VOC observations during TORERO and comparison with CAM-chem results

24-Jun-14 TORERO Data Workshop

TORERO TOGA – CAM-chem science team:

Eric Apel, Becky Hornbrook, Alan Hills (NCAR/ACD)

Jean- Francois Lamarque, Doug Kinnison, Simone Tilmes

The Trace Organic Gas Analyzer (TOGA)

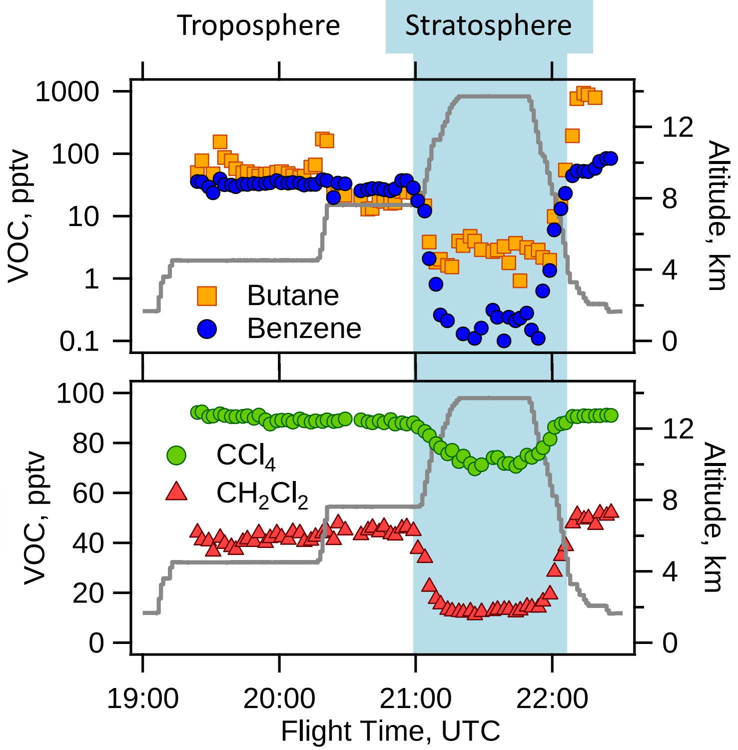
Eric Apel (PI), Alan Hills, Rebecca Hornbrook (ACD/NESL/NCAR)
Dan Riemer (Co-PI; University of Miami)

- VOCs needed to understand chemistry leading to trop O_3 and aerosols. Halogenated species can impact both trop and lower strat
- Designed specifically for the G-V
- Maiden research voyage – **TORERO 2 min time res**
- Designed to have very low **LOD ppt to sub – pptv** detection limits, over 45 VOC measured simultaneously

Sample data:
DC3 Test Flight 2

Pollutants

Greenhouse gases



TOGA compounds

Hydrocarbons	Propane 1-Butene *i*-Butene Butane *i*-Butane Benzene Toluene Ethyl Benzene *t*-2-Butene *c*-2-Butene Pentane 1,3-Butadiene Limonene	Isoprene *t*-2-Pentene *c*-2-Pentene *i*-Pentane *o*-Xylene *m/p*-Xylene 1,3,5-Trimethylbenzene 1,2,4-Trimethylbenzene α-Pinene β-Pinene Camphene Myrcene	
Oxygenates	Acetaldehyde Propanal Butanal Pentanal Methacrolein Methyl Vinyl Ketone Methyl Butenol	Methanol Ethanol Acetone Butanone 2-Pentanone 3-Pentanone Methyl t-Butyl Ether	
Halocarbons	Chloroform ($CHCl_3$)	Tetrachloromethane (CCl_4)	dibromomethane
	Methylene chloride (CH_2Cl_2)	CFC-113	diodomethane
	Methyl chloride (CH_3Cl)	HCFC-141b	bromocjhloromethane
	Methyl bromide (CH_3Br)	HCFC-134a	bromoiodomethane
	Tetrachloroethane (CH_2Cl_4)	1,2-Dichloroethane ($C_2H_4Cl_2$)	chloroiodomethane
	Tetrachloroethylene (C_2Cl_4)	Methyl Iodide (CH_3I)	
	Bromoform	iodoform	
Nitrogen and sulfur compounds	Acetonitrile Dimethyl Sulfide (DMS)	DMSO?	

Preliminary Lucy Carpenter/Stephen Andrews analysis vs. various standards

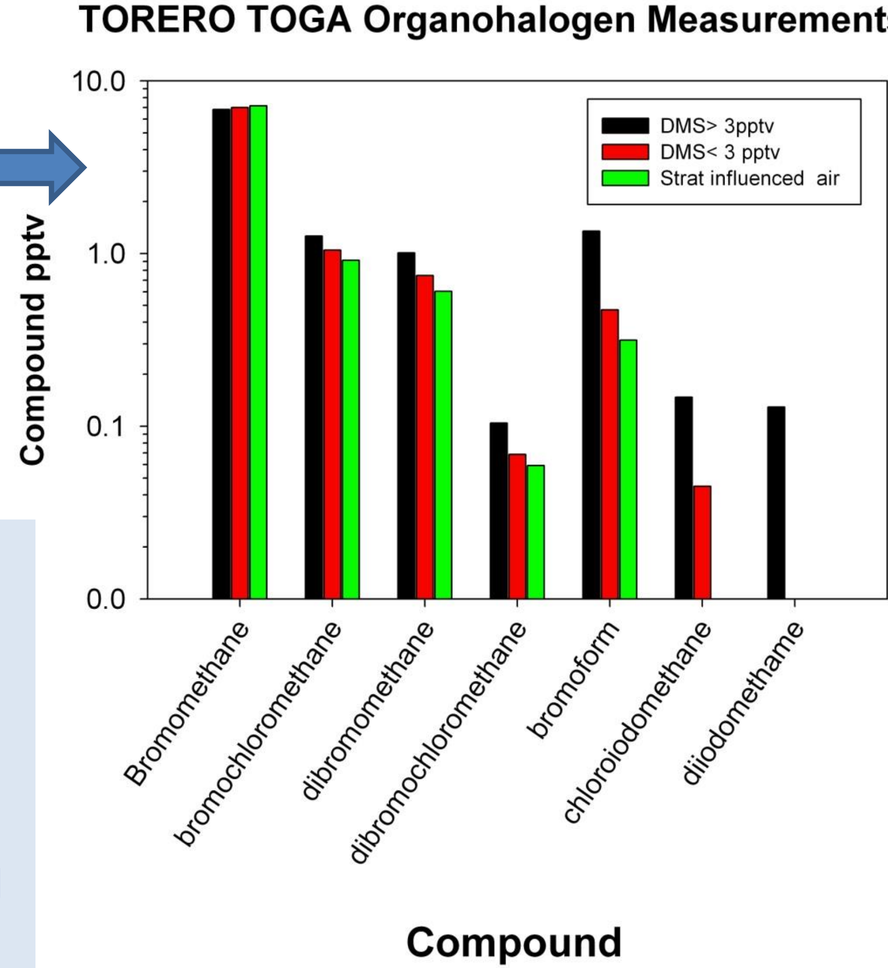
Compound	vs. NCAR Lab	vs. NOAA Air spike	vs. NOAA gravimetric	vs. NCAR in-flight cals
CH_3I	3.50	2.75		3.71
CH_2Br_2	2.25	2.04	2.39	2.13
$CHBr_3$		5.14	5.89	4.60
CH_2I_2	0.83	1.12	0.50	0.72
CH_2BrCl	7.43	5.87		6.71
$CHBr_2Cl$		3.53		1.64
CH_2IBr	1.79	1.49	2.03	1.72

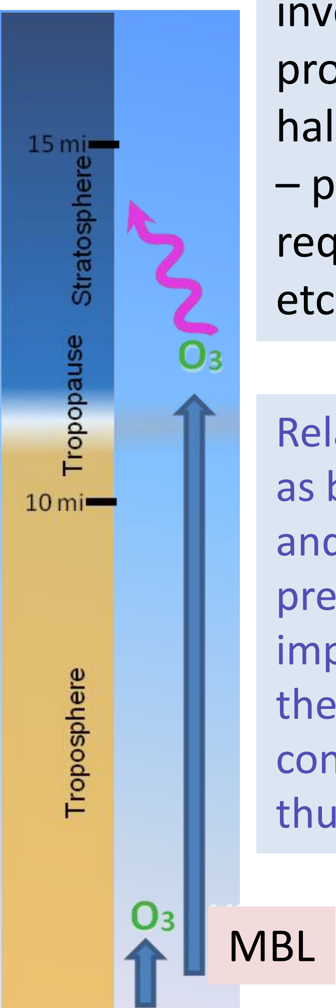
NOAA Gases

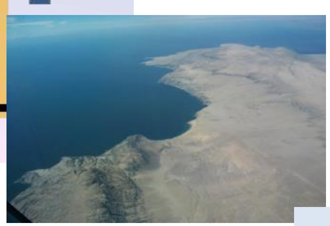
NCAR Gases

Canister Gases

Ultra-high sensitivity needed to investigate some chemical processes such as the inorganic halogen/organo-halogen species – parts per quadrillion sensitivity required (see Carpenter, Atlas, etc.)







Relatively stable organic halogens such as bromomethane, bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2), emitted predominantly from the oceans, can impact the MBL and be transported to the lower stratosphere and make a contribution to total bromine levels and thus to stratospheric ozone depletion.

Build on previous studies

VSLS – defined as less then 6 mo.

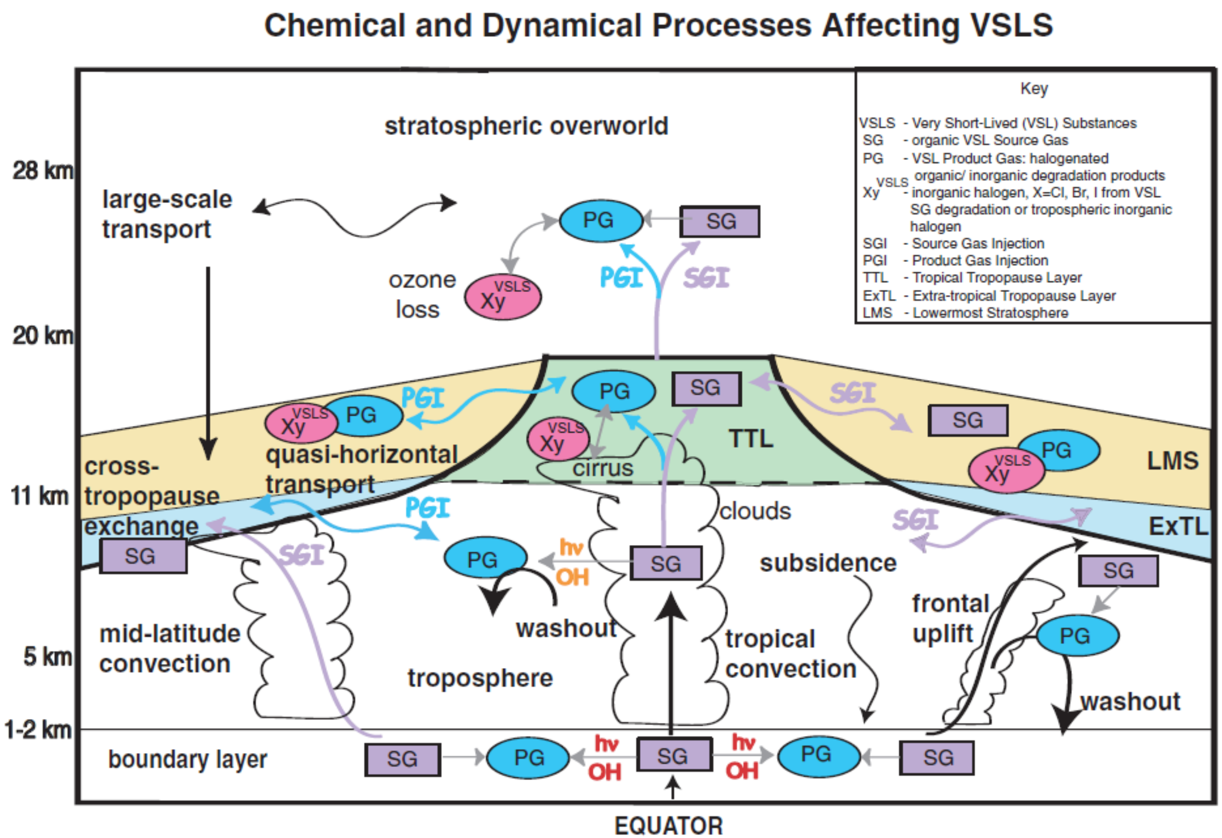
Bromomethane ≈ 1 year
Bromoform ≈ 1 month
Dibromomethane ≈ 4 months
Chloroiodomethane ≈ 2 hours (LOD TOGA = 0.03 pptv)
Diiodomethane ≈ 5 minutes (LOD TOGA 0.03 pptv)

J-F Lamarque and D. Kinnison ACD – CAM-chem

Recent updates to modeling VSL halogen chemistry in CAM-Chem

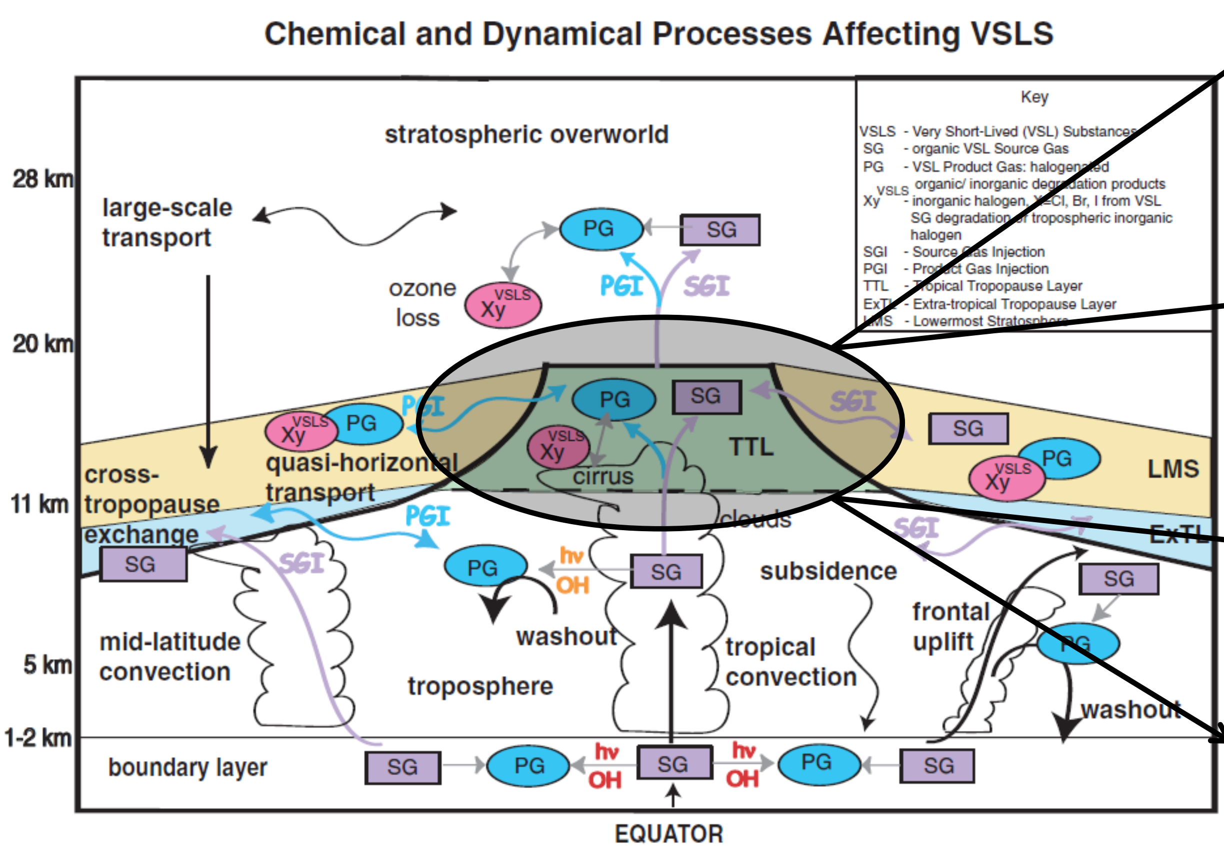
D. Kinnison & J.-F. Lamarque (NCAR, USA)
A. Saiz-Lopez (CSIC, Spain)
R. Fernandez (UNC, Argentina)
R. Salawitch (U. Maryland, USA)

Motivation



SG_{VSL} bromocarbons are converted to $PG_{VSL}= Br_y$ in the TTL before/while being injected to the stratosphere

Physical-chemistry processes



Heterogeneous recycling Over ice particles

Washout efficiencies and photochemical lifetime

Strength of convection

Entrainment from the MBL

SG_{VSL} bromocarbons are converted to $PG_{VSL} = Br_y$ in the TTL before/while being injected to the stratosphere

On-going work

- Updated (to the CONTRAST model setup and version) simulations for TORERO and CONTRAST at horizontal resolution of ≈ 1^o
- Planning (end of summer) high-resolution (≈ $1/4^o$) for both periods

Extensive recent developments in the representation of VSL halogen chemistry and emissions

- Ordonez, C., J.-F. Lamarque, S. Tilmes, D. Kinnison, E. Atlas, D. Blake, G. Sousa Santos, G. Brasseur and A. Saiz-Lopez, Atmos. Chem. Phys., 12, 1423–1447, 2012.
- Saiz-Lopez, A., J.-F. Lamarque, D. Kinnison, S. Tilmes, C. Ordonez, J. J. Orlando, A. J. Conley, J. M. C. Plane, A. Mahajan, G. Sousa Santos, E. Atlas, D. R. Blake, S. P. Sander, S. M. Schauffler, A. M. Thompson and , Atmos. Chem. Phys., 12, 3939–3949., 2012.
- Fernandez, R. P., R. Salawitch, D. E. Kinnison, J.-F. Lamarque and A. Saiz-Lopez, Bromine partitioning in the tropical tropopause layer: implications for stratospheric injection. Submitted to *Atmos. Chem. Phys. Disc*., 2014.

Organohalogens and DMS

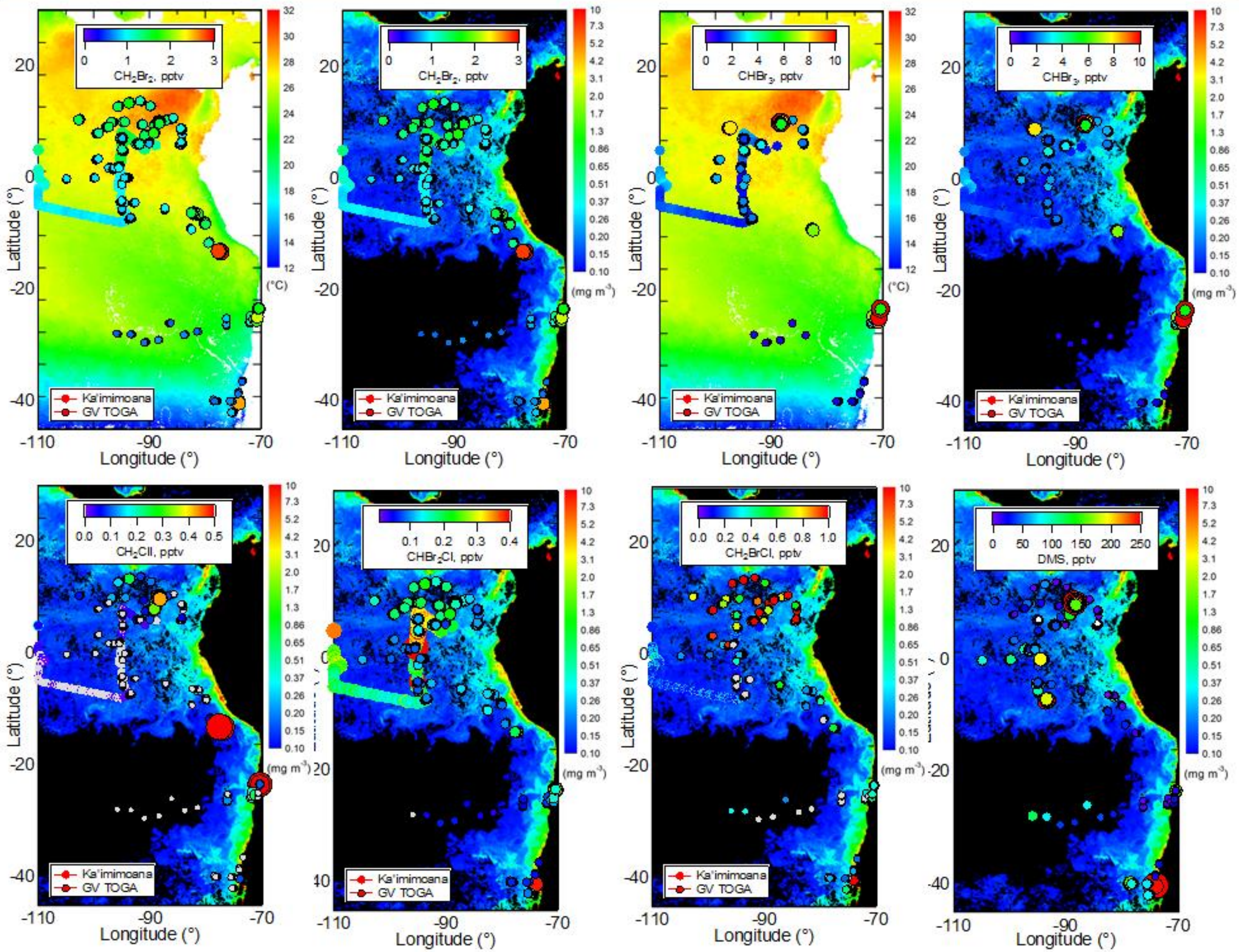
Dibromomethane – CH_2Br_2
Bromoform – $CHBr_3$
Others…
methyl iodide CH_3I
chloroiodomethane – CH_2ICl
dibromochloromethane – $CHBr_2Cl$

From 2012
Fall AGU poster:

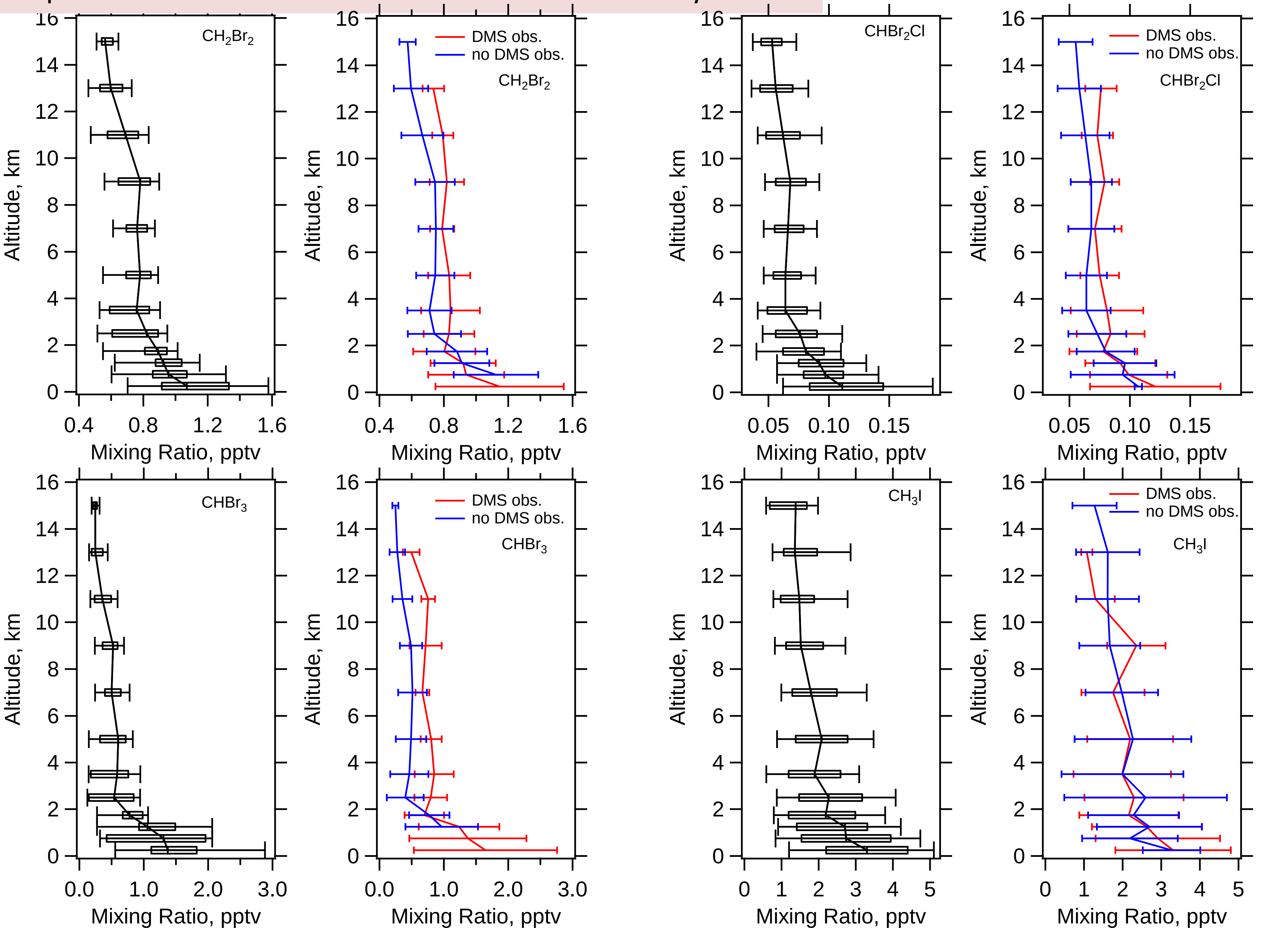
Marine Boundary Layer Organohalogens

Figure 3. TOGA data from the MBL (< 500 m) and U. of York data on surface maps of MODIS sea surface temperatures (SST) and Chlorophyll-a (Chl-a).

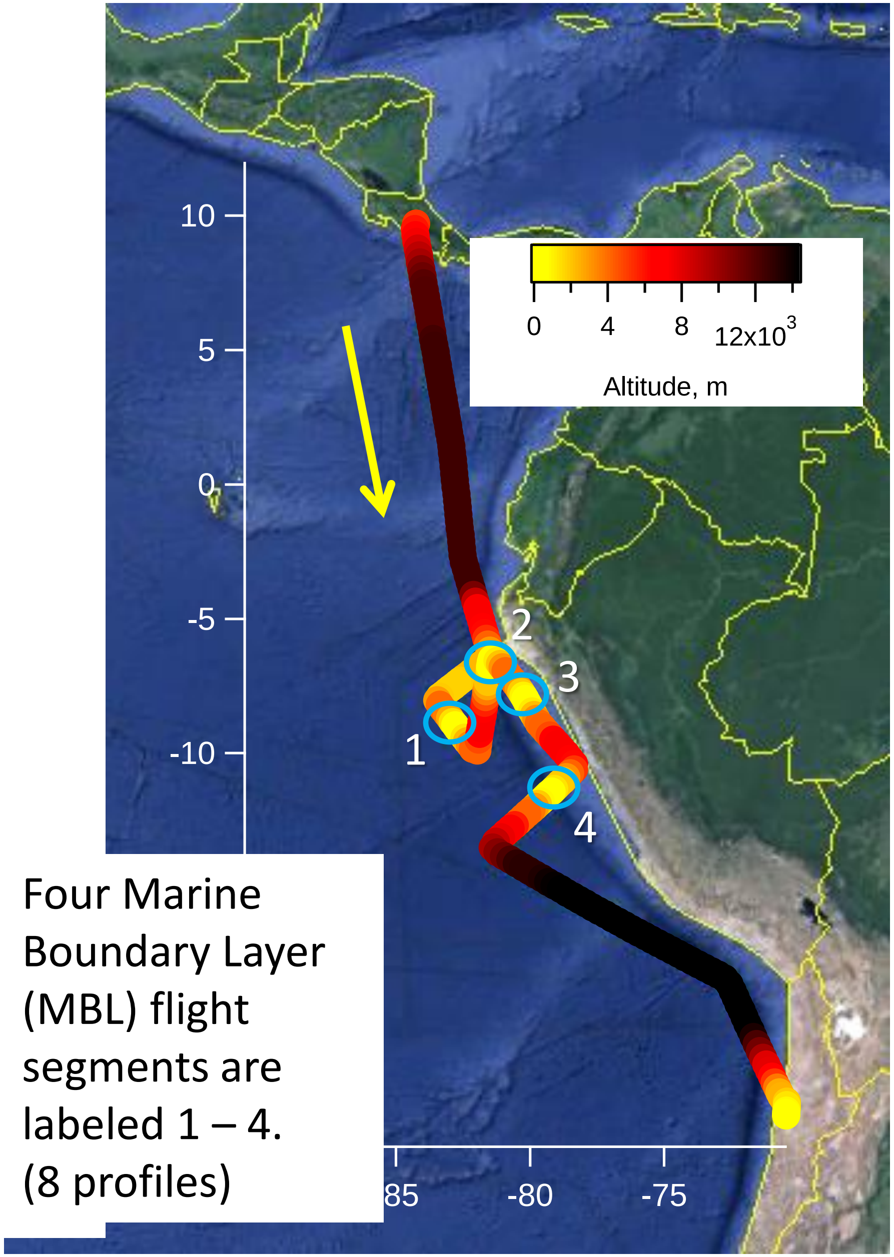
Emissions of Organohalogens and DMS are Similar, and yet not fully dependent on sea surface T (SST), or Chlorophyll-a, but there are similarities.



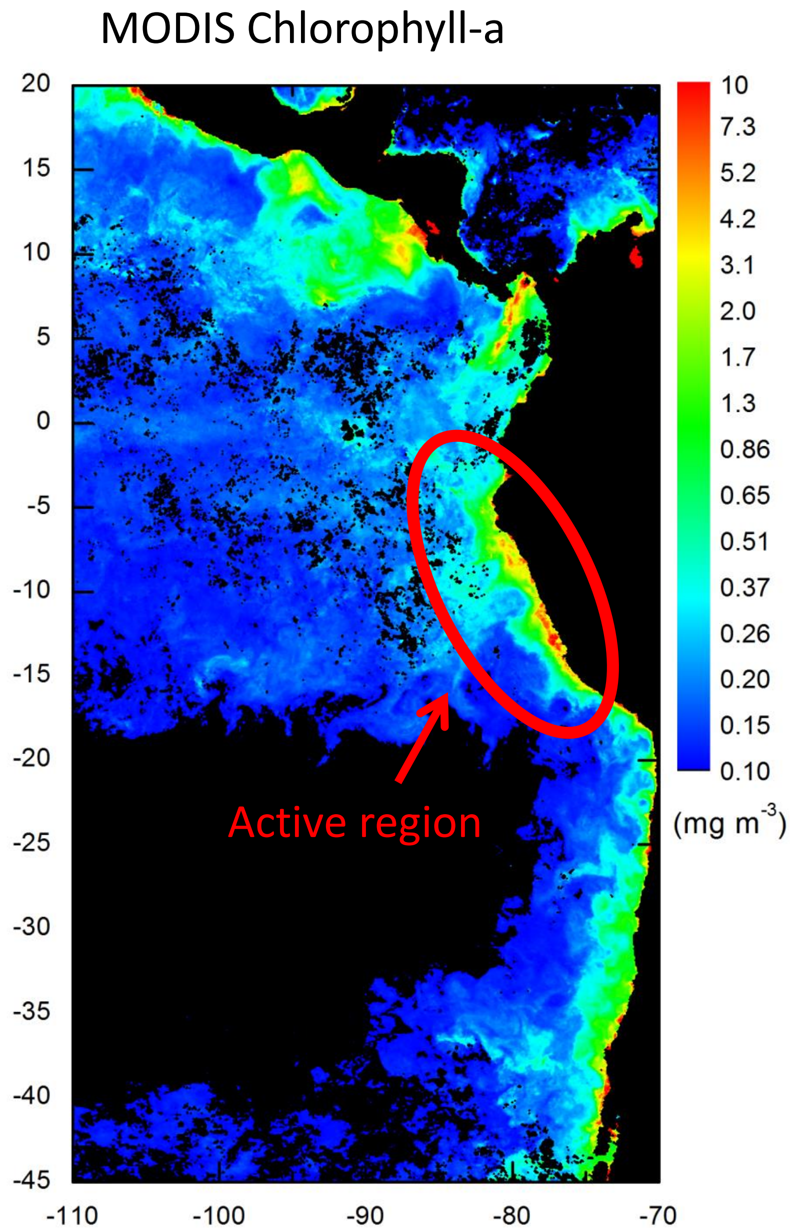
Impact of convection on brominated VSLS and methyl iodide



RF01 – coastal emissions, continental outflow

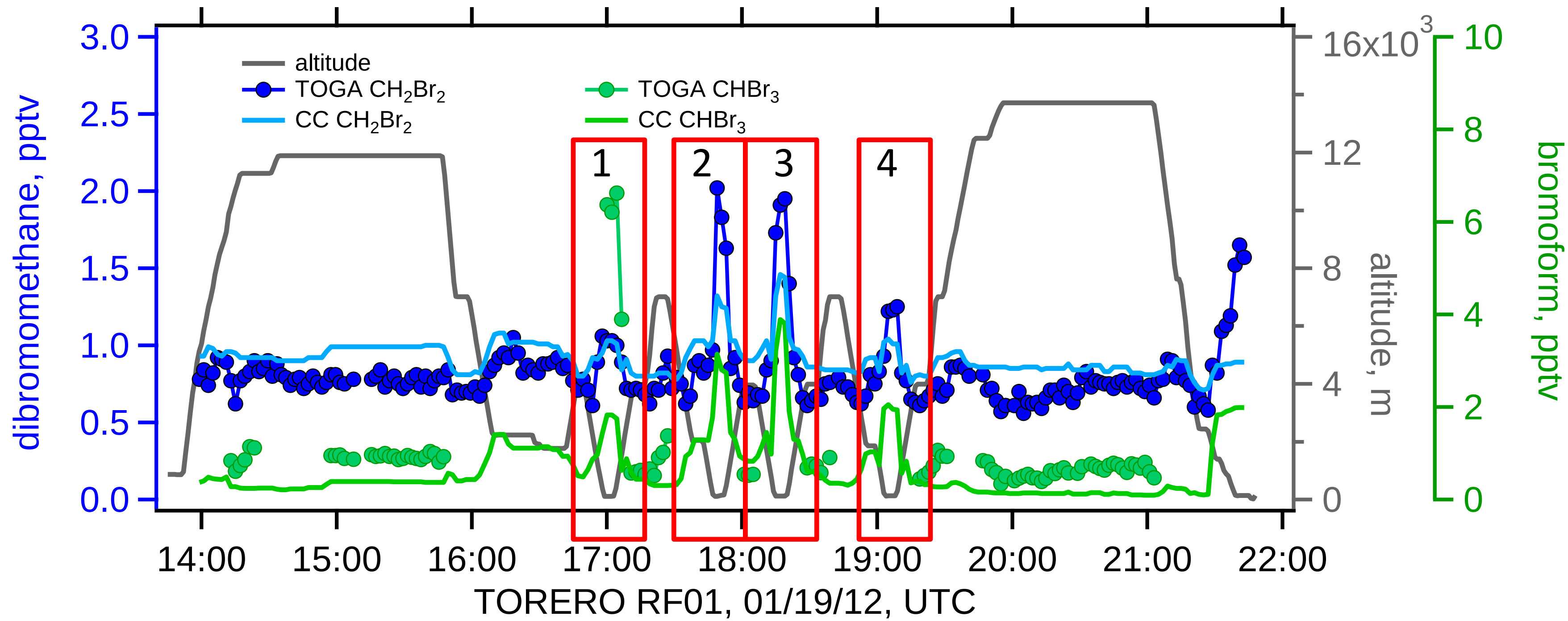


Four Marine Boundary Layer (MBL) flight segments are labeled 1 – 4. (8 profiles)



TORERO RF01.

Transit from Costa Rica to Chile, with profiling off the western coast of Peru.



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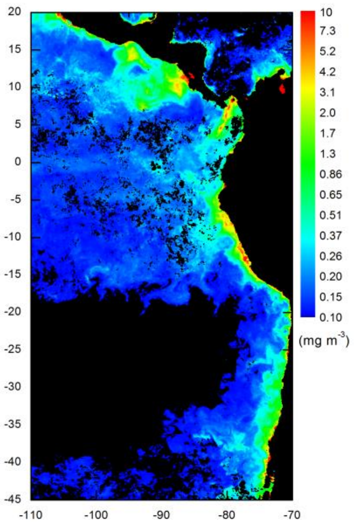
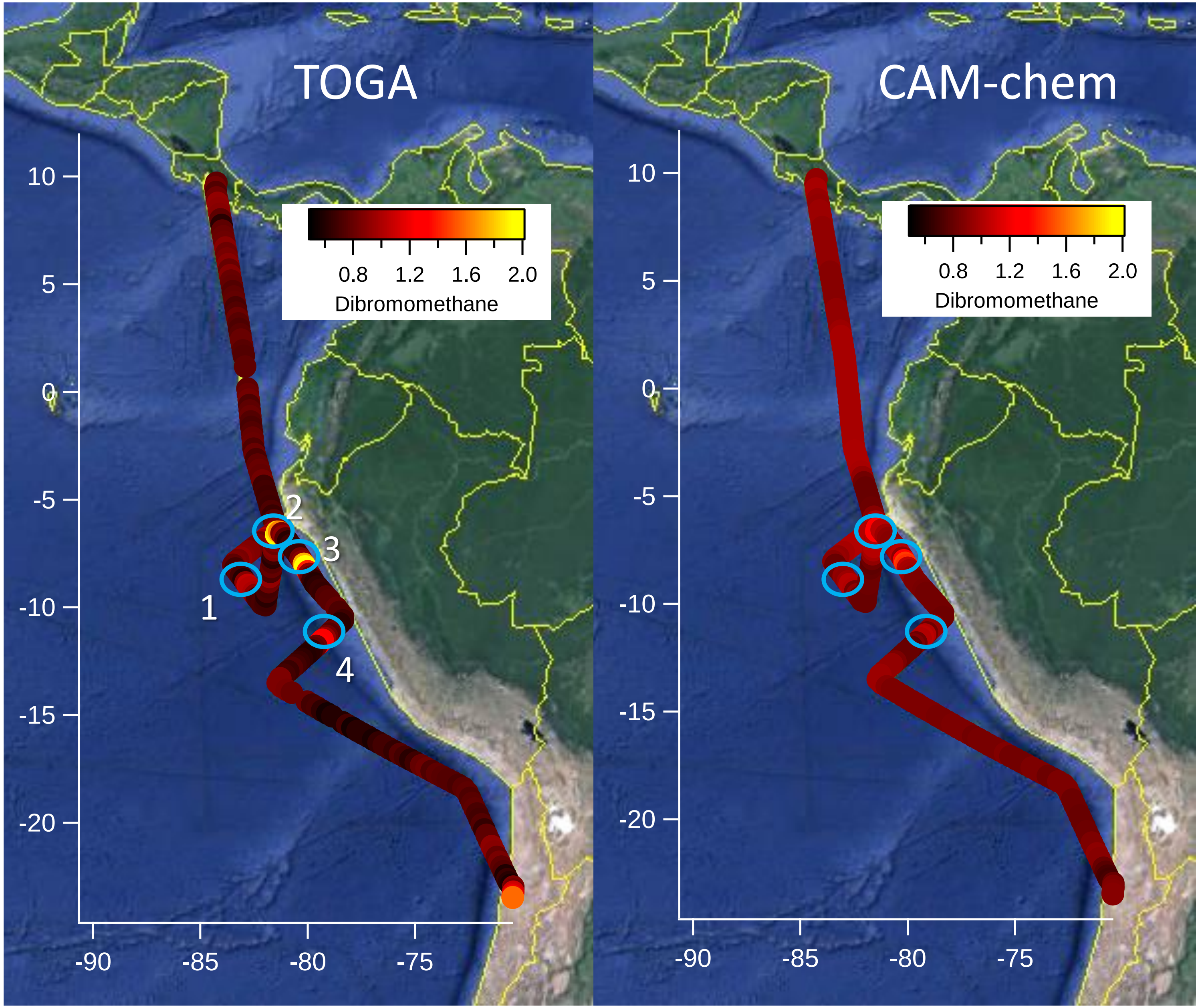
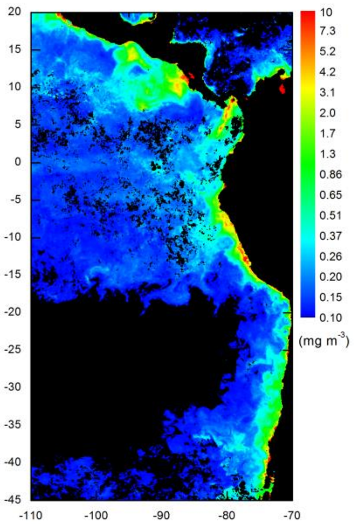
From RF01

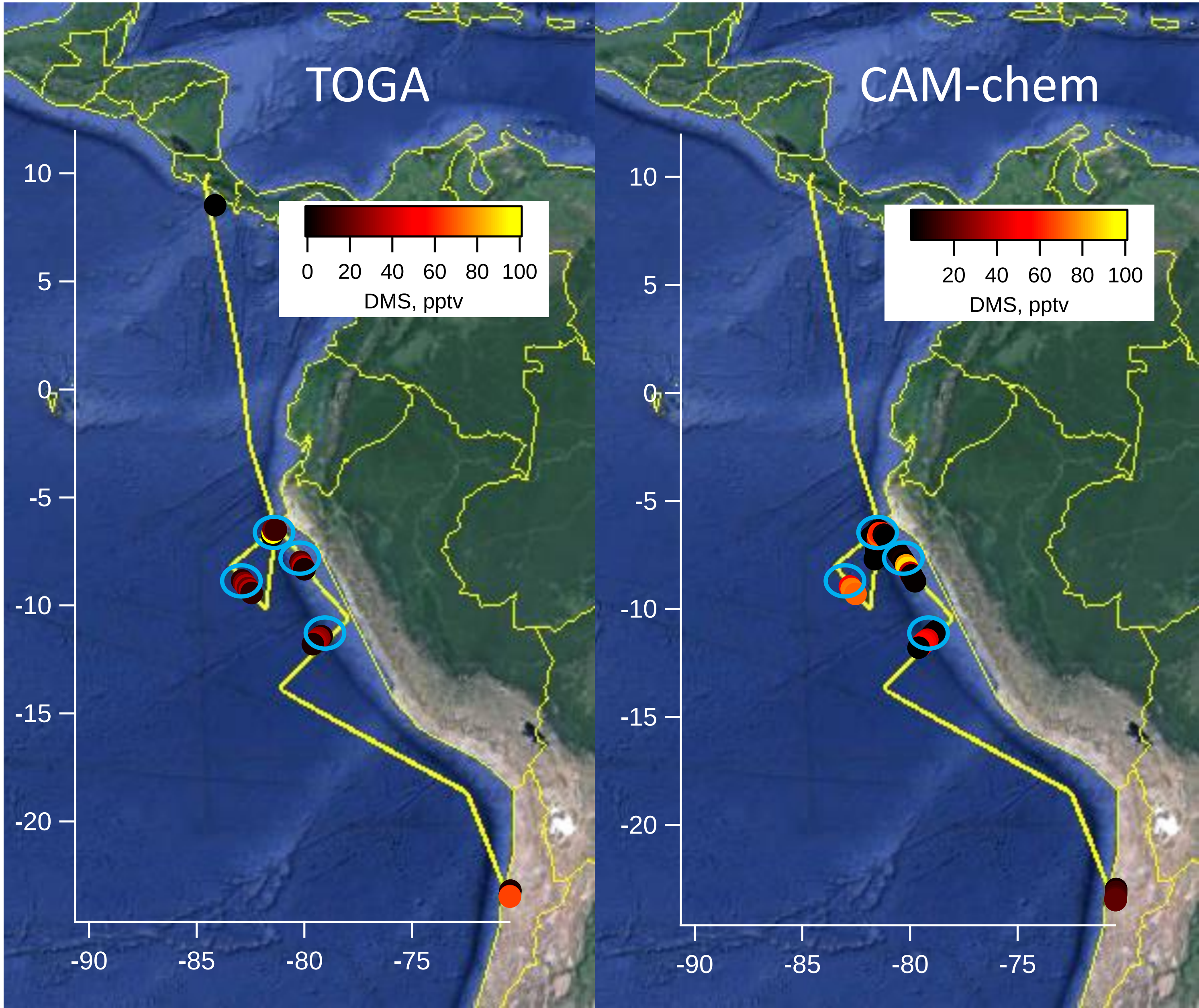




CAM-chem and TOGA CH_2Br_2 agree to within a factor of two.

From RF01

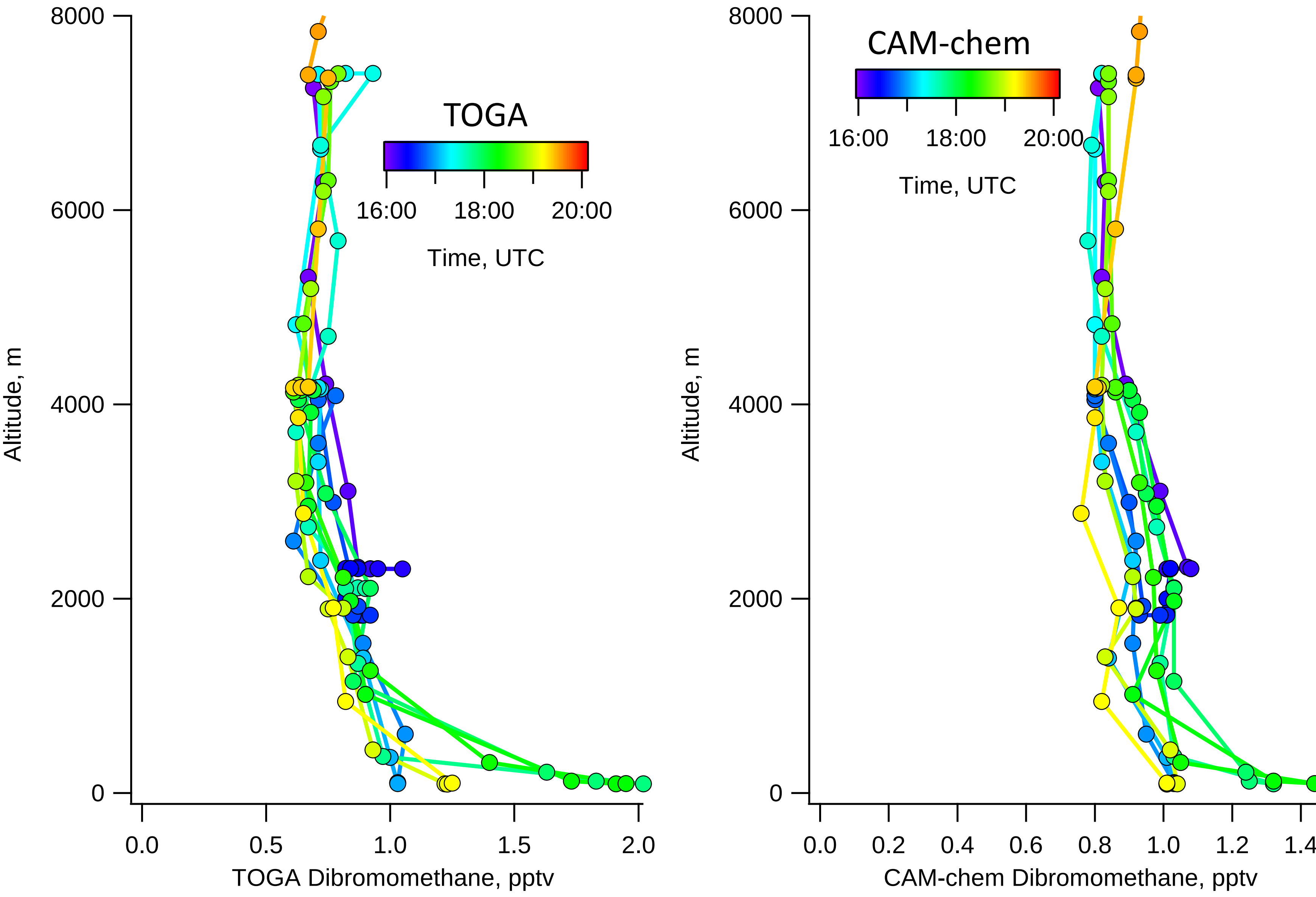




CAM-chem and TOGA DMS agree to within a factor of two.

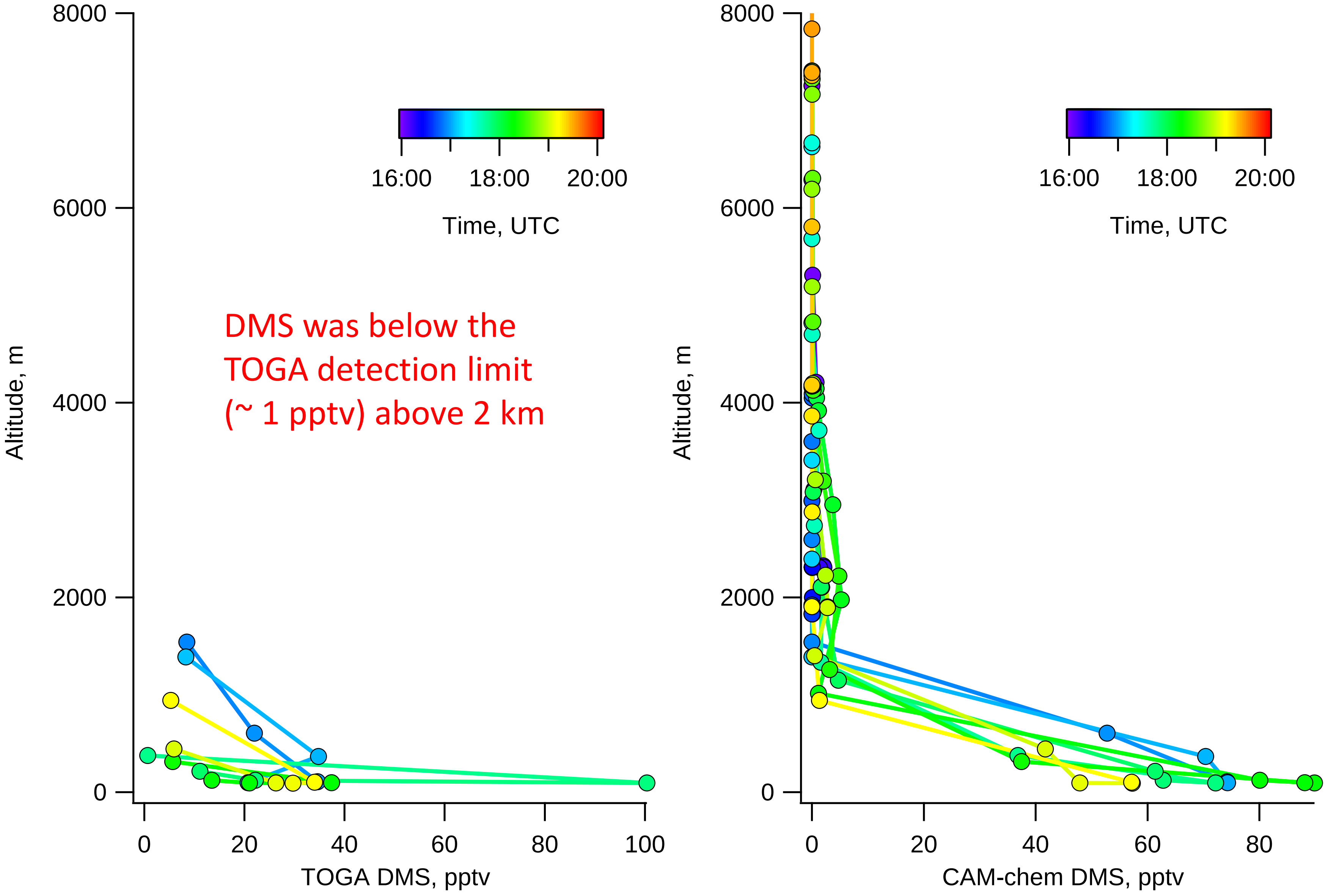
RF01: 8 profiles off the west coast of Peru

CAM-chem organohalogens and dibromomethane in good agreement with measurements.

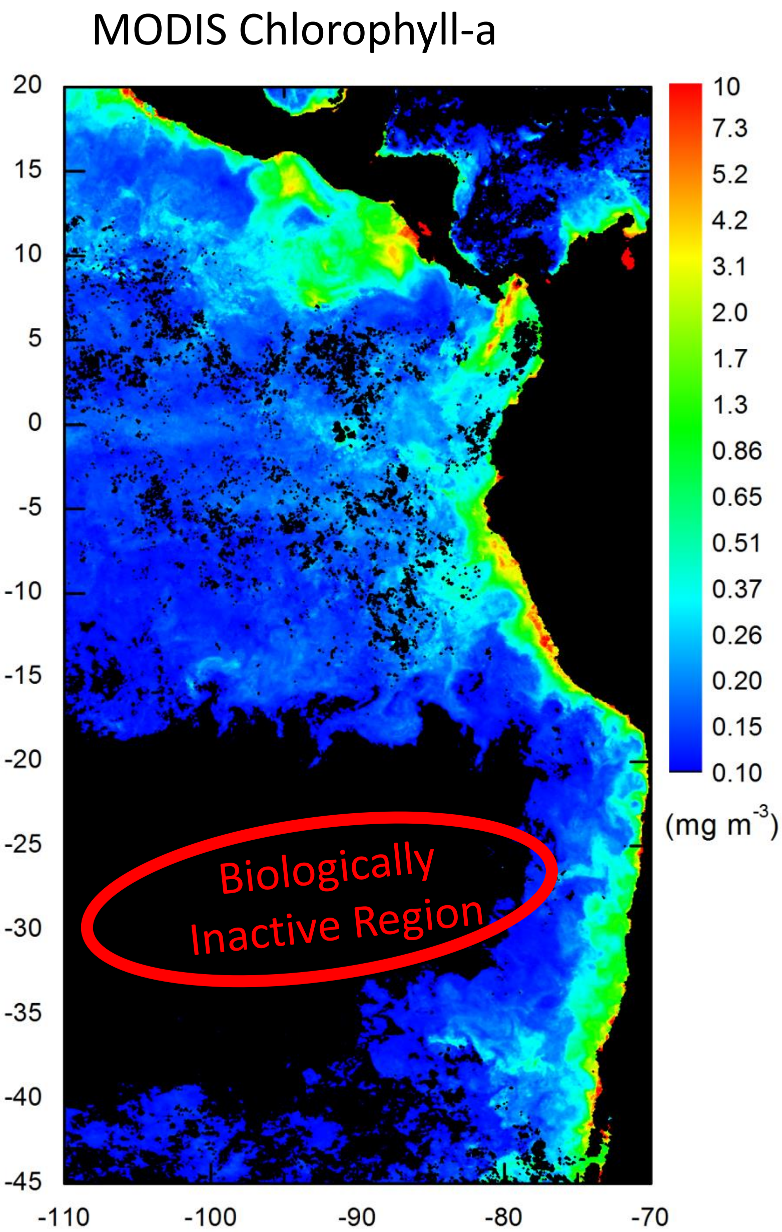


RF01: 8 profiles off the west coast of Peru

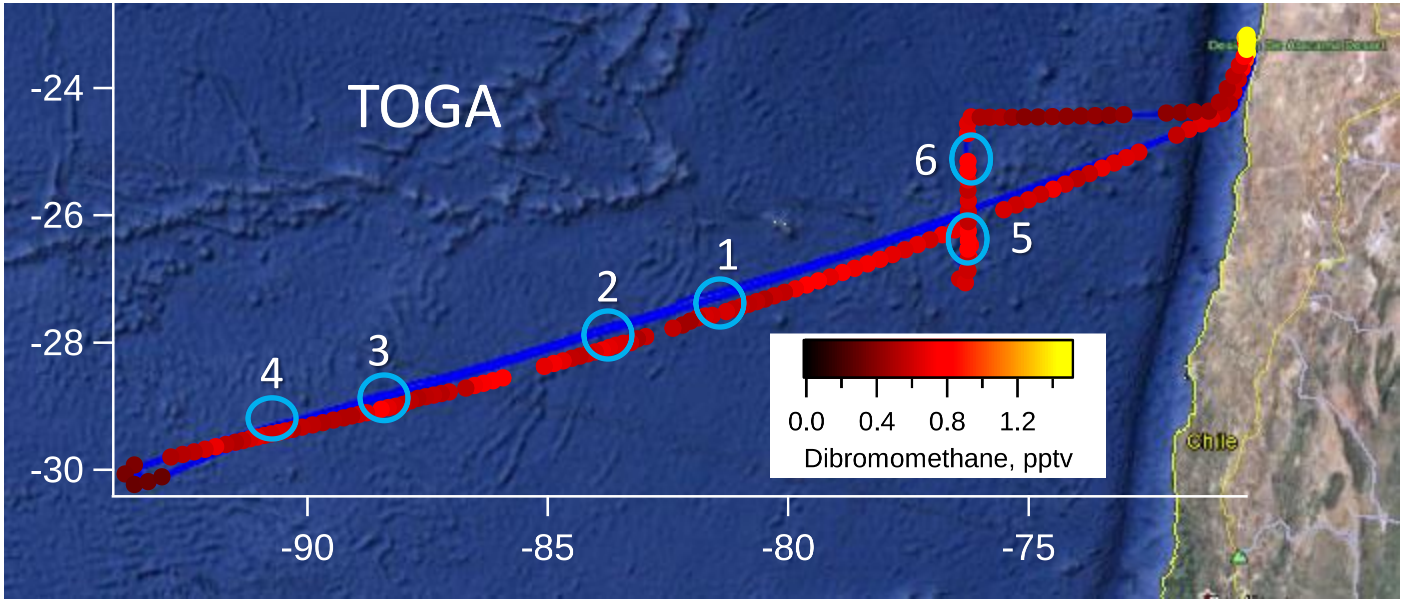
CAM-chem organohalogens and DMS in good agreement with obs.

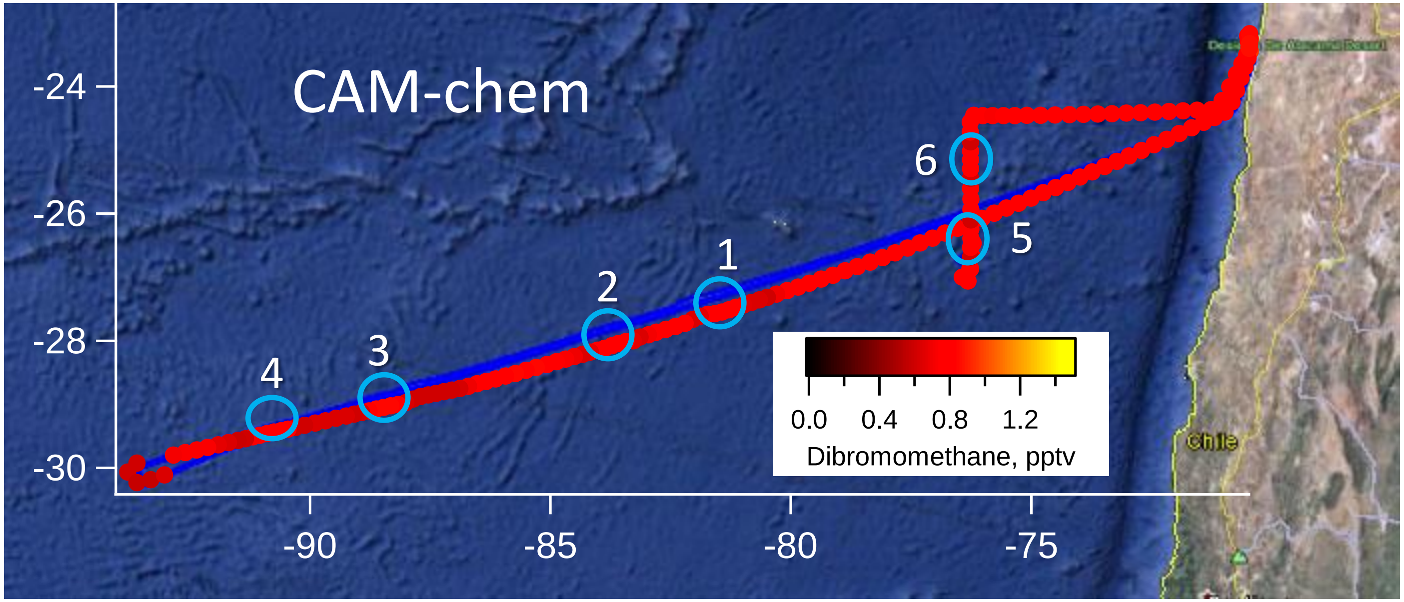


RF05 – oligotrophic ocean



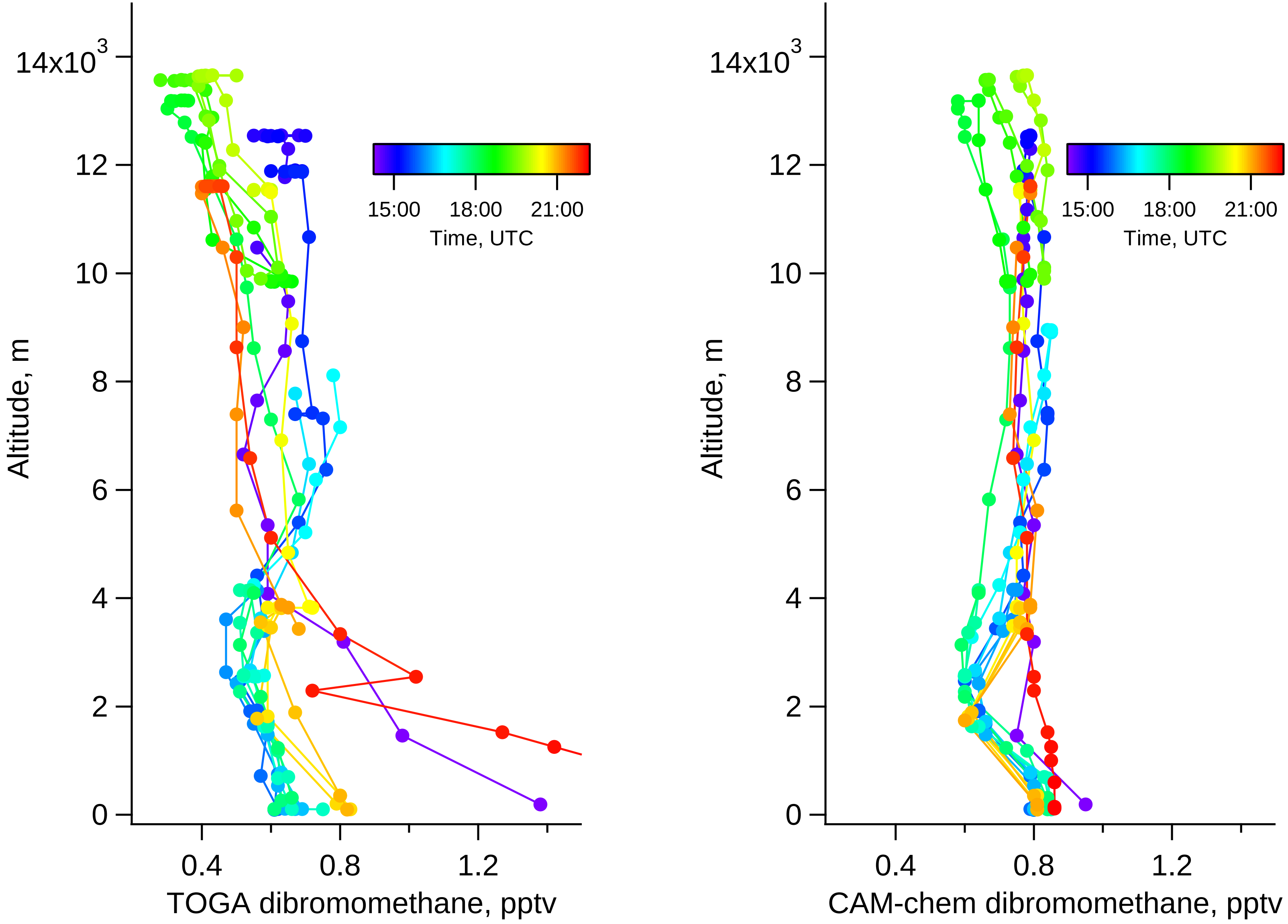
RF05 – oligotrophic ocean





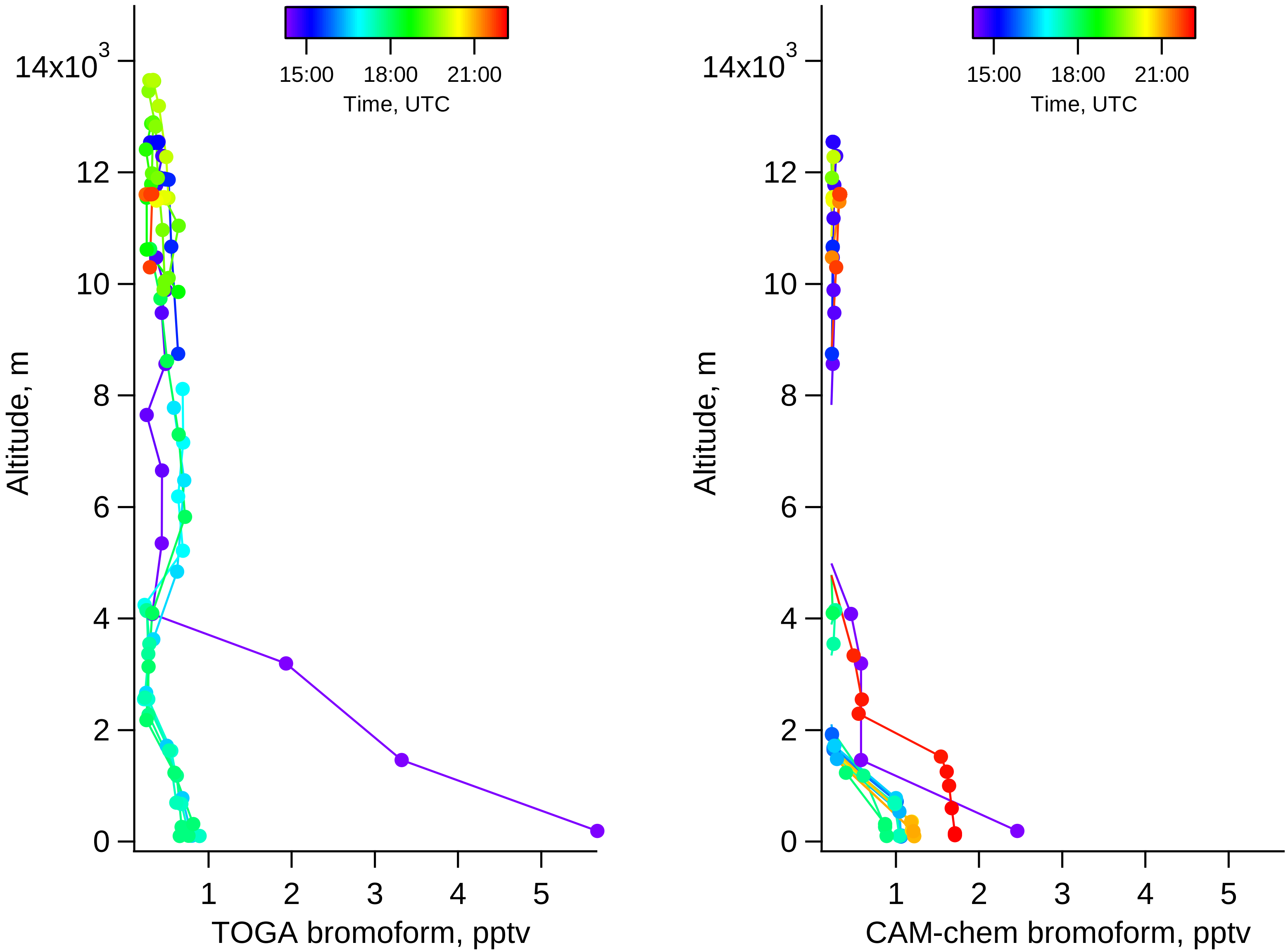
RF05 – oligotrophic ocean

Model and obs. Are very similar, with the exception of take-off and landing.
Dibromo in MBL runs 1 – 4 were slightly lower than CAM-chem predicts.



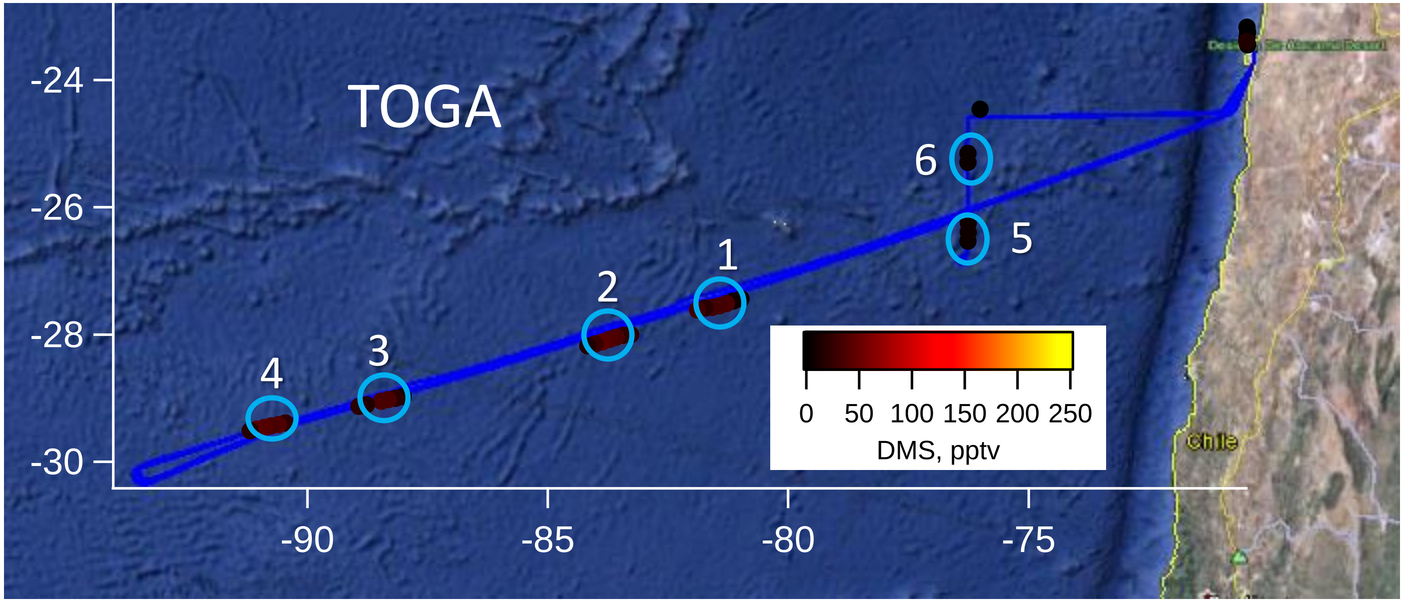
RF05 – oligotrophic ocean

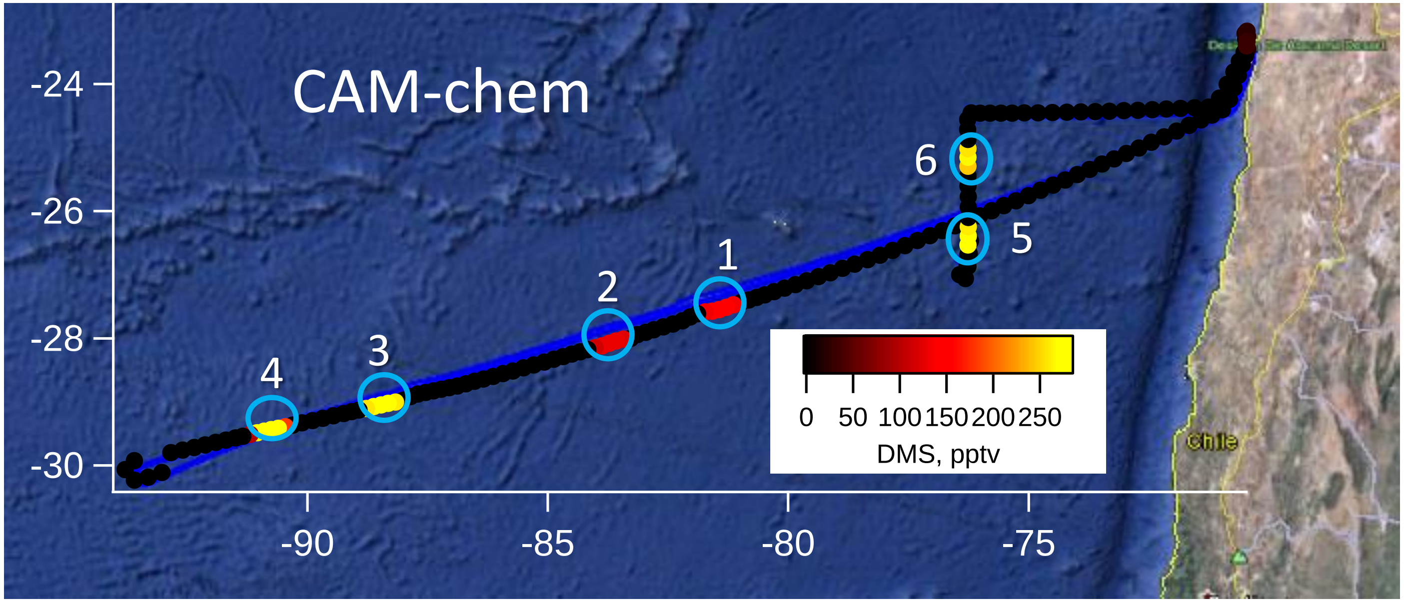
Model and obs. very similar, and relatively low (~ 1 ppt) in the oligotrophic ocean MBL.



RF05 – oligotrophic ocean

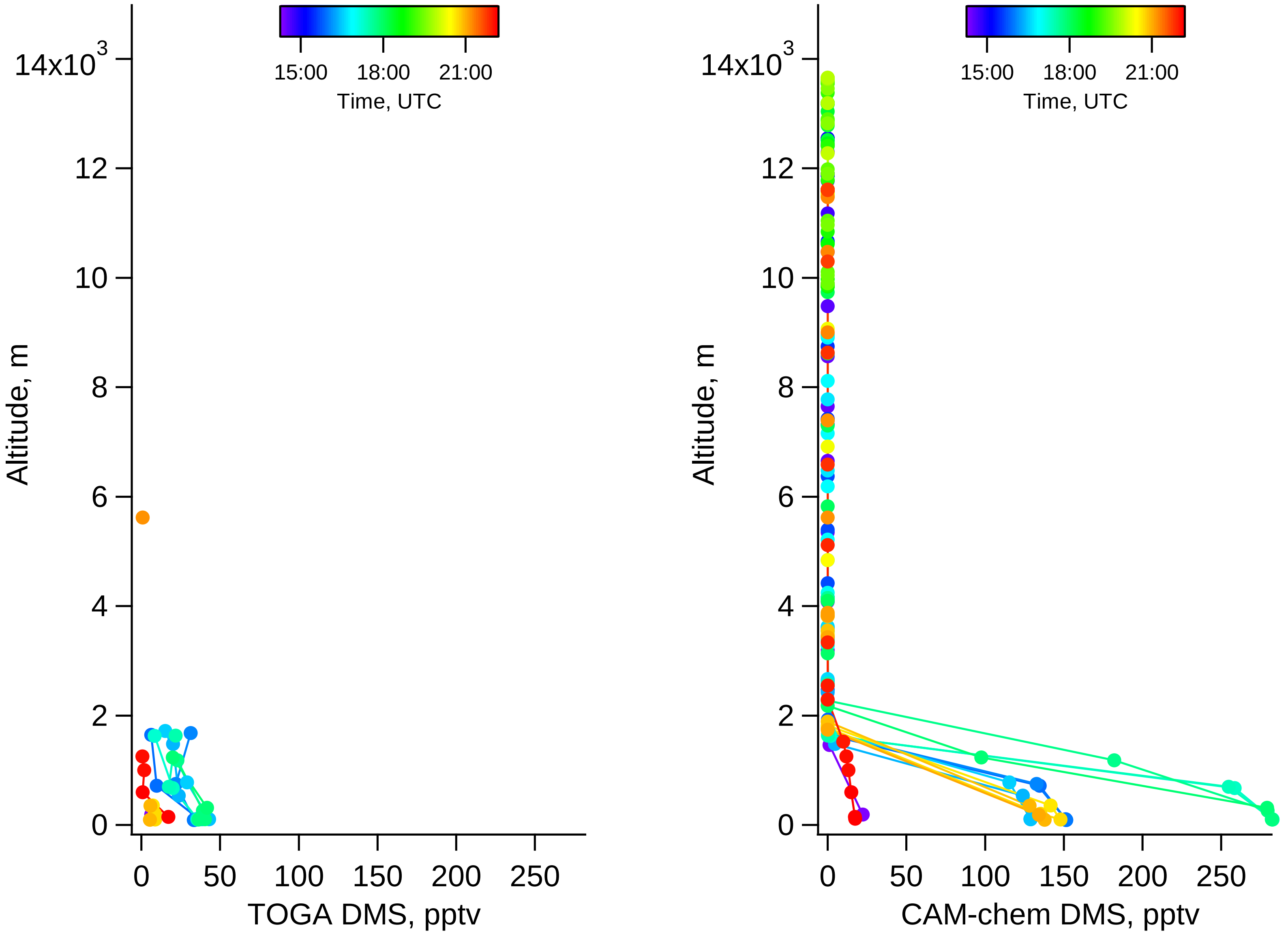
TOGA DMS
Is significantly
Lower than
CAM-chem
DMS in all
MBL runs.



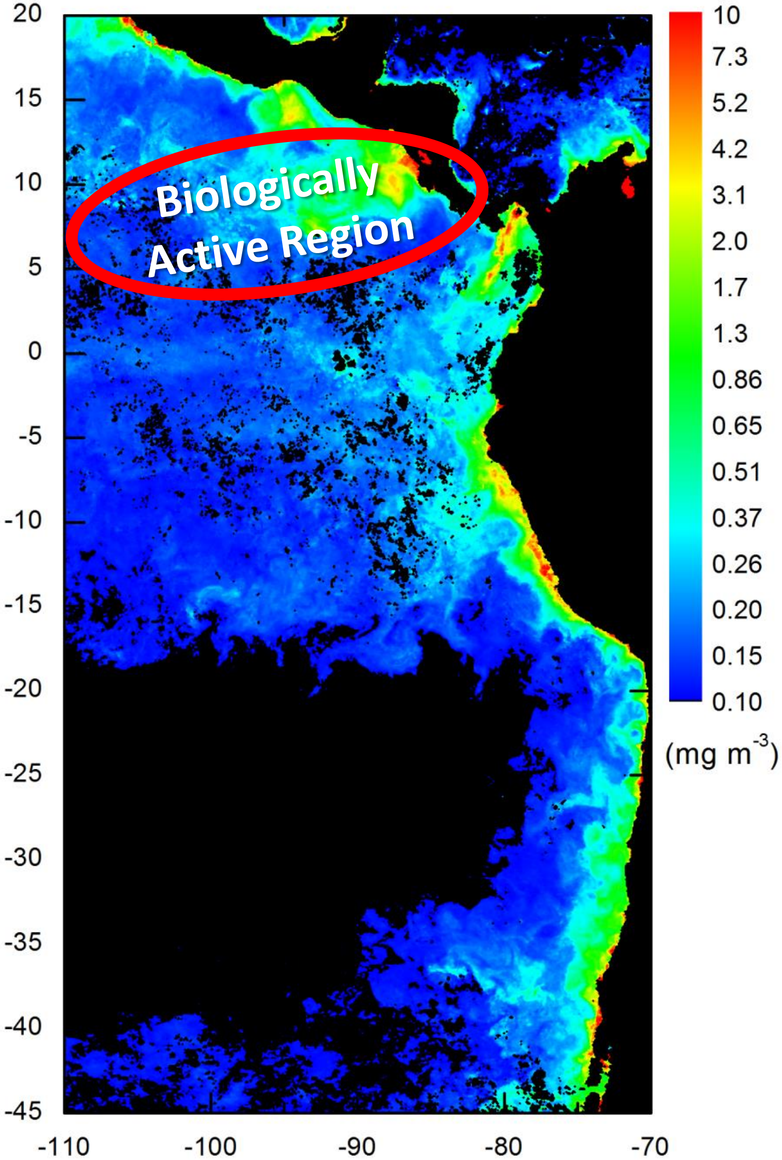


RF05 – oligotrophic ocean

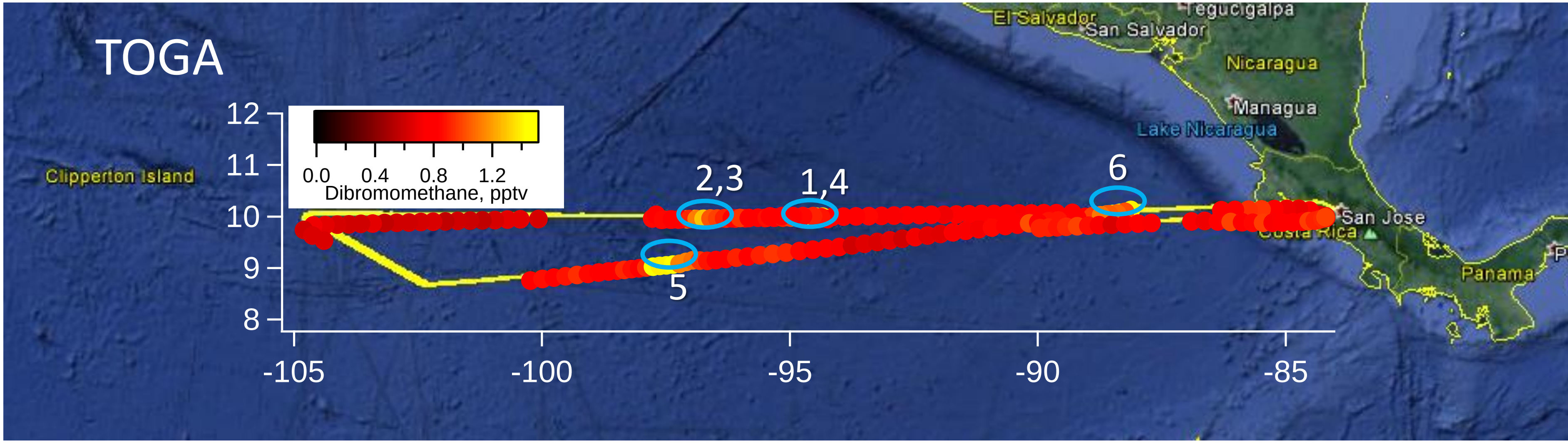
Model DMS >> TOGA DMS. Largest disagreement at the furthest two MBL runs.

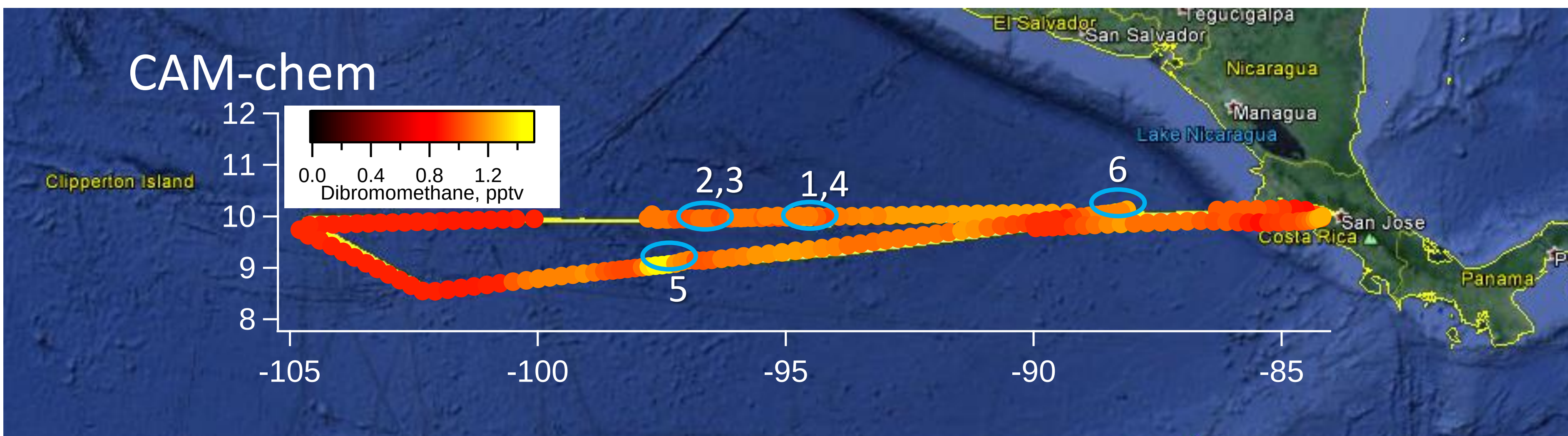


RF12 – biologically active region/convected MBL



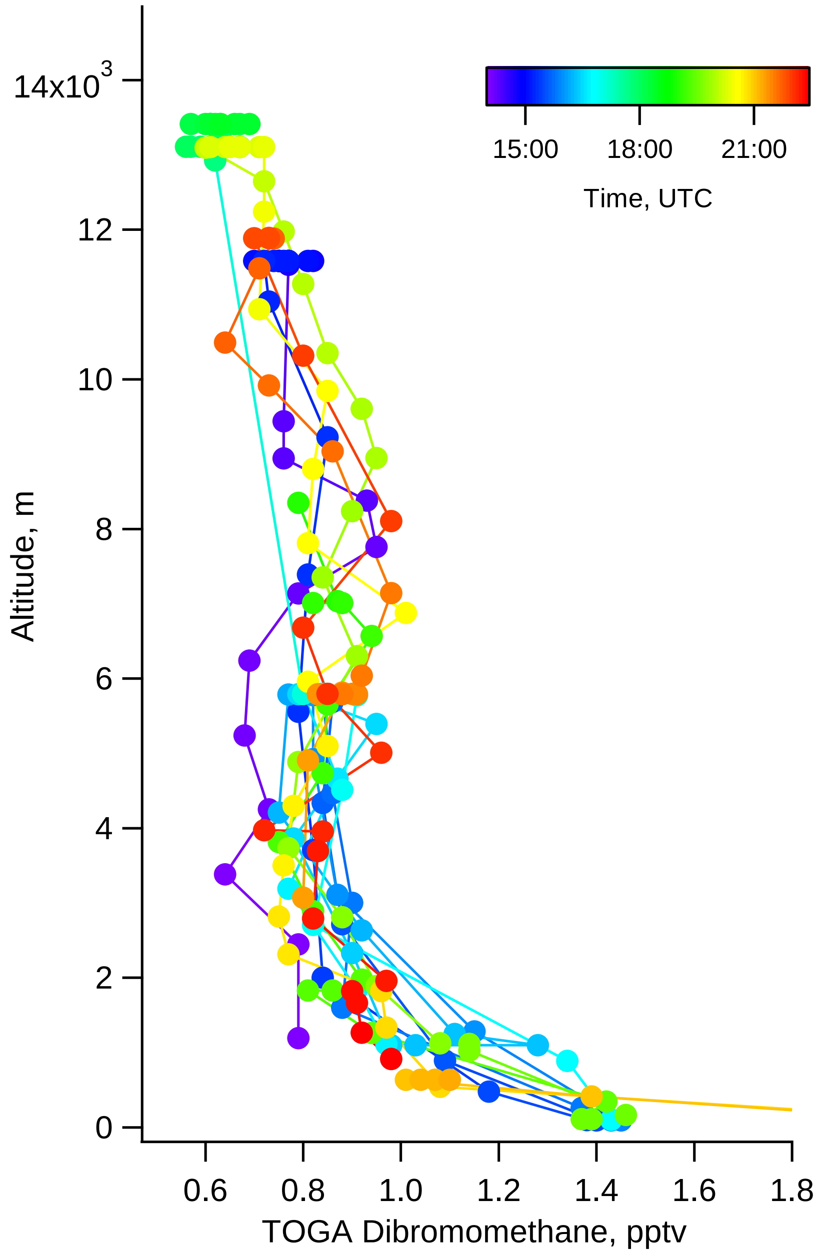
RF12 – biologically active region

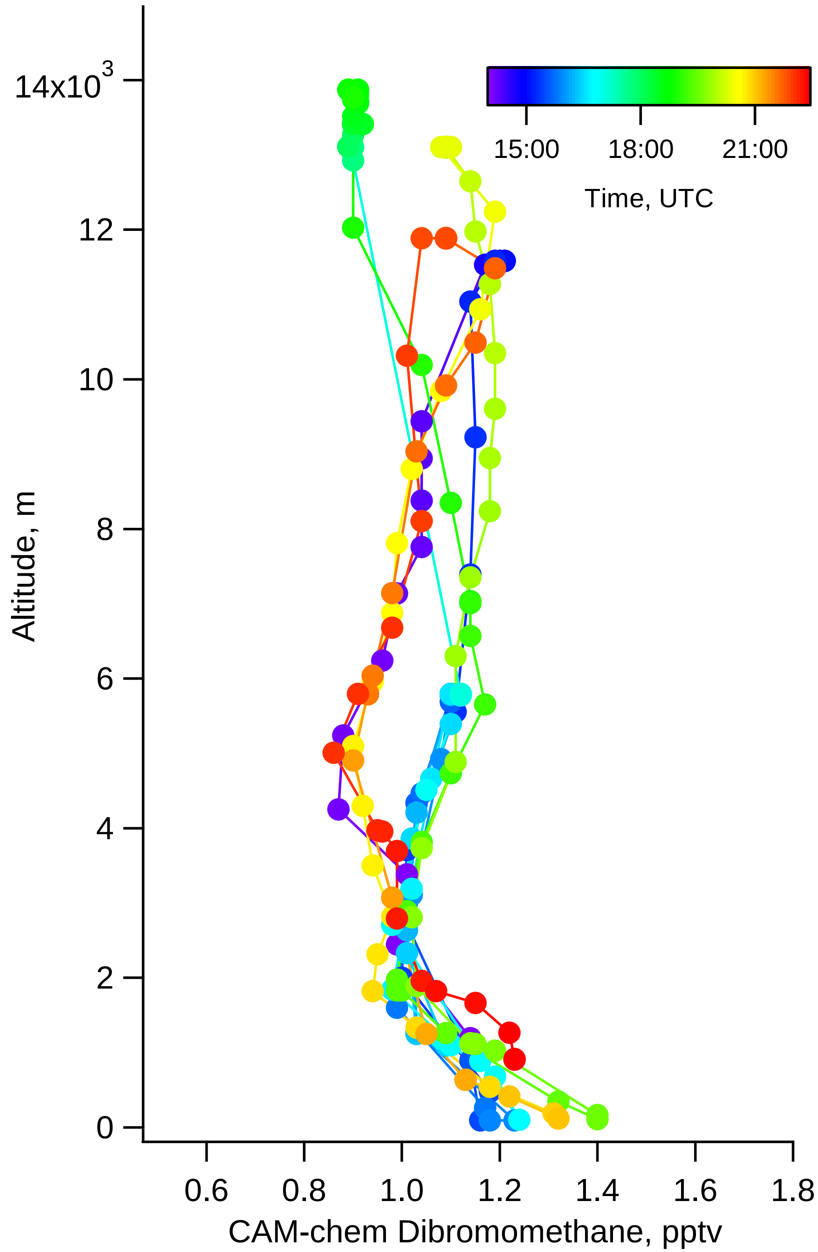




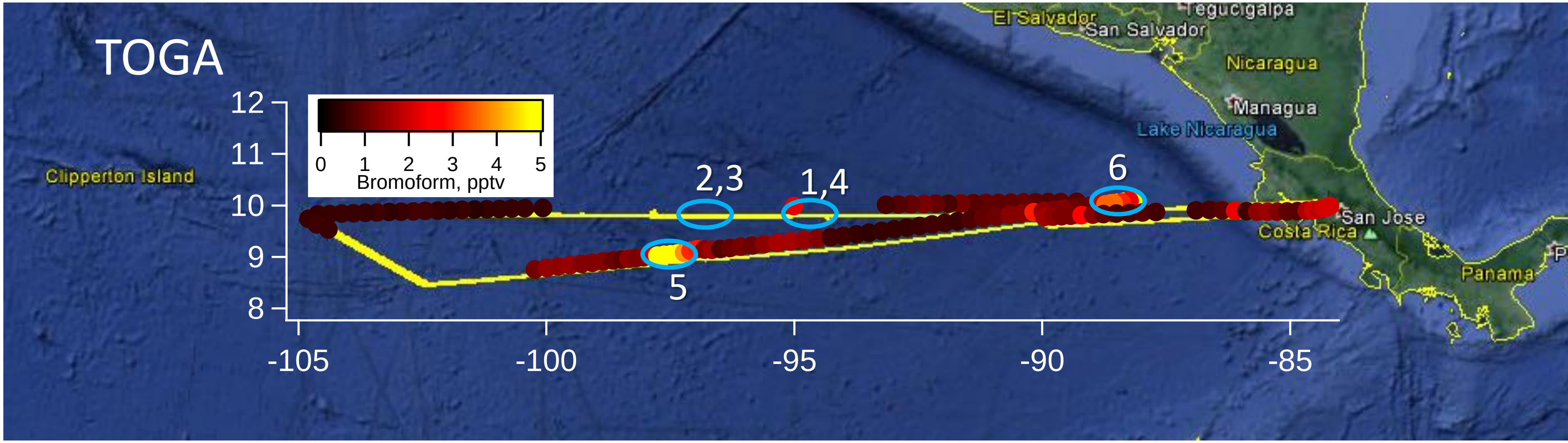
RF12 – biologically active region

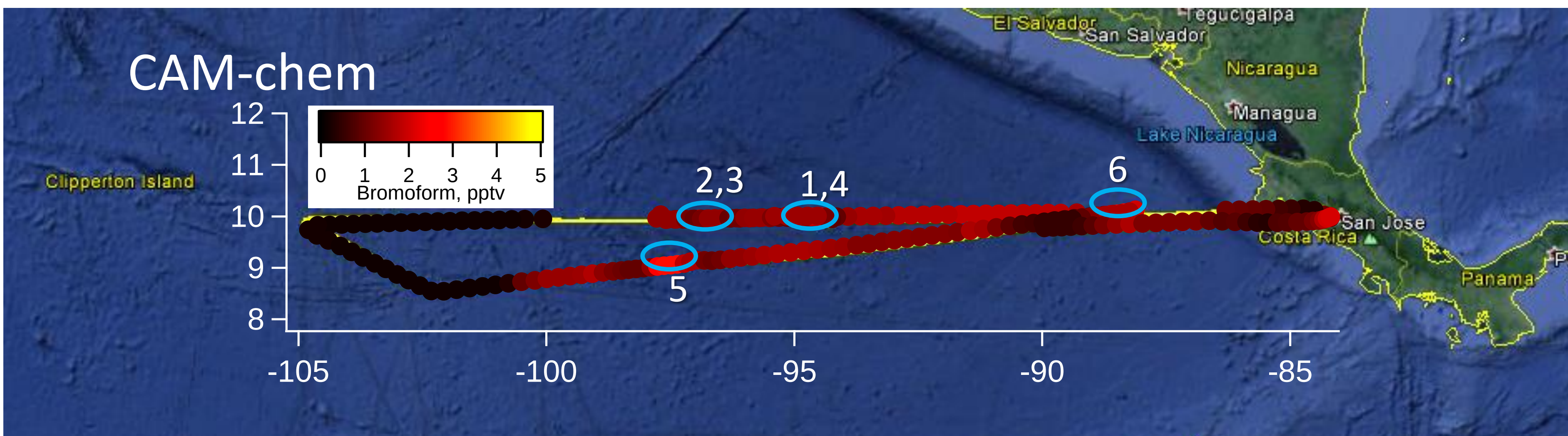
Observations are a little higher than the model at the surface, and lower aloft.





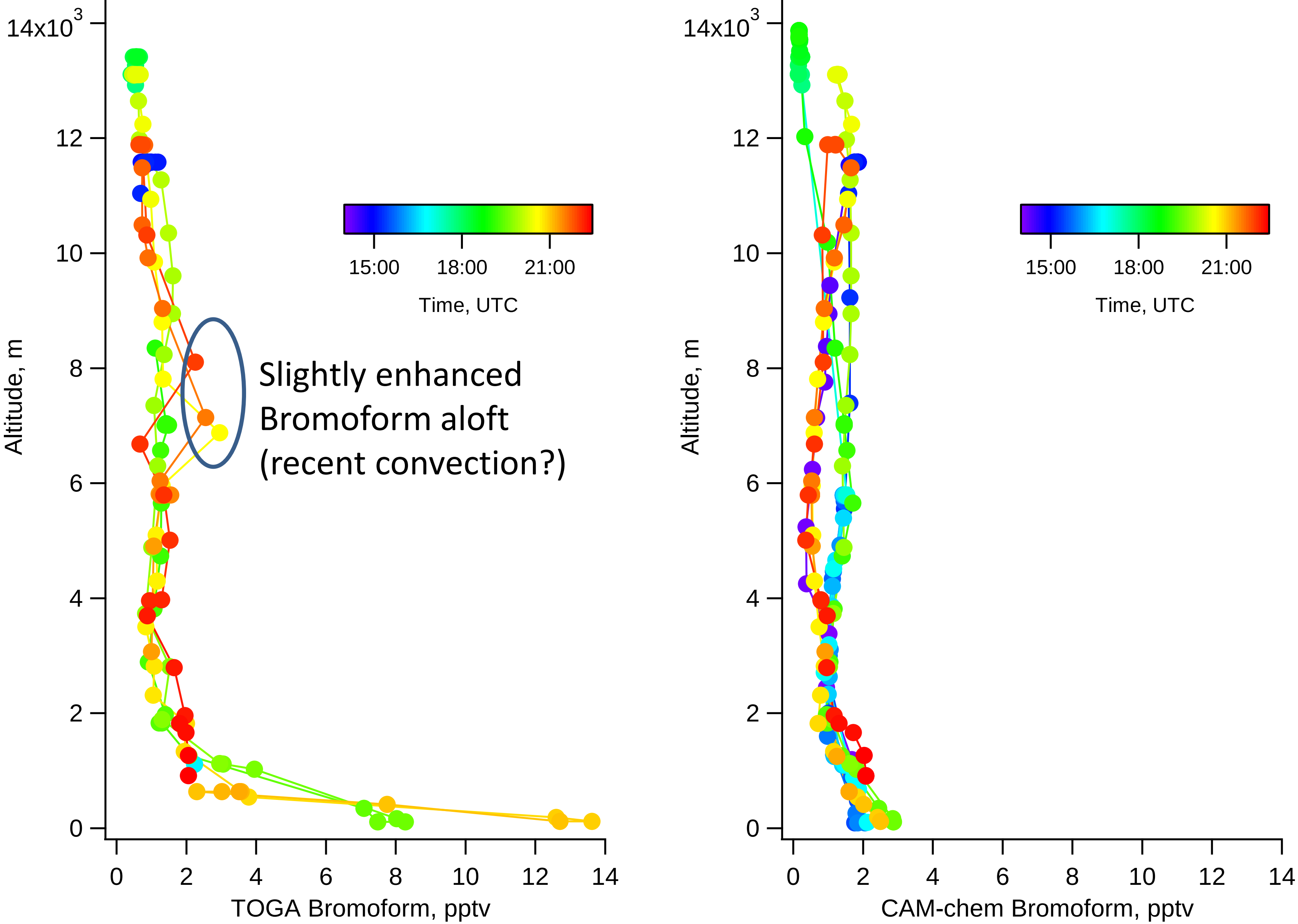
RF12 – biologically active region





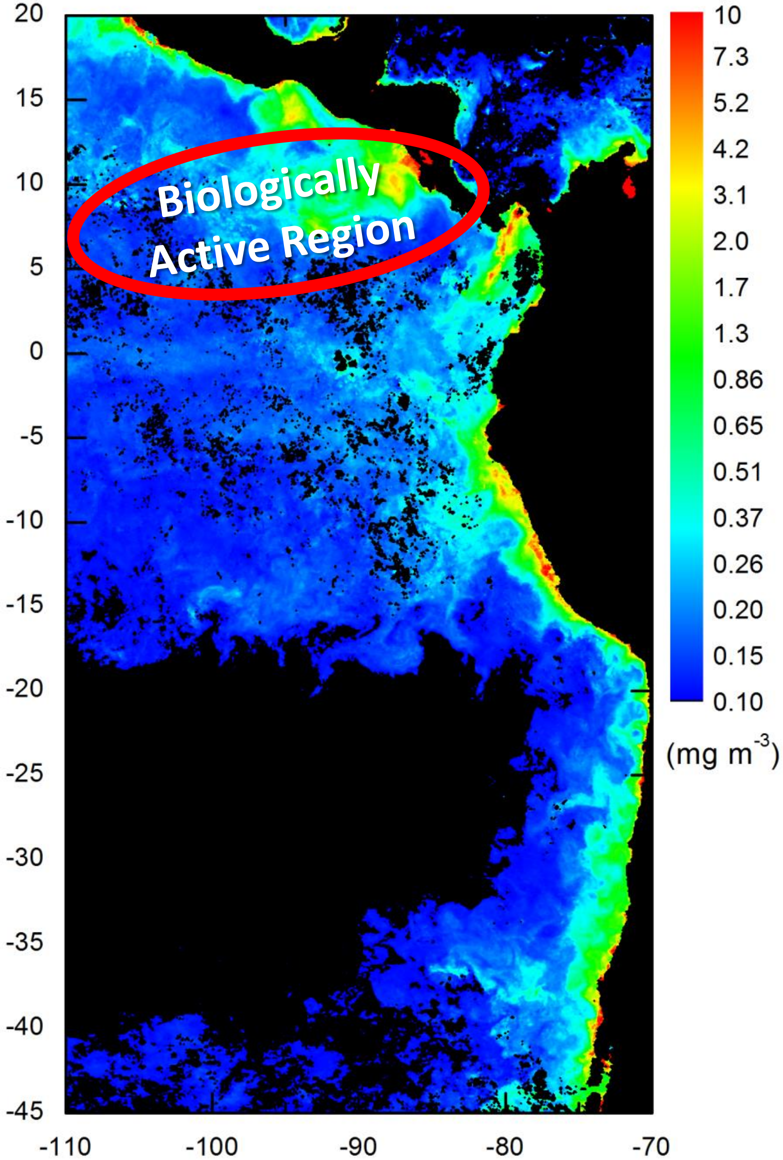
RF12 – biologically active region

Observations are much higher at the surface than the model predicts, but similar aloft.



RF15 – biologically active region

MODIS Chlorophyll-a



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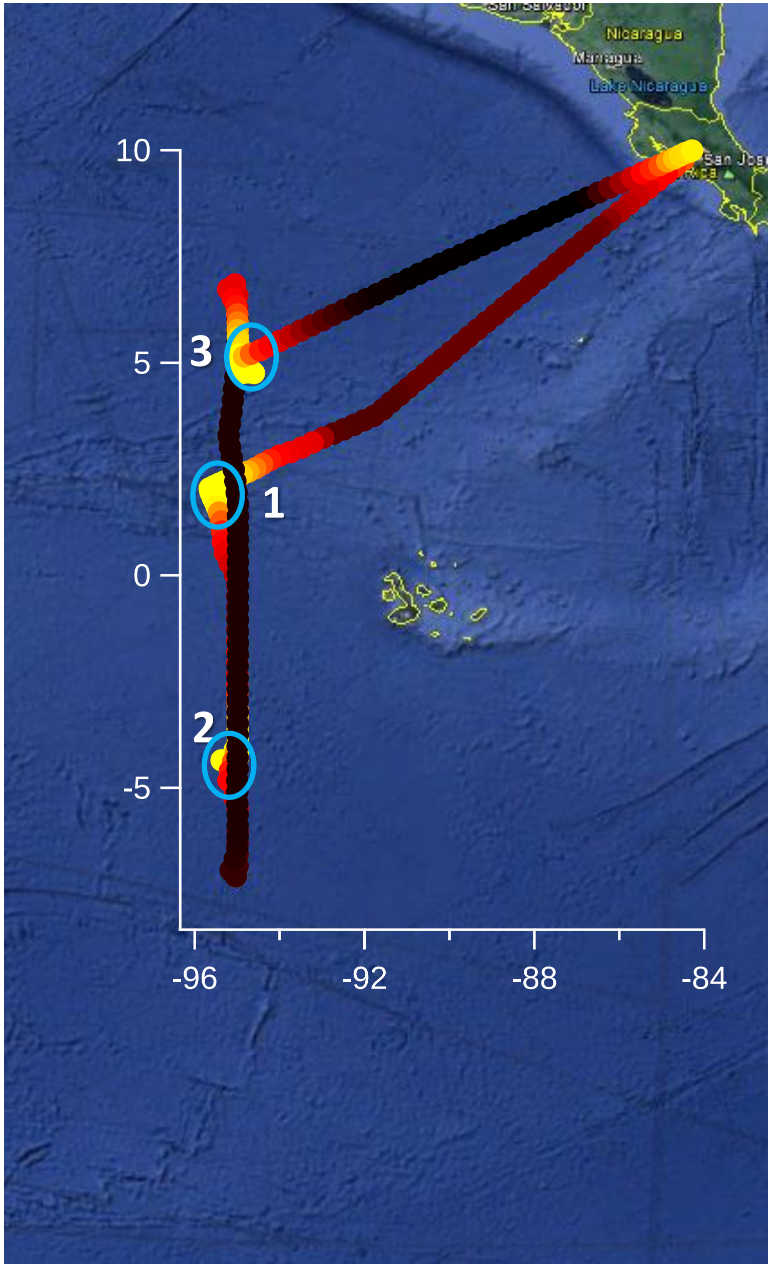

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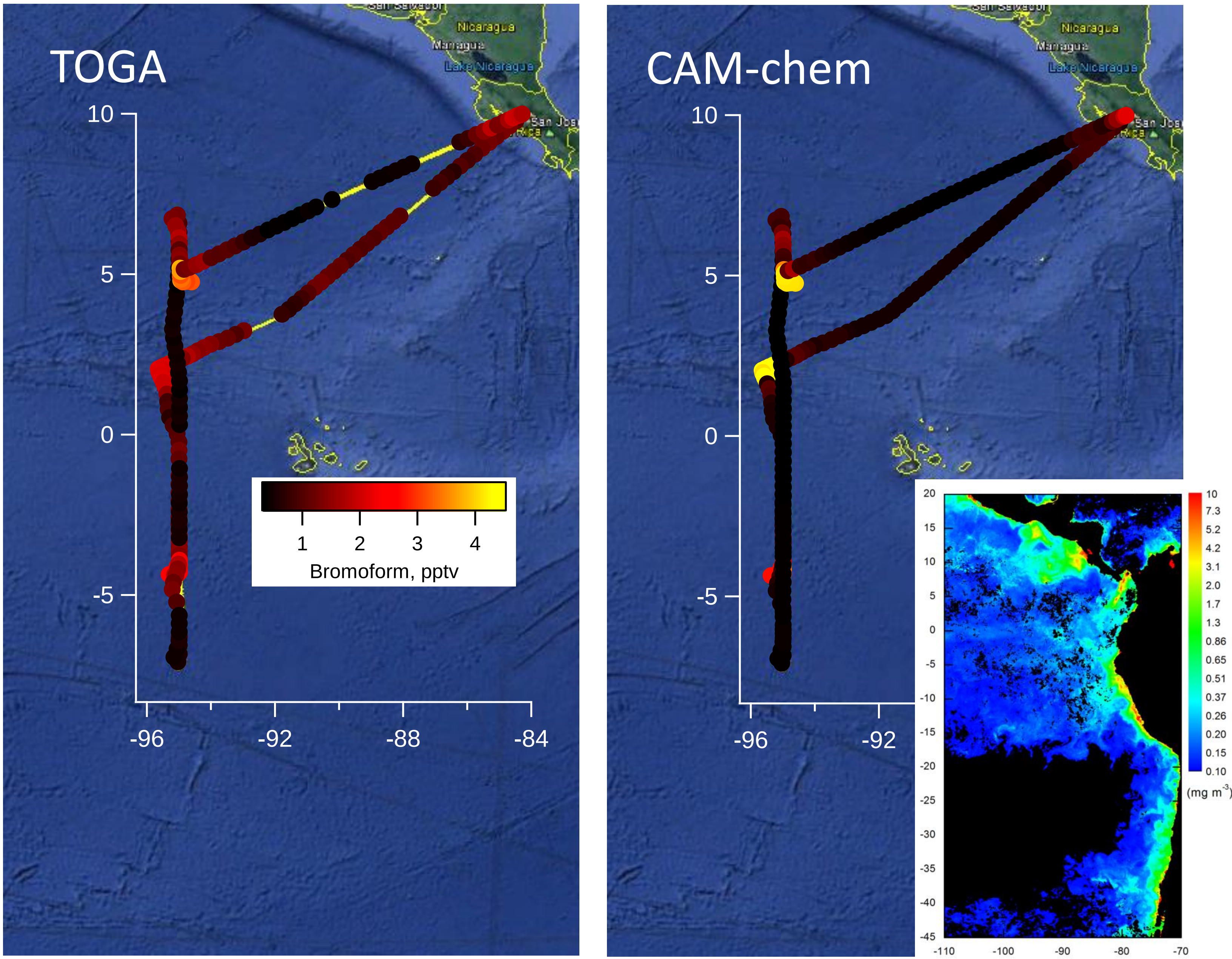

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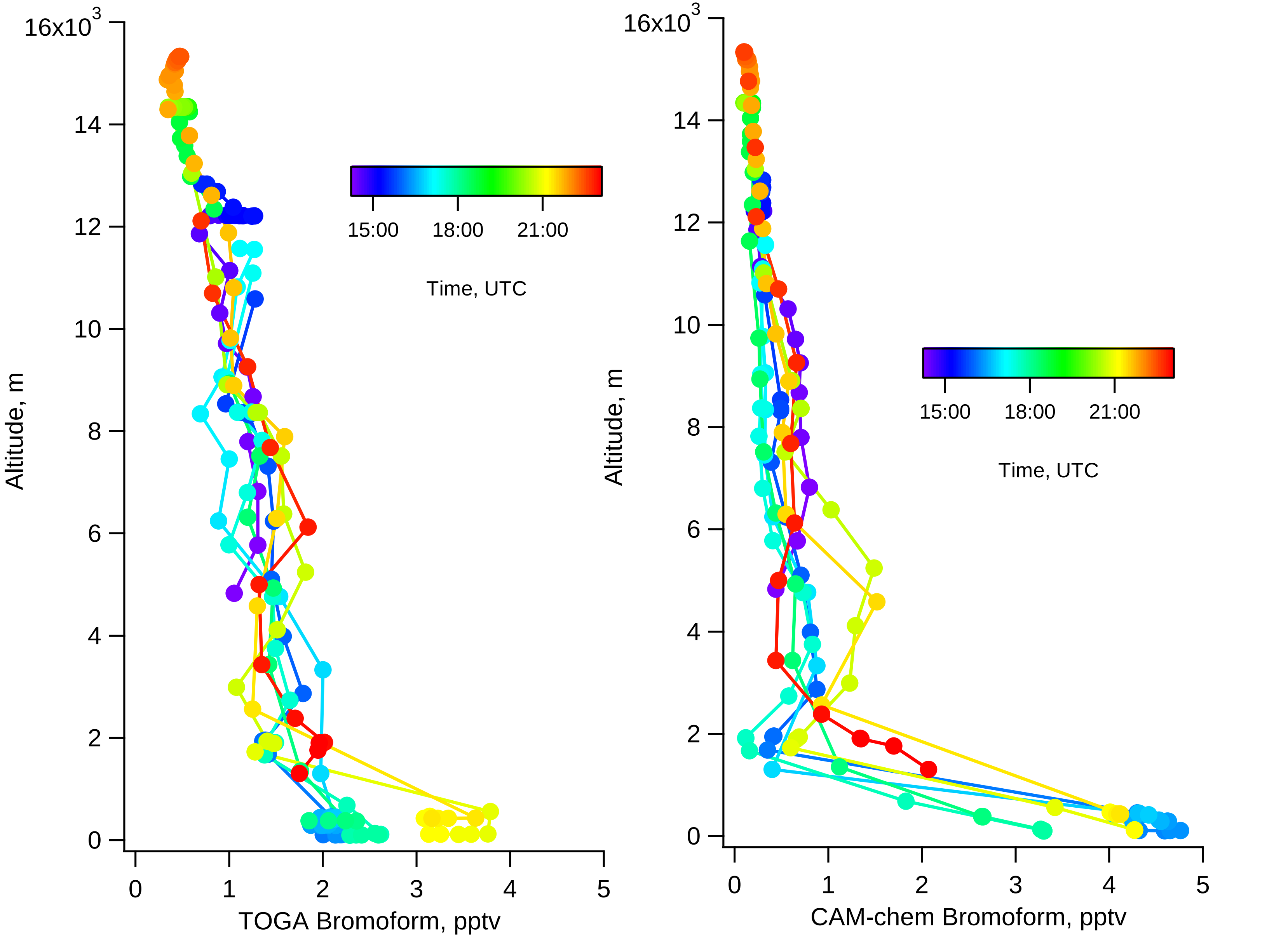

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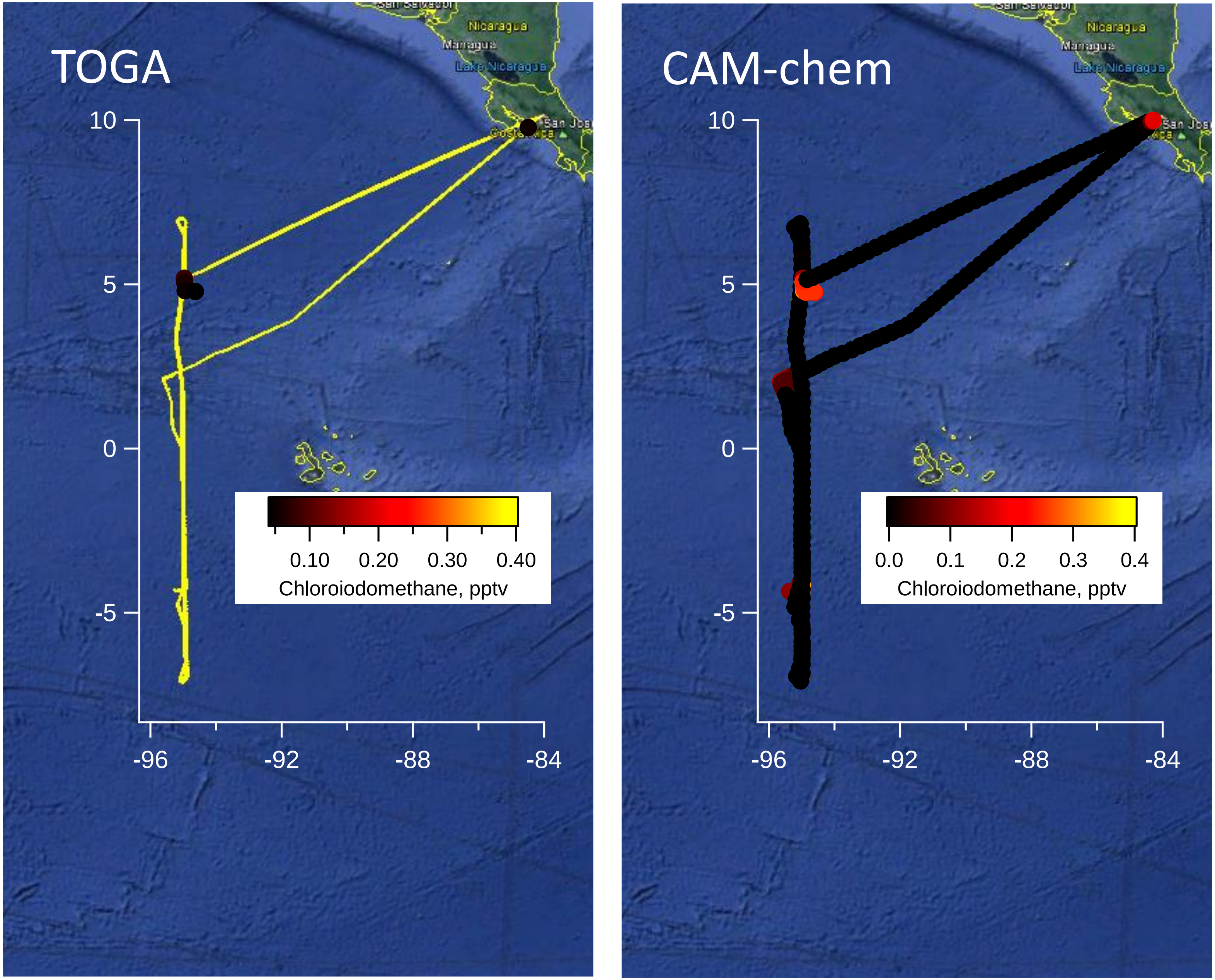

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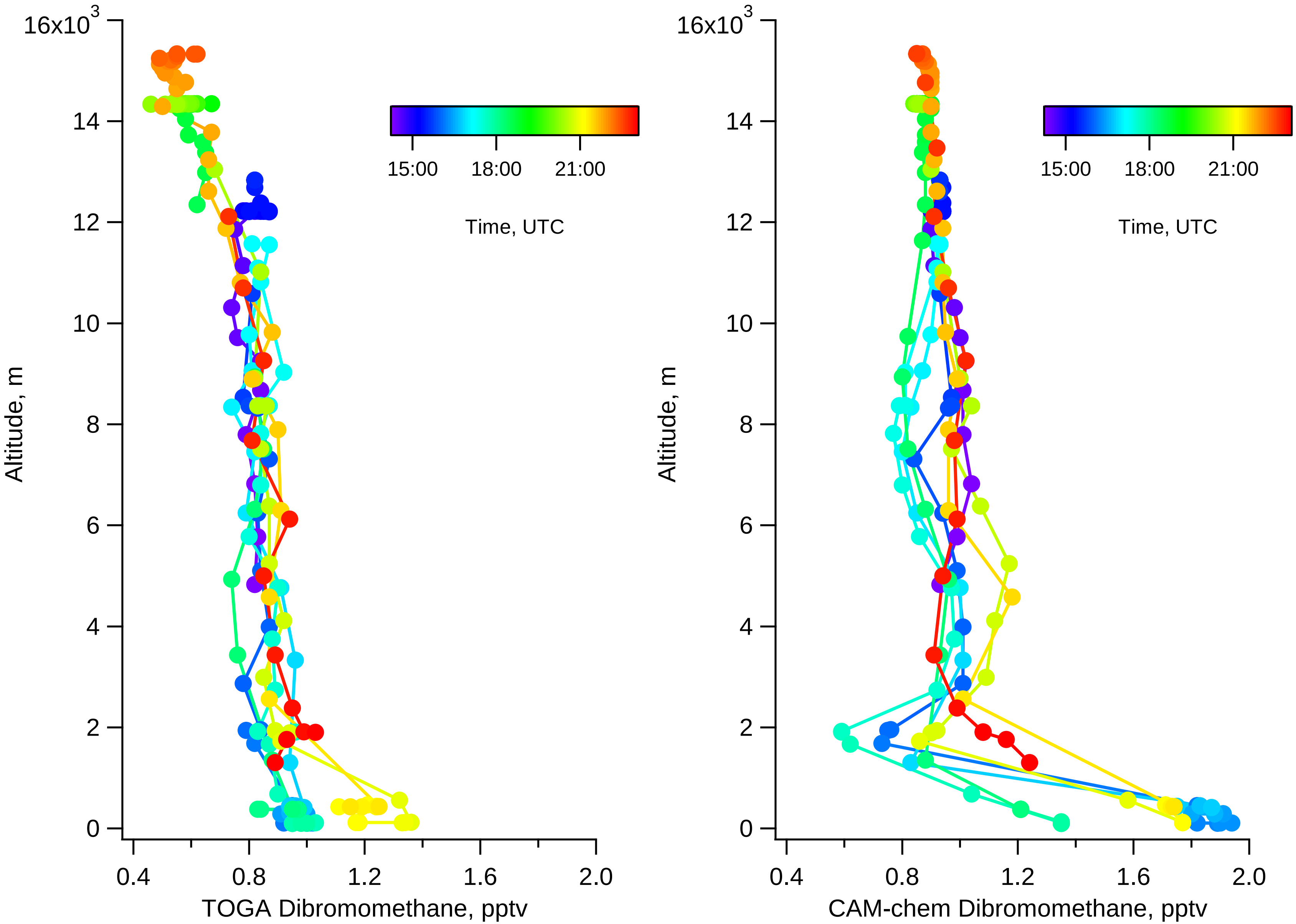
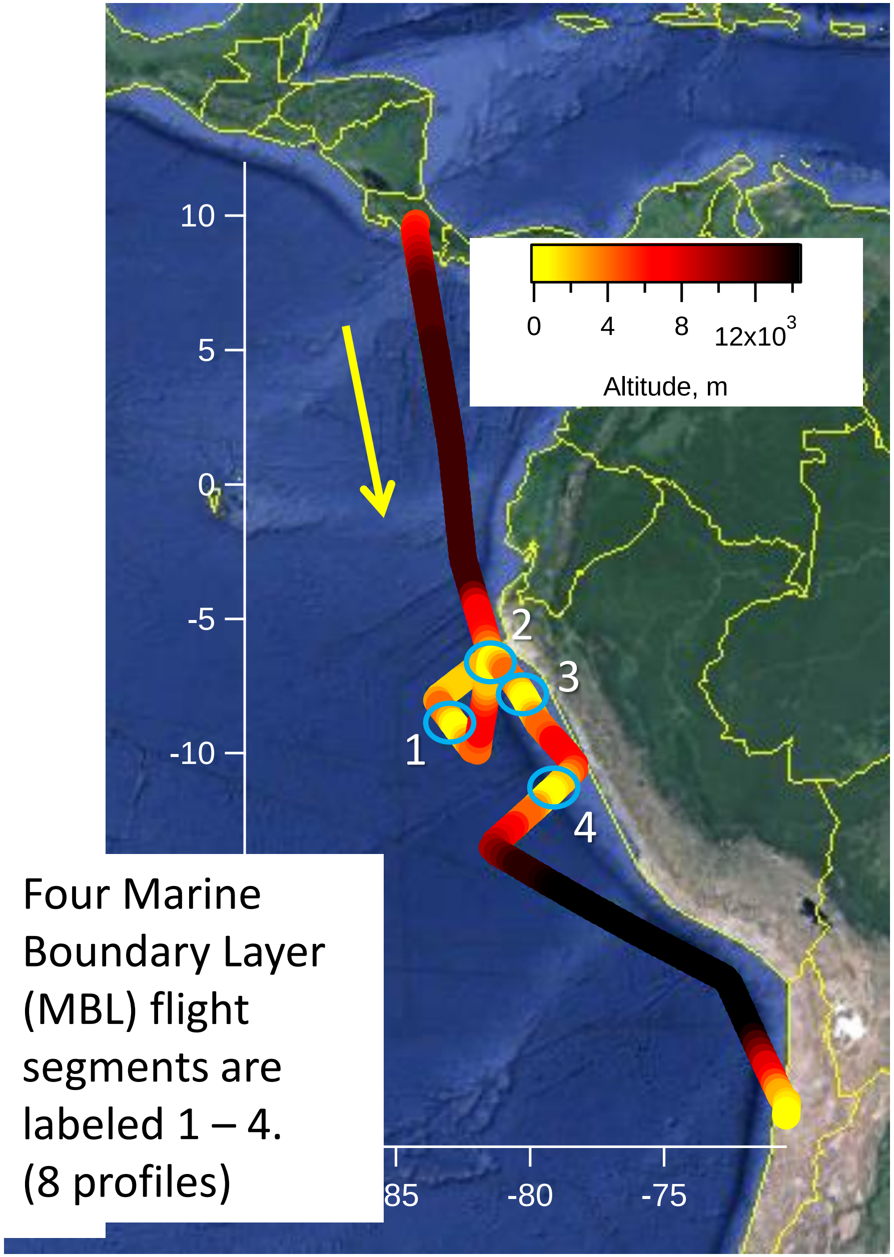


Anthropogenic/Biomass Burning/Ocean Tracers

n-butane
benzene
toluene
acetylene (CAM-chem)
acetone*, acetonitrile
Formaldehyde*, Acetaldehyde*

*also have other natural sources

RF01 – coastal emissions, continental outflow



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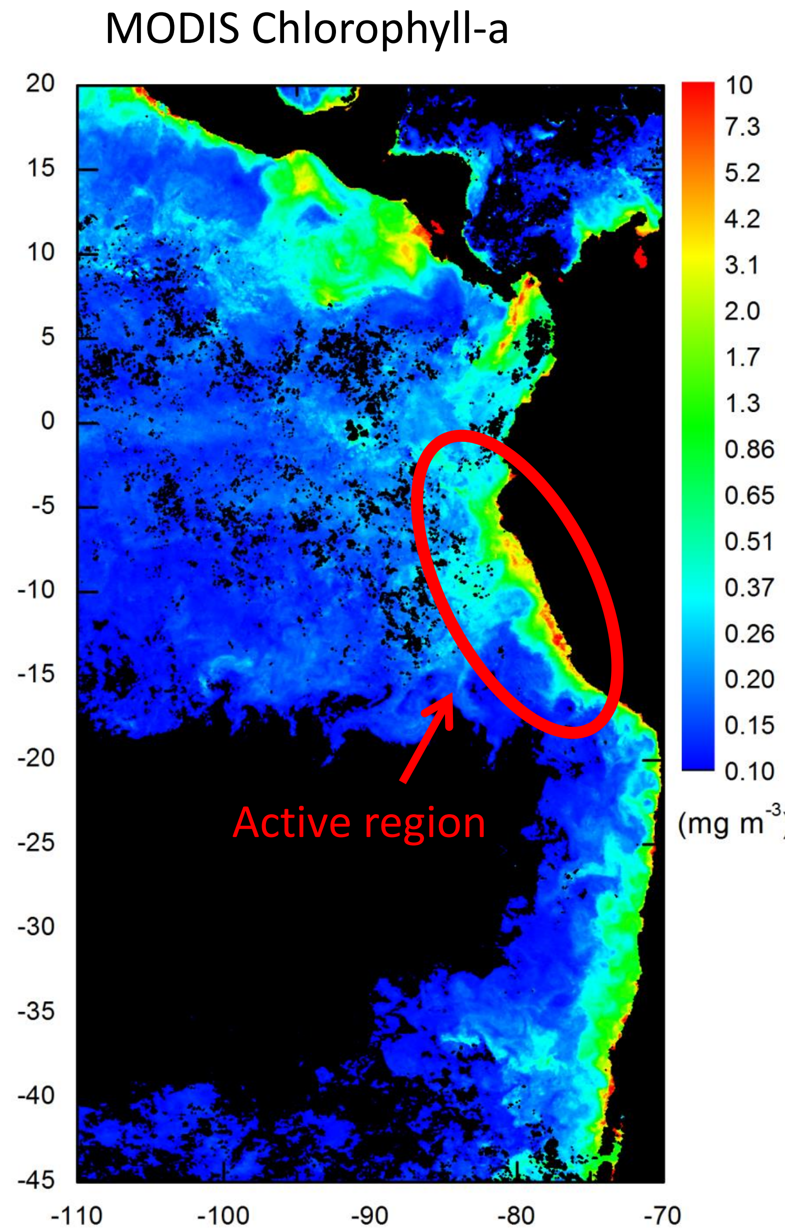
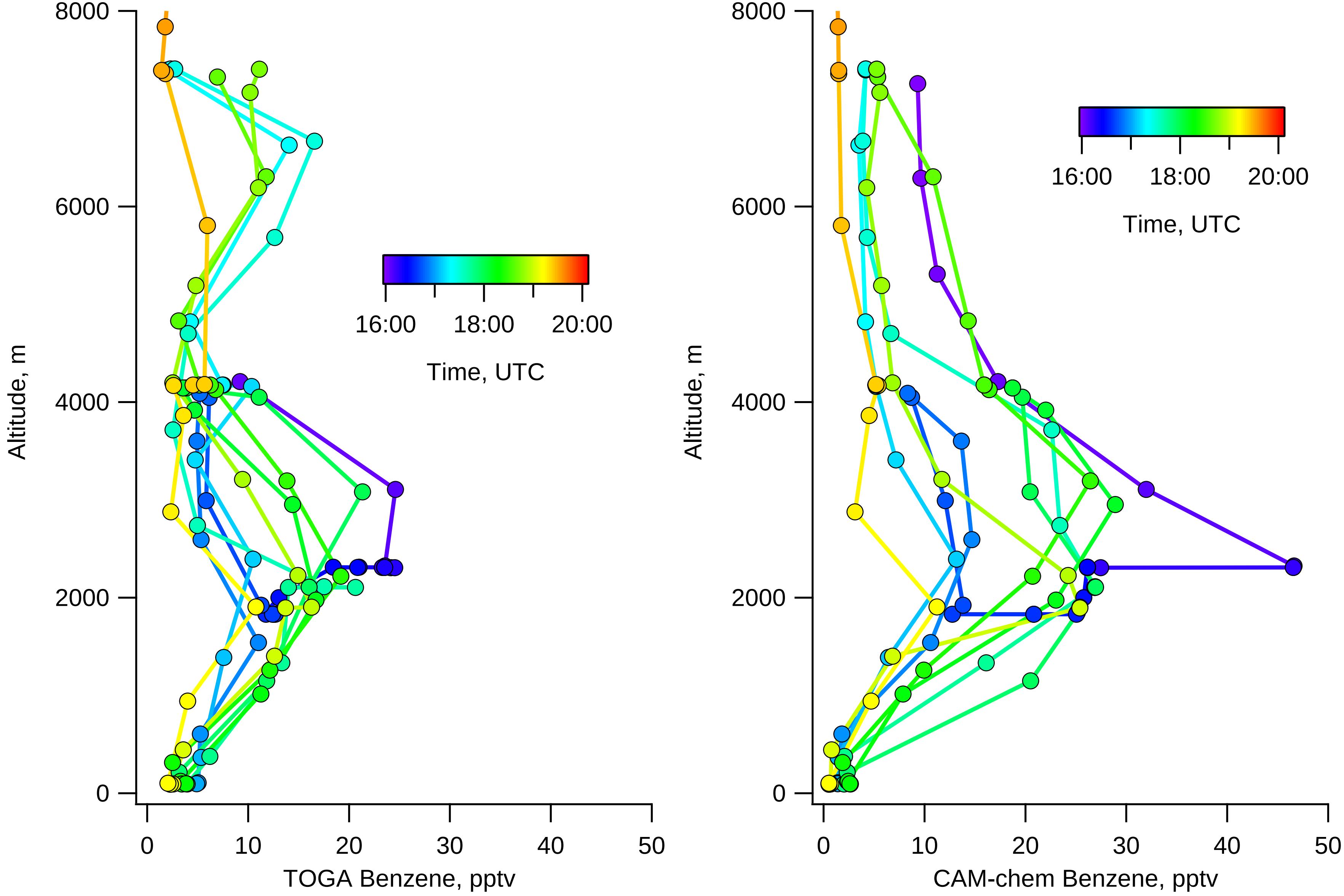


RF01: 8 profiles off the west coast of Peru

CAM-chem captured the pollution layer aloft at ~ 2-3 km



RF05 – oligotrophic ocean

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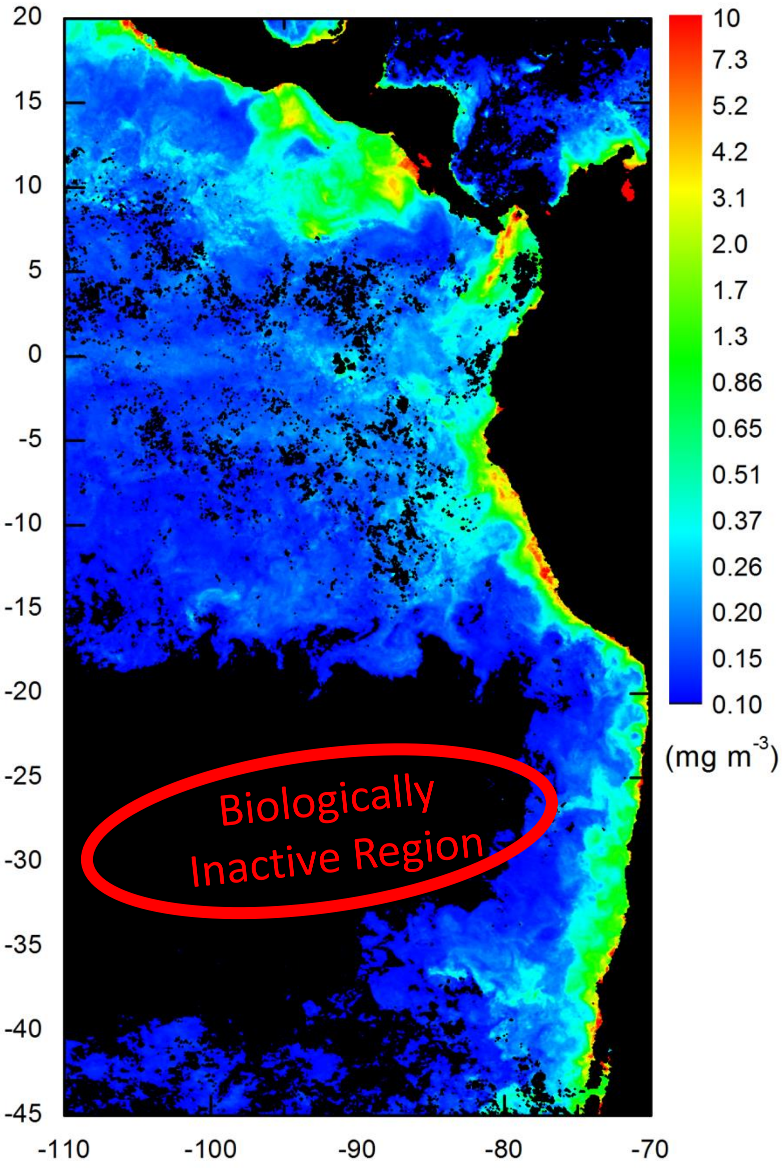
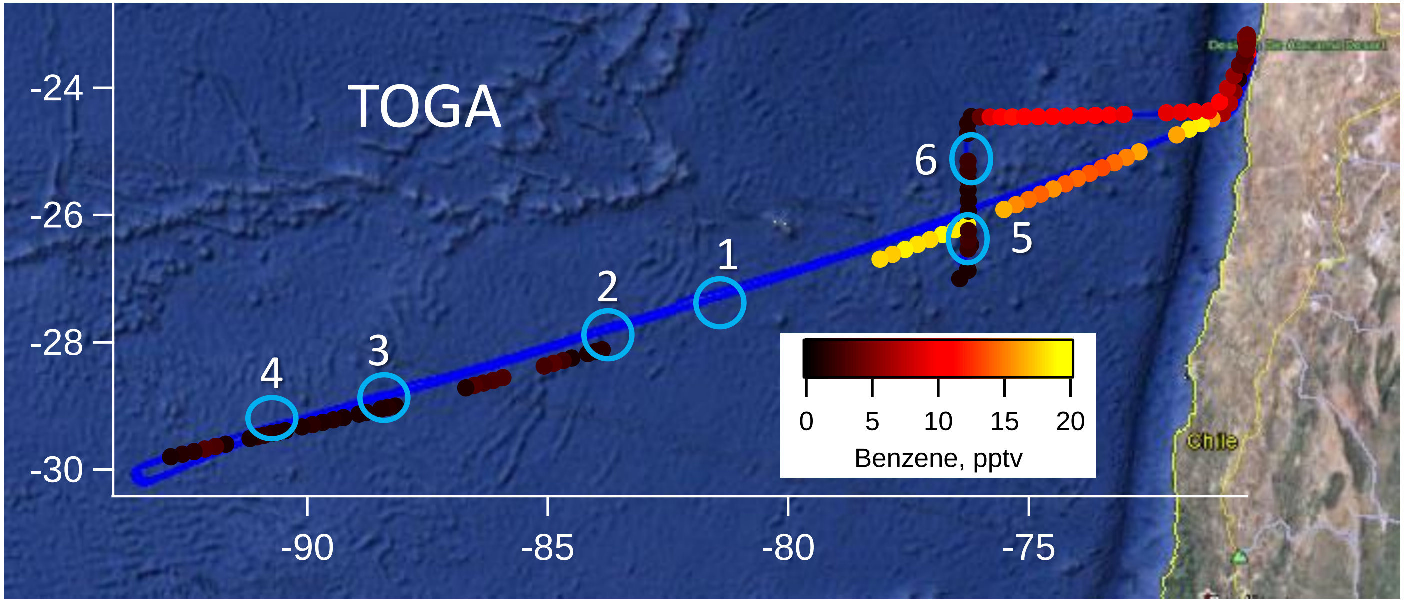
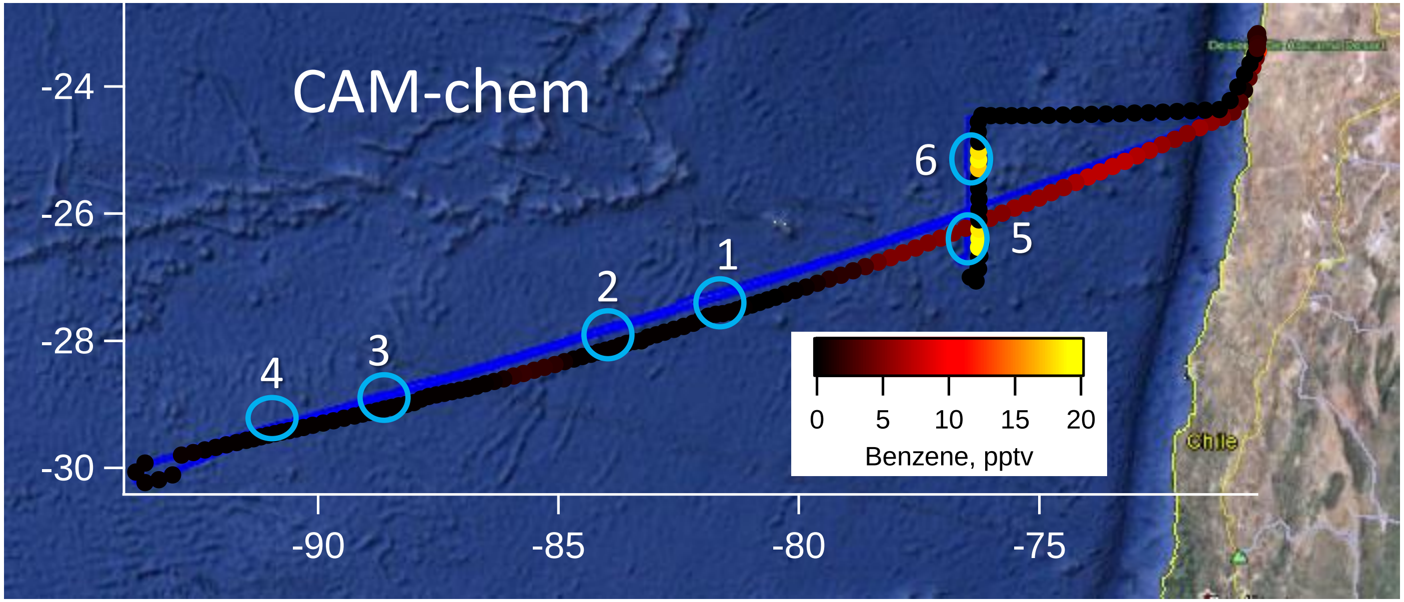


RF05 – oligotrophic ocean

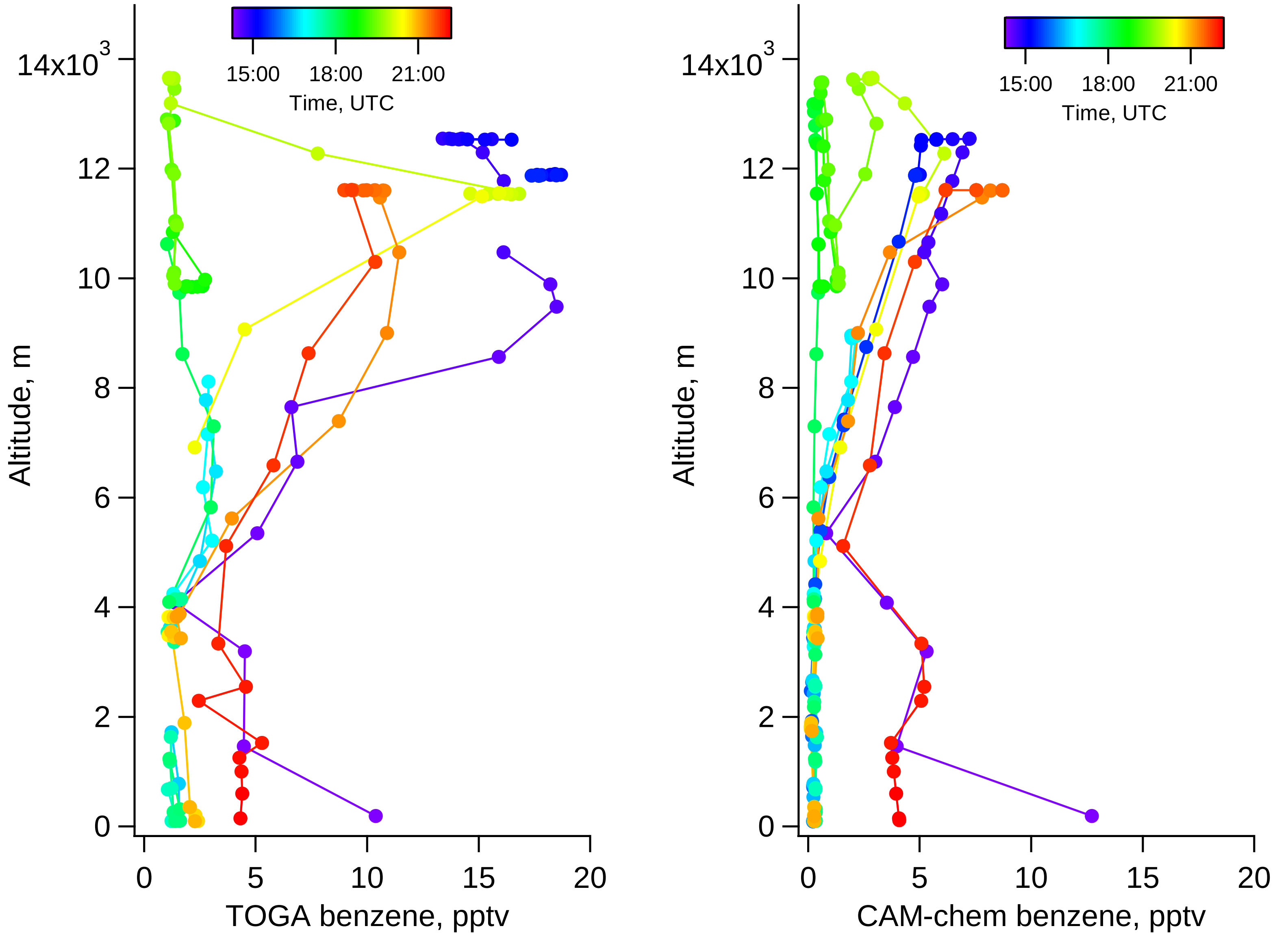
TOGA benzene





RF05 – oligotrophic ocean

benzene



RF12 – biologically active region/convected MBL

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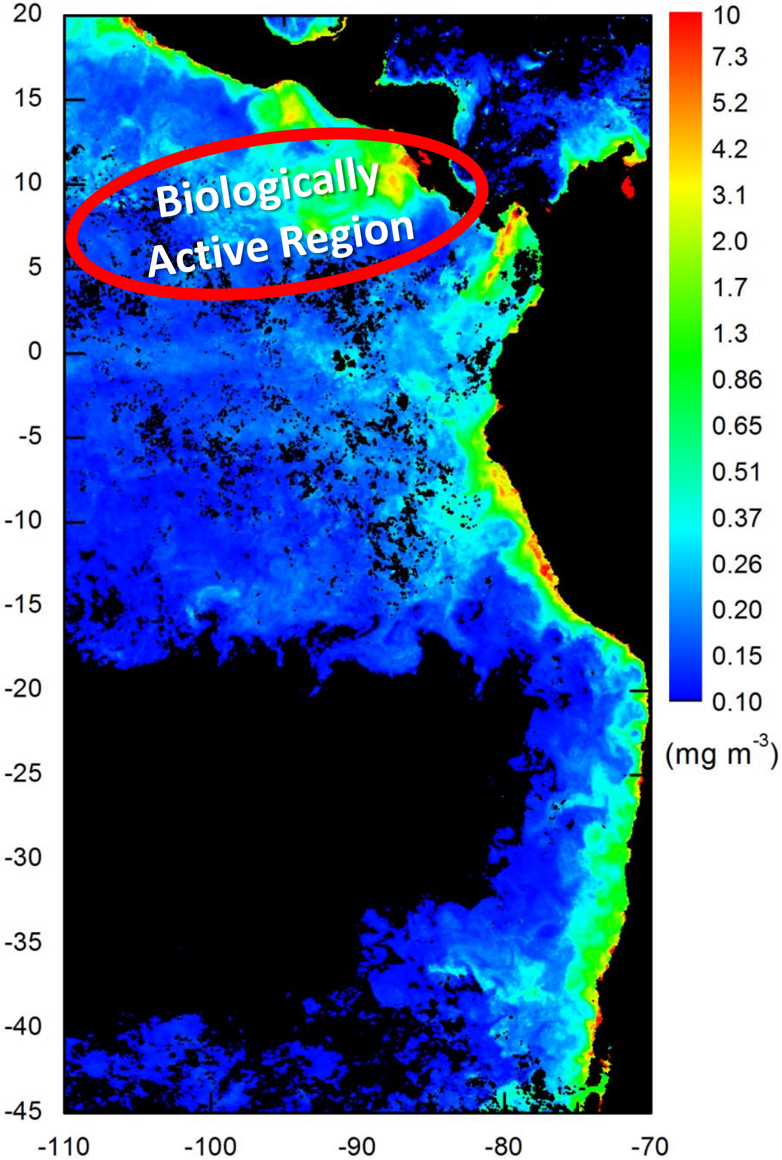

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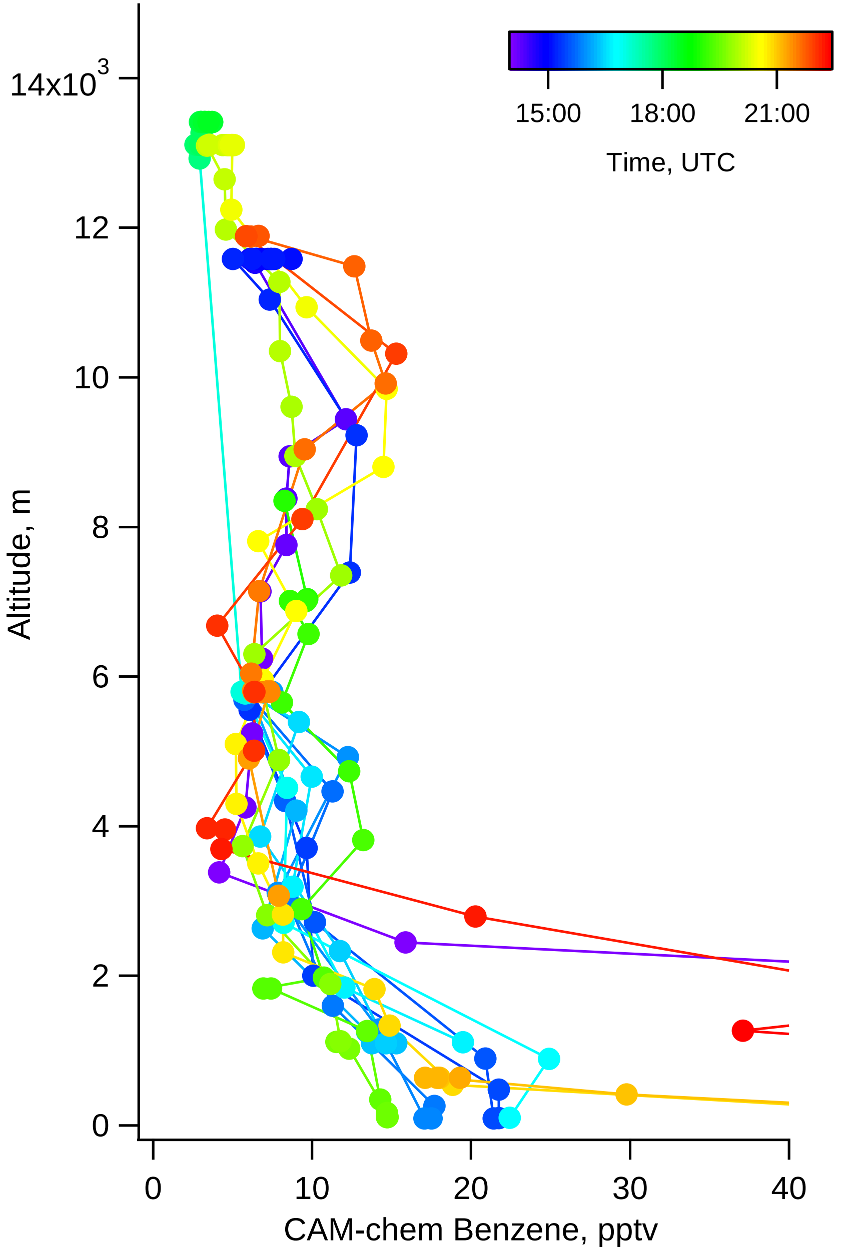
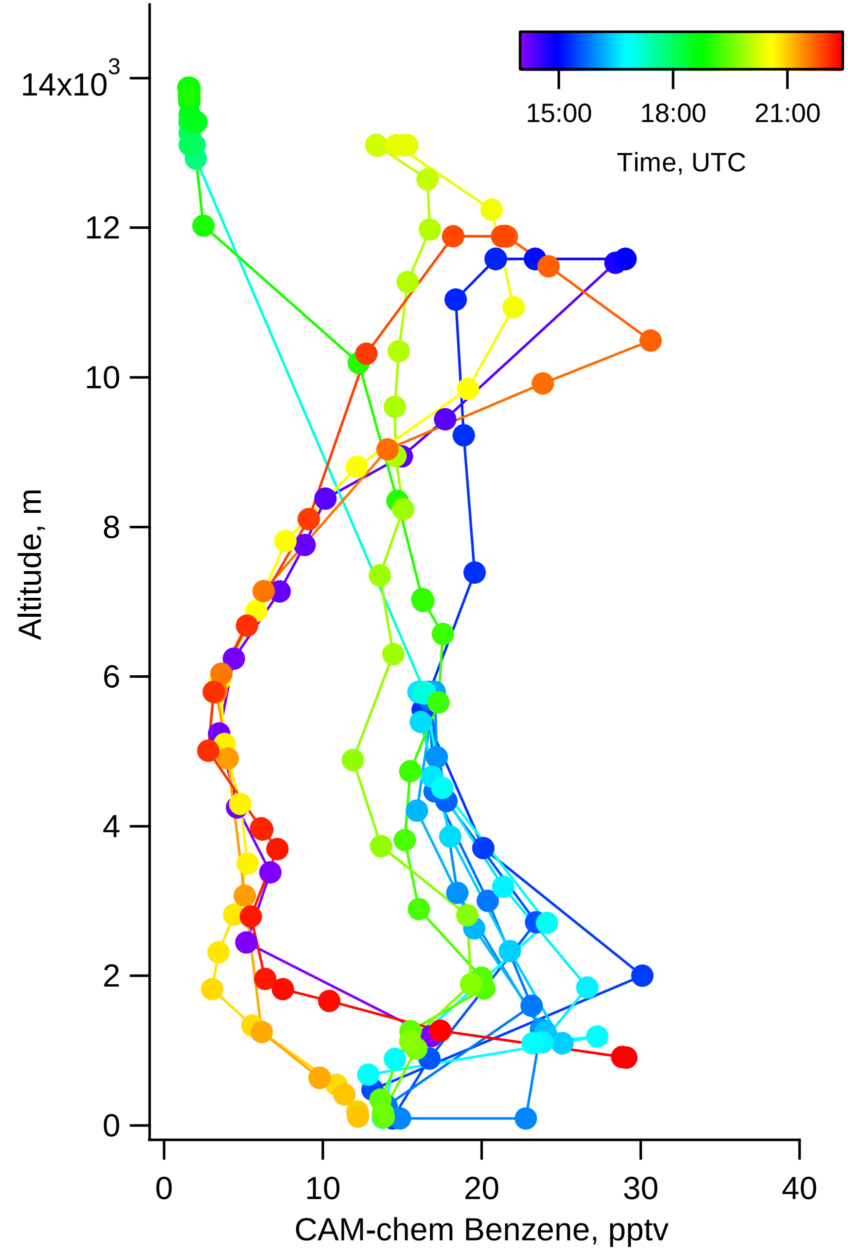
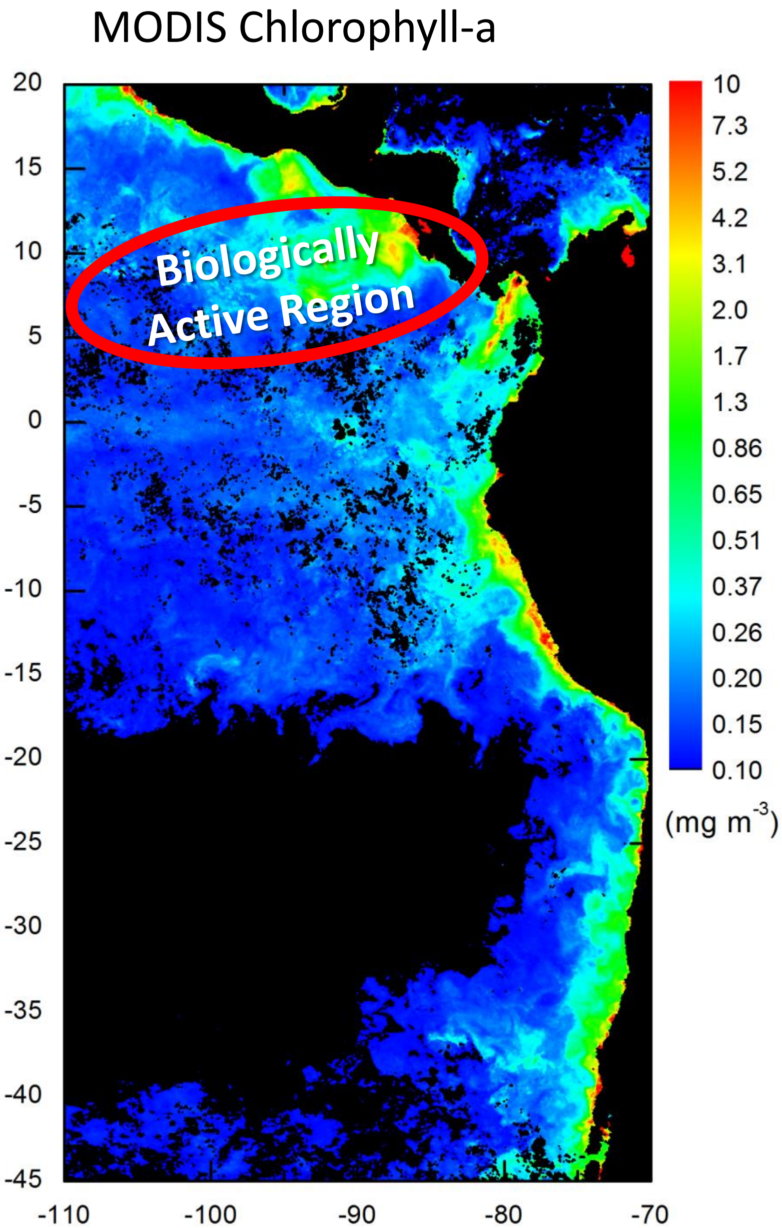




RF15 – biologically active region



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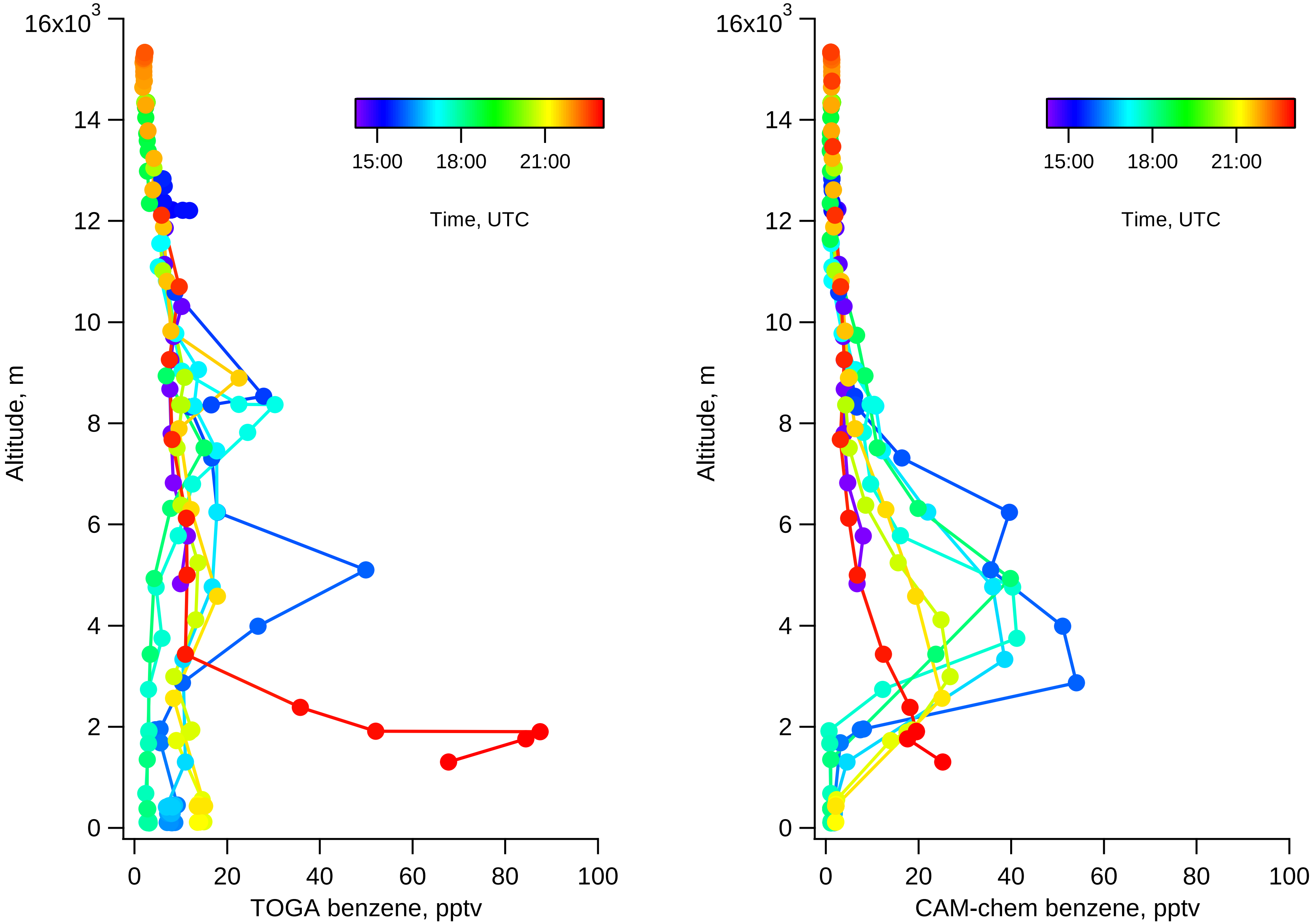


Oxygenated VOCs

acetone (CH_3COCH_3)

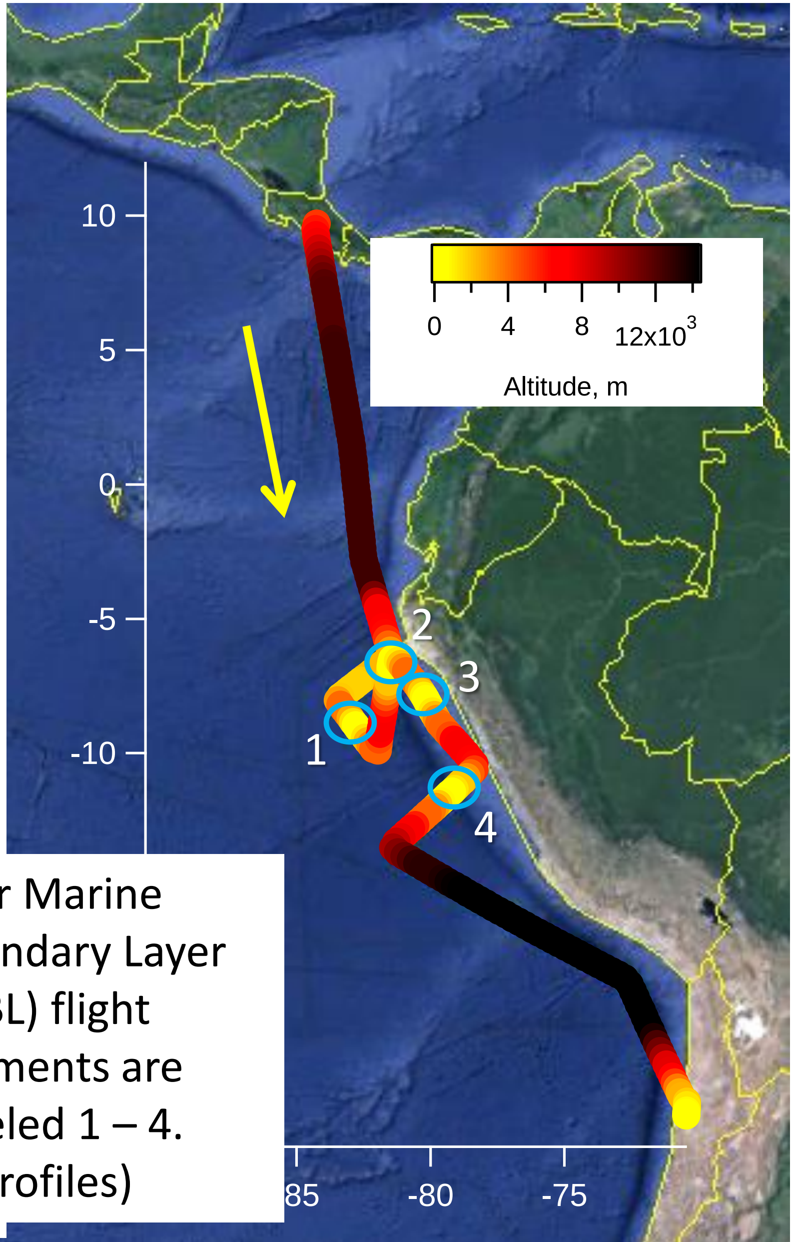
formaldehyde (HCHO)

acetaldehyde (CH_3CHO)

methanol (CH_3OH)

Butanone/Methyl Ethyl Ketone (MEK)

RF01 – coastal emissions, continental outflow



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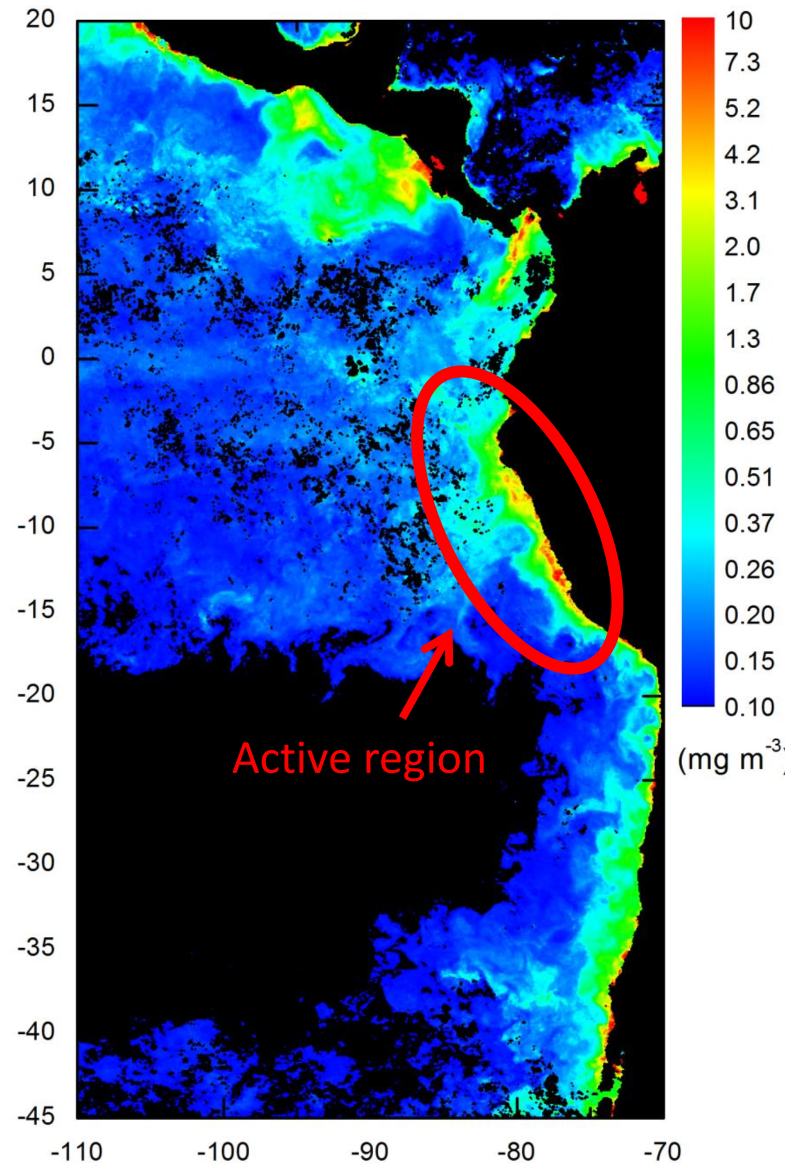
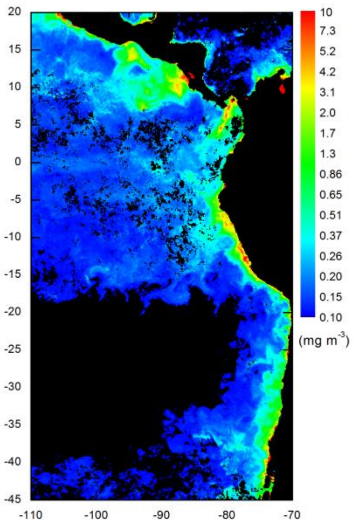
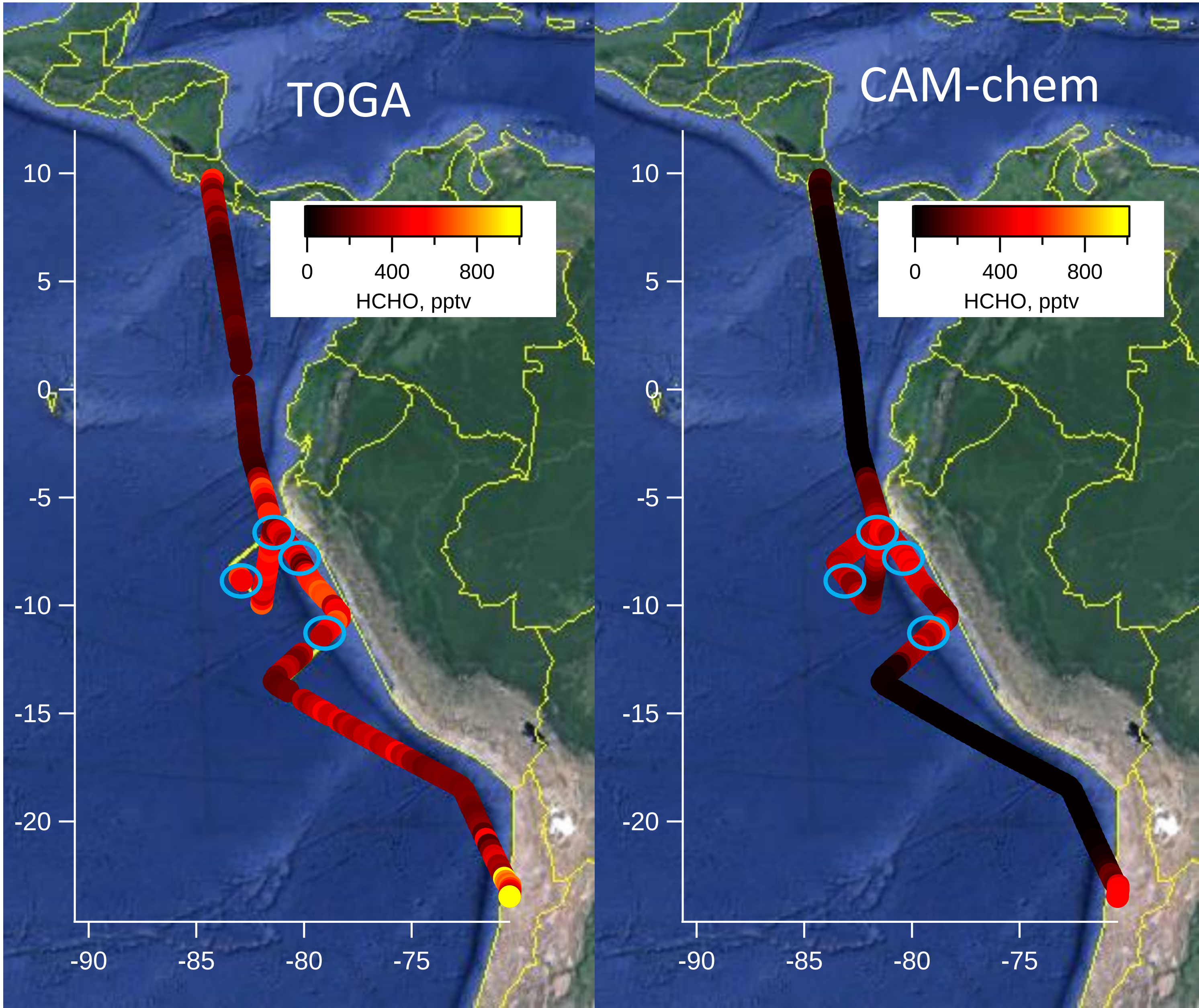


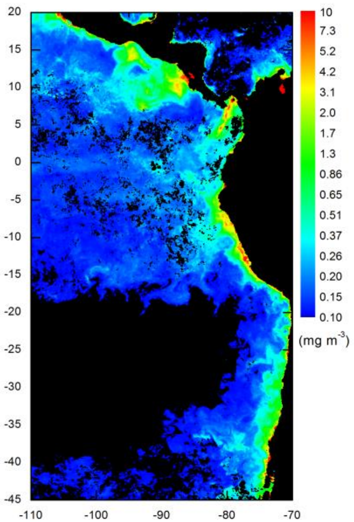
From RF01

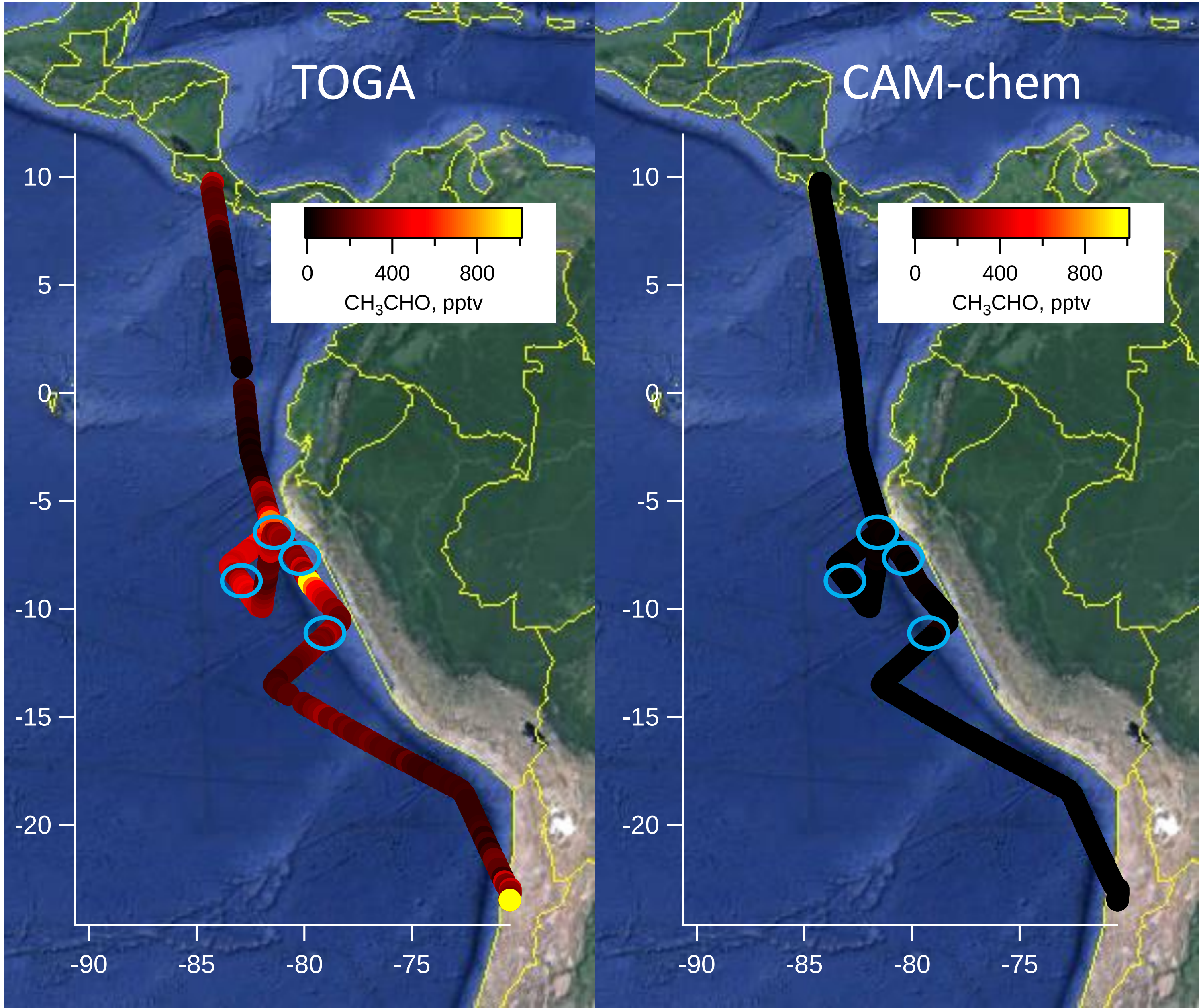




CAM-chem HCHO appears to capture
The pollution off the coast, but is lower than TOGA in high altitude flight segments.

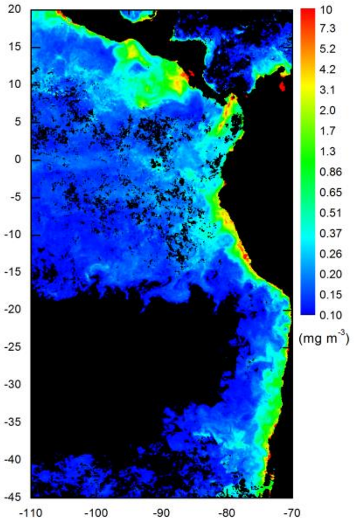
From RF01



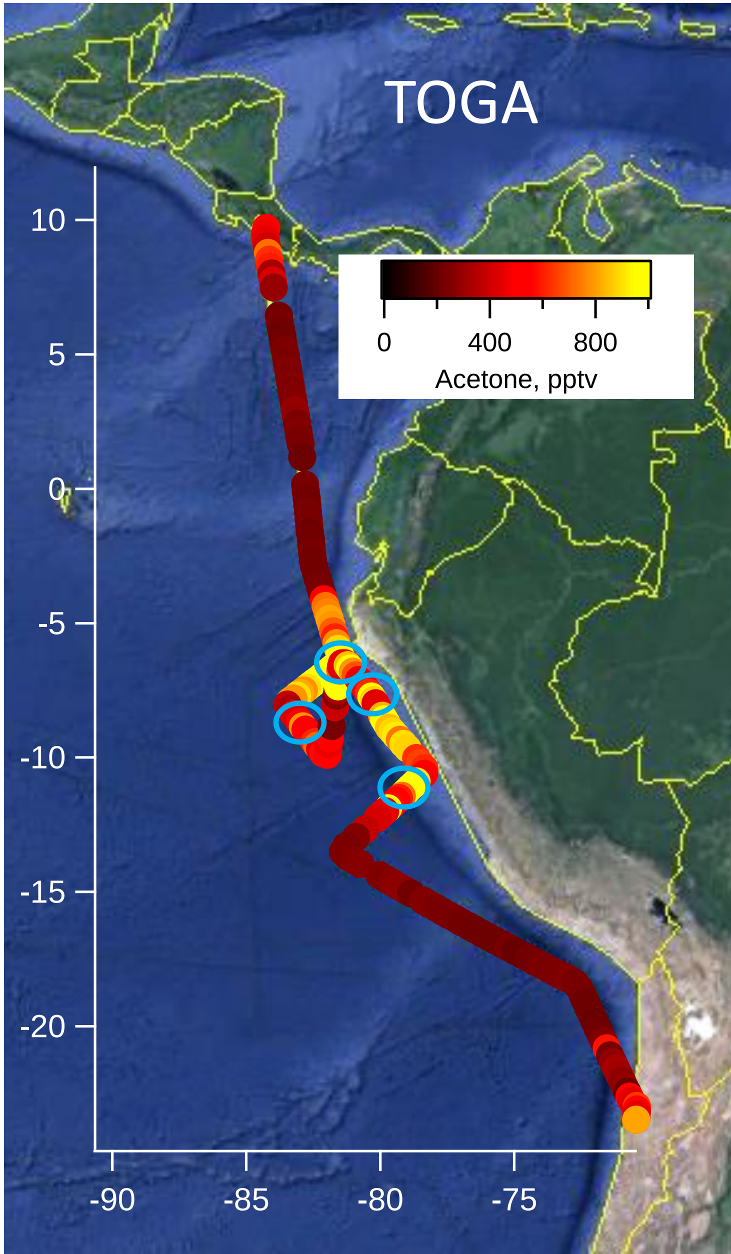


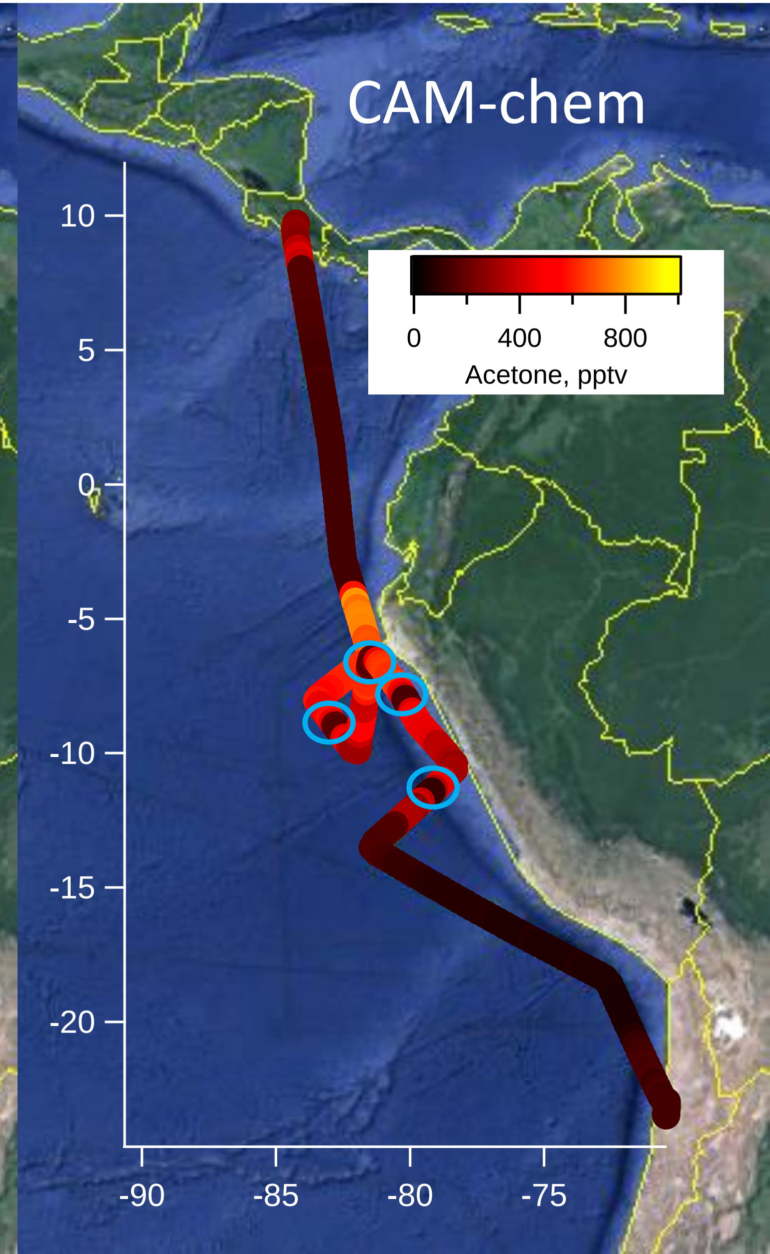
CAM-chem acetaldehyde *very low* in contrast to TOGA observations.

From RF01



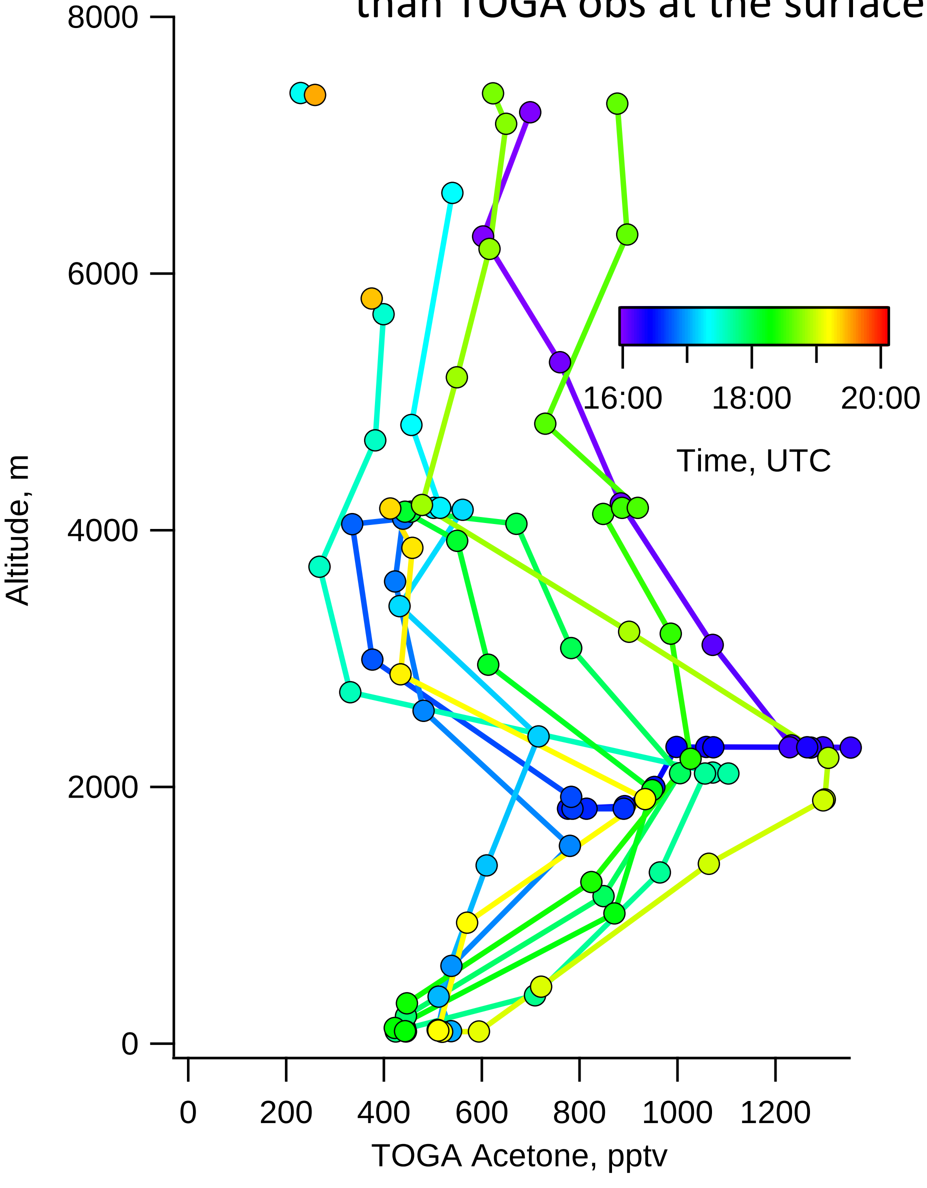
CAM-chem and TOGA acetone are both lower at the surface…

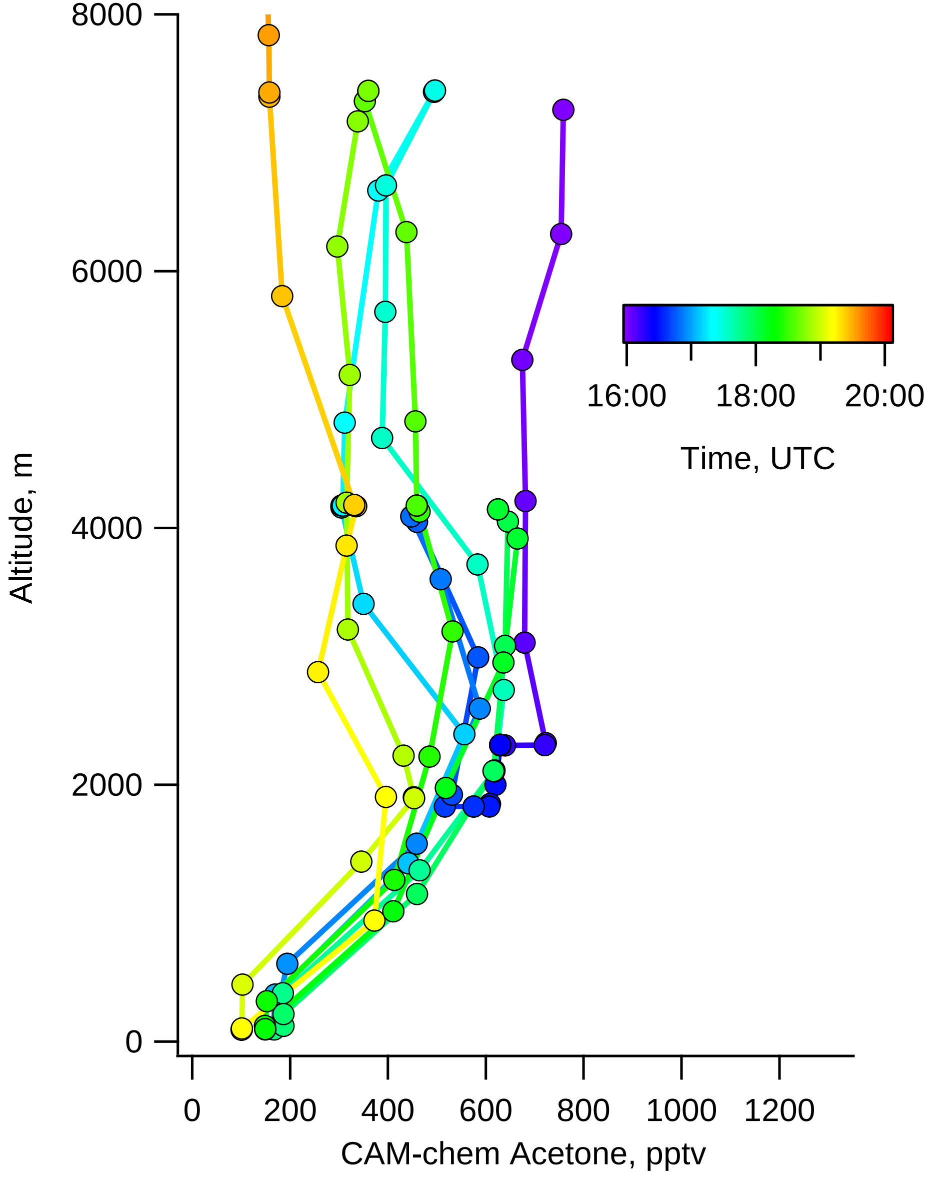




RF01: 8 profiles off the west coast of Peru

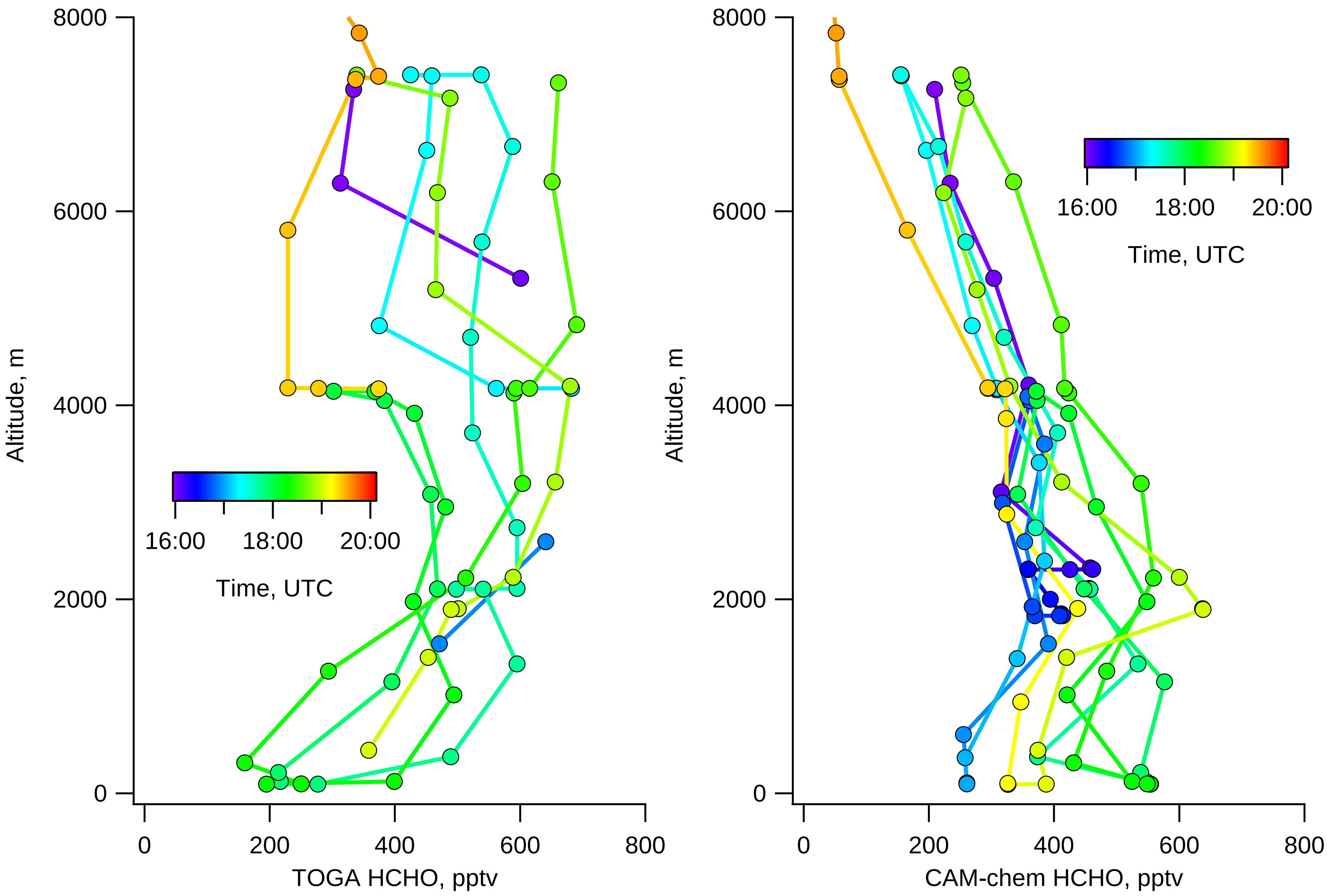
CAM-chem captured the pollution layer aloft at ~ 2-3 km, but is lower than TOGA obs at the surface.





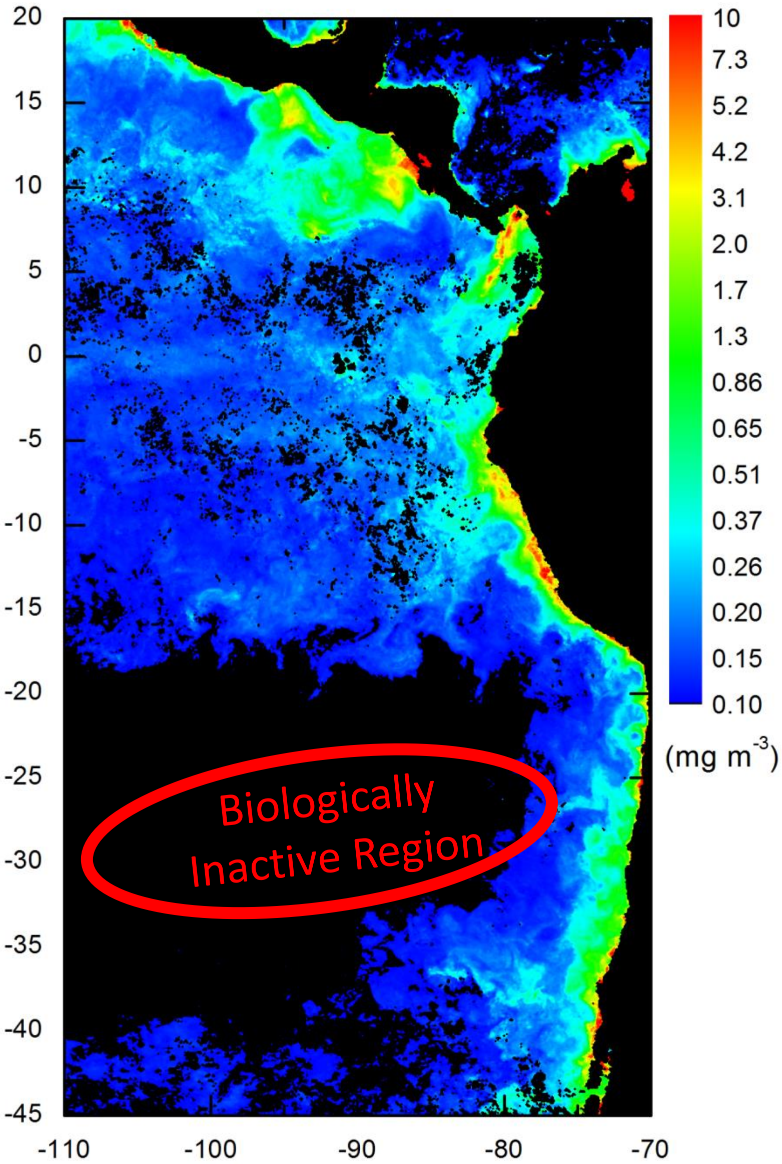
RF01: 8 profiles off the west coast of Peru

CAM-chem HCHO agrees nominally with TOGA.

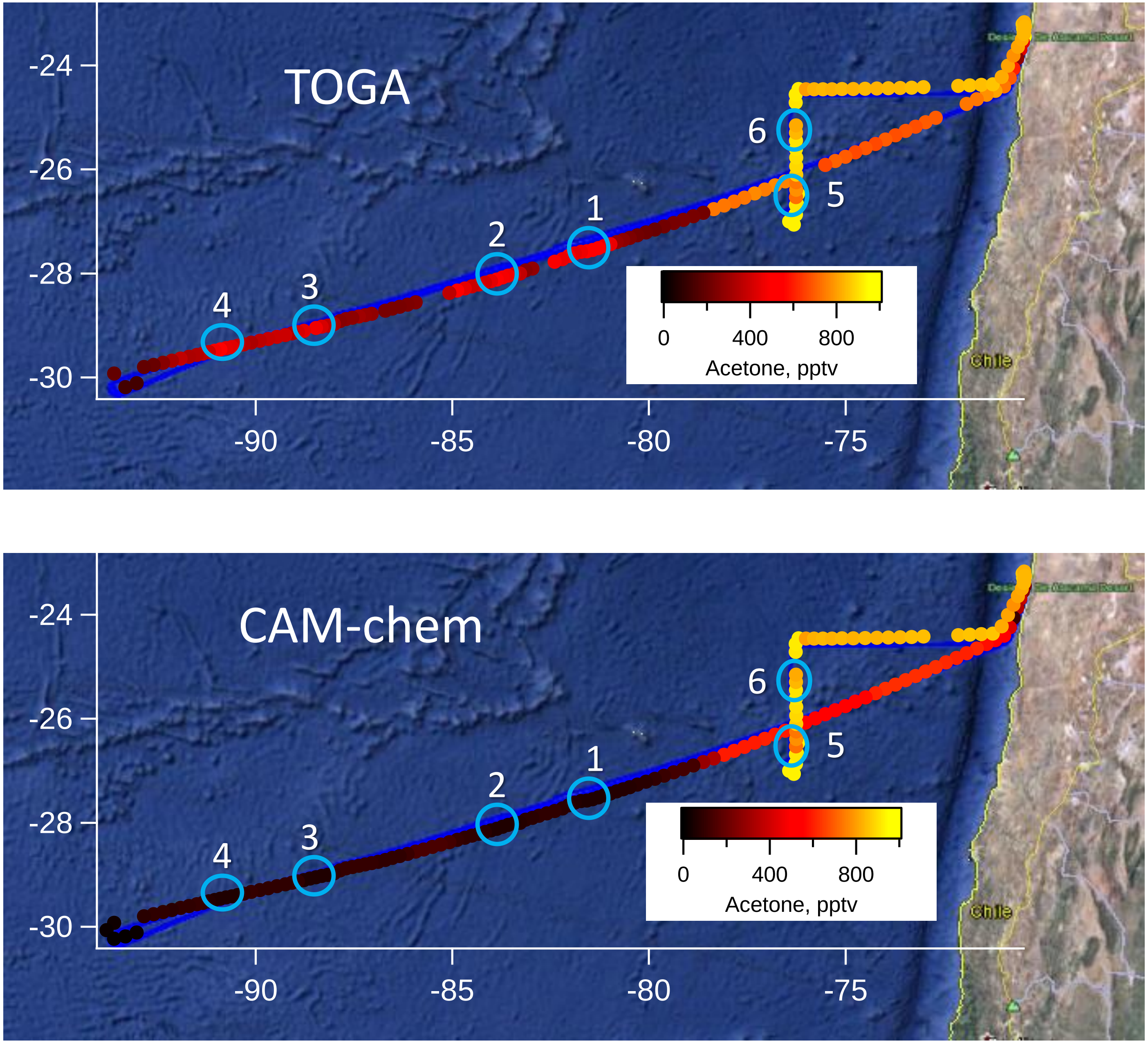


RF05 – oligotrophic ocean

MODIS Chlorophyll-a

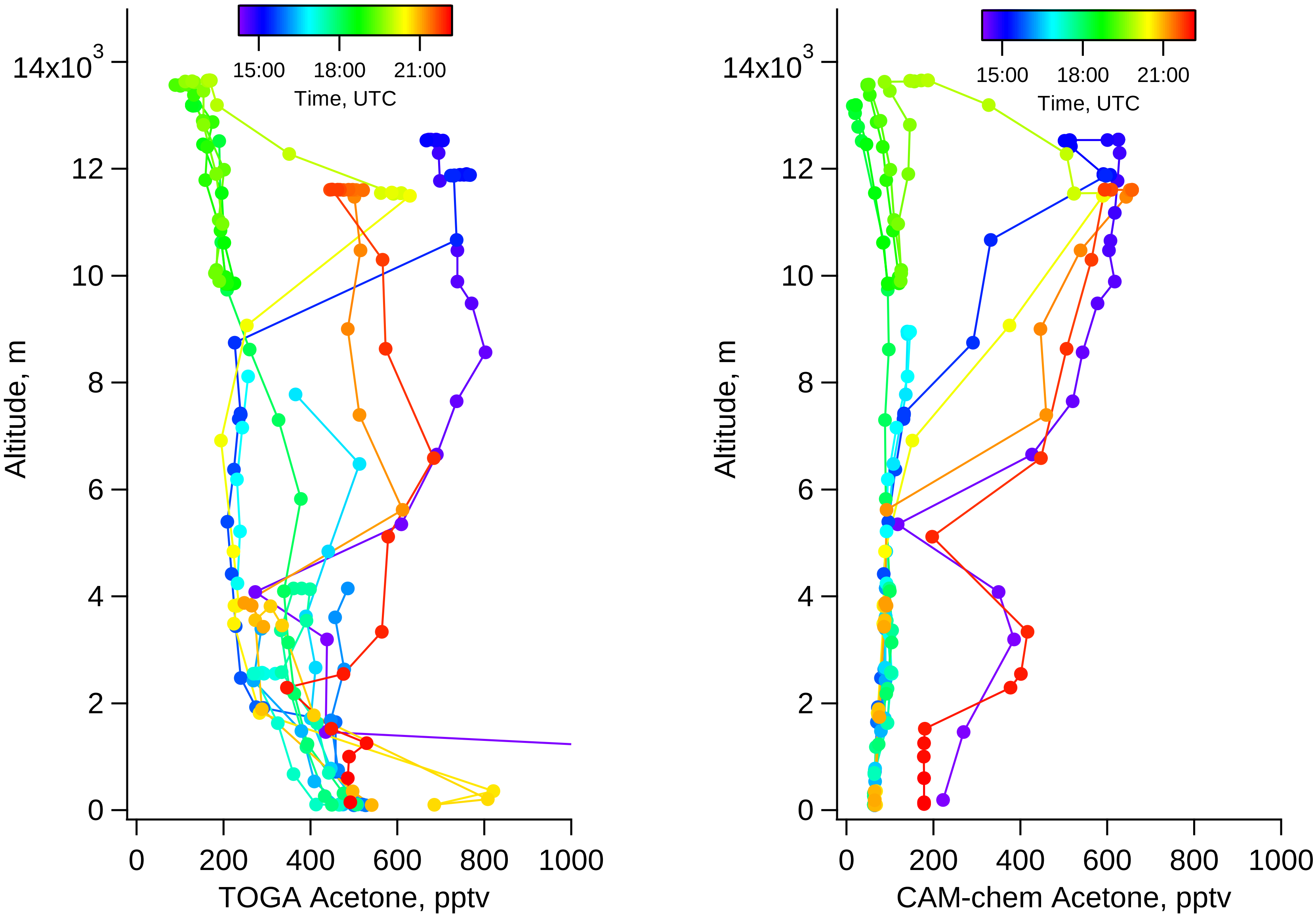


RF05 – oligotrophic ocean

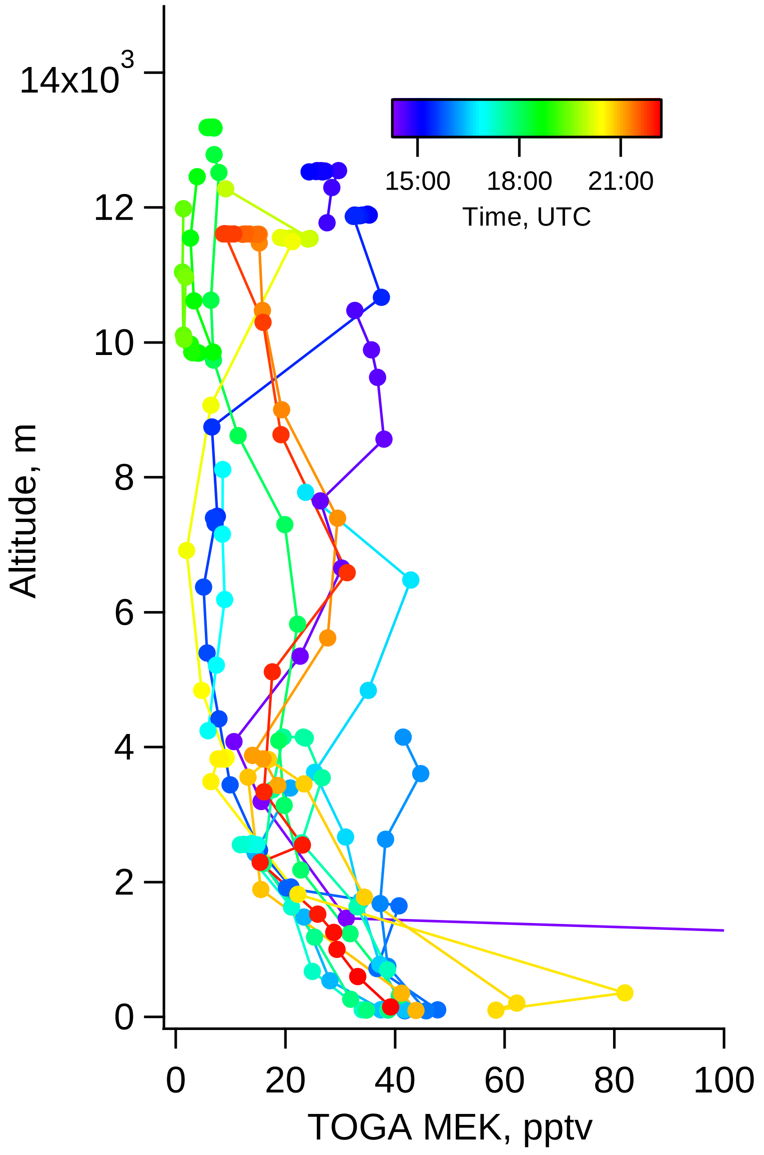


RF05 – oligotrophic ocean

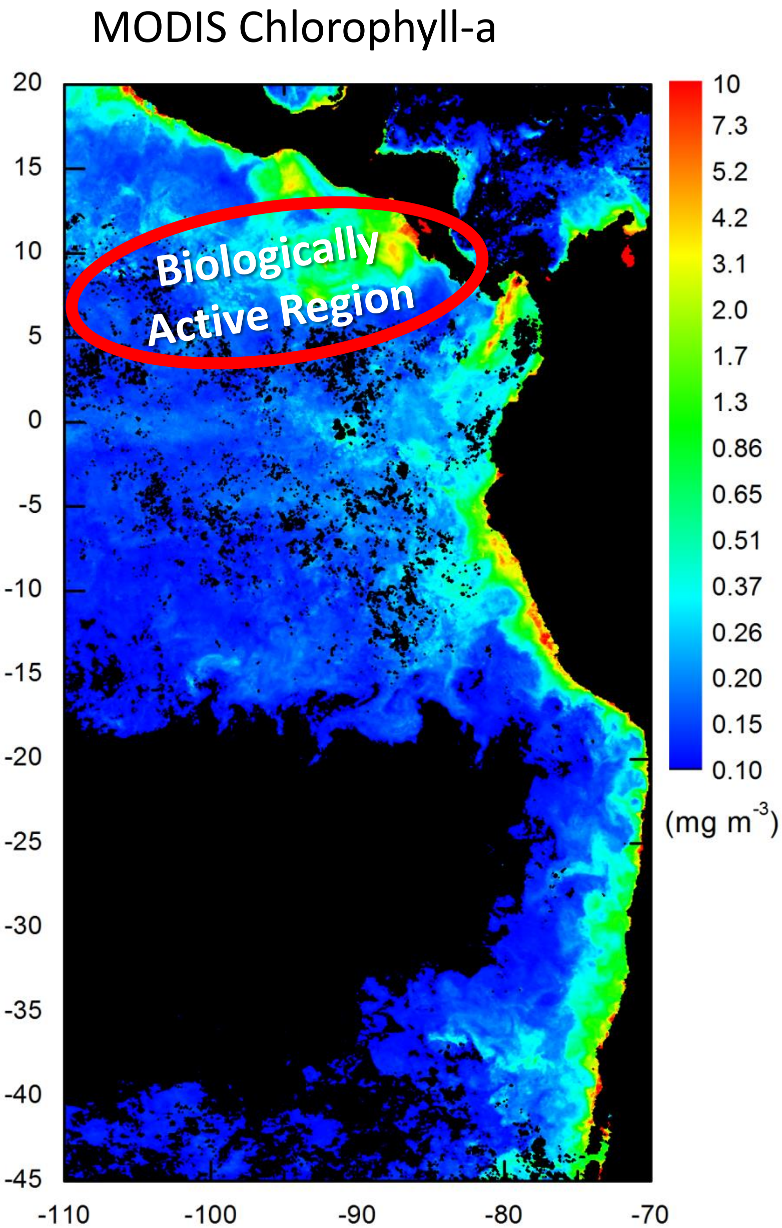
CAM-chem acetone << TOGA obs. near the oligotrophic surface and the transition layer.



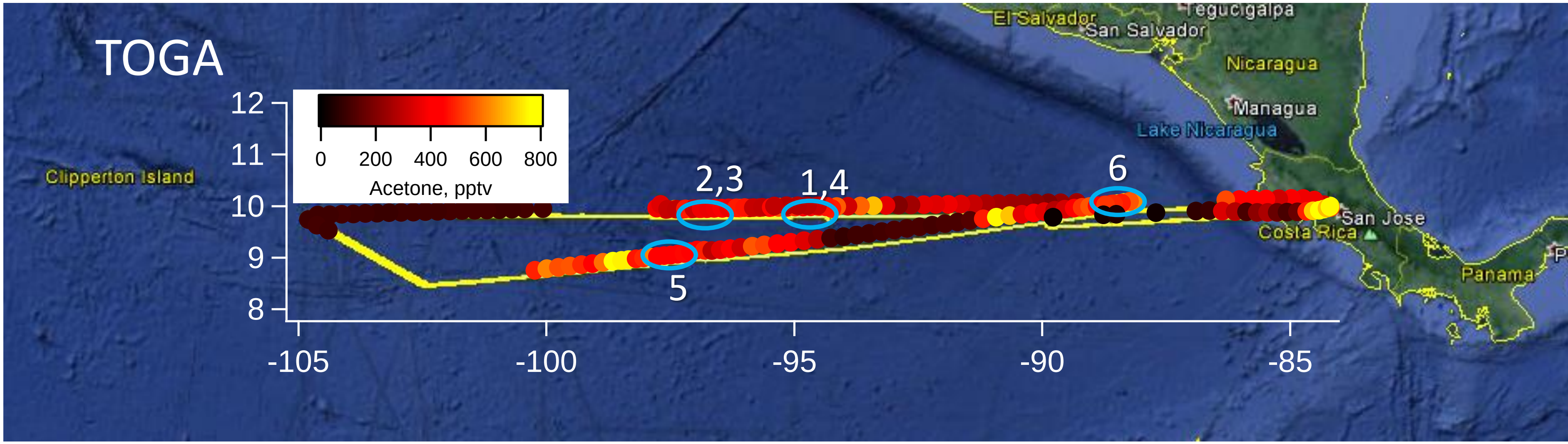
RF05 – oligotrophic ocean

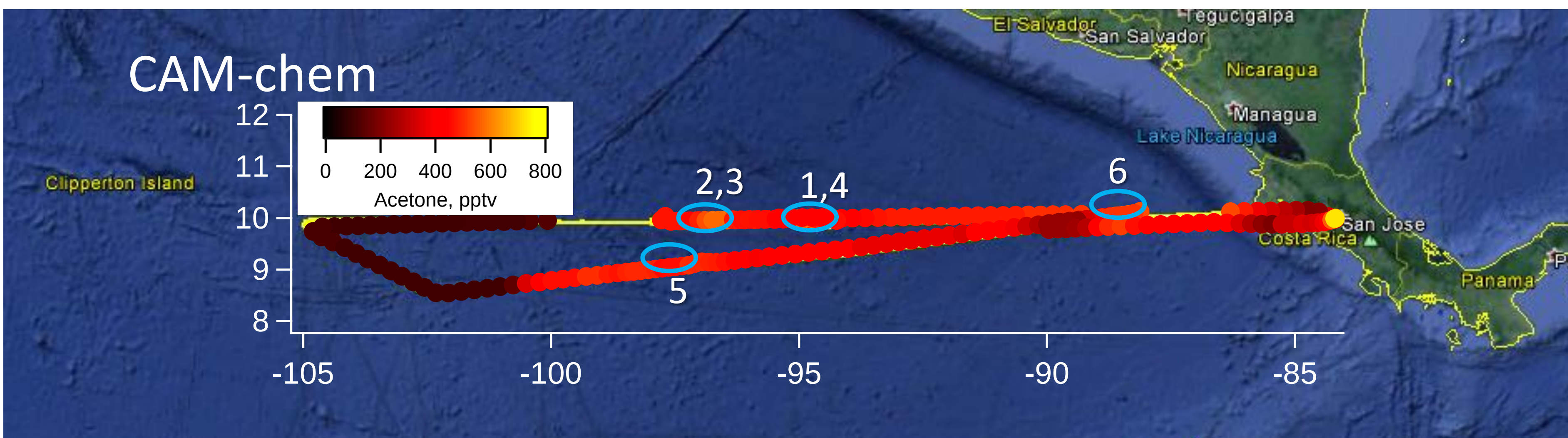


RF12 – biologically active region/convected MBL

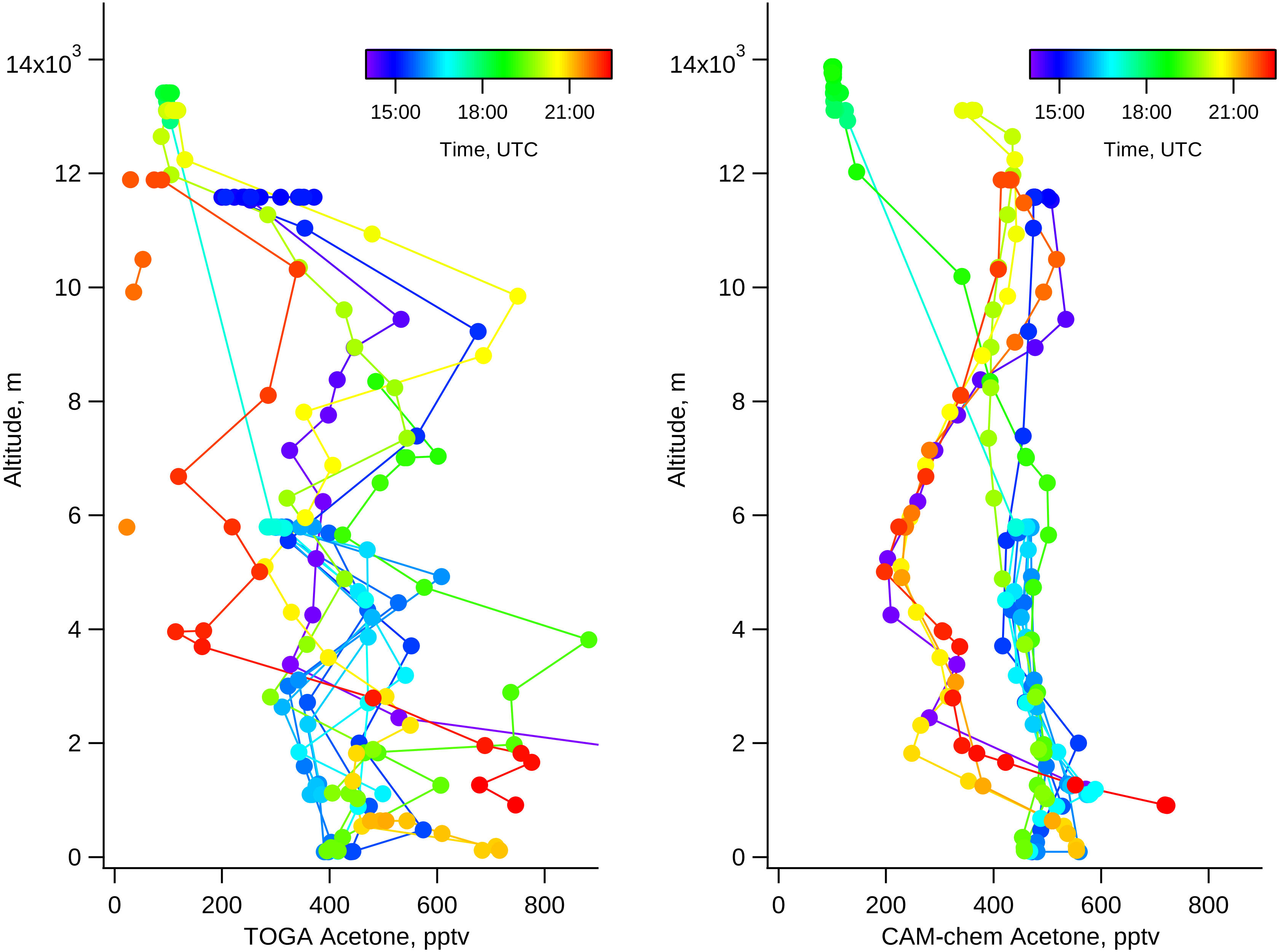


RF12 – biologically active region

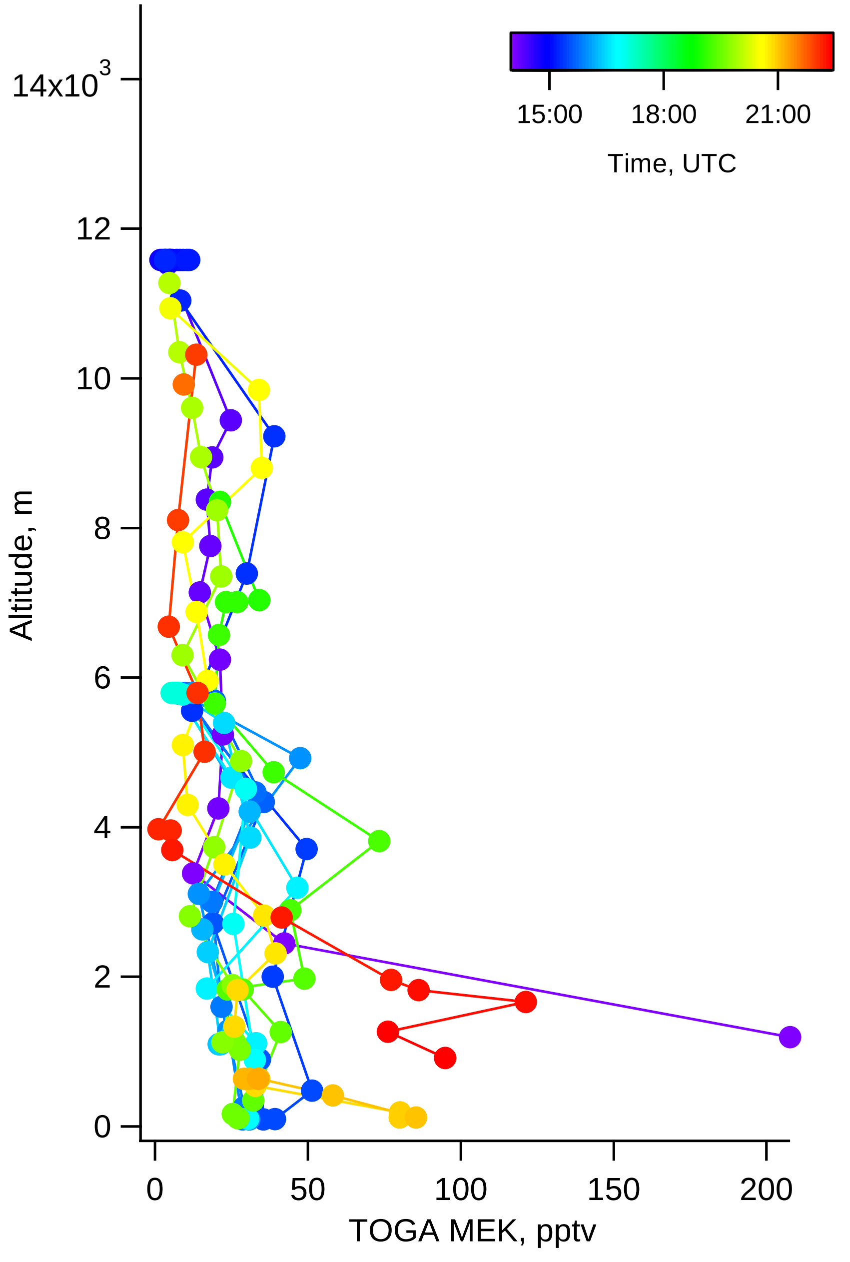




RF12 – biologically active region

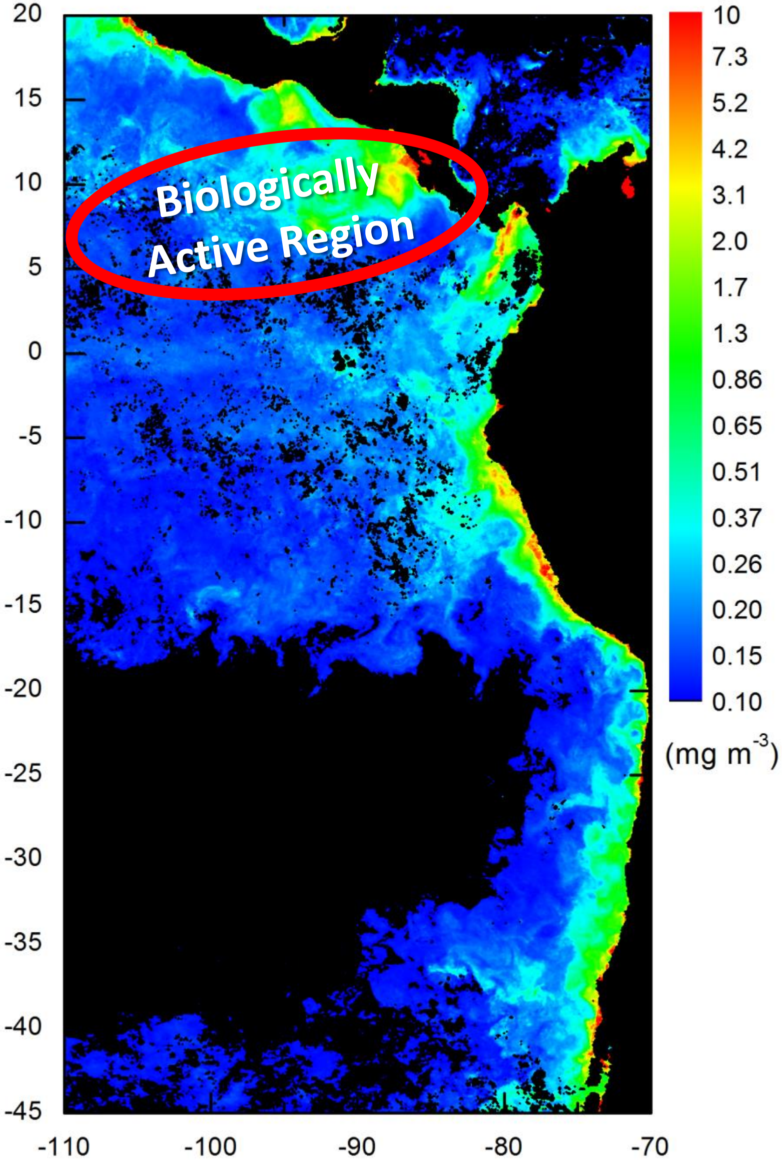


RF12 – biologically active region

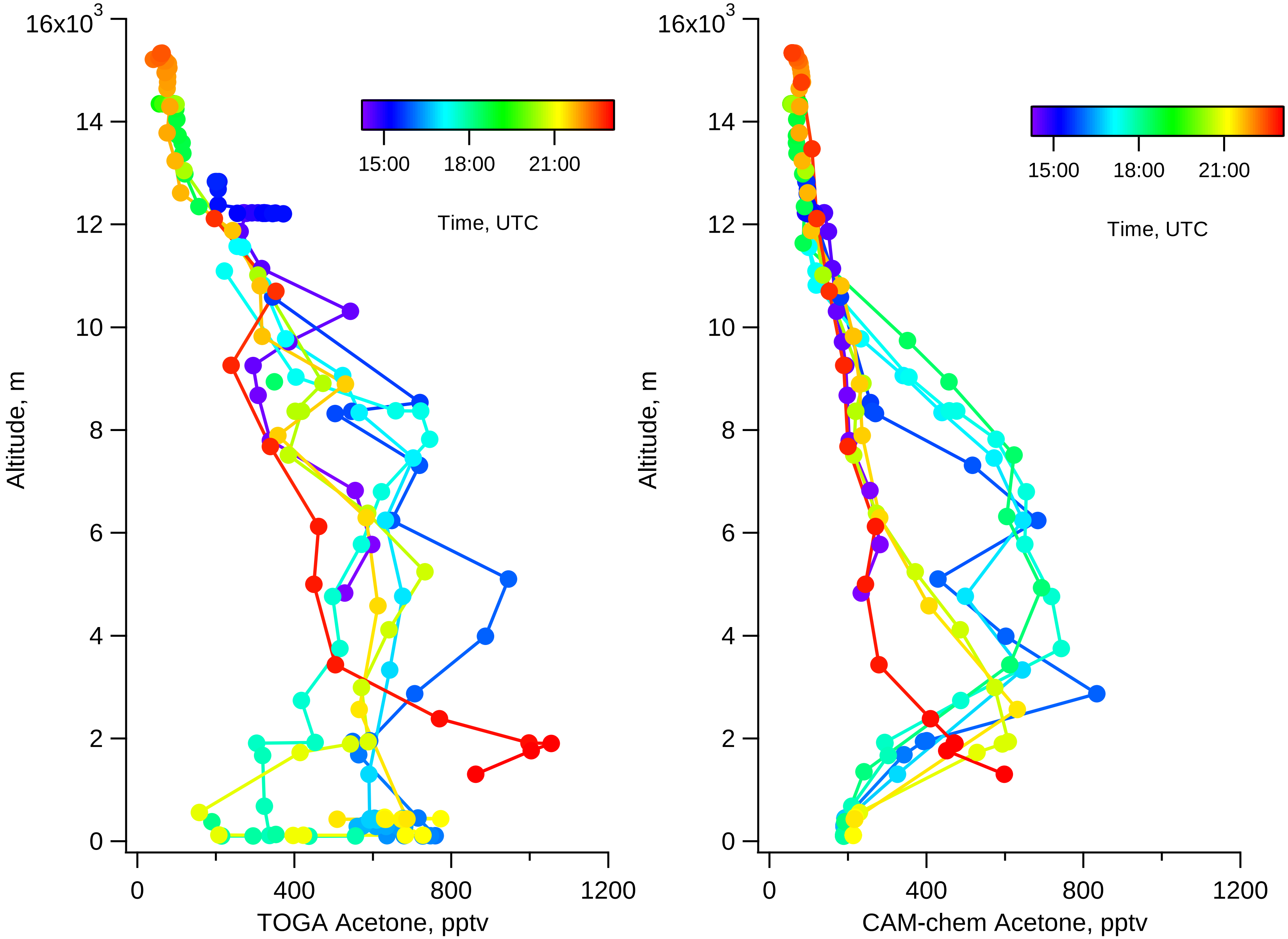


RF15 – biologically active region

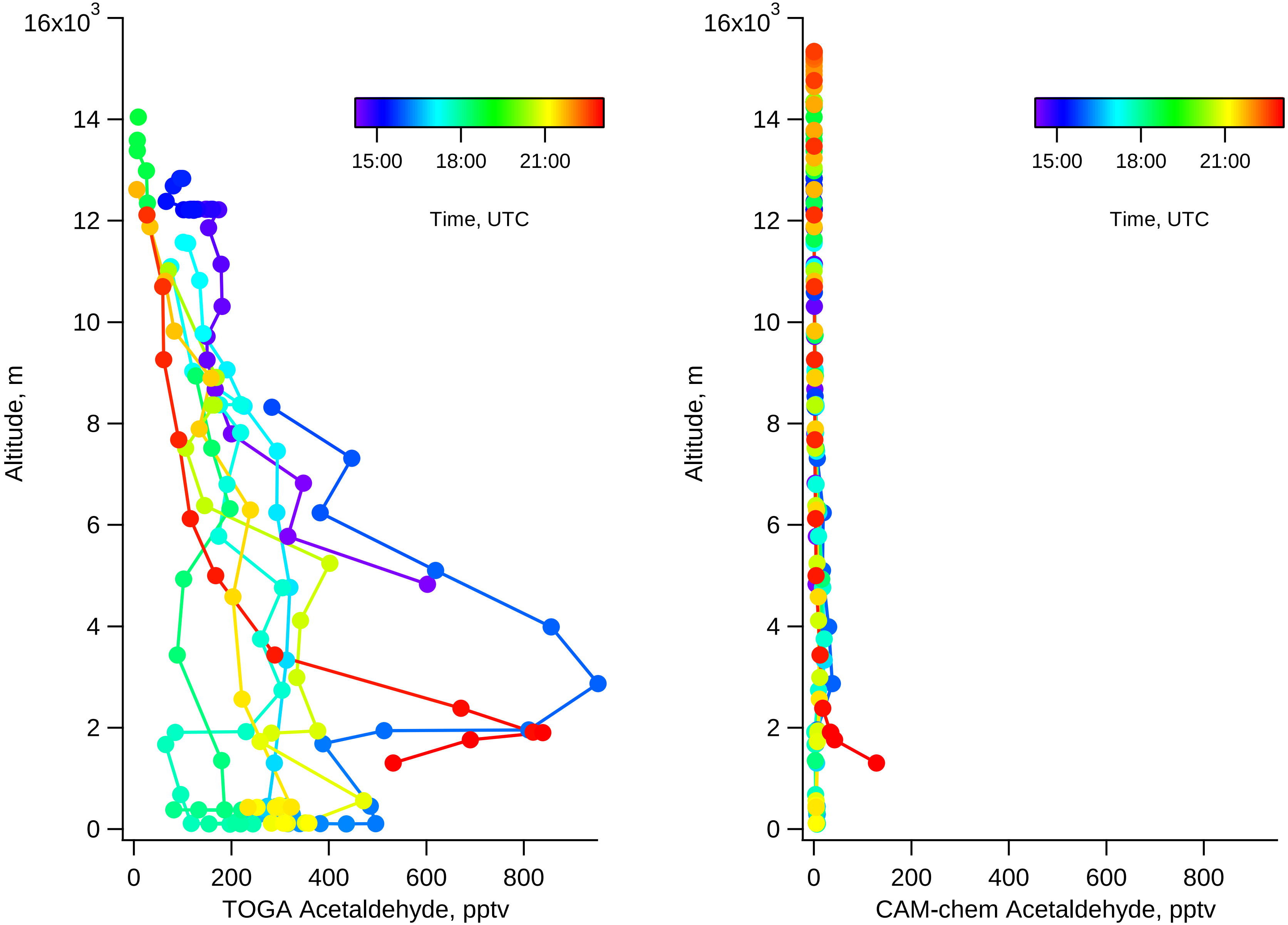
MODIS Chlorophyll-a



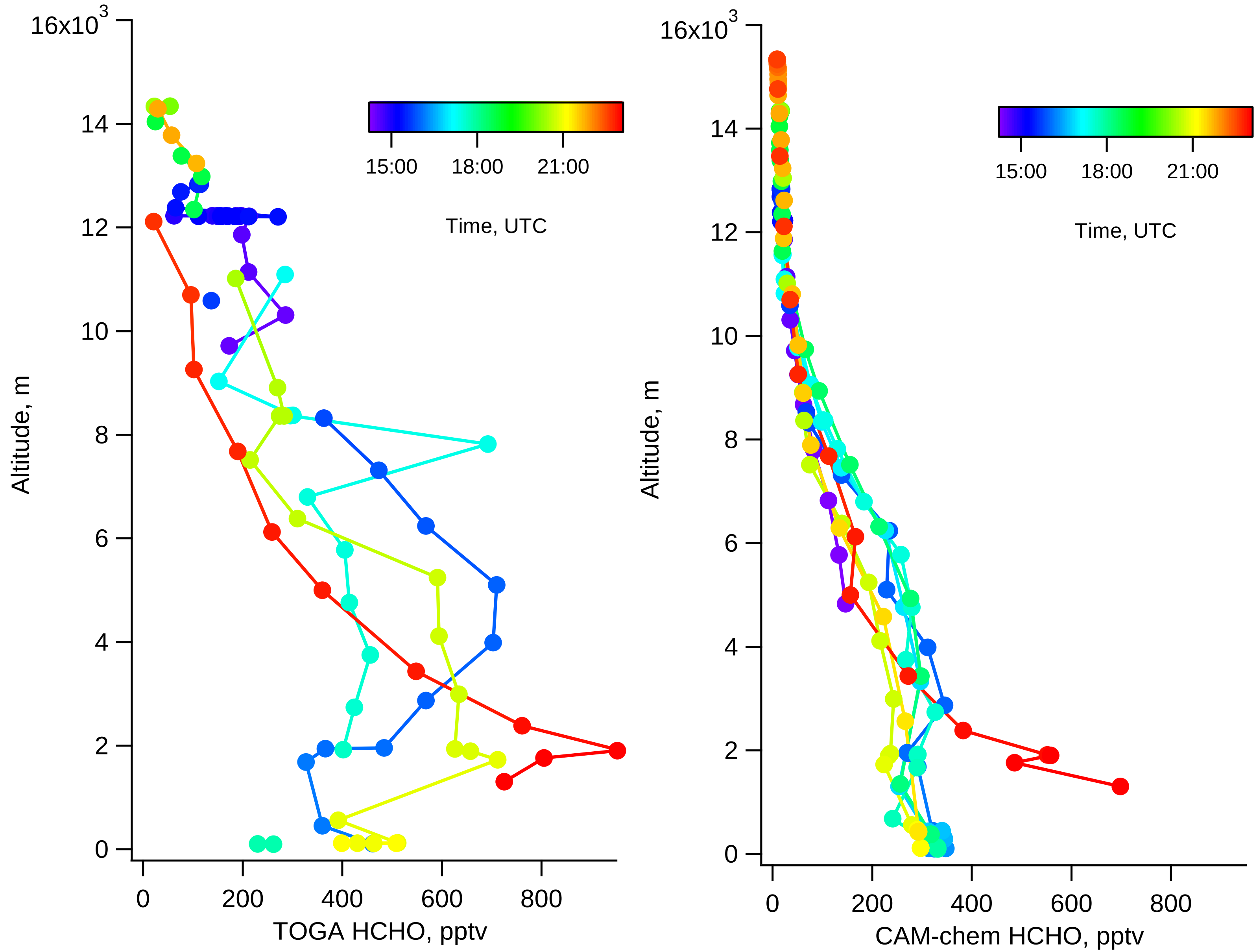
RF15 – biologically active region



RF15 – biologically active region



RF15 – biologically active region



Next Steps

- TOGA/CAM-chem comparison – remainder of flights
- Assess organohalogen and DMS emission inventory
- Investigate OVOC production/loss over ocean
- Convection of species emitted from the ocean

- TORERO relevant papers:
  - OVOCs in the remote troposphere
  - TOGA paper
  - Comparison of observed organohalogens and recent CAM-chem model results