Preliminary Measurements from TORERO with the Trace Organic Gas Analyzer (TOGA)

Eric Apel

Becky Hornbrook – July, 2012

Alan Hills, D. Riemer

NCAR

Key Topics

Atmospheric Chemistry

Emissions, transformations, and redistribution of trace gases affect the global environment

- Oxidative capacity (ability of atmosphere to cleanse itself)
- Ozone (health and ecosystem effects, radiative - climate)
- Radiative and health effects from nucleation and growth of ultrafine particles
- stratospheric/trop ozone depletion from VSL halogenated species

Recent experiment that address unresolved or outstanding issues relevant to these topics and the results of which are globally significant

- **TORERO** – GV/ ship study – CR and Chile – release and transport of trace species from coastal and open ocean waters

Tropical **O**cean t**R**oposphere **E**xchange of **R**eactive halogen species and **O**xygenated VOC

R. Volkamer PI

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

TORERO Science Hypothesis

Hypothesis #1: Ocean sources of oxygenated VOC (OVOC) and reactive halogen species (RHS) impact atmospheric composition in the MBL, and in the FT as a result of deep convective transport.

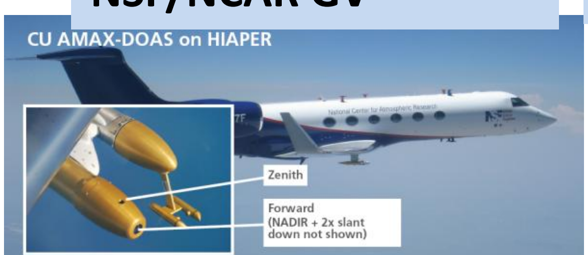
Hypothesis #2: The gas fluxes across the air-sea boundary vary between the oligotrophic and mesotrophic ocean, and coastal upwelling.

Hypotheses #3: Reactive gases released from the ocean are relevant to chemistry and climate.

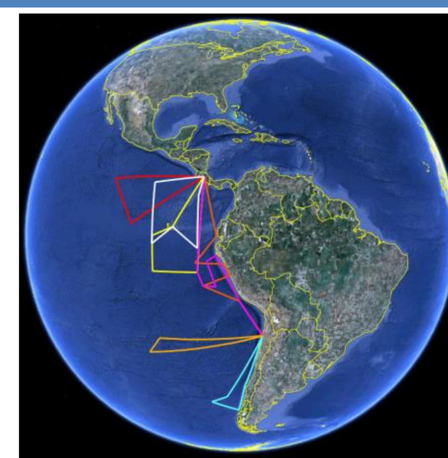
TORERO: measures for the first time simultaneously bromine and iodine oxide radicals, and organic precursor molecules.

Halogens destroy heat trapping tropospheric ozone, modify oxidative capacity, and oxidize mercury.

NSF/NCAR GV



NOAA RV Ka'imimoana



The Trace Organic Gas Analyzer (TOGA)

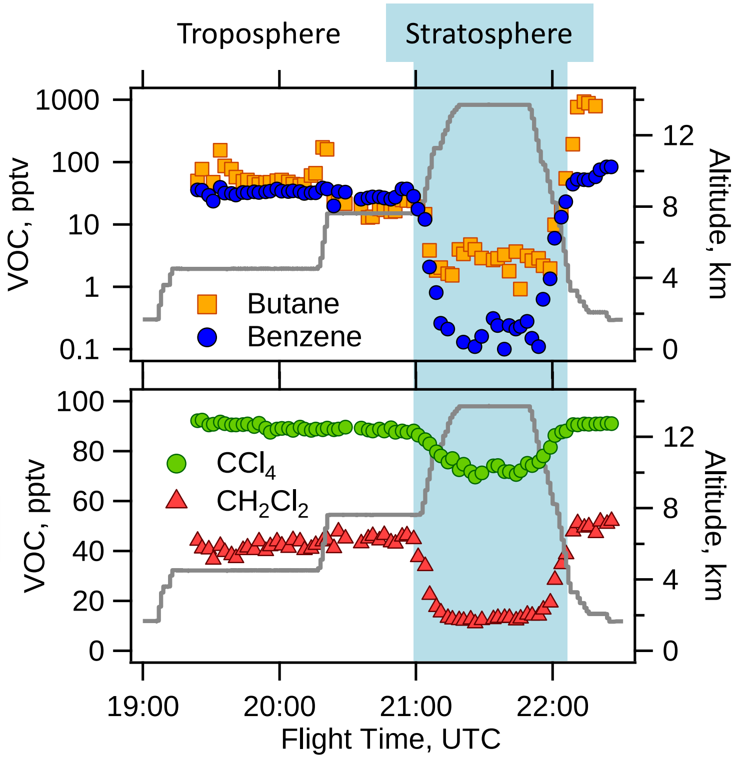
Eric Apel (PI), Alan Hills, Rebecca Hornbrook (ACD/NESL/NCAR)
Dan Riemer (Co-PI; University of Miami)

- 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

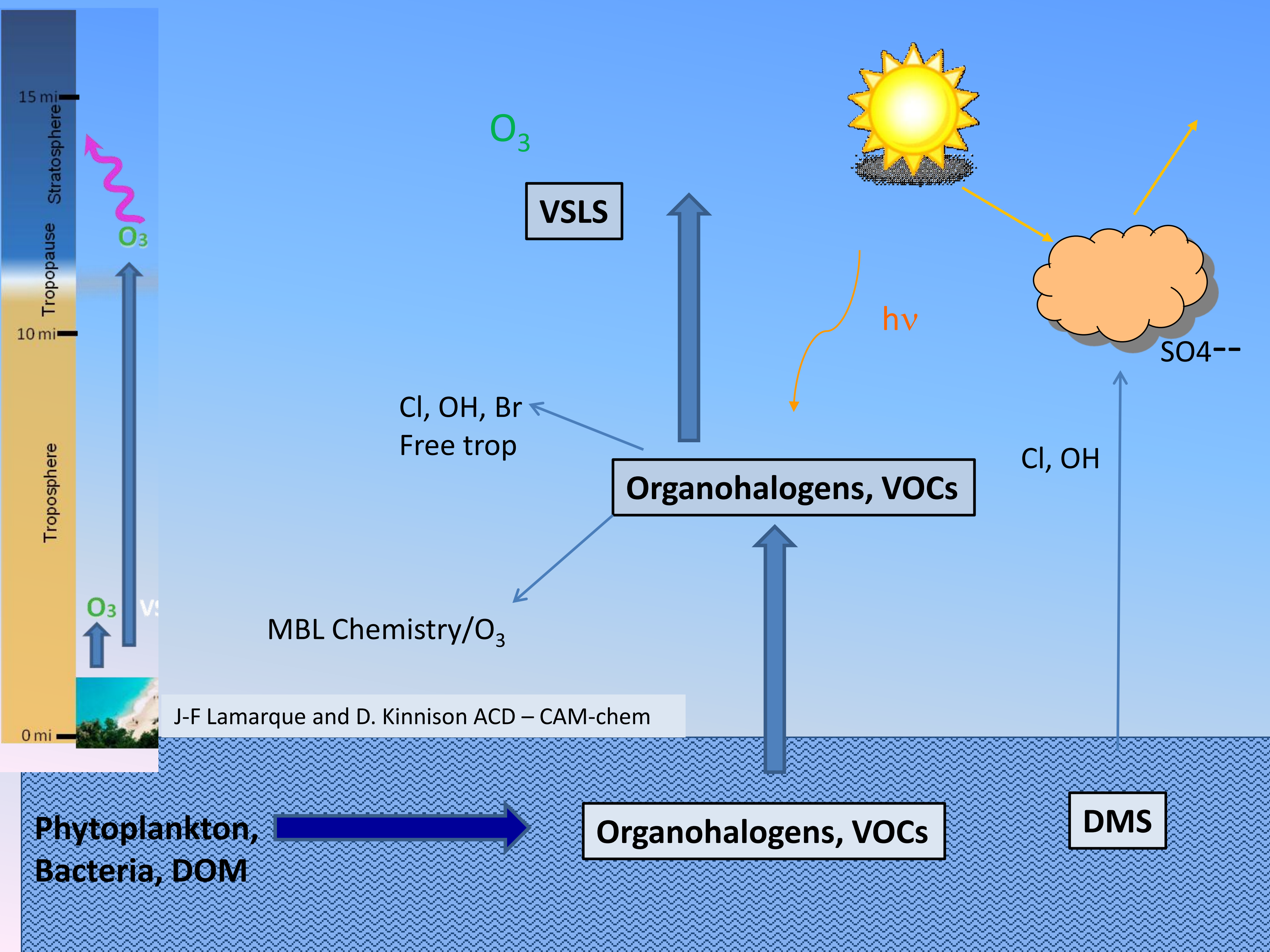
Greenhouse gases



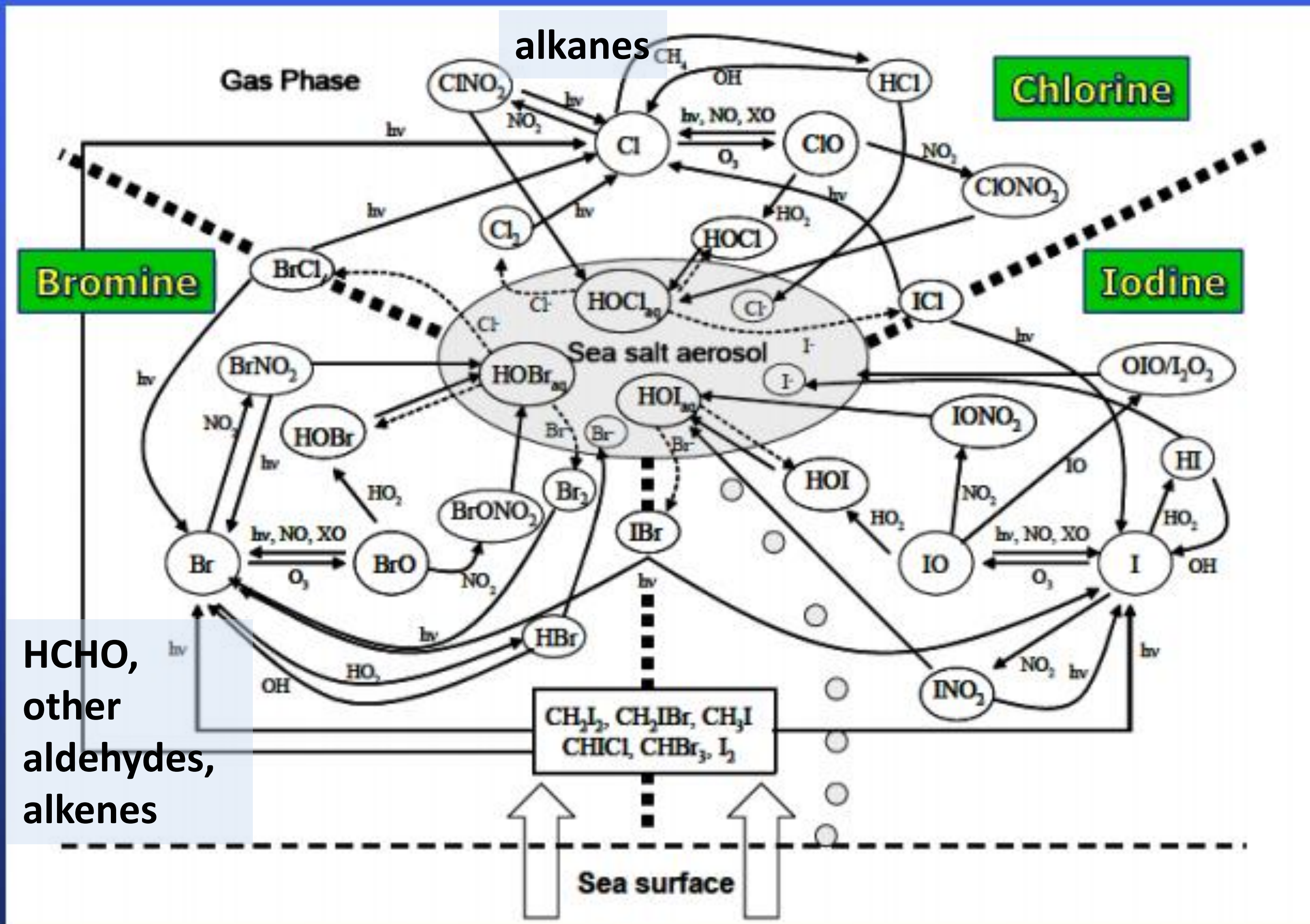
TOGA compounds

Hydrocarbons	Propane	Isoprene	
	1-Butene	*t*-2-Pentene	
	i-Butene	*c*-2-Pentene	
	Butane	*i*-Pentane	
	i-Butane	*o*-Xylene	
	Benzene	*m/p*-Xylene	
	Toluene	1,3,5-Trimethylbenzene	
	Ethyl Benzene	1,2,4-Trimethylbenzene	
	t-2-Butene	α-Pinene	
	c-2-Butene	β-Pinene	
	Pentane	Camphene	
	1,3-Butadiene	Myrcene	
	Limonene		
Oxygenates	Acetaldehyde	Methanol	
	Propanal	Ethanol	
	Butanal	Acetone	
	Pentanal	Butanone	
	Methacrolein	2-Pentanone	
	Methyl Vinyl Ketone	3-Pentanone	
	Methyl Butenol	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	DMSO?	
	Dimethyl Sulfide (DMS)		


TORERO
National Science Foundation


15 mi
Stratosphere
Tropopause
10 mi
Troposphere
0 mi
O_3
O_3
O_3
VSLS
hν
SO4--
Cl, OH, Br
Free trop
Organohalogens, VOCs
Cl, OH
MBL Chemistry/O_3
J-F Lamarque and D. Kinnison ACD – CAM-chem
Phytoplankton,
Bacteria, DOM
Organohalogens, VOCs
DMS

Tropospheric Halogen Chemistry



Montzka, Reimann, et al.

Table 1-4. Lifetimes for very short-lived halogenated source gases.

Compound	Local Lifetime from Previous Assessments (τ_{local}), days	OH Lifetime[1] (τ_{OH}), days	Photolysis Lifetime from Previous Assessments (τ_{local}), days	New Local Lifetime, (τ_{local}), days		Notes
Chlorocarbons						
CH_2Cl_2	140	144	> 15000	144		2, 8
$CHCl_3$	150	149	> 15000	149		2, 8
CH_3CH_2Cl	30	39		39		2
CH_2ClCH_2Cl	70	65		65		4
$CH_3CH_2CH_2Cl$		14		14		5
$CHClCCl_2$		4.9	> 15000	4.9		3, 8
CCl_2CCl_2	99	90		90		3
$CH_3CHClCH_3$		18		18		5
Bromocarbons						
CH_2Br_2	120	123	5000	123		2, 8
$CHBr_3$	26	76	36	24		2, 8
CH_2BrCl	150	137	15000	137		2, 8
$CHBrCl_2$	78	121	222	78		6, 8
$CHBr_2Cl$	69	94	161	59		7, 8
CH_3CH_2Br	34	41		41		2
CH_2BrCH_2Br	55	70		70		4
n-C_3H_7Br	13	12.8	> 1200	12.8		3, 8
iso-C_3H_7Br		16.7		16.7		3
Iodocarbons						
CH_3I	7	158	7 (4–12)	7		4, 8
CF_3I	4	860	not determined	4		2
CH_2ClI	0.1		0.1	0.1	2 hrs	8
CH_2BrI	0.04		0.04	0.04		8
CH_2I_2	0.003		0.003	0.003	5 min	8

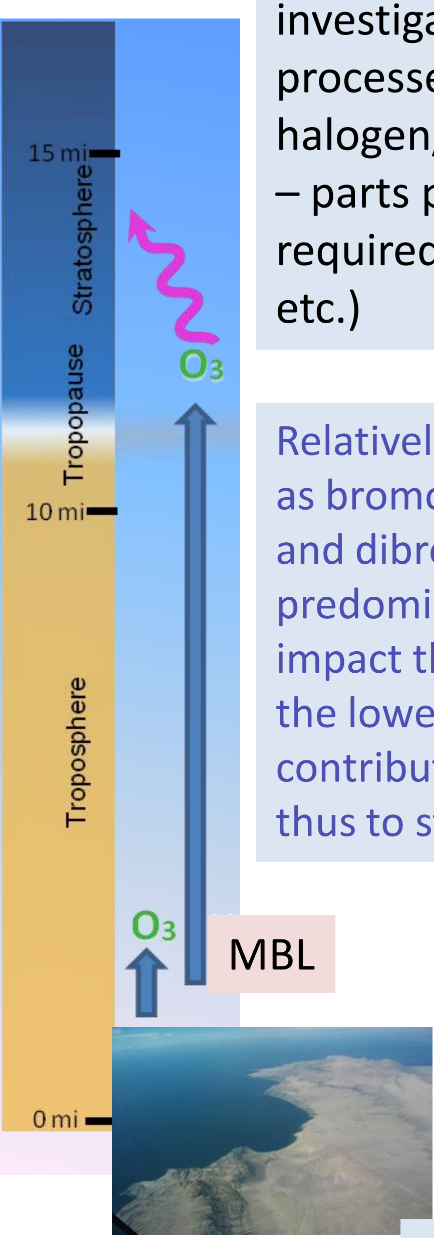
Preliminary Lucy Carpenter/Stephen Andrews analysis vs. various standards

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

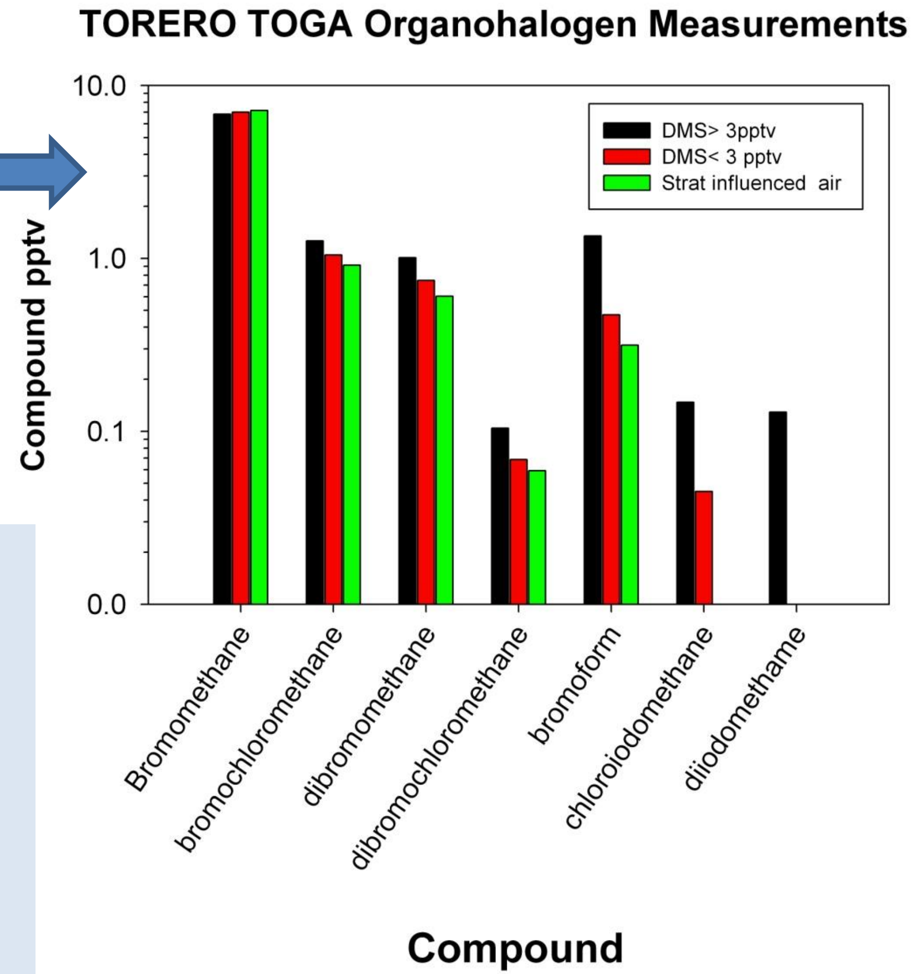
NOAA Gases

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

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

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)

DMS

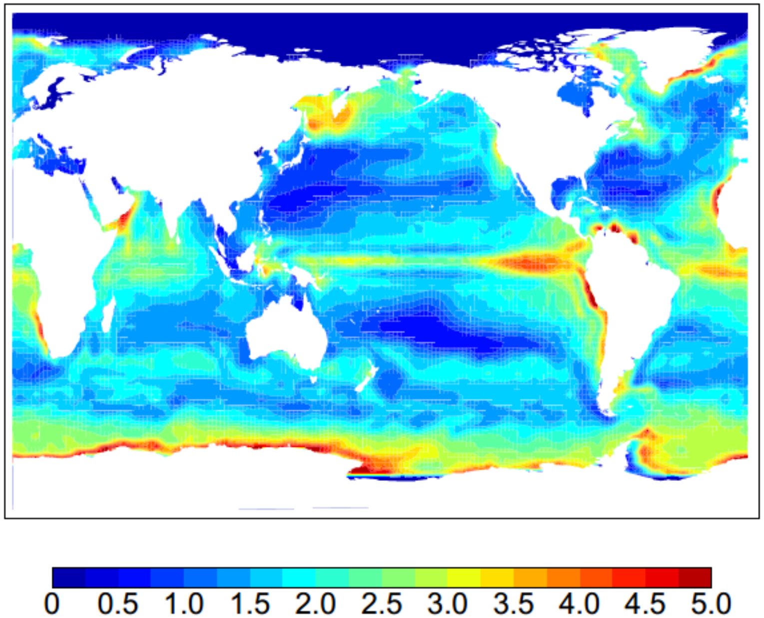
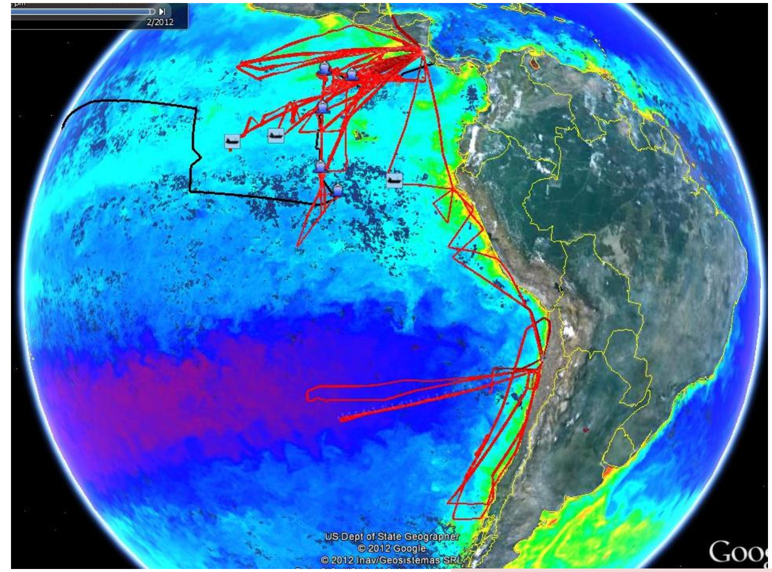
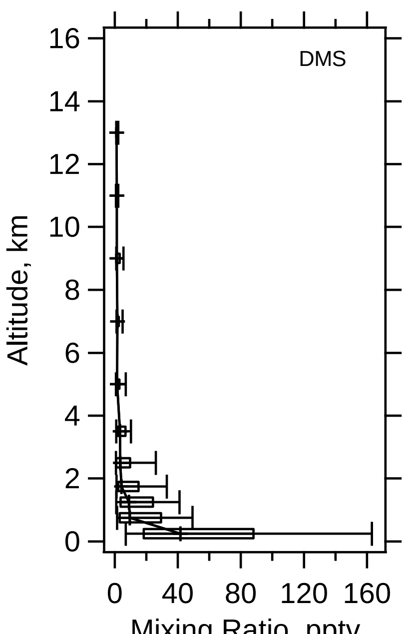


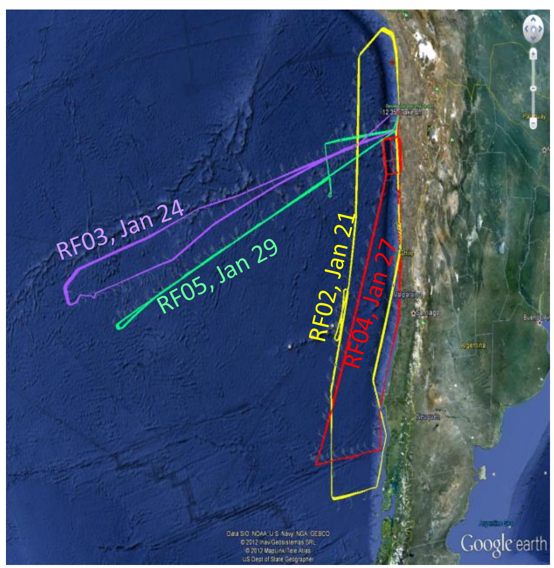
Fig. 1. Modeled annual mean DMS sea surface concentration. Units are nmol/l.

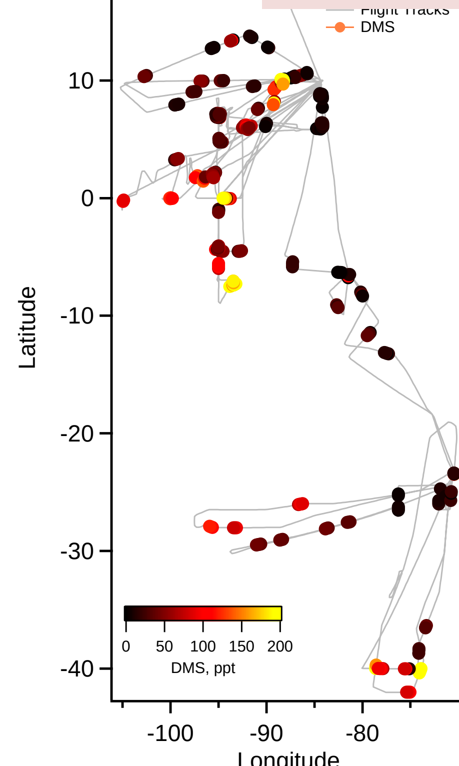
Kloster et al., 2005, Biogeosciences Discussions



DMS "mapping"





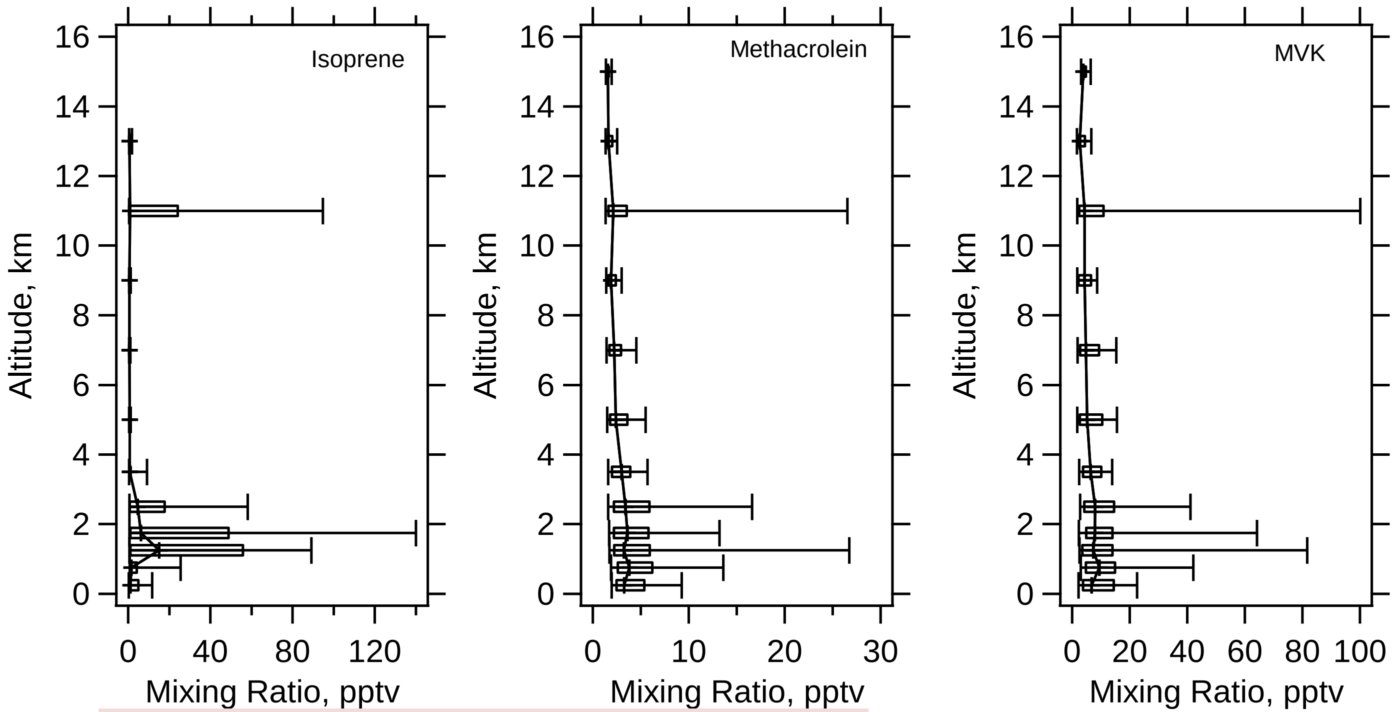


Biogenic compounds from ocean – impact on SOA etc.

very little isoprene observed in this study 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

Isoprene consistent with bottom-up GEOS-Chem w/ isoprene source

Arnold et al., ACP, 2009

GEOS Chem – no isop source

Bottom-up GEOS Chem – w/ isop source

w/ top-down estimate

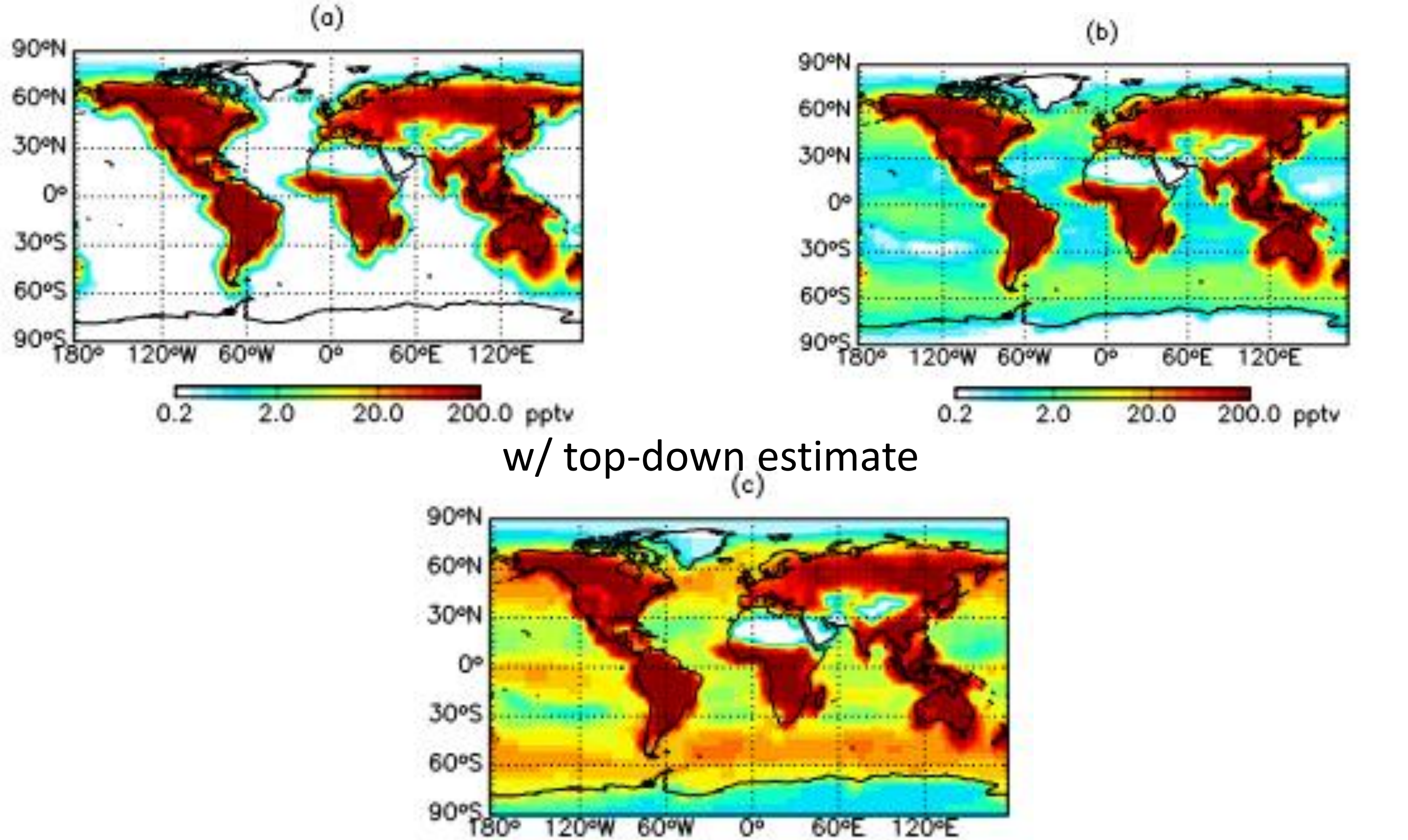
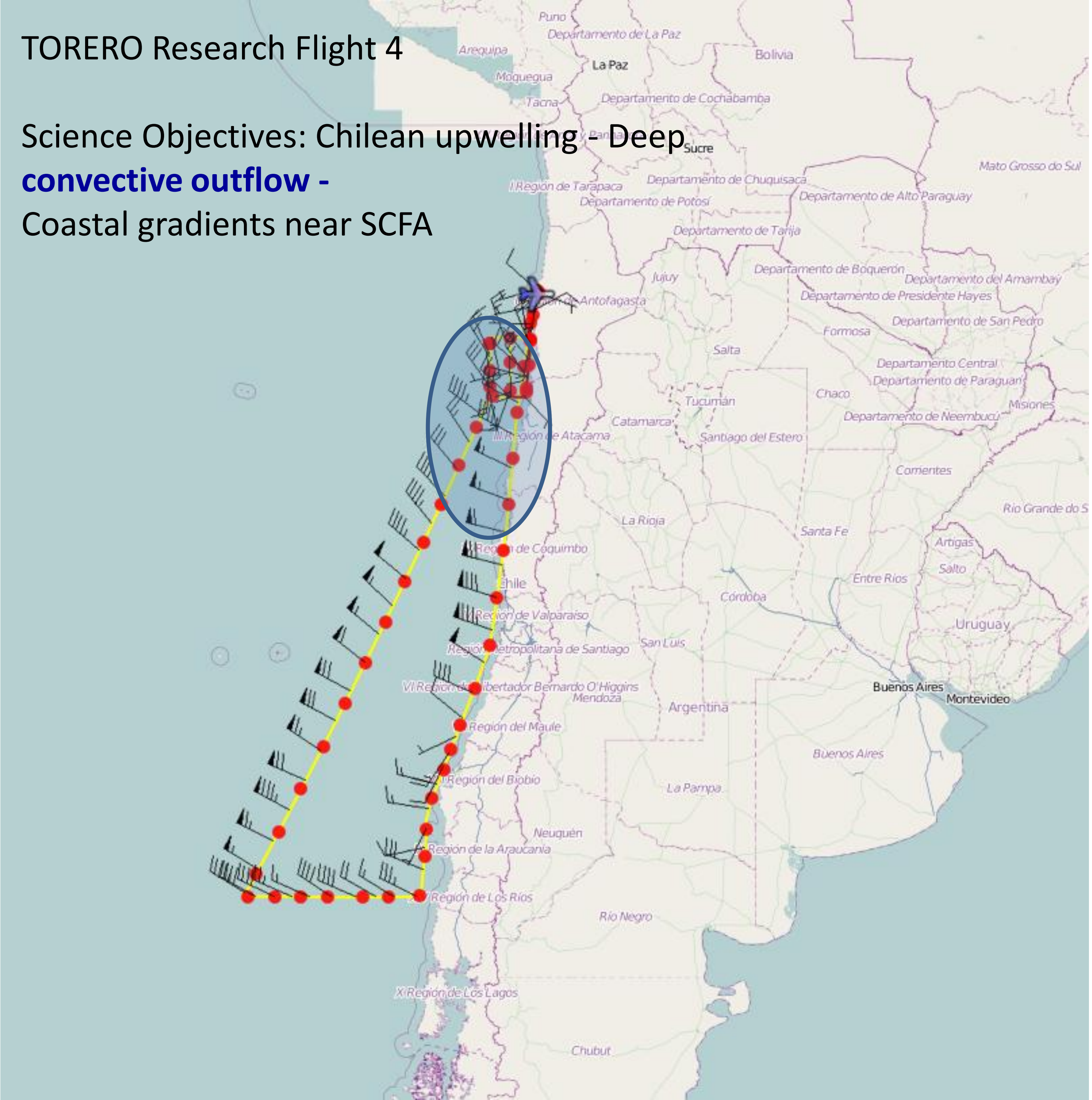


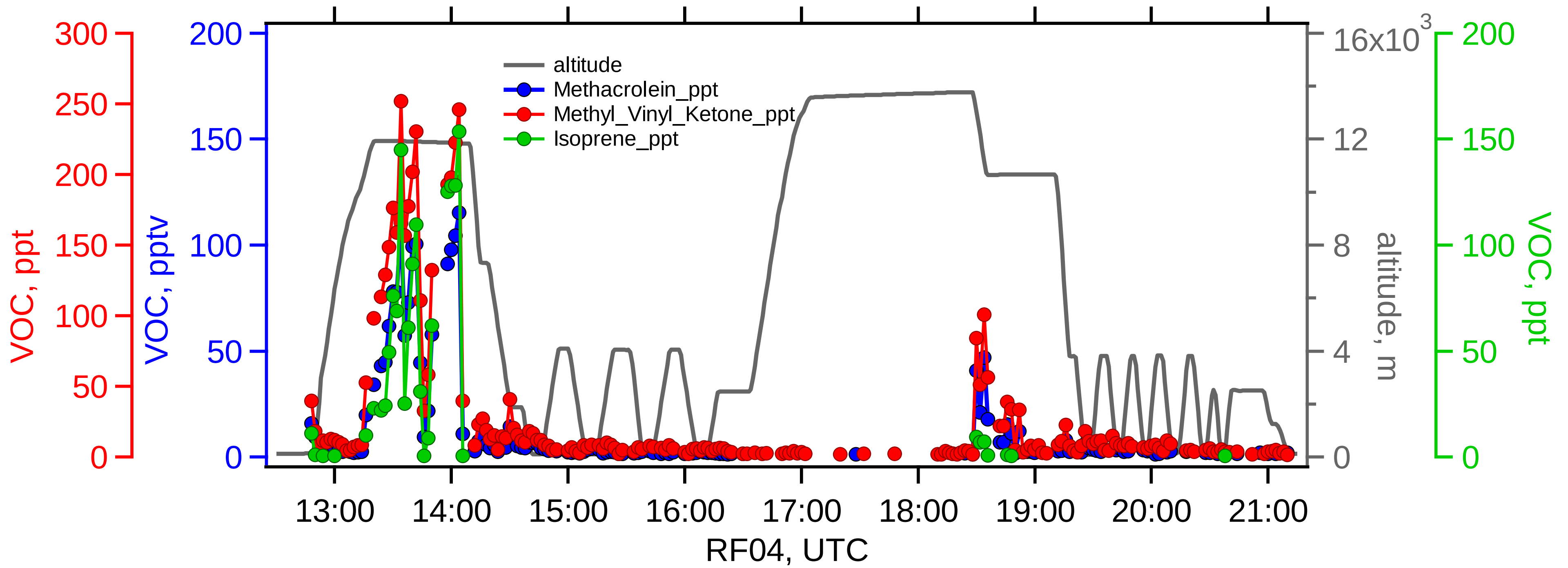
Fig. 2. (a–c) Annual mean surface atmospheric isoprene concentrations from the GEOS-CHEM model for year 2000 from simulations **(a)** without an oceanic isoprene source, **(b)** with the 0.31 Tg/yr "bottom-up" source estimate, and **(c)** with the 1.9 Tg/yr "top-down" source estimate. **(d)** Ratio of annual mean surface atmospheric isoprene concentrations from the 1.9 Tg/yr oceanic source to the no oceanic isoprene source simulations (c/a). Note colour scale is saturated at highest and lowest colour-bar values.

TORERO Research Flight 4

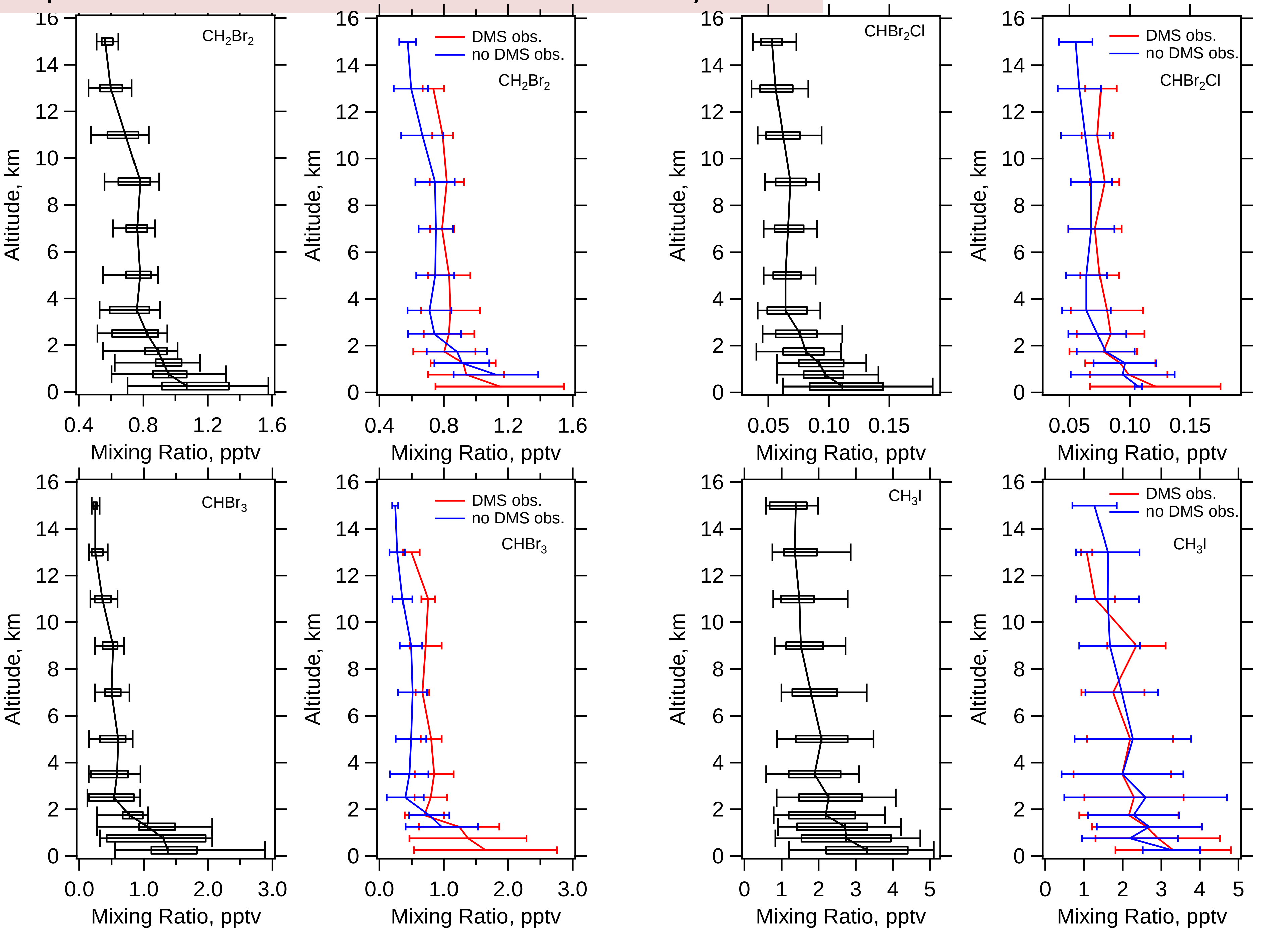
Science Objectives: Chilean upwelling - Deep **convective outflow -**
Coastal gradients near SCFA



TOGA Measurements of convected species off coast of South America

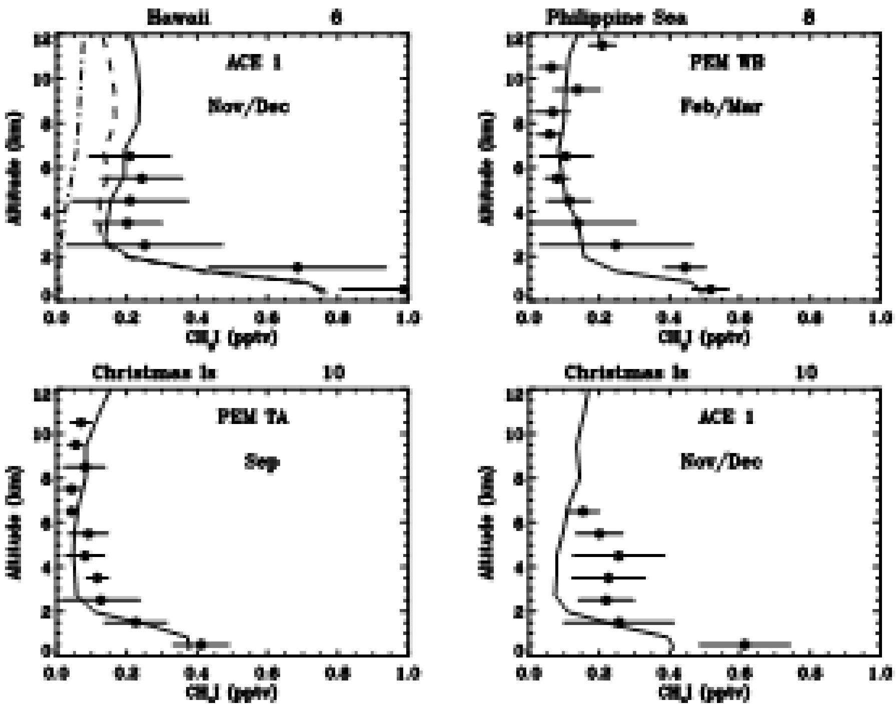


Impact of convection on brominated VSLS and methyl iodide

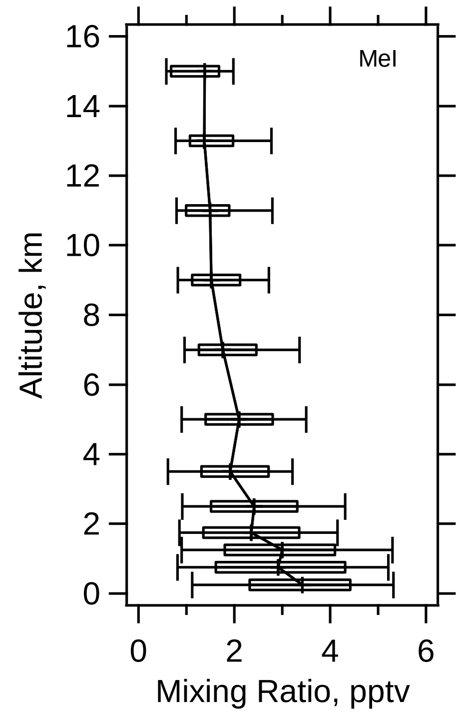


CH3I

Some Previous Measurements



TOGA TORERO



Bell et al.,

Long-lived semi-soluble species

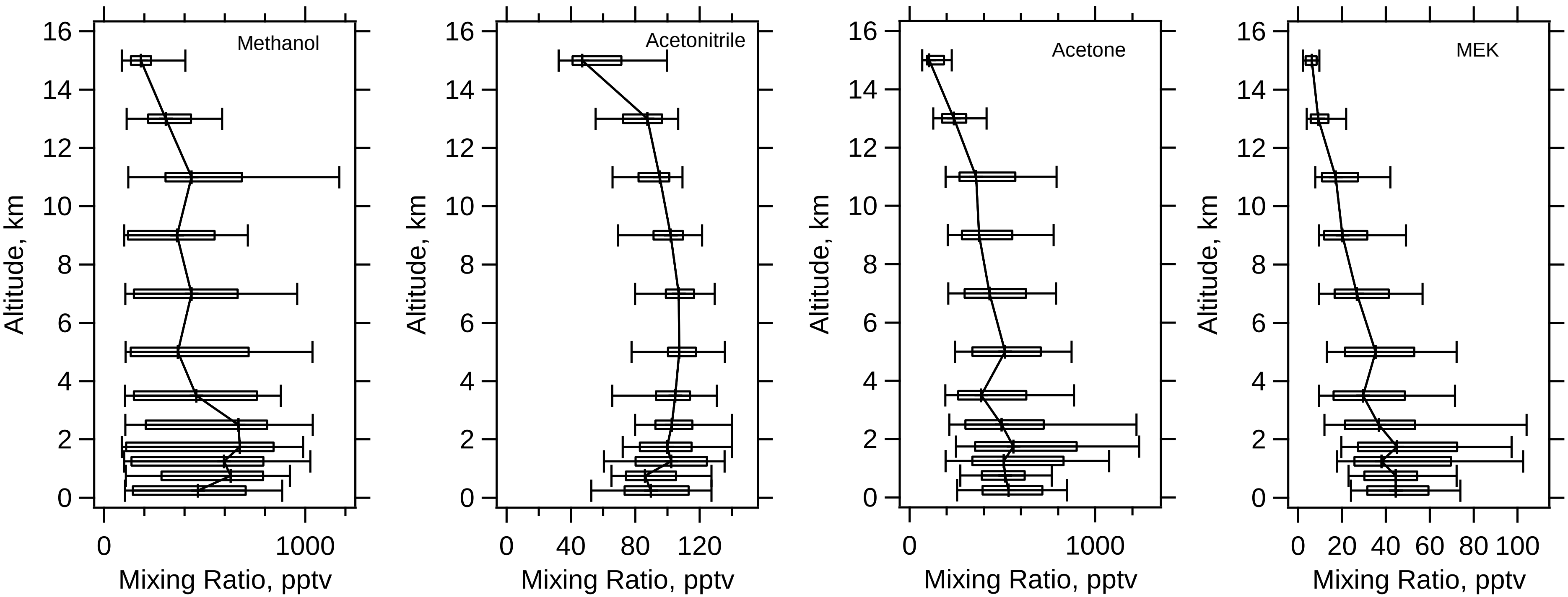
Methanol ~ 10 days, biogenic, BB, anthro, photochem

CH_3CN ~ months, BB (not much here)

Acetone ~ 1 month (14 days)

MEK ~ 10 days

TORERO TOGA Measurements

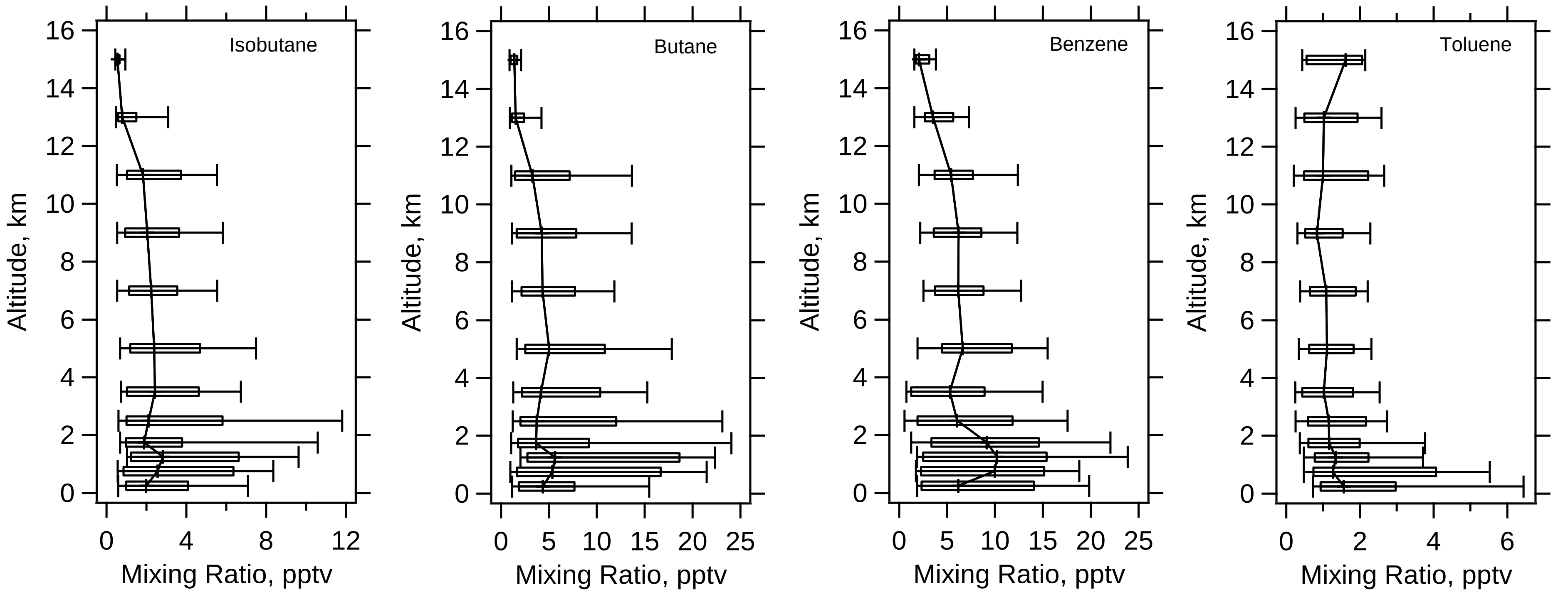


TORERO TOGA Measurements

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

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

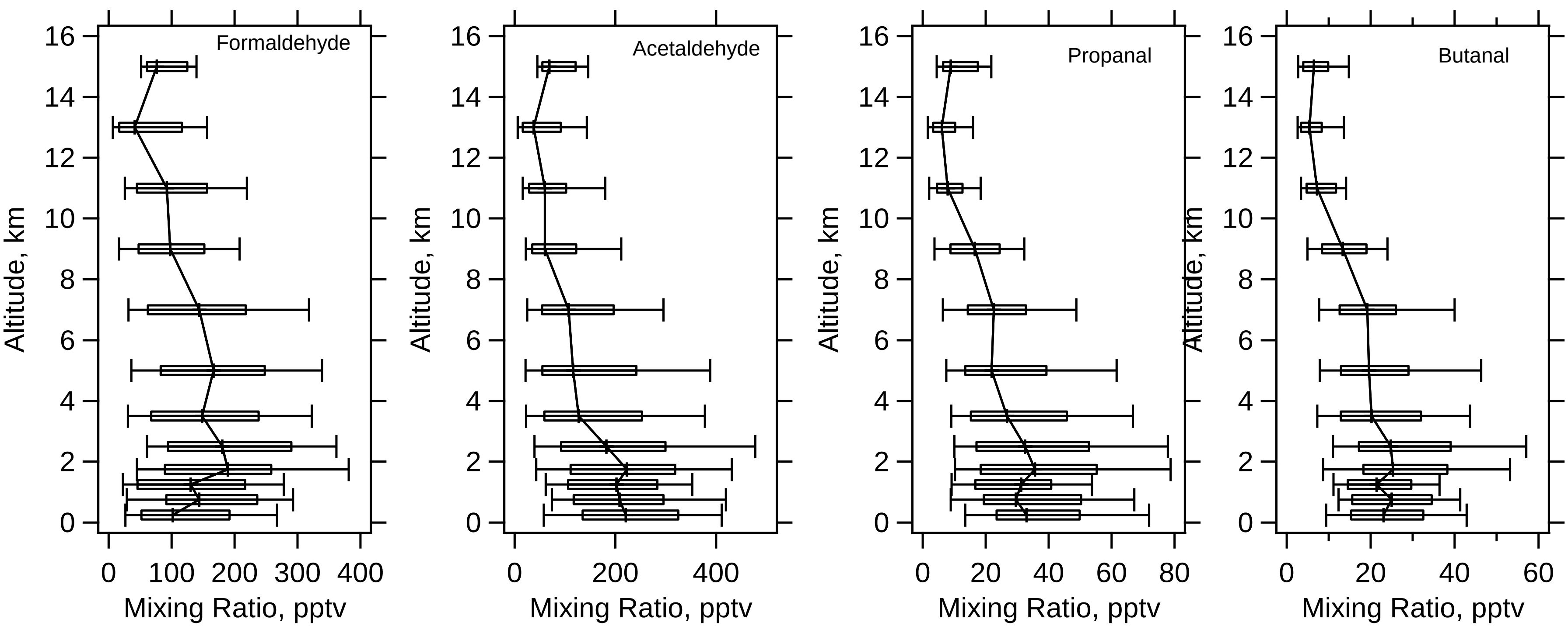
Butanes τ ~ week, Benzene ~ 1 month, toluene ~ days

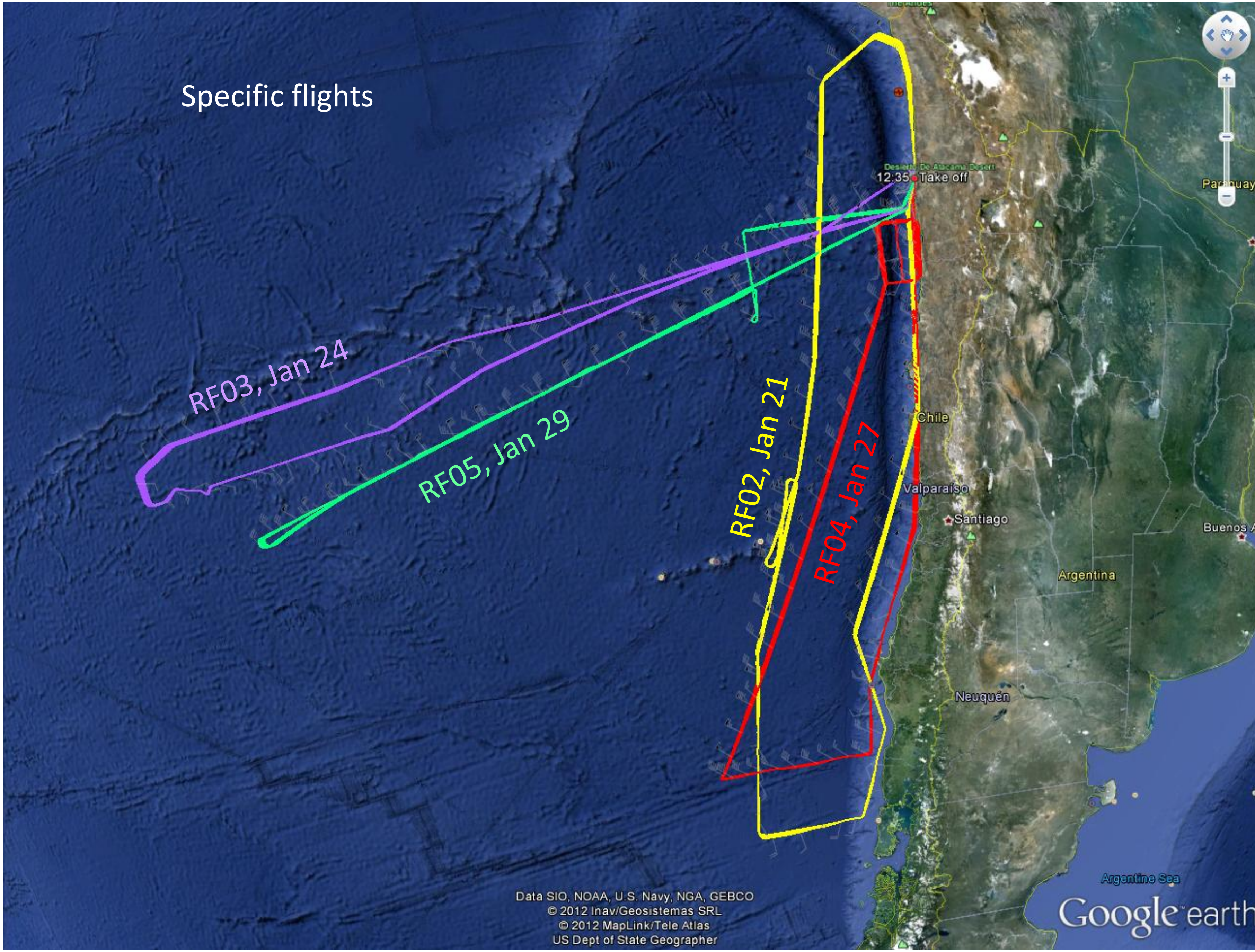


Short-lived OVOCs

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

Others – all have short lifetimes





Specific flights
RF03, Jan 24
RF05, Jan 29
RF02, Jan 21
RF04, Jan 27
12:35 Take off
Desierto De Atacama Desert
Chile
Valparaíso
Santiago
Buenos Air
Argentina
Neuquén
Paraguay
Argentine Sea
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
© 2012 Inav/Geosistemas SRL
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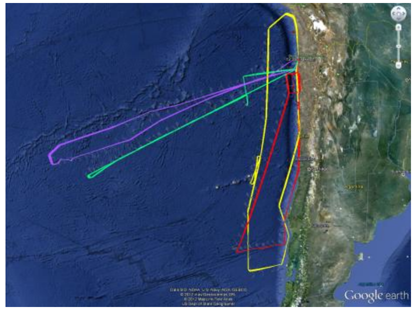
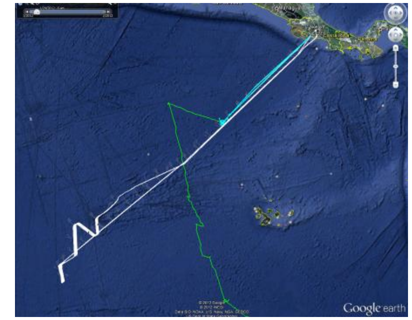
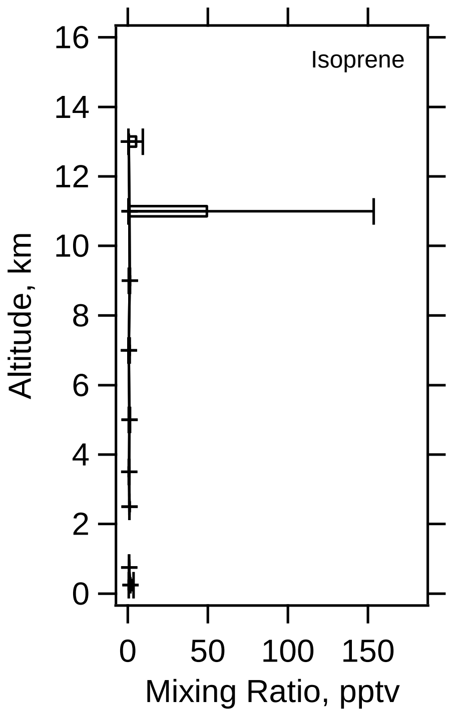
US Dept of State Geographer
Google earth

Convection -Isoprene

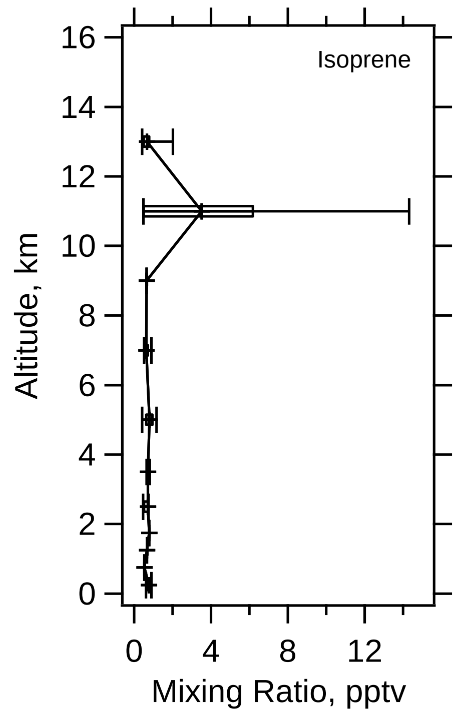




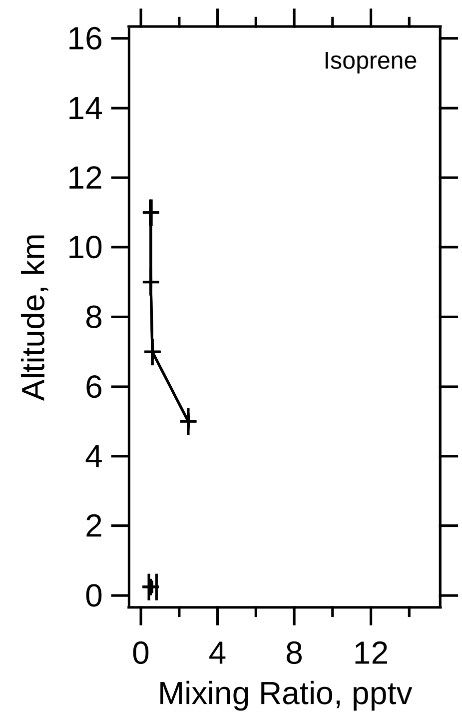
RF02 and RF04



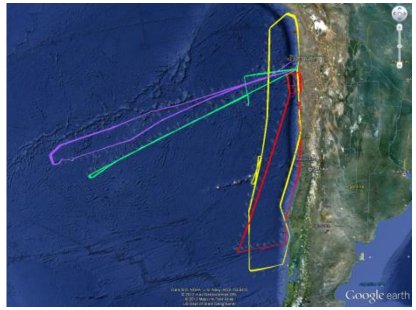
RF03 and RF05

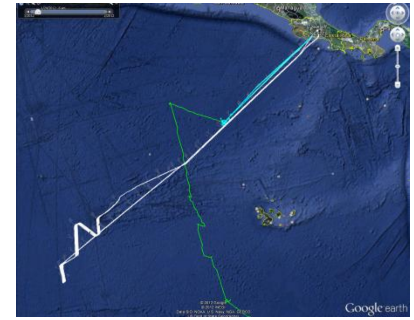


RF08 and RF17

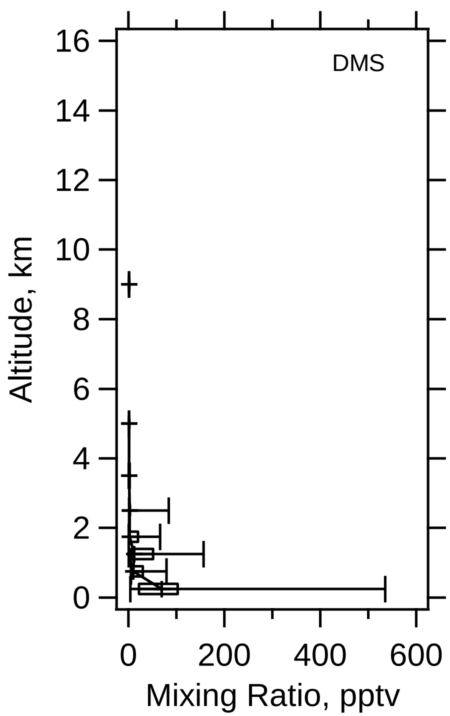


DMS

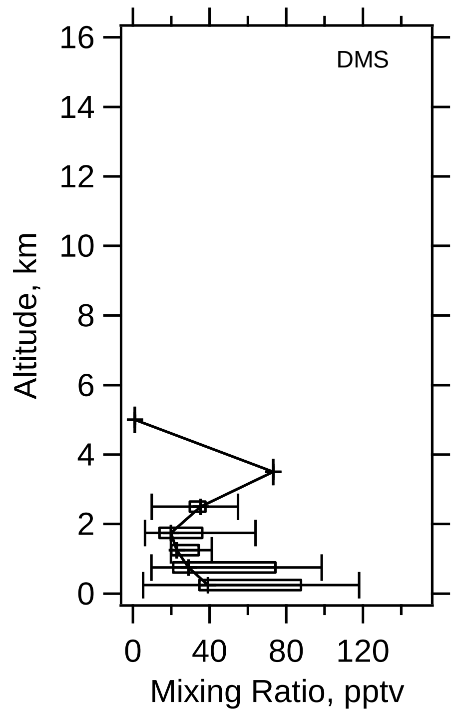




RF02 and RF04



RF03 and RF05



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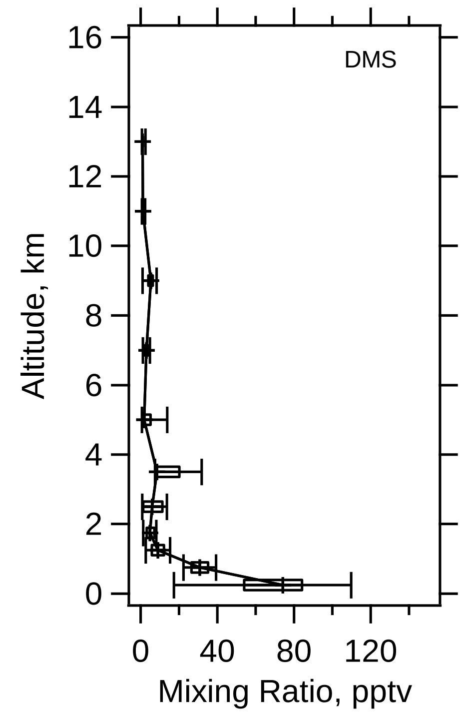
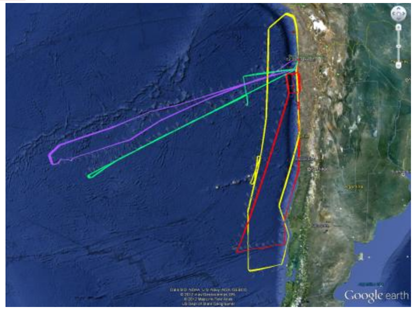
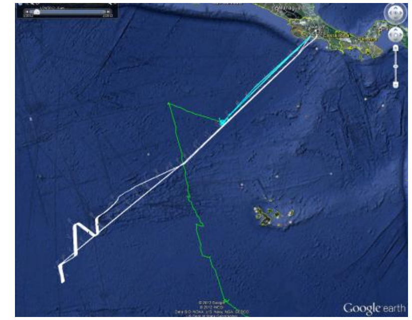
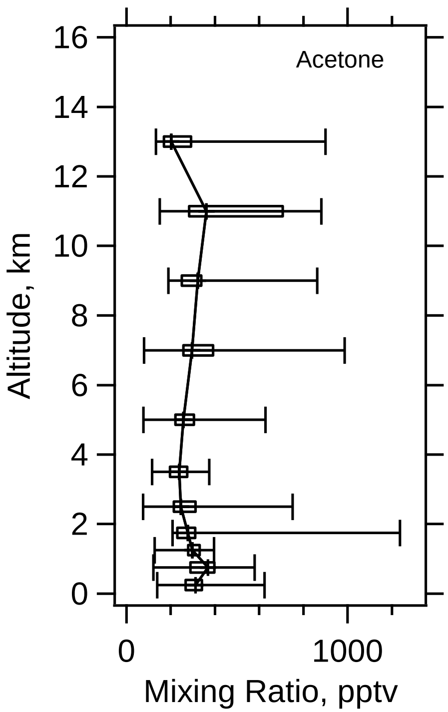


Acetone

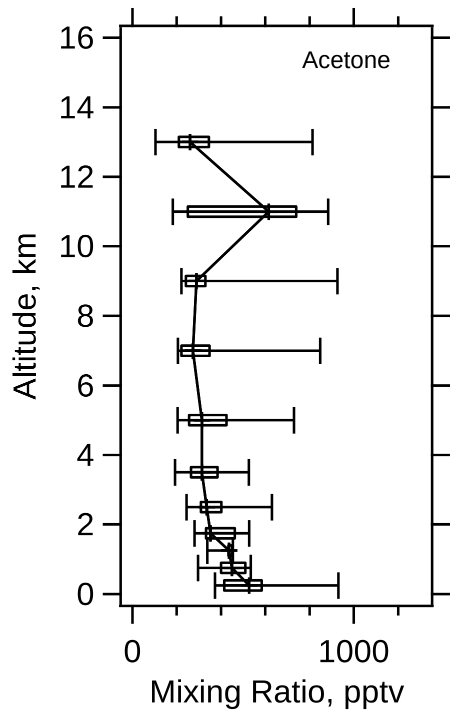




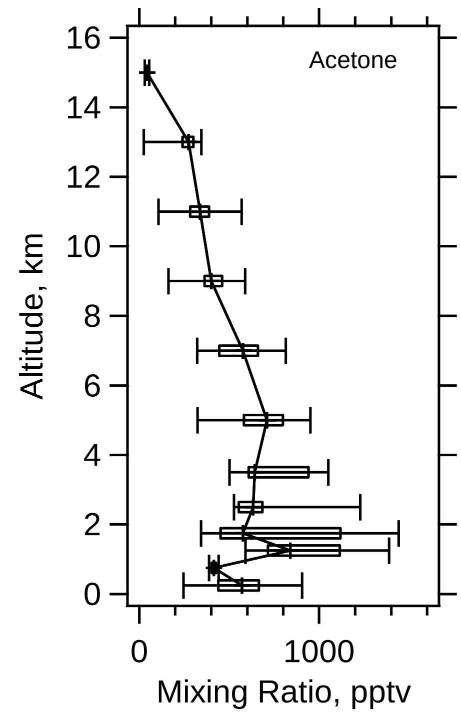
RF02 and RF04



RF03 and RF05



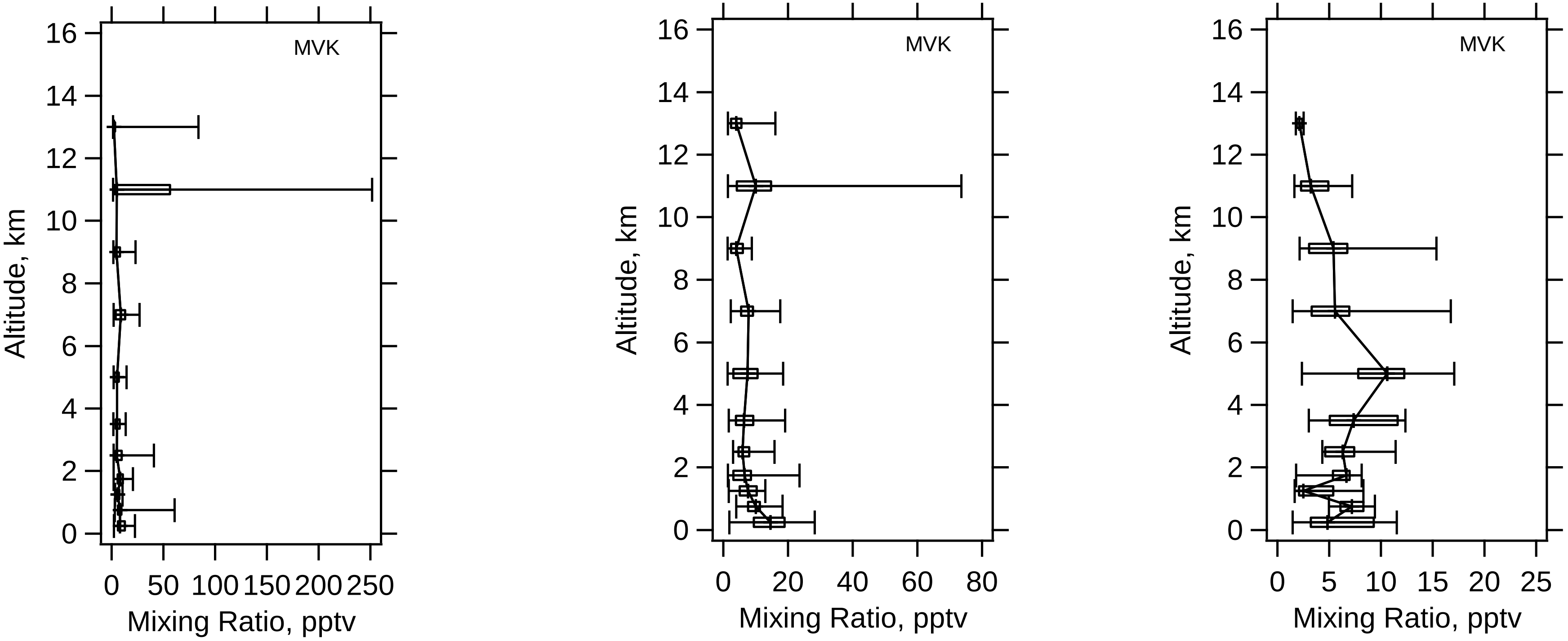
RF08 and RF17



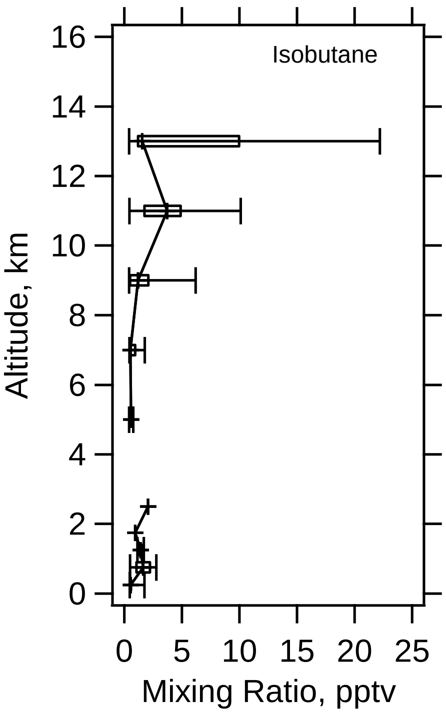
RF02 and RF04

RF03 and RF05

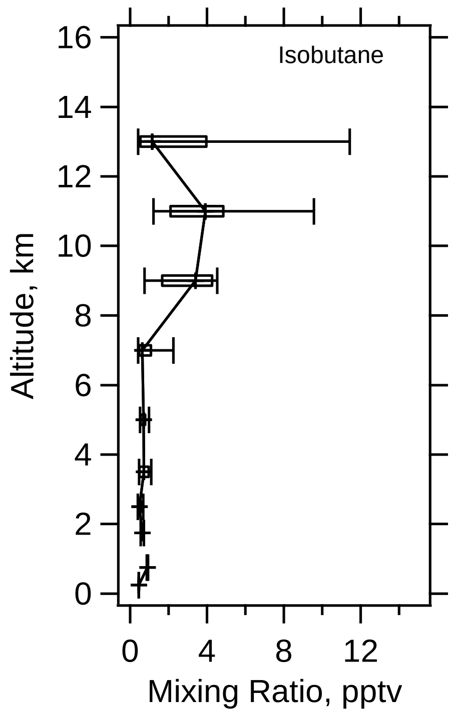
RF08 and RF17



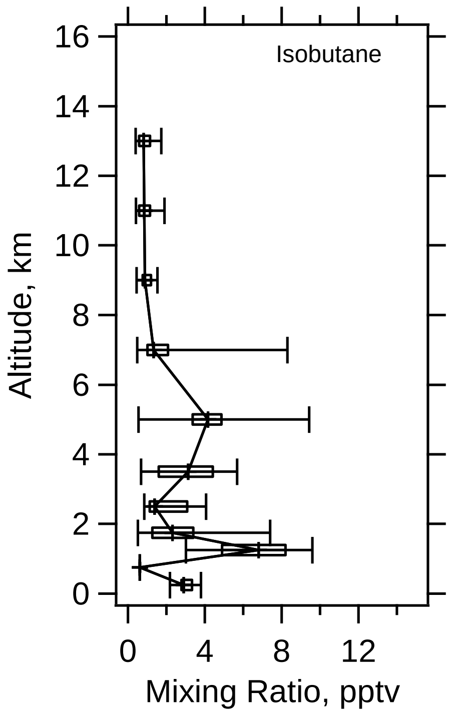
RF02 and RF04



RF03 and RF05

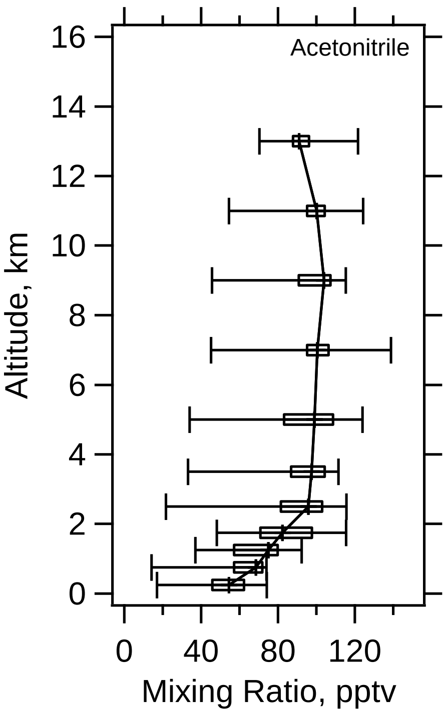


RF08 and RF17

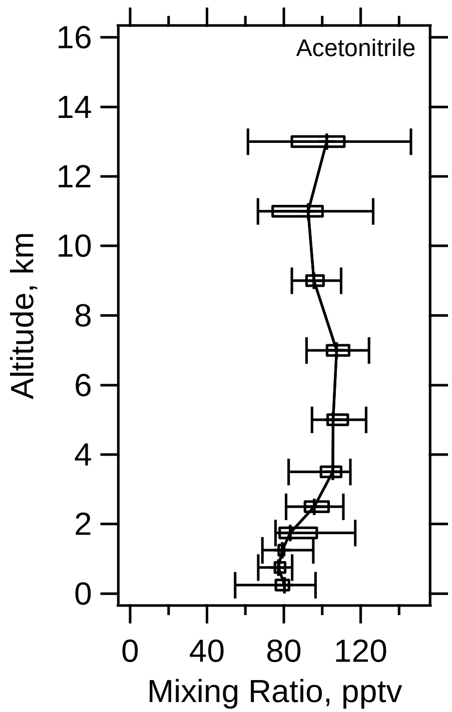


Biomass burning

RF02 and RF04



RF03 and RF05



RF08 and RF17