CONTRAST

Observations of VOCs in the upper troposphere: Sources and chemistry

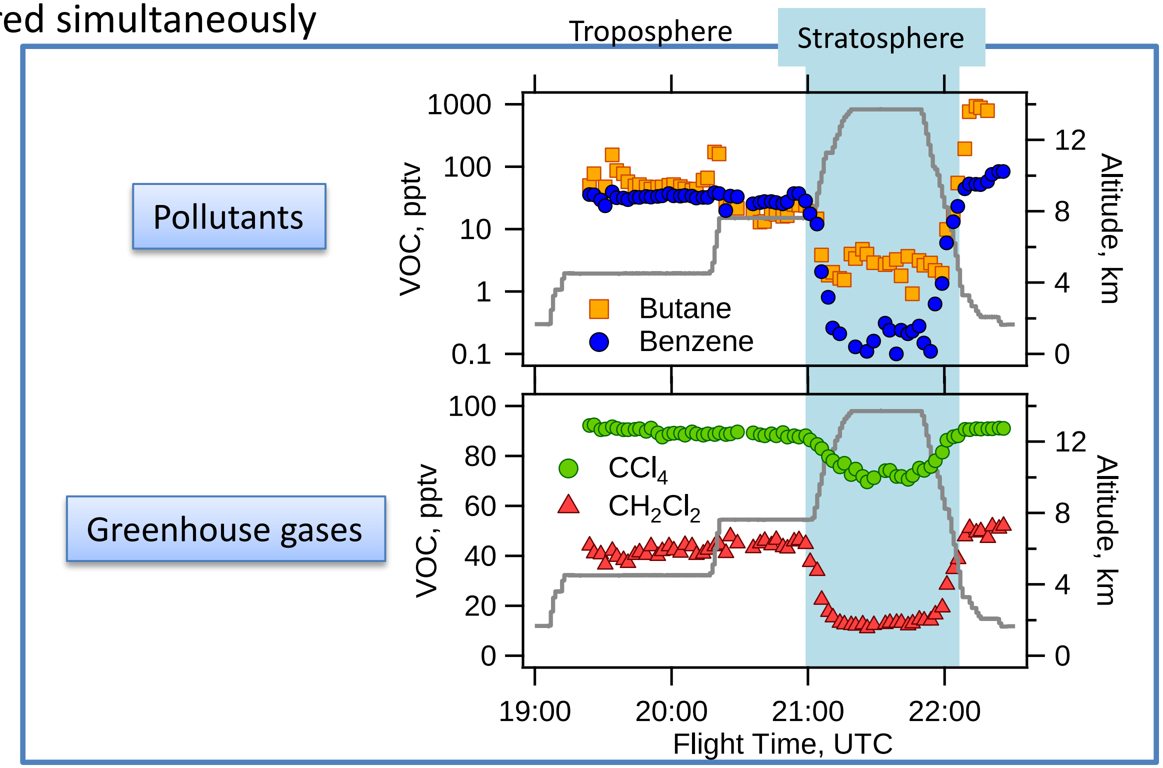
Eric Apel, Becky Hornbrook, Alan Hills, Dan Riemer

NCAR

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 – also DC3 and NOMADSS
- Designed to have very low LOD ppt to sub – pptv detection limits, over 70 VOC measured simultaneously



Atmospheric Chemistry Considerations

The photochemical budget of O_3 in the tropical TTL is determined by the strength of inputs of chemical precursors from convection and lightning.

O_3, H_2O, CO, CH_4, NO_x, hv – allow for model estimates of odd oxygen and HO_x

But…VOCs can also supply HO_x

. Species that photolyze – e.g., acetone, HCHO

Oxygenated VOC photolysis increases HOx levels and promotes the formation of PAN in the UT, altering O_3 photochemistry.

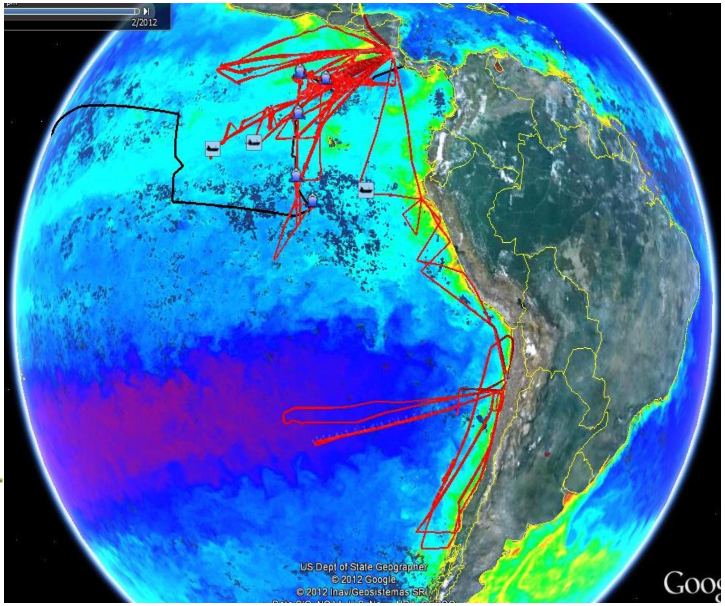
Previously: Measurements of OH in tropical UT demonstrated that the HOx source from the reaction of O^1D with H_2O is insufficient to explain the concentrations of this radical. Acetone suggested as a possible source of some of the missing OH (Wennberg et al., 1998).

Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated VOC

R. Volkamer PI, University of Colorado

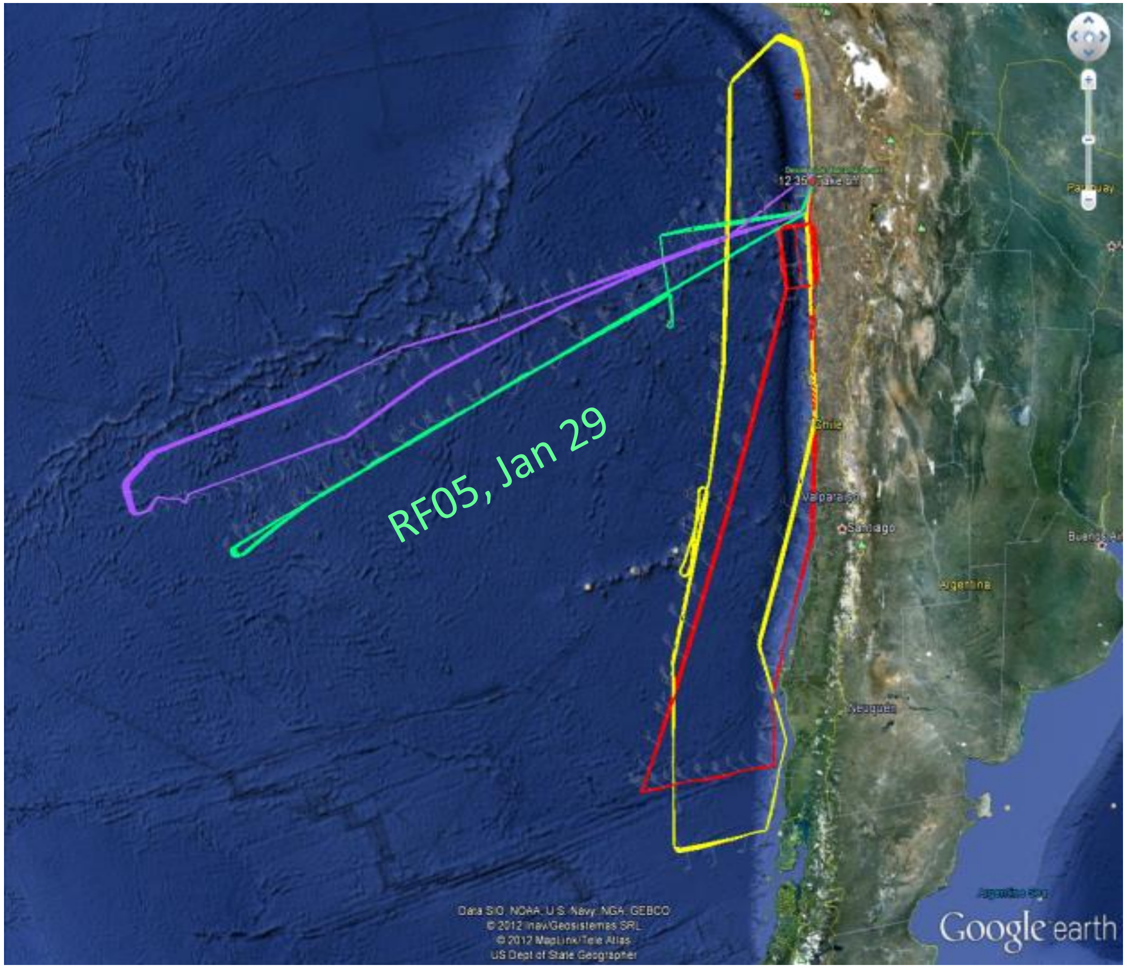
The scientific objective of the TORERO project was to study the release and transport of halogenated gases and oxidized VOCs in the Eastern Tropical Pacific during the season of high biologic productivity.

Jan-18-Feb 29
Antofagasta, Chile
San Jose, Costa Rica

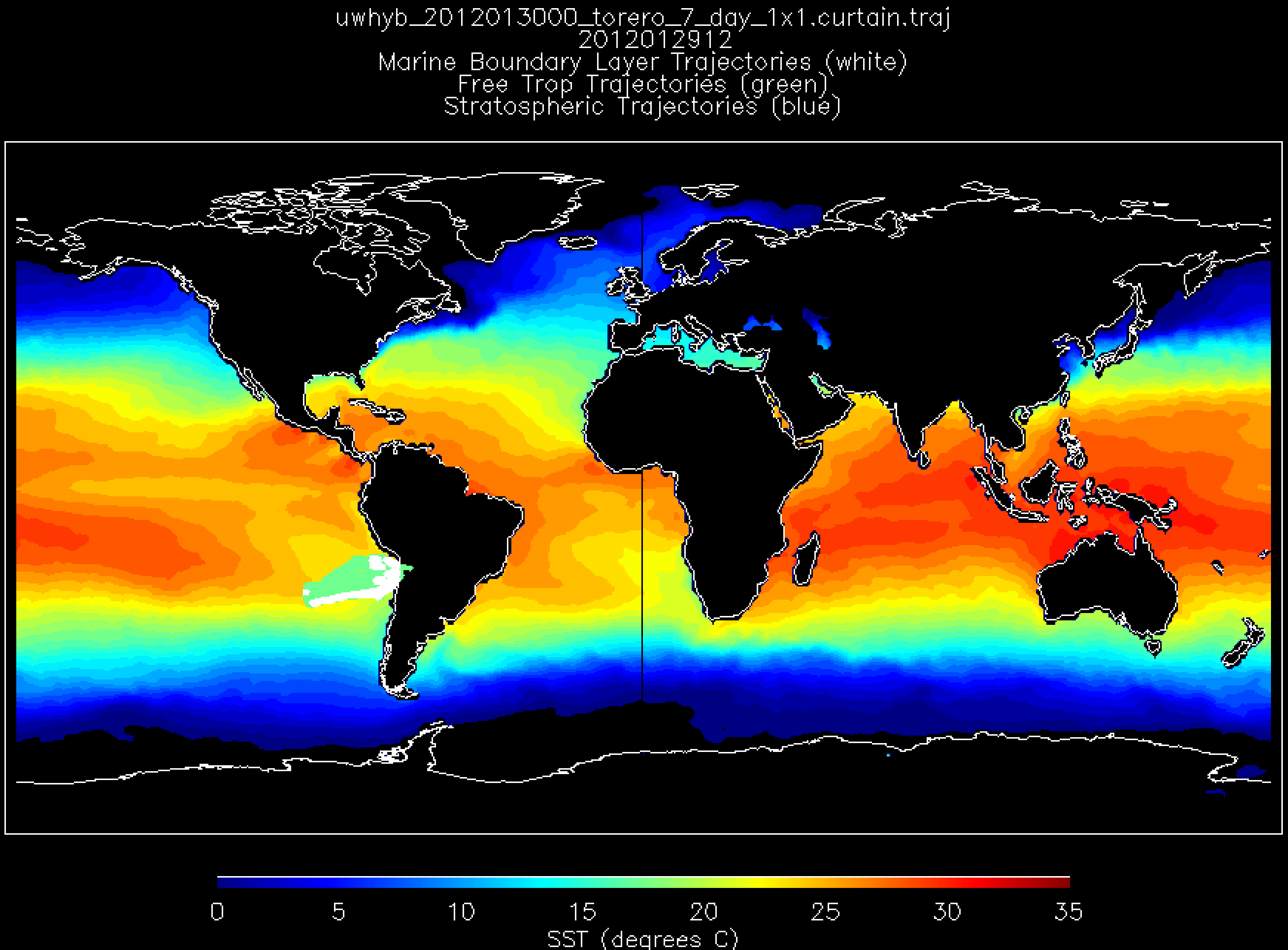


TORERO VOC Data

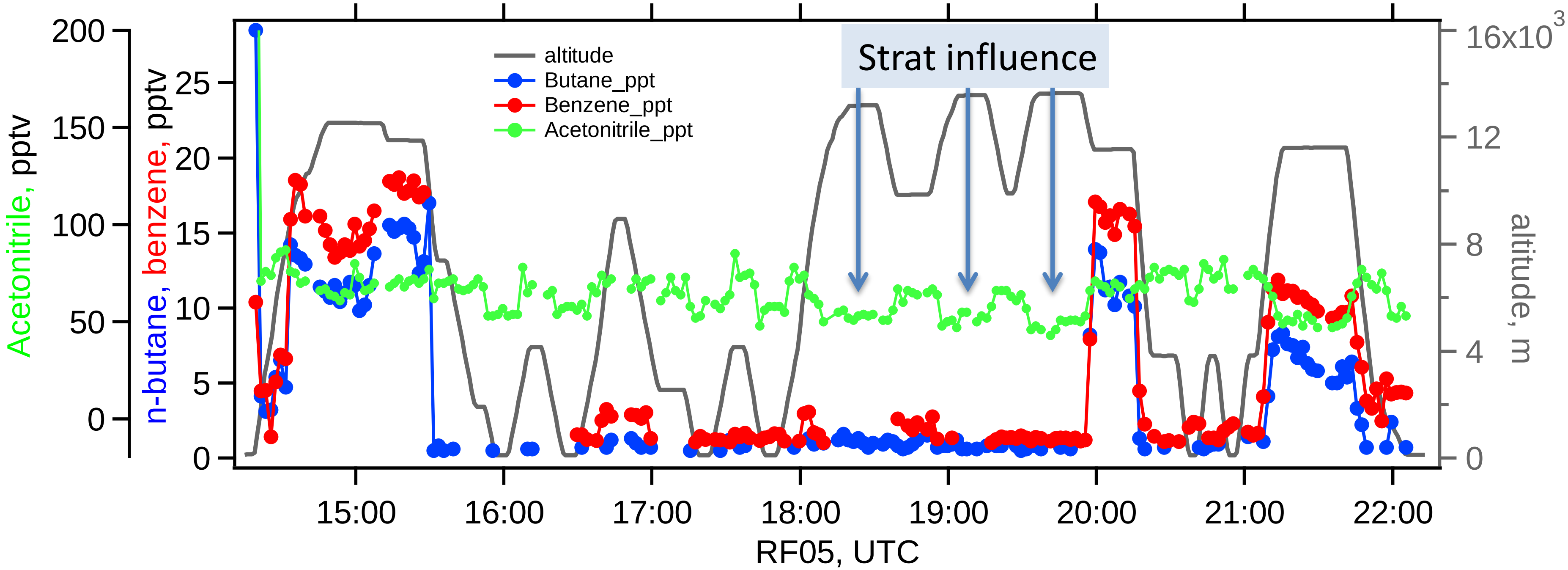
TORERO Acetone Data Example RF05

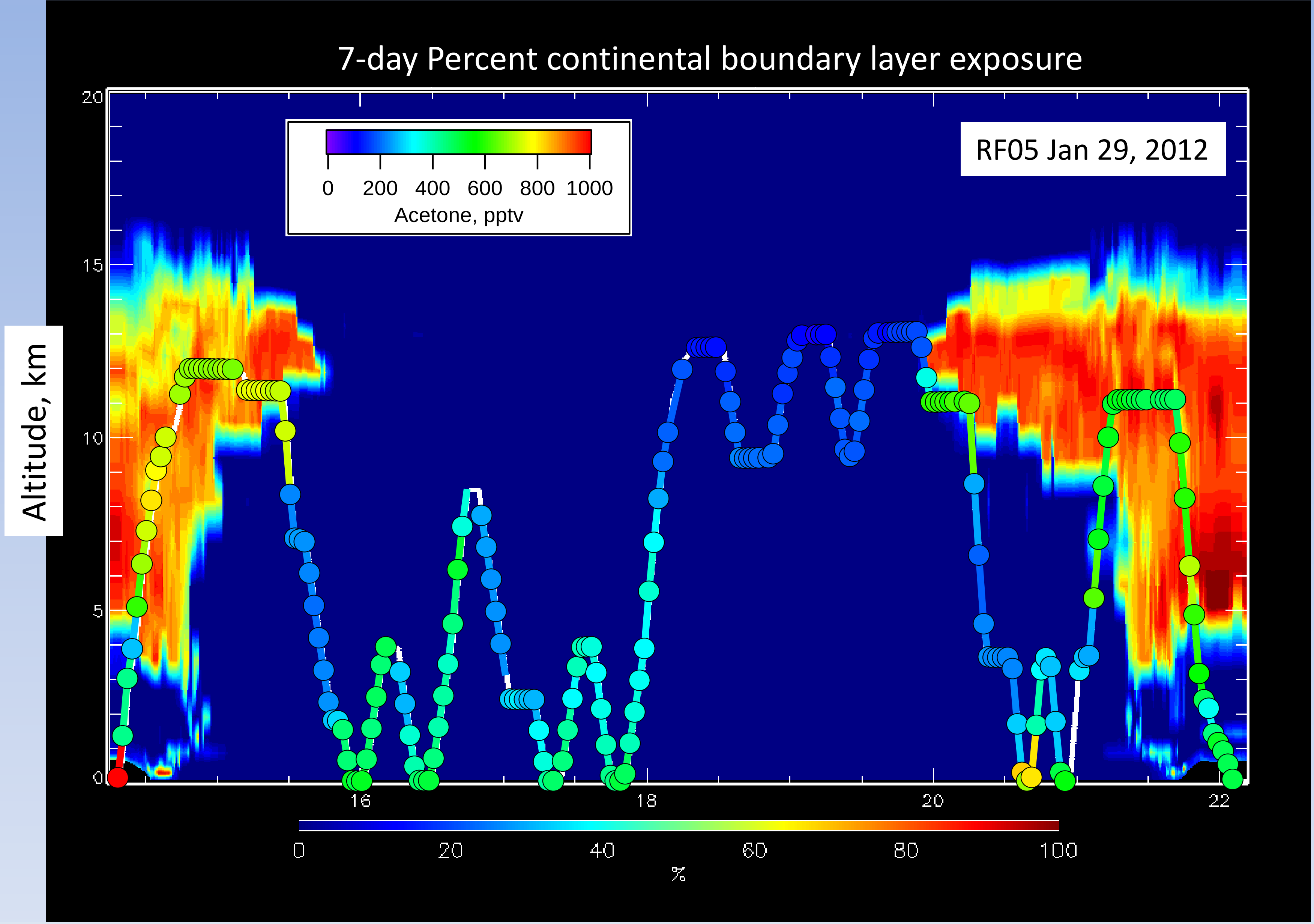


TORERO Research Flight 5



Measurements of OVOC precursors: very low – confirms little continental influence





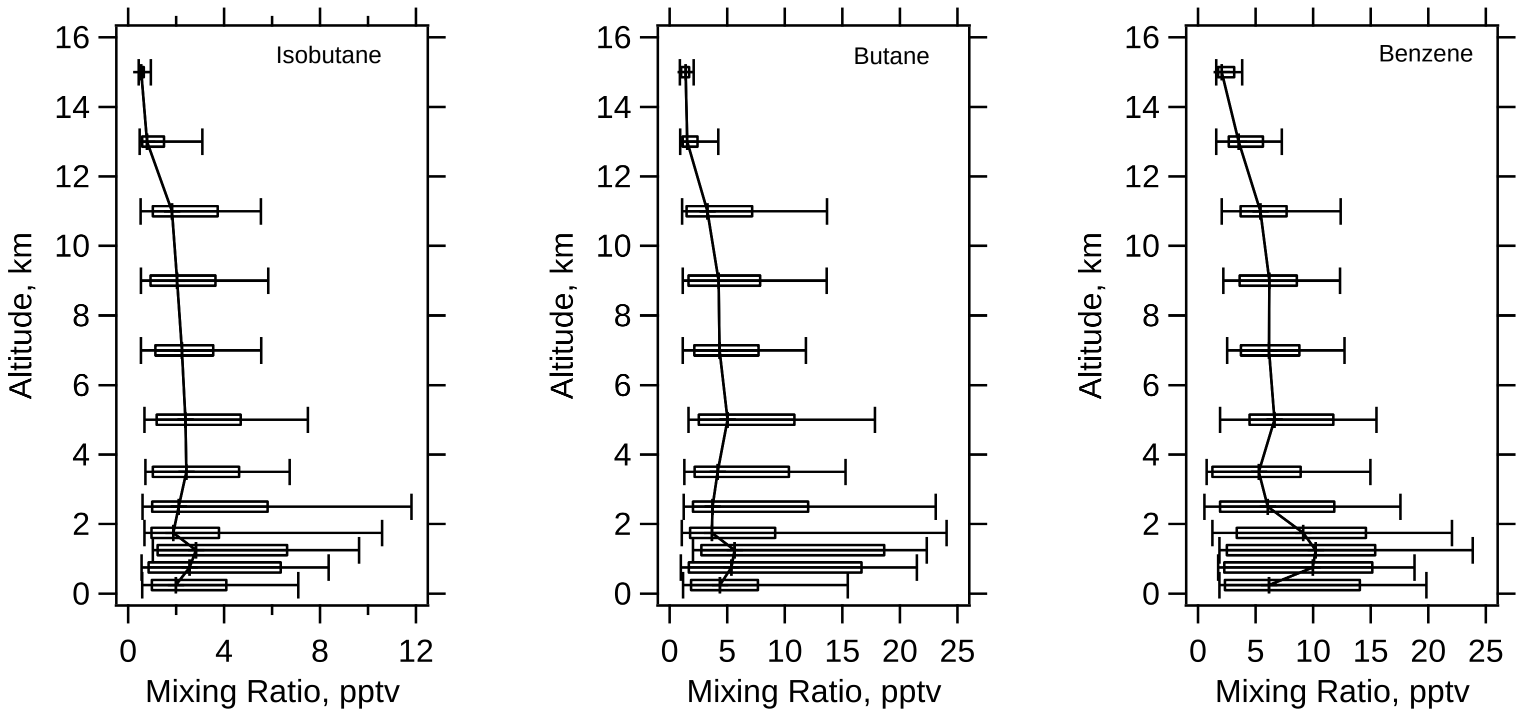
Three-dimensional back-trajectory calculations are used to construct reverse domain-filled (RDF) fields along aircraft flight tracks by sampling RAQMS along the back-trajectories following Fairlie et al., [2007]. (Courtesy of B. Pierce)

TORERO TOGA Measurements

Anthropogenic (BB) compounds – Tracers from over ocean-only data

Note low MRs of species – very little overall anthro /BB influence

Butanes τ ~ week, Benzene ~ 1 month



Long-lived semi-soluble species

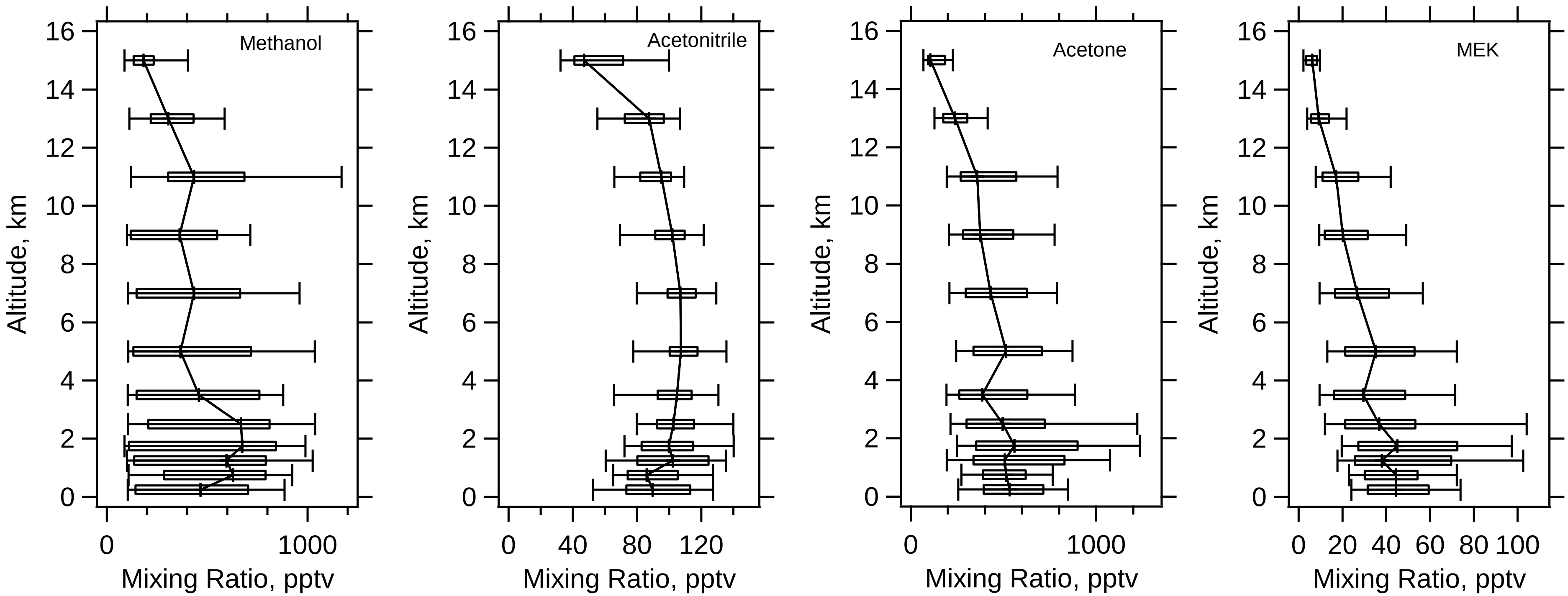
Methanol ~ 10 days, biogenic, BB, anthro, photochem

CH_3CN ~ months, BB (not much here)

Acetone ~ 1 month (14 days)

MEK ~ 10 days

TORERO TOGA Measurements

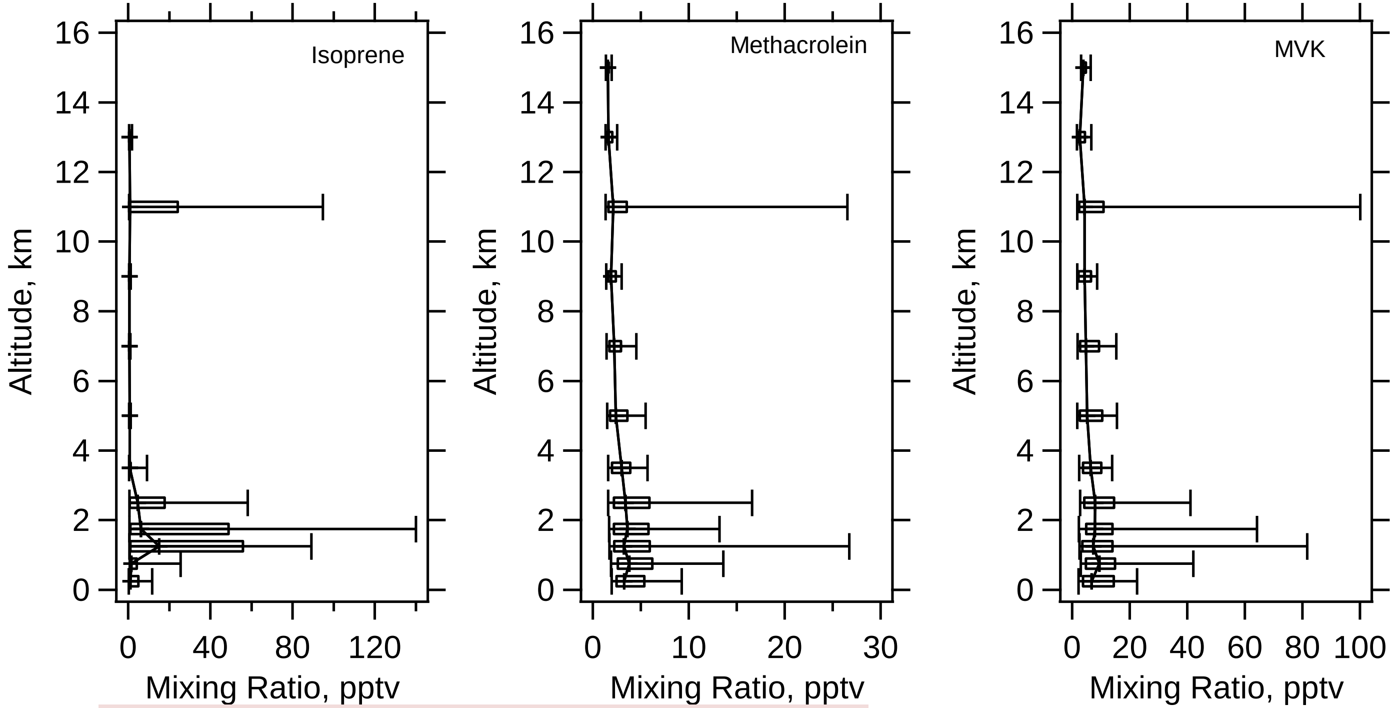


Biogenic compounds from ocean – impact on SOA etc.

very little isoprene observed in this study (TORERO) from oceans

Open question: 8 Tg/yr global source of organic marine aerosol (Spracklen et al., 2008)

Virtually no terpenes observed –very low MRs



Avg. isoprene w/ DMS> 20 = 1.1 pptv
Avg. terpenes w/ DMS> 20 = 0.4 pptv

Short-lived OVOCs

Aldehydes – formaldehyde – many sources incl. methane, methanol, MeOOH, CH_3CHO, etc

Others – all have short lifetimes

Formaldehyde

Acetaldeyde

Propanal

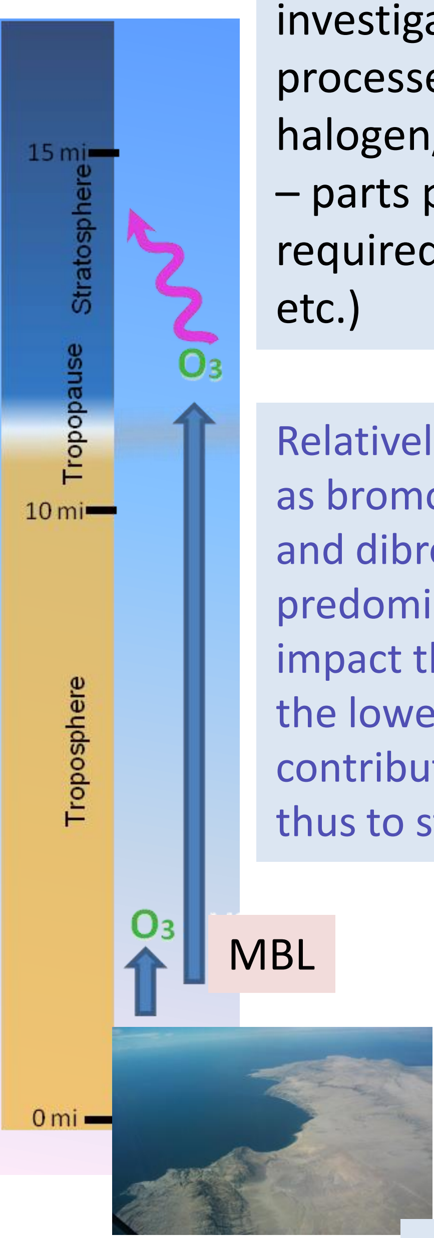
Butanal

CONTRAST Hypothesis: CH_2Br_2, $CHBr_3$, and other VSL bromocarbons will be elevated in air parcels that have undergone recent deep convection.

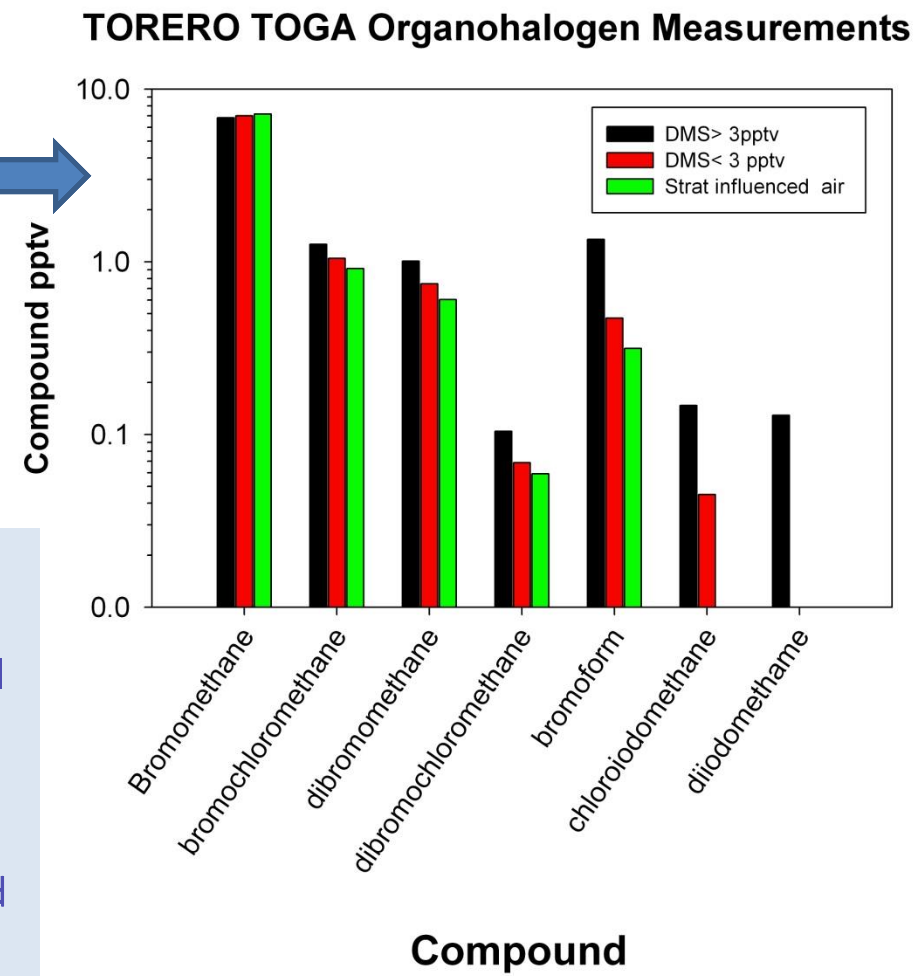
The low O_3 environment of air undergoing recent, deep convection will increase the atmospheric lifetime of halocarbons lost by reaction with OH

Table 1. Lifetime at 5 km, 275 K

Chemical	τ_{OH} (days)	τ_J (days)	τ_{TOTAL} (days)
$CHBr_3$	100	36	26
CH_2Br_2	120	5000	120
CH_2BrCl	150	15000	150



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

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

DMS

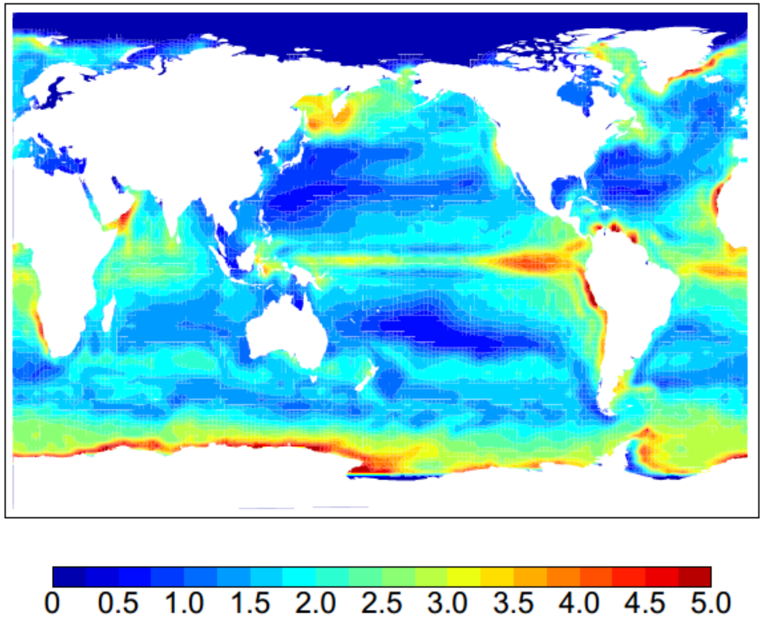
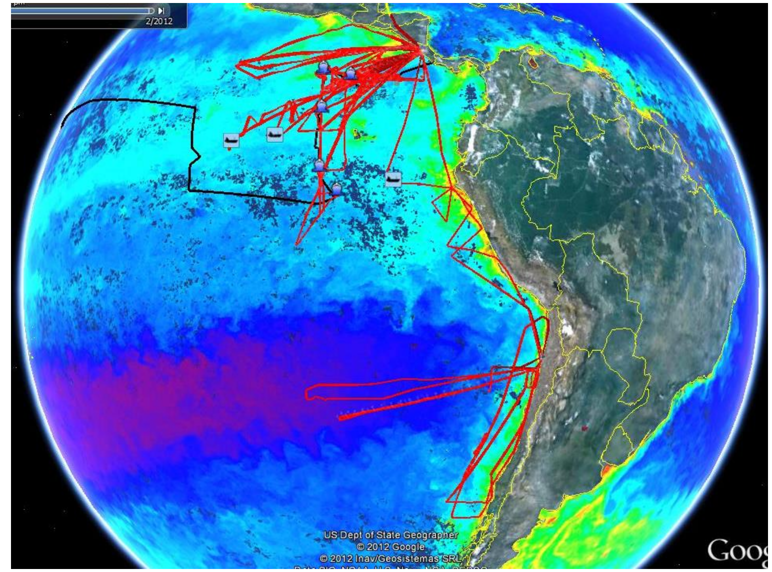
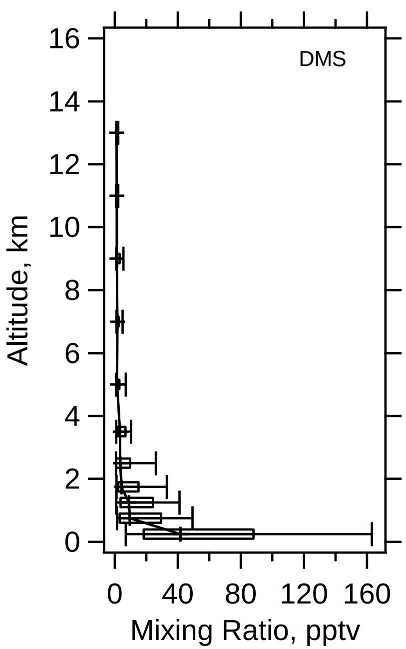
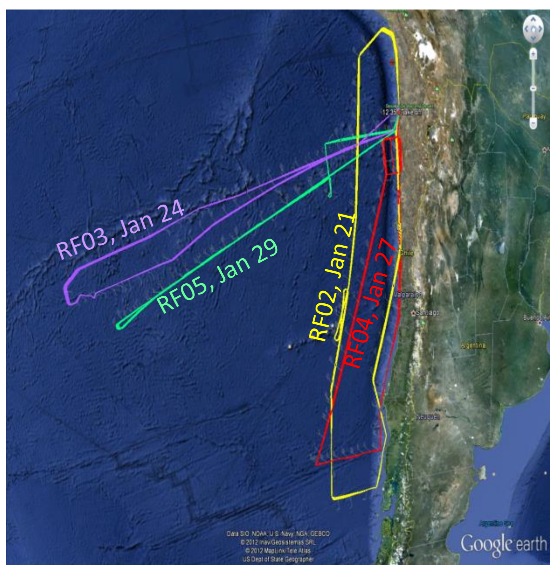


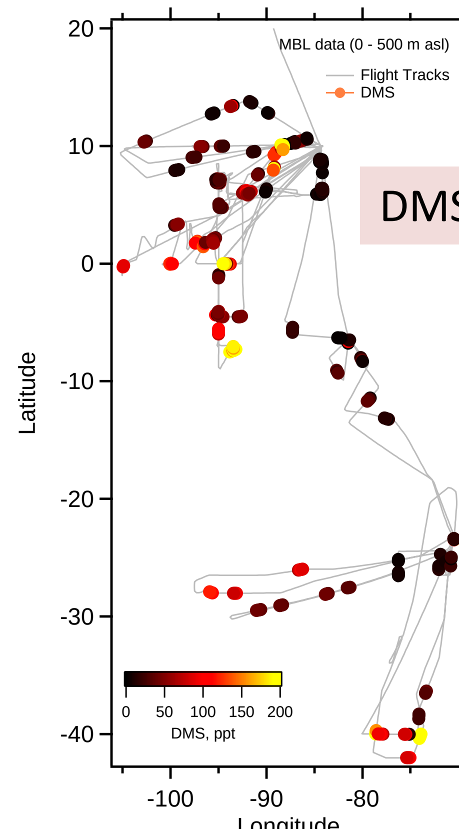
Fig. 1. Modeled annual mean DMS sea surface concentration. Units are nmol/l.

Kloster et al., 2005, Biogeosciences Discussions



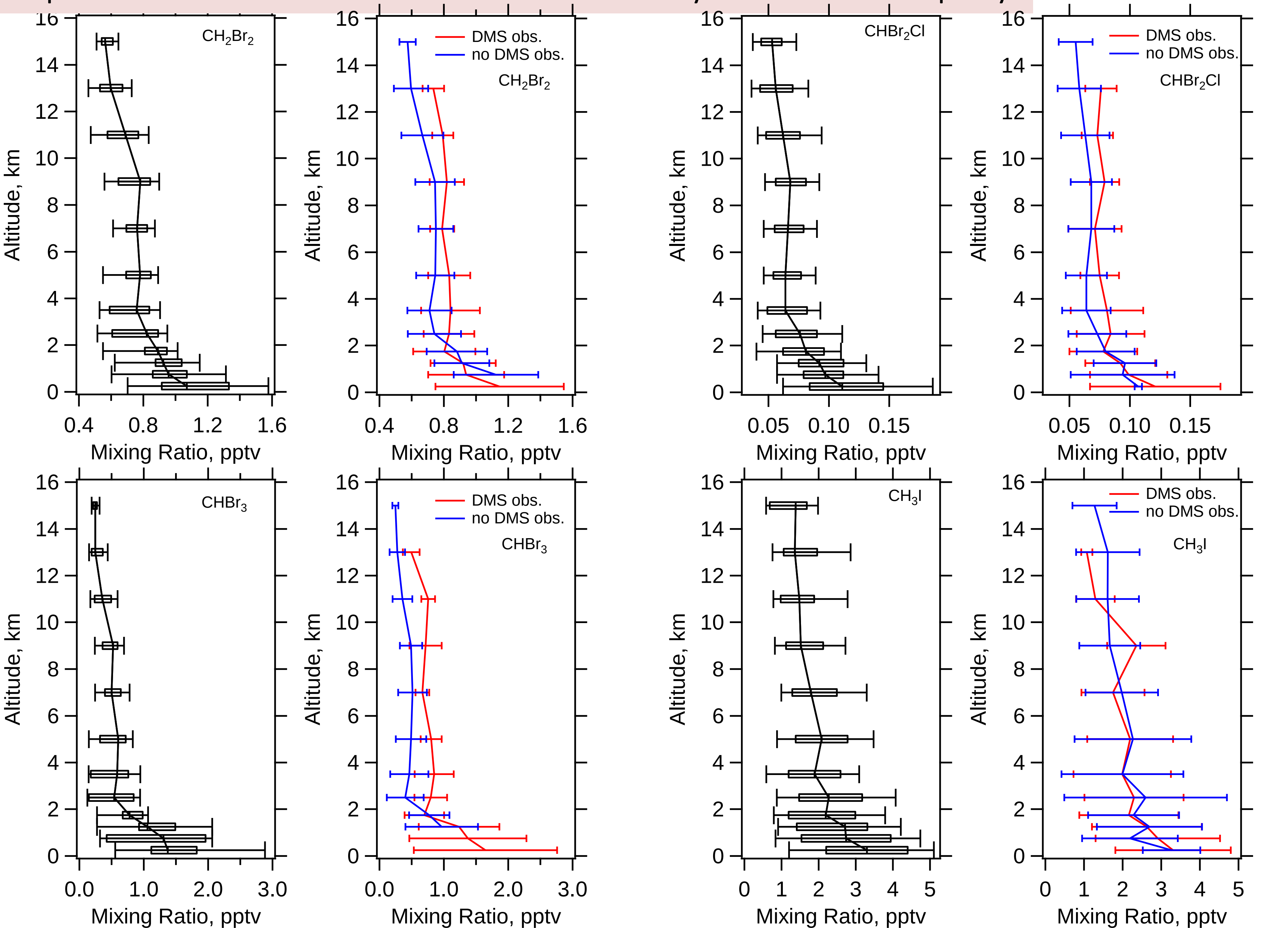




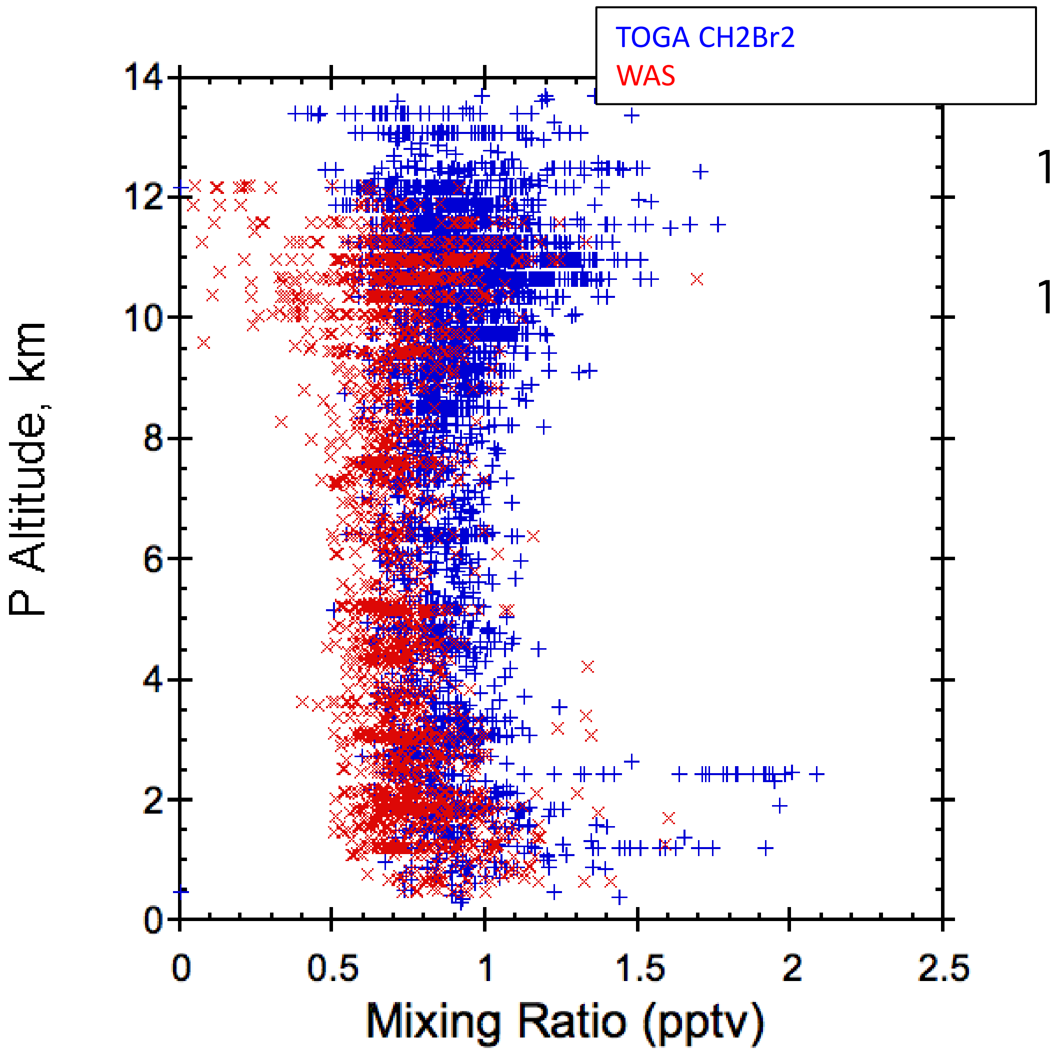


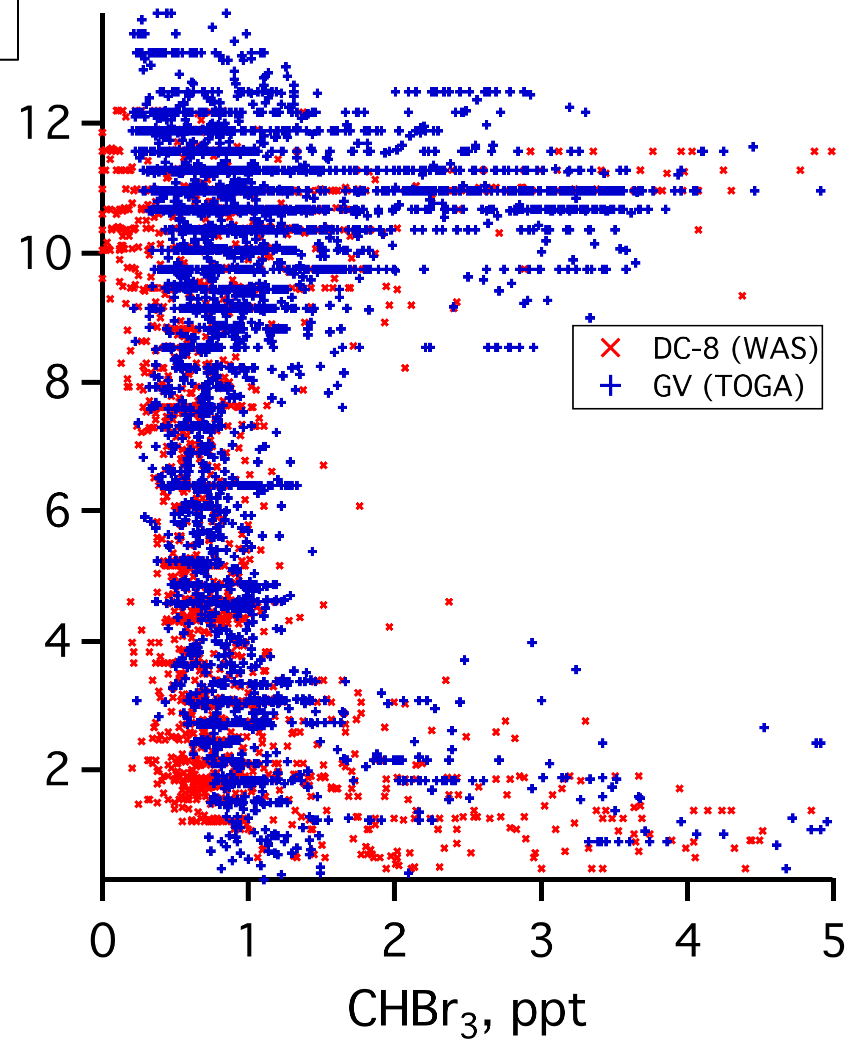
DMS “mapping”

Impact of convection on brominated VSLS and methyl iodide – DMS as proxy



2012 DC-3 Campaign

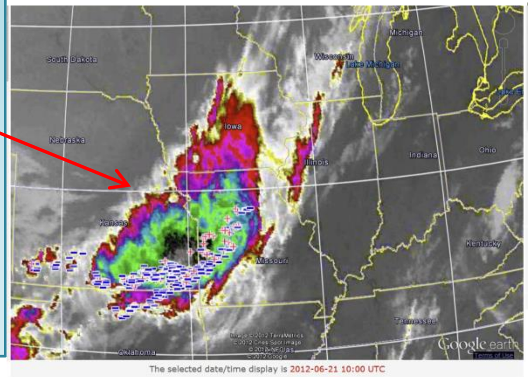




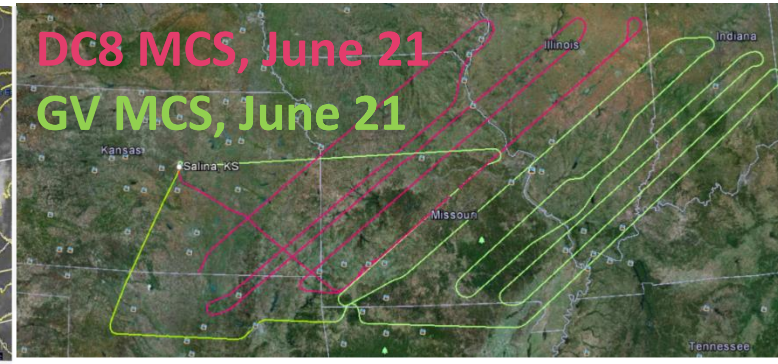
DC3 2013 June 21 MCS Flight - Following the photochemistry after convection

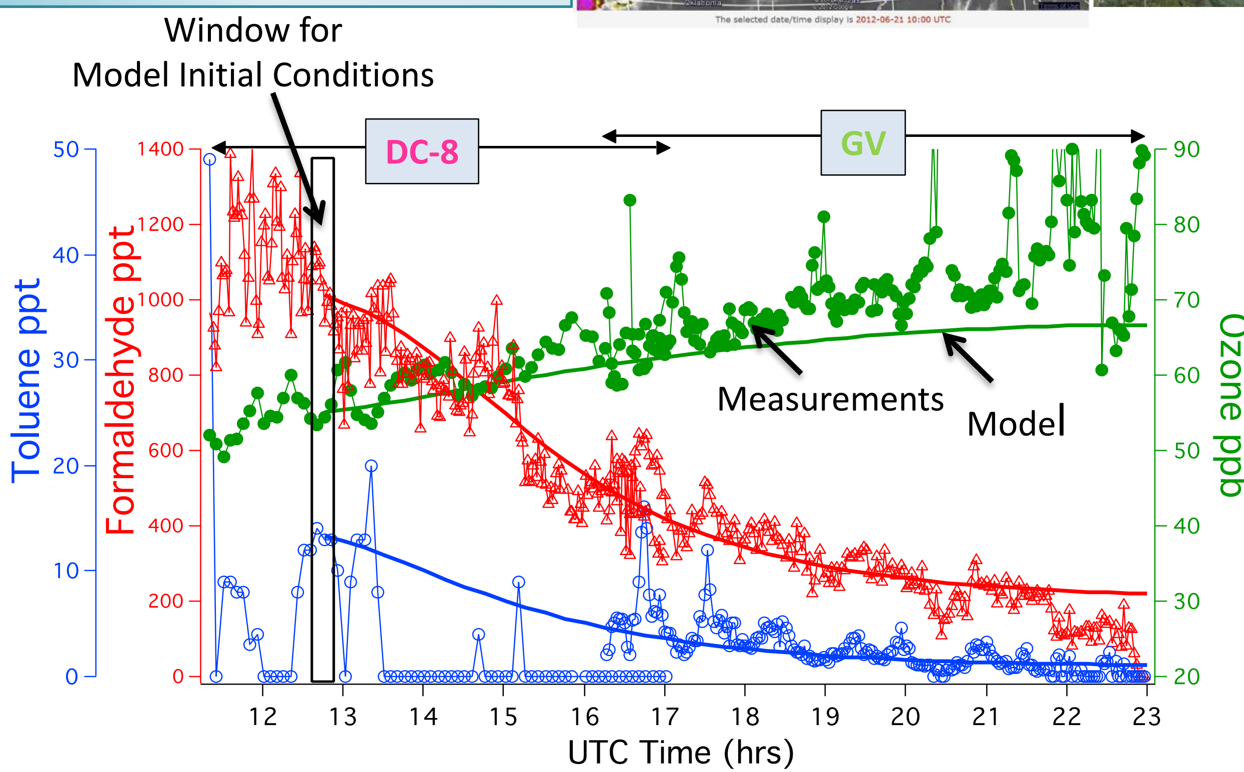
During the DC3 experiment we had the exceptional opportunity to study the outflow from an MCS (mesoscale convective system).

The highly instrumented GV aircraft followed the highly instrumented DC8 aircraft in a daylong study of the outflow from the previous night's MCS.



Flight tracks





- All measurements shown above 10 km
- MM predicts VOCs well – ozone underpredicted
- Photochemistry produces ozone in outflow (at 10 km altitude) – spikes probably represent strat intrusion
- TOGA measures toluene and other VOCs that contribute to formaldehyde and ozone formation to 1 pptv with high accuracy

GV Measurements: VOCs – ***TOGA*** (Apel, Hills, Hornbrook, NCAR/ACD; Riemer, U. Miami), O_3 (Campos, NCAR/ACD), Formaldehyde (Fried, NCAR/EOL)
DC8 Measurements: VOCs - Whole air sampler (Blake, UC-Irvine); O_3 (Ryerson, NOAA), Formaldehyde (Fried, NCAR/EOL)
NCAR Master Mechanism: Detailed 0-D model – Chemistry – Apel, Lee-Taylor, Madronich (NCAR/ACD)

Summary

TOGA VOC measurements will complement WAS + others and provide measurements for OVOC species as well at 2 min time resolution