Controls from a widespread surface ocean organic micro layer on atmospheric oxidative capacity

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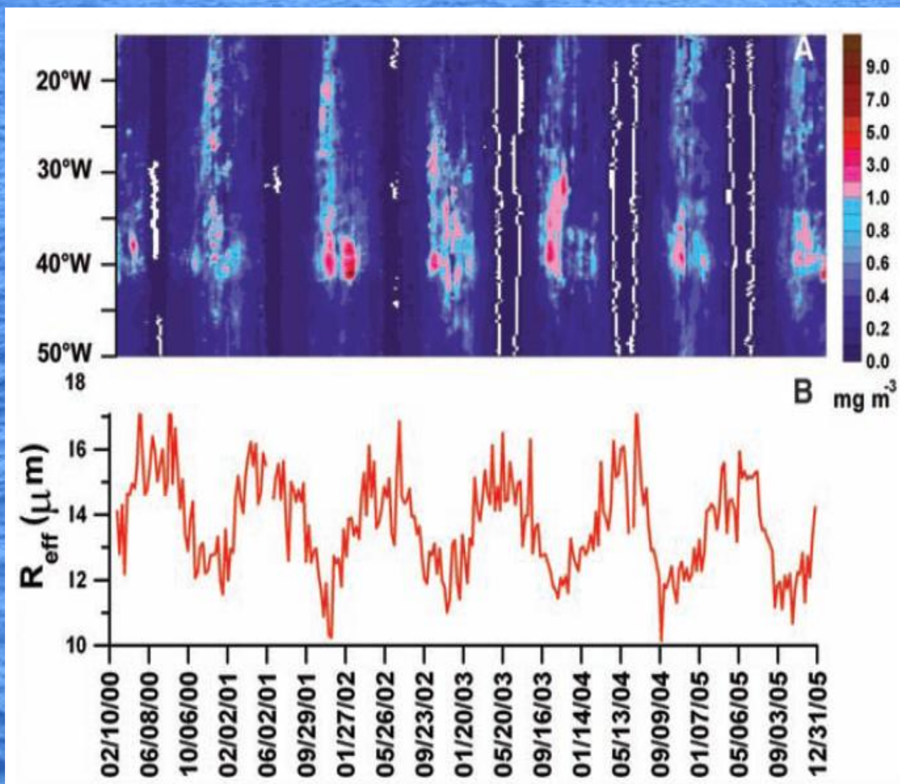
- Four cruises: IO, BrO, CHOCHO, HCHO, marine VOC, aerosols
- Organic carbon (and halogens) are relevant because
  - Modify oxidative capacity: influence on the reactive chemistry (OH, Br, Cl, I abundance) that determines the **removal rate (lifetime) of climate active gases** (e.g., methane, ozone, dimethyl sulfide) in the atmosphere
  - Modify aerosols: Number/Size (CCN), Optical properties

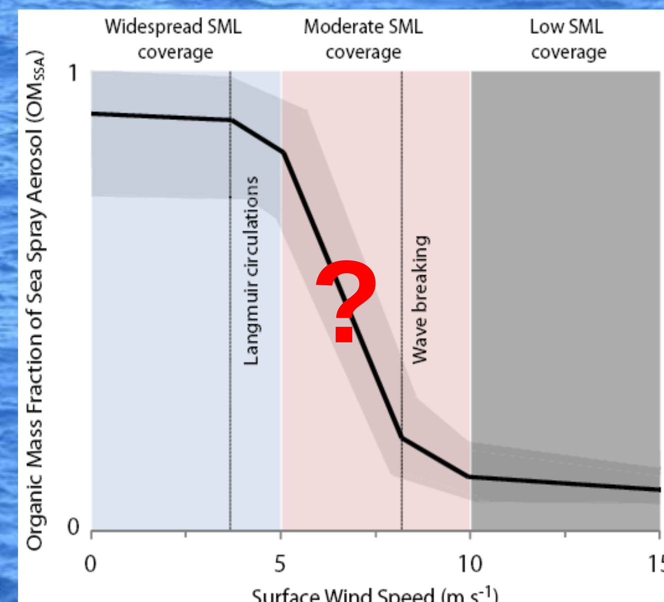
Ocean-aerosol-cloud interactions

Field evidence



Meskidze and Nenes, 2006

Secondary Organic Aerosol (SOA) ?

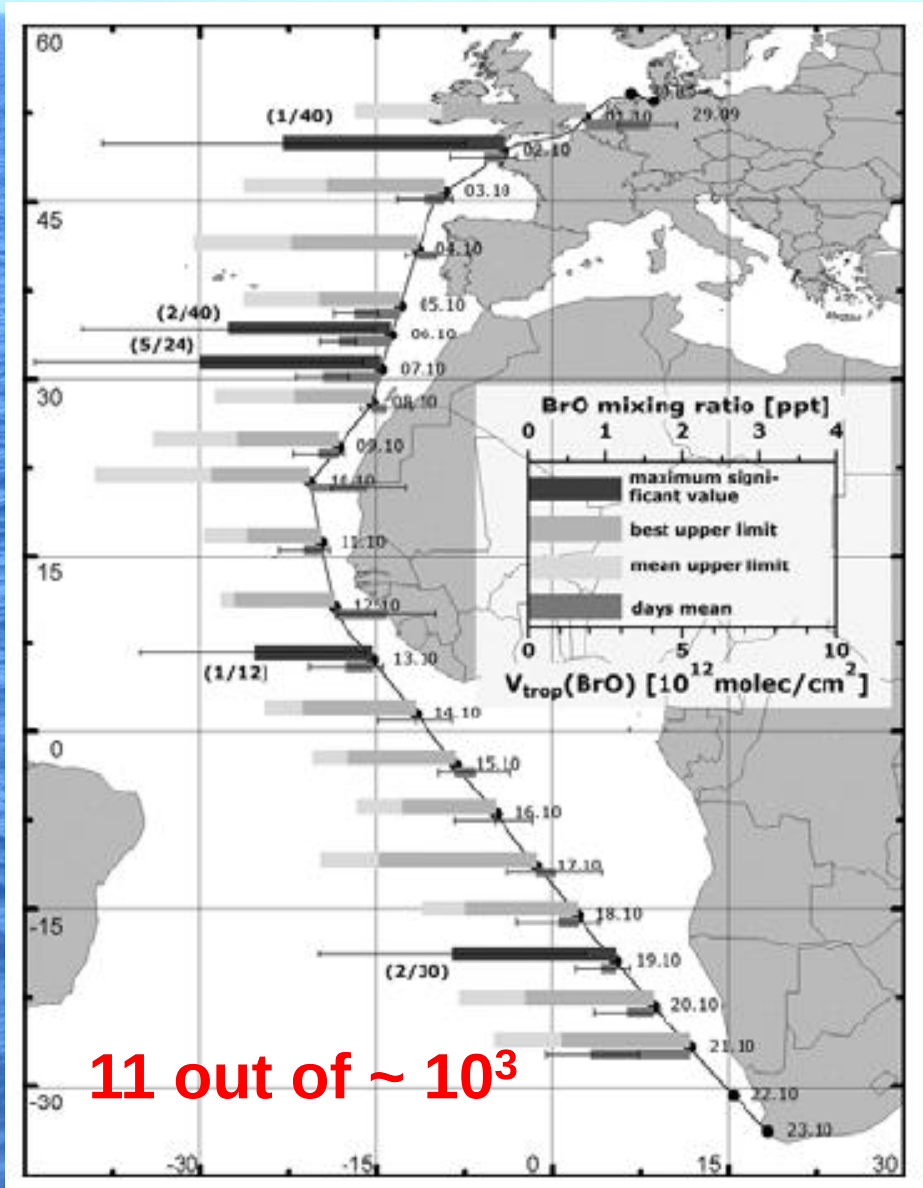


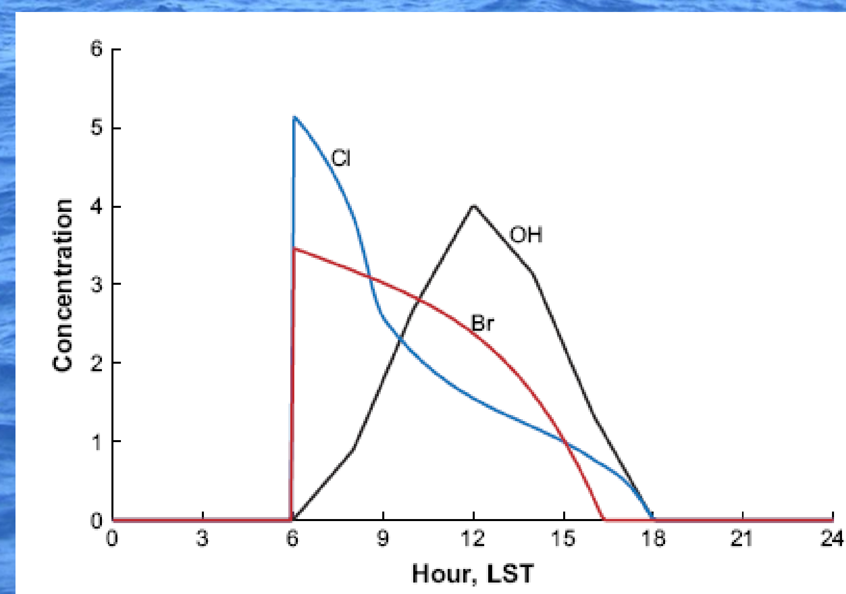
Gantt et al., 2011

OM_{SSA} is determined by organic enrichment at the air-sea interface, chemical composition of seawater, and aerosol size

How widespread is BrO over oceans?

- Field measurements: Leser et al., 2003, GRL; Martin et al., 2011
  - BrO over the Atlantic Ocean
- Models: Holmes et al., 2009; Ordonez et al., 2012
  - 2-3 ppt in most conditions





A smoking gun for other OVOCs

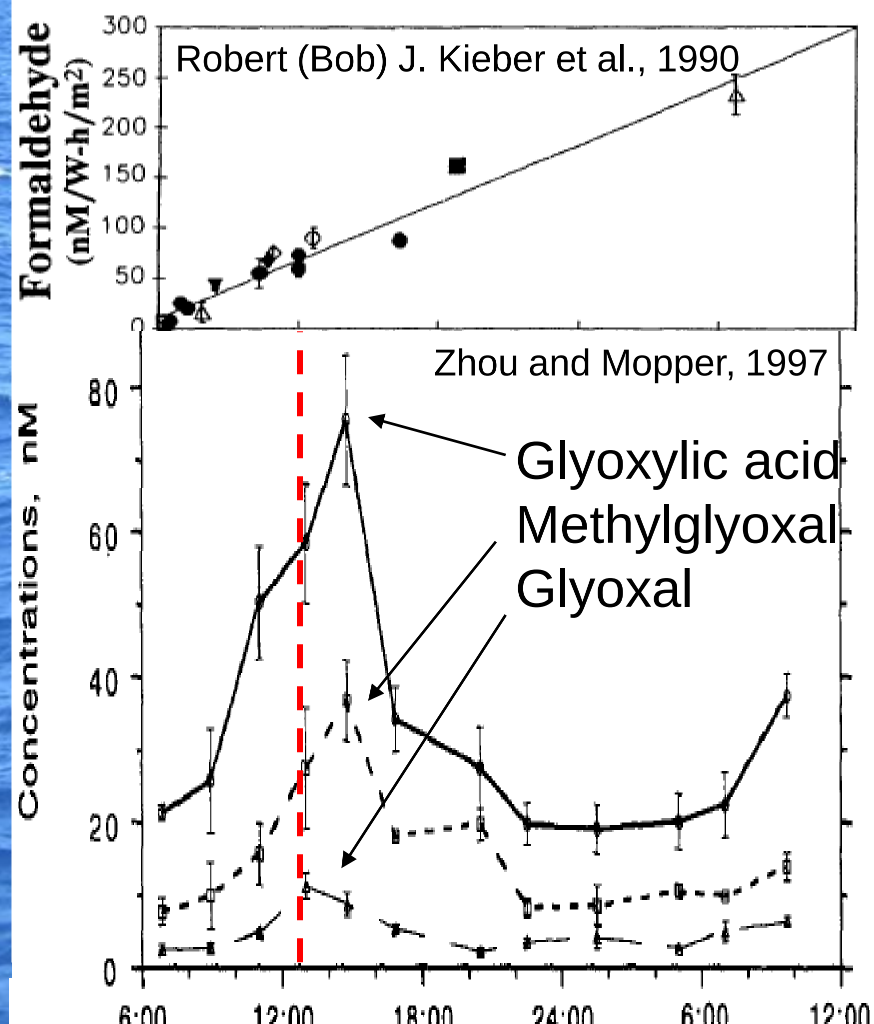
Table III. Typical Carbonyl Concentrations in Clean Marine Air, and Predicted and Measured Concentrations in Surface Open Ocean Seawater

compounds	concn in air,[a] ppb	predicted concn in seawater,[b] nM	measured concn in seawater,[c] nM
formaldehyde	0.4	1500	2–40
acetaldehyde	0.3	4	2–15
propanal	0.1	1	0.4–3
butanal	0.08	0.5	0.3–2
pentanal	0.1	0.5	0.2–5
hexanal	0.1	0.3	0.2–0.6
heptanal	0.1	0.2	0.2–0.5
octanal	0.1	0.1	0.2–0.7
nonanal	0.15	0.06	0.2–1
decanal	0.1	0.02	0.2–0.8
benzaldehyde	~0.01	0.3	ND[c]
acetone	0.3	10	3–50
butanone	0.05	0.8	0.5–2
glyoxal	0.08	30000	0.5–5
methylglyoxal	~0.01	300	0.1–1.5

[a] Typical carbonyl concentrations in the air over open Caribbean Sea and Sargasso Sea. [b] Predicted concentrations in seawater in equilibrium with atmosphere: [R′R″CO] = K^*P at 25 °C. [c] Carbonyl concentrations measured in South Sargasso Sea surface water. ND, not determined.

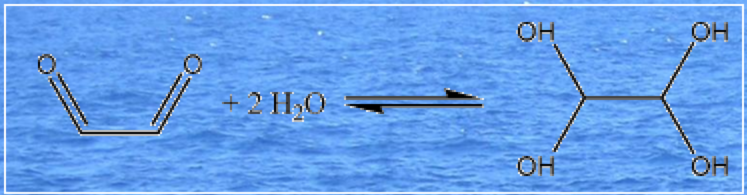
Zhou and Mopper, 1990, EST, 24, 1864

Photochemical source of biological substrates in

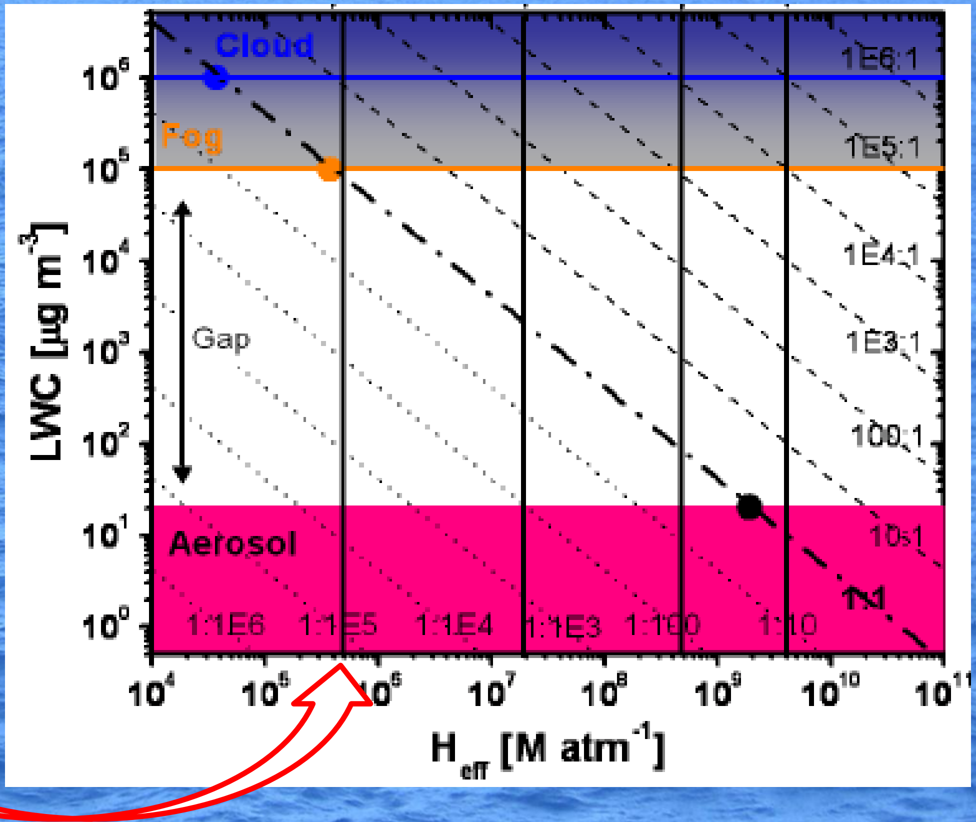


Glyoxal over the Sargasso Sea (80 ppt during the day)

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	$4x10^5$



Glyoxal is a source for SOA in clouds and aqueous aerosols

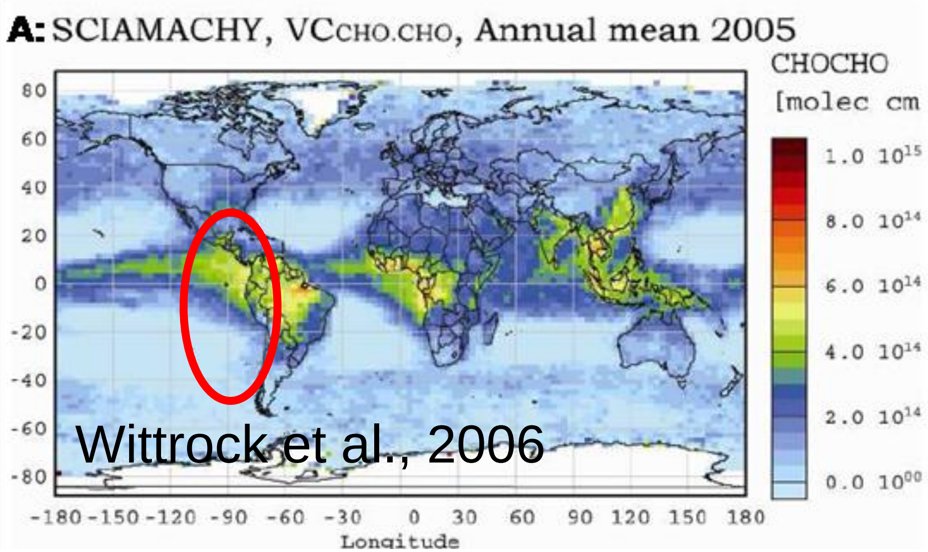
→ **Air-sea partitioning: shifted 10^7 towards the ocean**

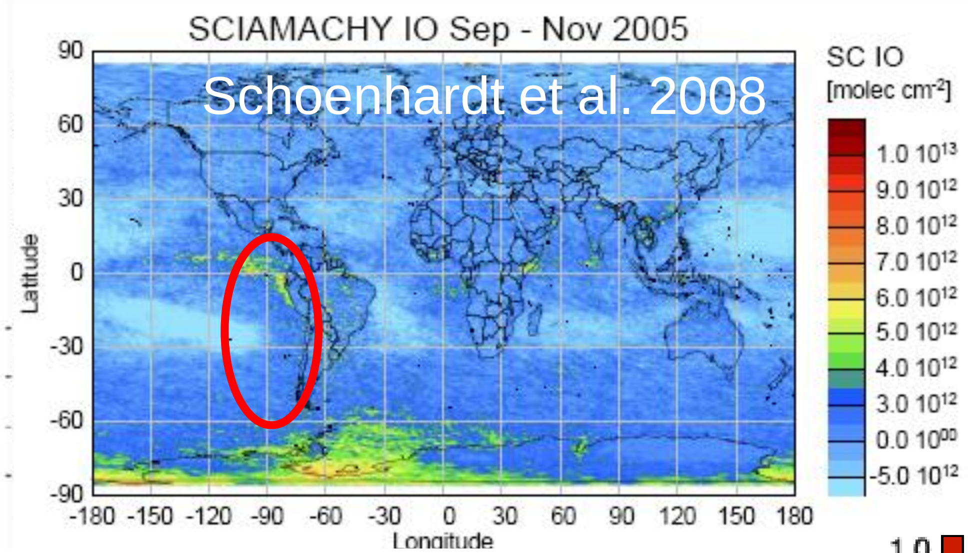
→ **Glyoxal must originate from an airborne source !**

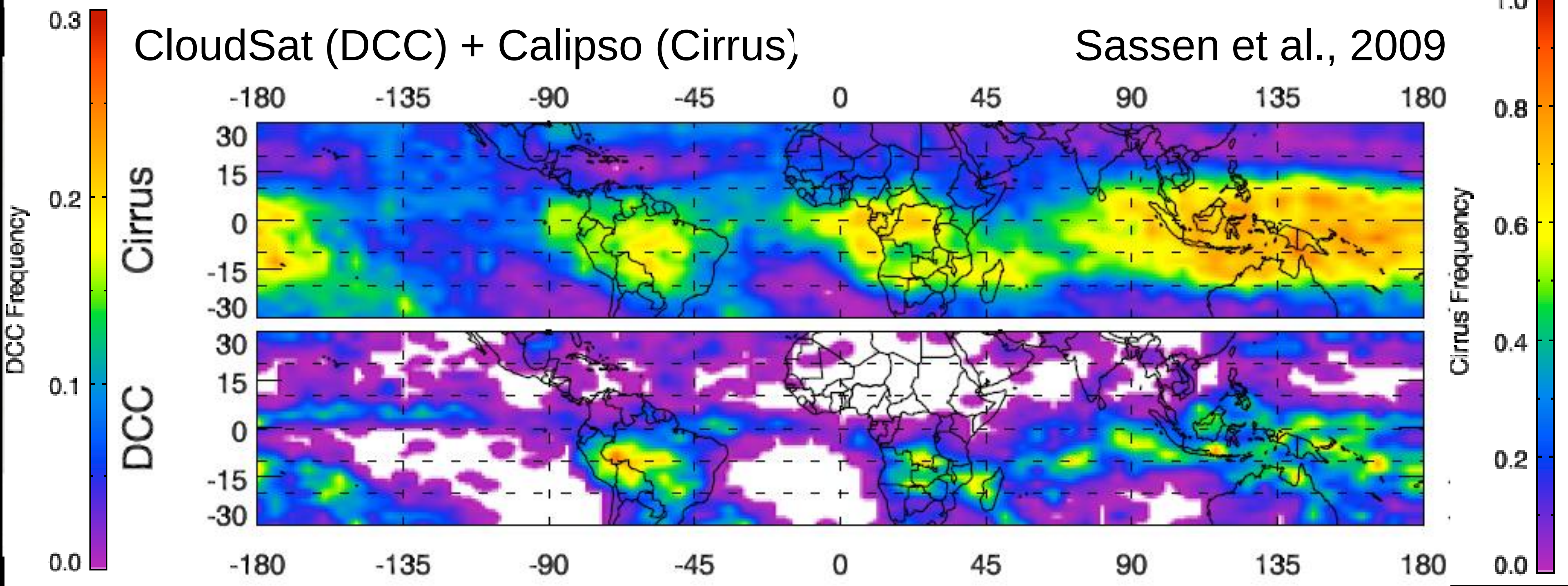
→ **Ocean is a sink for glyoxal**

Volkamer et al., 2009, ACP

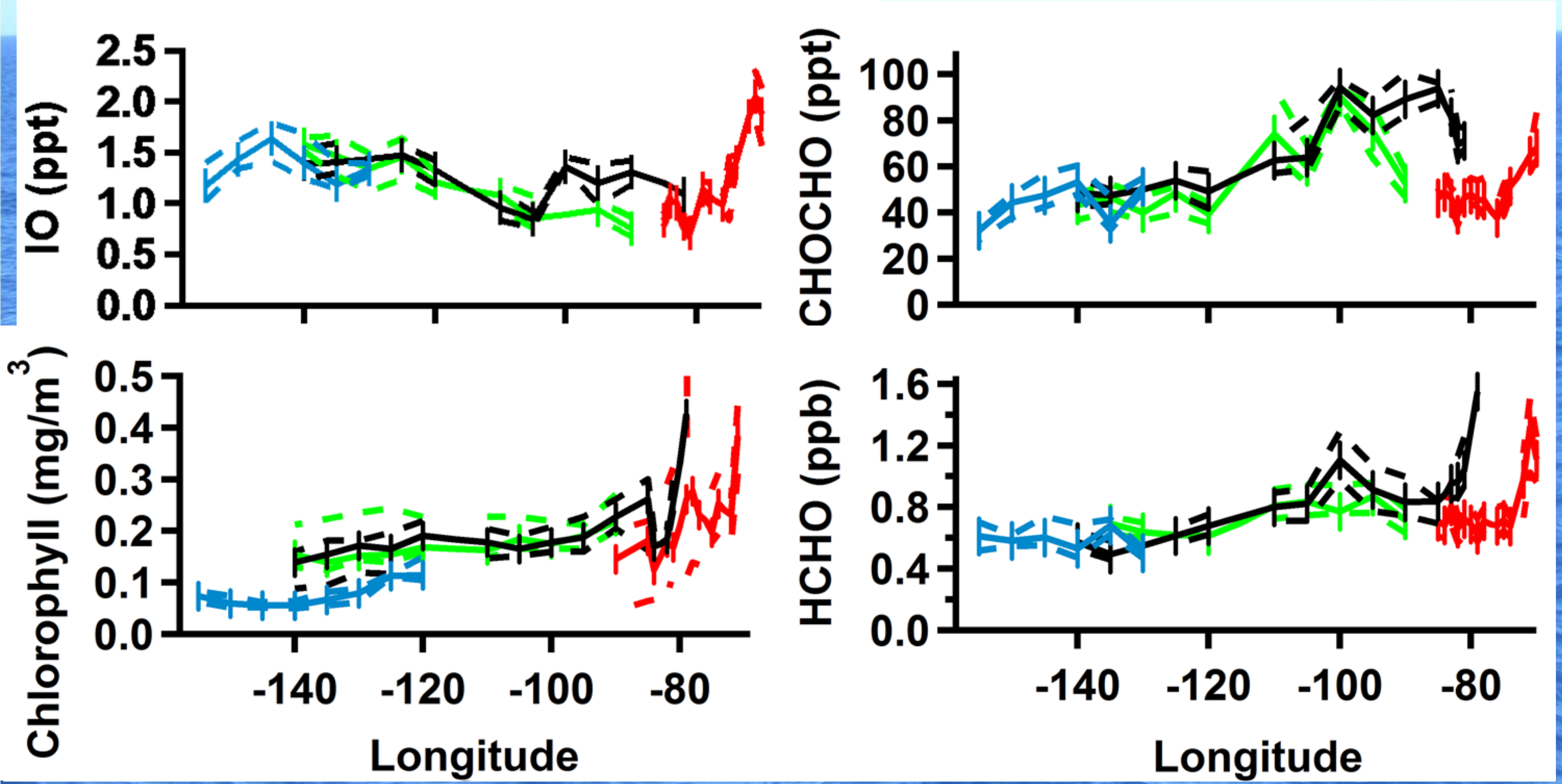
TORERO study area







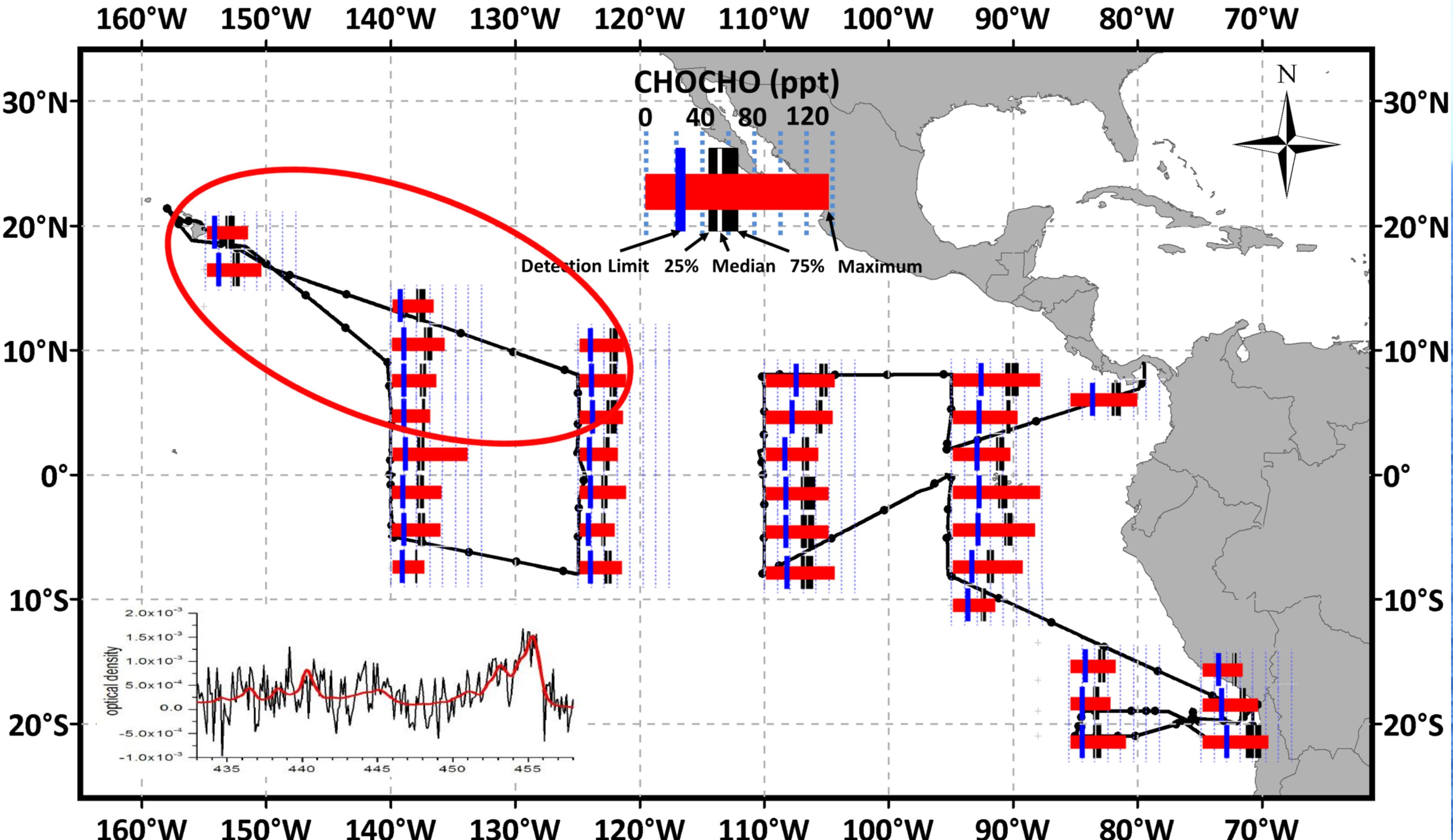
Longitude gradients



- IO: 0.5 – 2 ppt
- BrO: < 1 ppt
- Can organics modify halogen oxide abundances?

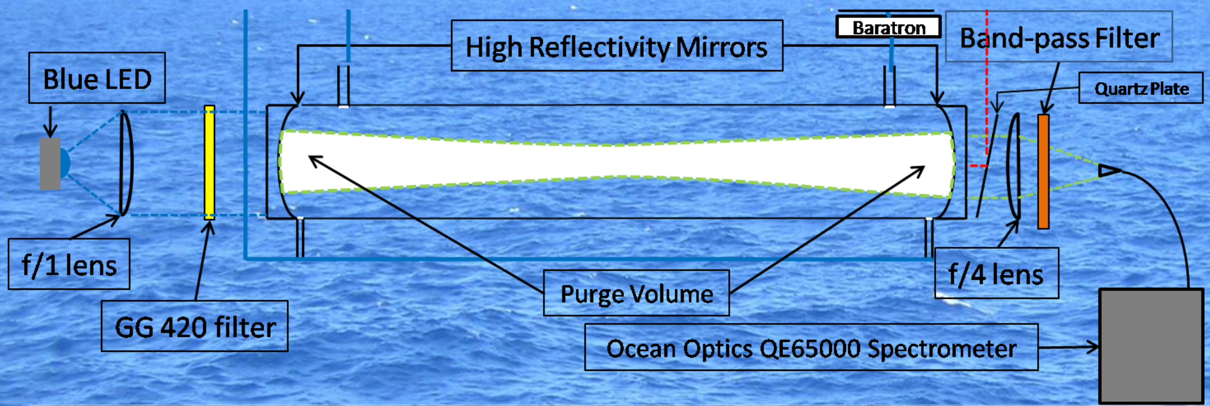
CHOCHO: 40-80 ppt

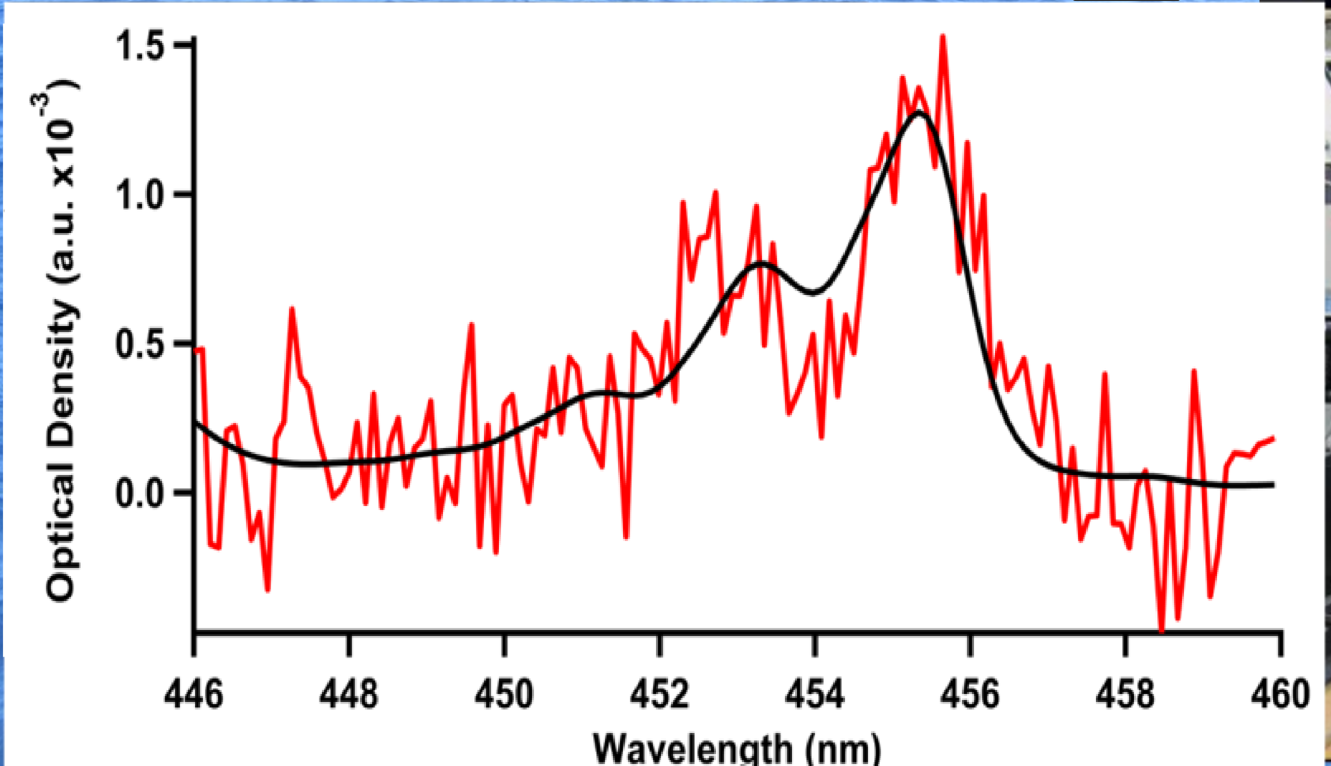
HCHO: 500ppt – 1 ppb



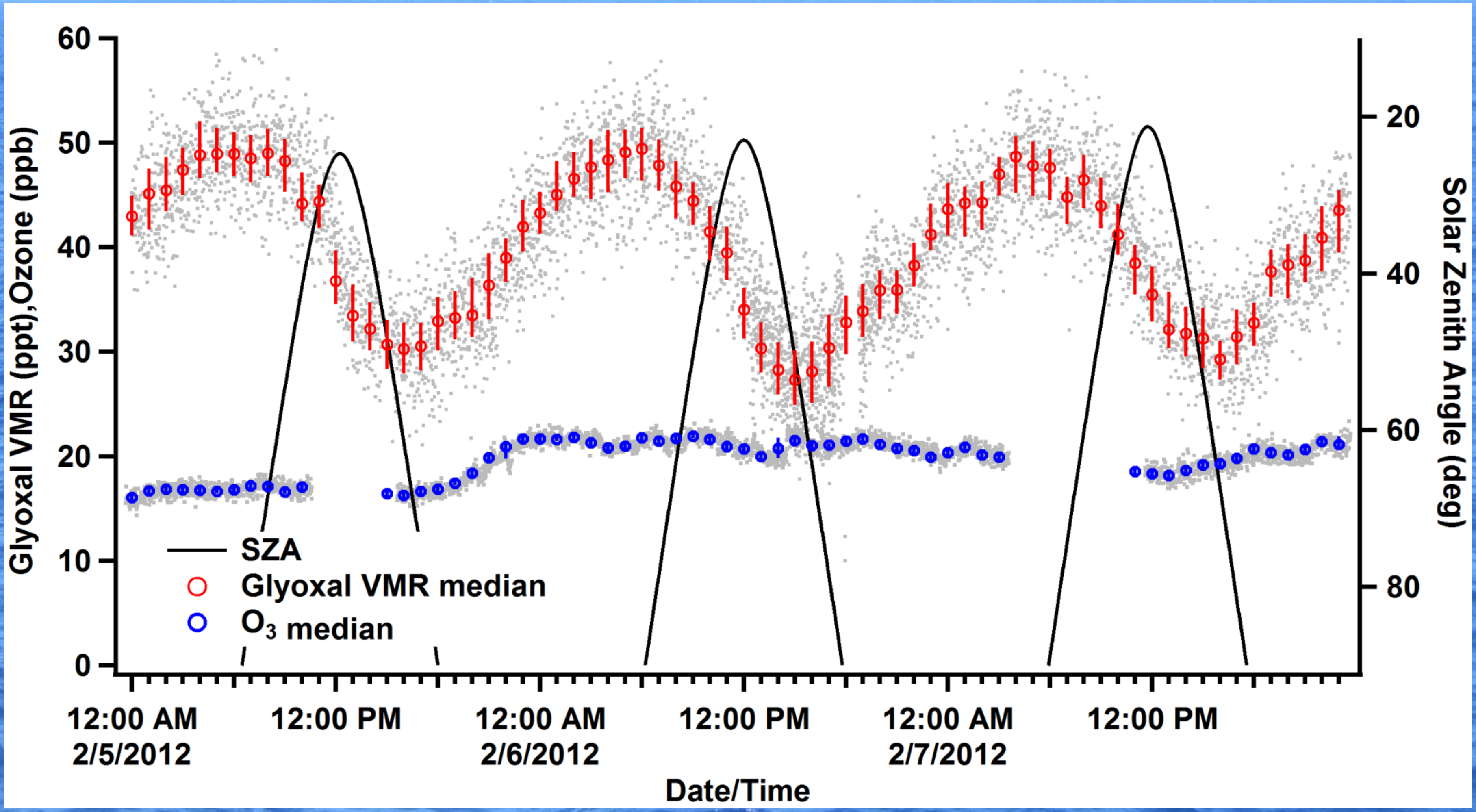
- Glyoxal is observed also over the oligotrophic ocean!
- Consistent with some satellites, but not with others.

Light Emitting Diode Cavity Enhanced DOAS (CU LED-CE-DOAS)





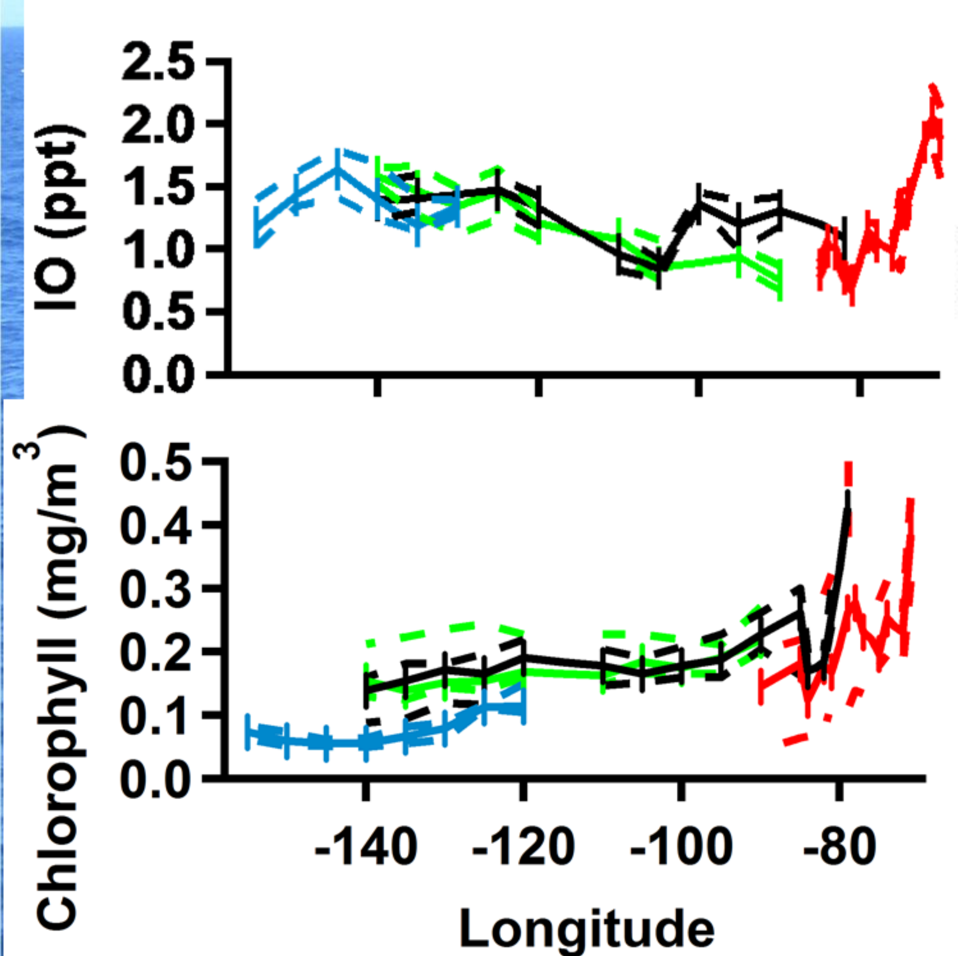
Diurnal cycle over the oligotrophic ocean carries mechanistic information

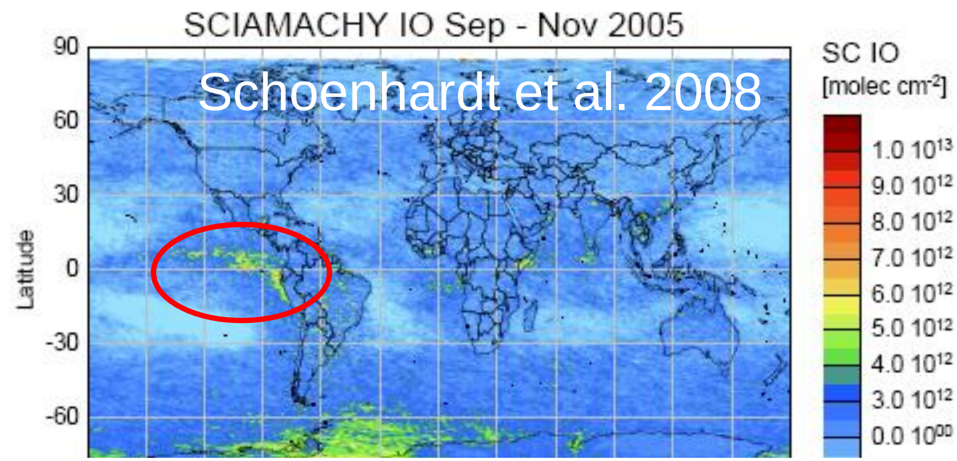


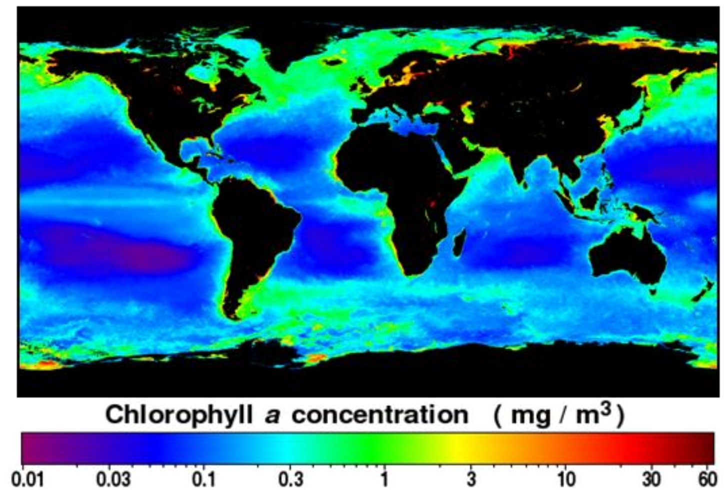
⇒ Night time increase is attributed to O_3 + DOM

⇒ Non-zero during day: photochemical mechanism

IO over the oligotrophic ocean

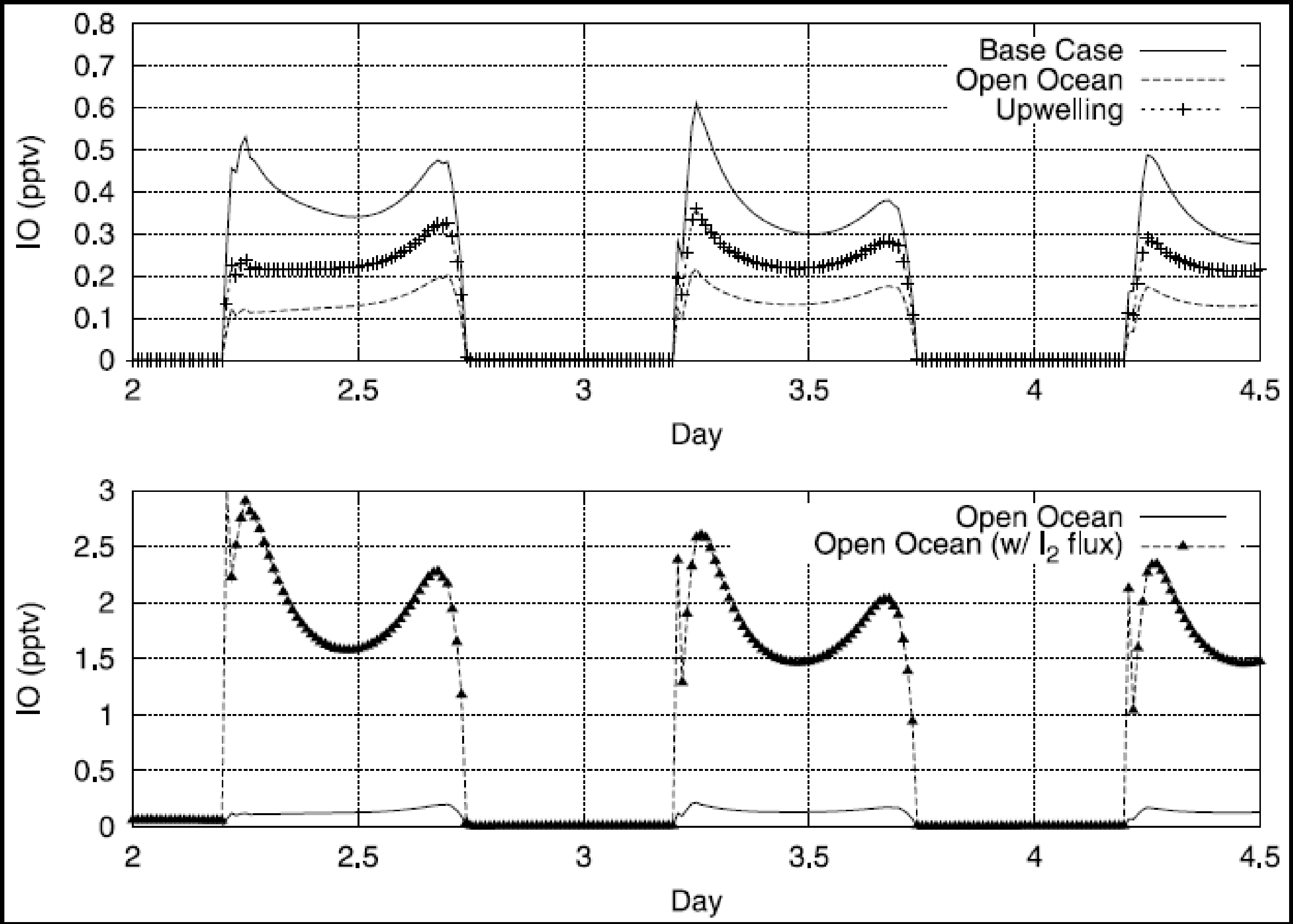






- Elevated IO over the oligotrophic ocean does not agree with the idea of iodine sources being primarily ‘biological’.
- Satellite IO shows (some) correlation with Chl-a

Reactive Iodine Species



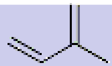
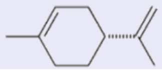
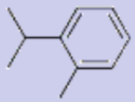
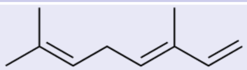
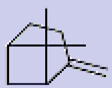
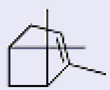
only organic iodine gases as iodine precursors (biological source)

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?

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	

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: gas-phase/heterogeneous process !

* 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 airborne DOM 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 DOM in the sea surface organic microlayer (or fine sea spray)

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

(Wurl et al. 2011; Russell et al., 2010)

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

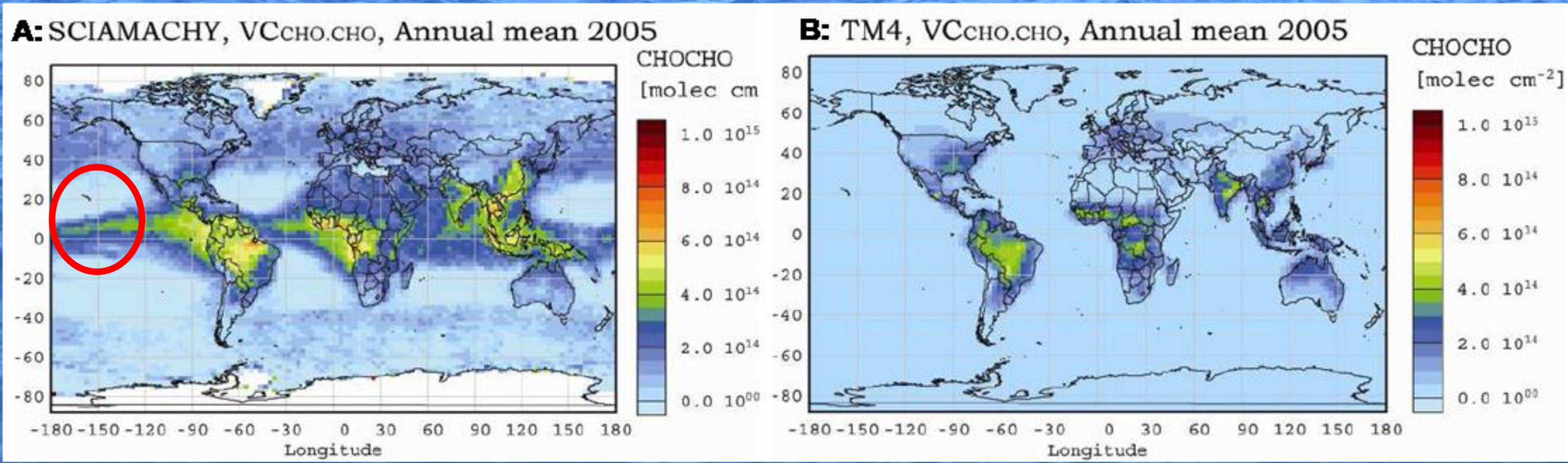
EF_X = Enrichment Factor = C_X / C_aq

The SML shows the highest EF for CHOCHO, but it appears to be sub-saturated in glyoxal (factor 320) => POA oxidation appears to be needed

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

Interim conclusions

- Glyoxal over oceans is attributed to airborne oxidation of DOM, or DOM oxidation products -> SML ?
- <u>OVOC source in absence of VOC</u>
- Aerosols or SML or DOM oxidation in the surface ocean? What is the formation mechanism? How big is the organic carbon flux?



Myriokefalitakis et al., 2008

Reaction of Organics with halogen atoms

- Cl: $10^{-13} < k_{VOC} < 10^{-10}$ cm^3/mol/s
  - τ_{Cl} < 0.2 sec (capped by CH_4)

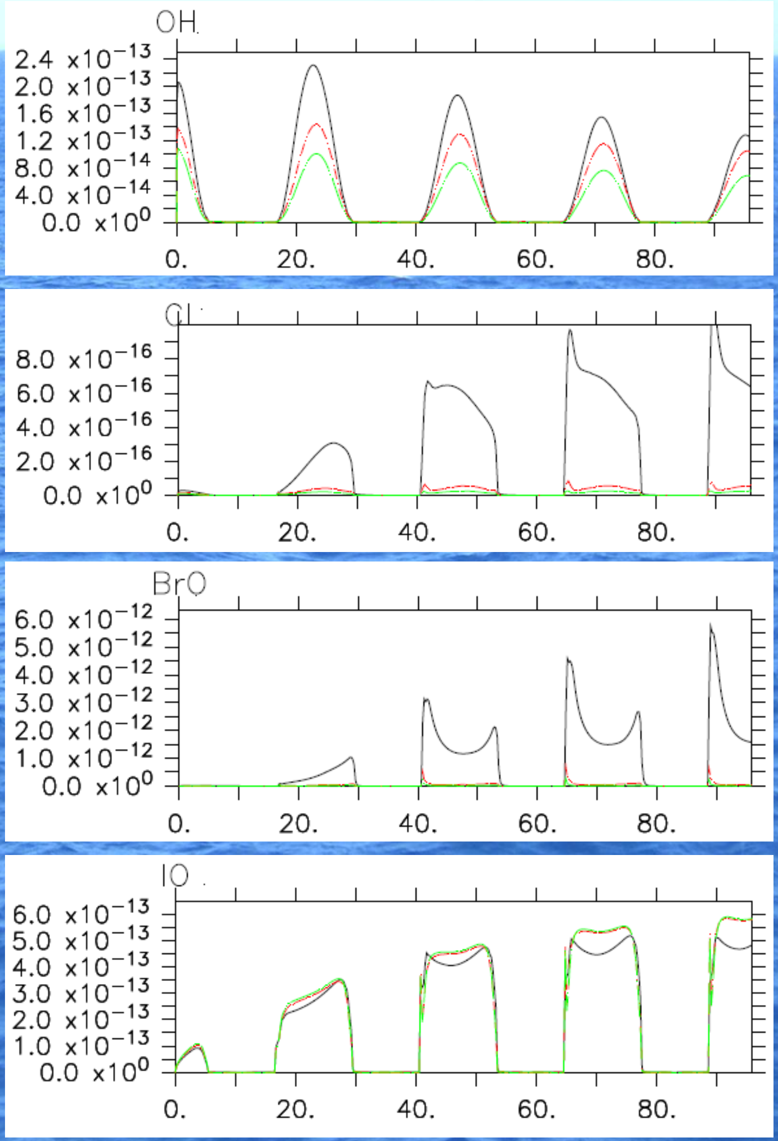
- Br: $10^{-12} < k_{OVOC} < 10^{-11}$ cm^3/mol/s
  - τ_{Br} < 4 sec (RCHO ~ 0.8 ppb)

- I: organic sink is inefficient (endothermic, but indirect effects might exist through coupling with Cl and Br chemistry)

Impact of OVOC on oxidative capacity

- Black: base case
- Red: +0.8 ppb HCHO
- Green: +1.8 ppb ALD2

- OH: strong reduction
- Cl: strong reduction
- Br: strong reduction
- I: insensitive



⇒ OVOC are efficient sinks for OH, Cl and Br

Reaction of Organics with halogen atoms

- Cl: $10^{-13} < k_{VOC} < 10^{-10}$ $cm^3/mol/s$
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  - $\tau_{Br} < 4$ sec (RCHO ~ 0.8 ppb)

Poster 21

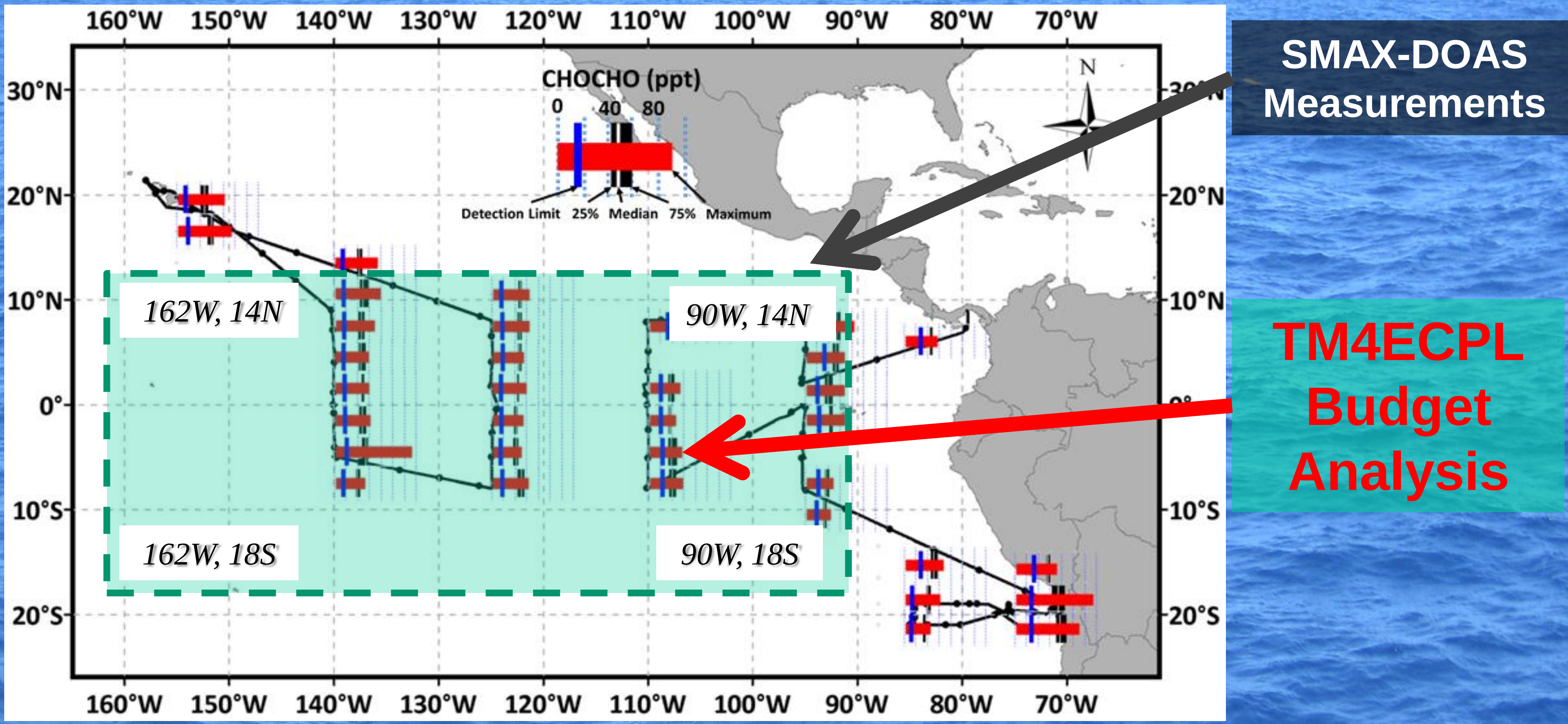
- I: organic sink is inefficient

⇒ OVOC levels are a relevant sink for BrO

⇒ Organics and iodine are weakly coupled in terms of their atmospheric chemistry

Organic carbon flux of glyoxal

TM4-ECPL global 3-d model : Myriokefalitakis et al., 2008; 2010; 2011



Simulations have been performed in 6°x4° resolution (longitude x latitude) in 34 vertical hybrid layers up to 0.1 hPa

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Kanakidou Maria mariak@chemistry.uoc.gr

Environmental Chemical Processes Laboratory
Chemistry Dept., University of Crete, Heraklion, Greece

Organic carbon flux from the ocean

		OCEANIC EMISSION				
COMPOUND	ROLE IN ATMOSPHERE	MASS FLUX	C FLUX	% OF TOTAL EMISSIONS	OTHER SOURCES	TOKEN REFERENCES
OVOC (glyoxal)		8 TgC/yr (SCIA) 16 – 41 TgC/yr				Myriofekalitakis et al. 2008 This work
Sulfur volatiles:						
DMS	Global sulfur budget Aerosol precursor: atmospheric acidity and cloud nucleation	14-29 TgC/yr		90%	Soils, plants	Kettle & Andreae 2000, Simó & Dachs 2002, Lana et al. 2010
COS	Precursor of stratospheric aerosol	0.30 TgS/yr	0.06 TgC/yr	50%	Soils, combustion	Kettle et al. 2002, Uher 2006, Sutharalingam et al. 2008
CS_2	COS precursor	0.15 TgS/yr	0.02 TgC/yr	25%	Soils, wetlands	Xie & Moore 1999, Watts 2000, Kettle et al. 2002
NMHC	Tropospheric (photo)chemistry, aerosol precursors and cloud nucleation	1-10 TgC/yr		minor	Plants, combustion	Plass-Dülmer et al. 1995, Broadgate et al. 1997, Yassaa et al. 2008, Arnold et al. 2009, Gantt et al. 2009
POA	Tropospheric (photo)chemistry, cloud nucleation	3-8 TgC/yr		minor?	Plants, soils, industrial, combustion	Spracklen et al. 2008, Roelofs 2008, Gantt et al. 2009

Table credit: Rafel Simo

- Ocean: ~ $7x10^5$ TgC DOM (about equal to atm. CO_2 mass)

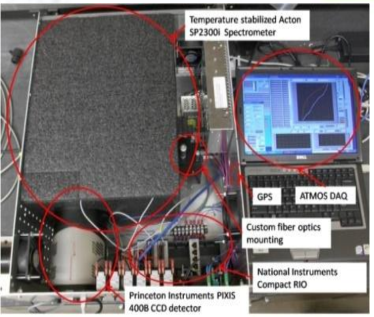
Conclusions

- OVOC strongly impact oxidative capacity in the remote MBL:
  - Reduce OH, Br, Cl radical abundances
  - Weak coupling also with I abundance (increases)
  - OVOC sink can explain 'missing BrO' over tropical Pacific Ocean
- A major organic carbon source from the ocean does involve DOM oxidation by O3 and photochemistry.
- This OVOC source is missing in atmospheric models, and creates model bias in our perception of Br and Cl radical abundances.
- Airborne measurements find elevated IO over most of the tropospheric air column above the Equatorial Pacific ocean. Reveal the potential that satellite maps may not indicate a boundary layer process (a-priori uncertainty in satellites).
- **Funding:**
NSF-ATM (CAREER award), NASA

The Volkamer Group

Atmospheric Trace Molecule Spectroscopy

http://www.colorado.edu/chemistry/volkamer



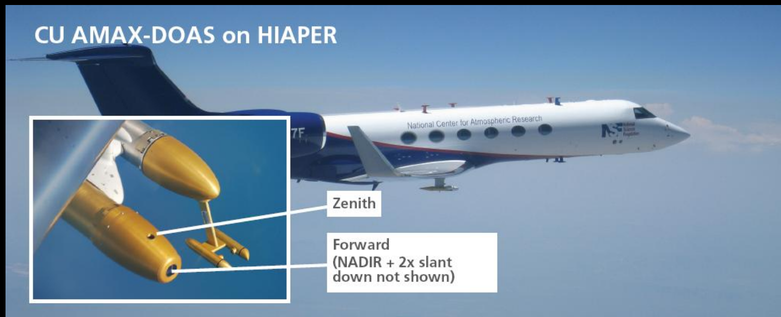
Thank you !

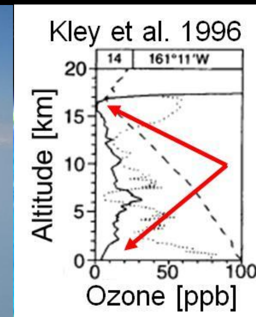
Band-pass Filter

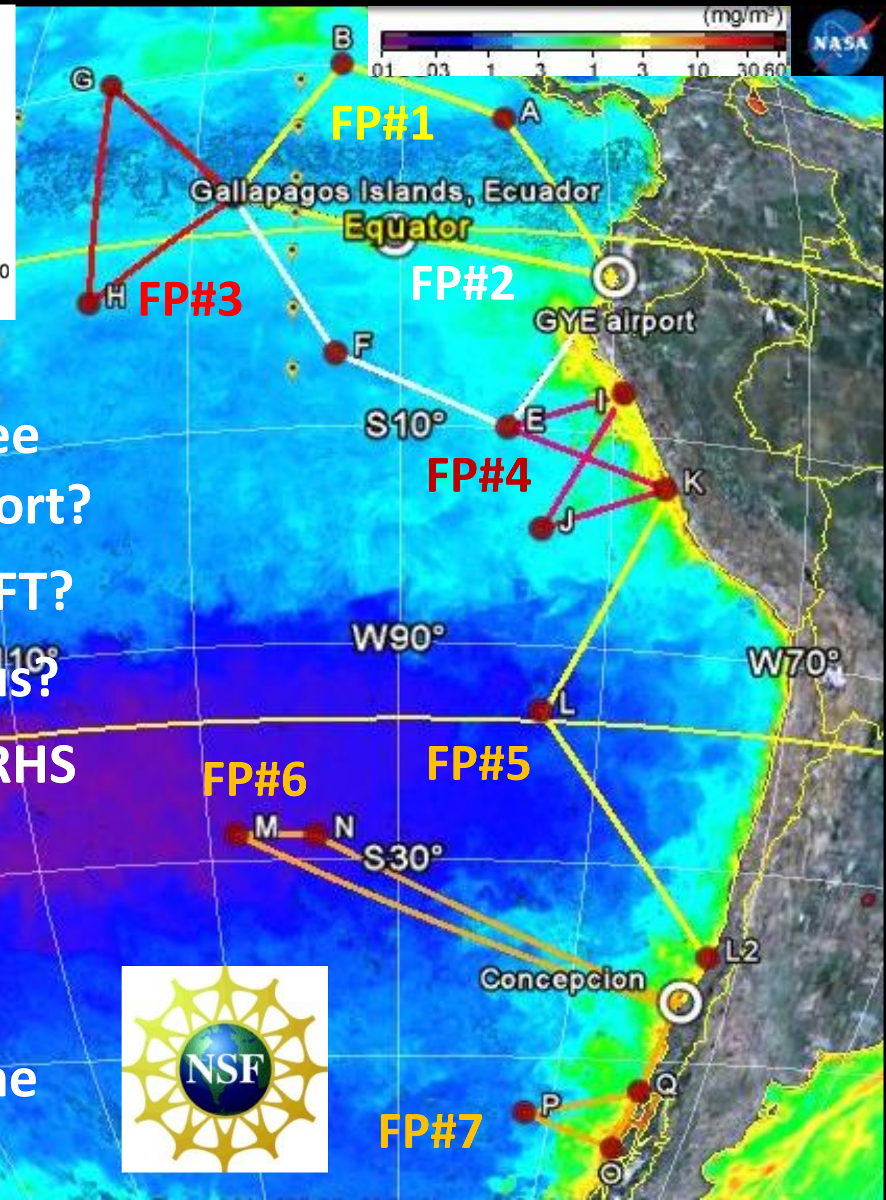
Job opening @ CU Boulder:
PhD project on AMAX-DOAS
rainer.volkamer@colorado.edu

Detector (CCD Spectrometer)

TORERO – Tropical Ocean tRoposphere Exchange of Reactive Halogen Species and OVOC (11Jan – 22Feb 2012)



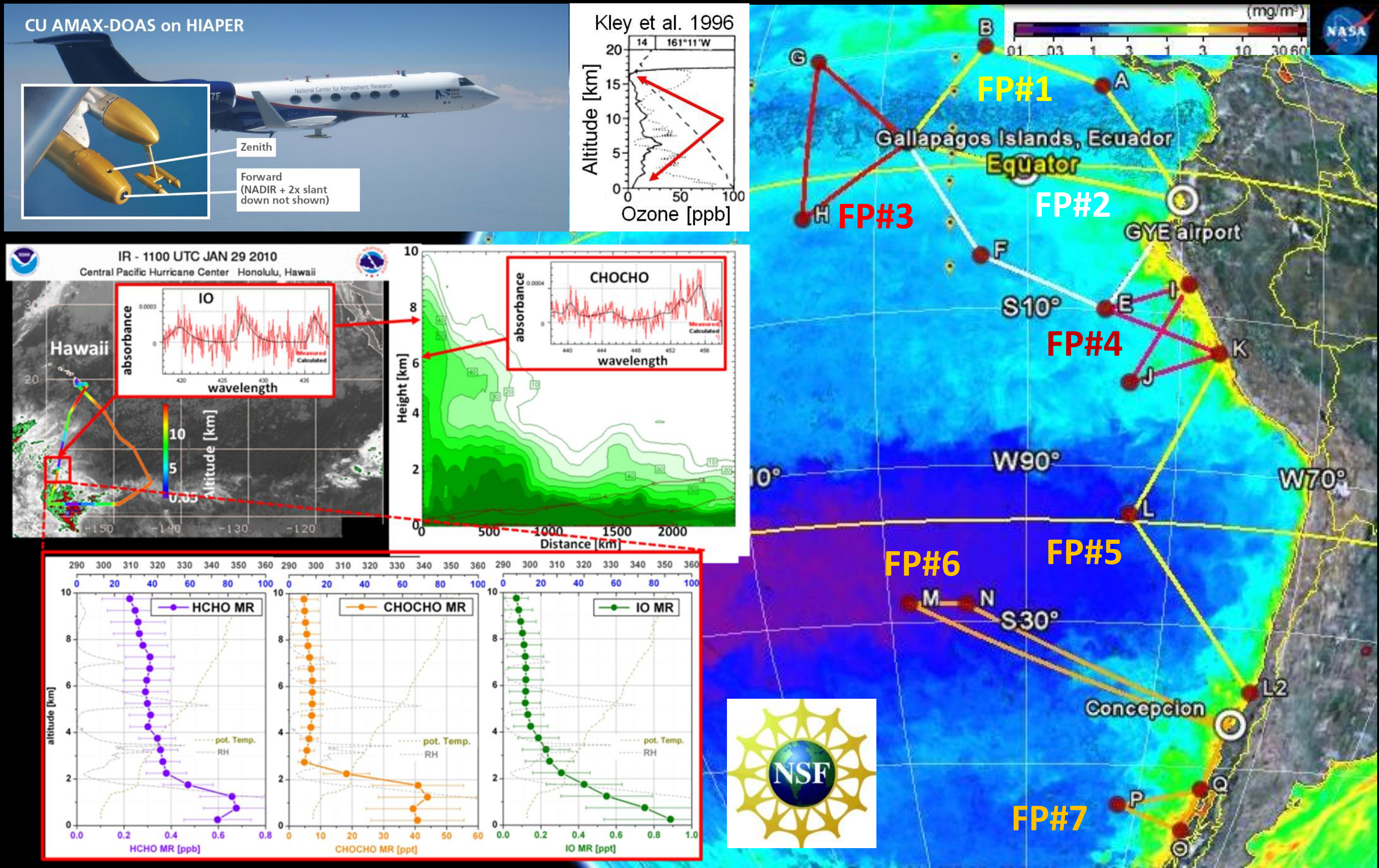




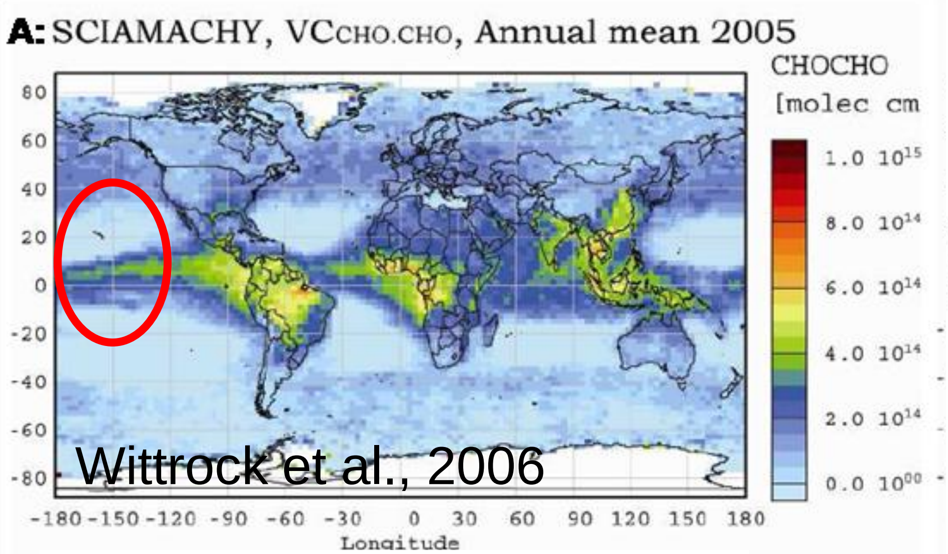
Science Questions:

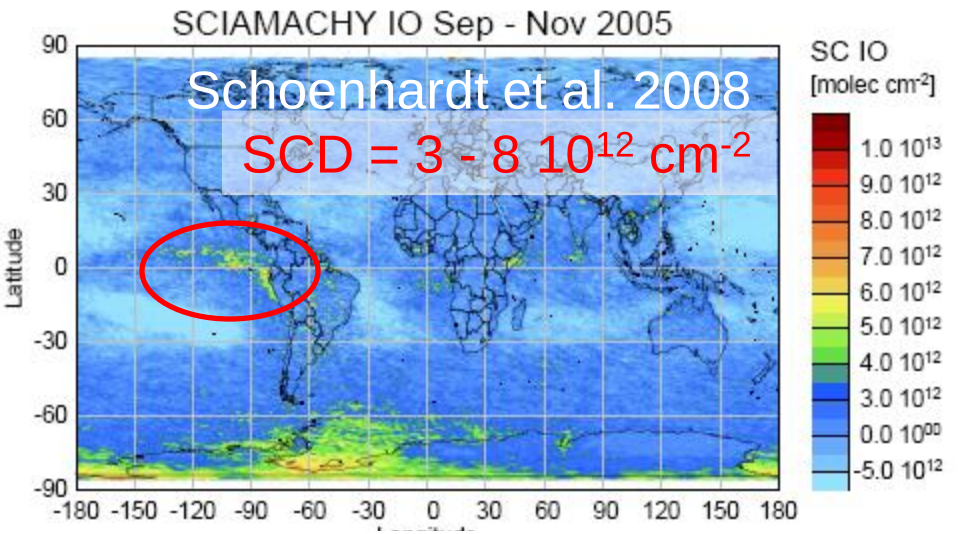
- How widespread is the impact on the free troposphere from deep convective transport?
- Do RIS trigger particle nucleation in the FT?
- Is there an effect of cirrus effective radius?
- How does the abundance of OVOC and RHS vary between areas with biologic activity, coastal upwelling and the ocean deserts?
- What is the role of Chl-a, CDOM?
- At what rate is ozone destroyed, methane oxidized, and aerosols formed?

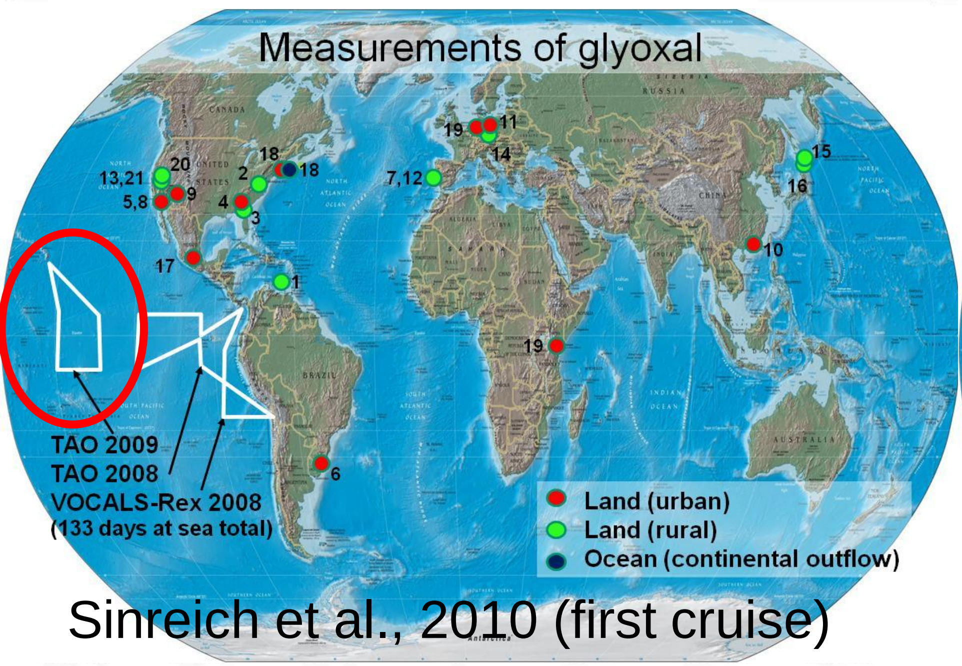
TORERO – Tropical Ocean tRoposphere Exchange of Reactive Halogen Species and OVOC (11Jan – 22Feb 2012)

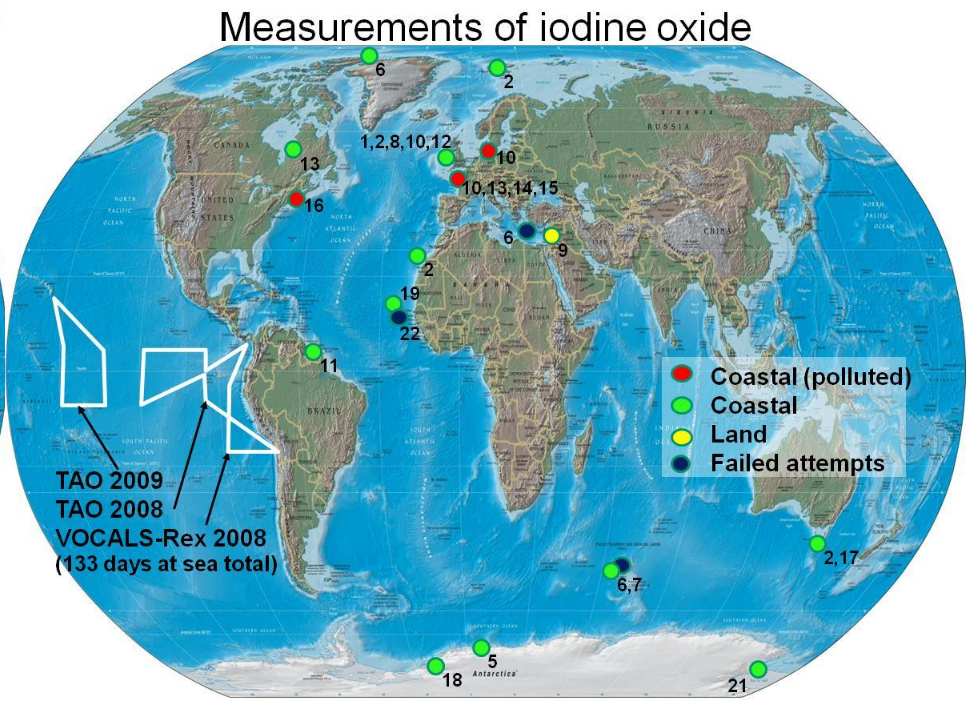


Glyoxal and IO over the open ocean?



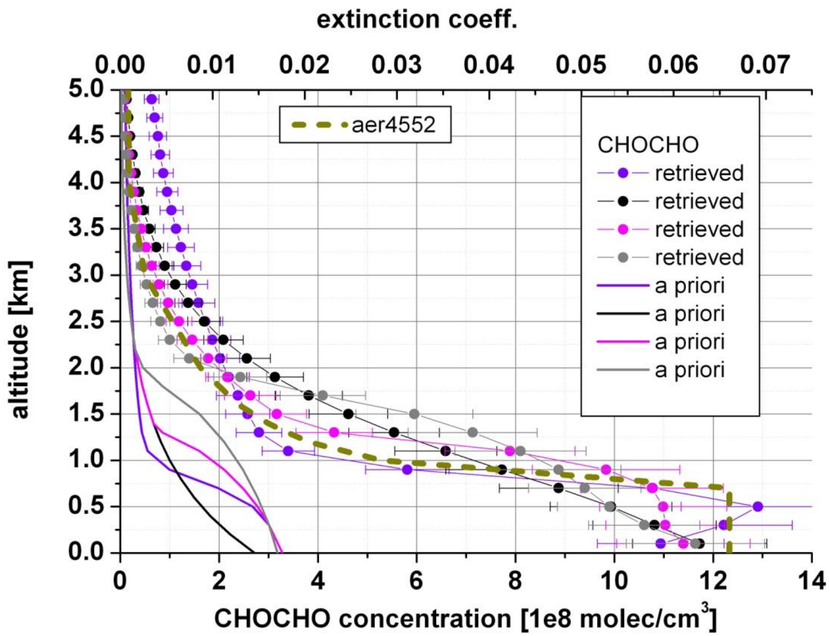


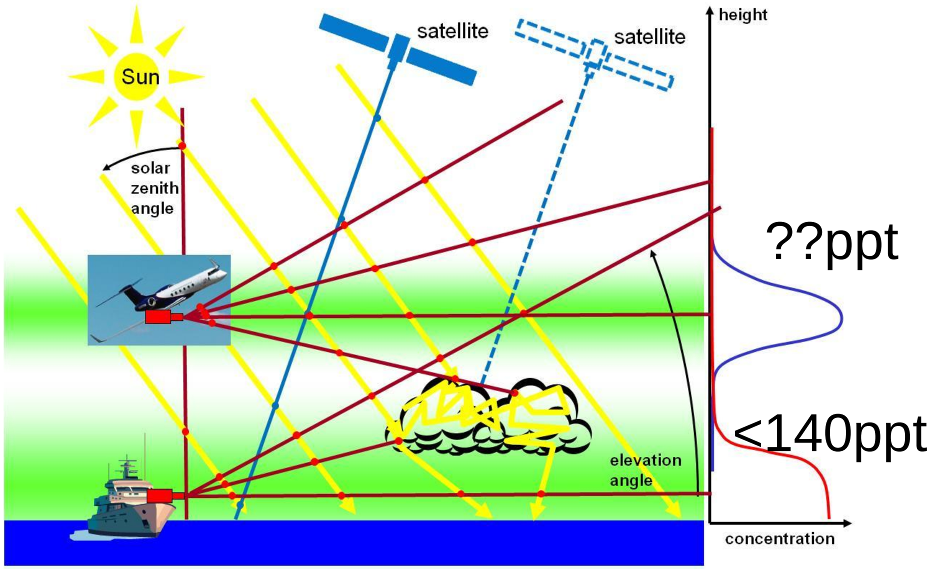




CU Ship MAX-DOAS

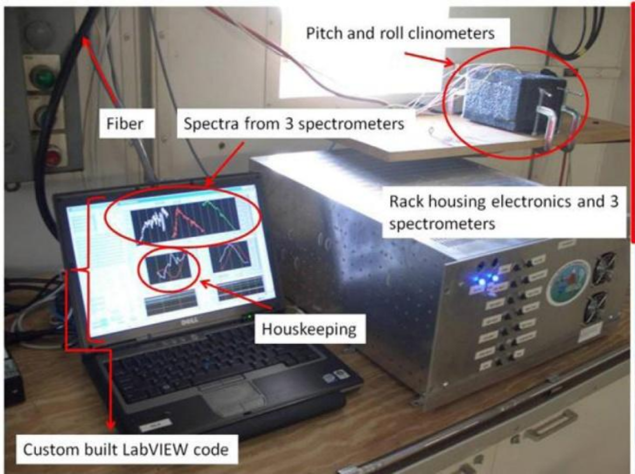
target gasses: CHOCHO, IO, NO_2, BrO, HCHO (OIO, I_2, SO_2)





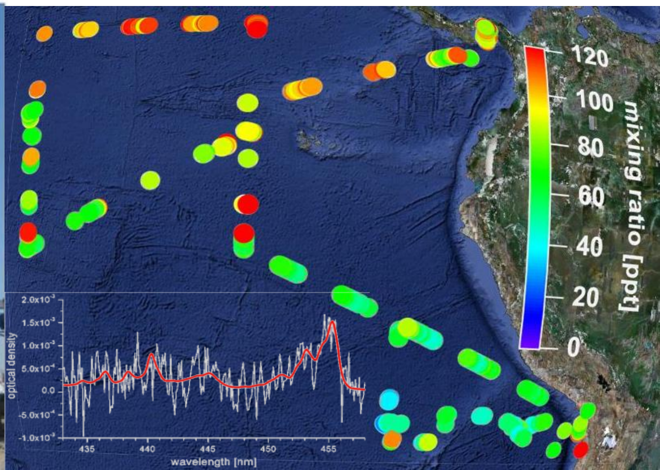
Sinreich et al., 2010, ACP

Inside: spectrometers/clinometers

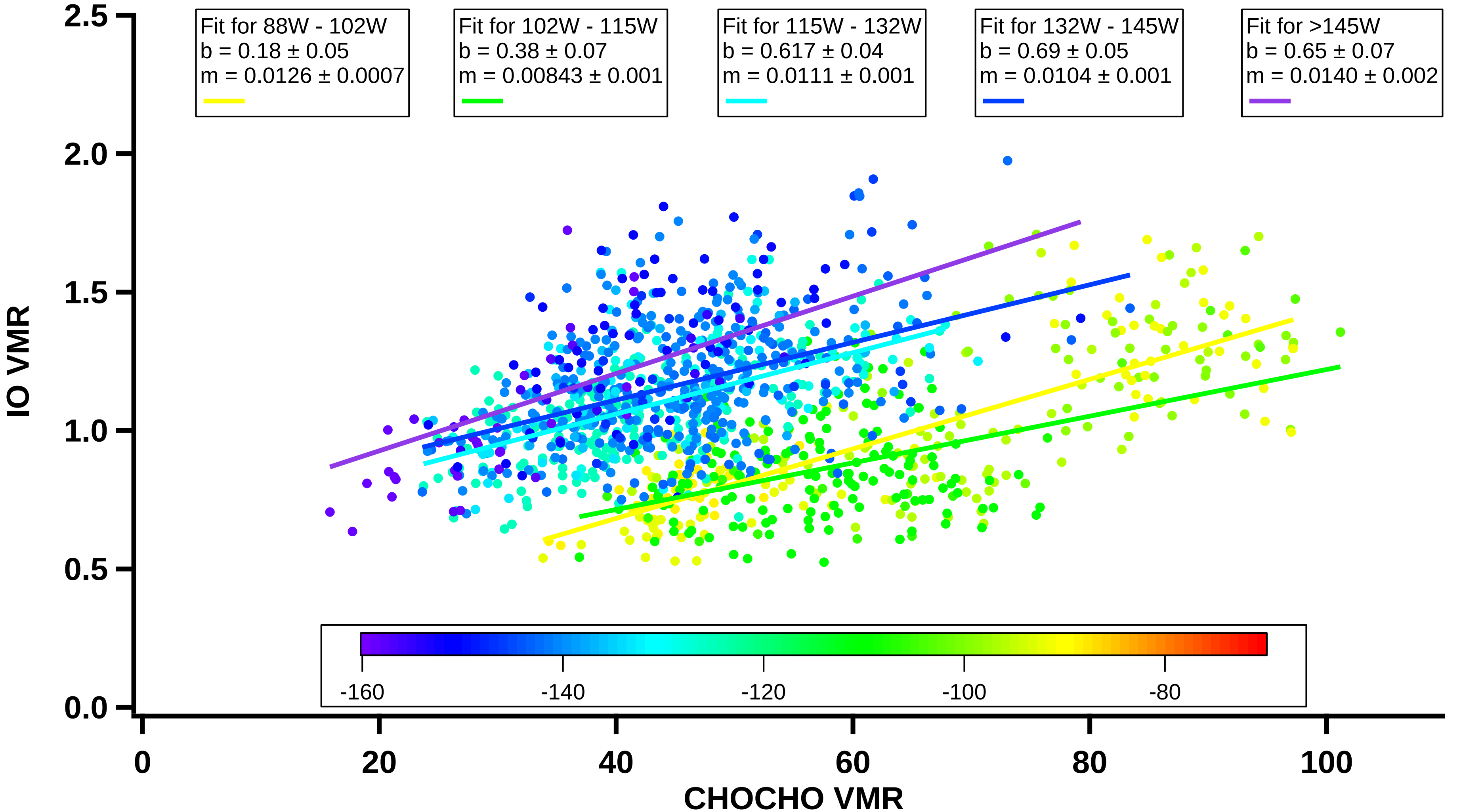


Outside: telescope

Cruise track (Oct08-Dec08)



Correlation: IO vs CHOCHO



- DOM oxidation rate and IO are positively correlated
- Increasing IO offset concentration towards the West!

Reaction mechanisms

Photo-redox chemistry: I_2 **(Cl_2,Br_2)**

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

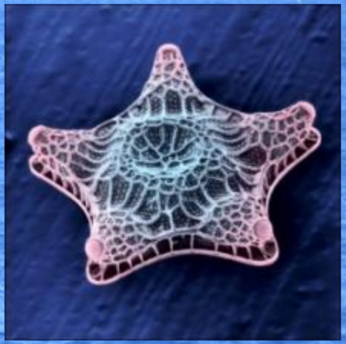
$I + I \rightarrow I_2$

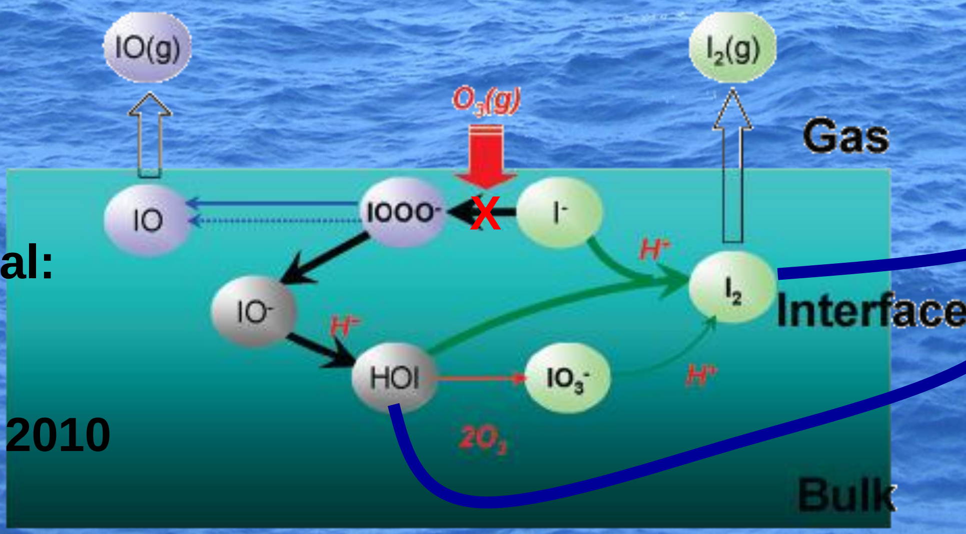
$I_2 + hv \rightarrow 2\ I$

$I + O_3 \rightarrow IO + O_2$

$OH, Cl, Br, O_3 + DOM \rightarrow \rightarrow CHOCHO, HCHO$

(chemical reason to accumulate I_2, but not Br_2 or Cl_2 => BrO)





CH_2ClI, CH_2I_2

DOM

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

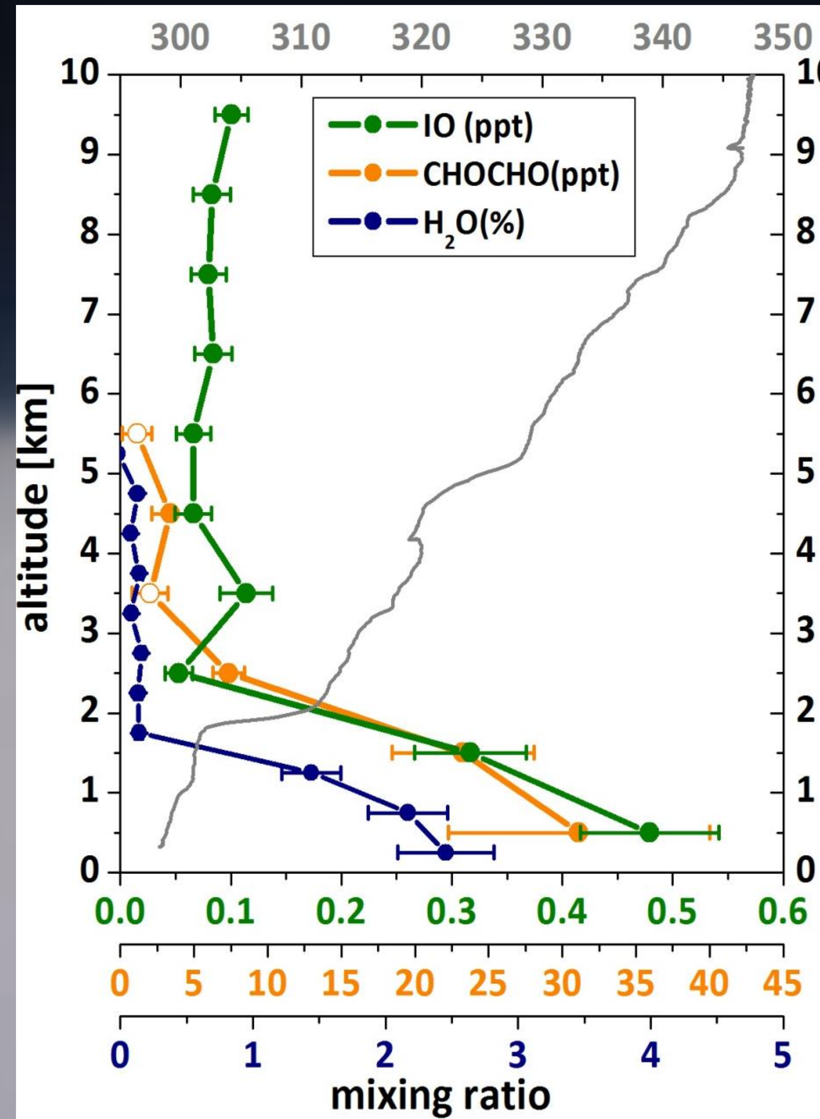
Martino et al: CH_2ClI, CH_2I_2 concentrations are very low (E. Atlas, pers. comm.)

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

IO in the tropical free troposphere

VCD IO [x1E12 molec./cm²]			
location	Total	MBL (800m)	Above 800m
ascent	2.79 (100%)	1.17 (41.9%)	1.62 (58.1%)

cloud cover	simulated satellite SCD IO [x1E12 molec./cm²]		
0%	4.58 (100%)	1.31 (28.6%)	3.27 (71.4%)
20%	4.62 (100%)	0.80 (17.3%)	3.82 (82.7%)
40%	4.64 (100%)	0.54 (11.6%)	4.1 (88.4%)



$$\sigma_{IO} = 2.7 \times 10^{-17} \text{ cm}^2$$

=> $\delta'_{MBL} < 3 \times 10^{-5}$

Only ~12% of satellite signal originates from within the MBL at moderate cloud cover