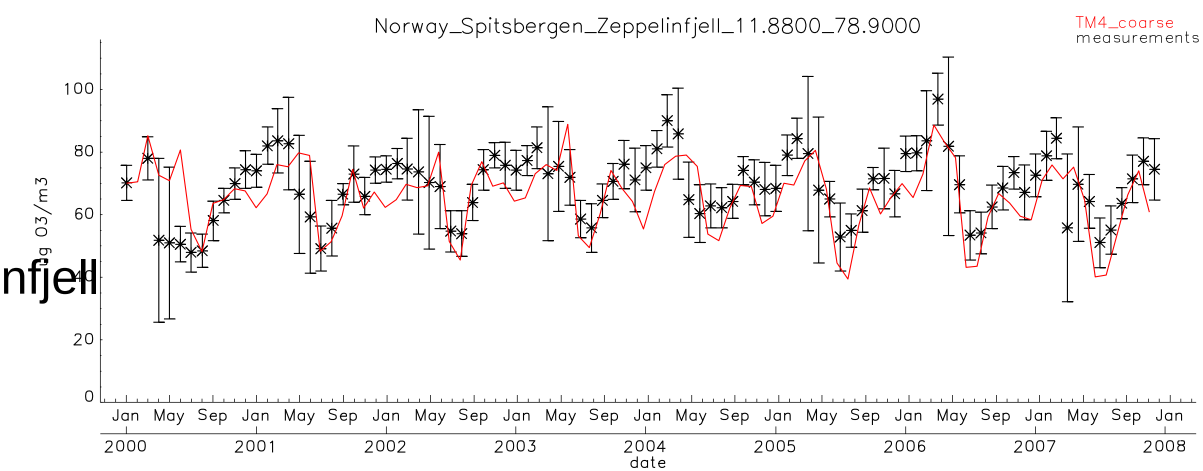
Ireland
Mace Head





United Kingdom
Strath Vaich Dam

Norway
Spitsbergen Zeppelinfjell



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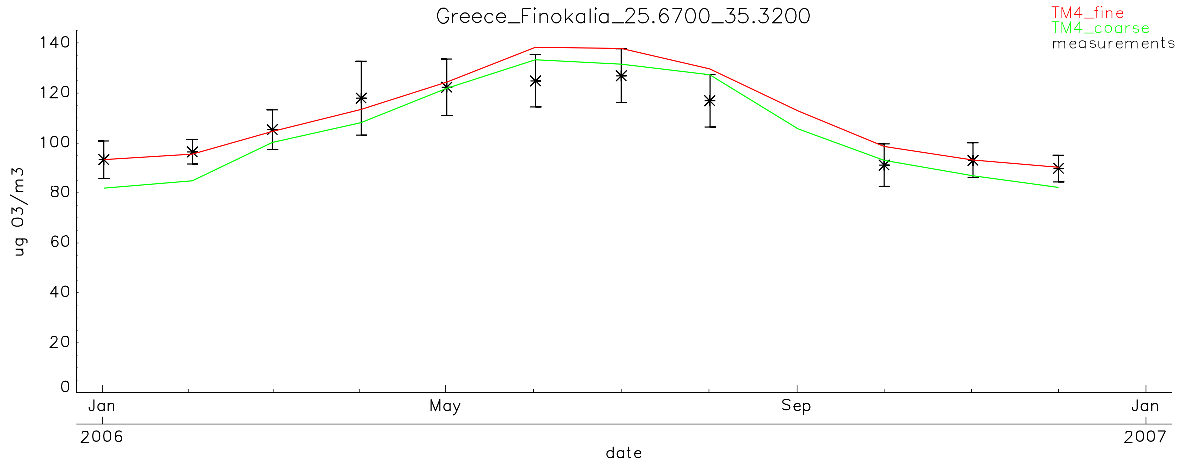
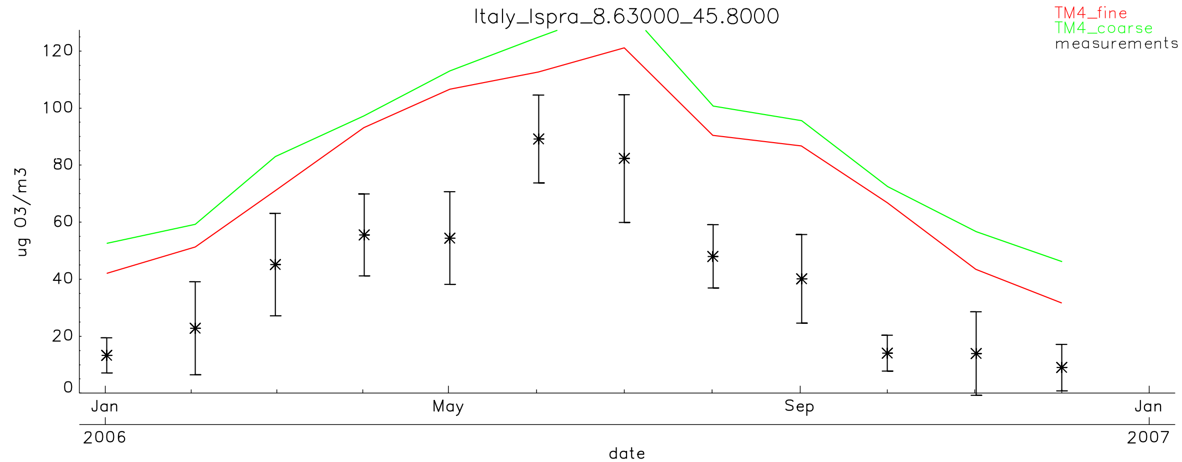
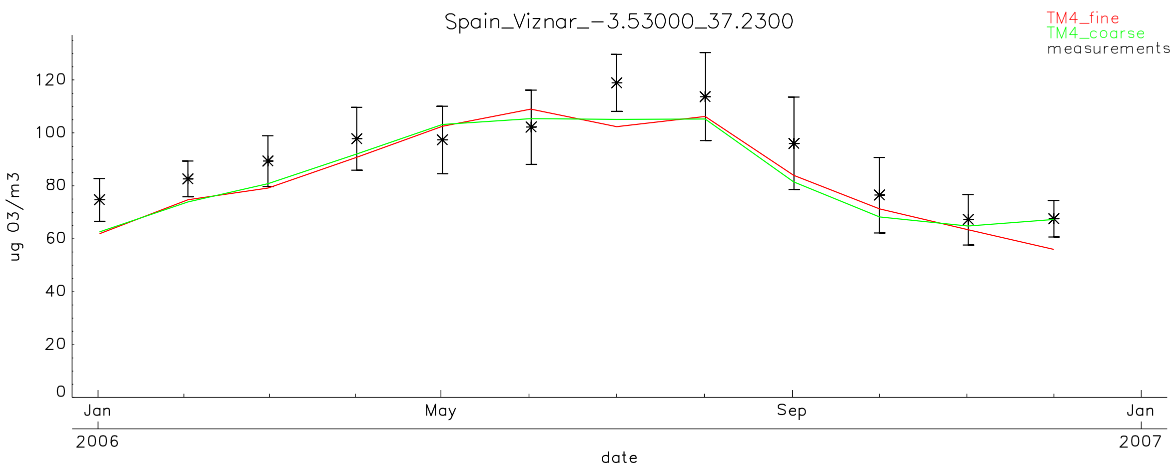
TM4-ECPL 3x2
TM4-ECPL-6x4
measurements



Greece
Finokalia

Italy
Ispra





Spain
Viznar

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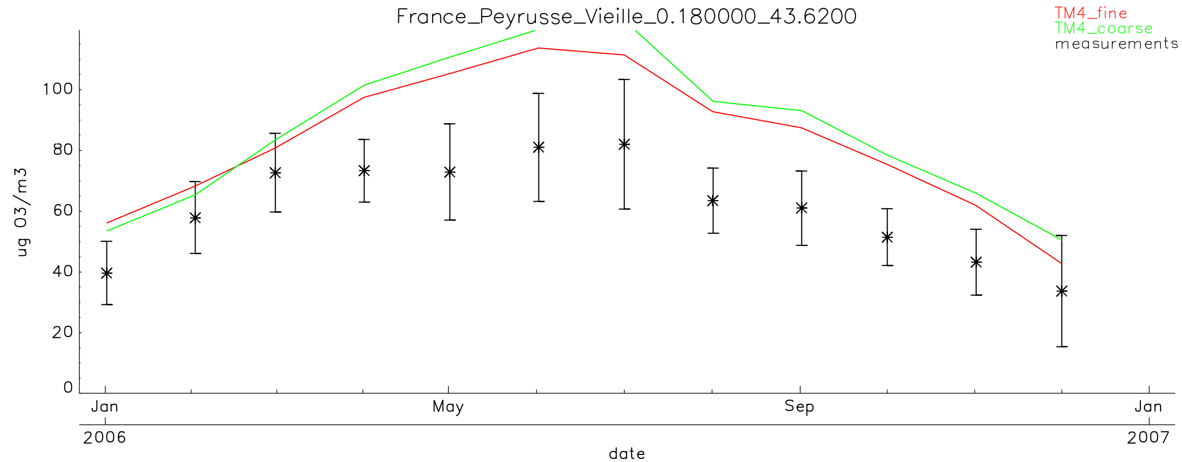
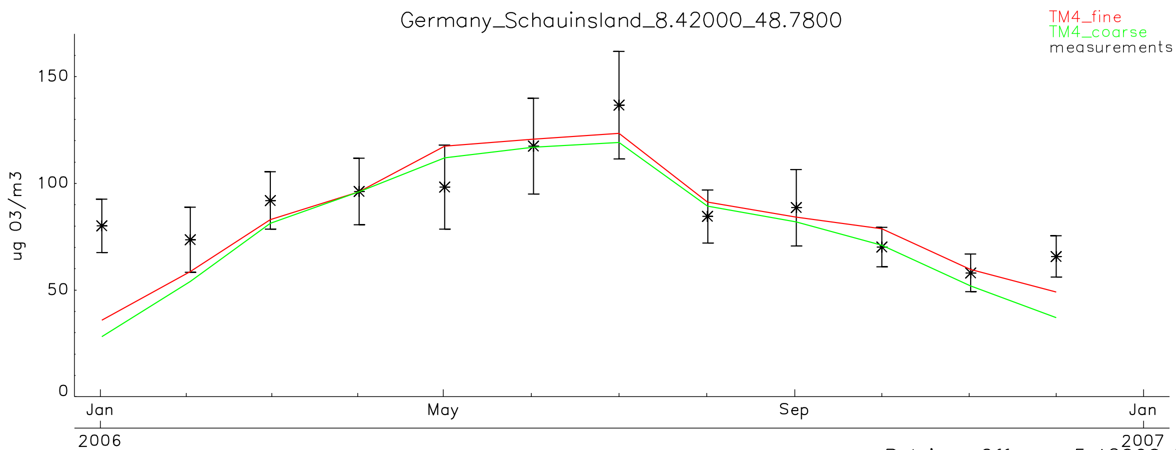
TM4-ECPL 3x2
TM4-ECPL-6x4
measurements

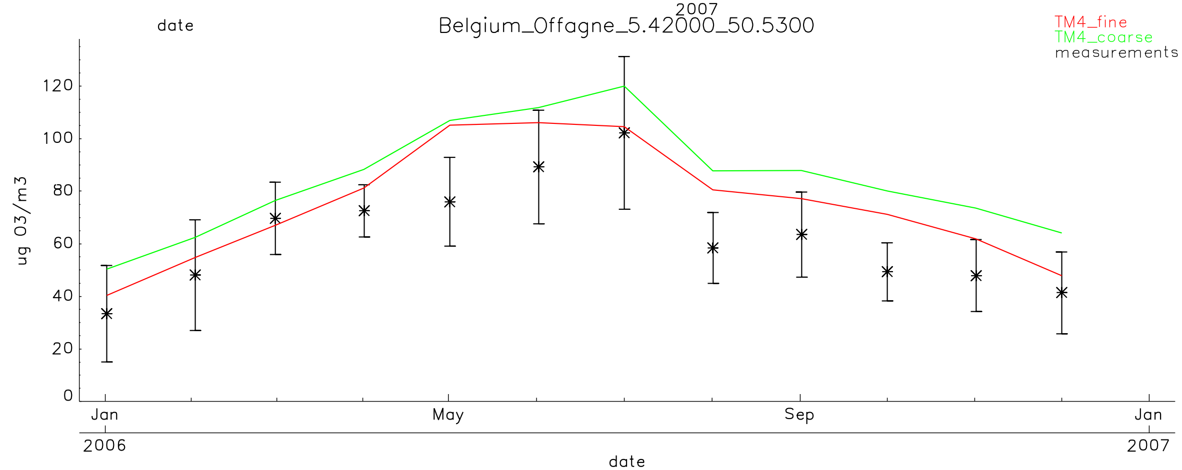
France
Peyrusse Vieille



Germany
Schauinsland



Belgium
Offagne



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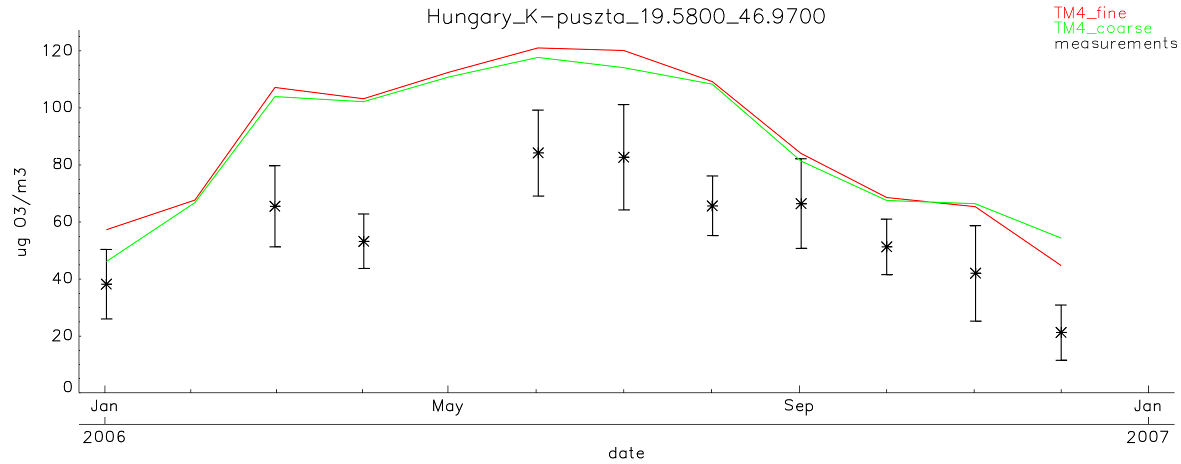
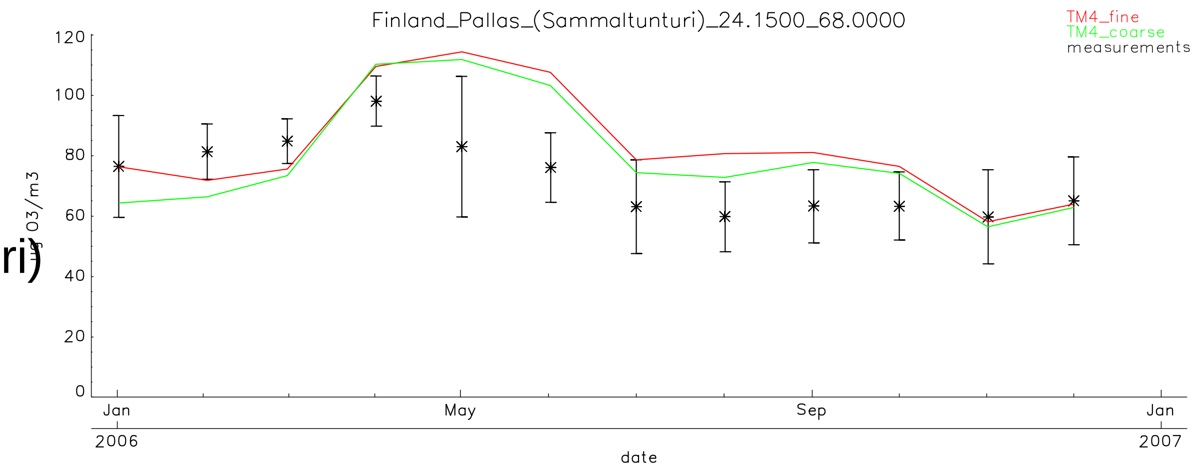
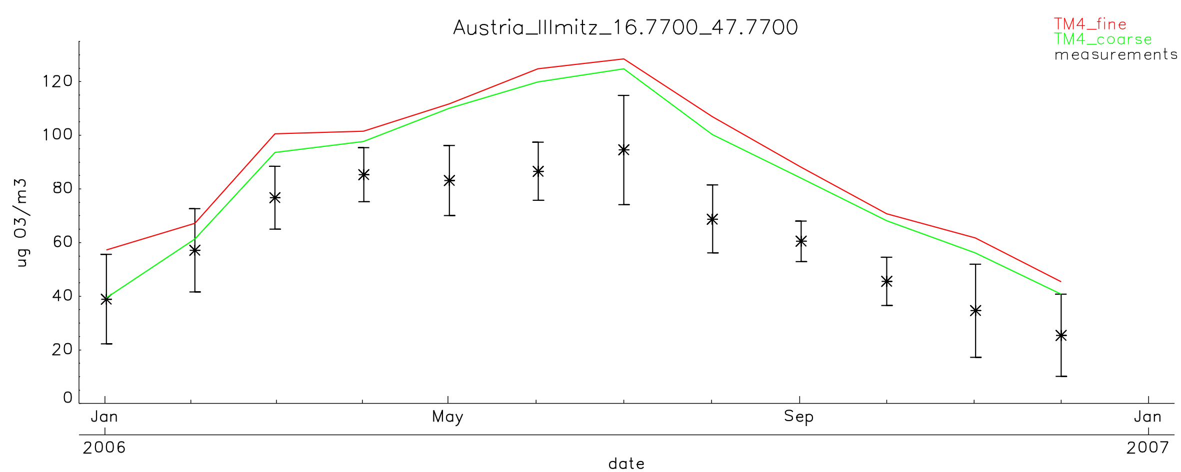
TM4-ECPL 3x2
TM4-ECPL-6x4
measurements



Hungary
K-puszta

Finland
Pallas (Sammaltunturi)

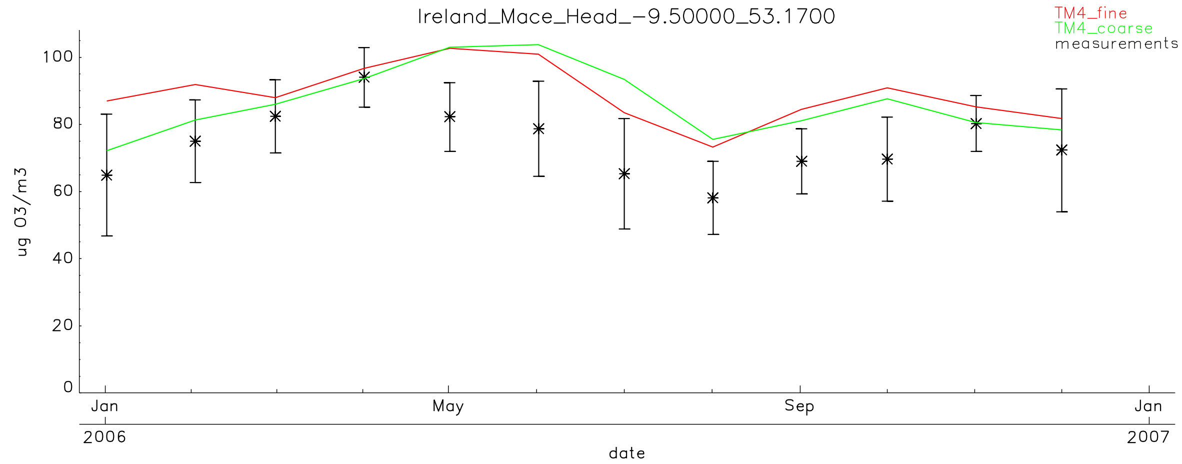


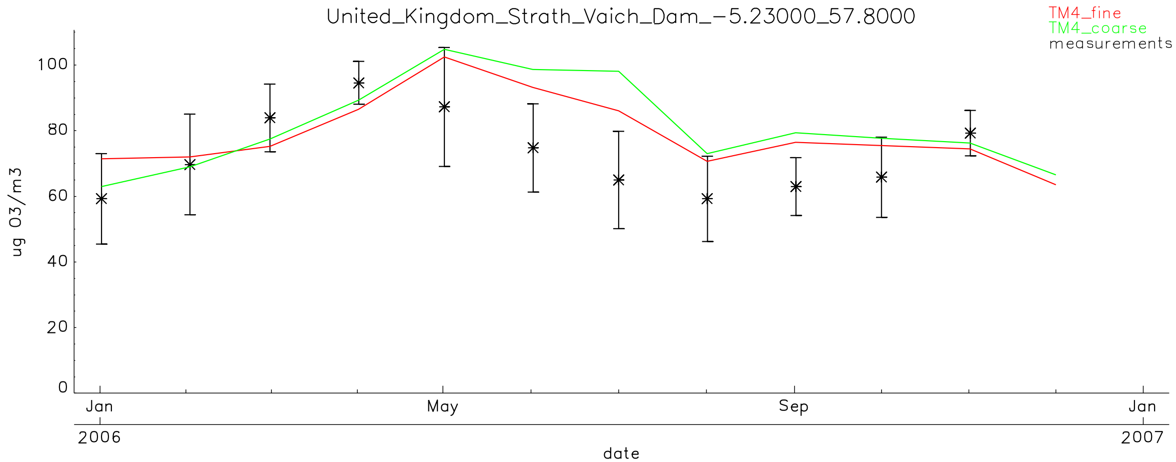


Austria
Illmitz

TM4-ECPL 3x2
TM4-ECPL-6x4
measurements

Ireland
Mace Head





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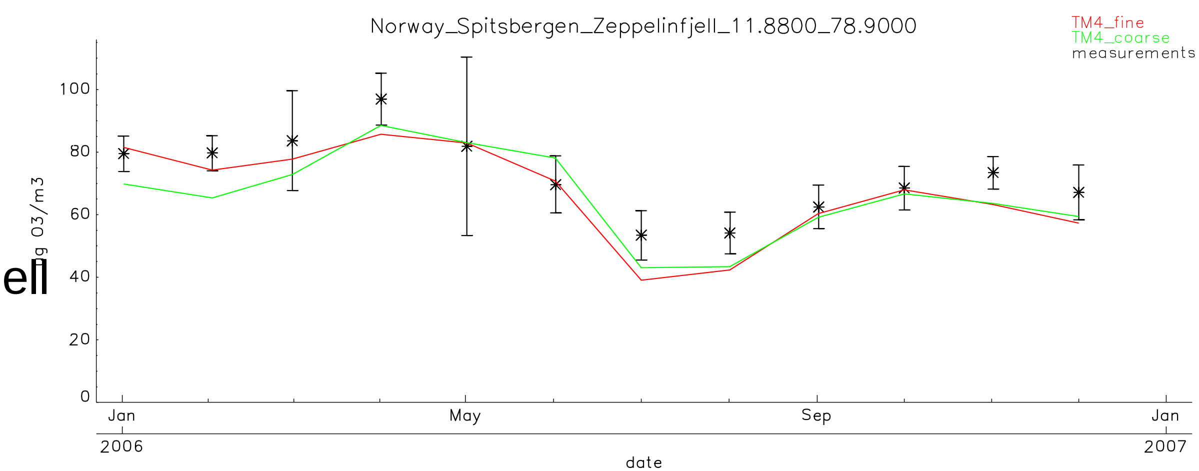
Strath Vaich Dam

Norway
Spitsbergen Zeppelinfjell



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1. Multiphase chemistry (Stelios)
2. Interannual model evaluation & AEROCOM (Nikos)

3. Other ongoing and future activities (Maria)

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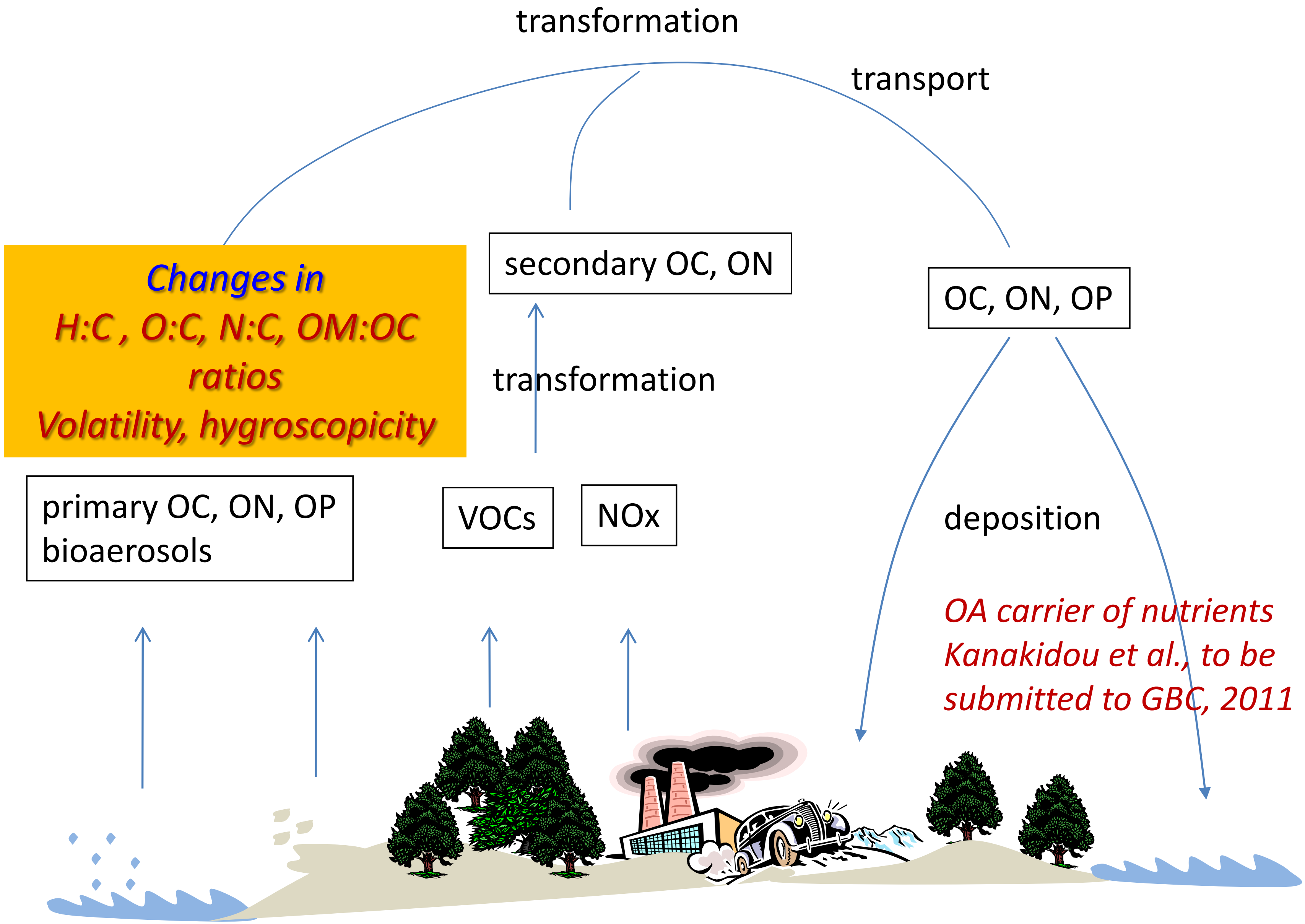
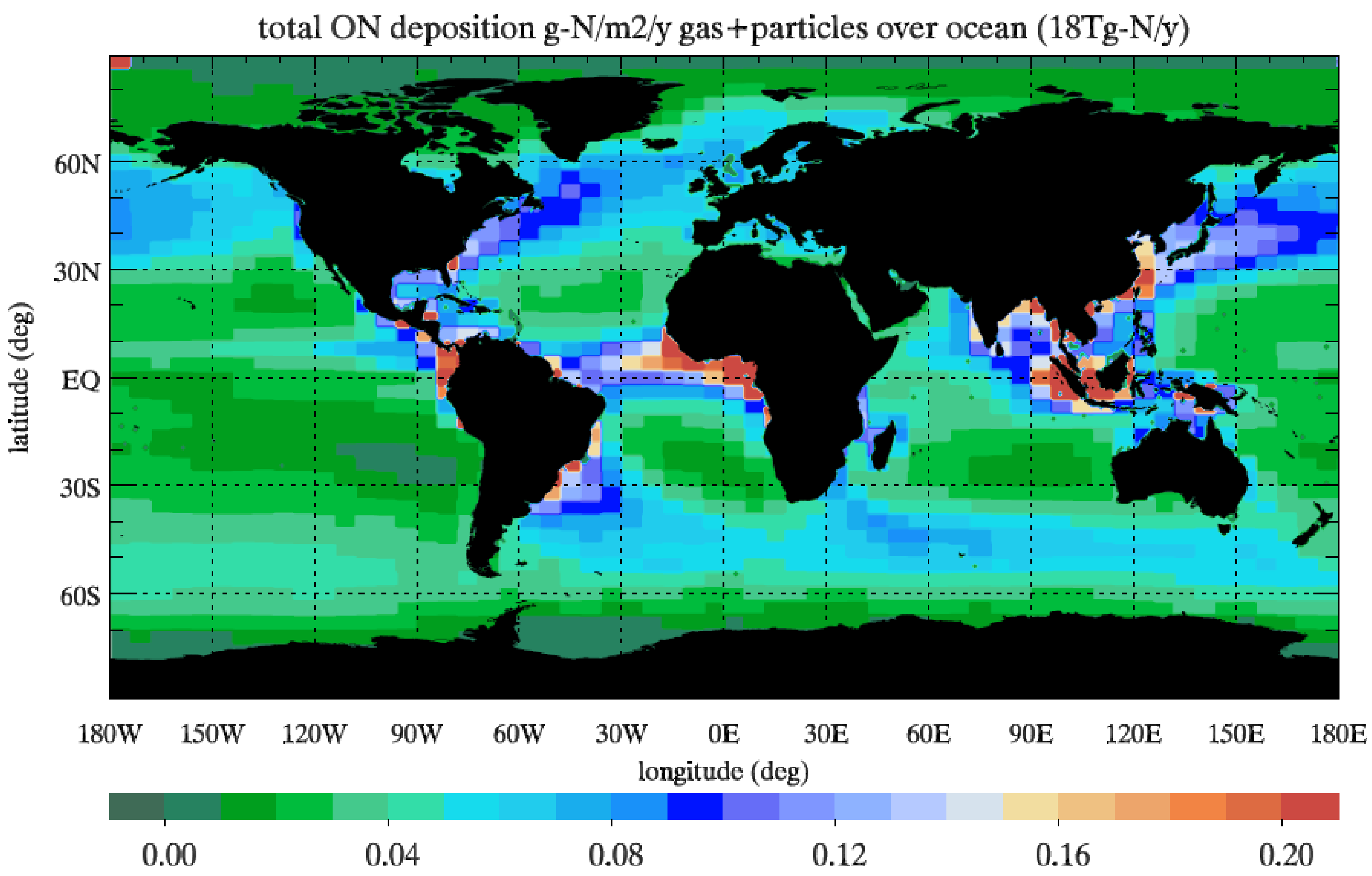
Organic aerosol - new perspectives– based on element ratios



Organic aerosol - new perspectives– based on element ratios



OA carrier of nutrients
Kanakidou et al., to be submitted to GBC, 2011
Contribution to GESAMP WG38

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Further work at ECPL

1. Sensitivity of model results to meteo, emissions, OA parameterisations
2. Interannual trends in oxidants + PM (past 20 years)
3. Oxidant and PM levels simulations – focus on Mediterranean
4. Budget analysis / import/export fluxes
5. Improve chemistry relevant parameterisations:
    1. OA parameterisations (volatility of POA, heterogeneous reactions, multiphase chemistry)
    2. oxidant chemistry (HOx recycling)
6. Sensitivity to emission location & height / geographic distribution/source receptor relationship/lifetime dependence
7. Impact of atmospheric deposition to the marine ecosystem (Mediterranean)