University of Colorado Boulder

CIRES

Comparison of ship and airborne observations of glyoxal and IO in the remote marine boundary layer

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TORERO WORKSHOP
06/24/2014

MOTIVATION

Importance of CHOCHO and IO:

- Both affect atmospheric oxidation capacity (HOx, NOx cycles)
- Both modify existing/form new particles that could act as CCN
- IO: catalytic ozone destruction
- CHOCHO: formation of Secondary Organic Aerosol (SOA)

Up to now:

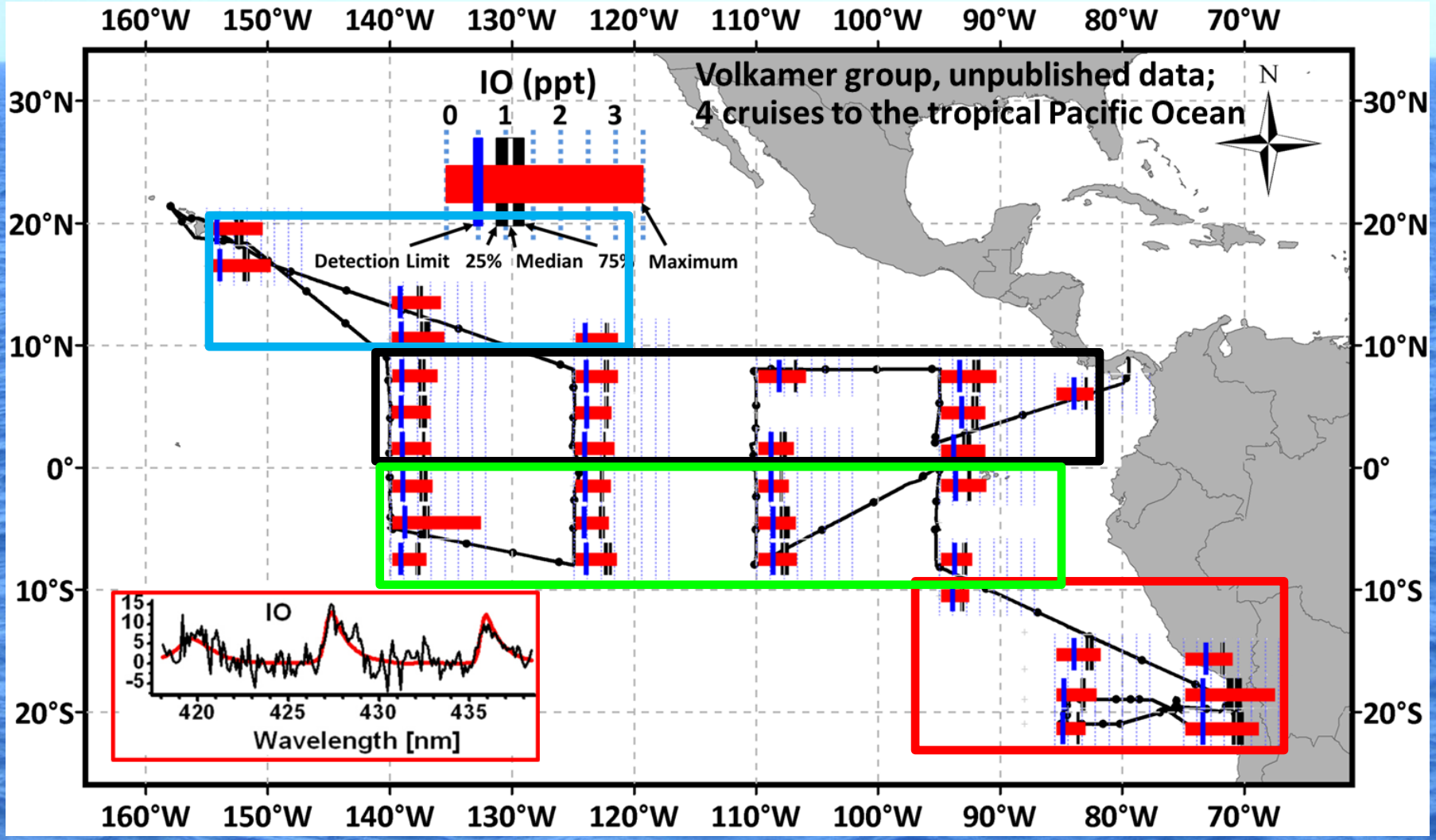
There have been numerous studies have detected CHOCHO and IO in (mainly) coastal-, Antarctic-, and sub-tropical MBL.
Recent studies detected IO in the free troposphere (Dix et al., 2013)

Open questions:

- Global distribution
- Source mechanisms

Poster:
Anthropogenic Triggers of Multiphase Chemistry of Glyoxal; Eleanor Waxman,

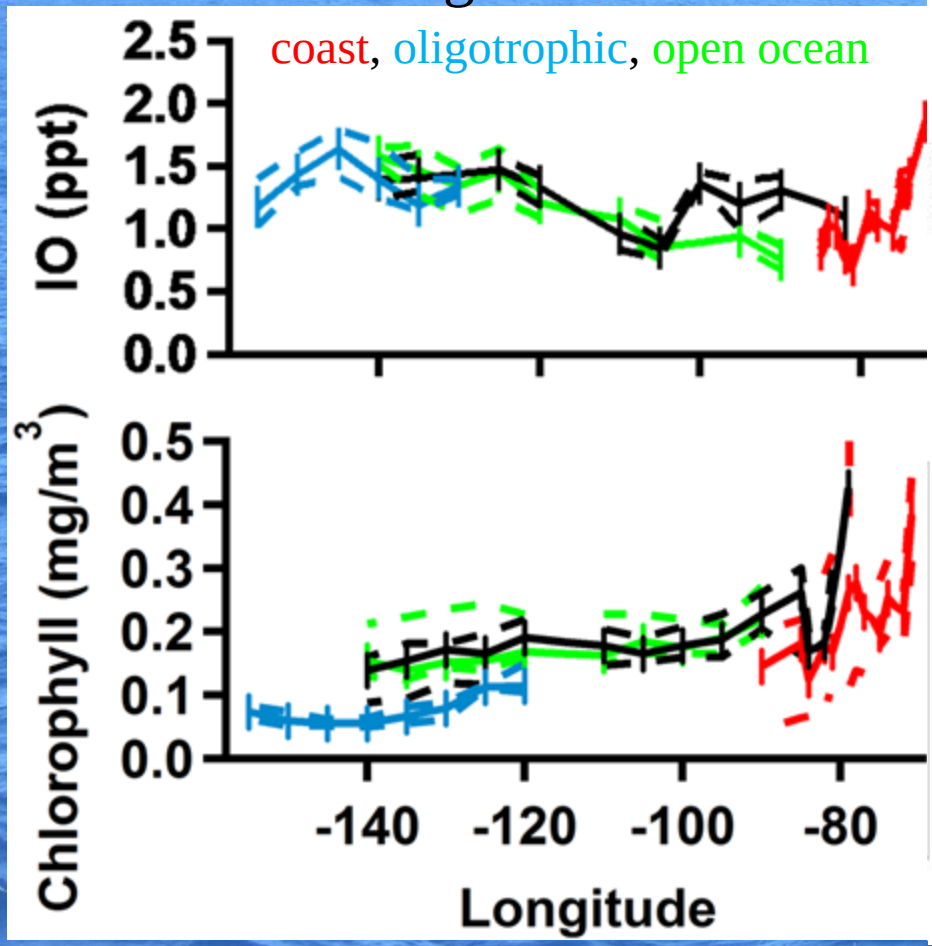
IO over the open ocean

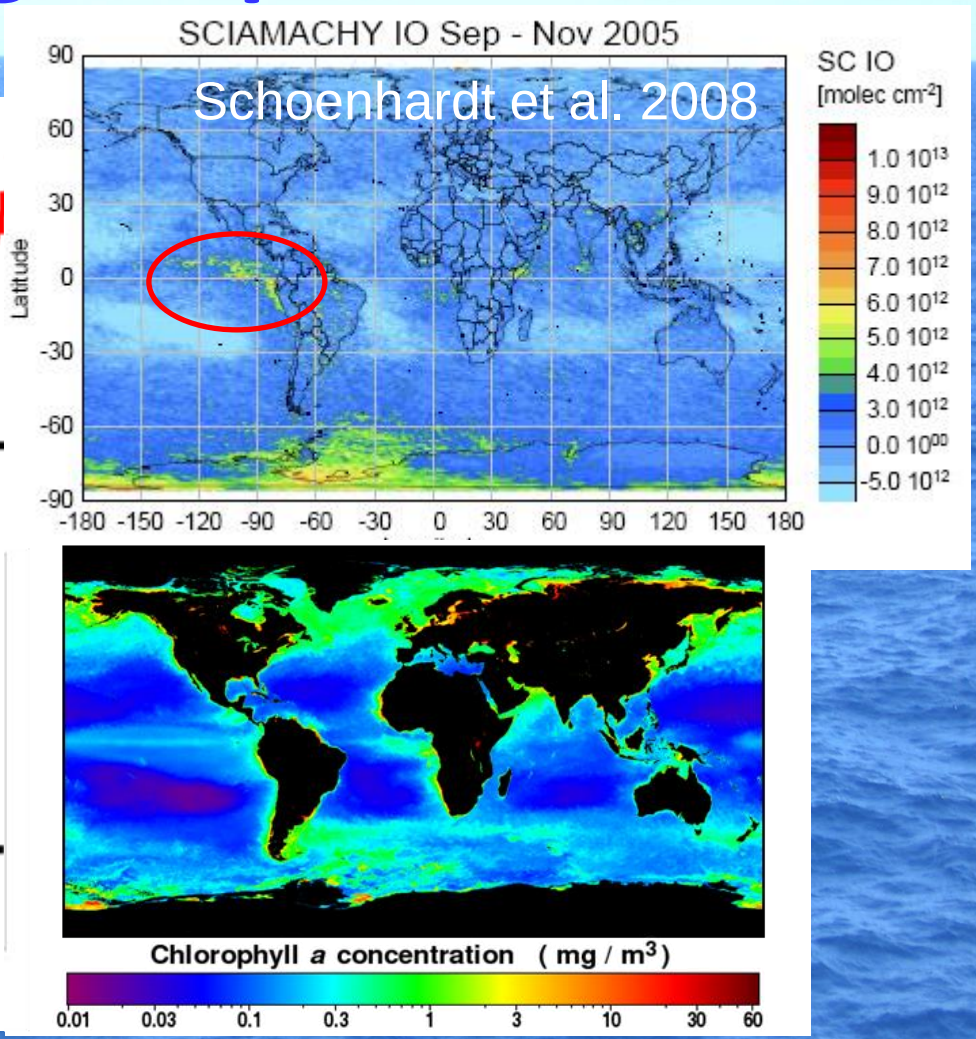


- Weak gradient of IO increasing from mesotrophic to oligotrophic ocean

IO over the oligotrophic ocean

Remote sensing: SMAX-DOAS

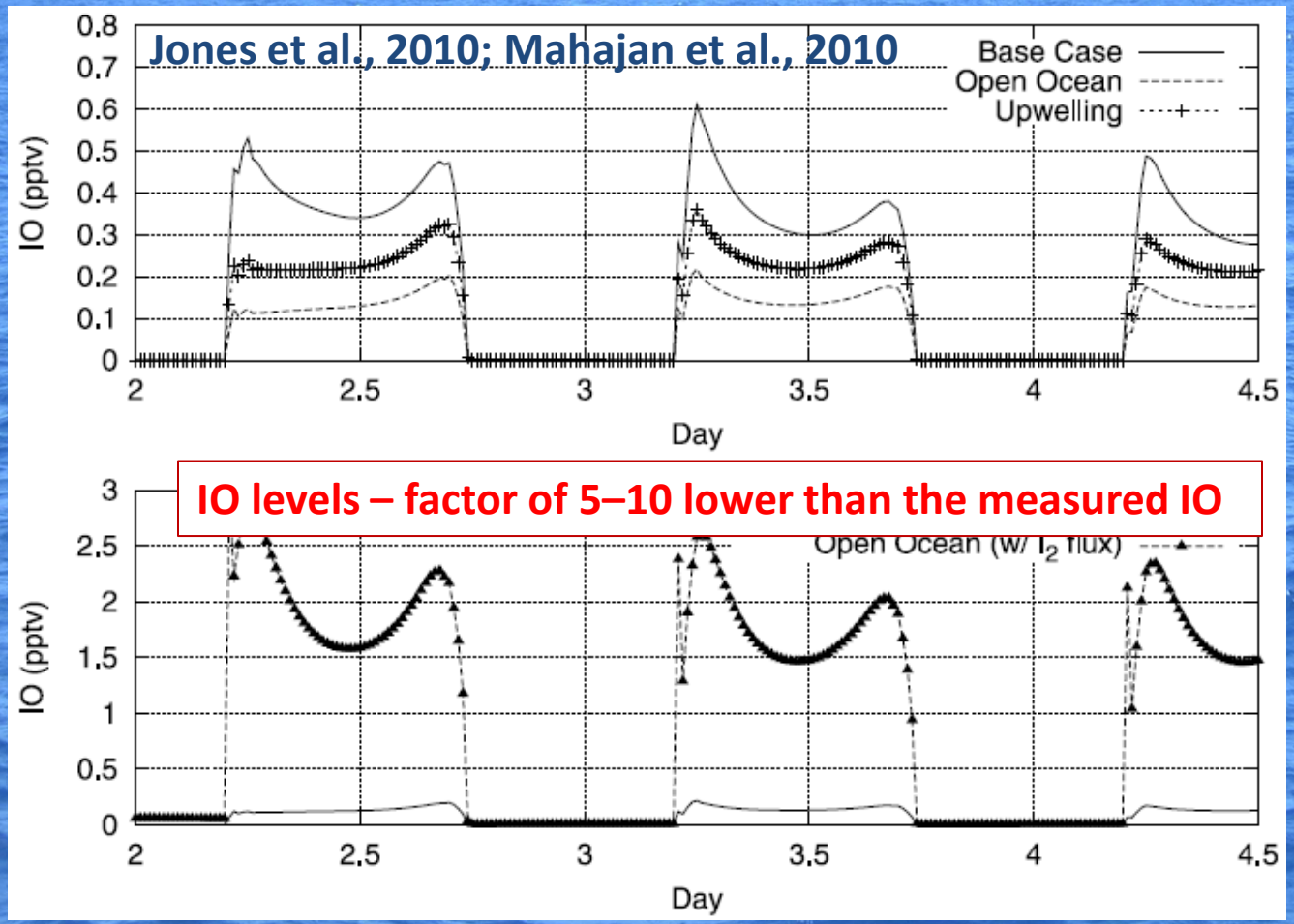




- **Elevated IO over the oligotrophic ocean does not agree with the idea of iodine sources being primarily 'biological'.**
- **Satellite IO shows (some) correlation with Chl-a**

Reactive Iodine Species

Could a comprehensive sea-air fluxes of VOIC could explain the IO levels?
Should it be possible to bring together their emissions to locally observed IO?



only organic iodine gases as iodine precursors (biological source)

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

Carpenter et al., 2013 proposed the formation of HOI

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

Global IO measurements with LP- and CE-DOAS

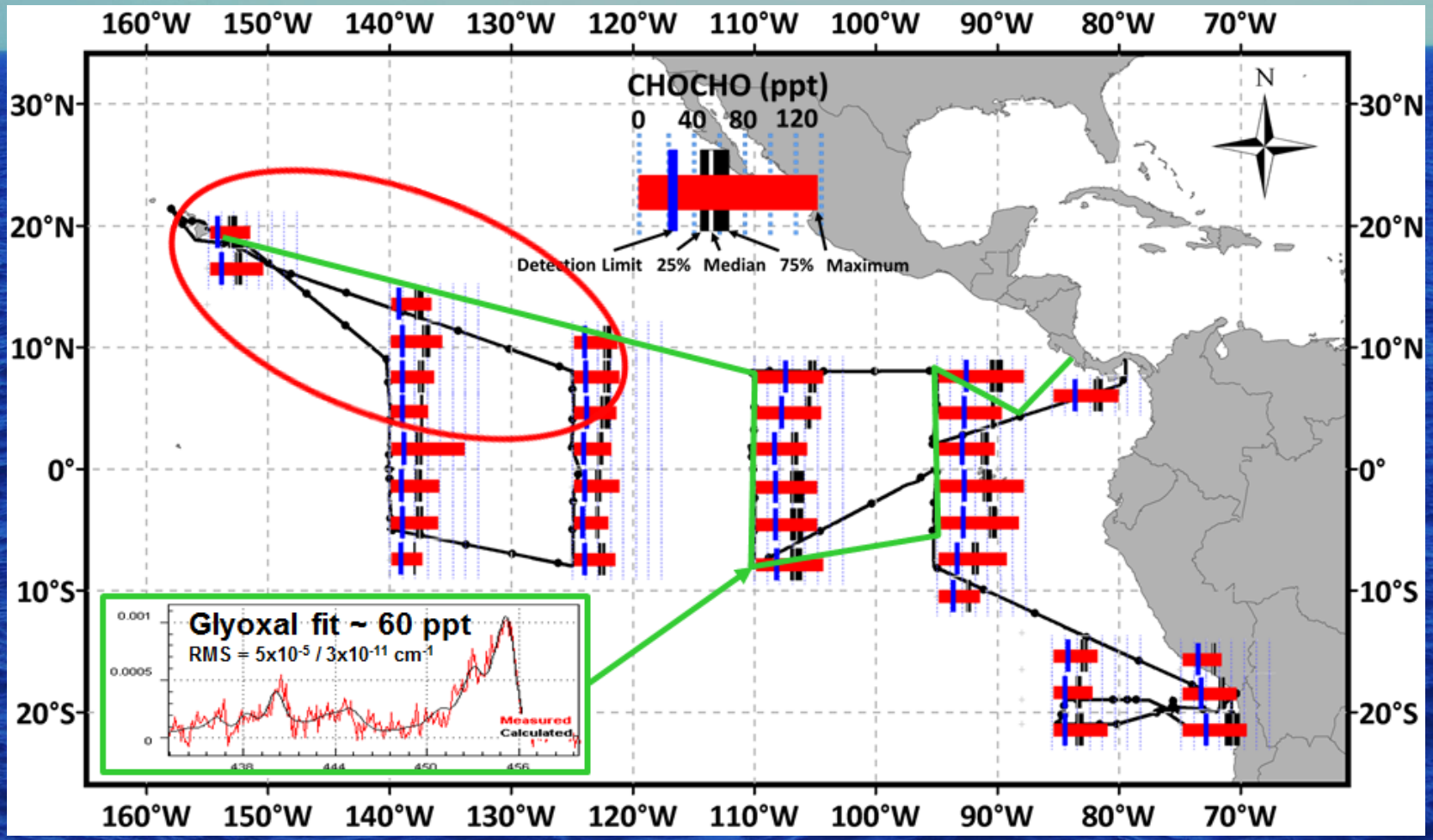
Data: D. Poehler (university of Heidelberg)

Location	Type	Period	Method	IO Value
Amundsen, Arctic	Polar	03 – 04/2008	LP	< DL 0.3ppt
Neumayer Station, Antarctica	Polar	02/2011	CE	< DL 1.5ppt
Scott [illegible]	[illegible]	[illegible]	[illegible]	[illegible]ppt
Ross [illegible]	[illegible]	[illegible]	[illegible]	[illegible]ppt
El [illegible]	[illegible]	[illegible]	[illegible]	[illegible]ppt
Ca [illegible]	[illegible]	[illegible]	[illegible]	[illegible]ppt
Ca [illegible]	[illegible]	[illegible]	[illegible]	[illegible]ppt
SHIVA-Sonne , West Pacific	Marine, Open Ocean	11/2011	CE	< DL 2.0ppt
SOPRAN P91, Peru, East Pacific	Marine, Upwelling Region	12/2012	CE	Up to 2.0ppt

Goal 1:
First comparison of IO in the MBL by different instruments/methods:
SMAX- and AMAX-DOAS (passive remote sensing)

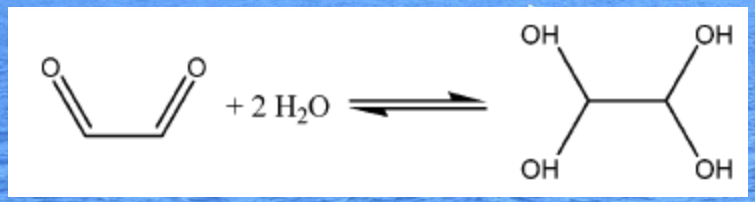
- How can we established confidence of the IO levels?
- Are IO concentrations below the observed DL atmospherically relevant?

Glyoxal over the open ocean

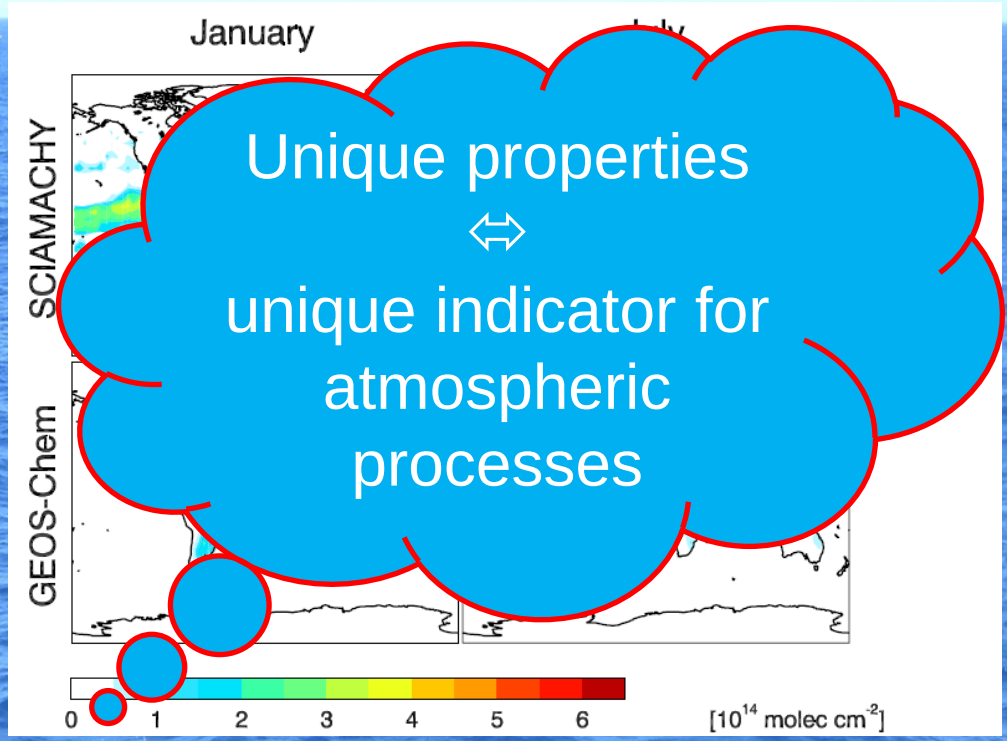


- Glyoxal is observed also over the oligotrophic ocean!
- Mahajan et al. (2014) reported average concentration of about 25 pptv with an upper limit of 40 pptv
- What is the source? What is the information content?

Glyoxal: physical and chemical properties



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



Fu et al (2008) JGR

Continental source: ~45 TgC/yr

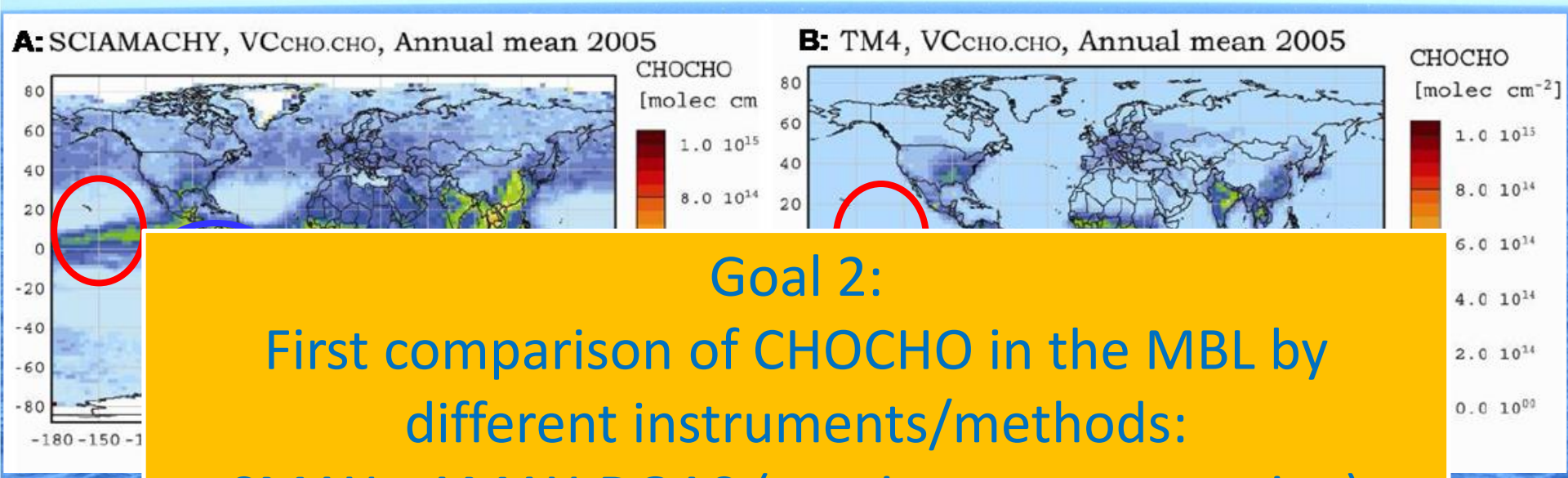
- 50% unaccounted
- 30% biogenic (i.e. isoprene)
- 14% anthropogenic
- 6% biomass burning

Atmospheric lifetime: ~ 2.5hrs

- 52% photolysis
- 18% OH
- 22% SOA in clouds/aerosols?
- 8% Dry/wet deposition

Stavrakou et al., 2009

Glyoxal over oceans remains unexplained



Goal 2:
First comparison of CHOCHO in the MBL by different instruments/methods:
SMAX-, AMAX-DOAS (passive remote sensing) and In-situ CE-DOAS (active)

2010

Lack … tes

- → Secondary VOCs can not account for most glyoxal
- → Glyoxal source probably from DOC
- → Previous comparison between SMAX-DOAS for glyoxal (Mahajan et al., 2014)

Stavrakou et al., 2009

Overall goal

- Despite efforts to quantify these species, uncertainties remain concerning the regional distribution of sources and sinks of these compounds and their impact on MBL chemistry
- Understand release processes of halogens at the air-sea interface
- Comparison of IO and Glyoxal levels using different instruments/retrievals.
- What is the vertical profile of IO and glyoxal during TORERO?
- We present CHOCHO and IO mixing ratios and altitude profiles at the time of one of the overflights of the GV aircraft over the vessel (Research flight 17, February 26, 2012) and compare values of three different devices as a case study.

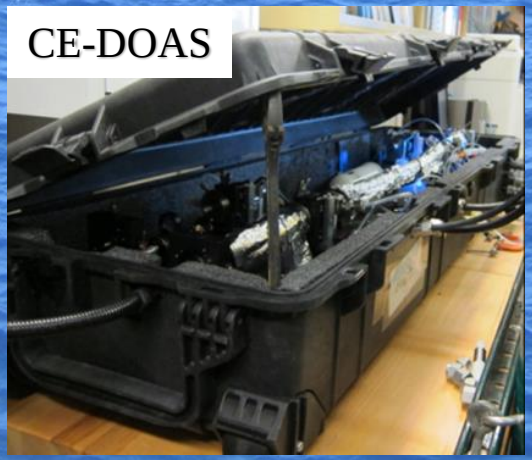
TORERO: instrumentation

- The scientific objective of the TORERO project was to study the release, transport and fate of reactive halogen gases and oxidized VOCs, and their effect on the atmospheric oxidation capacity in the Eastern Tropical Pacific Ocean during the season of high biological ocean productivity.

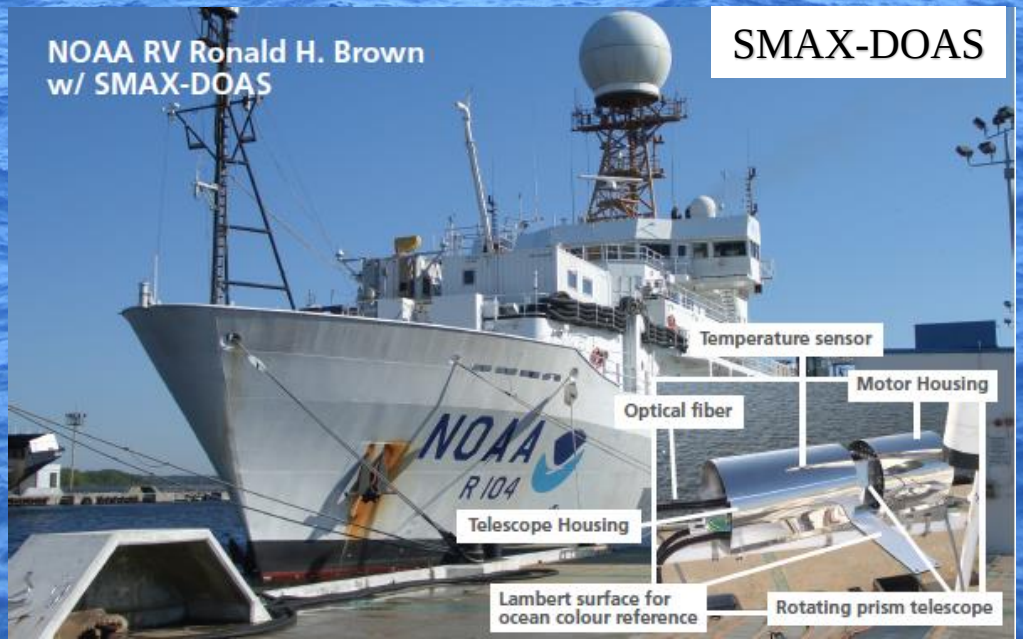
- The project utilized the NSF/GV aircraft: Aircraft - MAX-DOAS
- The cruise of the NOAA RVKa'imimoana: Ship - MAX-DOAS and CE-DOAS

AMAX-DOAS

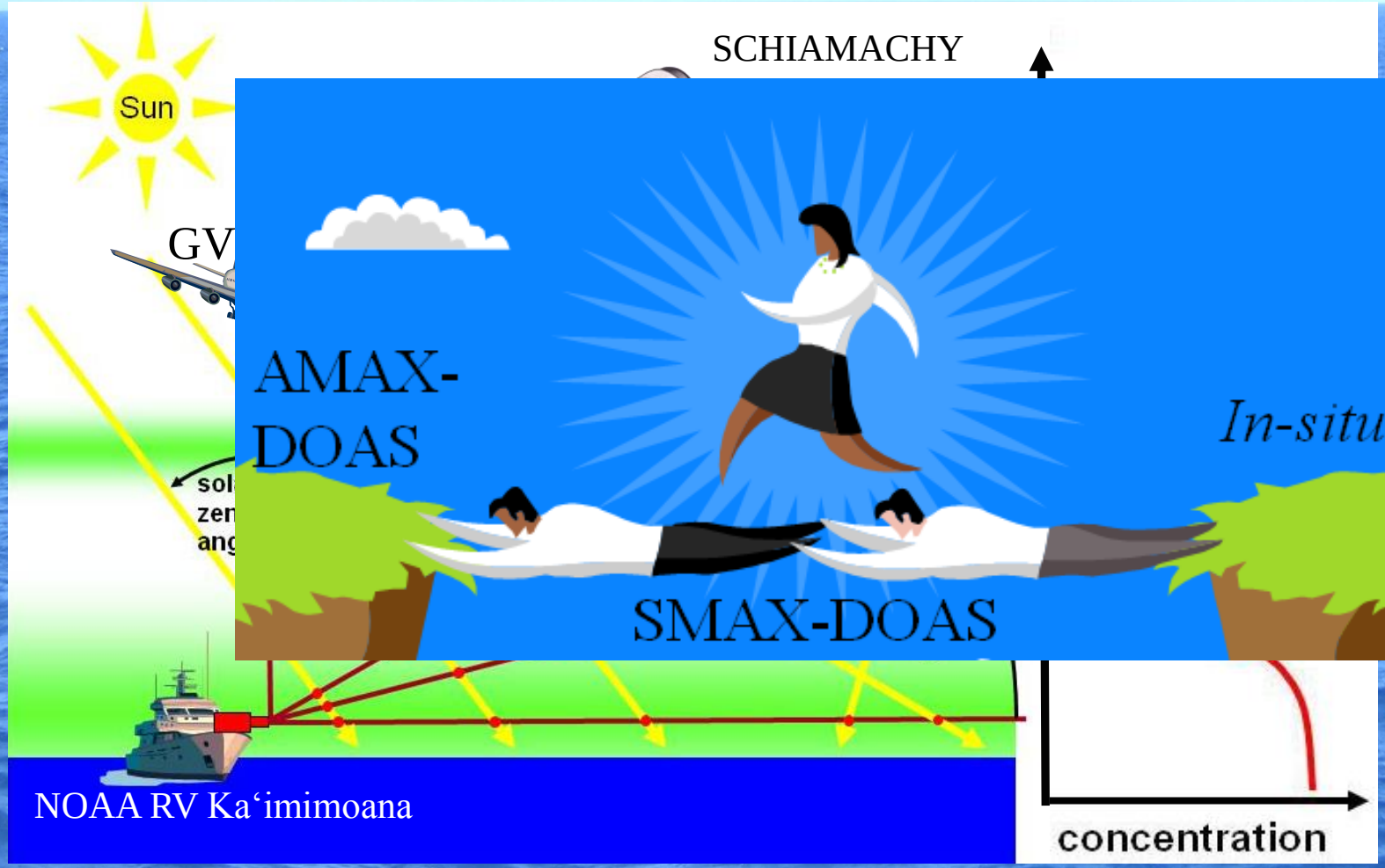
CE-DOAS



SMAX-DOAS

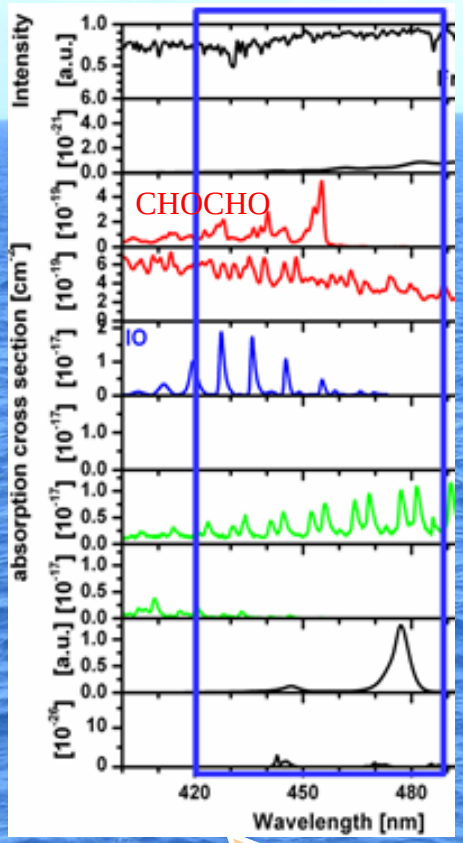


DOAS measurements devices



- Photons travel on parallel paths from the sun to the Earth‘s atmosphere
- The telescope collects photons from discrete viewing directions
- The lower the Elevation Angle the longer the light path through the BL

Trace gas inversion



DOAS-equation

Remove with polynomial

$$\frac{I(\lambda)}{Io(\lambda)} = \exp-\left[\underbrace{\sum \sigma_i'(\lambda) c_i l}_{\text{absorption}} + \underbrace{(\sigma_i^0 c_i + \alpha_{Ray}(\lambda) + \alpha_{Mie}(\lambda))l}_{\text{scattering}}\right]$$

Narrow band

Broad band extinction

DOAS-equation

$$\ln\left[\frac{I(\lambda)}{I_0(\lambda)}\right] = -\sum_i \sigma_i'(\lambda)\, SCD_i - \sum_p a_p \lambda^p + \text{Residual}(\lambda)$$

$$SCD = \int c_i(l)\, dl$$

Integrated absorber concentration c along the light path *l*

SCD

O_4

AMAX

CE-D

Path length

Trace gas VMR

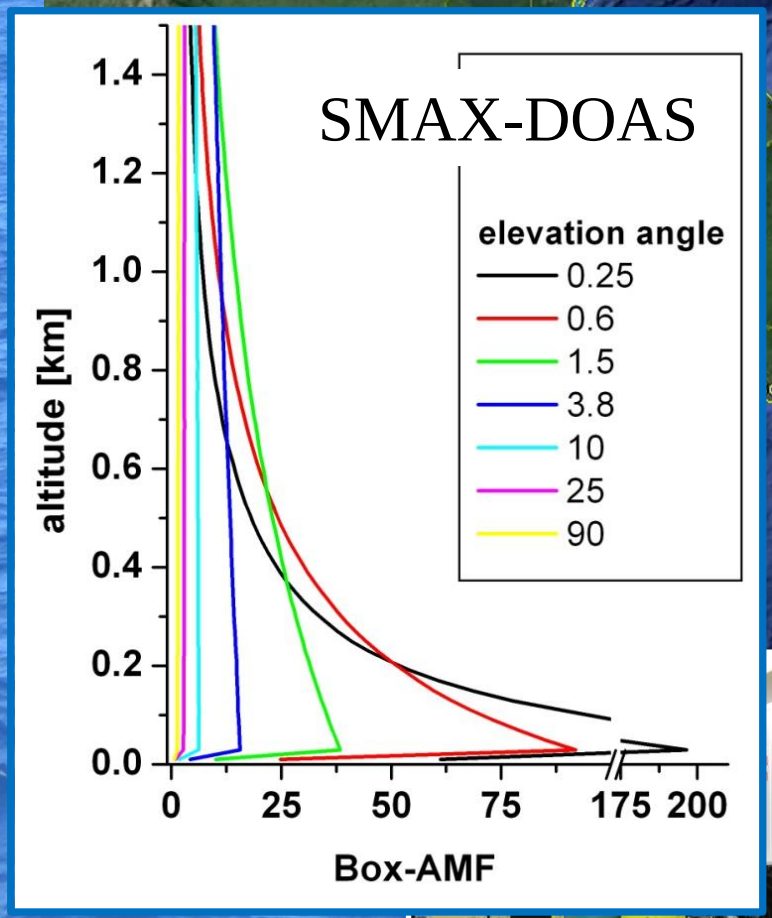
Poster:
AMAX-DOAS data interpretation: Comparison of optimal estimation and parameterization; Barbara Dix

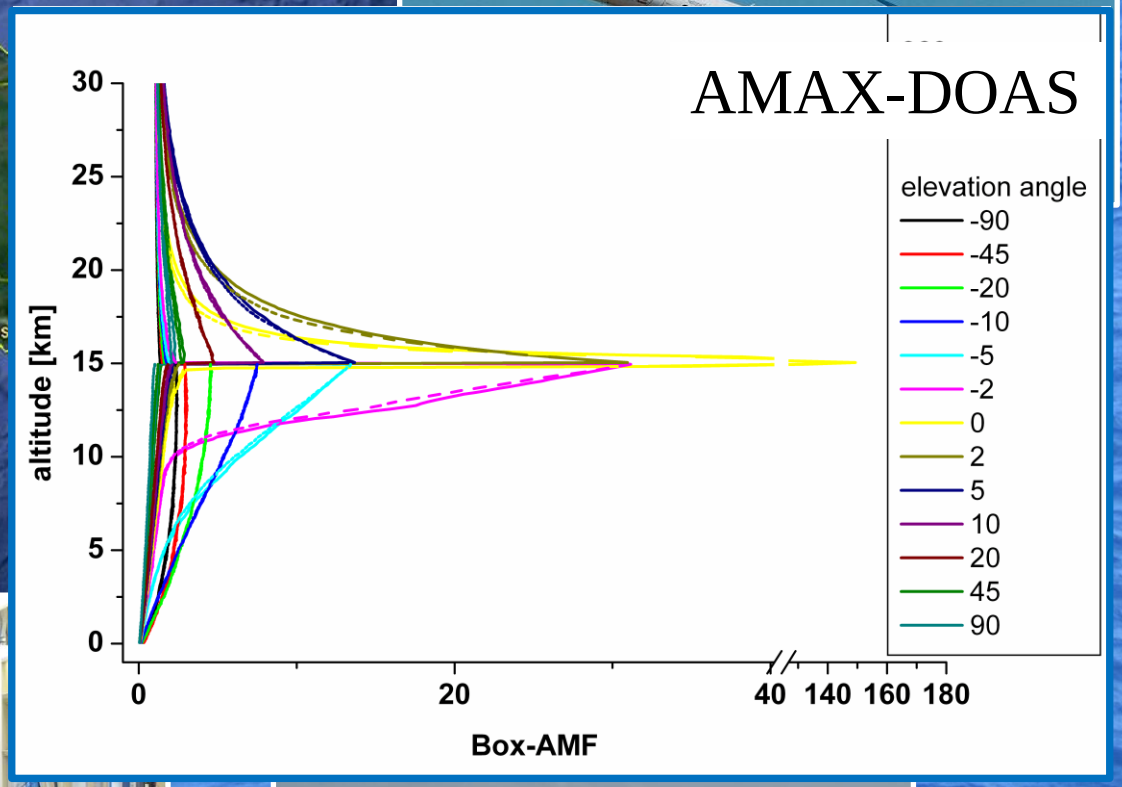
1) Optimal Estimation
2) Parameterization

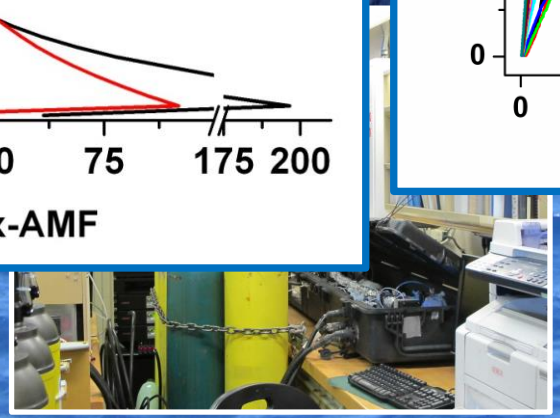
Trace gas profiles

Measurement Location: RF 17

(Optimized overpass for comparison)

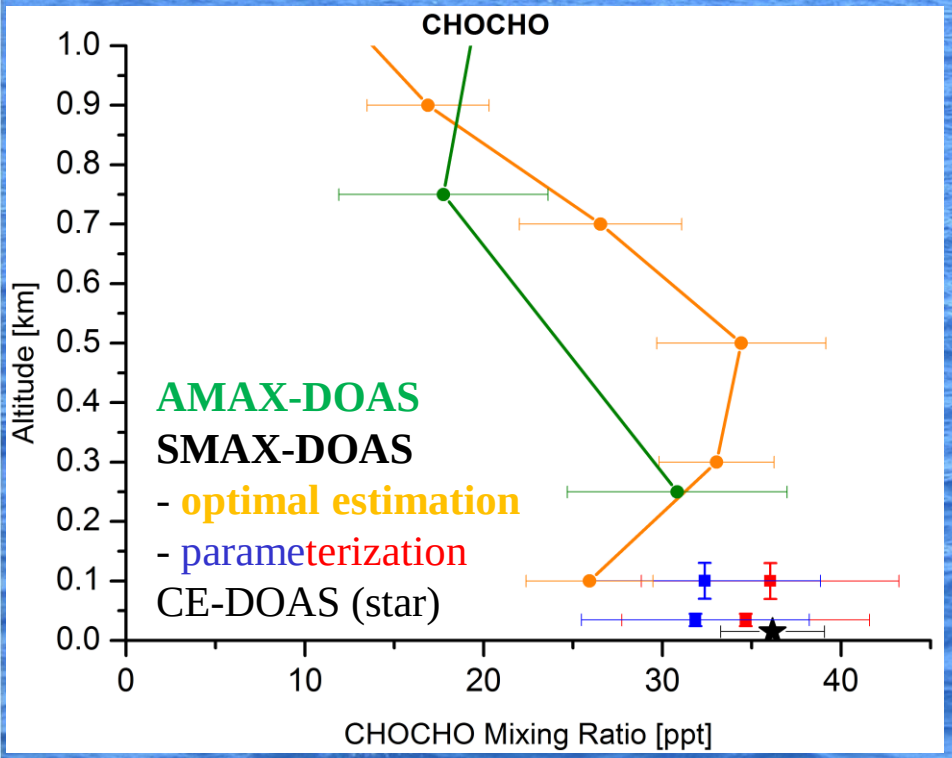




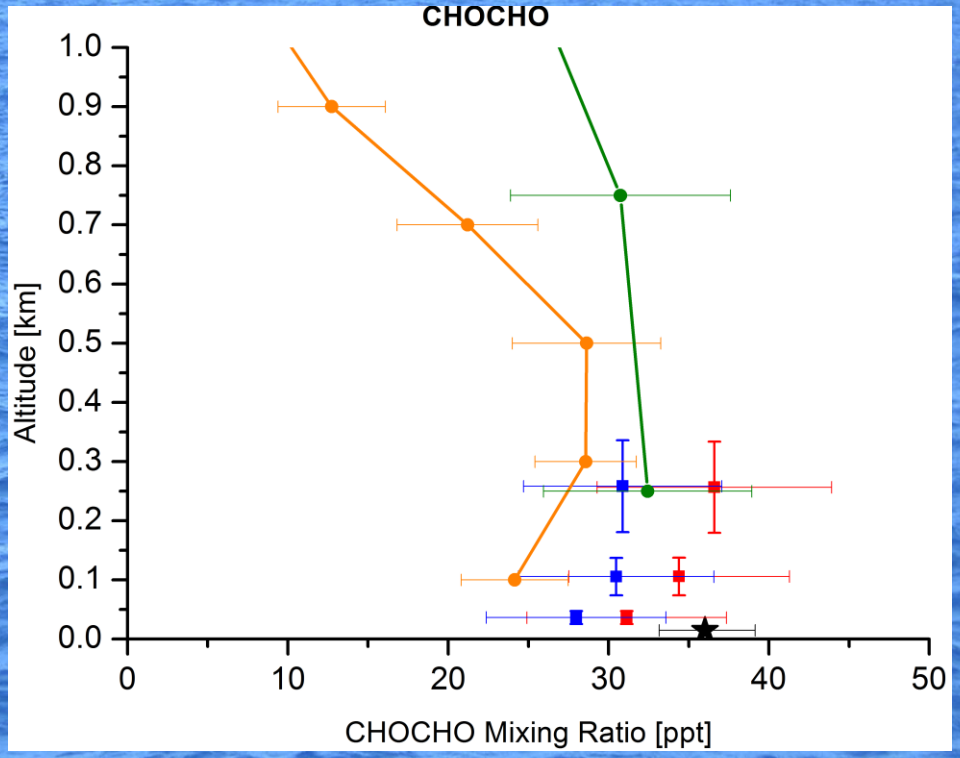


Measurements comparison: CHOCHO

Descent



Ascent

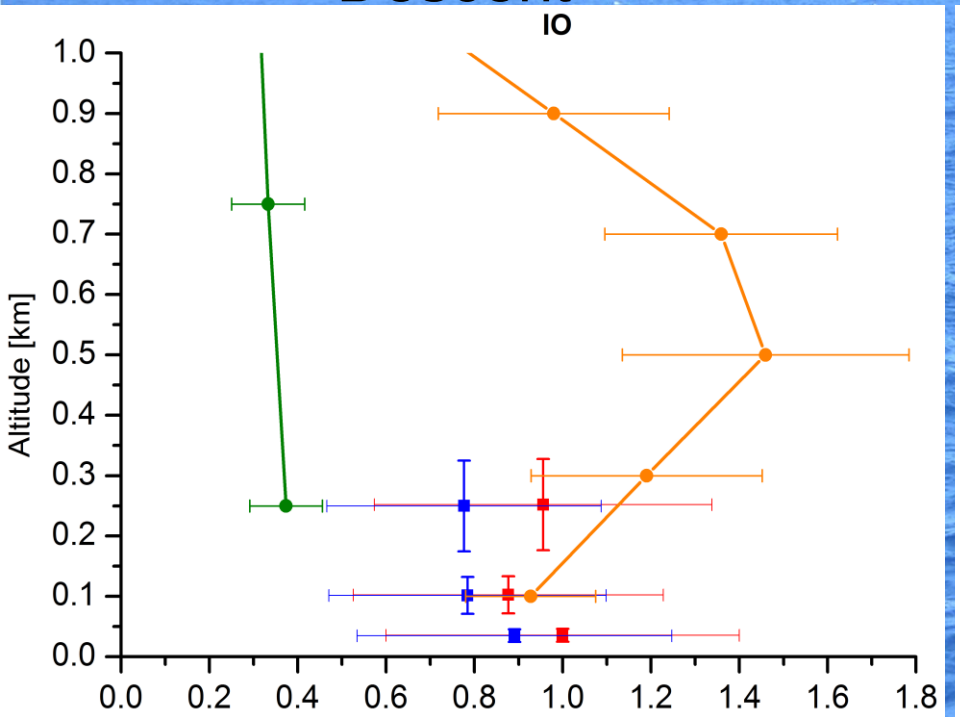


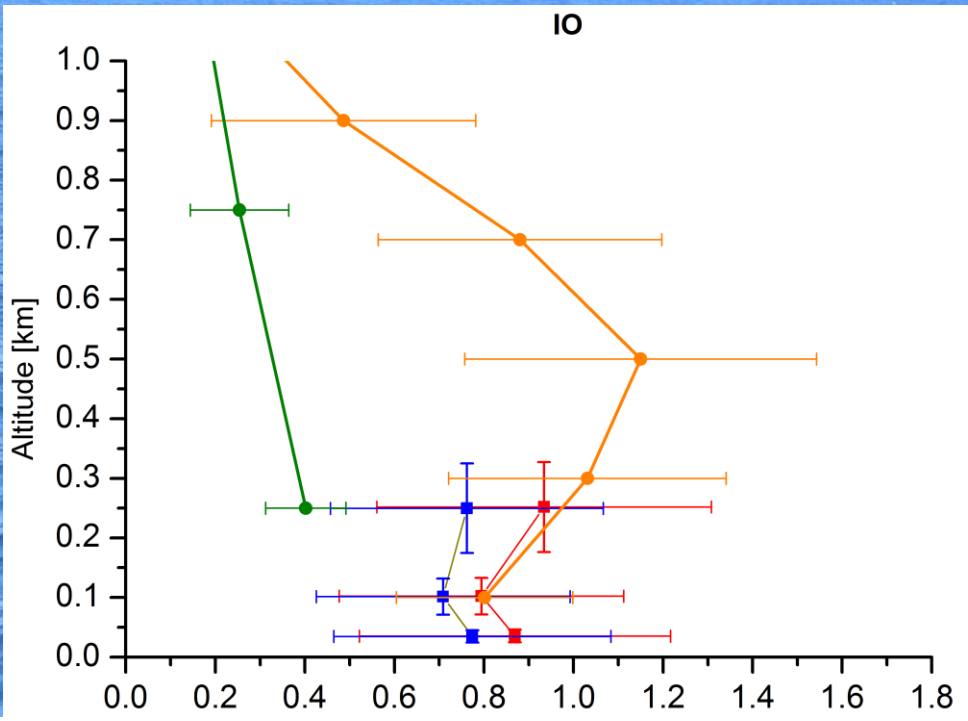
Consistent with Mahajan et al. (2014) → reported average concentration of about 25 pptv with an upper limit of 40 pptv

Measurements comparison: IO

Descent

Ascent



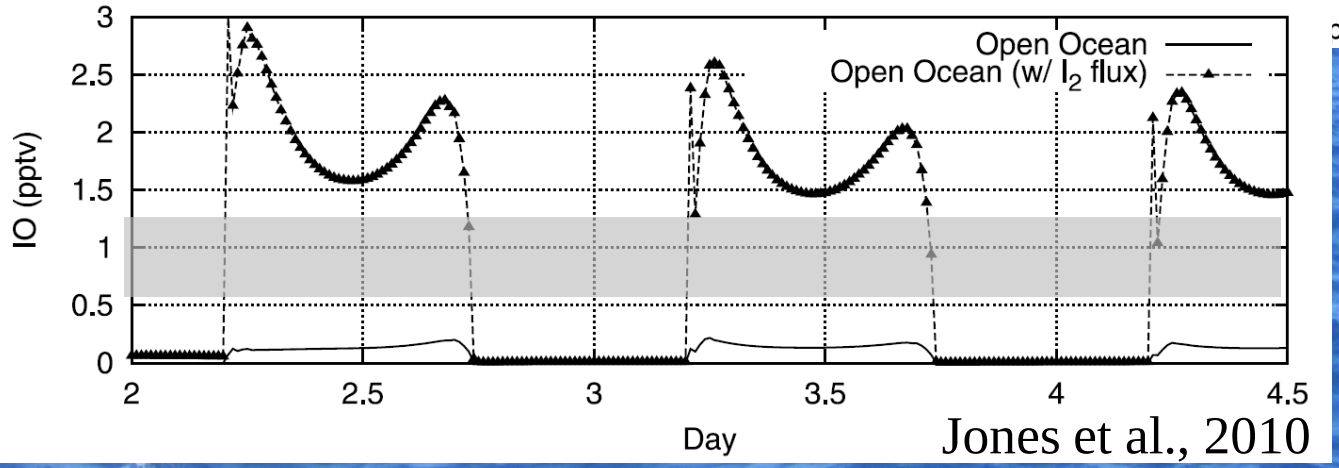


AMAX-DOA

SMAX-DOA

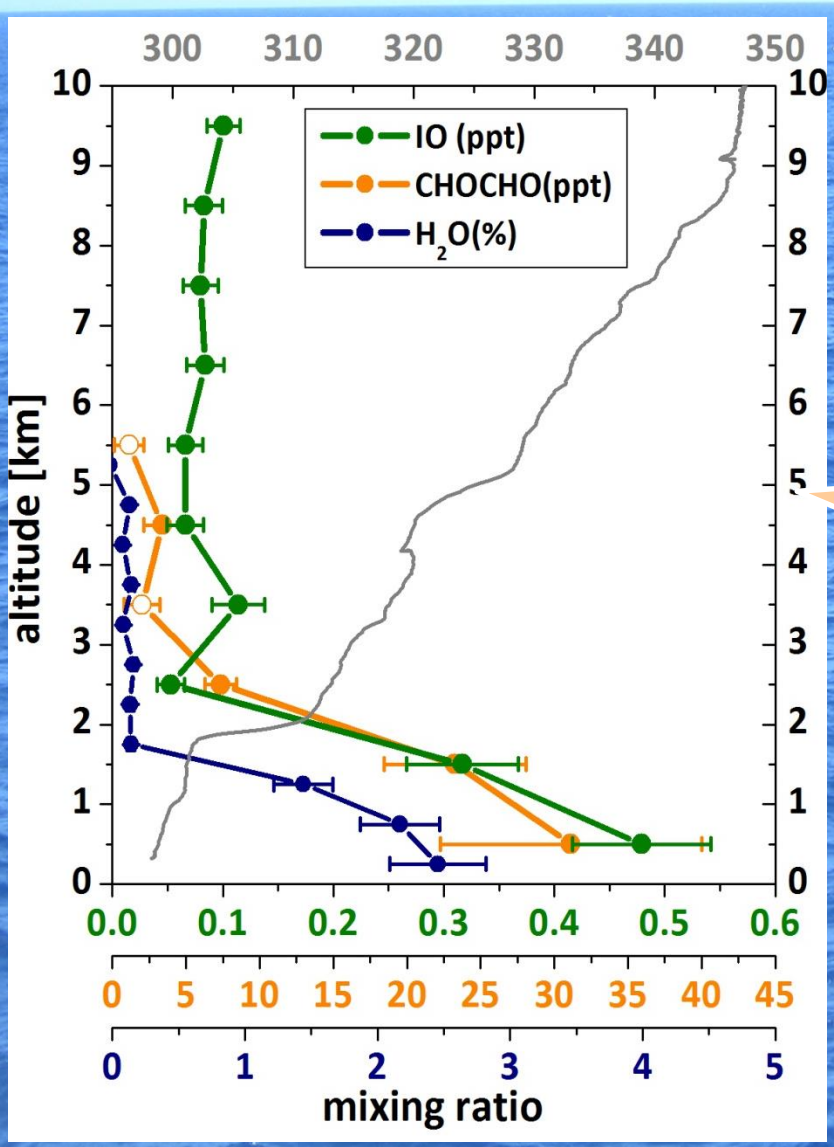
- optimal est
- parameteriz

CE-DOAS (s



Jones et al., 2010

IO in the tropical free troposphere



Poster:
Iodine Oxide vertical profile observations by CU AMAX-DOAS; Theodore Koenig

CONCLUSIONS

- Concentration of Glyoxal are consistent with three different instruments → agreement with previous measurements (Sinreich et al., 2010 - mean 63ppt +/- 22). Mahajan et al., 2014 is slightly on the low side (25 pptv with an upper limit of 40 pptv

- Cavity, SMAX-DOAS and AMAX-DOAS agree in MBL, and in some extent boundary layer profiles.

- Currently known sources of glyoxal are insufficient to explain the average MBL concentrations

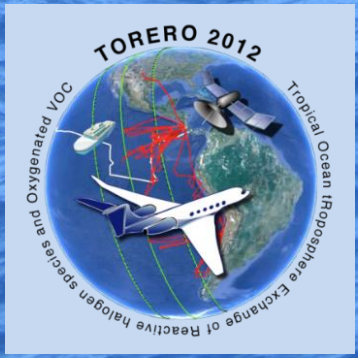
- Even though AMAX-DOAS is in the lower side of the concentration (~0.5ppt) and SMAX-DOAS (1ppt). Overall evidence suggests that there is a need for an iodine source (inorganic?), but magnitude is not well constrained.

- Include air sea fluxes of VOIC (ship and airborne) to understand the IO levels.

Acknowledgments

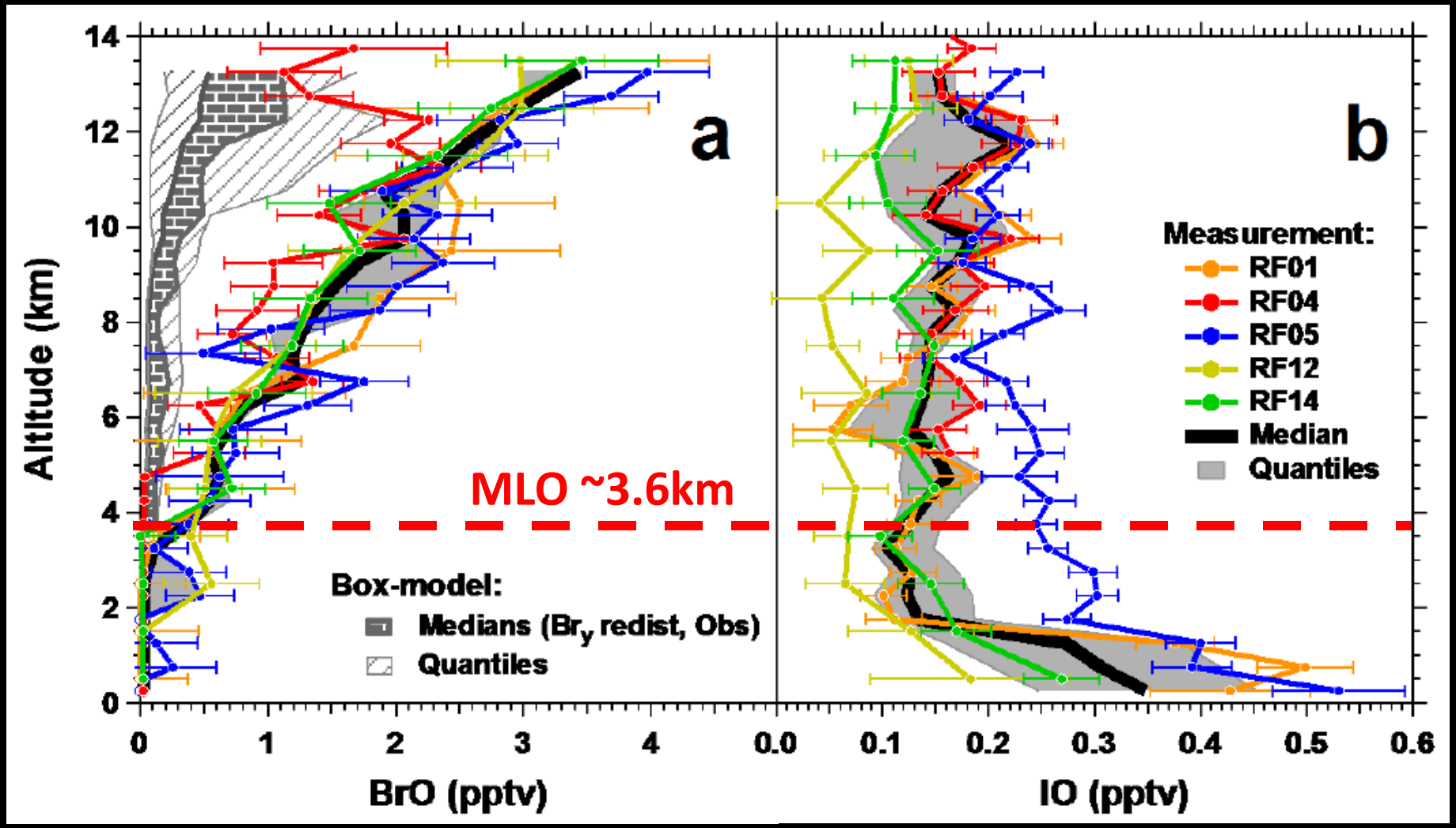
- NOAA RV Ka‘imimoana crew for support during TORERO (TAO arrays)
- Volkamer group for campaign participation/support
- T. Deutschmann for providing the McArtim radiative transfer code
- TORERO (Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated VOC) is funded by NSF award AGS-1104104 (PI: R. Volkamer)

Thanks



Additional slides

Vertical profiles & comparison with models



- GEOS-Chem: underestimates BrO by a factor 2-4
- Box-model (organohalogens, aerosol SA) -> even less BrO

Goal:

1) Glyoxal:

Sinreich et al., 2010 (mean 63ppt +/- 22) is consistent with measurements during TORERO (??)

Mahajan et al., 2014 is slightly on the low side

Cavity, SMAX-DOAS and AMAX-DOAS agree in MBL

2) IO:

Introduce the need for inorganic iodine sources?

Recent field evidence from Heidelberg is consistent with SMAX-DOAS over upwelling regions

AMAX-DOAS and SMAX-DOAS comparison

Overall evidence suggests that there is a need for an inorganic iodine source, but magnitude is not well constrained

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

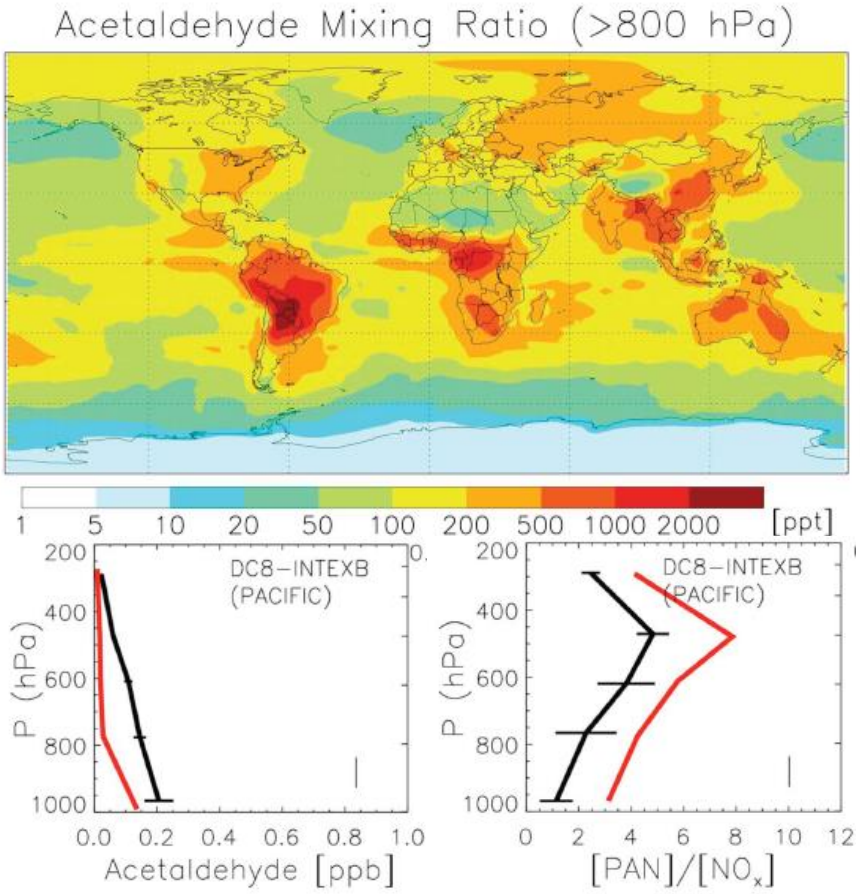
compounds	concn in air,[a] ppb	predicted concn in seawater,[b] nM	measured concn in seawater,[c] nM
formaldehyde	0.4	1500	2–40
acetaldehyde	0.3	4	2–15
propanal	0.1	1	0.4–3
butanal	0.08	0.5	0.3–2
pentanal	0.1	0.5	0.2–5
hexanal	0.1	0.3	0.2–0.6
heptanal	0.1	0.2	0.2–0.5
octanal	0.1	0.1	0.2–0.7
nonanal	0.15	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

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

Photochemical source of



Millet et al., 2009: ~57 TgC/yr

Explains observations <2km

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)

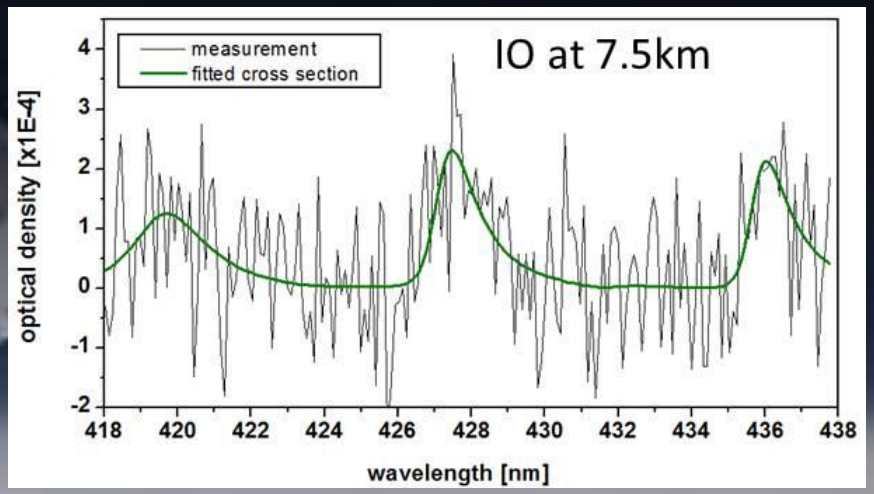
- Diffusion length scale: ~1 mm

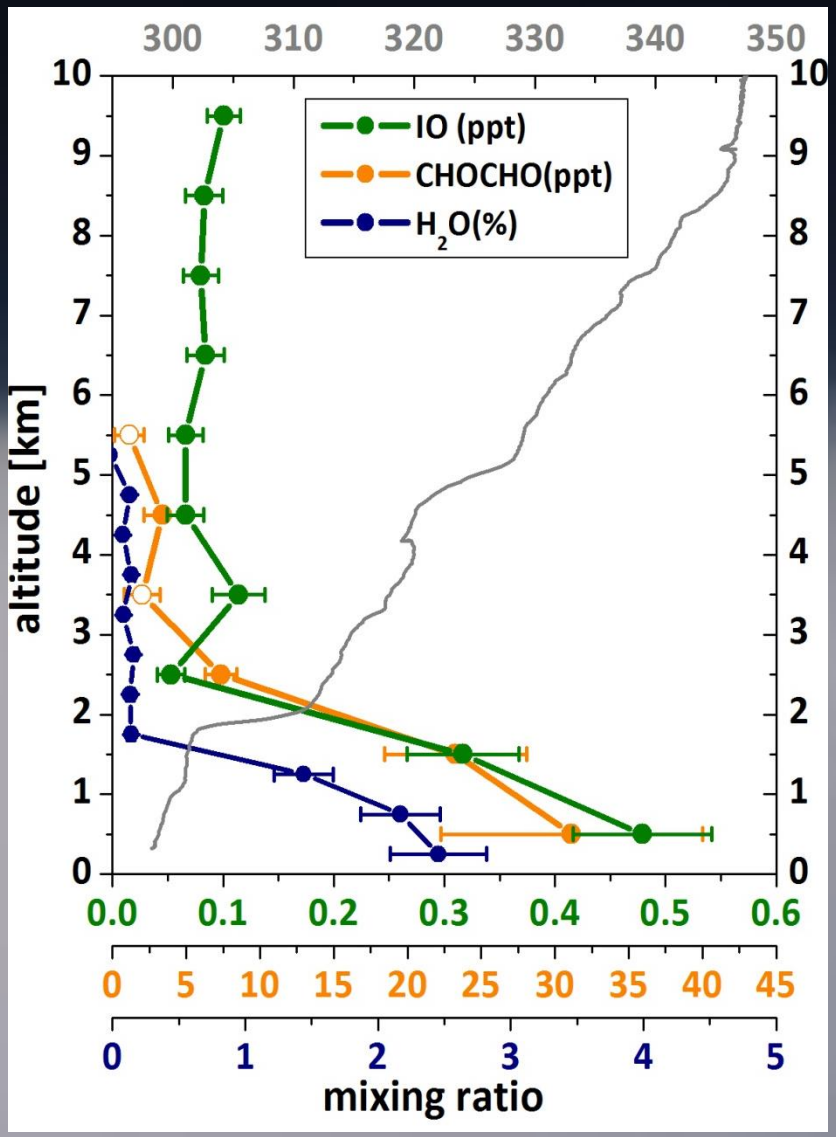
Recent evidence suggests that the surface organic micro layer (SML) is more stable than previously believed:

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

… atmospheric impacts ?

IO in the tropical free troposphere





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

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

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

Organic carbon flux from the ocean

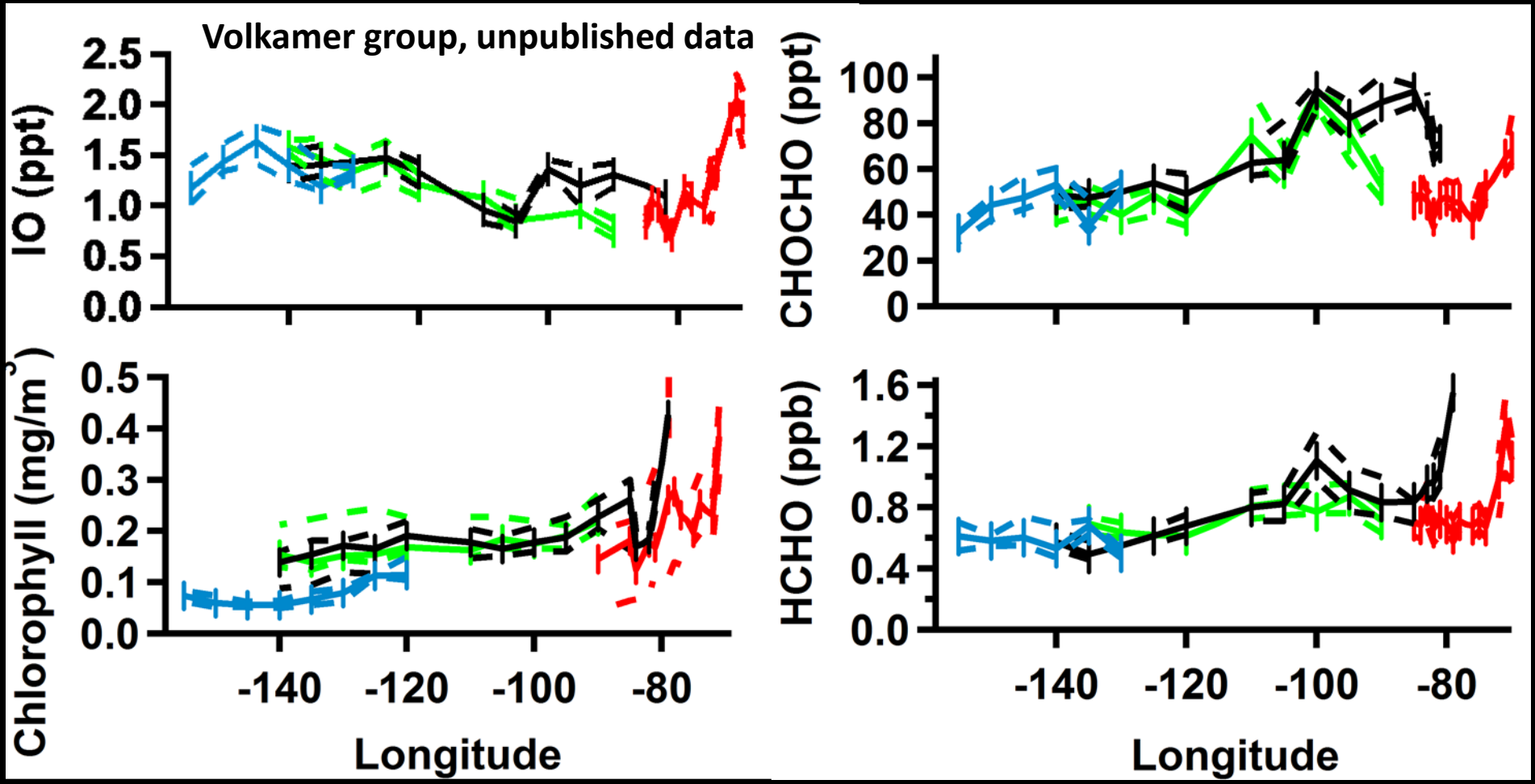
OCEANIC EMISSION

COMPOUND	ROLE IN ATMOSPHERE	MASS FLUX	C FLUX	% OF TOTAL EMISSIONS	OTHER SOURCES	TOKEN REFERENCES
Acetaldehyde Glyoxal		31 TgC/yr 8 TgC/yr (SCIA) 16 – 41 TgC/yr				Millet et al., 2009 Myriofekalitakis et al. 2008 This work
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: ~ 7×10^5 TgC DOM (about equal to atm. CO_2 mass)

INCREASING IO towards the oligotrophic ocean!



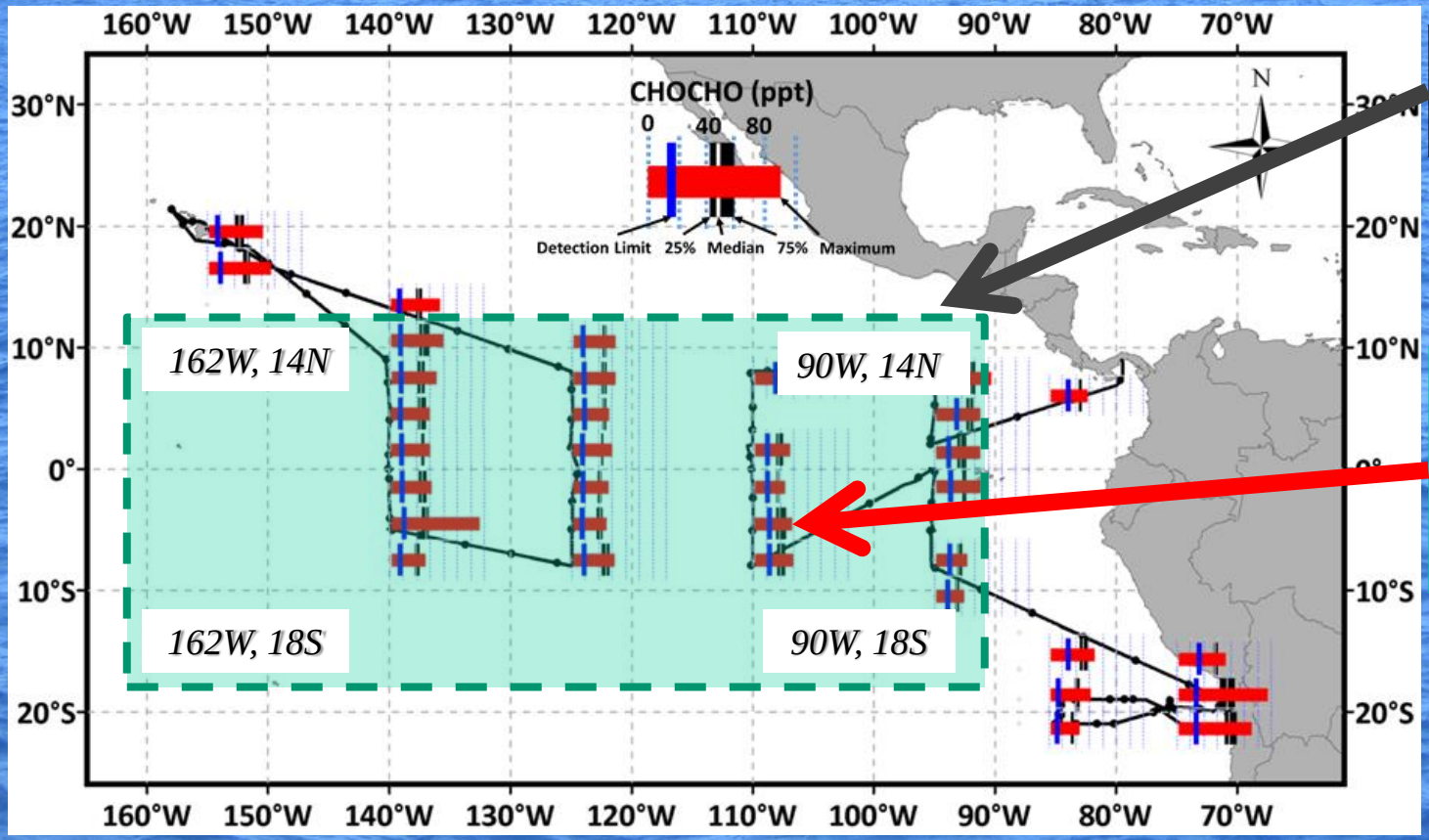
⇒ Anti-correlated with Chl-a => a non-biological source!

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

⇒ RIS speciation over the open ocean remains unclear!

Organic carbon flux of glyoxal

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



SMAX-DOAS Measurements

TM4ECPL Budget Analysis

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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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
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Sulfur volatiles:						
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- Ocean: ~ 7×10^5 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 is currently not understood, and missing in atmospheric models. This lack of understanding of organics 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

Job opening @ CU Boulder:
PhD project on AMAX-DOAS
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Interim Conclusions

- *Ours are the first limb-observations of BrO and IO in the tropics*
- *BrO is detected regularly above 2-4 km; BrO and IO are abundant throughout the air column*
  - *Consistent with the GOME-2 satellite, ground-based MAX-DOAS data (Theys et al., 2011)*
  - *~8 times higher than direct-sun profiles (Dorf et al.)*
  - *~2-4 times more than predicted by models*
- *Measurements support ~10-15 pptv Br_y in the tropical UTLS (~5-6 pptv Br_y unaccounted ?)*

Topic #1: Reactive Halogen Species

Photo-redox chemistry: I_2 (Cl_2,Br_2)

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%)

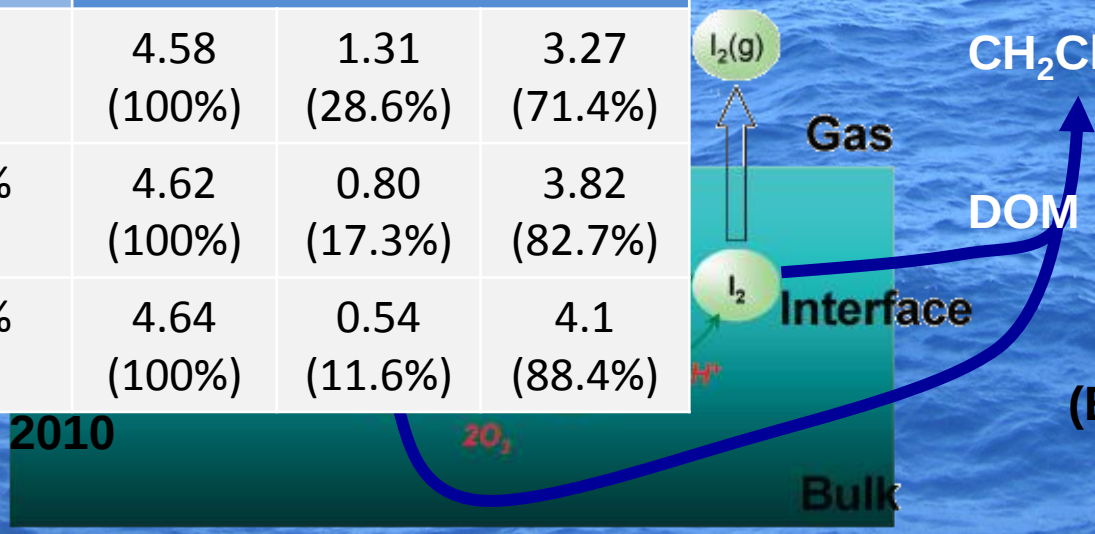
→ CHL/CDOM + I

→ I_2

→ 2 I

O + O_2

→ → DOC Products



Sakam
Inhibite
Organi
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