Reactive gas studies during ORCAS

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Scientific Motivations

- Emissions from productive Southern Ocean can have regional and global (?) impacts.
  - Reactive halocarbons
    - Oxidative processes / ozone depletion (tropospheric and stratospheric)
    - Aerosol formation
  - Organic nitrates
    - Marine origin/source of NOx
  - Sulfur species
    - DMS and aerosol formation
- Distributions and fluxes poorly characterized/or conflicting conclusions
  - Complex source/sink relationships
  - Mechanisms of production/loss also complex/variable
  - Limited information on links to biogeochemical processes
    - Pigments
    - Species dependence

Questions related to main ORCAS objectives:

- Can the combination of aircraft profiles and Lagrangian transport models effectively quantify the fluxes of halocarbons and other reactive gases from different regions over the Southern Ocean?

- What is the relationship of halocarbon fluxes and distributions to those of CO_2 and O_2?

- What are the trace gas signatures of sources from coastal Antarctica vs Southern Ocean?

- Can quantitative relationships be established between halocarbon fluxes and observations of ocean hyperspectral features?

- What are the main source regions of organic nitrates in the Southern Ocean atmosphere and how are they related to reactive halocarbons or other biogeochemical variables?

Questions related to main ORCAS objectives:

- What are the relative importance of emissions of halocarbons near the retreating ice edge versus the nearshore and open ocean environments vs the Argentine Basin?

- What are the vertical distributions and geographical variations of halocarbon and other reactive gases around the Southern Ocean?

- Are the observations of reactive gases consistent with existing model formulations (e.g. CAM-CHEM, etc.)?

- Can the relationships developed for trace gas emissions be translated/extrapolated to other productive ocean regions?

Organohalogens, DMS, Organic Nitrates

Dibromomethane – CH_2Br_2

Bromoform – $CHBr_3$

methyl iodide CH_3I

chloroiodomethane – CH_2ICl

Diiodomethane – CH_2II

dibromochloromethane – $CHBr_2Cl$

DMS

Methyl Nitrate

PEM-Tropics: $RONO_2$ high in tropics and Southern Ocean atmosphere

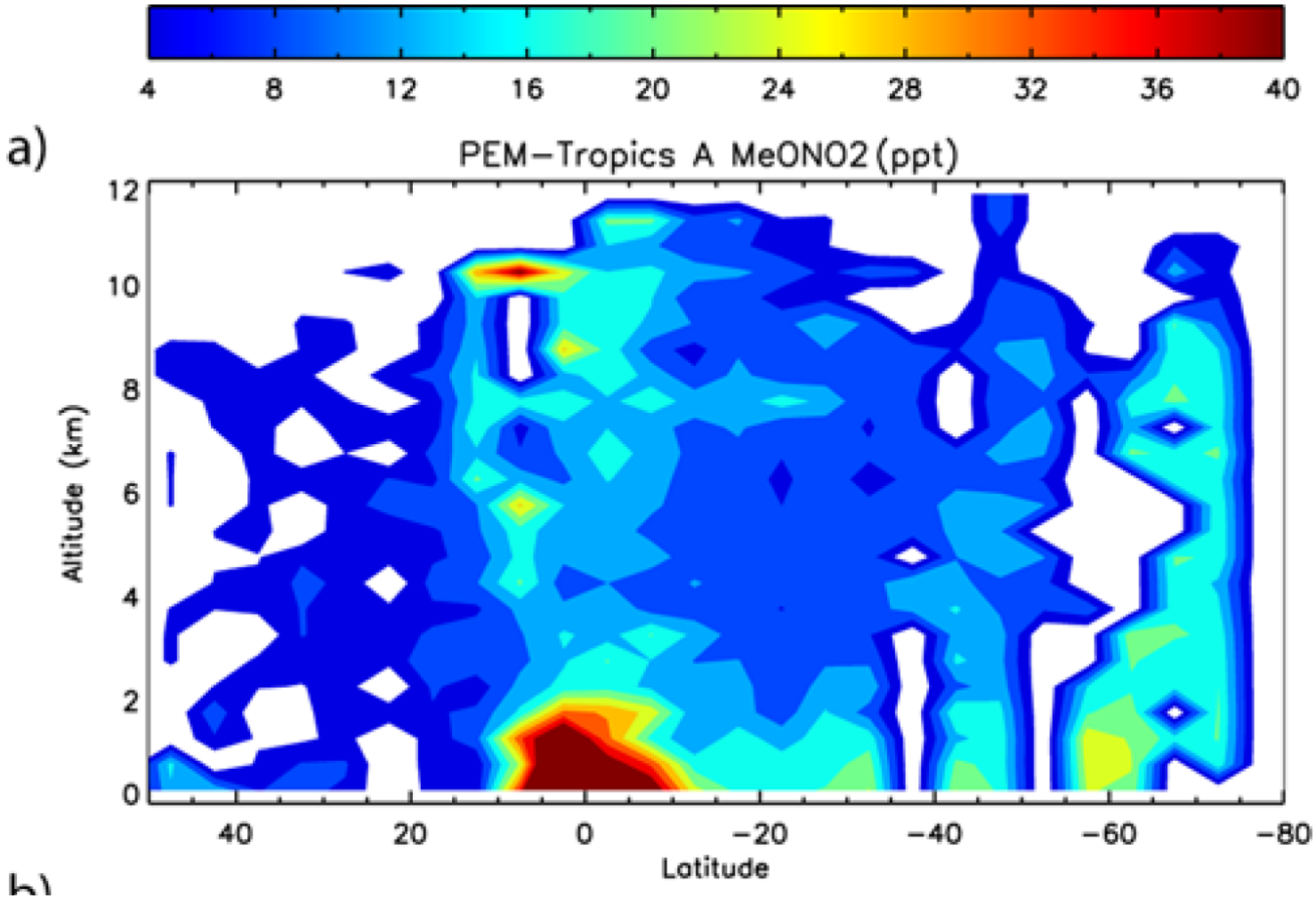


Figure from Neu et al., GRL, 2008.

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

e.g.,

Tropospheric Halogen Chemistry – CAM-chem representation

Halogenated sources from the ocean

- Emissions following Chl-a over tropics
- Catalytic release from sea-salt
- Do NOT have polar emission processes

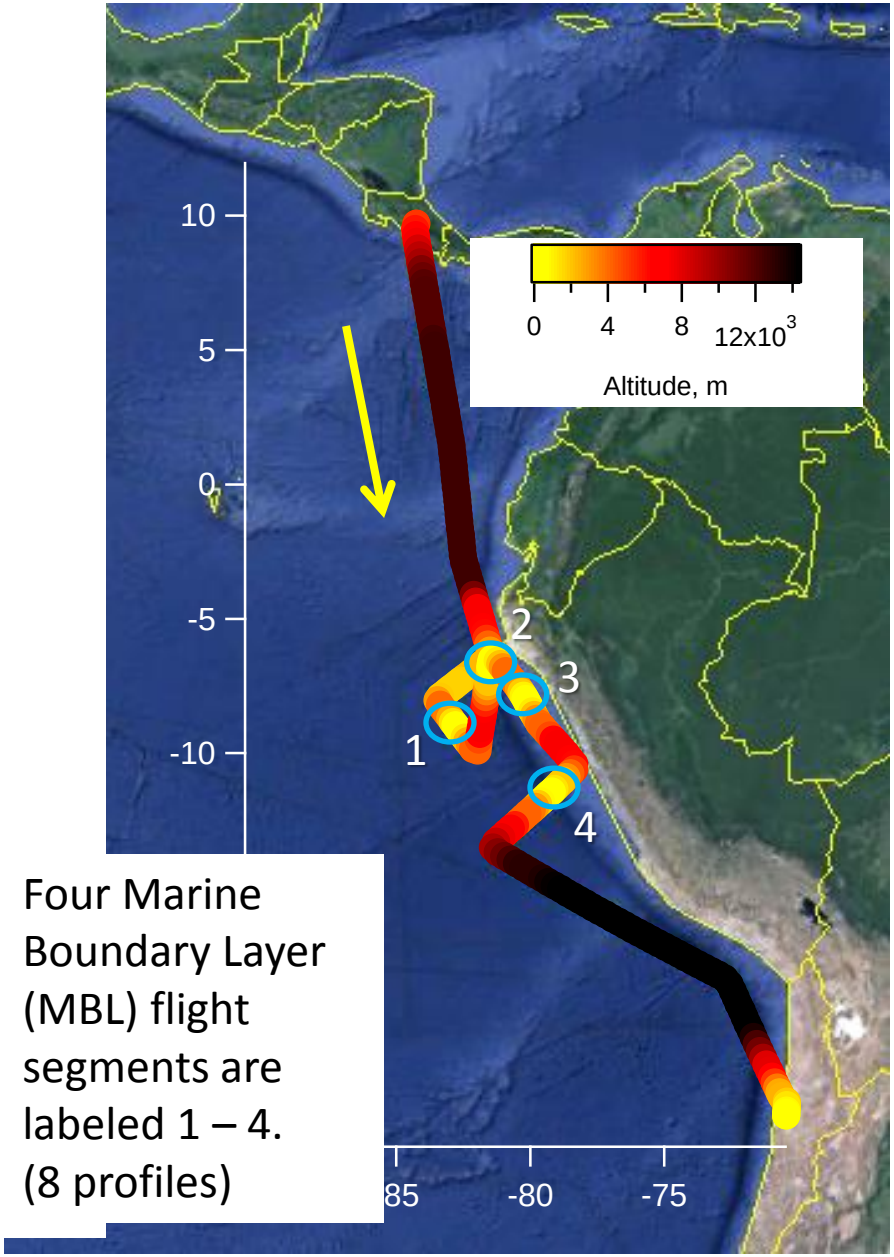
Chemical Processes

- Photochemistry (Cl, Br, and I)
- Dry/wet deposition
- 160 species, 427 reactions

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.

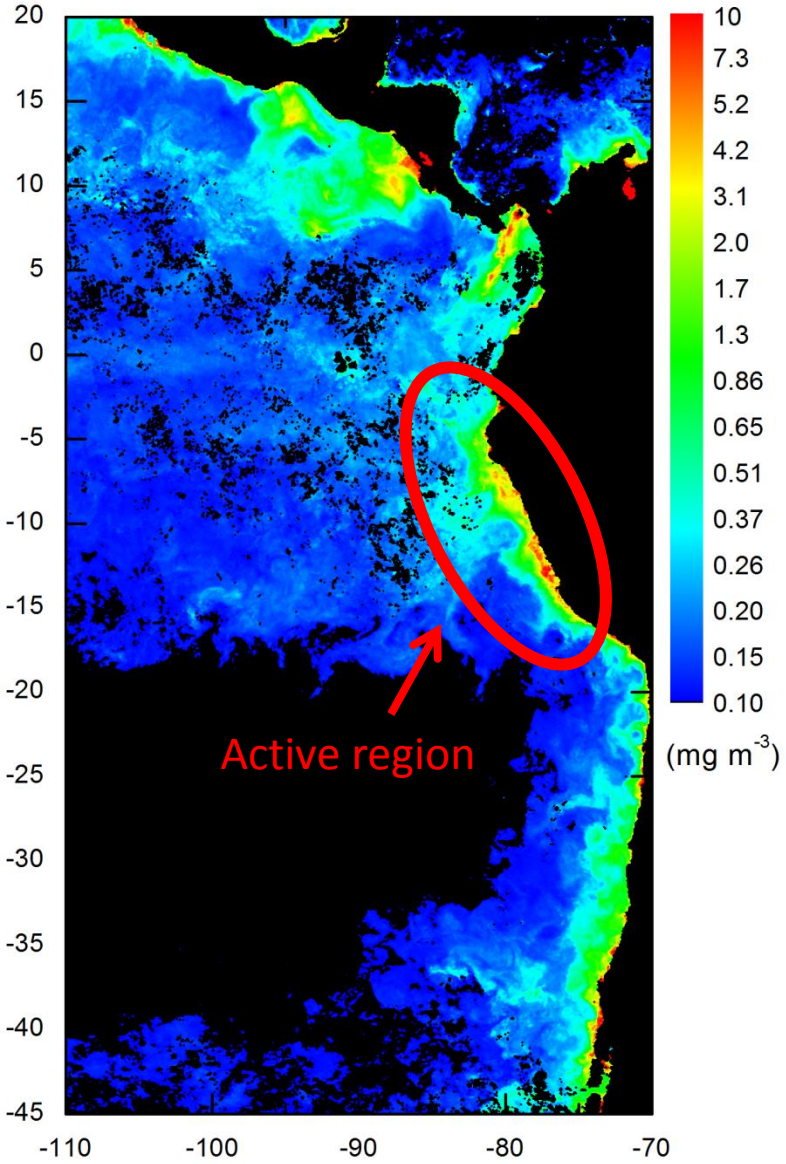
Fernandez, R. P., R. Salawitch, D. E. Kinnison, J.-F. Lamarque and A. Saiz-Lopez, Bromine partitioning in the tropical tropopause layer: implications for stratospheric injection. Submitted to *Atmos. Chem. Phys. Disc*., 2014.

TORERO - RF01 – coastal emissions, continental outflow



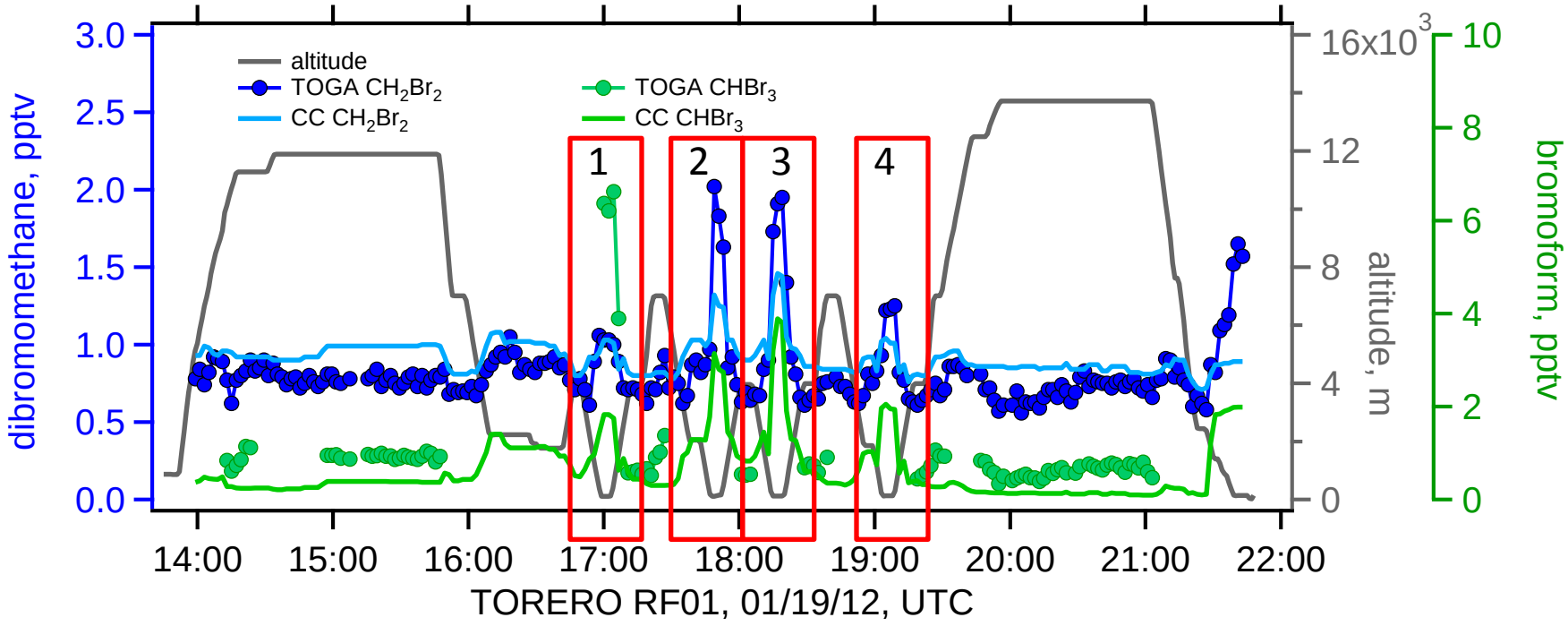
Four Marine Boundary Layer (MBL) flight segments are labeled 1 – 4. (8 profiles)

MODIS Chlorophyll-a



TORERO RF01.

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



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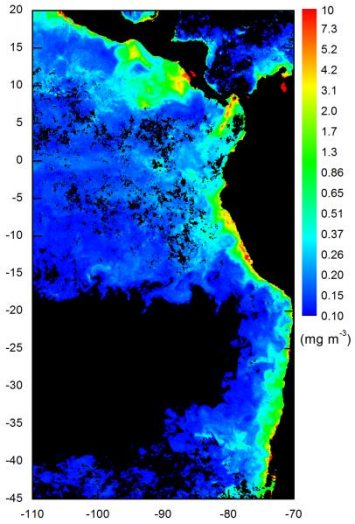
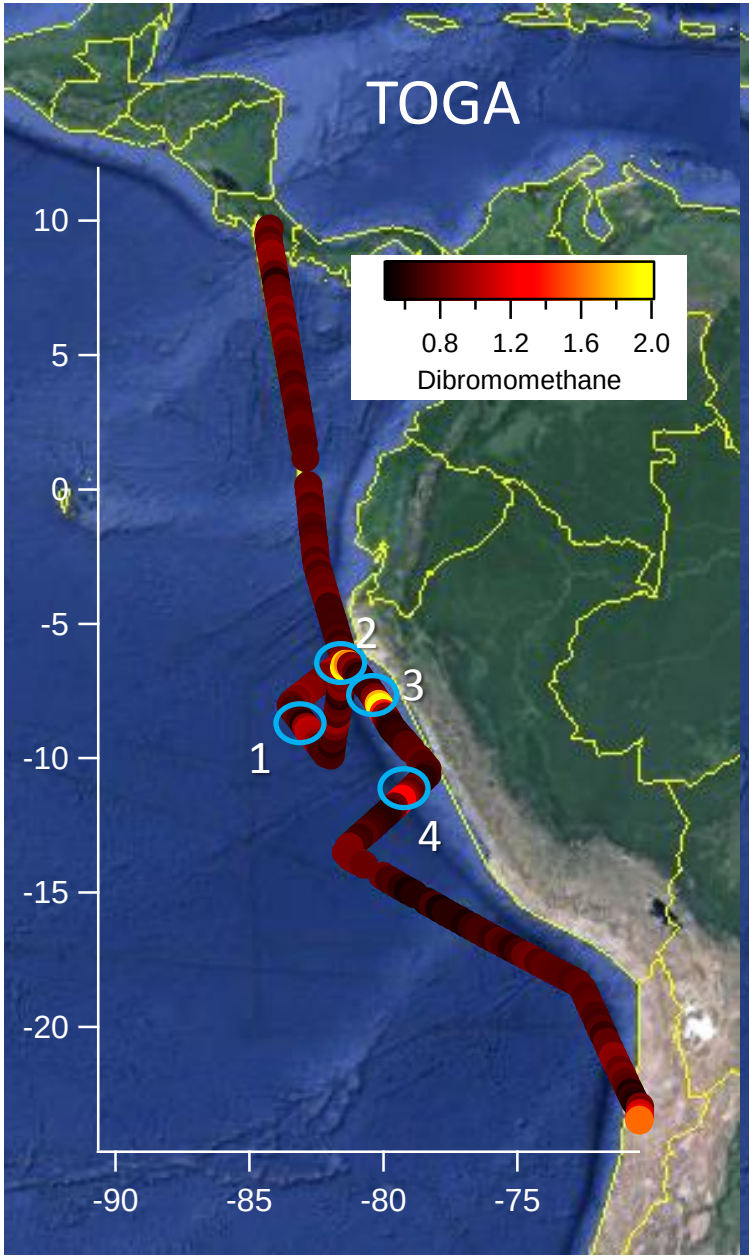
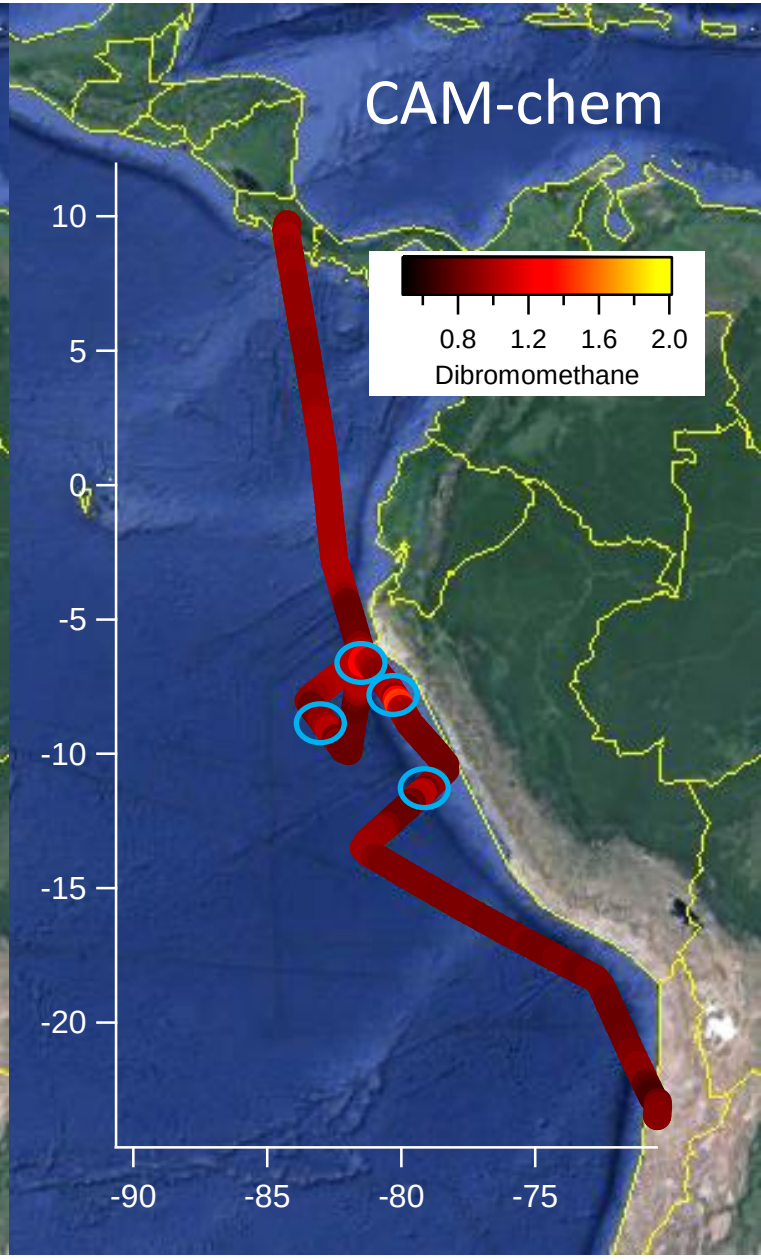
From RF01



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





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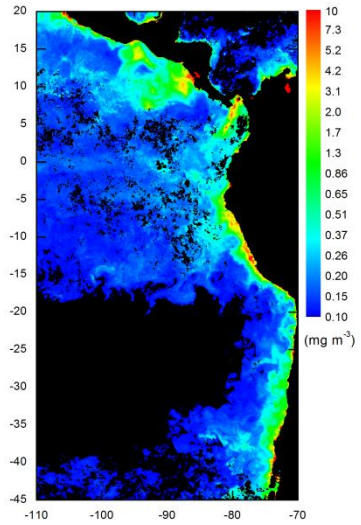
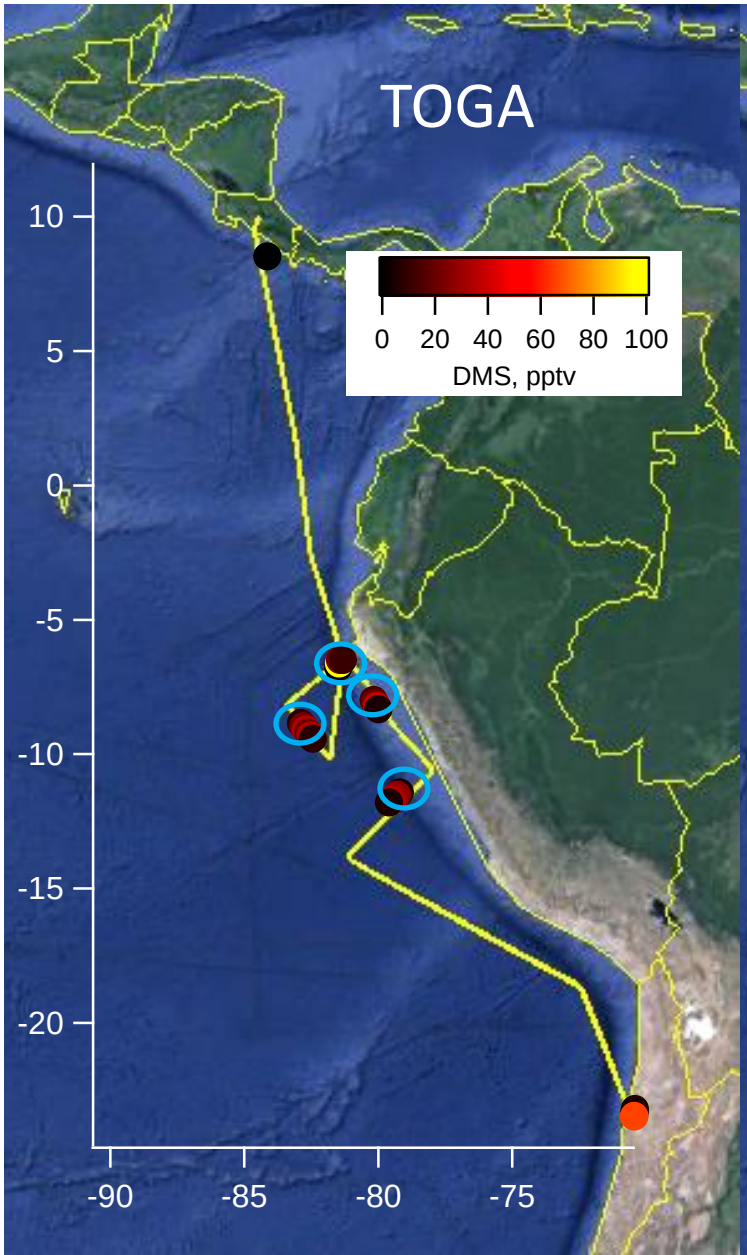
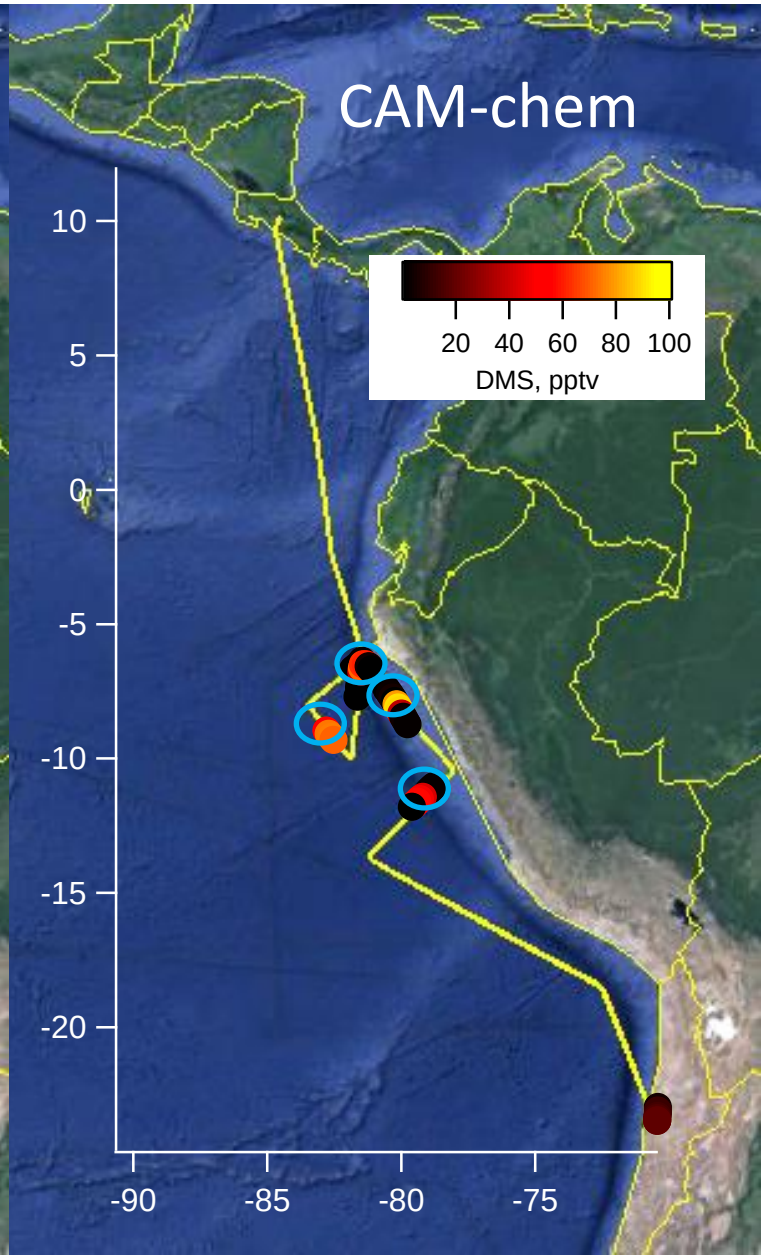


CAM-chem and TOGA DMS agree to within a factor of two.

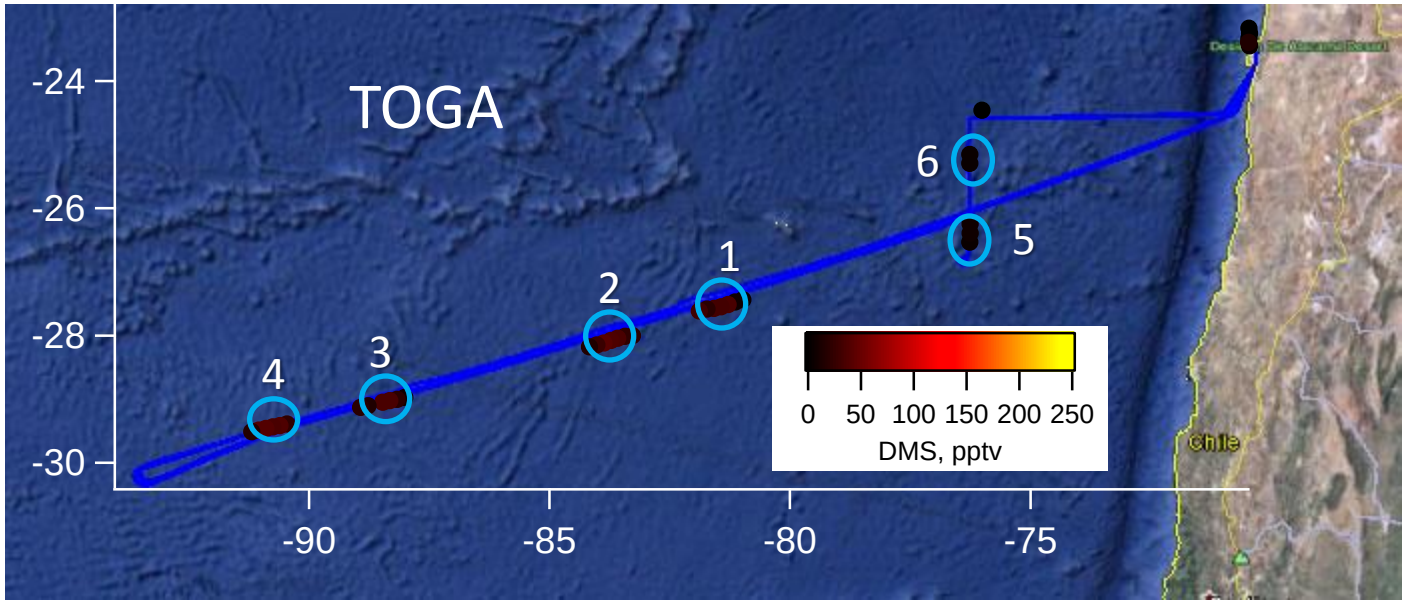
But not always that good….

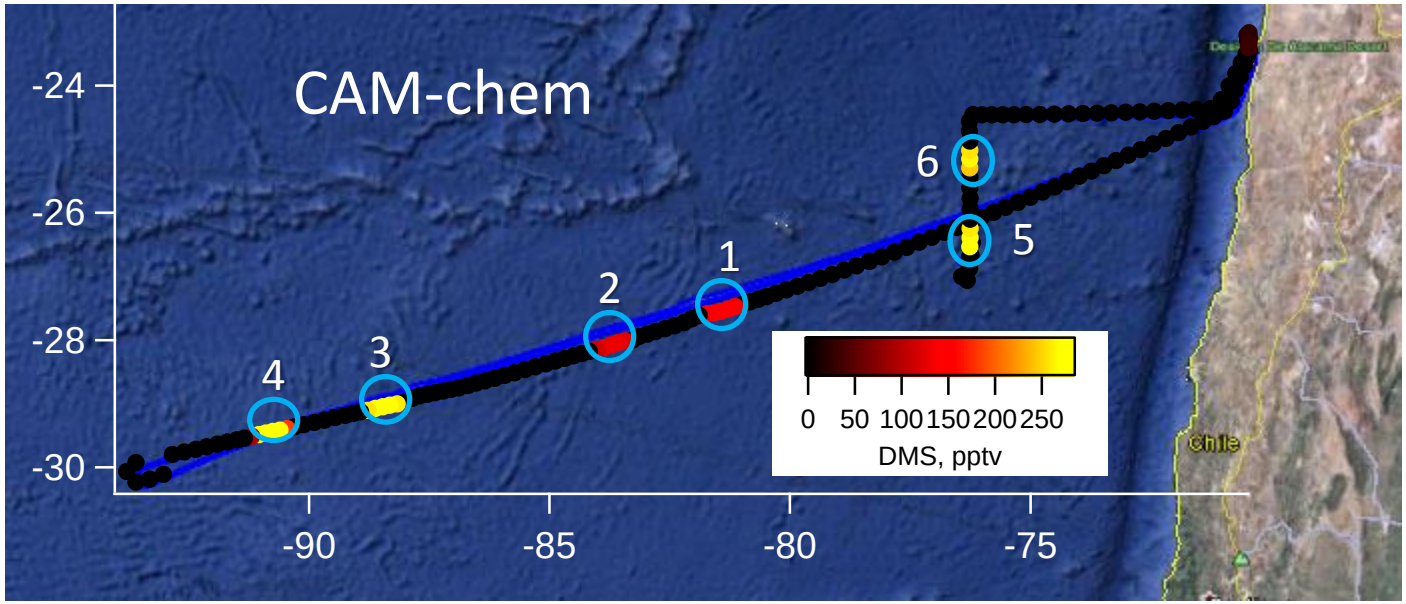




RF05 – oligotrophic ocean (non-productive)

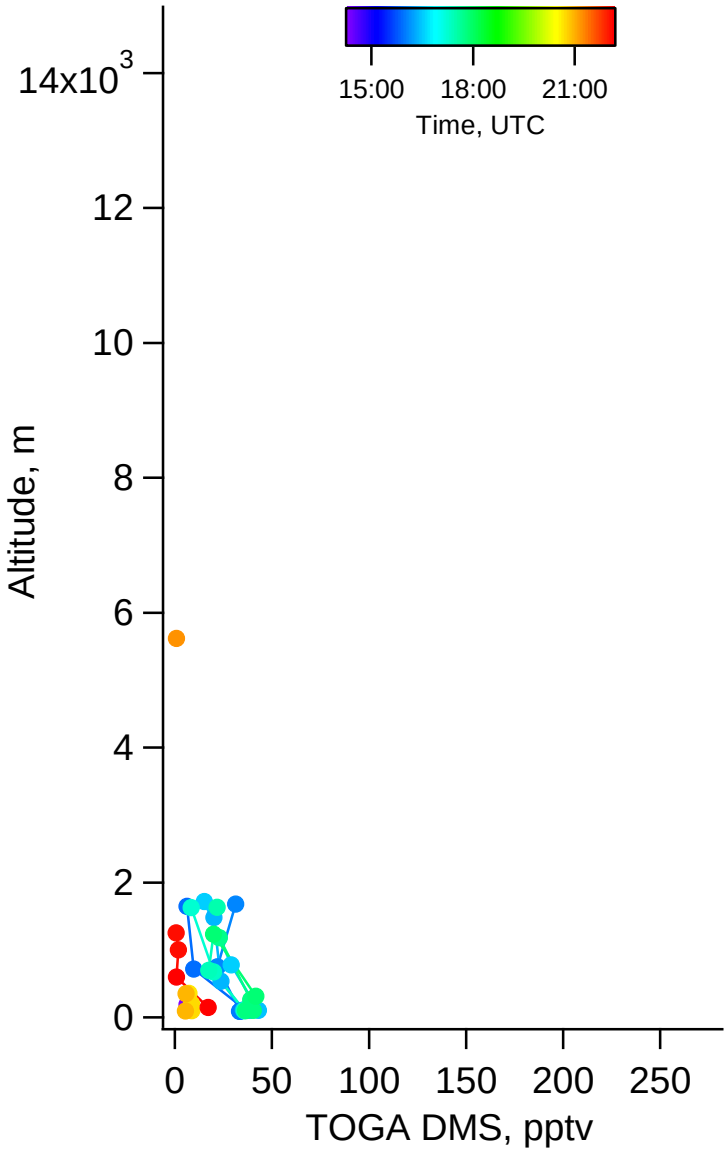
TOGA DMS
Is significantly
Lower than
CAM-chem
DMS in all
MBL runs.

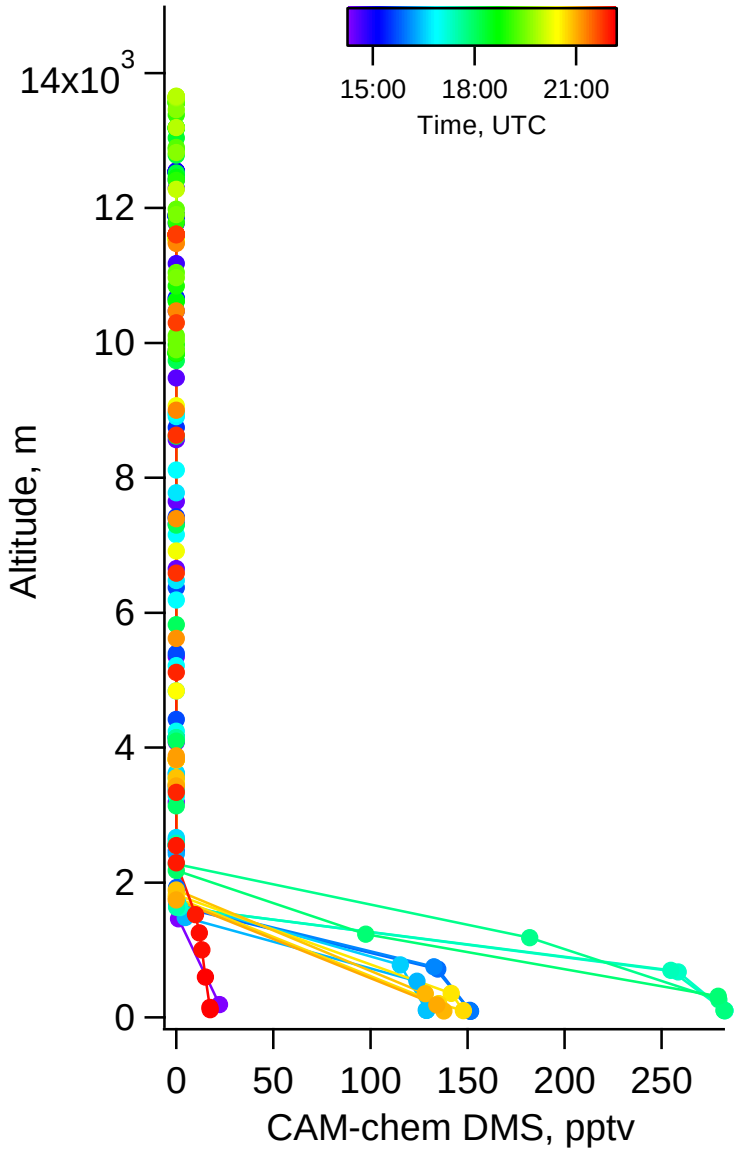




RF05 – oligotrophic ocean

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





Oxygenated VOCs

acetone (CH_3COCH_3)

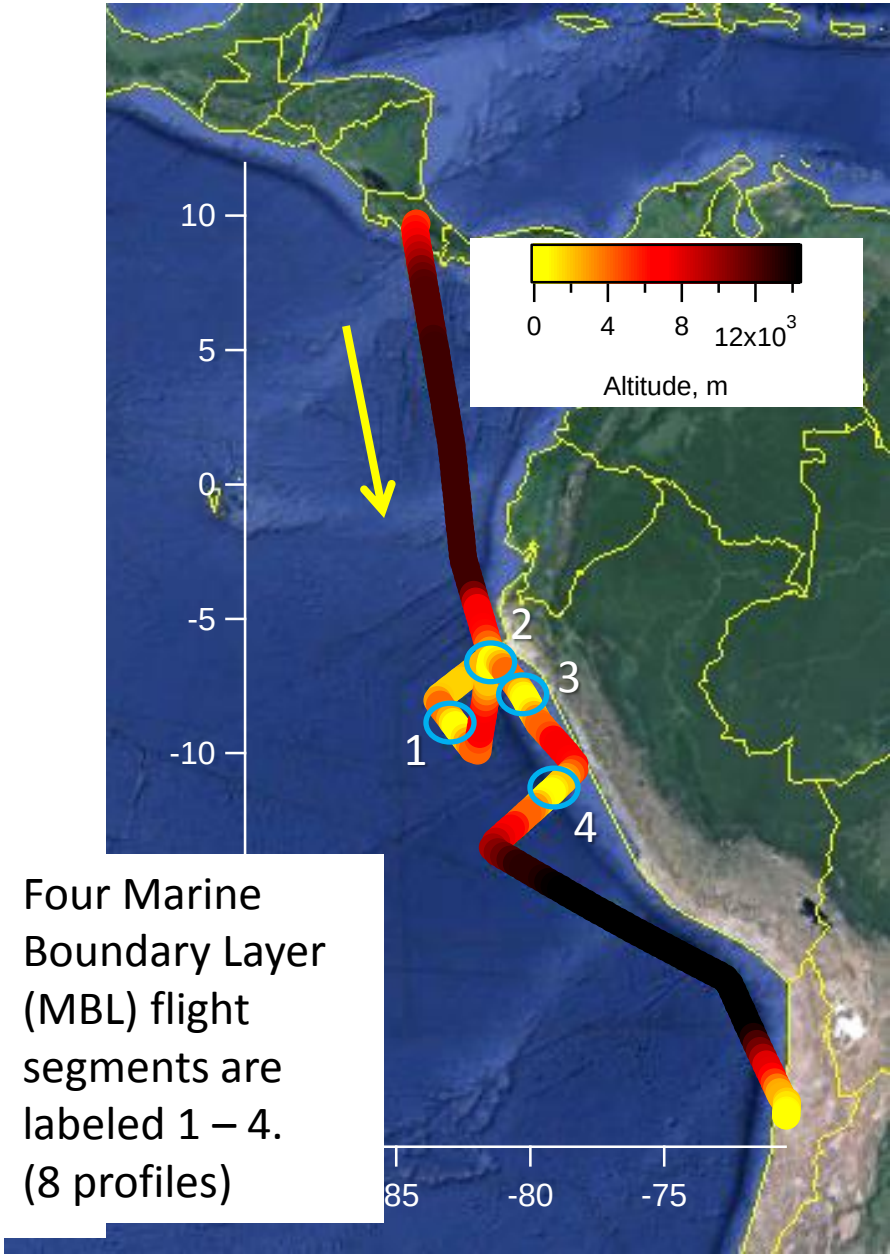
formaldehyde (HCHO)

acetaldehyde (CH_3CHO)

methanol (CH_3OH)

Butanone/Methyl Ethyl Ketone (MEK)

RF01 – coastal emissions, continental outflow



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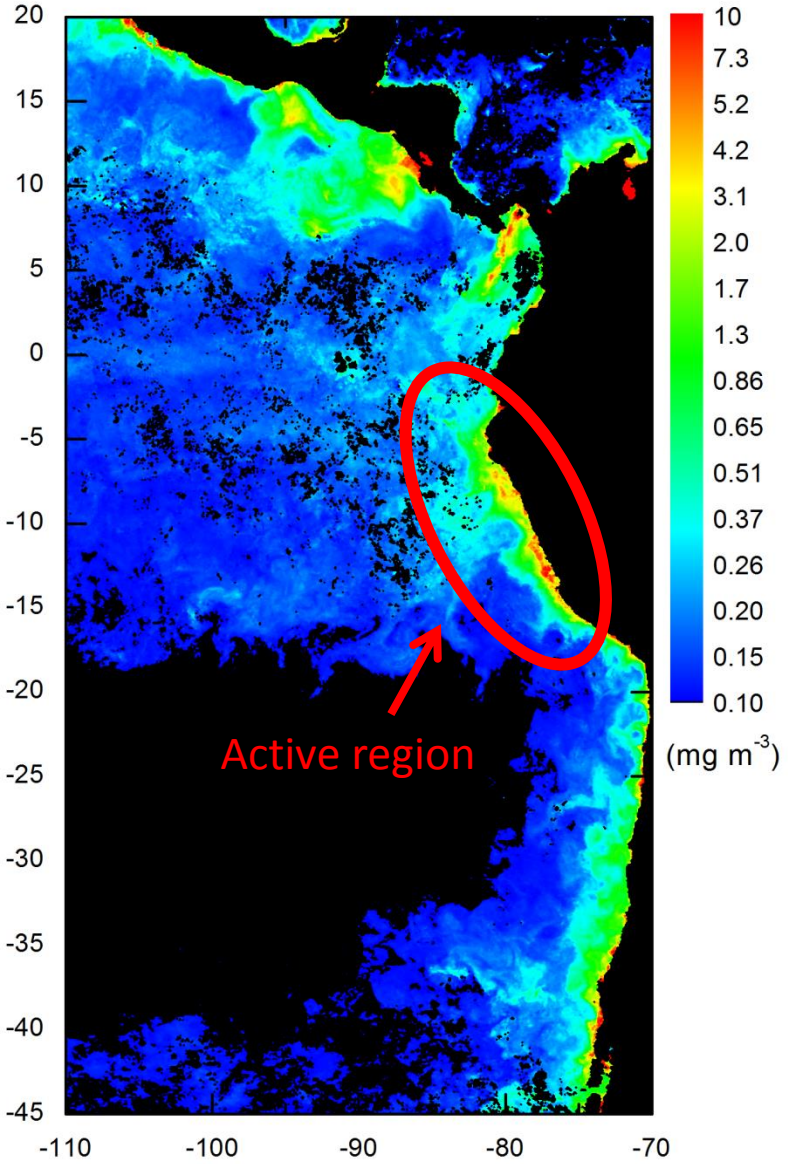
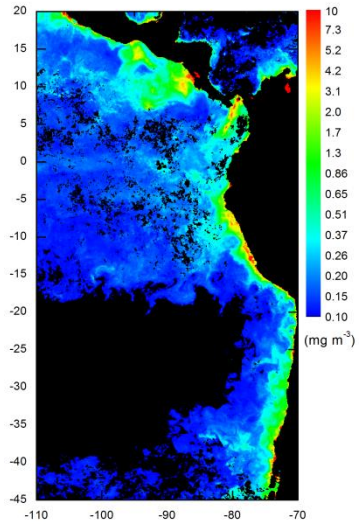
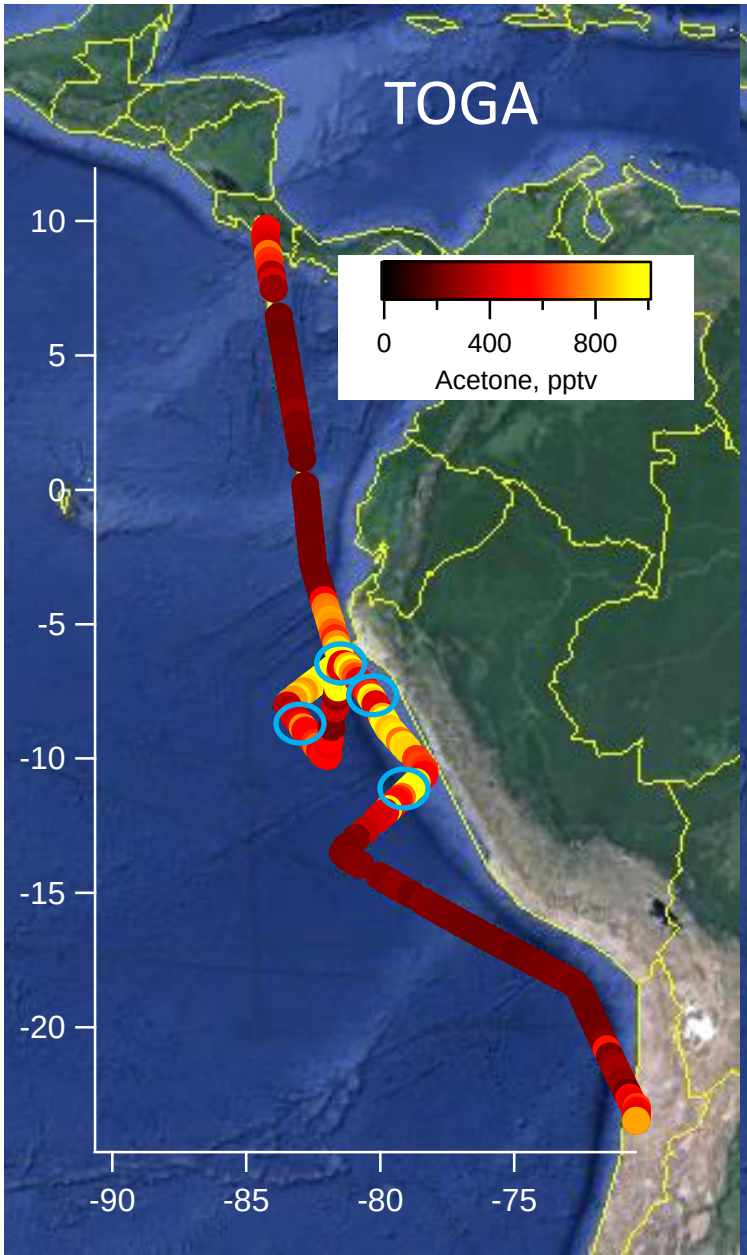
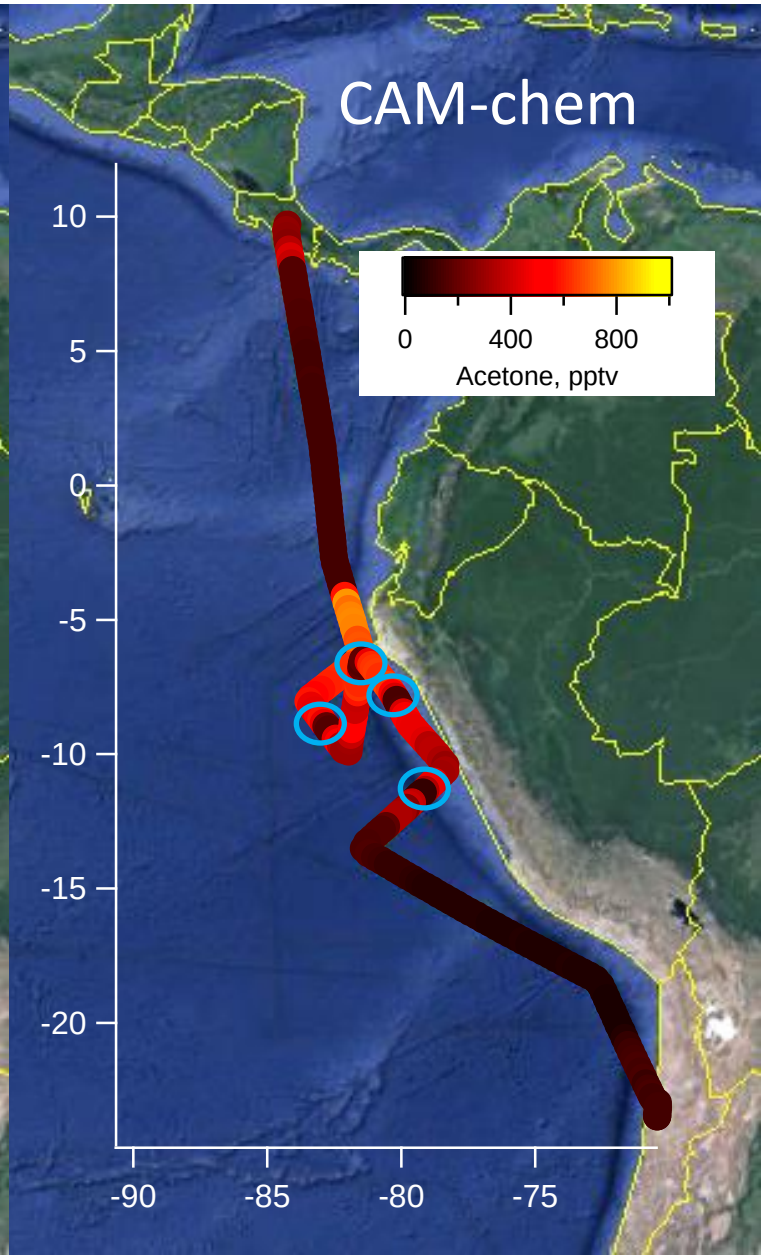


From RF01 - **Acetone**



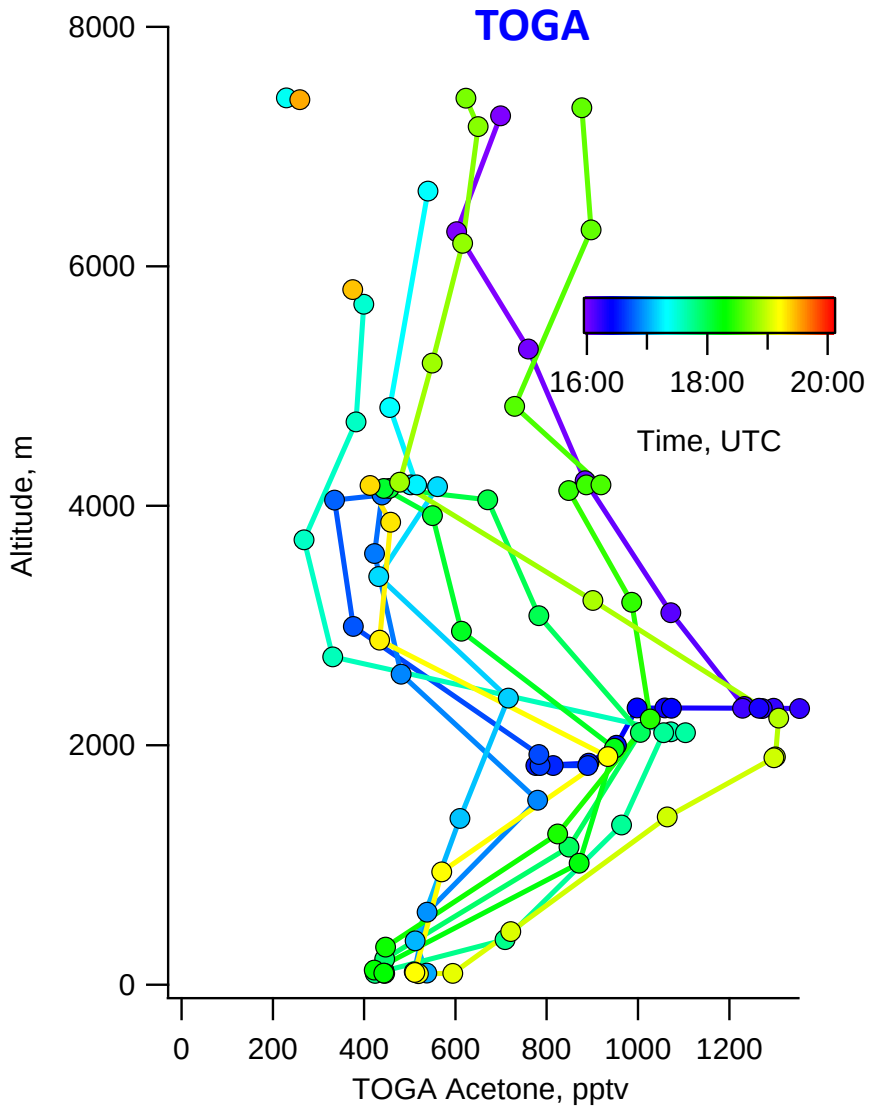
CAM-chem and TOGA acetone are both lower at the surface…

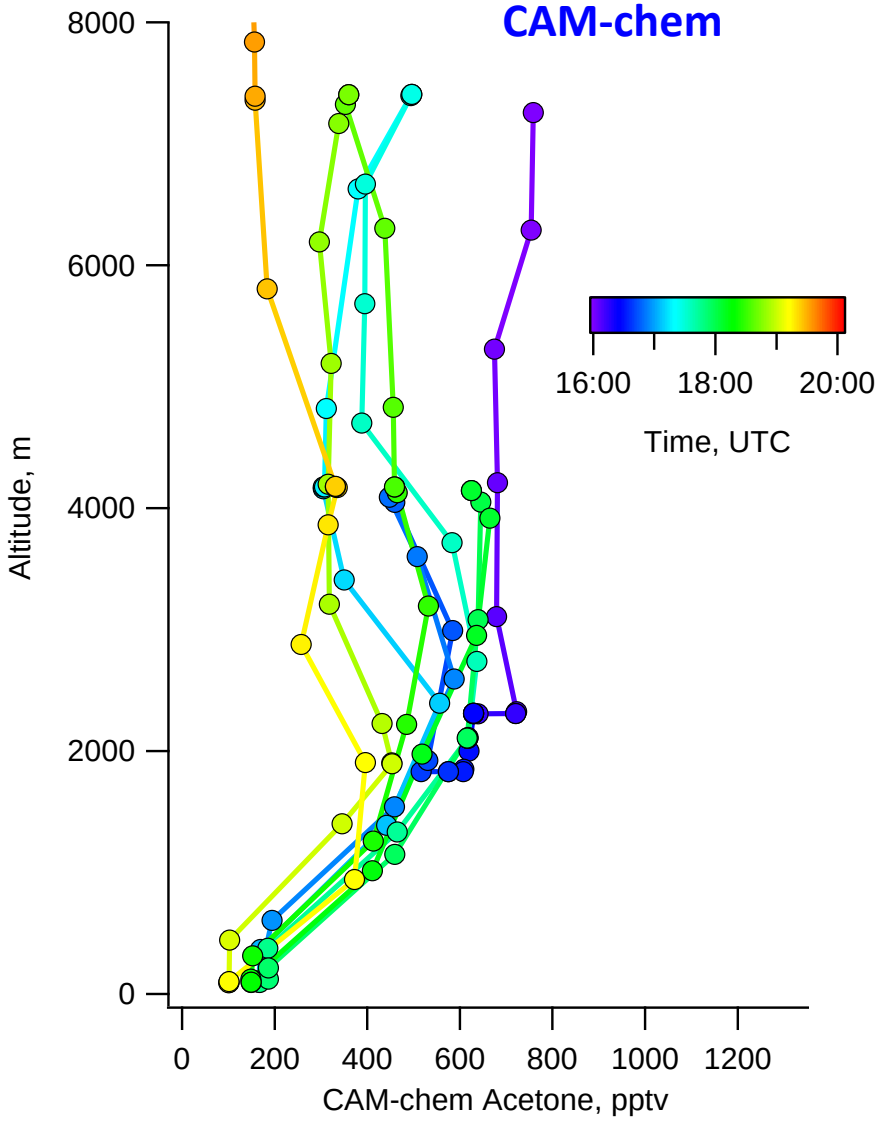




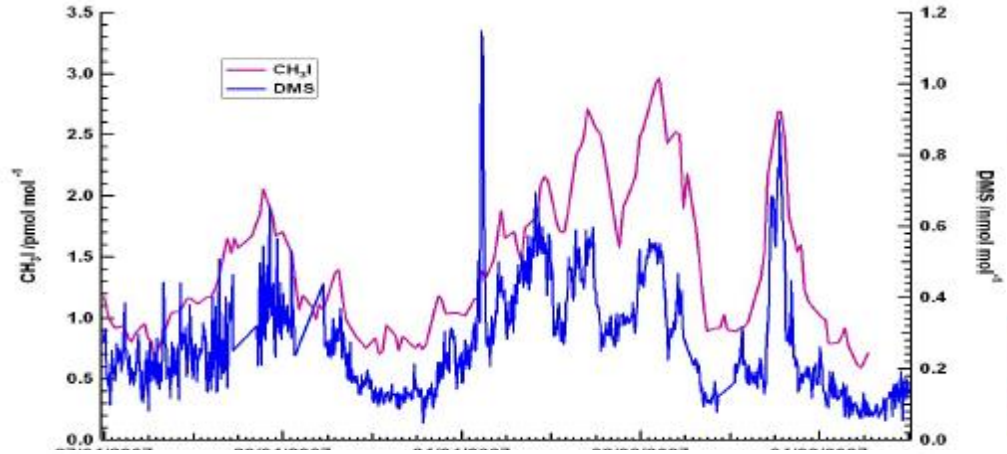
RF01: 8 profiles off the west coast of Peru

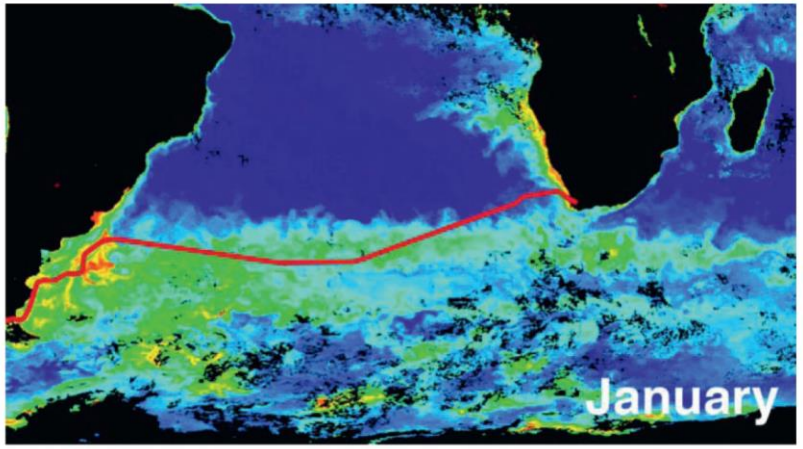
CAM-chem captured the pollution layer aloft at ~ 2-3 km, but is lower than TOGA obs at the surface.

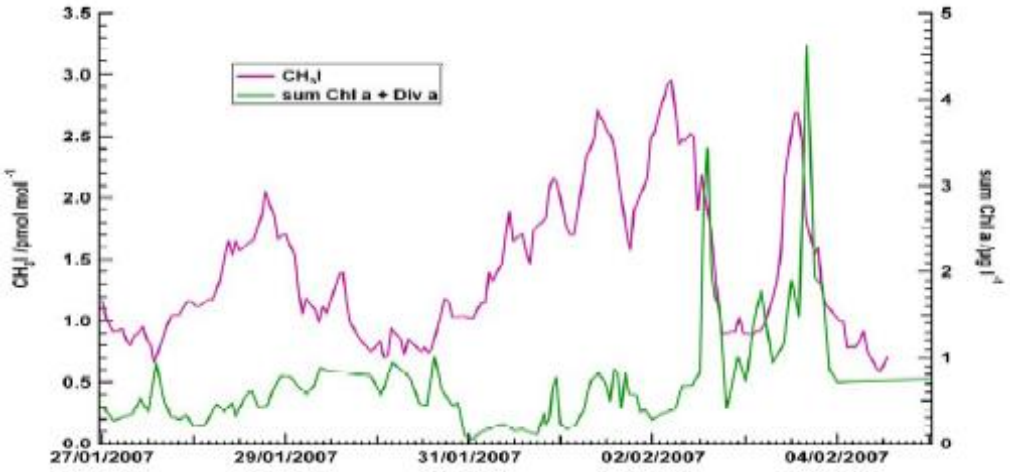




OOMPH cruise: DMS, CH3I and Chl*a*







Time series along cruise track (to Argentina): Good correlation between gases in atmosphere, but little consistent correlation to Chl a. Improved correlation considering back trajectories over productive areas (from retrospective satellite obs.)