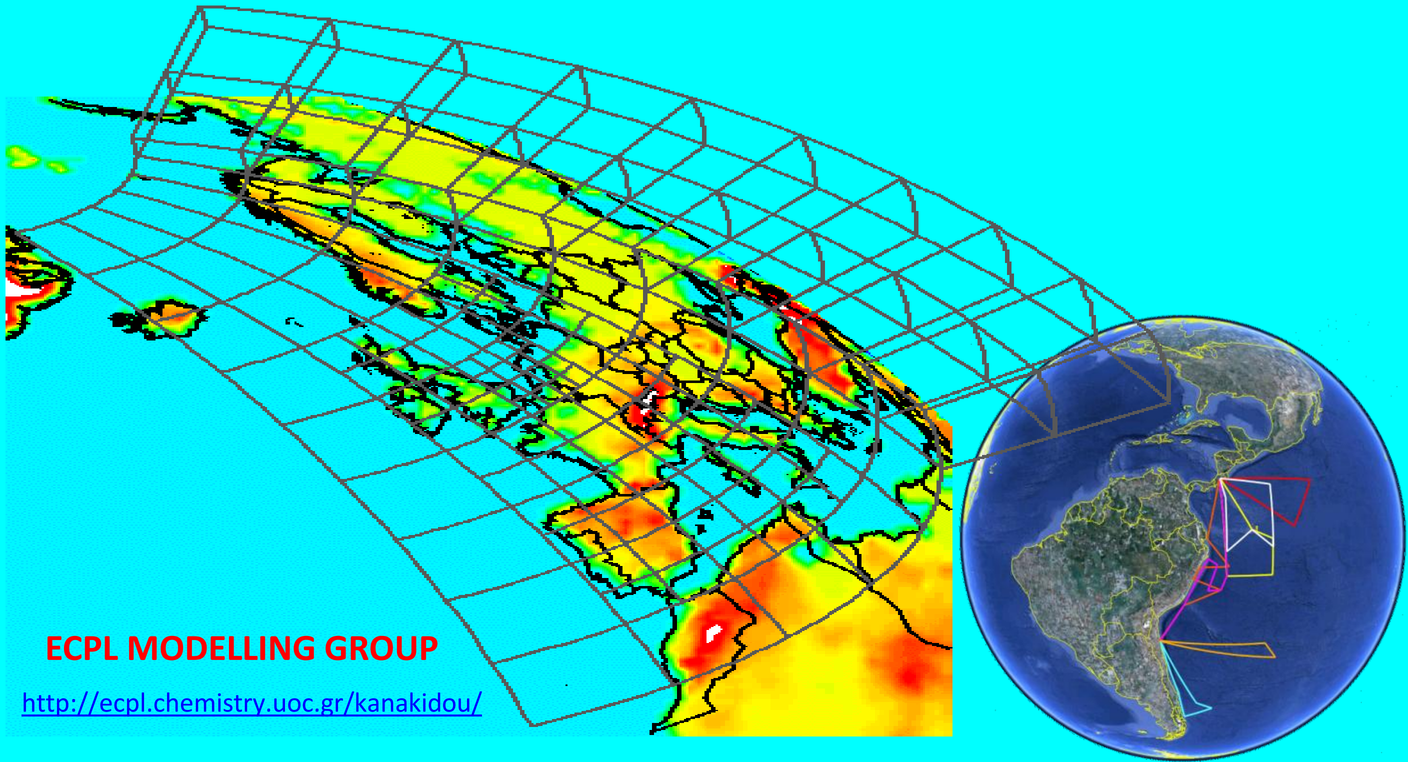
/// GLYOXAL (CHOCHO) Over Oceans \\\

"Reconciling TM4-ECPL model calculations with TORERO Observations"



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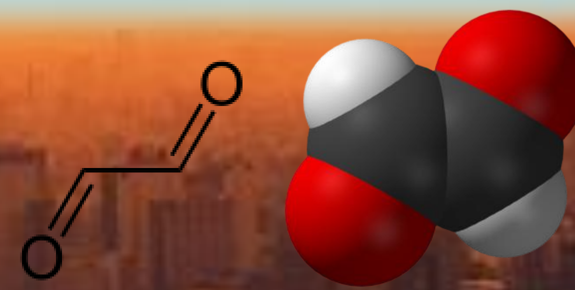
What is glyoxal ?
Why do we care?



CHOCHO

Glyoxal, the smallest dicarbonyl, which has recently been observed from space, is expected to provide indications on volatile organic compounds (VOC) oxidation and secondary aerosol formation in the troposphere

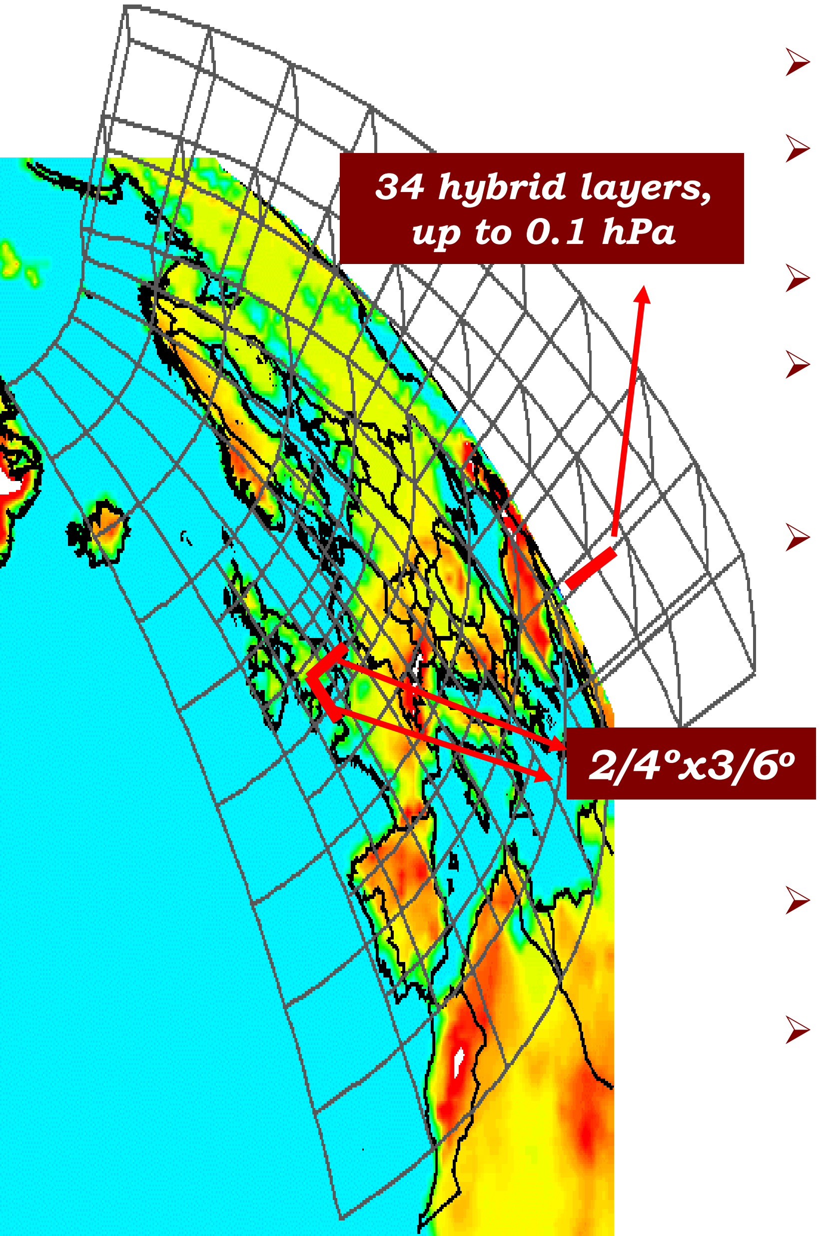
(air pollution and climate relevance)

Known Sources: Glyoxal is known to be mostly of natural (biosphere) origin and is produced during biogenic VOC oxidation.

It also has primary anthropogenic sources (vehicles) and is produced during biomass burning.

Known sinks: photolysis, reaction with OH, and NO_3, clouds & aerosols, deposition

TM4-ECPL Global 3D Model

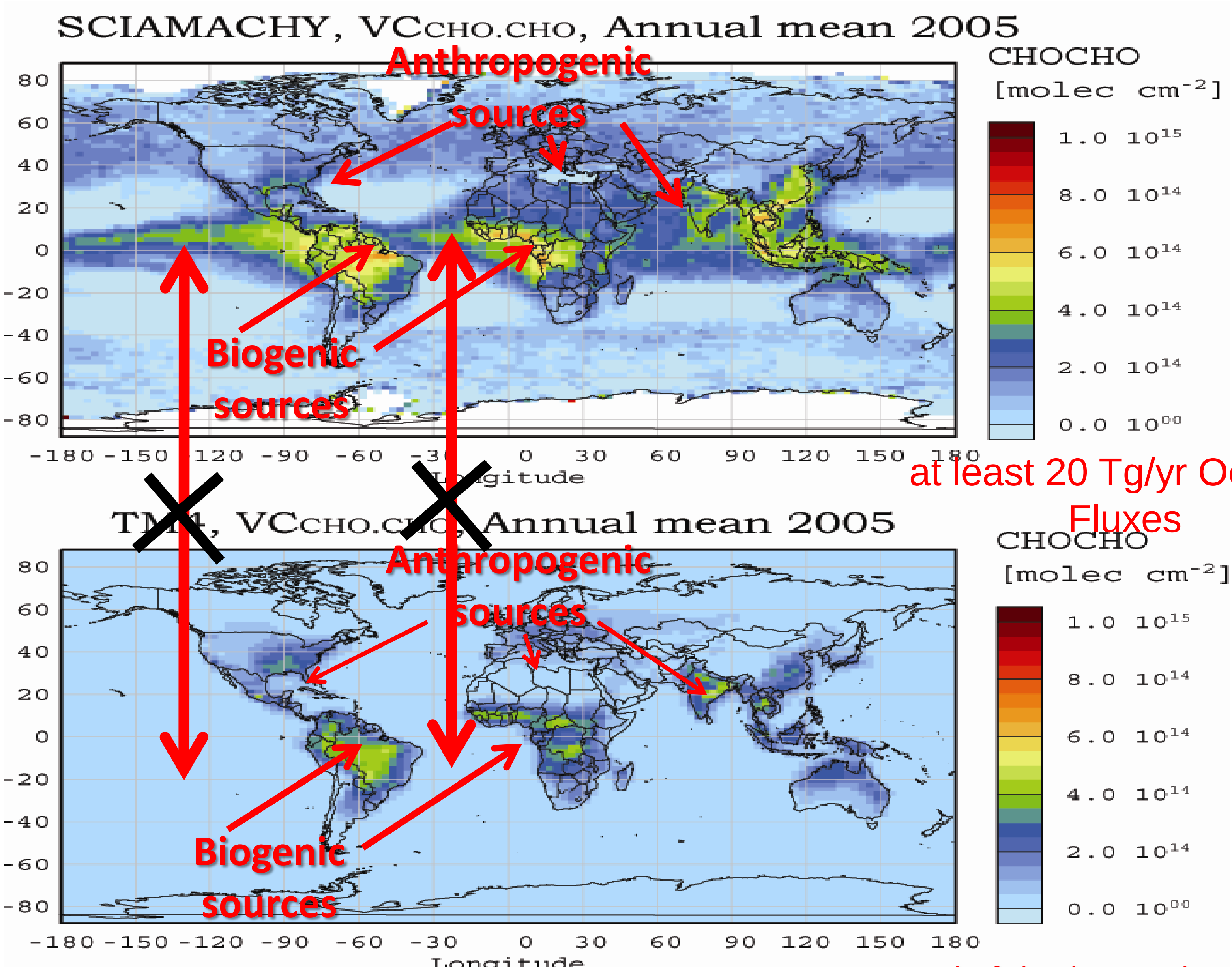


- Meteorology input from ECMWF – ERA-Interim project data-archive: 3 hourly data
- Anthropogenic emissions from CIRCE inventories (2000-2010)
- Biogenic Emissions from POET 2000 inventories have been adopted.
- Biomass Burning Emissions from GFED v3 (2000-2010)
- Marine emissions of POA, hydrocarbons and sea-salt particles and marine SOA are on-line parameterized in the model (Myriokefalitakis et al., Adv. Met., 2010)
- The model considers the sulfur and ammonia chemistry and the oxidation of C_1-C_5 Volatile Organic Compounds (VOC) including isoprene as well as a simplified terpenes and aromatic chemistry (Myriokefalitakis et al., ACP, 2008)

Multiphase chemistry as outlined in Myriokefalitakis et al., Atmos. Chem. Phys., 2011

- Gas-particle partitioning for inorganics is solved using ISORROPIA II (Fountoukis and Nenes, 2007)
- On-line gas-phase chemistry and secondary aerosol formation calculations together with primary carbonaceous, dust & sea-salt particles (Tsigaridis et al., ACP, 2006; Tsigaridis& Kanakidou Atmos. Environ., 2007)

Comparison with satellite observations– CHOCHO



at least 20 Tg/yr Oceanic Fluxes

Myriokefalitakis et al., ACP, 2008

Chemical Sources and Sinks of CHOCHO in TM4-ECPL

gas-phase

Table 1. Reactions taken into account in the TM4-ECPL model and describing CHOCHO production and destruction and the references for the rate coefficients, k, used in the model.

a)

Number	Reactions (Gas phase chemical production)	k	Reference
1	Isoprene+OH→0.03CHOCHO+products	2.7 E-11exp(390/T)	IUPAC (2006)
2	$C_2H_4+O_3+2O_2\rightarrow$0.0044CHOCHO+products	9.1 E-15exp(−2580/T)	IUPAC (2006)
3	$C_3H_6+O_3+2O_2\rightarrow$0.05CHOCHO+products	5.5 E-15exp(−1880/T)	IUPAC (2006)
4	C_2H_2+OH→0.635CHOCHO+products	3 bodies reaction	IUPAC (2006)
5	Benzene+OH→0.36CHOCHO+products	2.47 E-12exp(207.0/T)	Calvert et al. (2002)
6	Toluene+OH→0.306CHOCHO+products	5.96 E-12	Atkinson (1994)
7	Xylene+OH→0.319CHOCHO+products	1.72 E-11	Average of ortho-, meta-, para-isomers
8	$HOCH_2CHO+OH+O_2\rightarrow CHOCHO+HO_2+H_2O$	2.2 E-12	IUPAC (2006)

BVOC

AVOC

b)

Number	Reactions (Gas phase chemical destruction)	k	Reference
1	$CHOCHO+OH\rightarrow 2CO+HO_2+H_2O$	2.8×10^{-12}exp(340/T)	Feierabend et al. (2008)
2	$CHOCHO+NO_3+O_2\rightarrow HNO_3+HO_2+2CO$	1.2 E-15	upper limit estimate by I. Barnes (personal communication, 2007)
3	$CHOCHO+h\nu\rightarrow 2HO_2+2CO$	J_{CHOCHO}	IUPAC (2006)

Myriokefalitakis et al., ACP 2008

aqueous-phase

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 $1\,mol^{-1}\,s^{-1}$. Reaction rates are taken from Lim et al. (2005), unless referred differently. Reactions rates are calculated as follows: $k=k_{298}\exp\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right]$

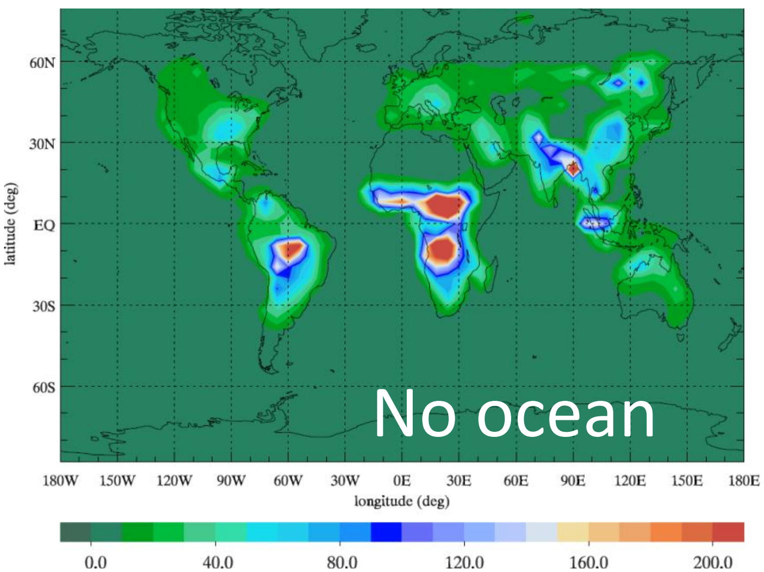
16	GLYAL + OH (+ O_2)	→	GLY + HO_2	1.0×10^{9}	1564 [d]
17	GLYAL + 2 OH (+ 2 O_2)	→	GLX + 2 HO_2 + 2 H_2O	5.0×10^{8}	1564 [d]
18	GLYAL + NO_3 (+ O_2)	→	GLX + HO_2 + NO_3^- + H^+	1.1×10^{7} [e]	
19	GLYAL + 2 NO_3 (+ O_2)	→	GLY + 2 NO_3^- + 2 H^+ + H_2O	5.5×10^{6} [g]	
20	GLY + OH (+ O_2)	→	GLX + HO_2 + H_2O	1.1×10^{9}	1564 [g]
21	GLY + OH	→	0.03GLX + 0.97 OXL + H_2O	3.1×10^{9} [h]	
22	GLY + NO_3 (+ O_2)	→	GLX + HO_2 + NO_3^- + H^+	6.3×10^{7} [f]	
23	GLY + $h\nu$/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] 2.4×10^{-4} (pH = 5) [j] 0.43 (pH = 7) [j]	

Myriokefalitakis et al., ACP 2011

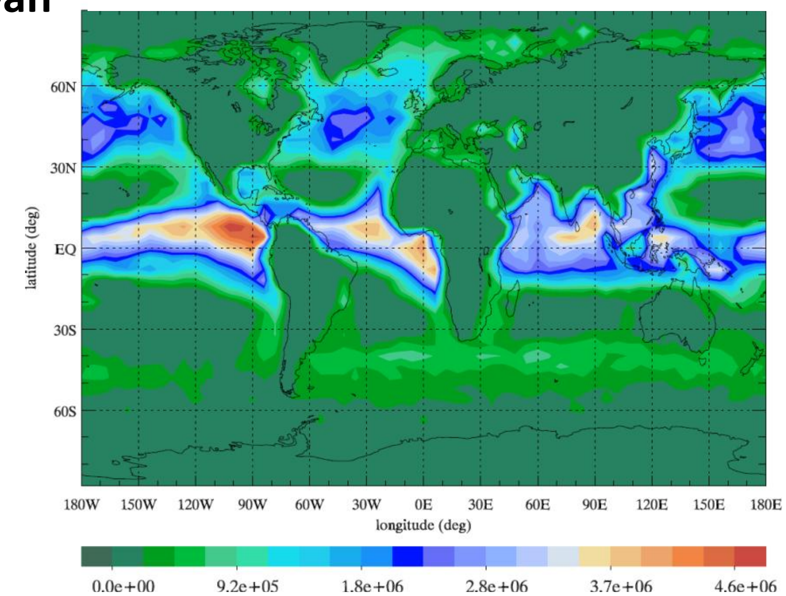
Oceanic Emission Contribution to CHOCHO

Annual mean

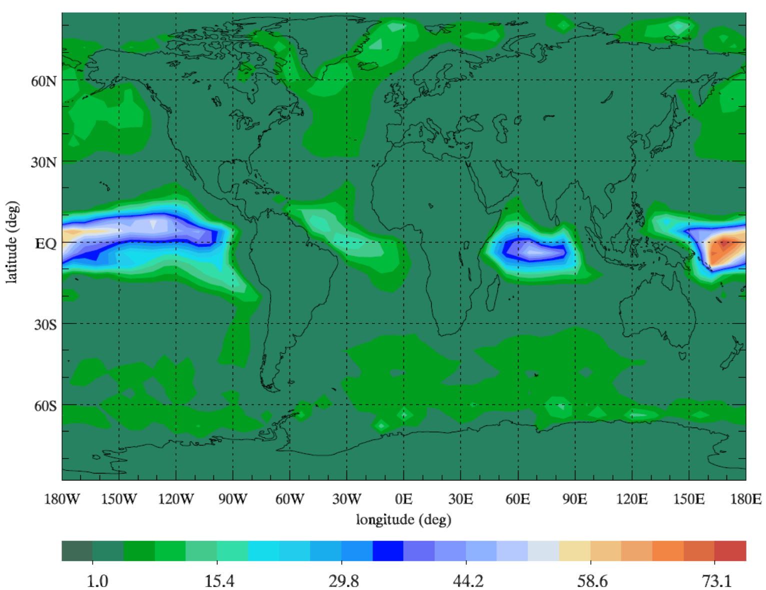
CHOCHO (pptv) surface



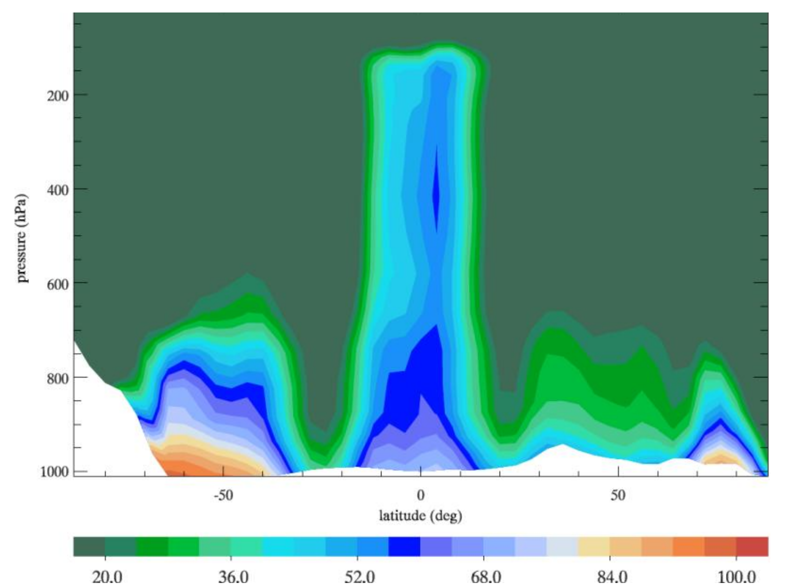
CHOCHO ocean source (kg/grid)



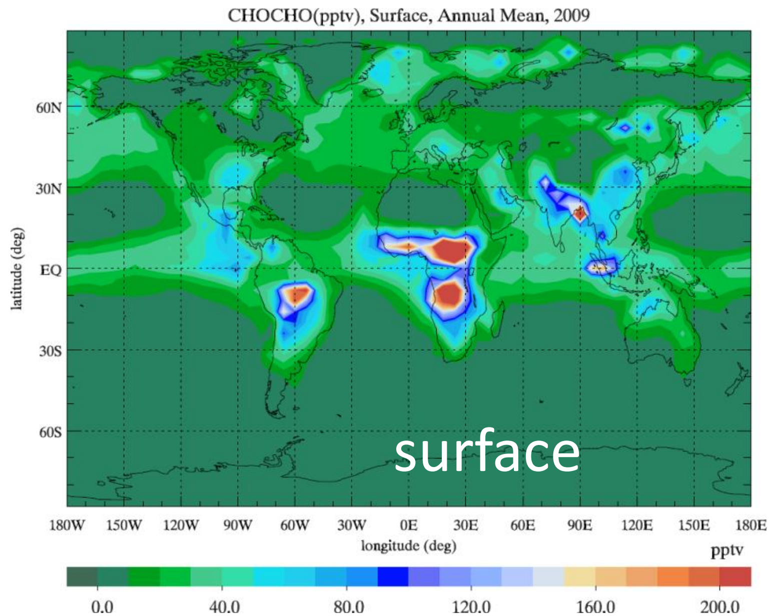
CHOCHO column ratio (0-500m) ocean/no_ocean

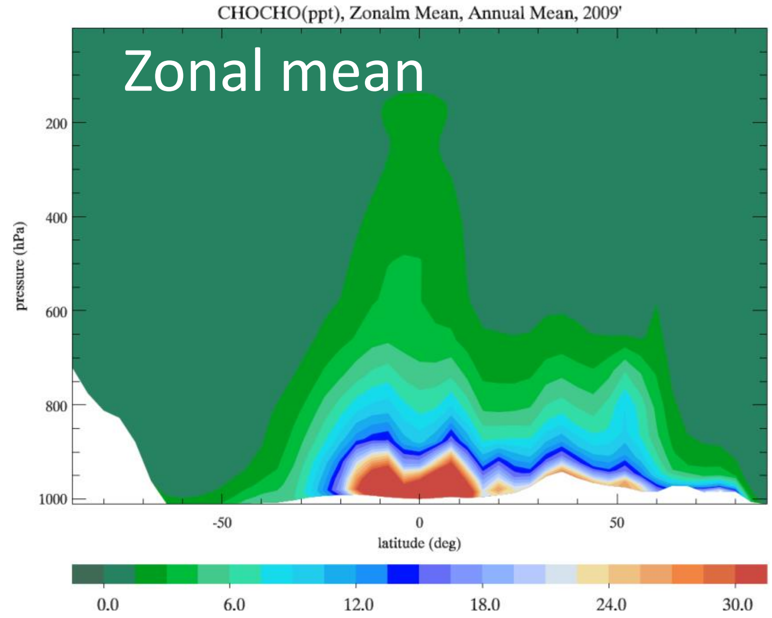


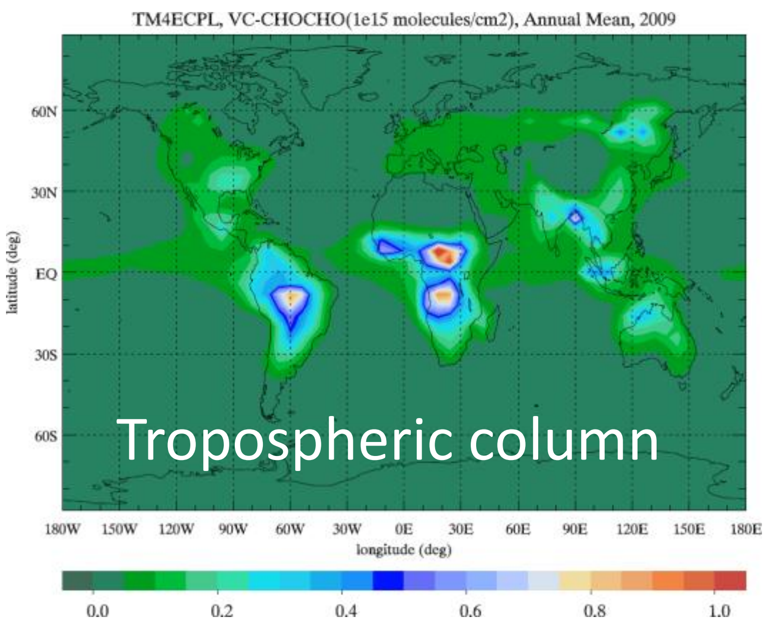
CHOCHO column ratio (0-500m) ocean/no_ocean zonal mean

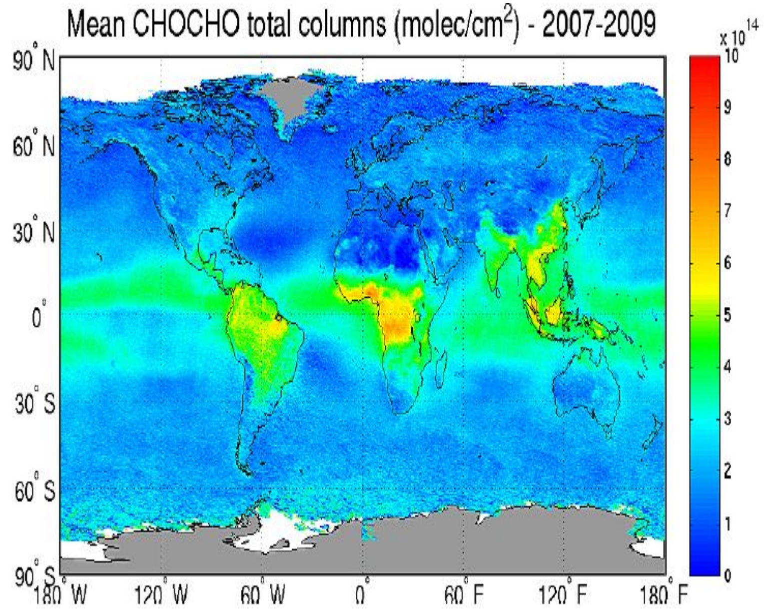


Global CHOCHO Distributions





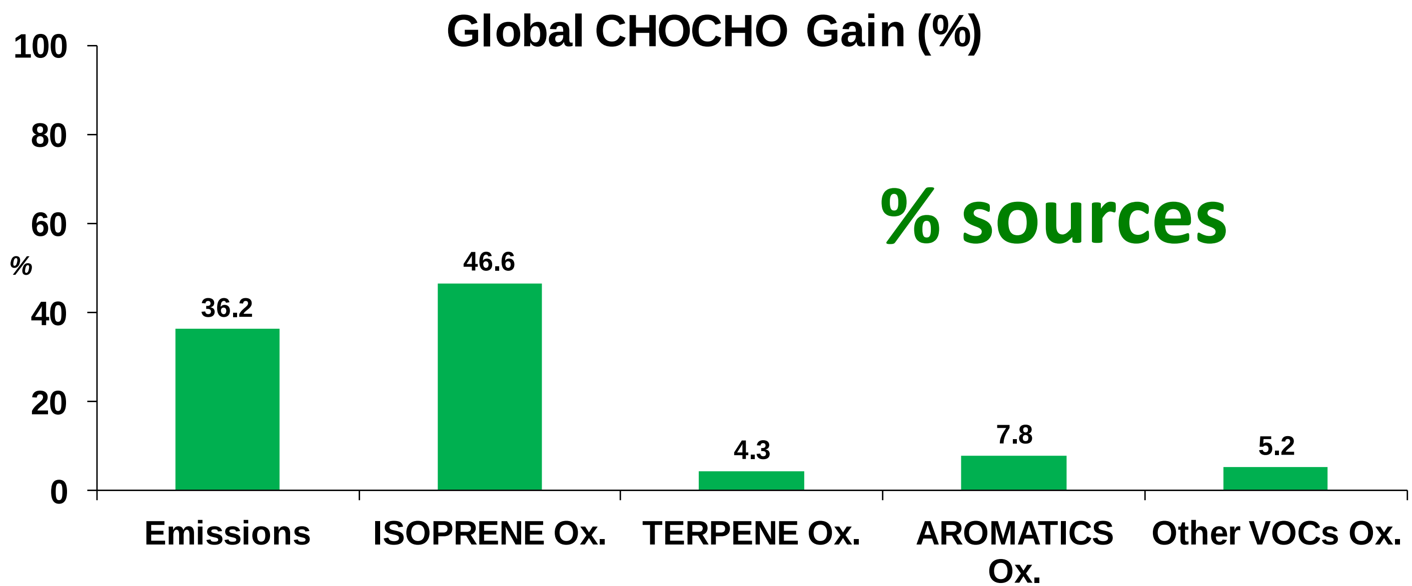




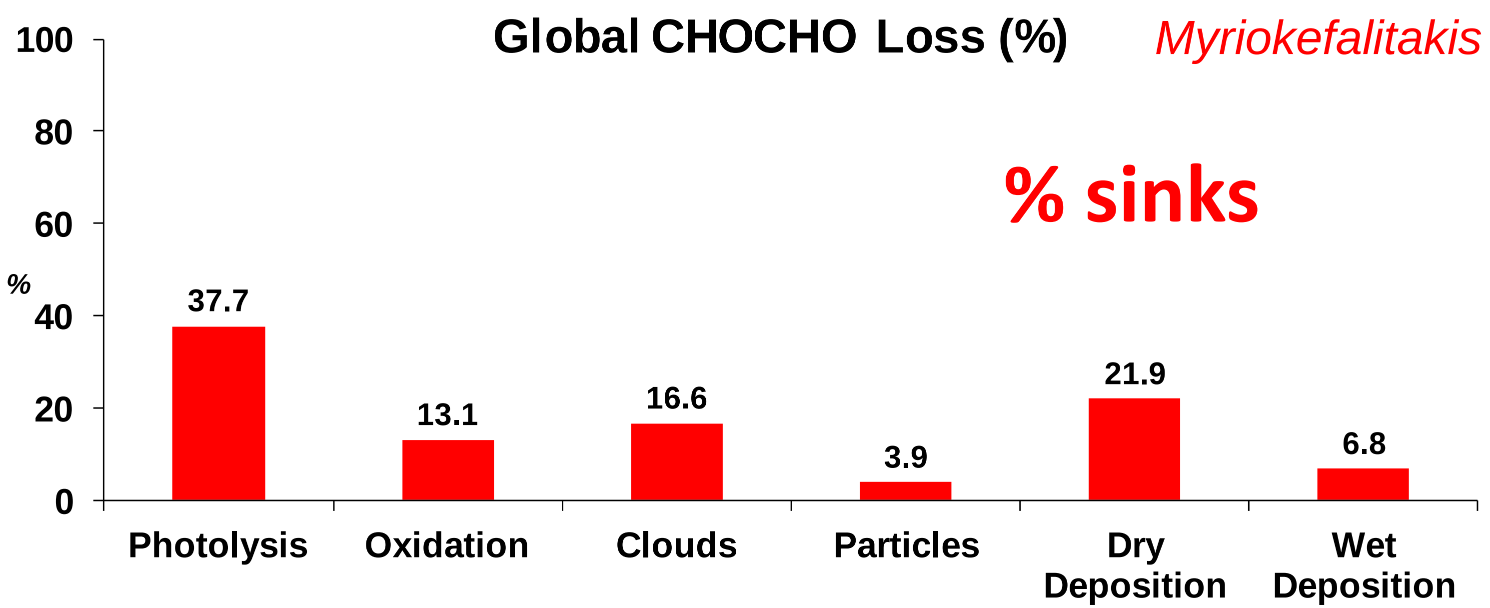
GOME 2- Satellite observations → at low cloud cover (<0.4)

Lerot et al ACP,10,12059, 2010

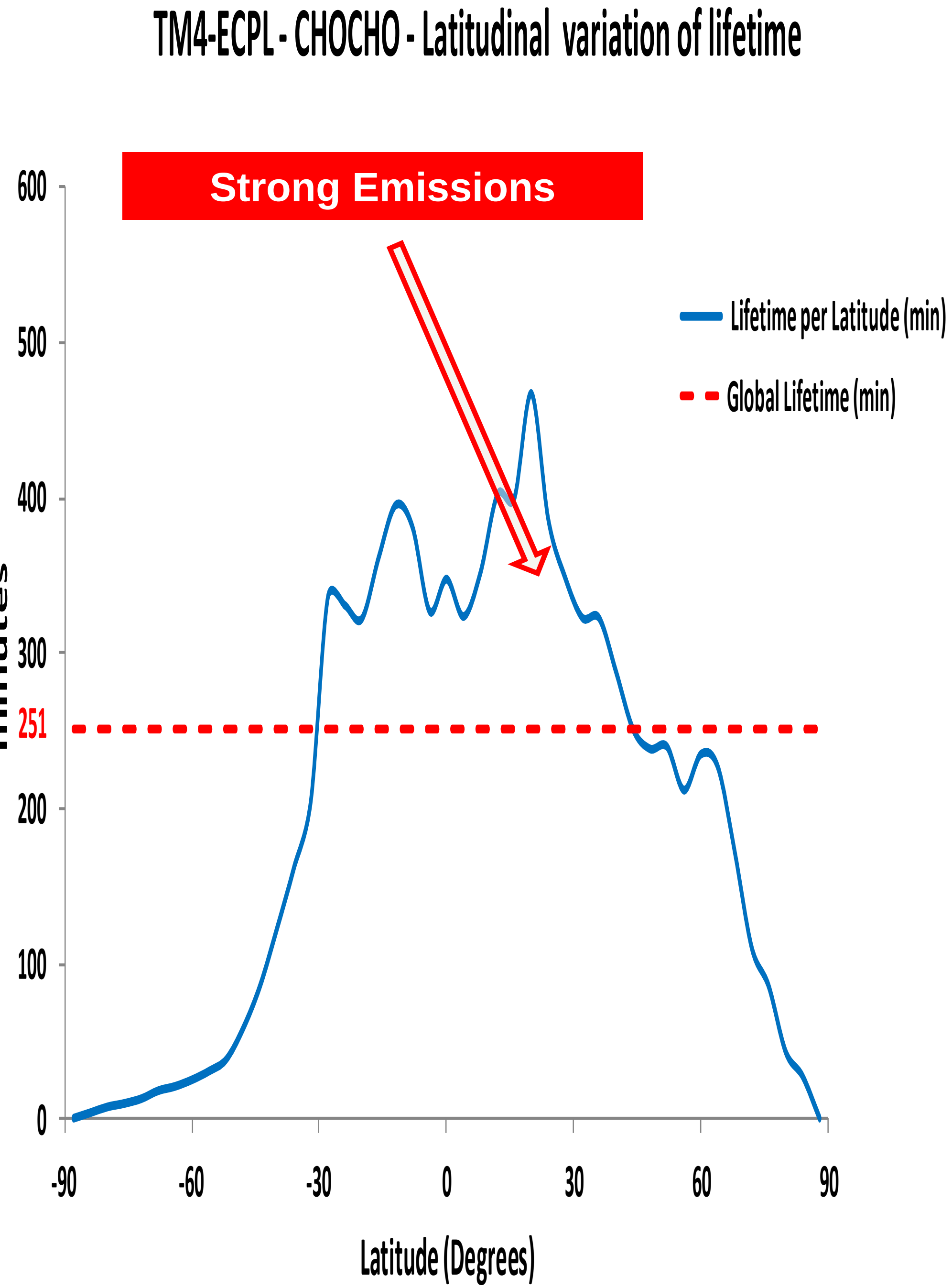
CHOCHO Budget Analysis

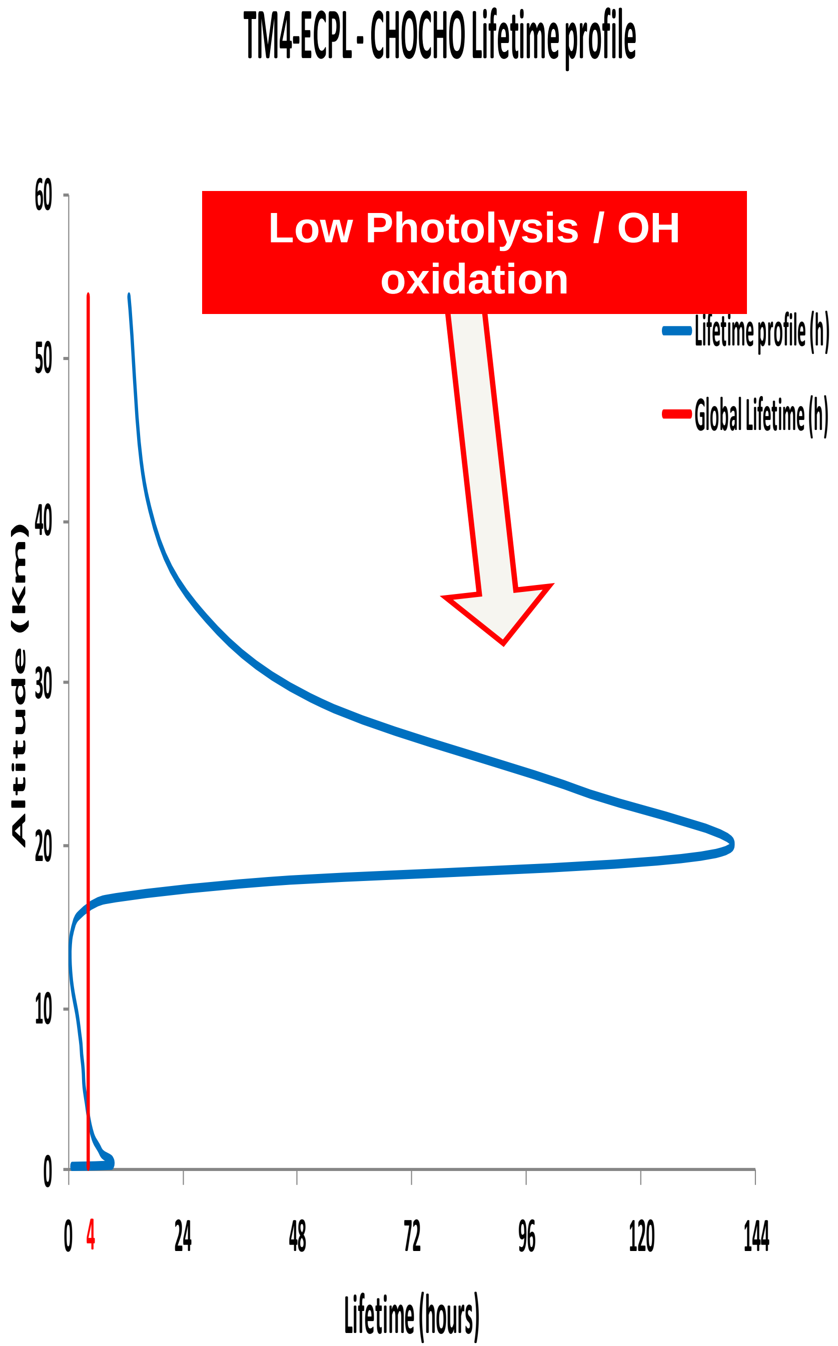


CHEM pro=	*~56*	*Tg CHOCHO/yr*	**TM4**
CHEM des=	*~48*	*Tg CHOCHO/yr*	**ECPL**



Myriokefalitakis et al., ACP, 2008

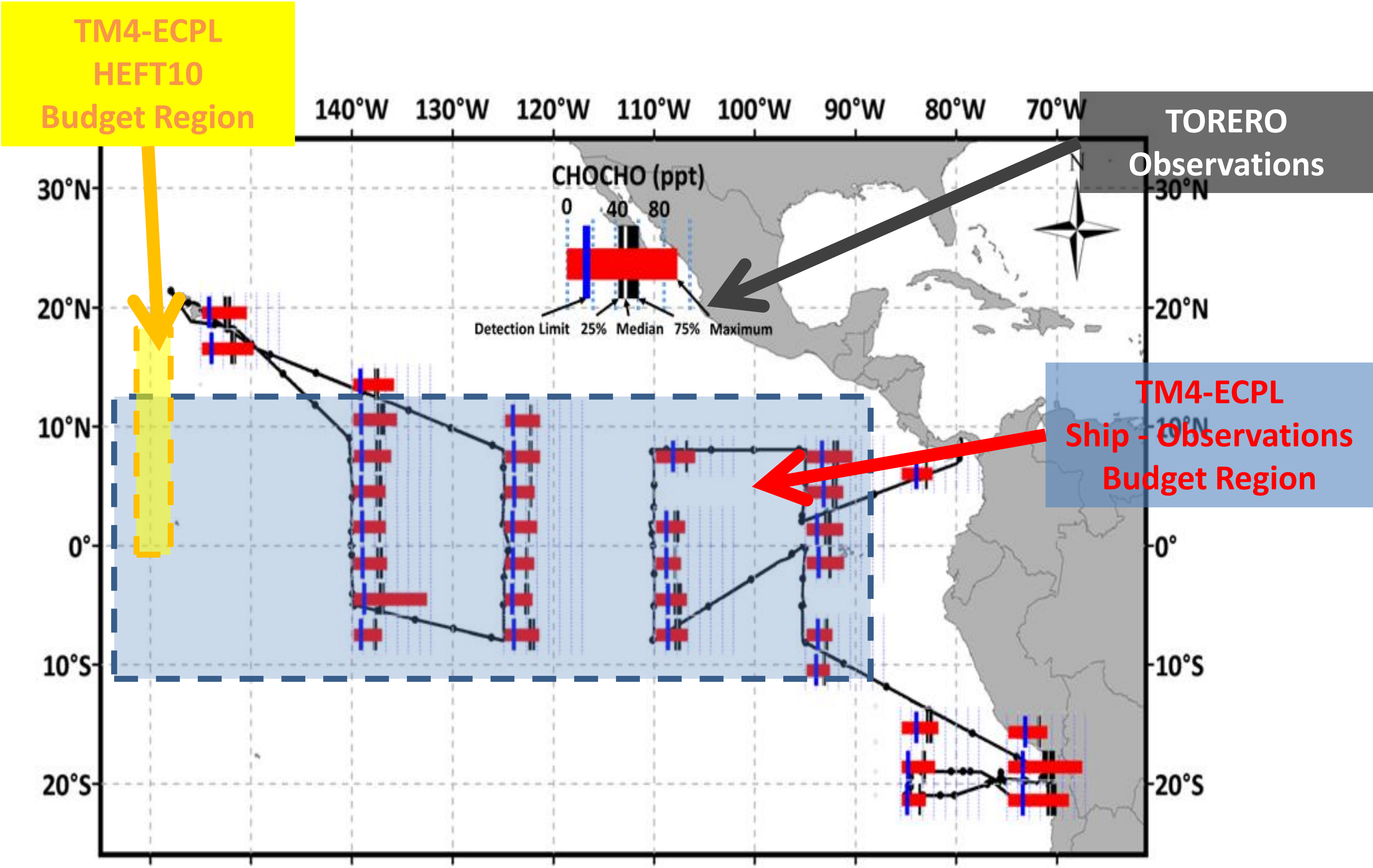

TM4-ECPL - CHOCHO - Latitudinal variation of lifetime
Strong Emissions
Lifetime per Latitude (min)
Global Lifetime (min)
600
500
400
300
251
200
100
0
-90
-60
-30
0
30
60
90
Latitude (Degrees)


TM4-ECPL - CHOCHO Lifetime profile
Low Photolysis / OH oxidation
Lifetime profile (h)
Global Lifetime (h)
Altitude (Km)
60
50
40
30
20
10
0
0
4
24
48
72
96
120
144
Lifetime (hours)

TORERO questions to be investigated

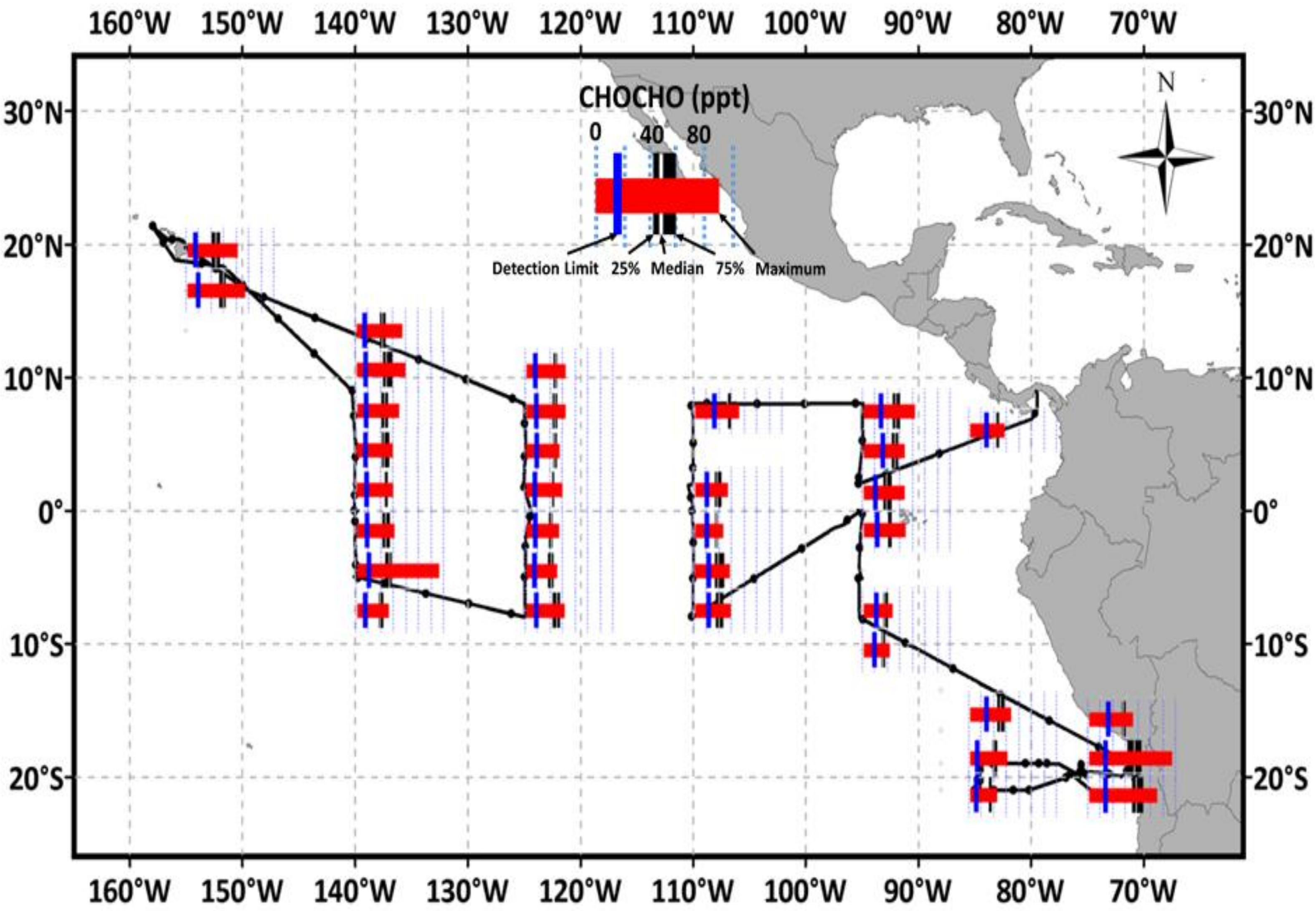
1. Atmospheric composition in MBL and comparison to that in FT
2. CHOCHO formation in the FT
3. Vertical distribution and lifetime of CHOCHO in the MBL and in the FT (spatial and temporal variability)
4. CHOCHO formation from VOC gas phase oxidation vs heterogeneous reactions sources.
5. Explanation of the discrepancies between global model simulations and satellites (ocean source?)
6. How relevant are ocean sources of OVOC on global scales?

TM4-ECPL Studied Regions



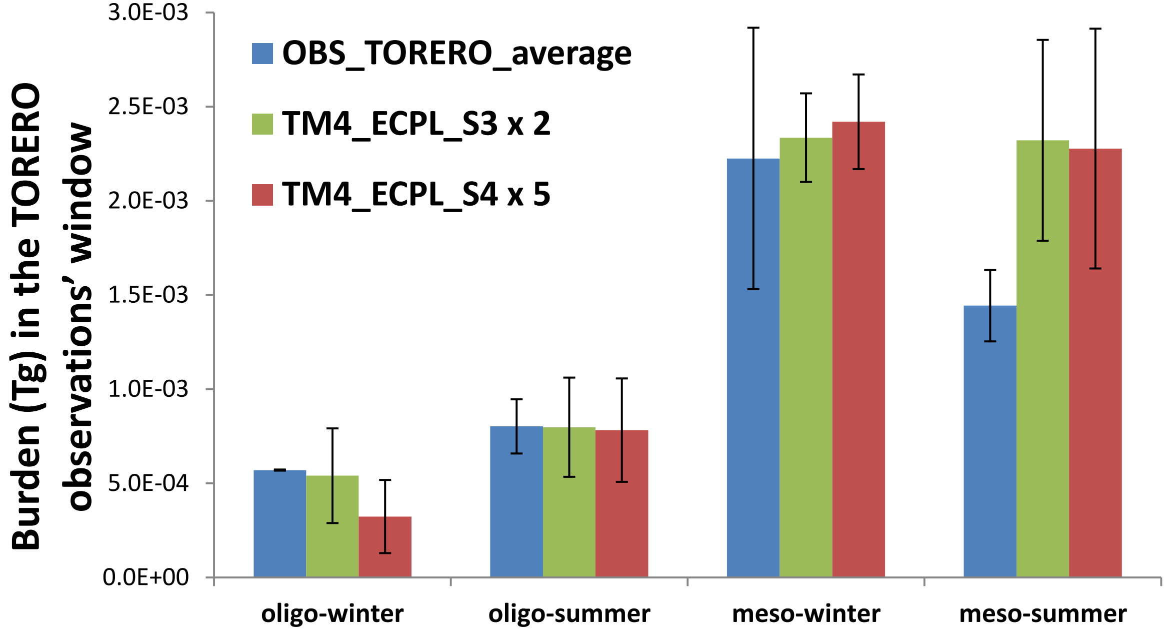
For this study, all budget analyses have been performed based on imulations in 6°x4° horizontal resolution (longitude x latitude) in 34 vertical hybrid layers from surface up to 0.1 hPa

Cruises Calculations



CHOCHO burdens
derived from Observations and from TM4-ECPL model

up to 1.8km in the oligotrophic & mesotrophic TORERO regions

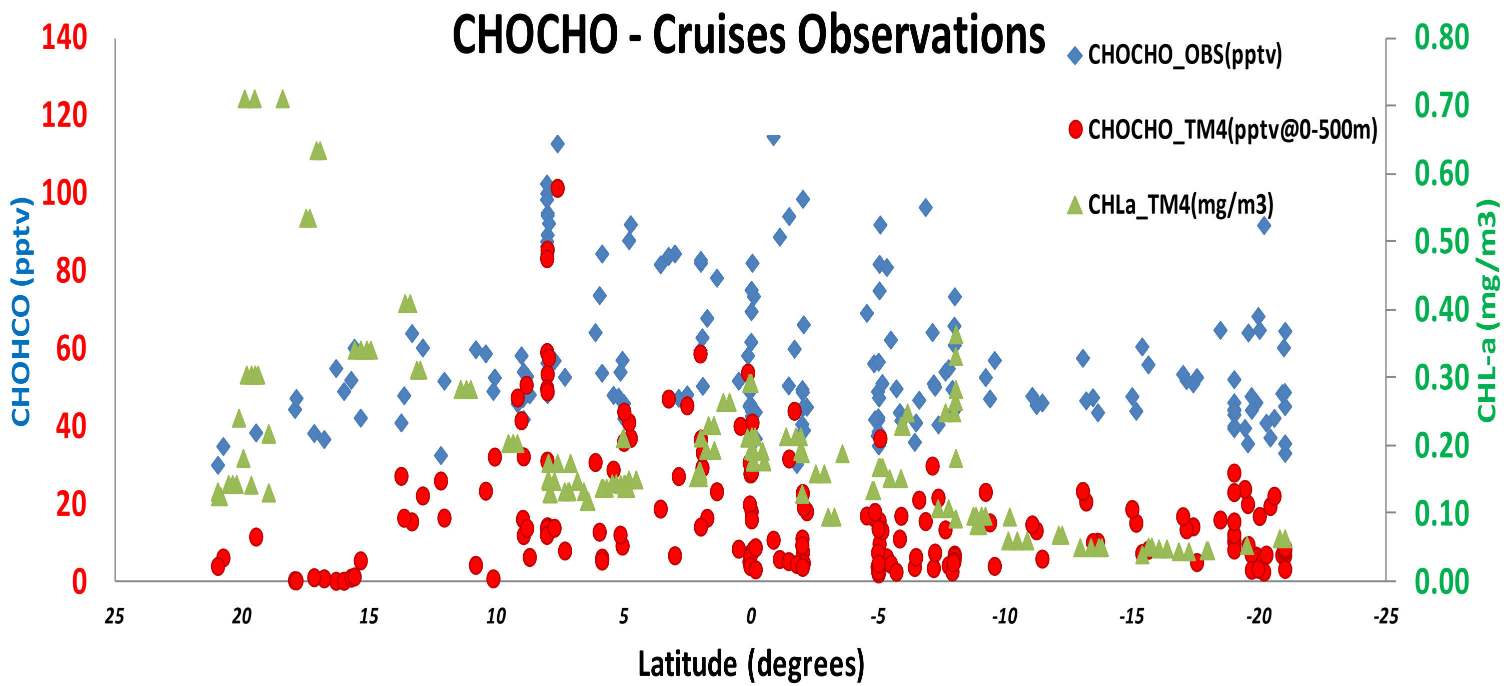


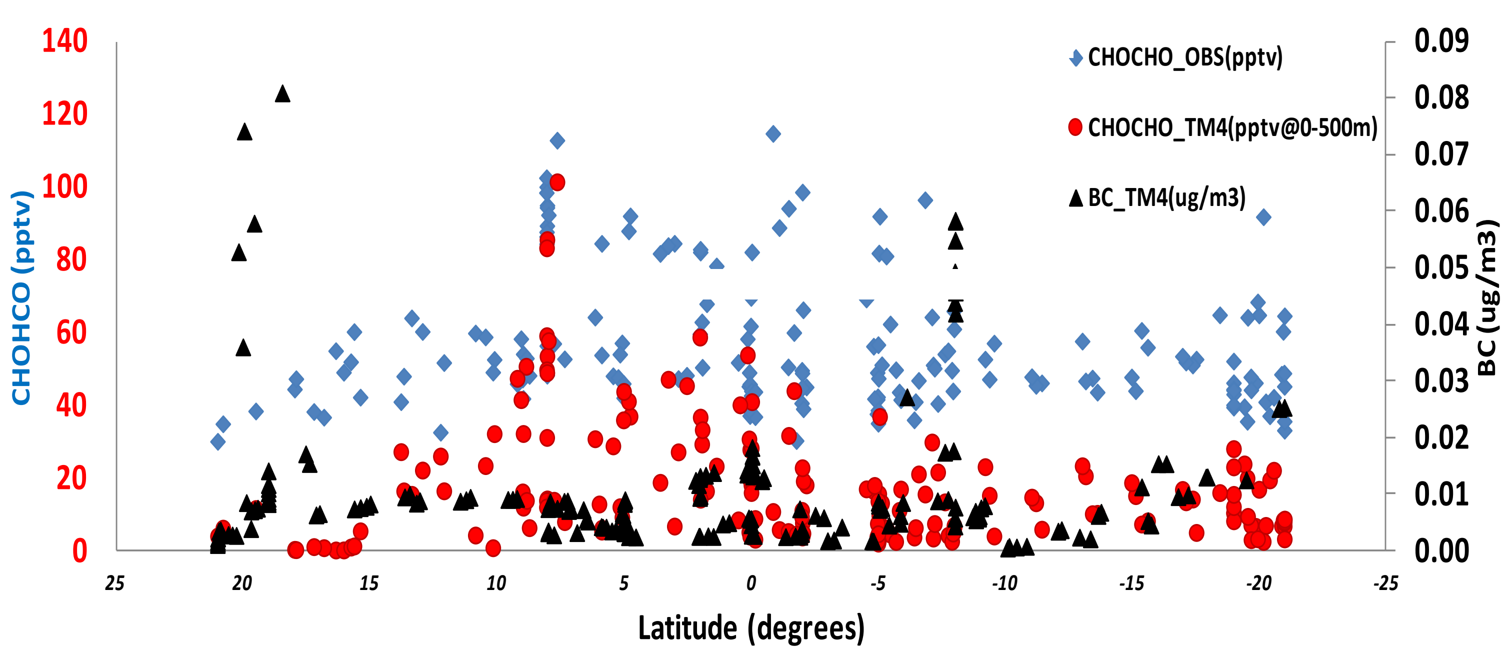
CHLa _Region - Period	OBS_TORERO (Average)	TM4_ECPL_S3 (24h Fluxes)	TM4_ECPL_S4 (Daylight Fluxes)
oligo-winter (Tg)	*5.7E-04 ± 3.0E-06*	*2.70E-04 ± 1.26E-04*	*6.5E-05 ± 3.9E-05*
oligo-summer (Tg)	*8.0E-04 ± 1.4E-04*	*3.99E-04 ± 1.32E-04*	*1.6E-04 ± 5.5E-05*
meso-winter (Tg)	*2.2E-03 ± 6.9E-04*	*1.17E-03 ± 1.18E-05*	*4.8E-04 ± 5.0E-05*
meso-summer (Tg)	*1.4E-03 ± 1.9E-04*	*1.16E-03 ± 2.67E-04*	*4.6E-04 ± 1.3E-04*

TM4-ECPL global model- Myriokefalitakis , Kanakidou

Cruises

CHOCHO Comparisons vs TM4-ECPL burdens up to 500m + Simulated land and ocean tracers

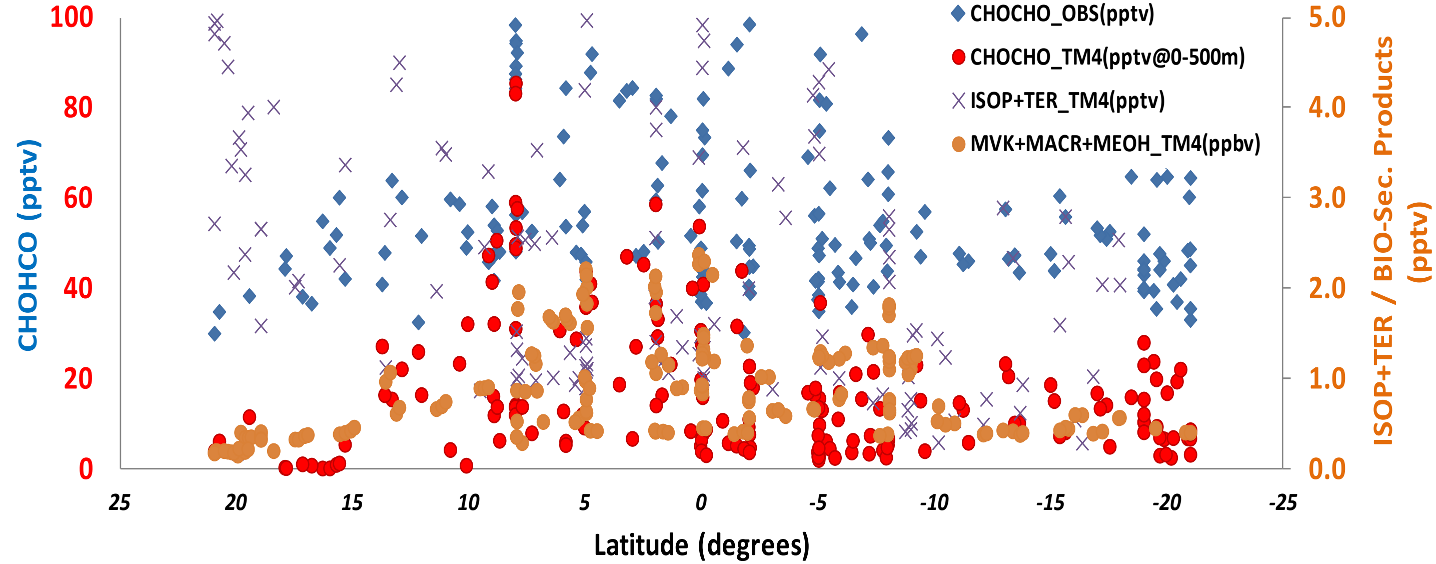


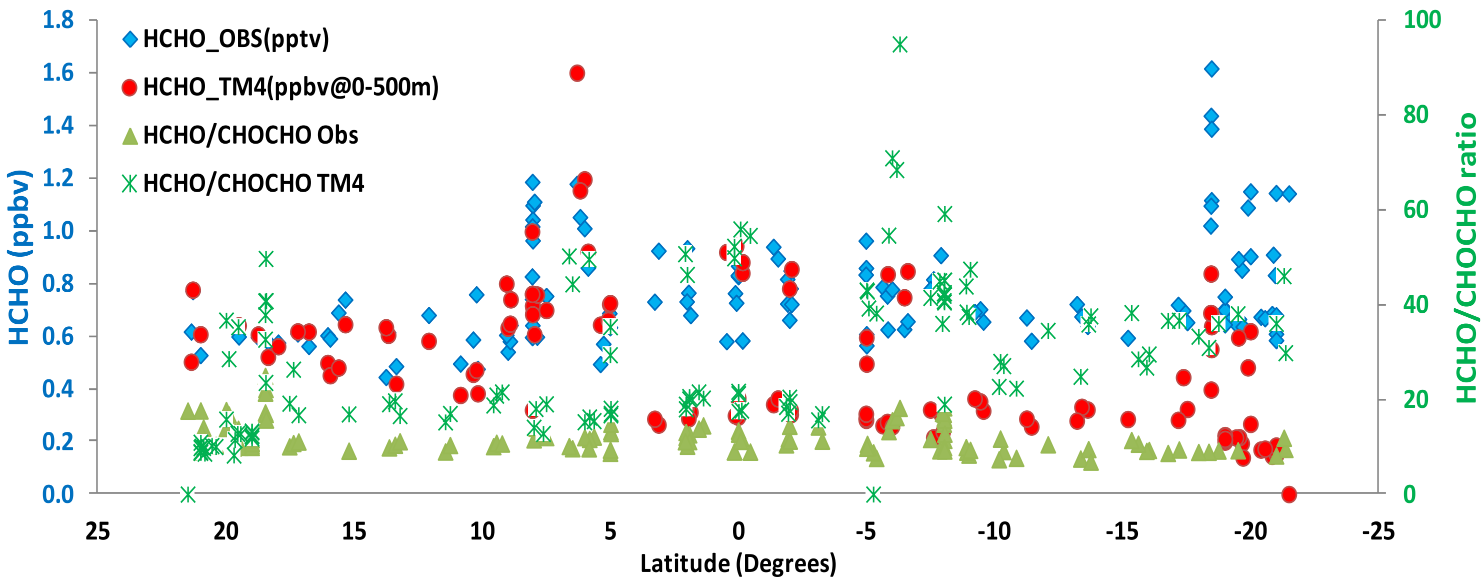


TM4-ECPL simulations in 3°x2° (longitude x latitude) & 34 vertical hybrid layers from surface up to 0.1hPa with 20 Tg/yr Global Oceanic Fluxes up to 1.8 Km for 24h integration

Cruises

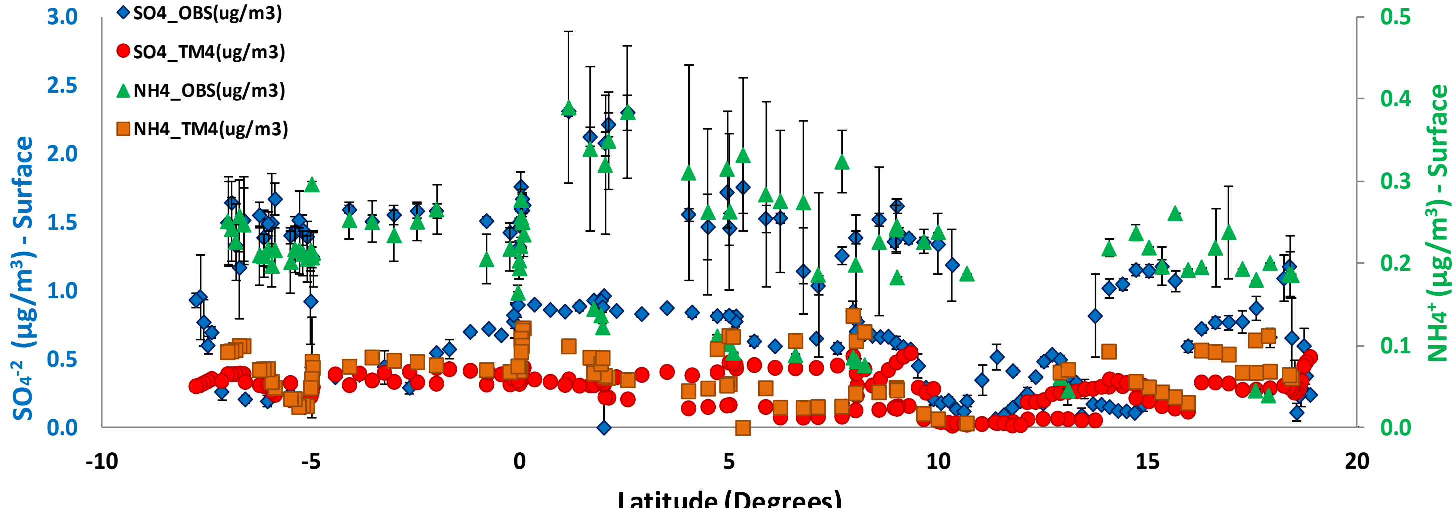
CHOCHO Comparisons vs TM4-ECPL burdens up to 500m + Simulated land and ocean tracers

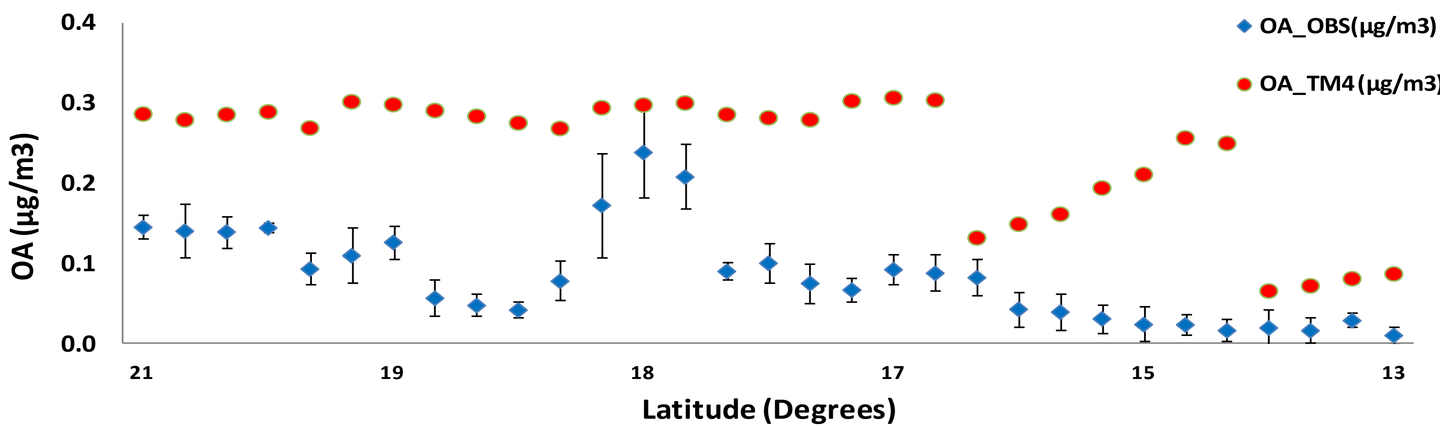


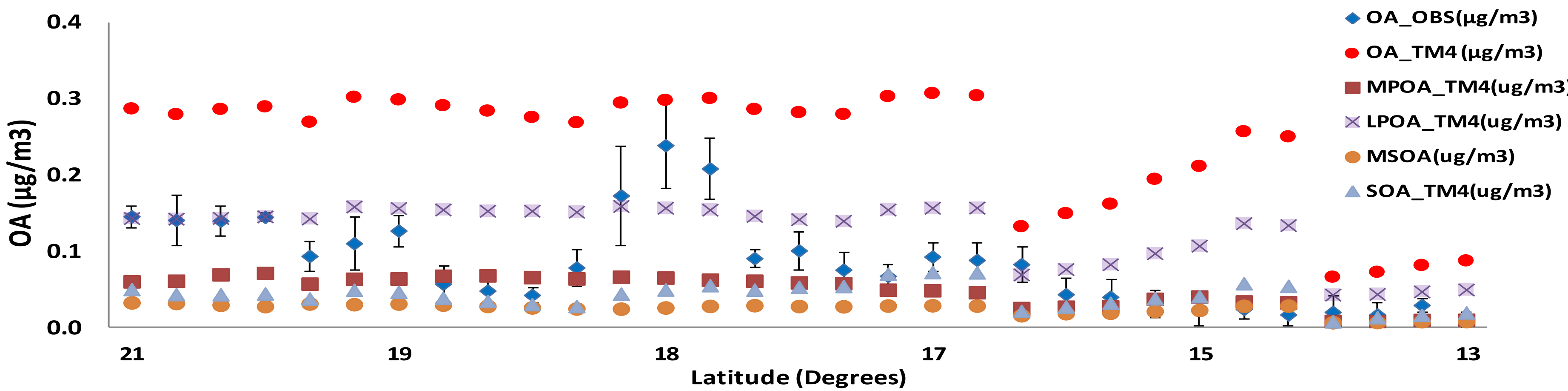


TM4-ECPL simulations in 3°x2° (longitude x latitude) & 34 vertical hybrid layers from surface up to 0.1hPa with 20 Tg/yr Global Oceanic Fluxes up to 1.8 Km for 24h integration

Cruises
PM Comparisons with TM4-ECPL simulations

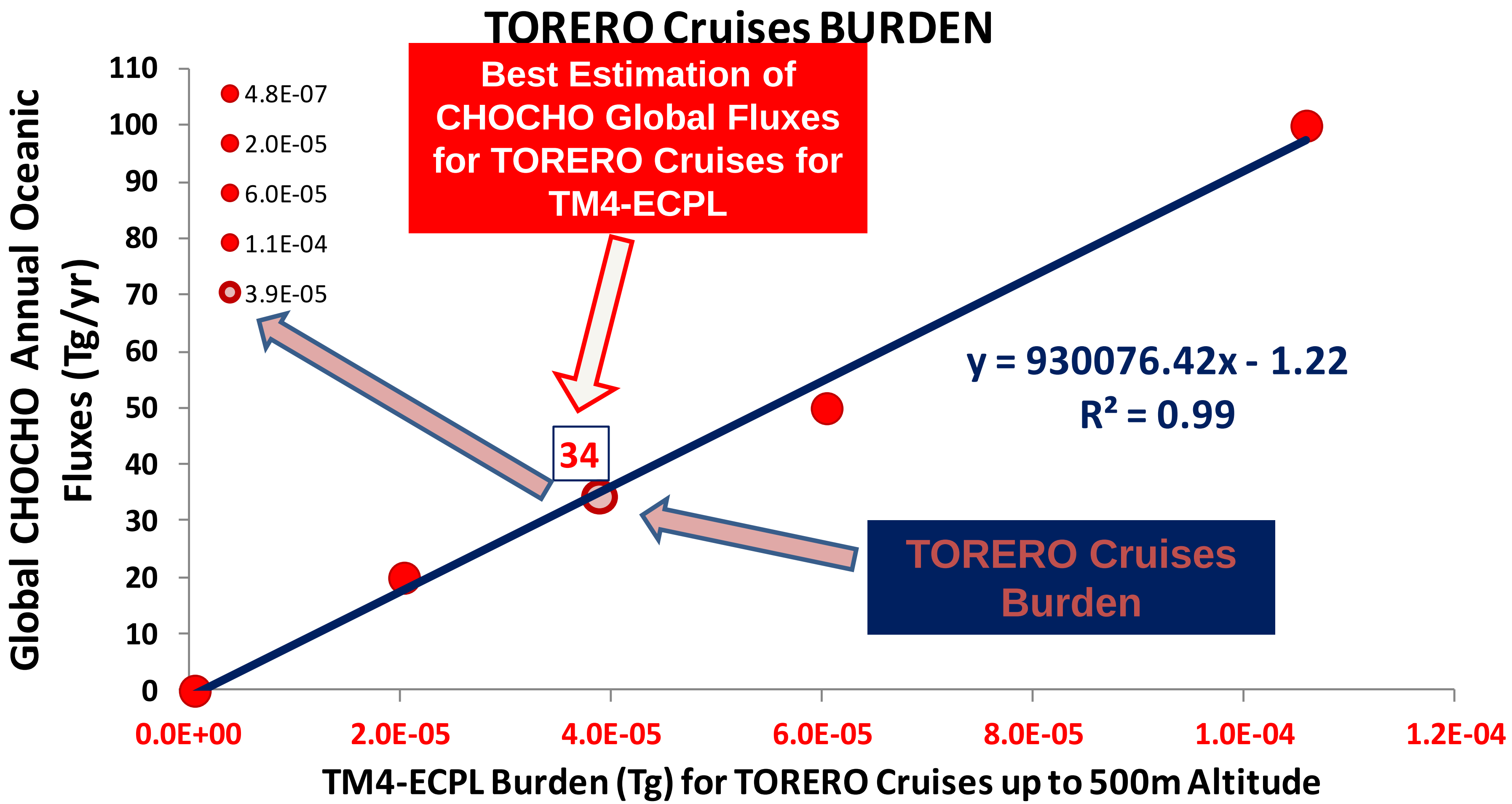




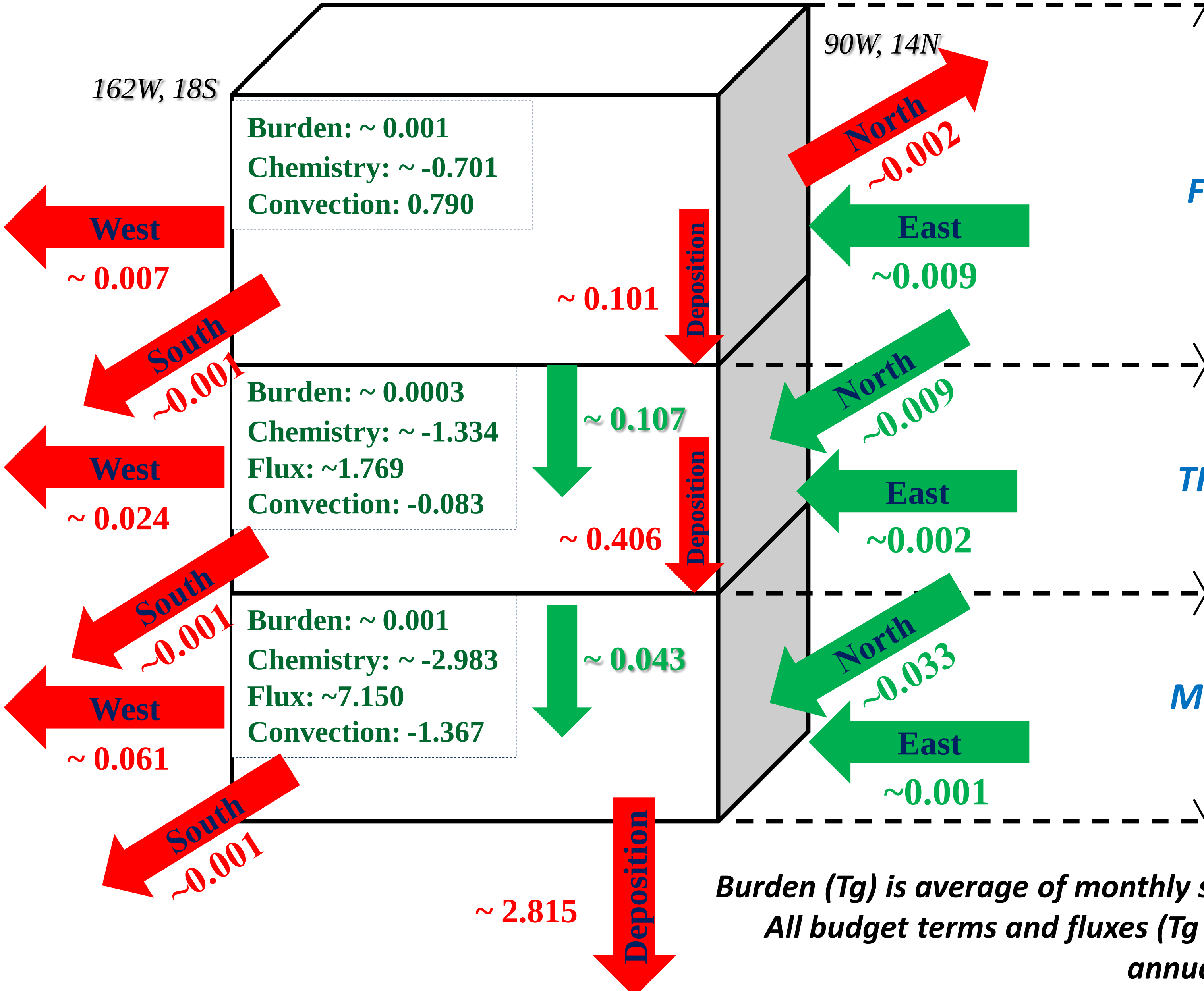


TM4-ECPL TORERO Cruises Simulations

Simulation	Description
S0	•*Without oceanic CHOCHO flux*
S1	•*Base Case - 20 Tg yr^{-1} CHOCHO oceanic flux from surface up to 1.8 Km*
S2	•*50 Tg yr^{-1} CHOCHO oceanic flux from surface up to 1.8 Km*
S3	•*100 Tg yr^{-1} CHOCHO oceanic flux from surface up to 1.8 Km*
S4	•*Best Case - 34 Tg yr^{-1} CHOCHO oceanic flux from surface up to 1.8 Km*

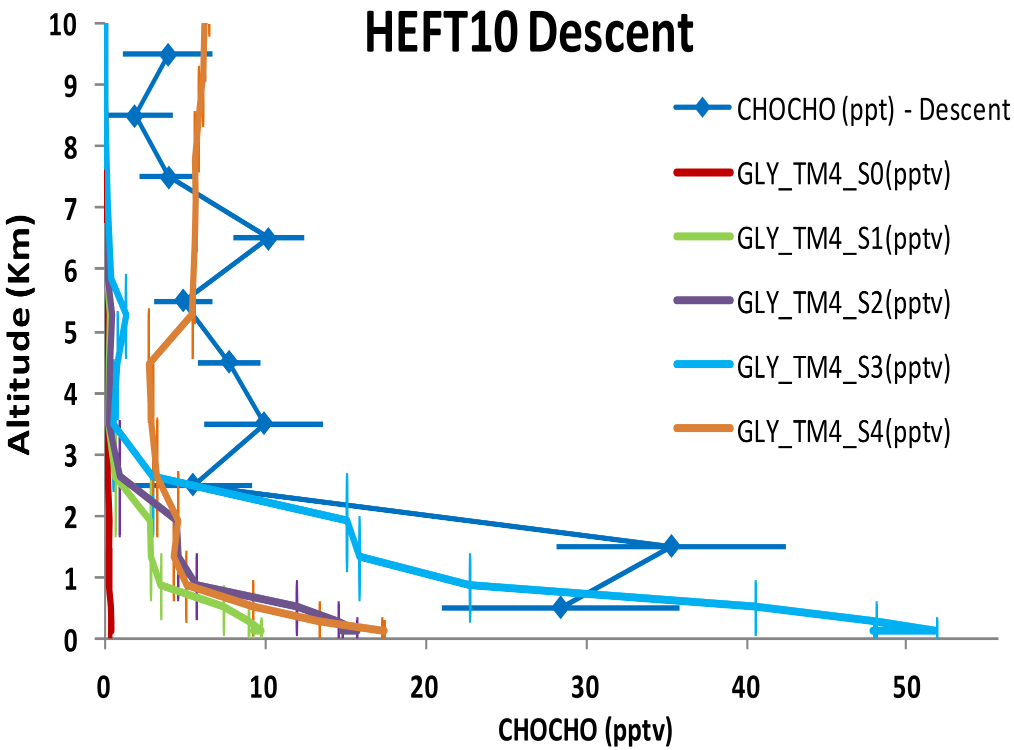


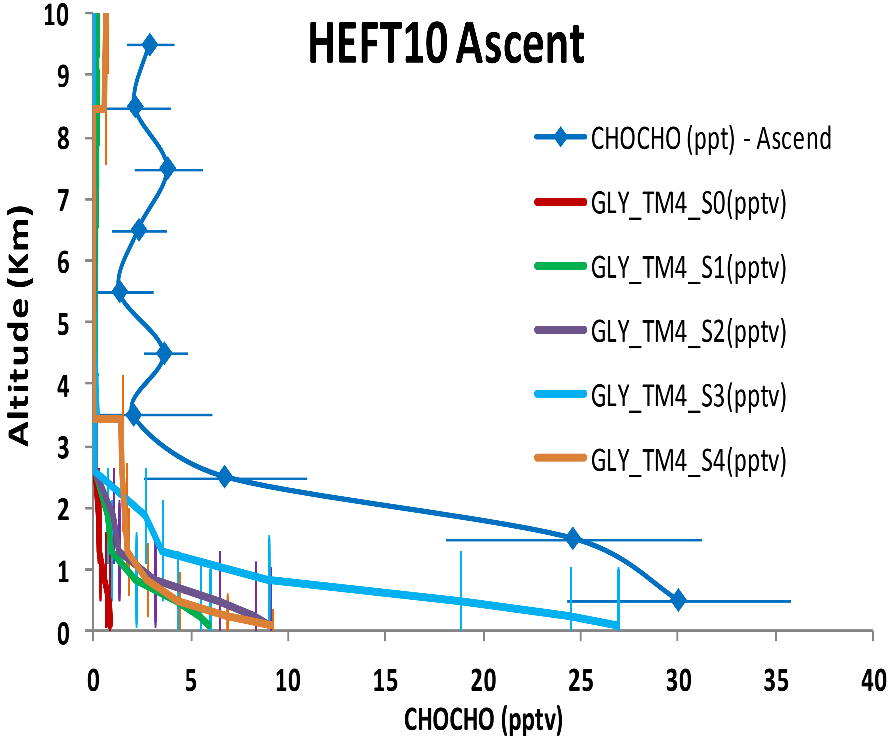
CHOCHO Schematic Budget for 2009 on TORERO Cruises Window for S4 Simulation (34 Tg Ocean GLY yr^{-1})



Burden (Tg) is average of monthly samples. All budget terms and fluxes (Tg yr^{-1}) are annual totals.

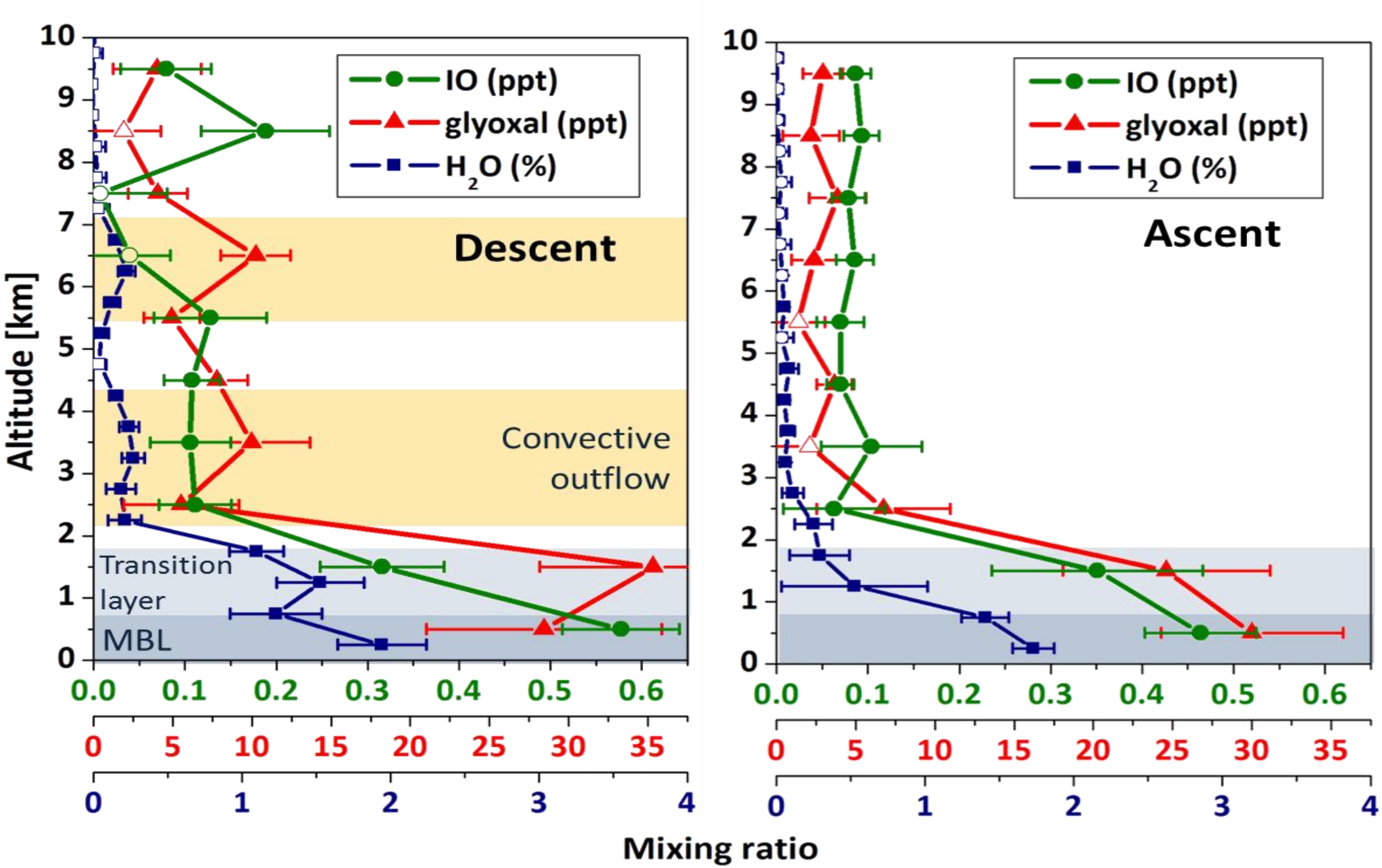
CHOCHO Validation of HEFT10 –Contribution of Fluxes Strength



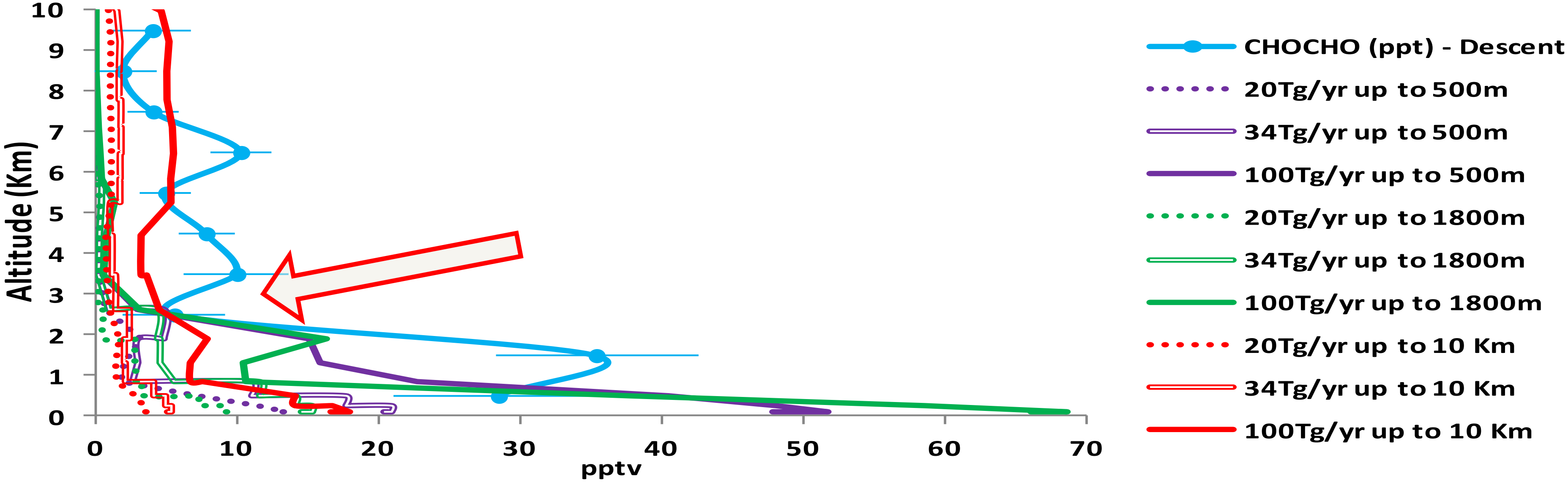


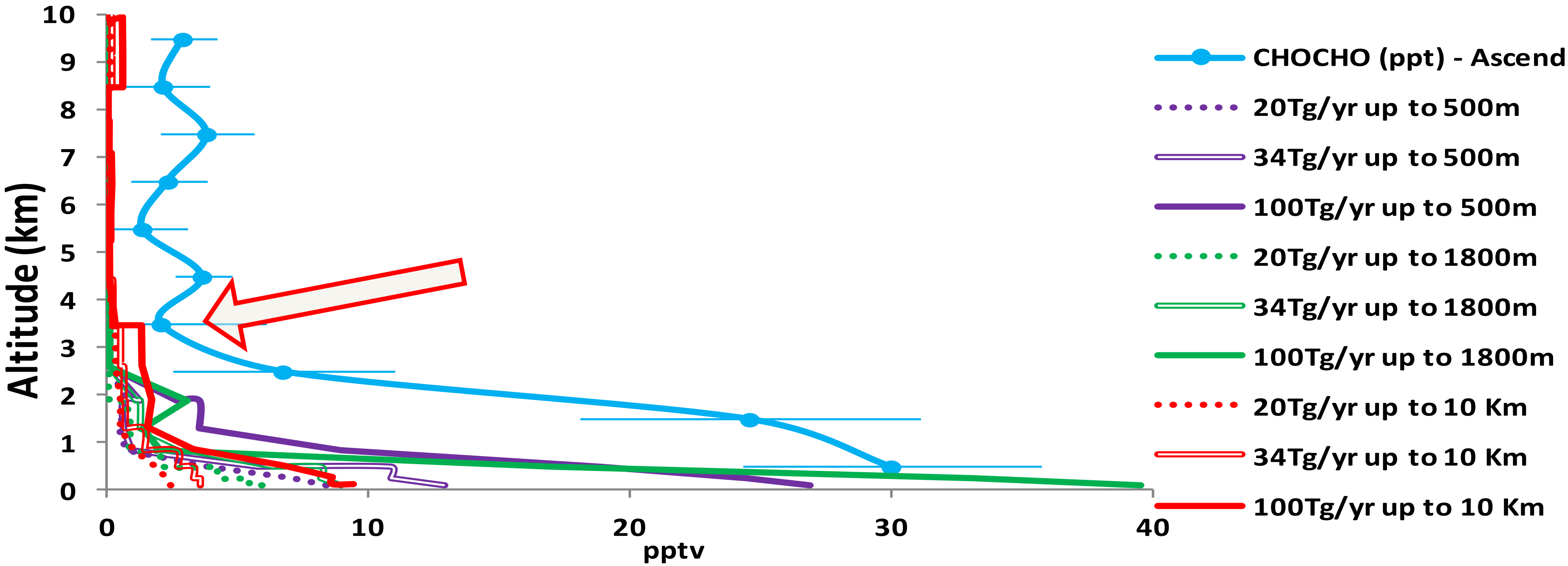
Simulations**	Description
S0	***without CHOCHO ocean fluxes***
S1	***with 20 Tg/yr CHOCHO ocean fluxes up to 1.8 Km (homogenously distributed at model's levels) - Published case scenario (see Myriokefalitakis et al., Adv. Meteor., 2010, doi:10.1155/2010/939171)***
S2	***with 34 Tg/yr CHOCHO ocean fluxes up to 1.8 Km (homogenously distributed at model's levels) - Best case scenario based on ship observation - TM4-ECPL comparison***
S3	***with 100 Tg/yr CHOCHO ocean fluxes up to 1.8 Km (homogenously distributed at model's levels) - Top estimate scenario***

Flights Calculations

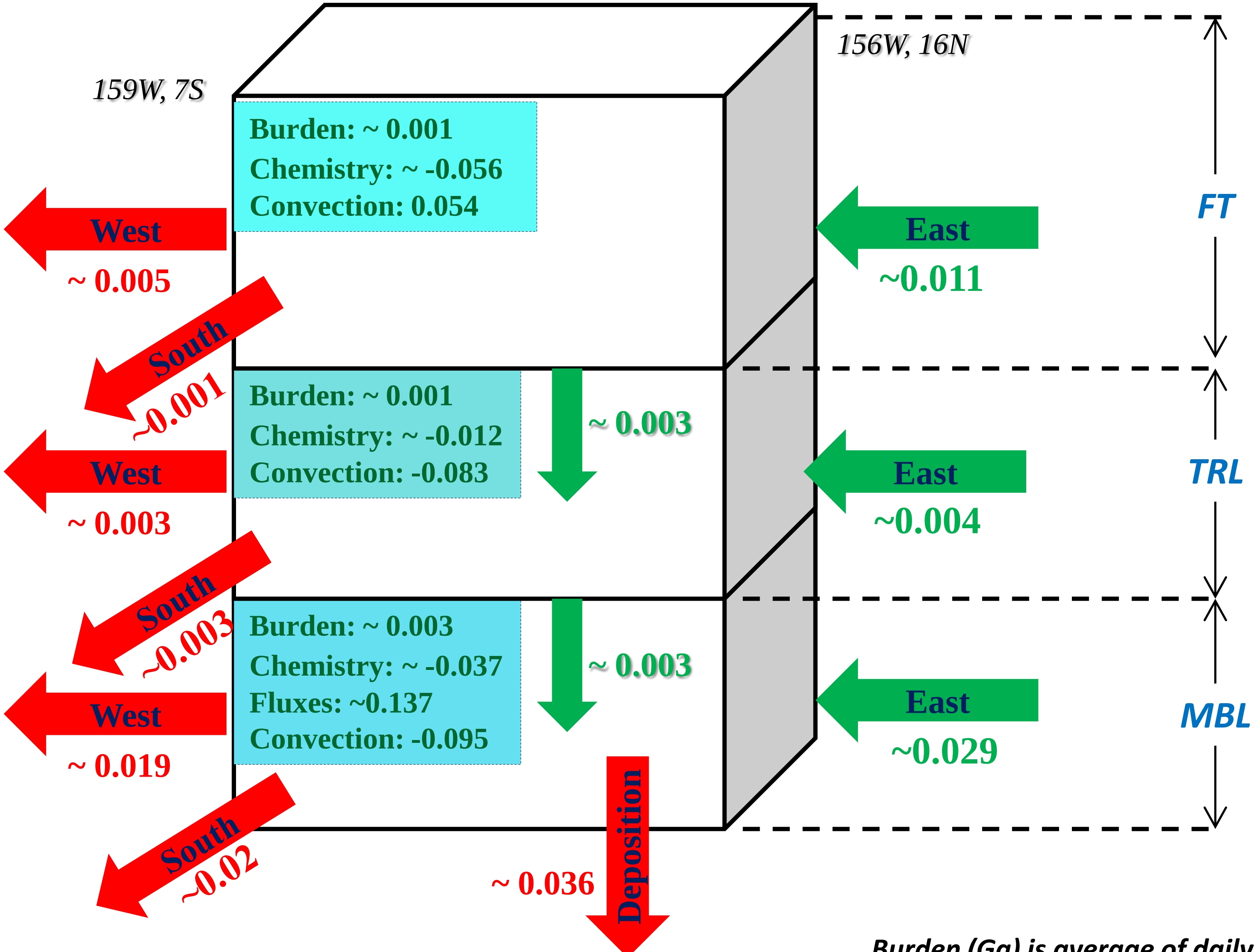


CHOCHO Validation of HEFT10 – Vertical Contribution of Fluxes



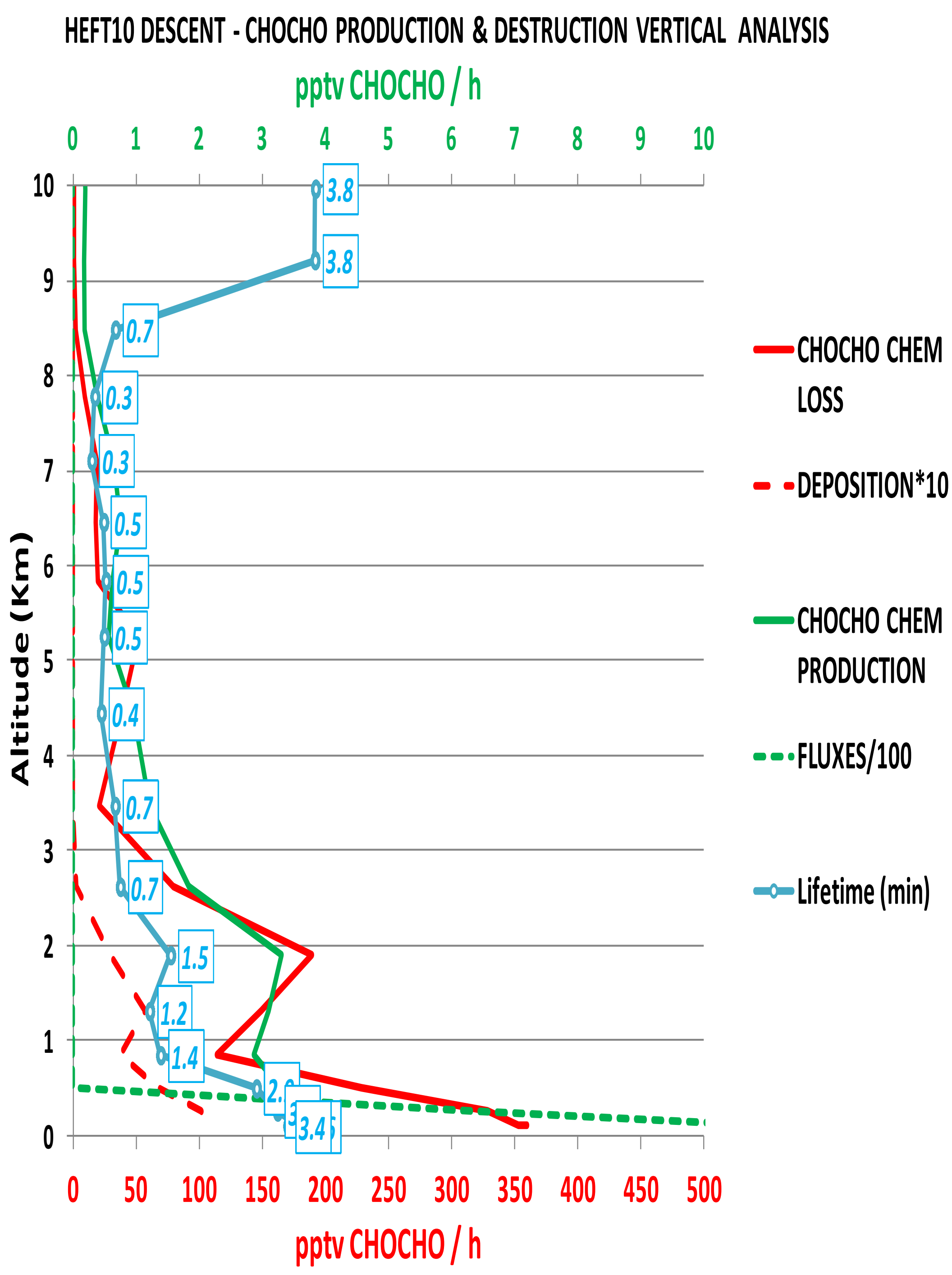


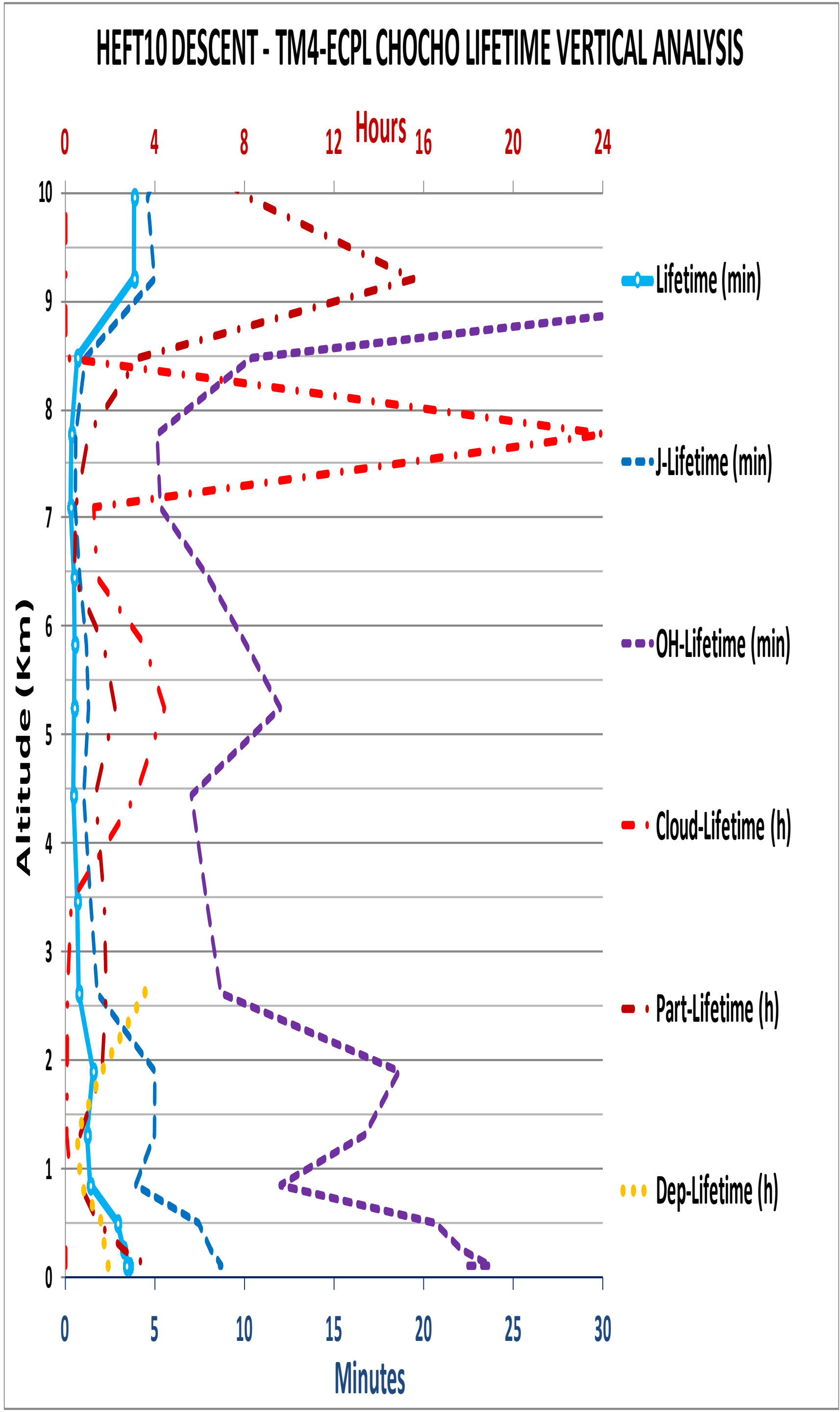
CHOCHO Schematic Budget for January 29-30-31 2010 on TORERO HEFT10 Domain

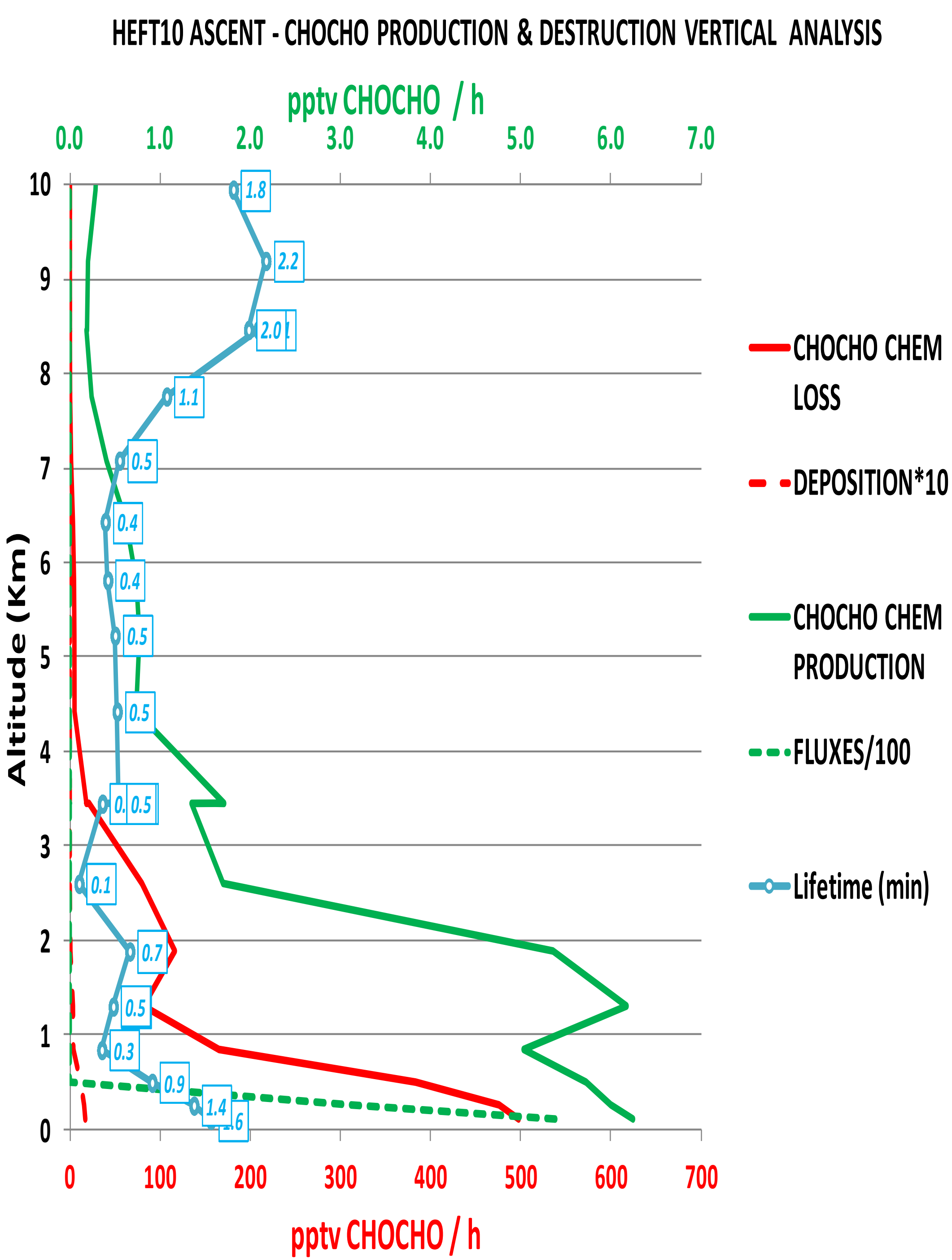


Burden (Gg) is average of daily samples.

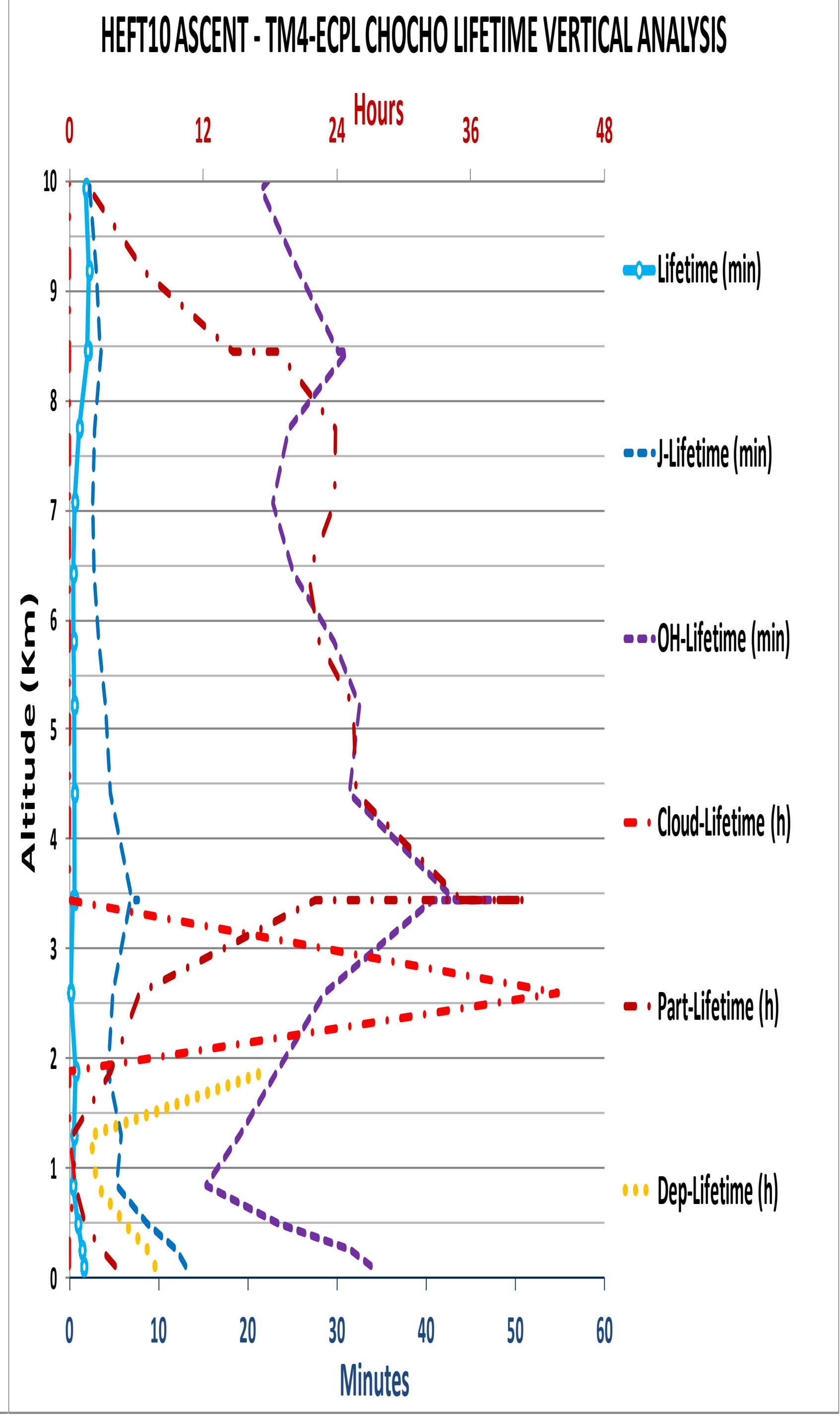
All budget terms and fluxes (Gg d^{-1}) are daily totals.


HEFT10 DESCENT - CHOCHO PRODUCTION & DESTRUCTION VERTICAL ANALYSIS
pptv CHOCHO / h
Altitude (Km)
pptv CHOCHO / h
CHOCHO CHEM LOSS
DEPOSITION*10
CHOCHO CHEM PRODUCTION
FLUXES/100
Lifetime (min)


HEFT10 DESCENT - TM4-ECPL CHOCHO LIFETIME VERTICAL ANALYSIS
Hours
Altitude (Km)
Minutes
Lifetime (min)
J-Lifetime (min)
OH-Lifetime (min)
Cloud-Lifetime (h)
Part-Lifetime (h)
Dep-Lifetime (h)



HEFT10 ASCENT - CHOCHO PRODUCTION & DESTRUCTION VERTICAL ANALYSIS
pptv CHOCHO / h
Altitude (Km)
pptv CHOCHO / h
CHOCHO CHEM LOSS
DEPOSITION*10
CHOCHO CHEM PRODUCTION
FLUXES/100
Lifetime (min)



HEFT10 ASCENT - TM4-ECPL CHOCHO LIFETIME VERTICAL ANALYSIS
Hours
Altitude (Km)
Minutes
Lifetime (min)
J-Lifetime (min)
OH-Lifetime (min)
Cloud-Lifetime (h)
Part-Lifetime (h)
Dep-Lifetime (h)