TORERO Science Objectives, Platforms and Activities

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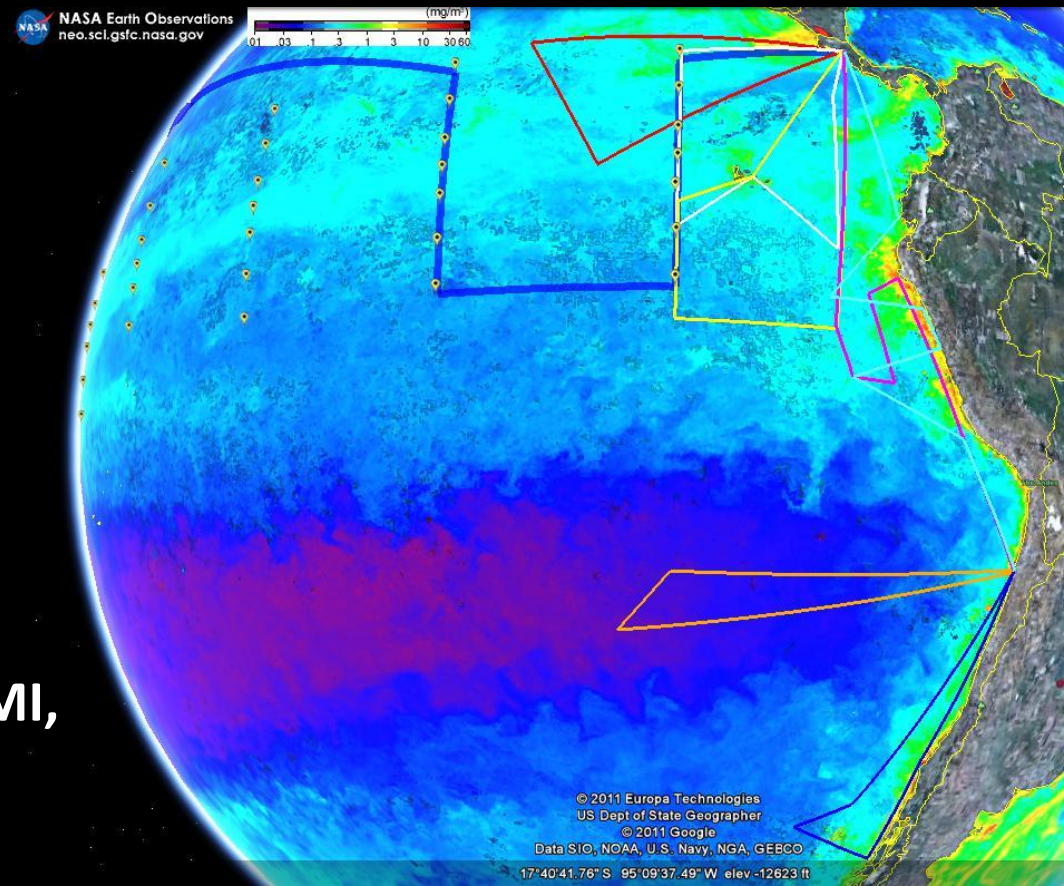
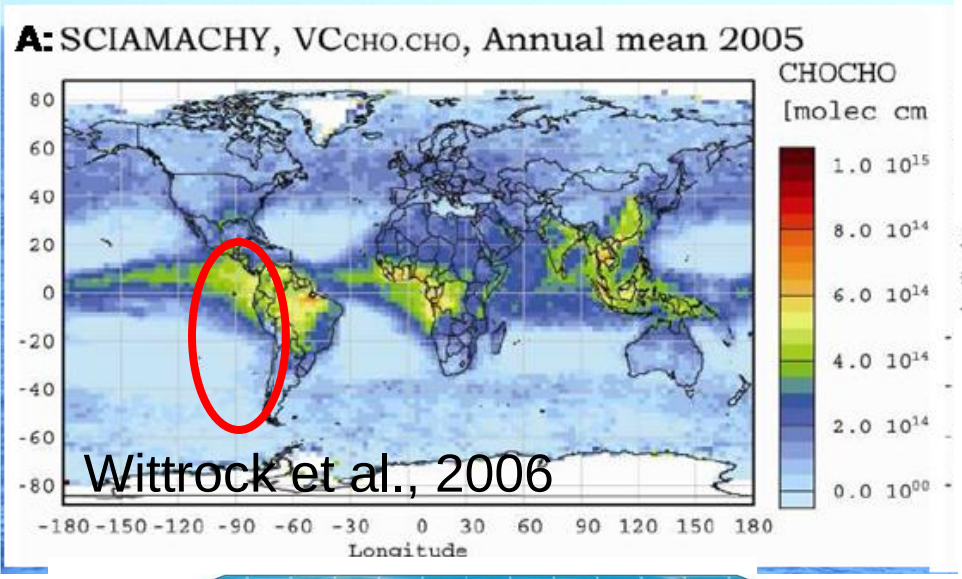
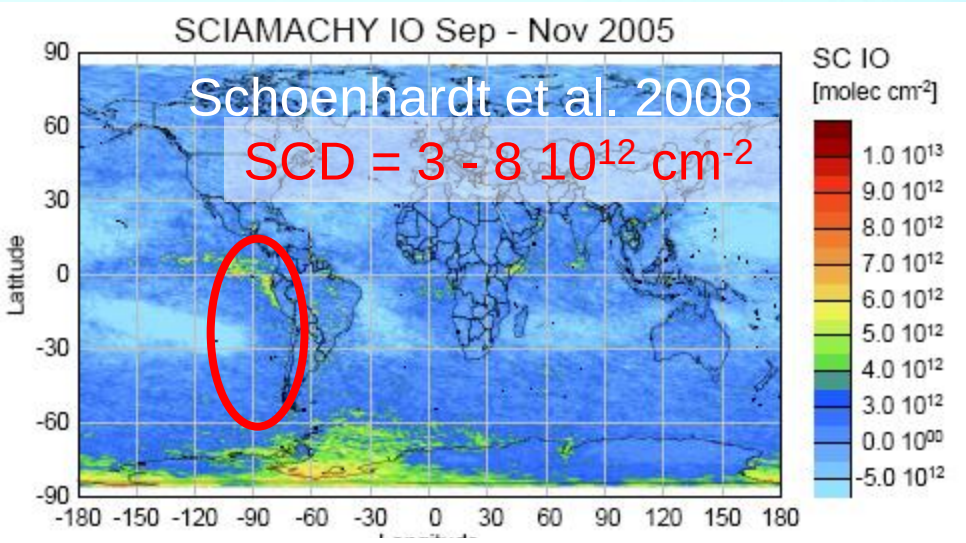
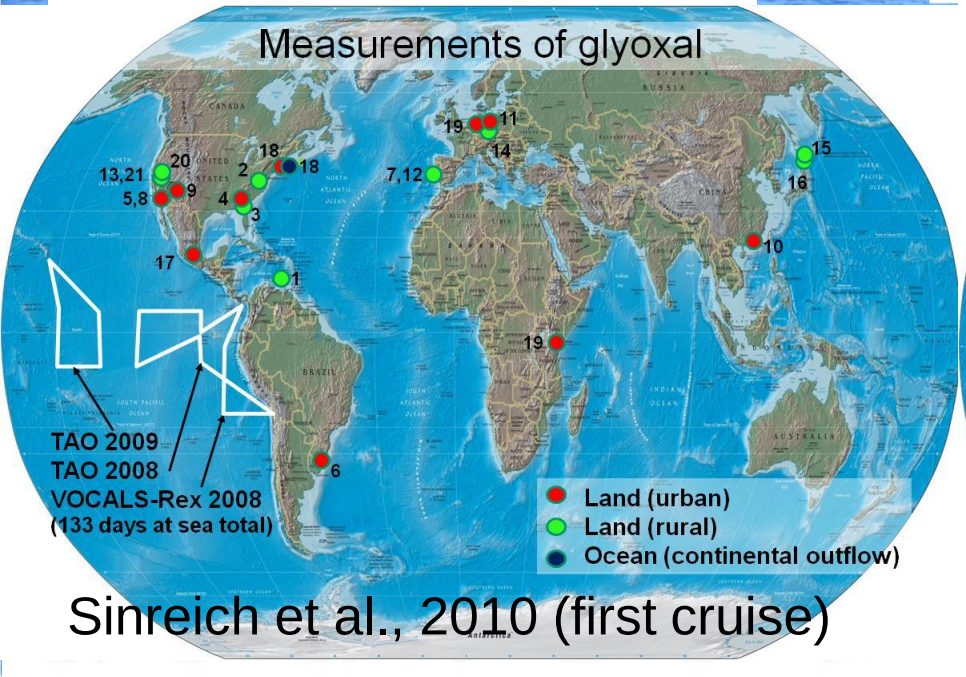
- **TORERO Motivation and Hypothesis**
  - **State of the Science**
  - **Synergistic aspects of experiment design**
- **Platforms and Activities:**
  - **NSF/NCAR GV aircraft (11 Jan – 22 Feb)**
  - **NOAA RV Ka'imimoana (21 Jan – 25 Feb)**
  - **Satellites: NASA A-Train (OMI, AQUA, MODIS), GOME2, SCIAMACHY, GOES-R/ABI**

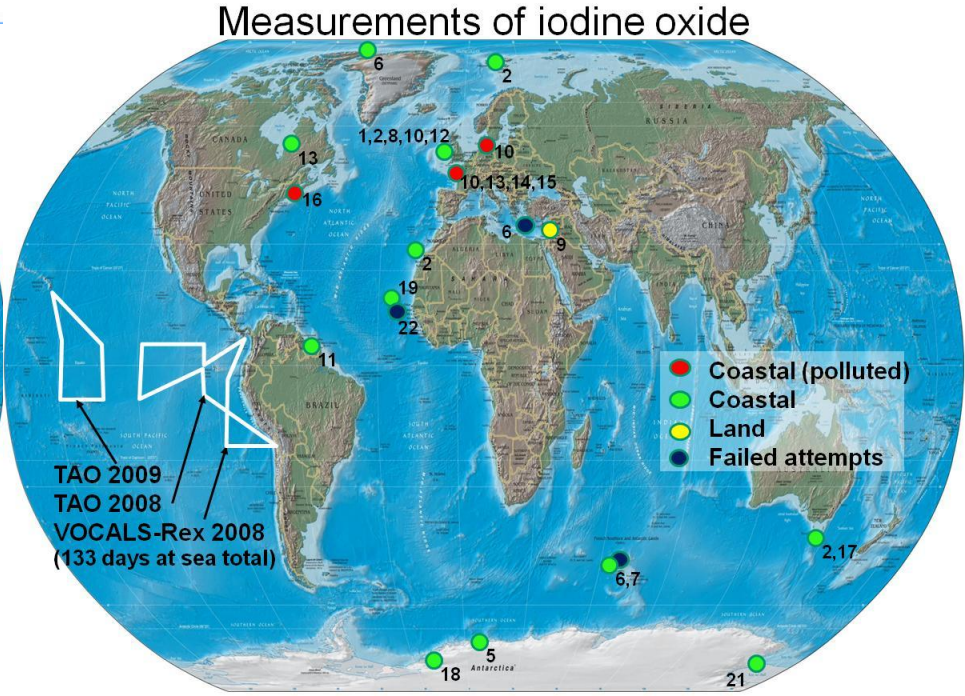


Glyoxal and IO over the open ocean?

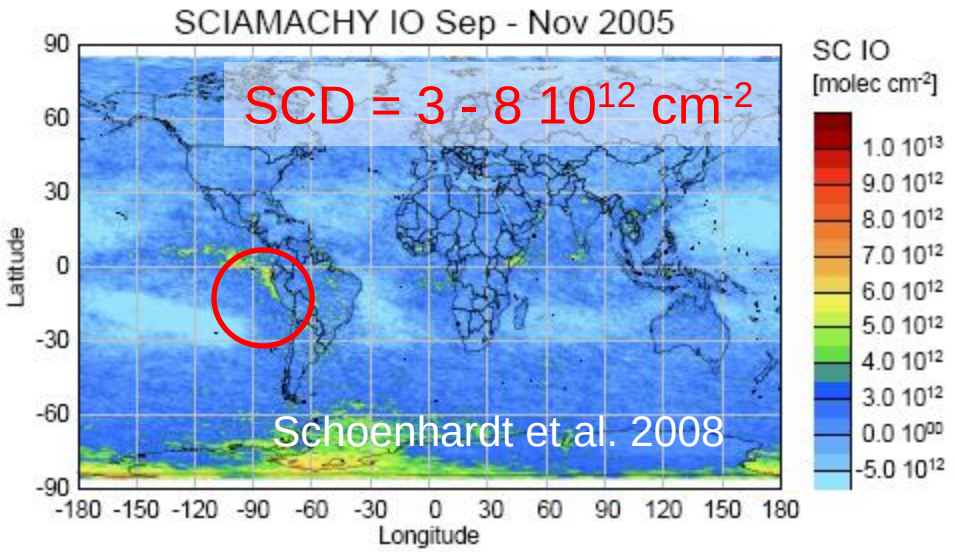


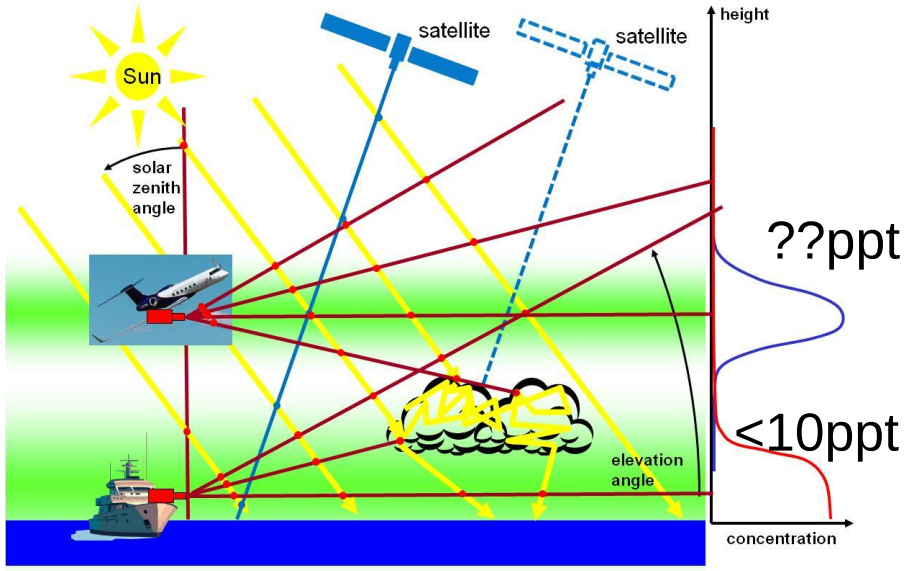






VOCALS-REx + TAO cruises in 2008

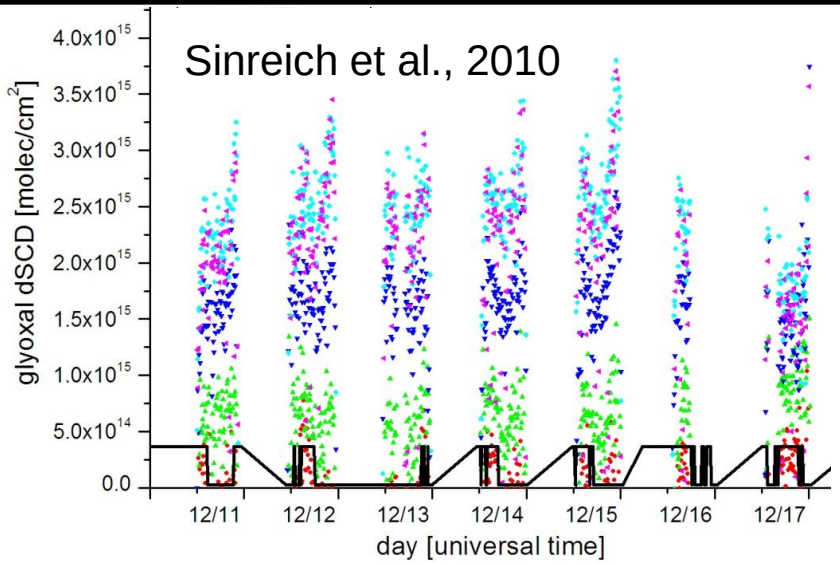


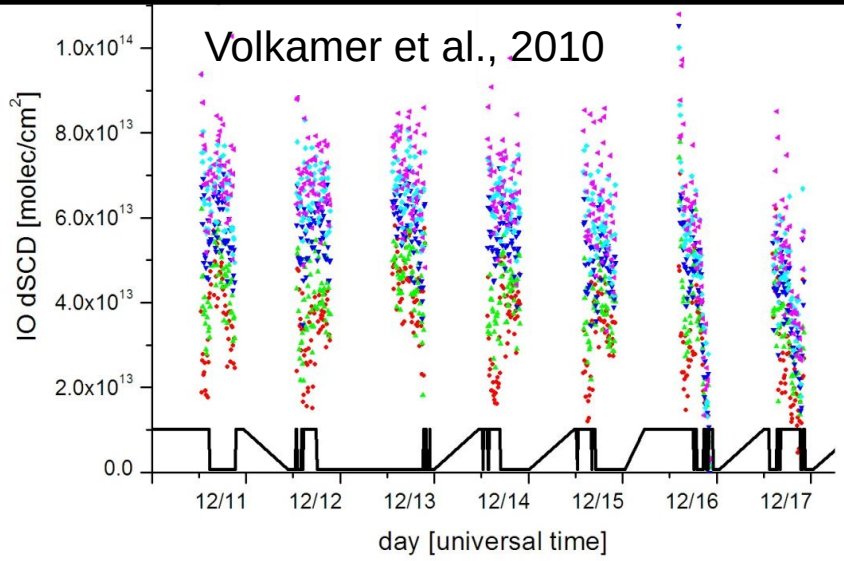


Strong (factor 10) dependence on the vertical profile (not directly measured)

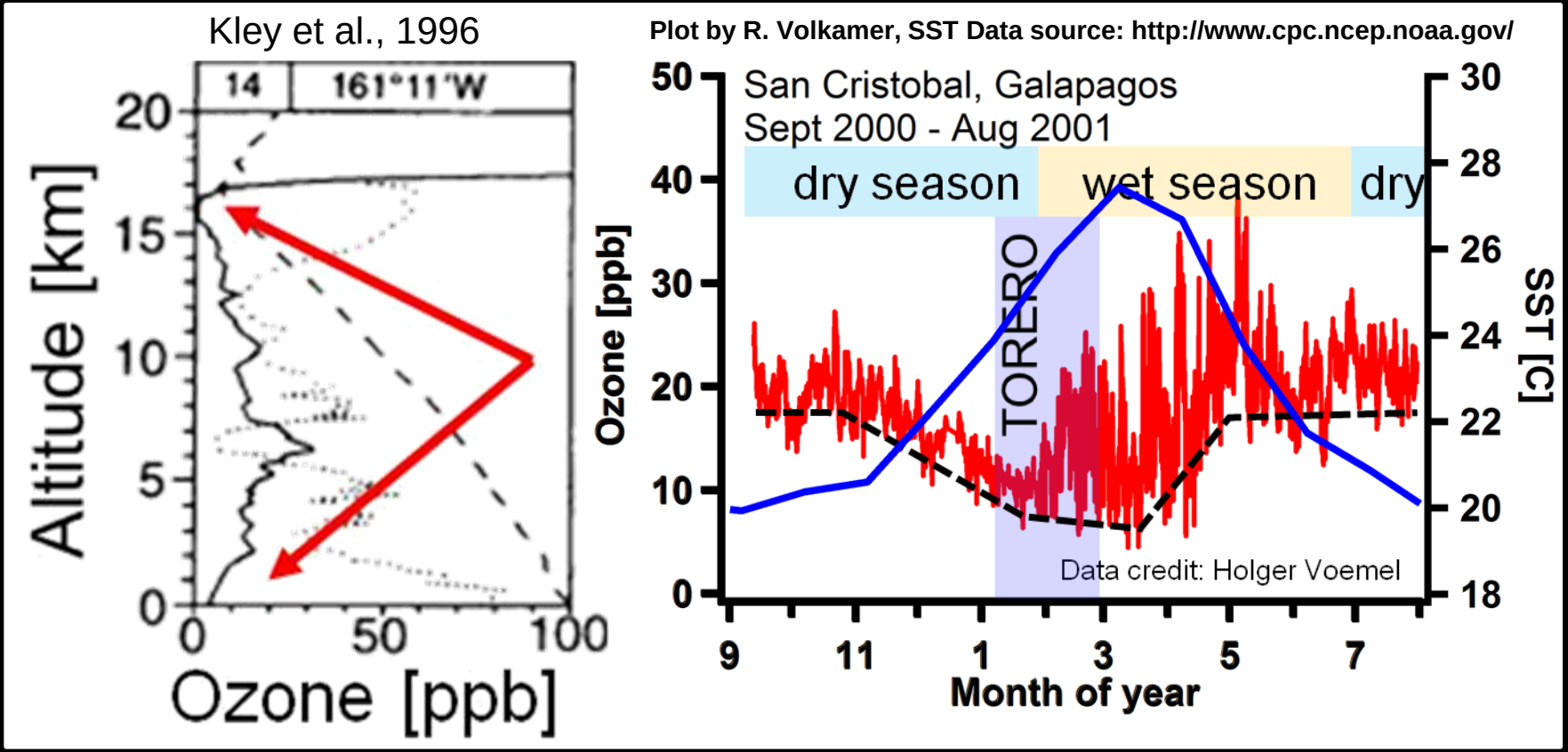
PBL_0-1km: VCD = 2 10^{13} cm^{-2}

FT_4-6km: VCD = 3 10^{12} cm^{-2}



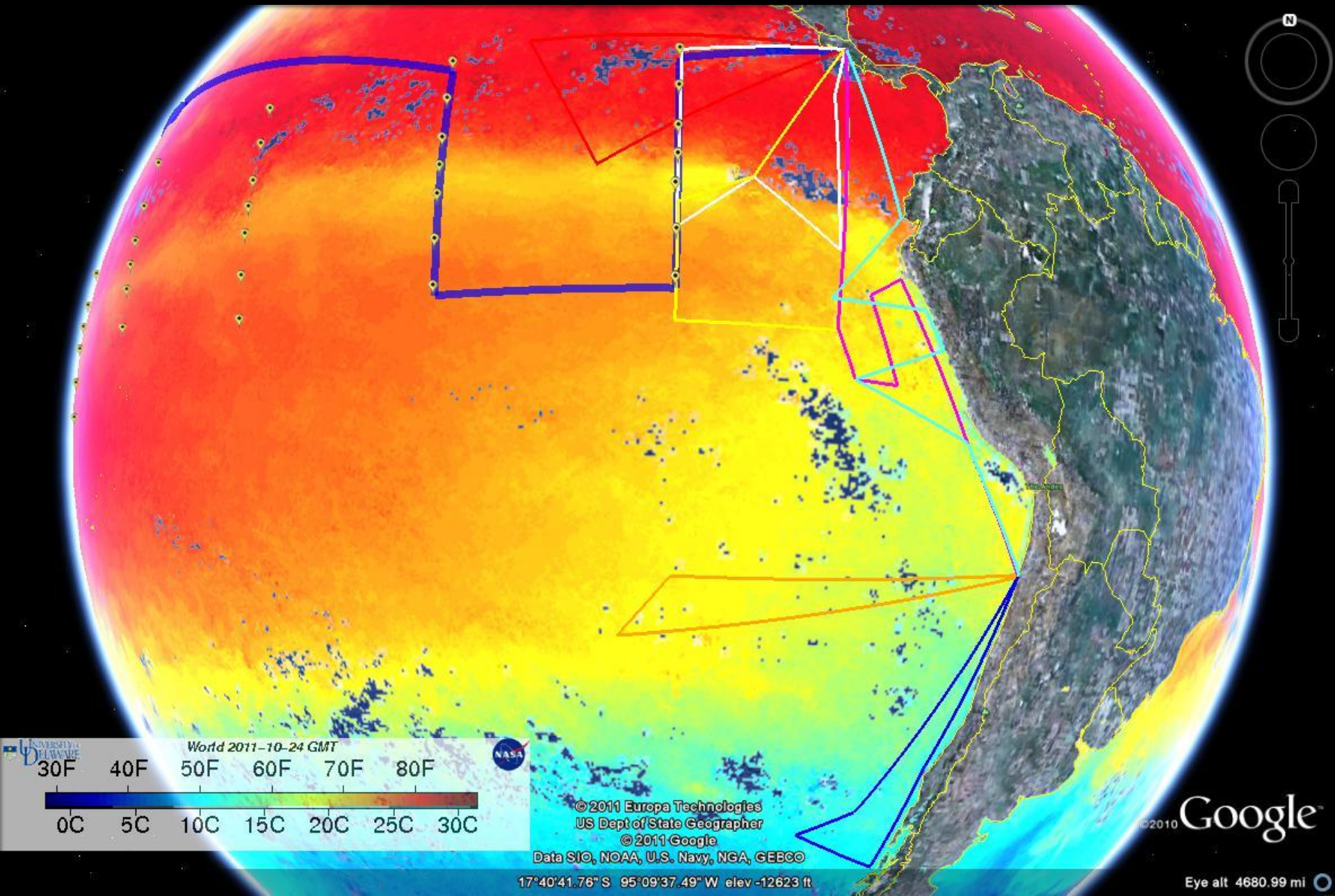


Timing of the TORERO Experiment

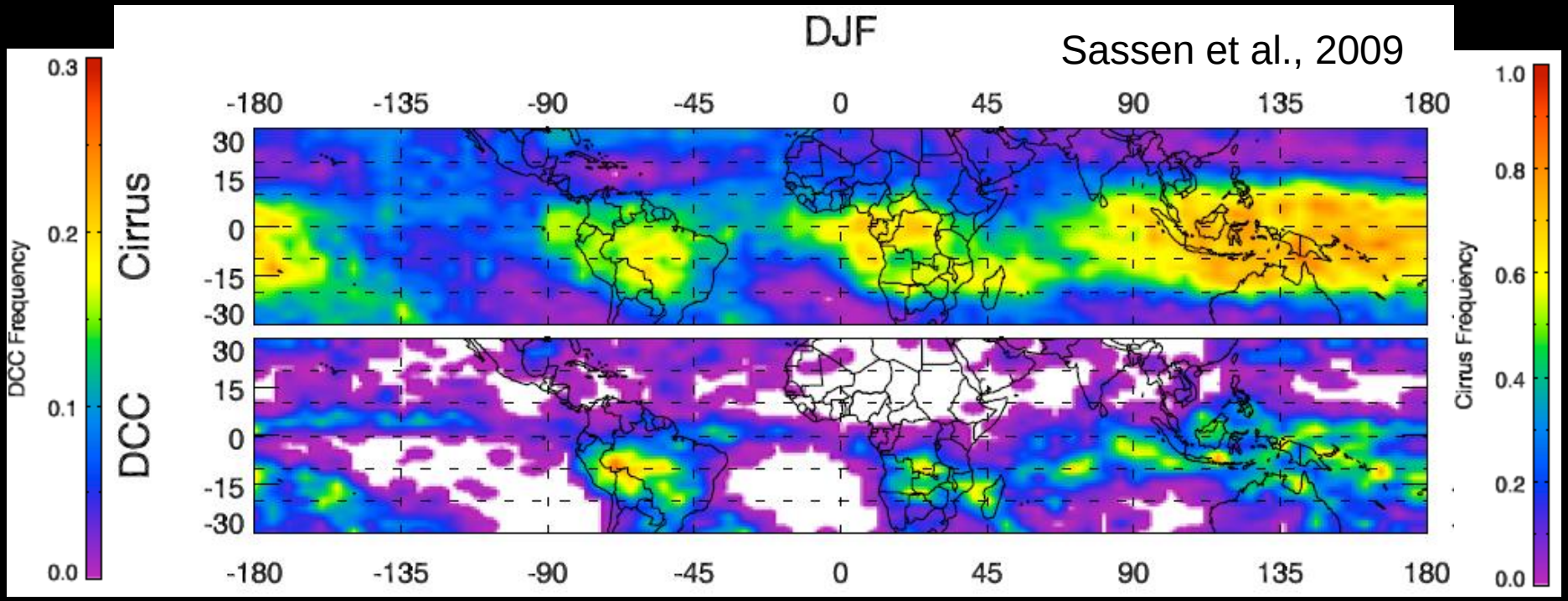


- Pronounced annual ozone cycle (min <10 ppb) at Galapagos (right)
- Vertical distribution could be suggestive of deep convective transport
- Is low O3 in MBL controlled by changes in chemistry or transport?
- SST link may point to relevance of surface ocean dynamics?

Annual mean SST in the TORERO study area



Deep convective clouds (DCC) – CloudSat
Cirrus clouds – CALIPSO



- Cirrus: 30 - 60% (North of 15N latitude); infrequent for forward deployment to Chile
- DCC: <10% chance during most flights; up to 15% chance off the Coast of Peru

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.

- Does the ocean provide a source or a sink of oxidants to the free troposphere?
- What is the vertical distribution of RHS, OVOC, reactive forms of mercury, and particles?
- Is iodine a source for new particles in the free troposphere?
- What can we learn about the chemical composition of cirrus clouds, and do they bias the satellite view of aerosols, and reactive gases?

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

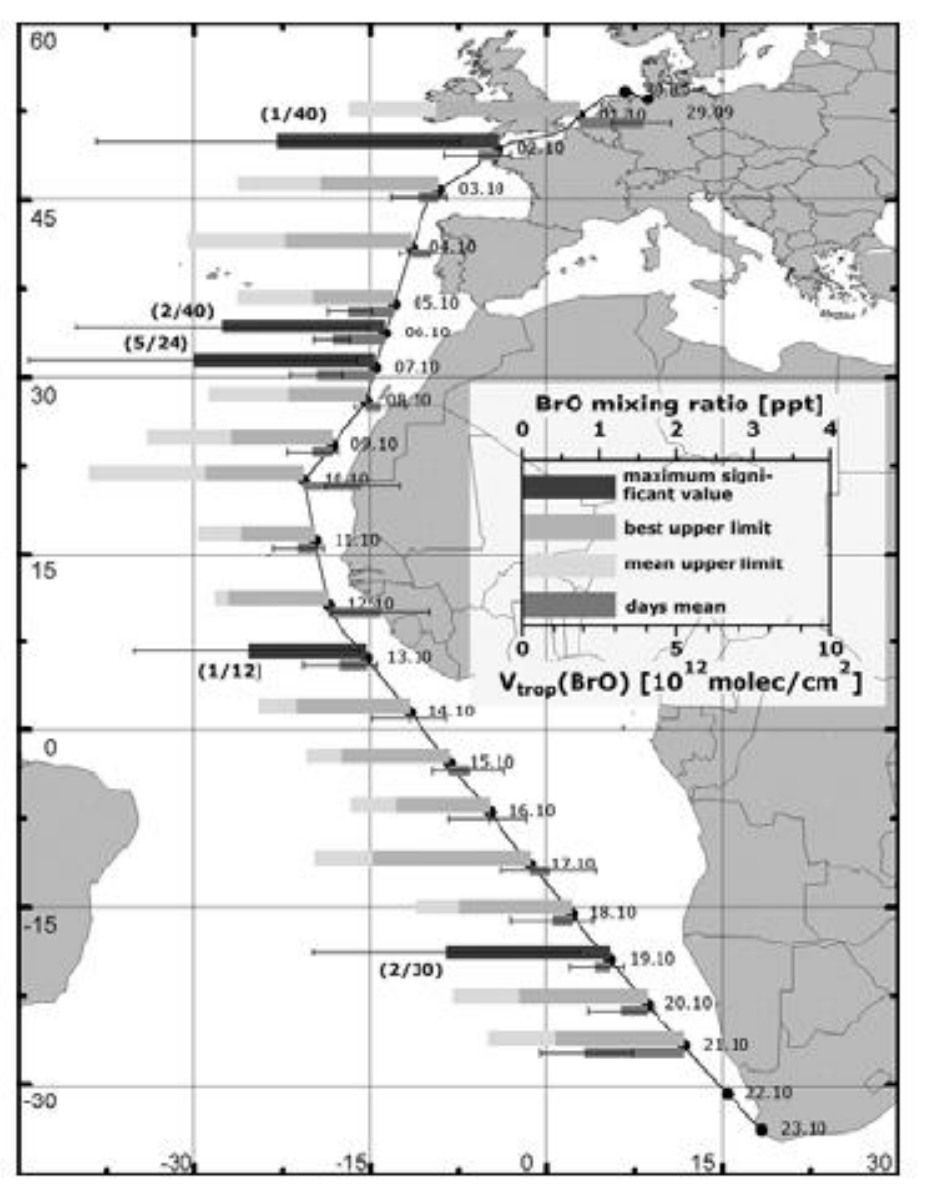
- What are the horizontal gradients in concentrations from the coastal to the open ocean?
- Is the sea surface organic microlayer controlling the fluxes of RHS, OVOC, and CO2?
- What is the chemical speciation of RHS and OVOC, and how does it vary between different ocean environments?

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

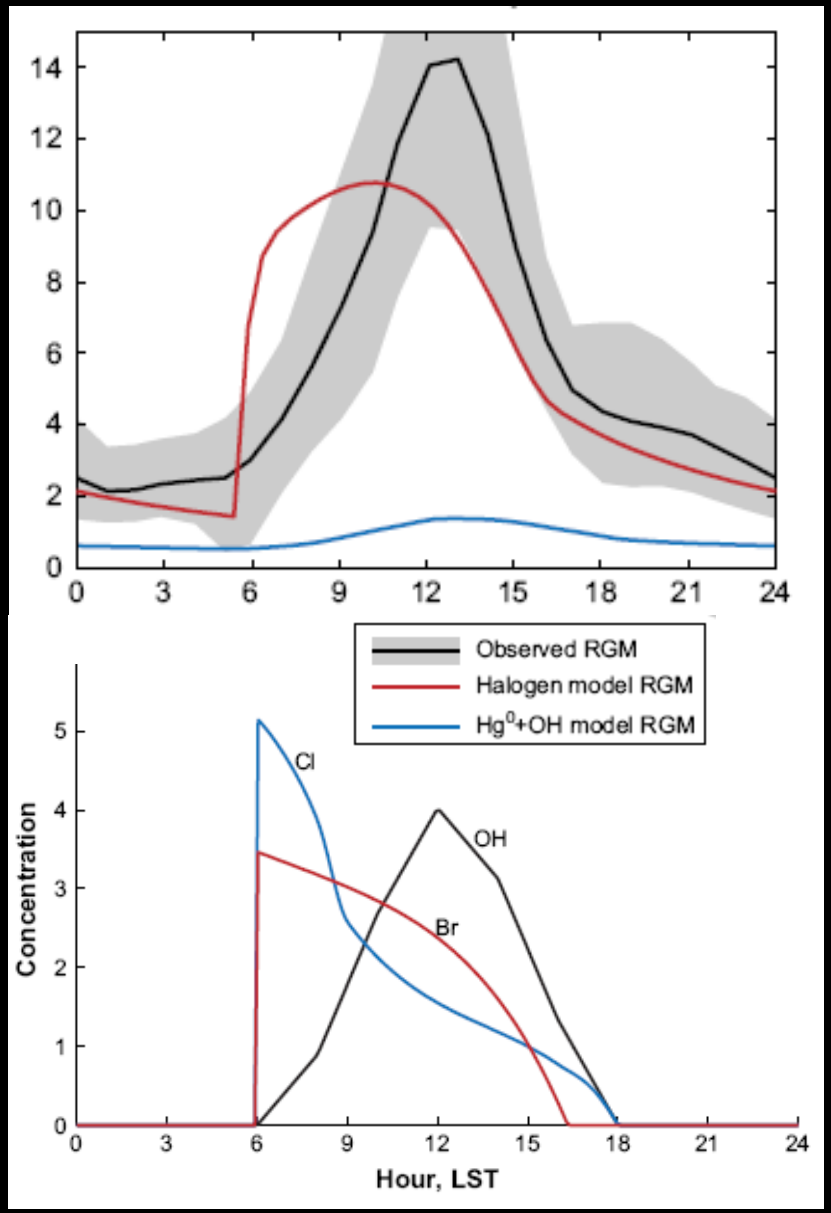
- At what rate is O3 destroyed, methane oxidized, and aerosol formed?
- What factors control the low BrO observed over the tropical Pacific Ocean?
- How relevant are ocean sources of OVOC and RHS on global scales?

Topic #1: Reactive Halogen Species

- Relevance of bromine: destroys tropospheric ozone, oxidizes mercury, impacts oxidative capacity (HOx)
  - Numerous studies have detected BrO in coastal-, arctic-, mid-latitude-, sub-tropical MBL; fewer studies in the tropical MBL and in the free troposphere
- Relevance of iodine: destroys tropospheric ozone, impacts oxidative capacity (HOx), can form new particles
  - Mostly coastal studies; numerous studies have detected IO in coastal-, antarctic-, and sub-tropical MBL; recent studies detect IO in the free troposphere

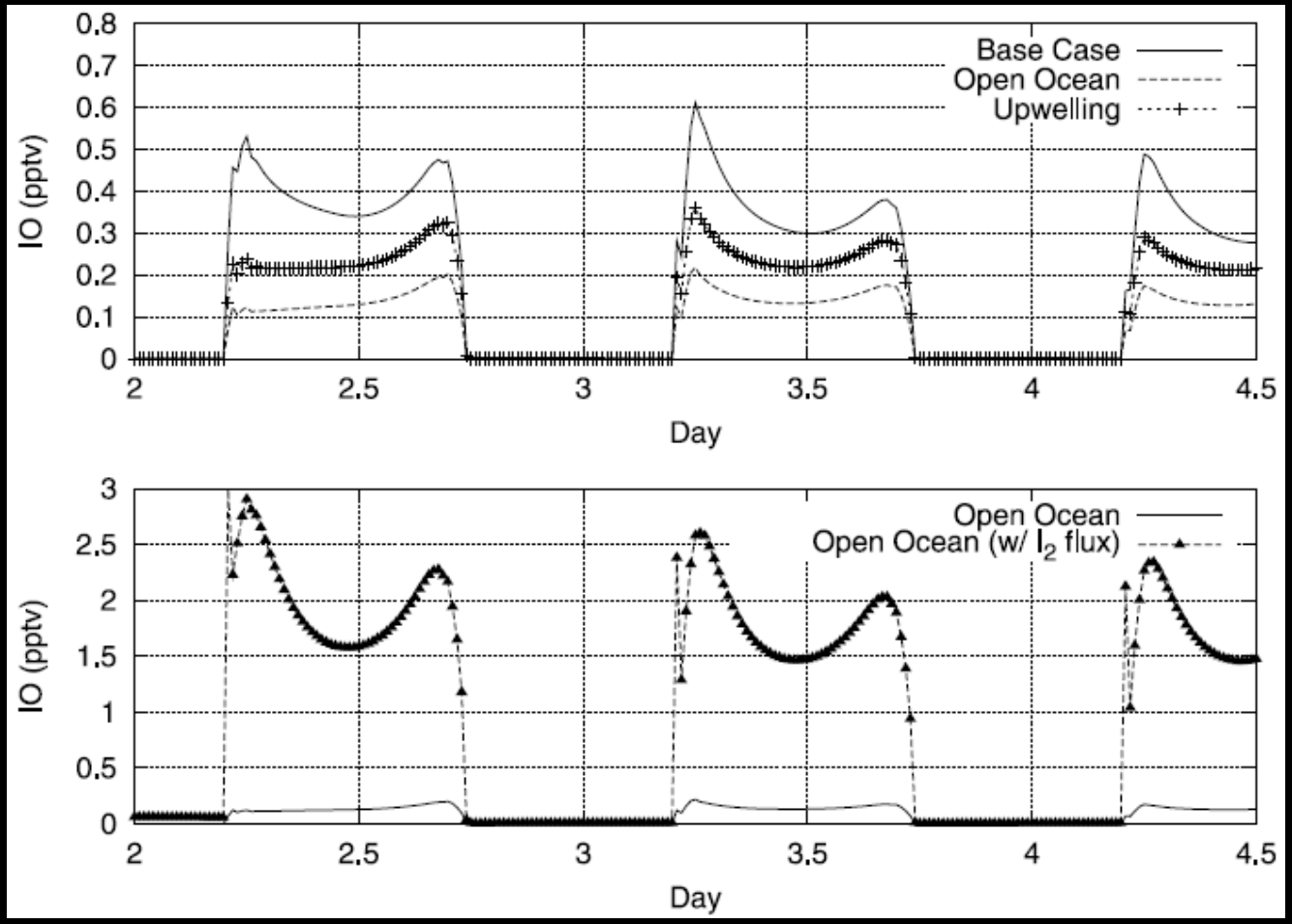


Leser et al., 2003



Holmes et al., 2009; Geos-Chem:
~ 2ppt BrO under most conditions

Topic #1: Reactive Iodine Species



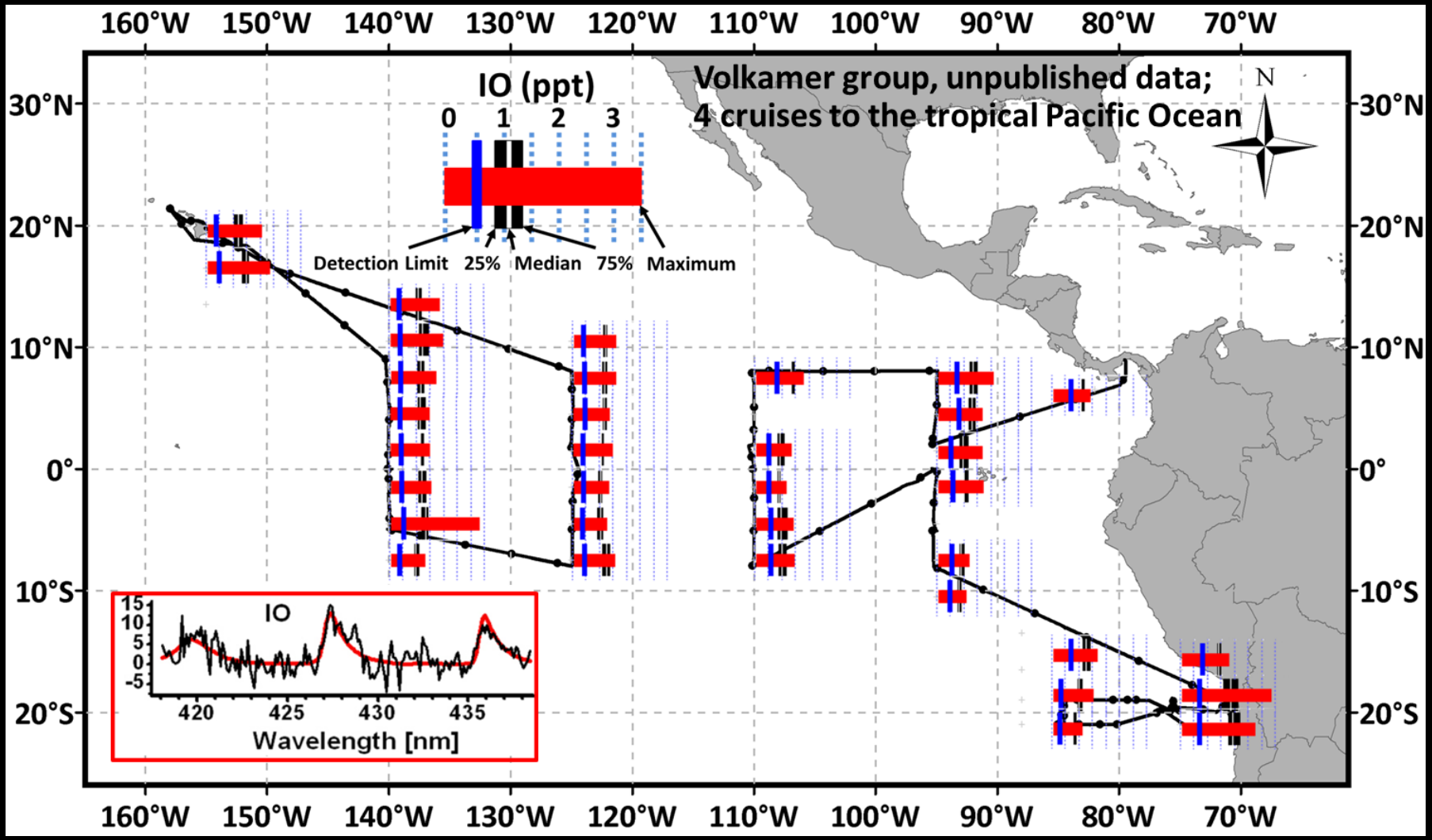
only organic iodine gases as iodine precursors (biological source)

organic iodine ("open ocean") and additional flux of I_2

Jones et al., 2010; Mahajan et al., 2010

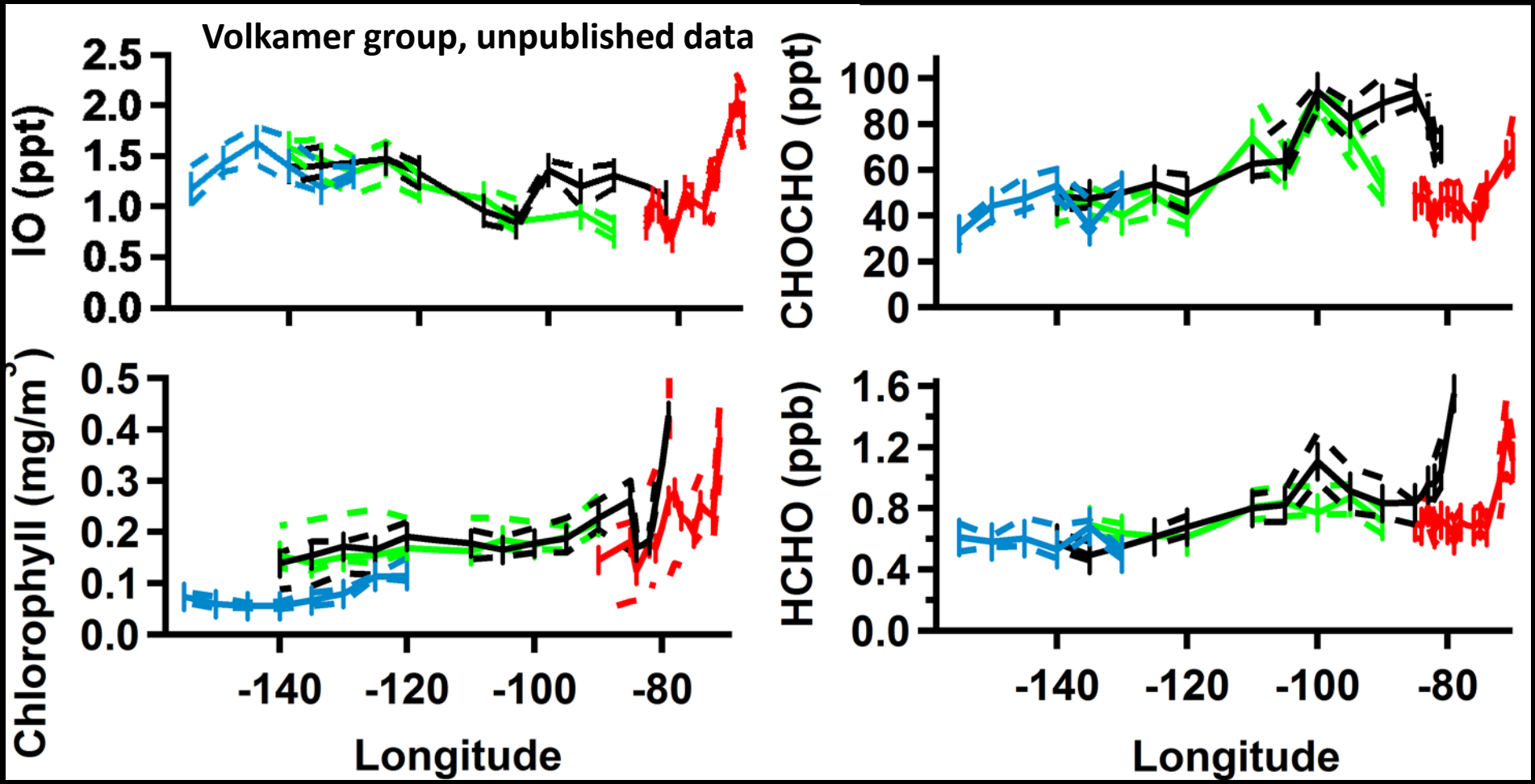
- Organic precursors alone are not sufficient.
- An inorganic iodine precursor?

Iodine oxide over the open ocean



- **Strong gradients in the TORERO study area**

INCREASING IO towards the oligotrophic ocean!



⇒ Anti-correlated with Chl-a => a non-biological source!

⇒ Opposite gradients inside the MBL than apparent from space ?!

⇒ RIS speciation over the open ocean remains unclear!

Topic #1: Reactive Halogen Species

Photo-redox chemistry: I_2 (Cl_2,Br_2)

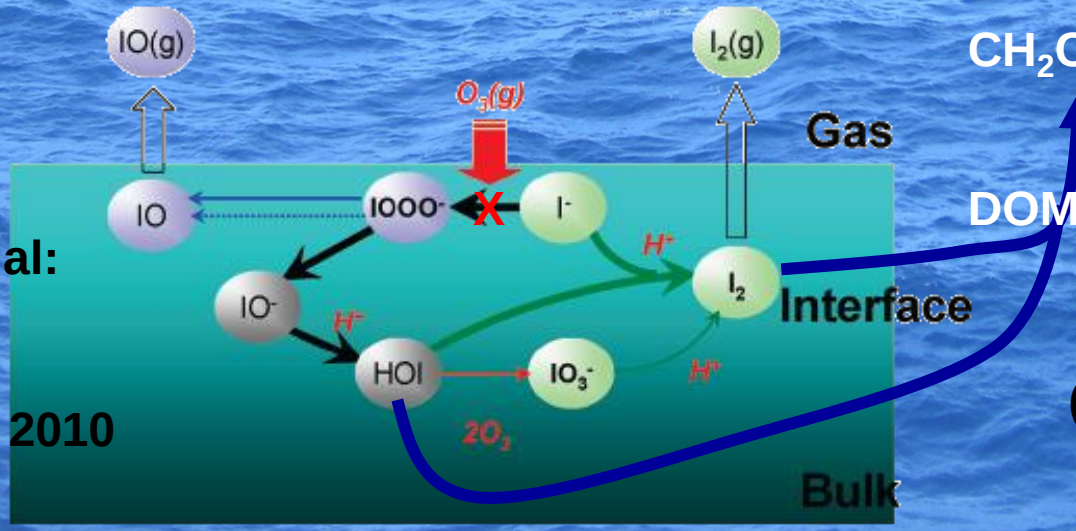
$$CHL^+/CDOM^+ + I^- \rightarrow CHL/CDOM + I$$

$$I + I \rightarrow I_2$$

$$I_2 + h\nu \rightarrow 2\,I$$

$$I + O_3 \rightarrow IO + O_2$$

$$OH, Cl, Br, O_3 + DOC \rightarrow \rightarrow DOC\ Products$$



CH_2ClI, CH_2I_2

DOM

Sakamoto et al: Inhibited by Organics Hayase et al. 2010

Martino et al: CH_2ClI, CH_2I_2 concentrations are very low (E. Atlas, pers. comm.)

Martino et al., 2009, GRL; Reeser et al., 2009, JPC; Jammoul et al., 2009; Hayase et al., 2010, JPC

TORERO observations topic #1

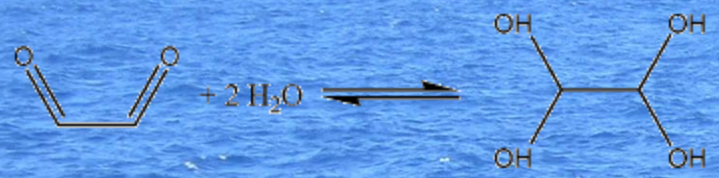
- NSF/NCAR GV: speciation, radical source fluxes, radical abundances, rate of aerosol loss, horizontal and vertical distributions
  - RHS speciation (TOGA), J-values (HARP), BrO and IO radicals (CU AMAX-DOAS), aerosol surface area (UHSAS), nucleation mode (2-channel NMASS), Chl-a and CDOM (HARP - irradiances)
- NOAA RV Ka'imimoana: speciation, source fluxes (gradient method), radical abundances, diurnal variations over the oligotrophic, mesotrophic, and coastal ocean, vertical distributions (lower 1.5km)
  - Organic RHS speciation in water column and gas-phase (GC-MS), I2 and XY (denuders), BrO and IO radicals (CU SMAX-DOAS), IO (CU LED-CE-DOAS)

Topic #2: OVOC over the ocean

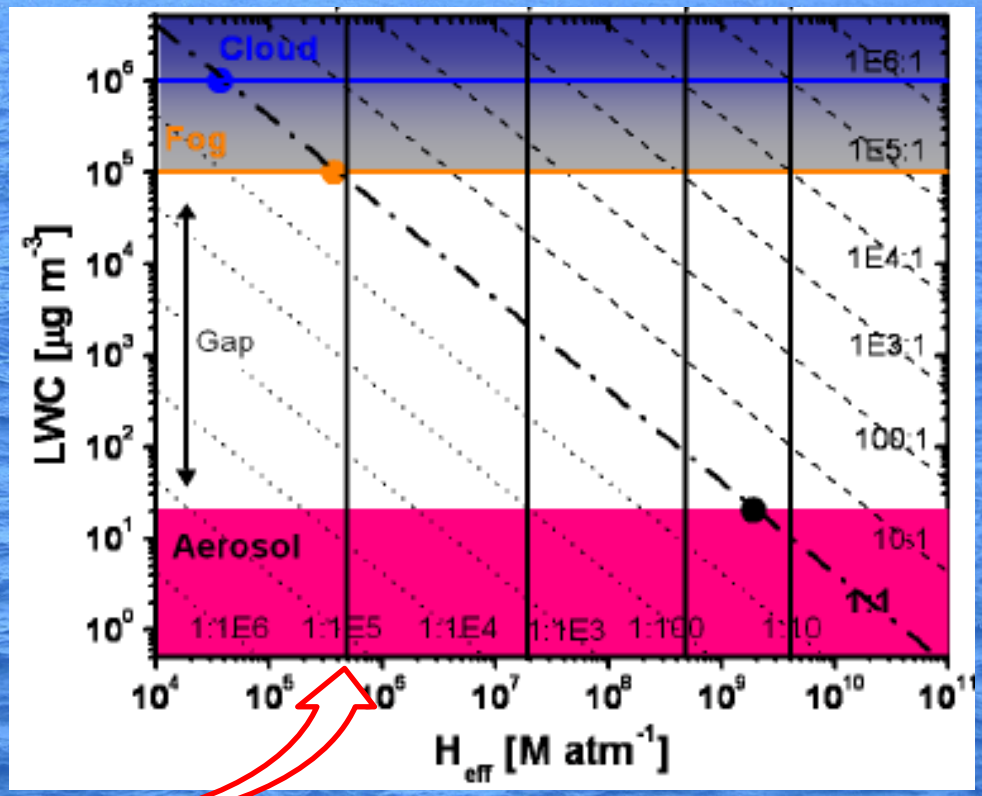
- Relevance of OVOC: affect oxidative capacity (HOx), are sink for bromine atoms, some OVOC add to SOA formation (repartitioning), aerosol-cloud interaction
  - VOC source of isoprene is estimated 1 Tg/yr
  - OVOC source 10 to 100 times larger, and can compete with land sources from VOC oxidation for acetaldehyde and glyoxal, possibly others? (Myriokefalitakis et al., 2008; Millet et al., 2010)
  - Source mechanism is not yet understood: solubility challenge for very soluble compounds (Zhou and Mopper, 1997; Sinreich et al., 2010)

  => water soluble OVOC indicate missing processes
- Glyoxal indicates the rate of SML oxidation: SML can reduce CO2 uptake to the ocean

Glyoxal: solubility and air-sea partitioning



O/C [au/au]	1	2
P^0 [atm]	0.3	~ 10^{-6}
C* [ug m^{-3}]	~10^9	~ 10^4
H_{eff} [M atm^{-1}]	~5	4x10^5



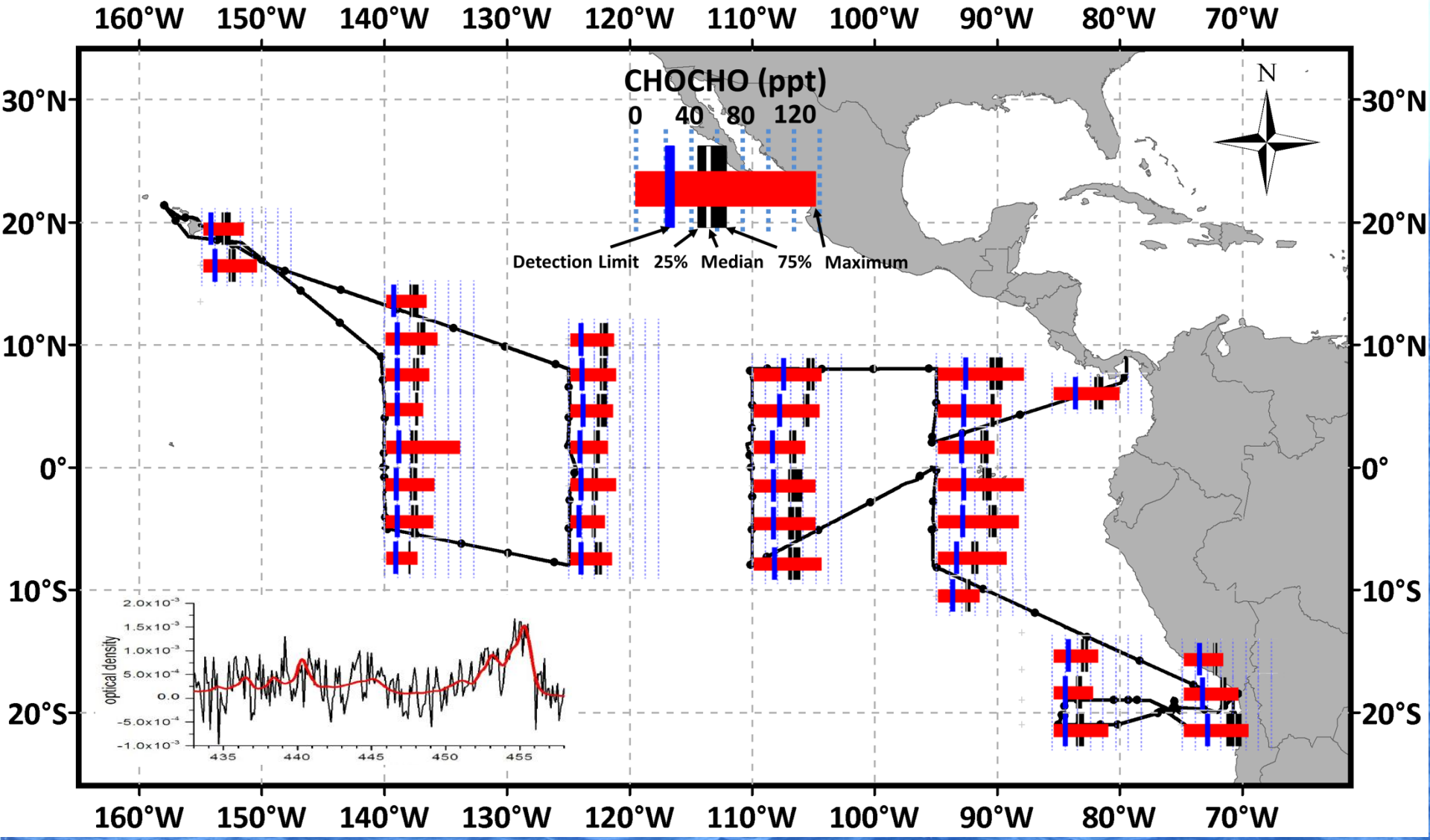
Cloud droplet: 90% of glyoxal$_g$ will partition into the droplet

Air-sea partitioning: shifted 10^7 towards the ocean!

➔ Glyoxal must originate from an airborne source !

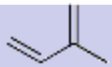
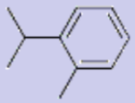
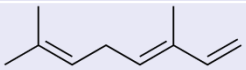
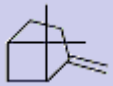
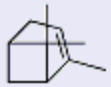
➔ Glyoxal flux is directed into the ocean!

Zhou and Mopper, 1990, EST; Volkamer et al., 2009, ACP; Sinreich et al., 2010, ACP



- Glyoxal is observed also over the oligotrophic ocean!
- What is the source? What is the information content?

GC-MS measurements of VOC precursors

VOC		VMR ave (ppt)	VMR max	Yield (%)	Glyoxal (ppt)
Isoprene		10	30	8	2 - 5
Limonene*		21	80	0.5	< 0.8
o-Cymene*		2.4	13	8	< 0.2
Z-b-Ocimene*		1.1	7.6	< 4	< 0.6
b-Pinene*		1.2	4.5	5	< 0.5
a-Pinene		0.8	2.1	NA	

Collaboration w/ Alex Guenther, NCAR/ACD

First isoprene measurements in the study area

Found consistent with prediction by Arnold et al., 2009

Σ Glyoxal = 2-7 ppt

Isoprene and 9 monoterpenes were identified
concentrations are low, i.e., can explain <10% of the glyoxal source in terms of secondary VOC chemistry.

=> Secondary VOC can not account for most glyoxal

=> Glyoxal source is from Dissolved Organic Carbon (DOC)!

* b-pinene yield: MCMv3.1, o/p-cymene yield: taken as o/p-xylene, limonene yield: unpublished data; assuming [OH] = 3 10^6 molec/cm^3 and a glyoxal lifetime of 1.5 hrs

Glyoxal: Indicator for surface DOC oxidation

- Vertical diffusivity in the thermocline:

  0.15 $cm^2\ s^{-1}$ (Ledwell et al.)

- Hydration rate:

  $k_{hydr} = 7\ s^{-1}$ (Creighton et al., 1988)

- Diffusion length scale: ~1.5 mm

➔ Glyoxal source: Oxidation of surface organic microlayer (or fine sea spray aerosol)

➔ Glyoxal indicates: widespread presence of a surface organic microlayer!

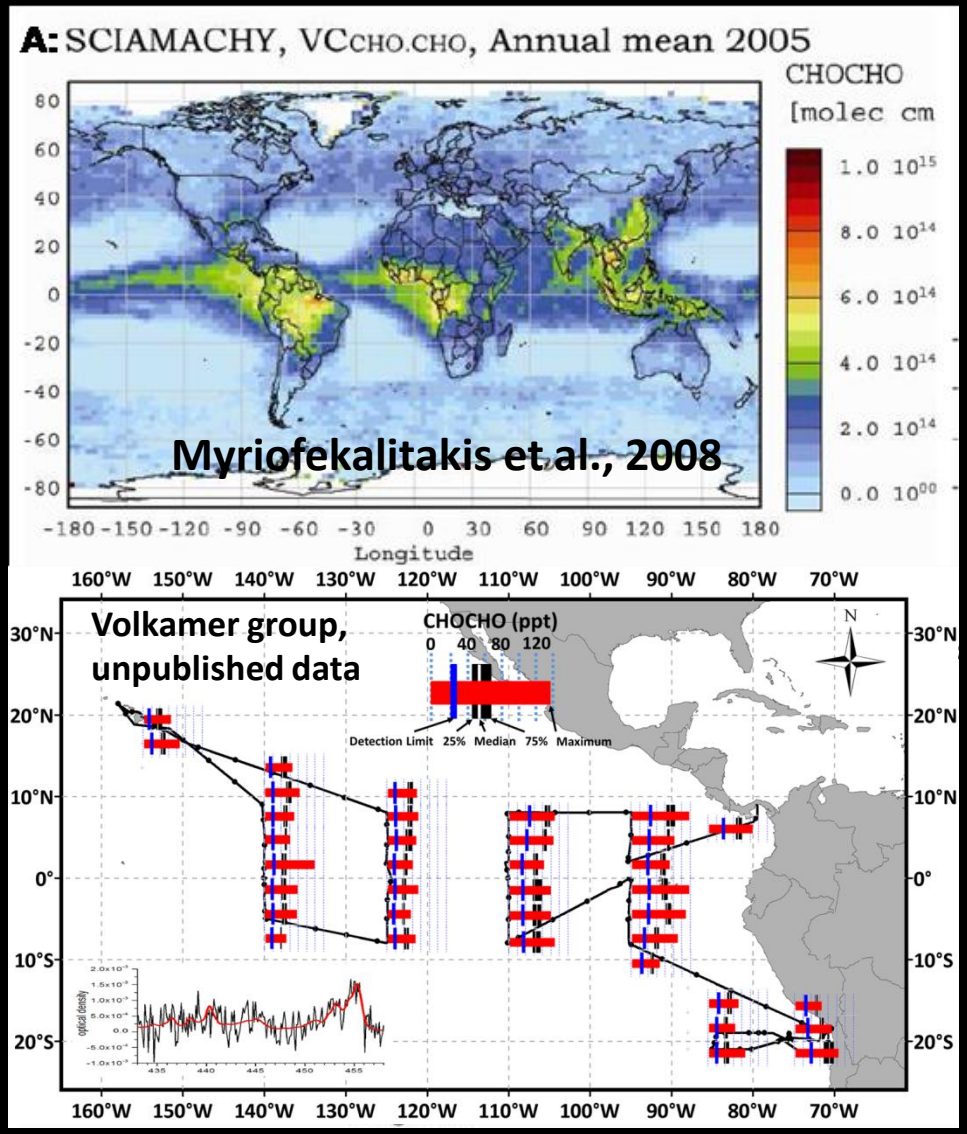
Enrichment factors

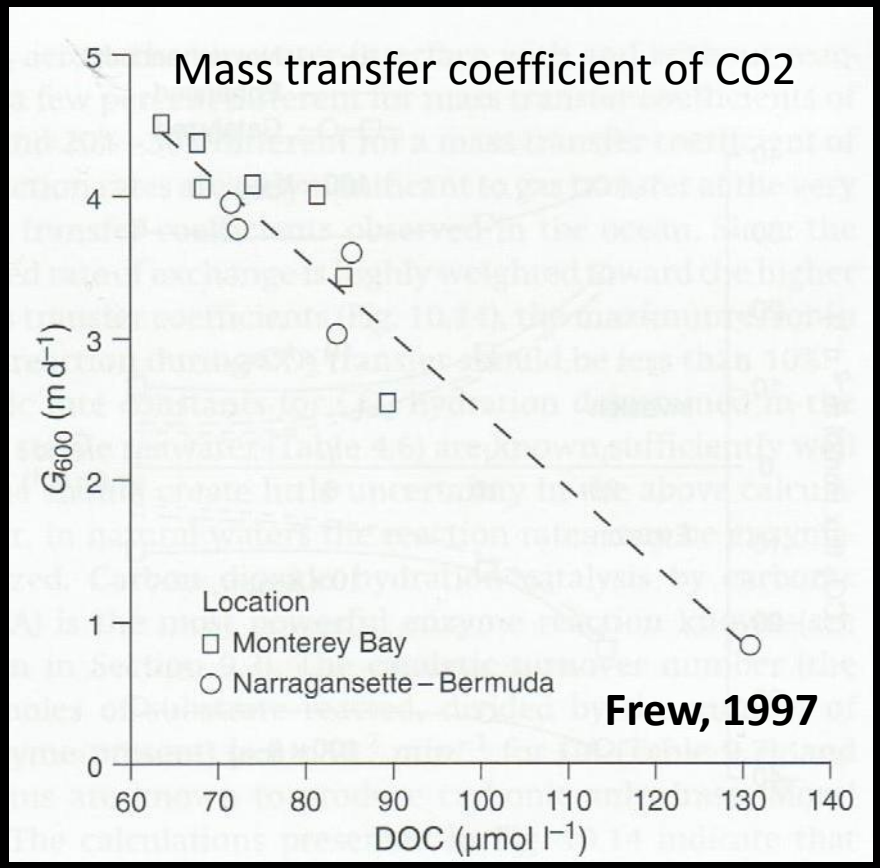
Measured parameter	Henry's Law H_{eff} [M/atm]	EF_SML	EF_Air
Total Dissolved Carbon (TDC)		1.0 – 4.0	
HCHO	3,700	8.9	43
CHOCHO	420,000	21.1	6720
CH_3COCHO	4,000	14.9	27
CH_3CHO	13	11.1	0.3

EF_X = Enrichment Factor = C_X / C_aq

Zhou and Mopper, 1990, Zhou and Mopper,1997; this work

Glyoxal is assigned to indicate the rate of SML oxidation





The presence of soluble surfactant reduces the liquid-phase transfer velocities (Asher 1996)

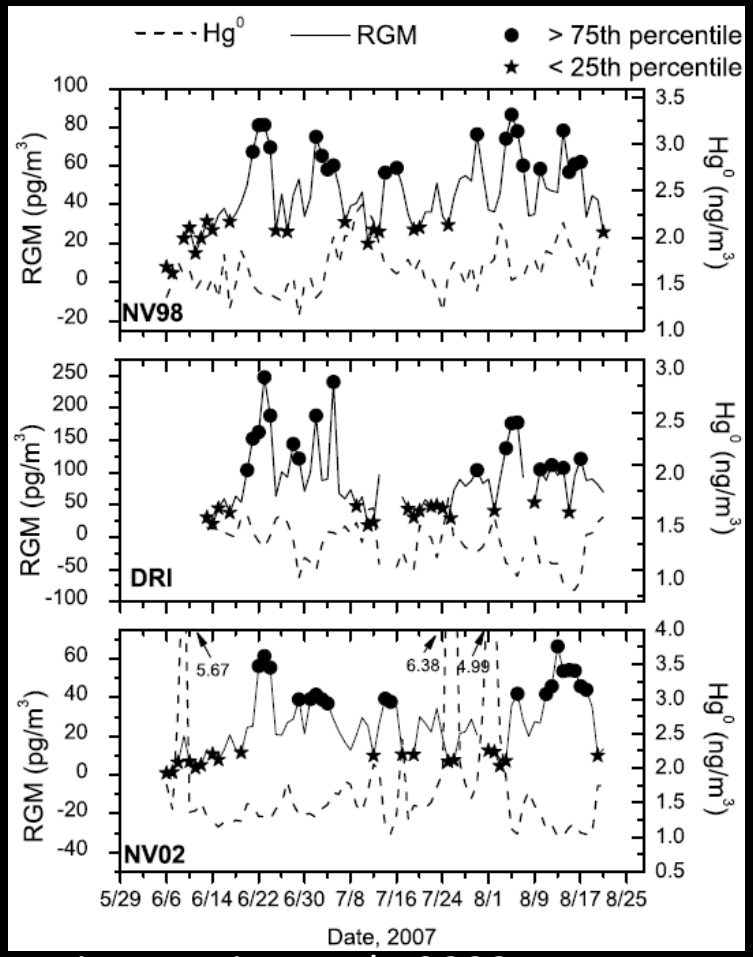
⇒Implications for CO2 fluxes into the ocean?

⇒ Spatial correspondence between OVOC and CDOM ?

TORERO observations topic #2

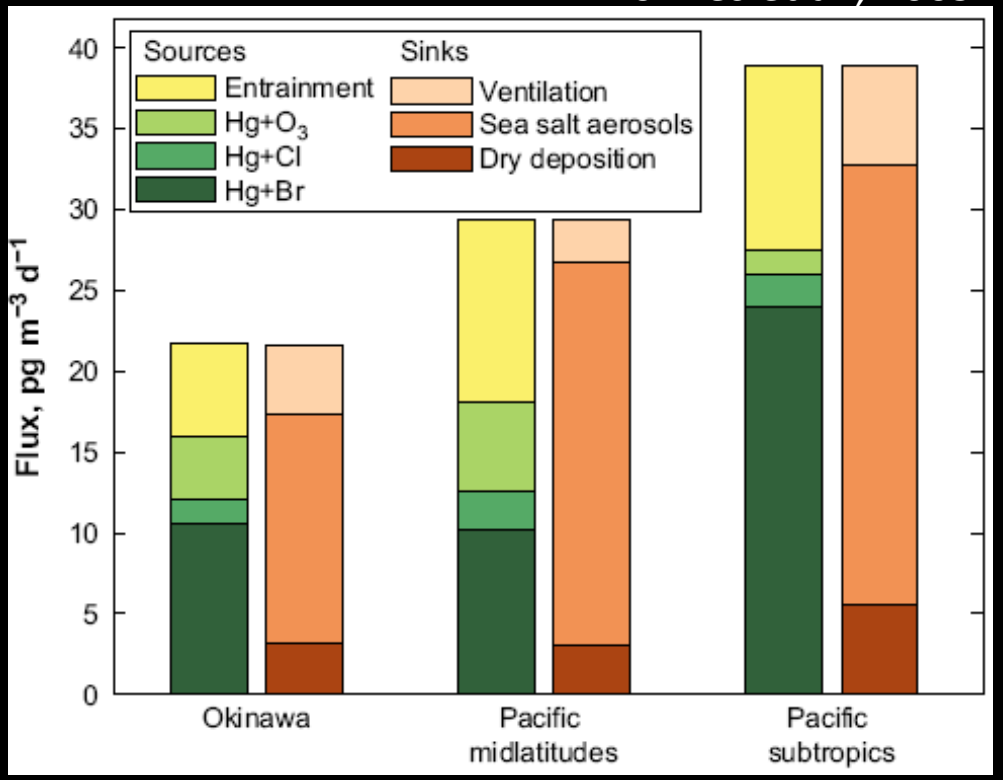
- NSF/NCAR GV: OVOC speciation, source fluxes, abundances, horizontal and vertical distributions
  - VOC and OVOC speciation and abundances (TOGA, AMAX-DOAS), J-values, Chl-a and CDOM (HARP), CO (Fluorescence?), CO2 and CH4 (Picarro)
- NOAA RV Ka'imimoana: Eddy covariance fluxes of CO2, and relaxed fluxed for Glyoxal (indicator for SML coverage), diurnal variations over the oligotrophic, mesotrophic, and coastal ocean, vertical distributions (lower 1.5km)
  - CO2 in gas-phase (Picarro, 13C?), and pCO2 in water
  - CHOCHO and aerosol extinction (CU LED-CE-DOAS)
  - Acoustic Doppler Current Profiler (ADCP)
  - HCHO, CHOCHO (CU SMAX-DOAS) vertical profiles

Topic #3: Atmospheric Mercury



Weiss-Penzias et al., 2009

Holmes et al., 2009



$$\mathrm{Hg^0 + Br \xrightarrow{M} HgBr} \qquad 1.1 \times 10^{-12}\,(T/298)^{-2.37}$$

$$\mathrm{HgBr \xrightarrow{M} Hg^0 + Br} \qquad 1.2 \times 10^{10}\exp(-8357/T)$$

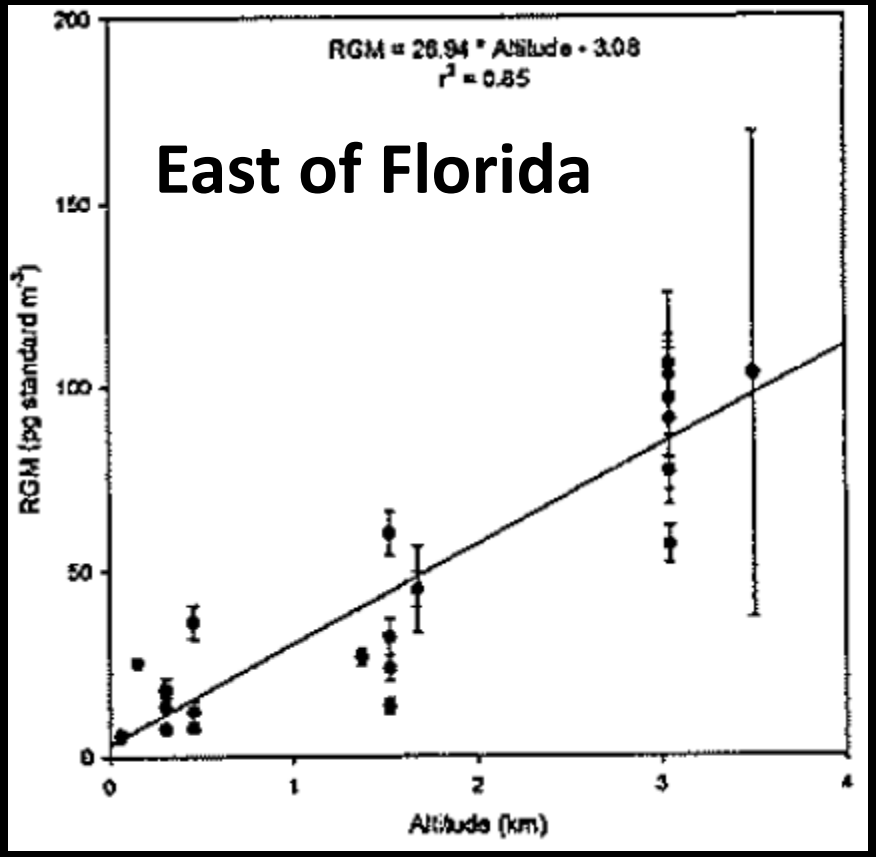
$$\mathrm{HgBr + Br \xrightarrow{M} HgBr_2} \qquad 2.5 \times 10^{-10}\,(T/298)^{-0.57}$$

Is there a pool of reactive gaseous mercury, RGM, in the FT?

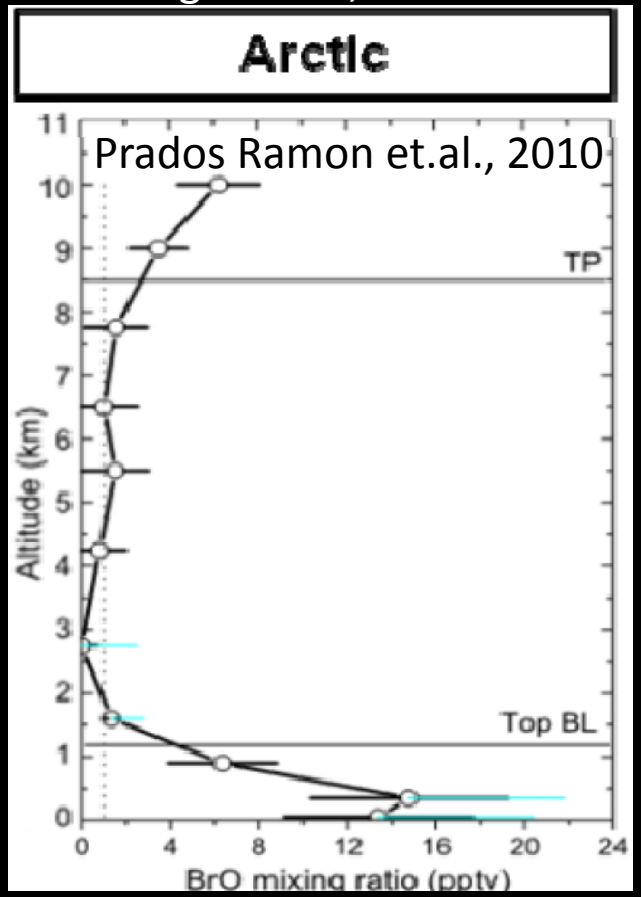
Is there a hemispheric Br atom background in the FT?

Topic #3: Atmospheric Mercury

Fitzenberger et al., 2000



Landis et al., 2005



- Many high-altitude particles contained Hg! (Murphy et al., 1998)
- Few RGM measurements available in the FT.
- BrO ubiquitous in the FT? Uncertainties remain...

Fitzenberger et al., 2000; van Roozendael et al., 2002; Ebinghaus et al., 2002; Salawitch et al., 2005; Theys et al., 2007; Prados-Ramon et al., 2010; Heue et al., 2010; Coburn et al., 2011

TORERO observations topic #3

- NSF/NCAR GV: horizontal and vertical distributions of RGM, O3 and BrO
  - RGM (KCl denuders),
  - O3 (UV-absorption),
  - BrO radicals (CU AMAX-DOAS)

Topic #4: O3 and water vapor

- The paucity of ozone and water vapor data in the tropical FT presents an obstacle to gaining a wider perspective on the chemistry and climate effects of O3 and water vapor changes in the tropical FT (and lower stratosphere)
- NSF/NCAR GV: O3 and water vapor
- NOAA RV Ka'imimoana : O3/water vapor sonde launches?

Flight Planning

Discussion Remote Sensing

Instrument	Species / Parameters	Detection limit / Accuracy / Comment	Time / Space resolution	PI / Institution
CU AMAX-DOAS	IO BrO OClO NO_2 HCHO CHOCHO	0.1 ppt 1 ppt 0.7 ppt 10 ppt 120 ppt 3 ppt	Acquisition: 2-30 sec Profile scan: 1-5 mins Vertical resolution: ~ few 100 m– few km	Rainer Volkamer (CU Boulder)
HARP	Photon actinic flux: J_{O3}, J_{NO2}, J_{OVOC}, J_{RX}, J_{IxOy}, etc. Hyper spectral irradiance Surface albedo Cloud optical depth + Percent cloud cover Cloud/Aerosol eff. radius Single scattering albedo Asymmetry parameter	~ 9 % (280–680 nm) < 5 % (260–2217 nm) < 3 % ~ 3 % ~ 5 % ± 0.03 ~ 0.1	0.1 – 3 sec 1 sec inferred by difference from hyper spectral irradiance data	Sam Hall (NCAR/ACD) Sebastian Schmidt (CU Boulder)
GV-HSRL	Aerosol Backscatter, Depolarization, Extinction altitude profiles	$1x10^{-9}$ m^{-1} sr^{-1} ~ 1% $2x10^{-8}$ cm^{-1}	Acquisition: 0.5 sec Profile time: 3-5 mins Vertical res.: 7.5 m Range: 30 km	Ed Eloranta (U Wisconsin)
Microwave Temperature Profiler	Altitude temperature profile	1 K (near plane) < 2 K (within 6km from plane)	Profile scan: 18 sec Vertical resolution: ~150 m to few km	Julie Haggerty (NCAR/RAF)

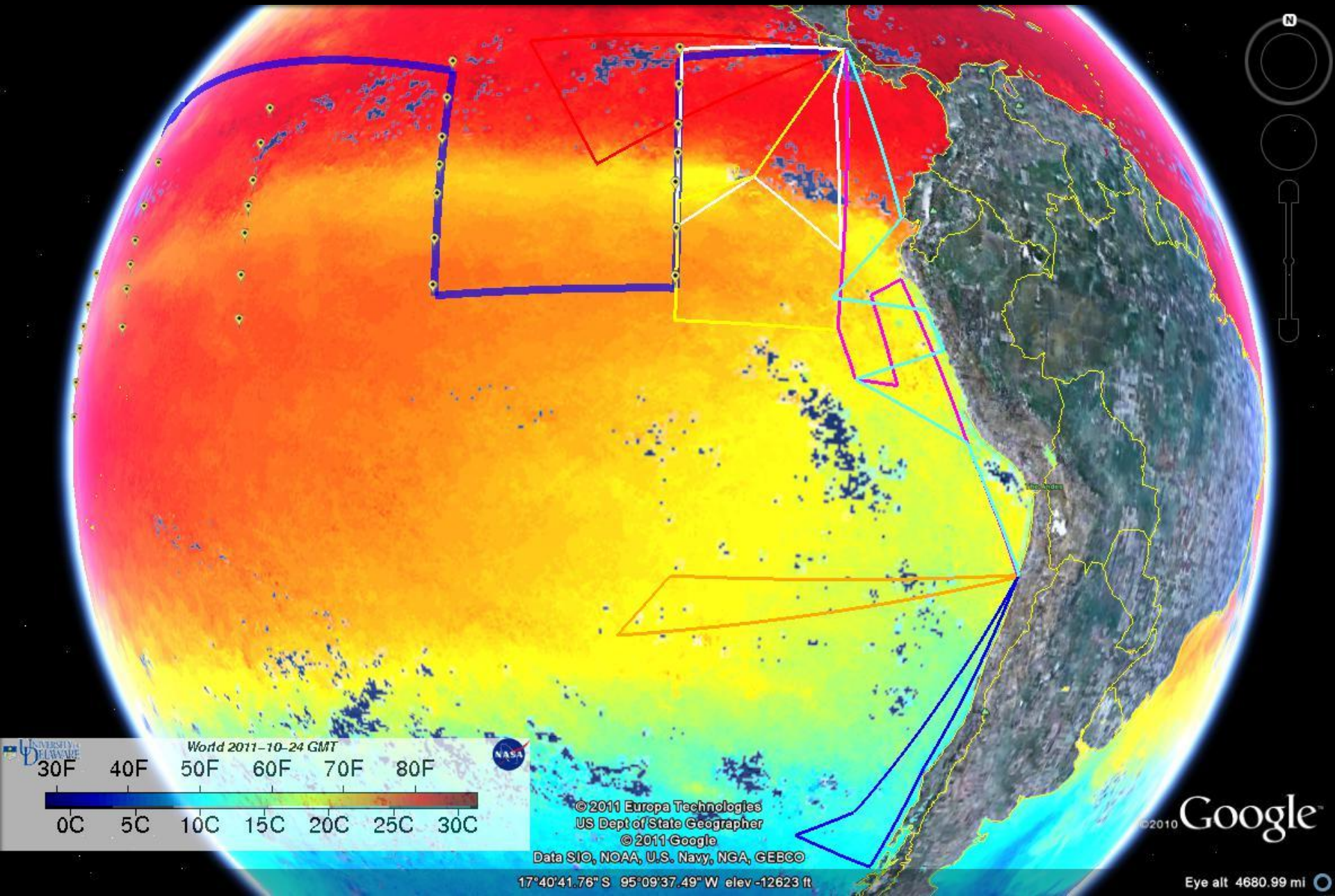
Discussion in-situ instruments

TOGA-HIAPER	Alkylhalides (incl. CH_2X_2, CH_2XY, CH_3X, C_3H_7X) VOC (incl. DMS, C_5H_8, monoterpenes) OVOC (incl. CH_3CHO, DMSO, C_2H_5OH, acetone, MACR, MVK, acetonitrile)	0.1 - 1 ppt* 3 - 10 ppt* 3 - 10 ppt*	2 mins * Detection limits are a function of how many species are measured simultaneously. Upper limits: ~50 species	Eric Apel (NCAR/ACD)
O_3	O_3	$1.5x10^{10}$ molec cm^{-3}	1 sec	Ru-Shaun Gao (NOAA/ESRL)
VCSEL	Water vapor	< 1 ppm	0.04 sec	Stuart Beaton (NCAR/RAF)
Hygrometers	Water vapor	± 0.1°C	10 - 120 sec	EOL facility instrument
CO	CO	2 ppb	3 sec	Frank Flocke (NCAR/ACD)
CN / NMASS	Aerosol number (nucleation mode)	0.2 # cm^{-3} (integral # / 6 and 15 nm cutoff)	1 sec	Dave Rogers (NCAR/RAF) Chuck Brock (NOAA/ESRL)
UHSAS	Aerosol size distribution	1 cm^{-3} (60-1000 nm)	1 sec	EOL facility instrument
Cloud droplet probes	Cloud droplet size distribution	2-50 µm	1 sec	EOL facility instrument
Cloud 2-D imaging spectrometers	Distinguish ice and water droplets / Cloud droplet size distribution	18-640 µm 25-1600 µm	N/A	EOL facility instrument
DVR	Video stream	Forward view	1 sec	EOL facility instrument
Ozone/water vapor sonde launches from the surface (ship /Galapagos Island)	Water vapor O_3 GPS Position Temperature Pressure	< 0.8 ppm < 3 ppb ~ 25 m < 0.5 K	Vertical res.: ~50m	Rainer Volkamer (CU Boulder) Holger Voemel (CIRES/DWD)

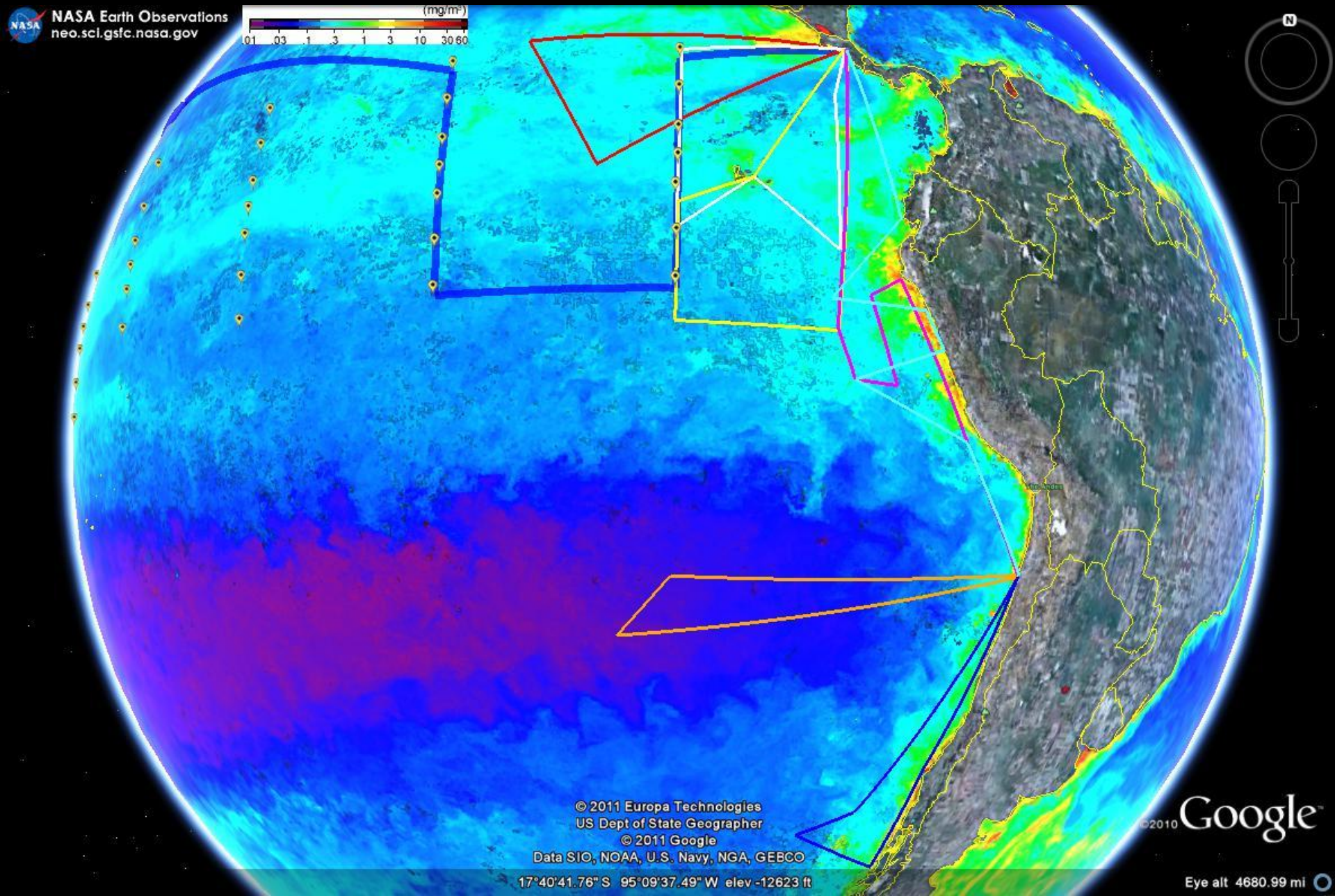
Synergistic use of remote sensing and in-situ observations Bridging Spatial Scales

- Variable time resolution translates into different spatial scales that are probed:
  - Example: HIAPER-TOGA (2mins) corresponds to 14km or 26km in the MBL and FT
  - AMAX-DOAS and HSRL: ~3-5 mins, corresponding to 25 to 65km
  - LIDAR vs passive remote sensor spatial mismatch!
- Resolution atmospheric models:
  - ~30km for WRF; ~15km for RAQMS (in RDF mode); ~60km for GEOS-Chem;
  - ~300km for RAQMS in forecast mode; ~300km for TM4-ECPL
- Satellite footprints:
  - ~13x24km2 for OMI;
  - ~30x60km2 for SCIAMACHY;
  - ~40x80km2 for GOME-2
- Ocean eddies: ~100 km, DCC features: ~50 to 300km; Cirrus: up to 1000km.
- The finest scale variability is expected in coastal stretches that will be sampled by flight legs parallel to the coast, with increasing distance to the coast (e.g., circles around Galapagos Islands).
- Vertical profiles consist of steep rises, alternating segments of climb/descent, and segments at constant flight altitude (~10mins) to allow for repetitive sampling by all instruments at any given altitude.

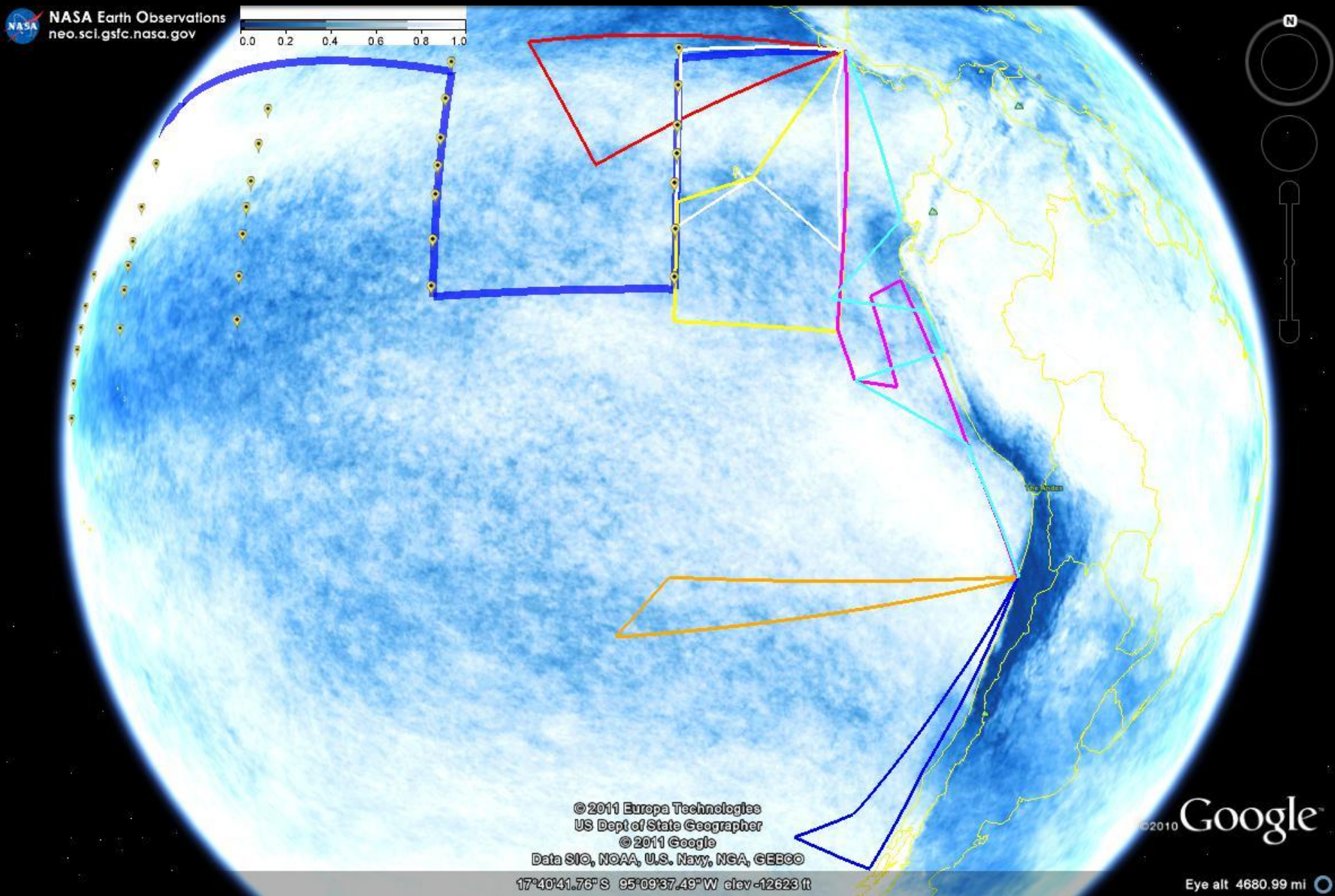
Annual mean SST in the TORERO study area



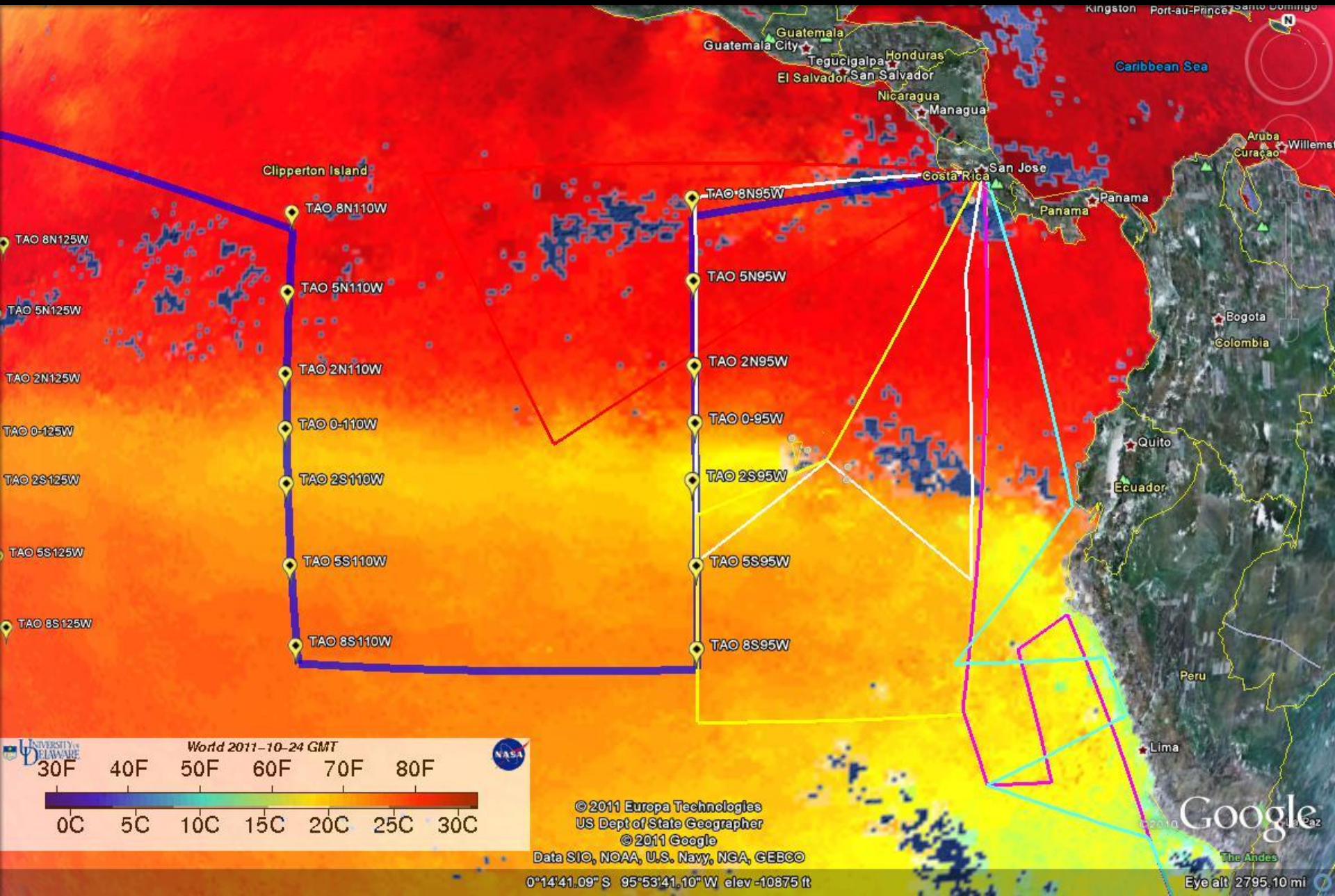
Chl-a during Jan/Feb 2009 in the TORERO study area



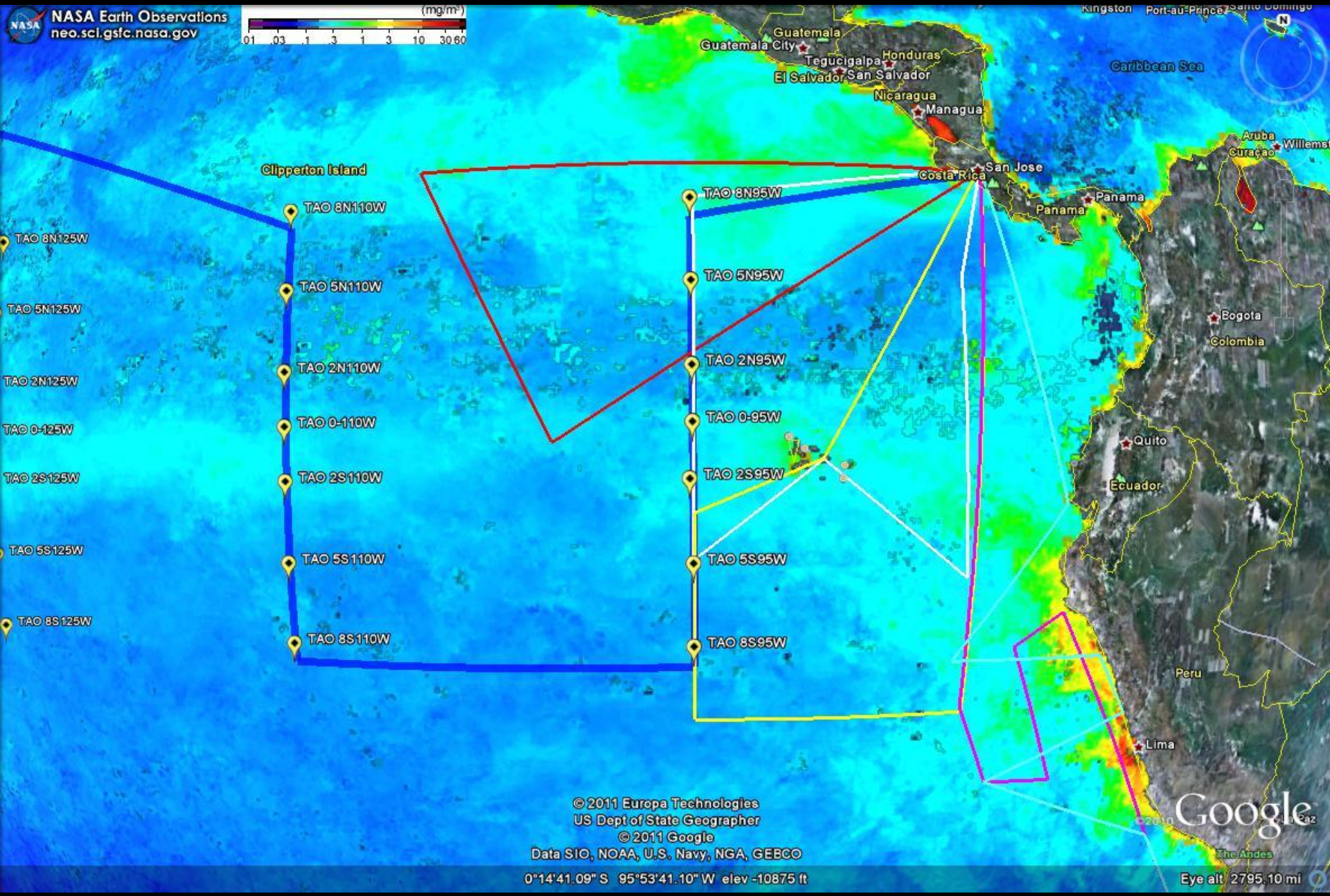
Annual mean cloudiness in the TORERO study area



Annual mean SST in the TORERO study area



Chl-a during Jan/Feb 2009 in the TORERO study area



Annual mean cloudiness in the TORERO study area