

*at interfaces*

# Novel chemistry in the tropical troposphere

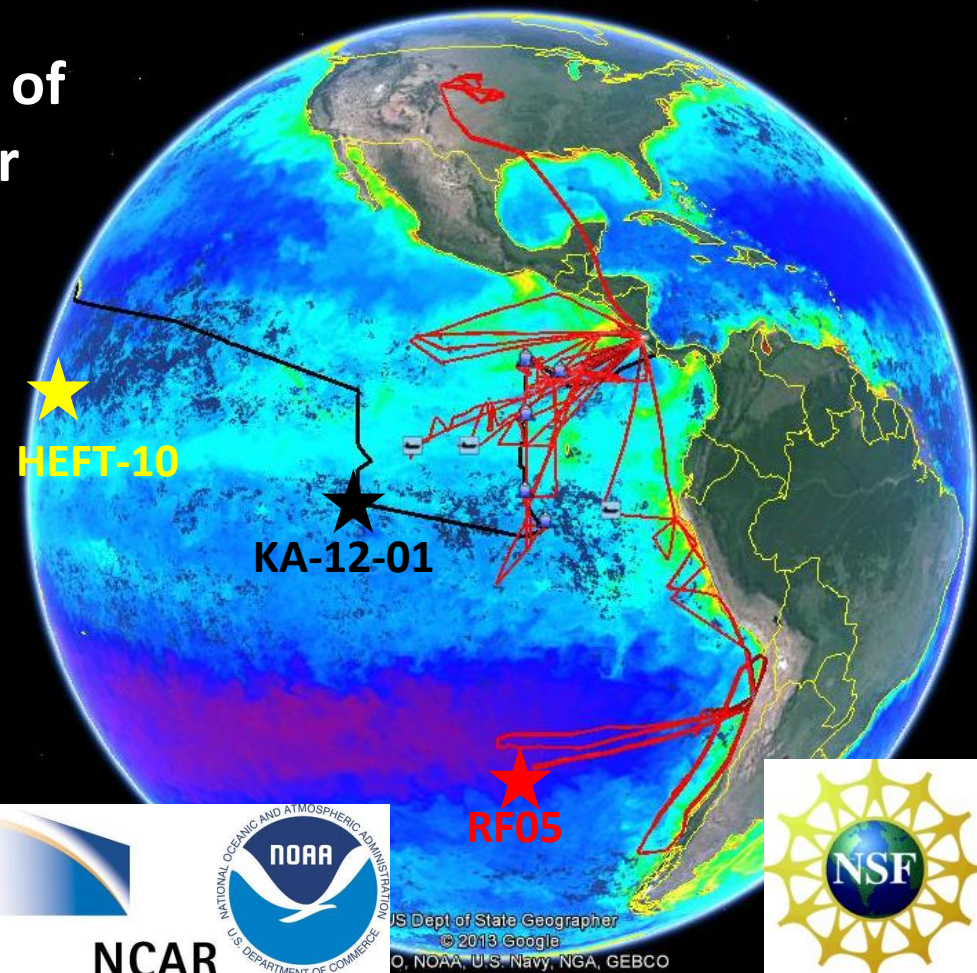
Rainer Volkamer

Sean Coburn, Siyuan Wang, Barbara Dix, Brad Pierce, Rebecca Hornbrook,  
Eric Apel, Roland von Glasow, Maria Kanakidou and Team TORERO

Objectives: study air-sea exchange of oxygenated VOC and halogens over the full tropospheric air column

→ Field observations: Free troposphere, marine boundary layer, **oligotrophic ocean**

→ Modeling: heterogeneous chemistry, oxidative capacity



# Examples for heterogeneous chemistry that is relevant to air quality & climate

Stratospheric ozone – PSCs

Bromine activation/recycling

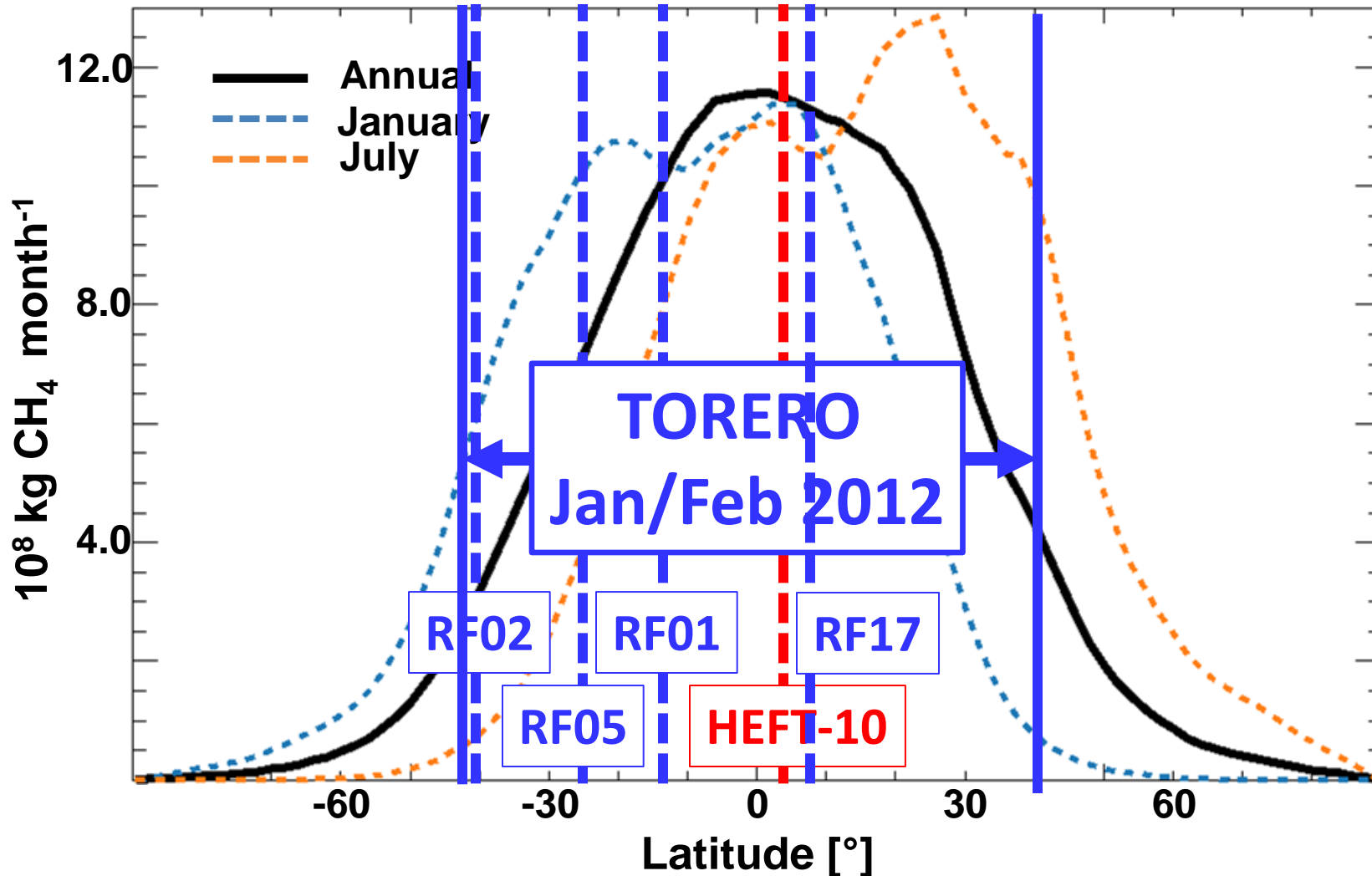
$\text{N}_2\text{O}_5$  hydrolysis

Iodine recycling

Organic carbon at interfaces

# Oxidation of long-lived gases by OH is mostly in tropics

## monthly methane oxidation (GEOS-Chem)



# CDOM Photochemistry: a smoking gun...

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

compounds	concn in air, <sup>a</sup> ppb	predicted concn in seawater, <sup>b</sup> nM	measured concn in seawater, <sup>c</sup> 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 <sup>c</sup>
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

<sup>a</sup>Typical carbonyl concentrations in the air over open Caribbean Sea and Sargasso Sea. <sup>b</sup>Predicted concentrations in seawater in equilibrium with atmosphere:  $[R'R''CO] = K \cdot P$  at 25 °C. <sup>c</sup>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 by GC-MS

## Photochemical source of biological substrates in sea water: implications for carbon cycling

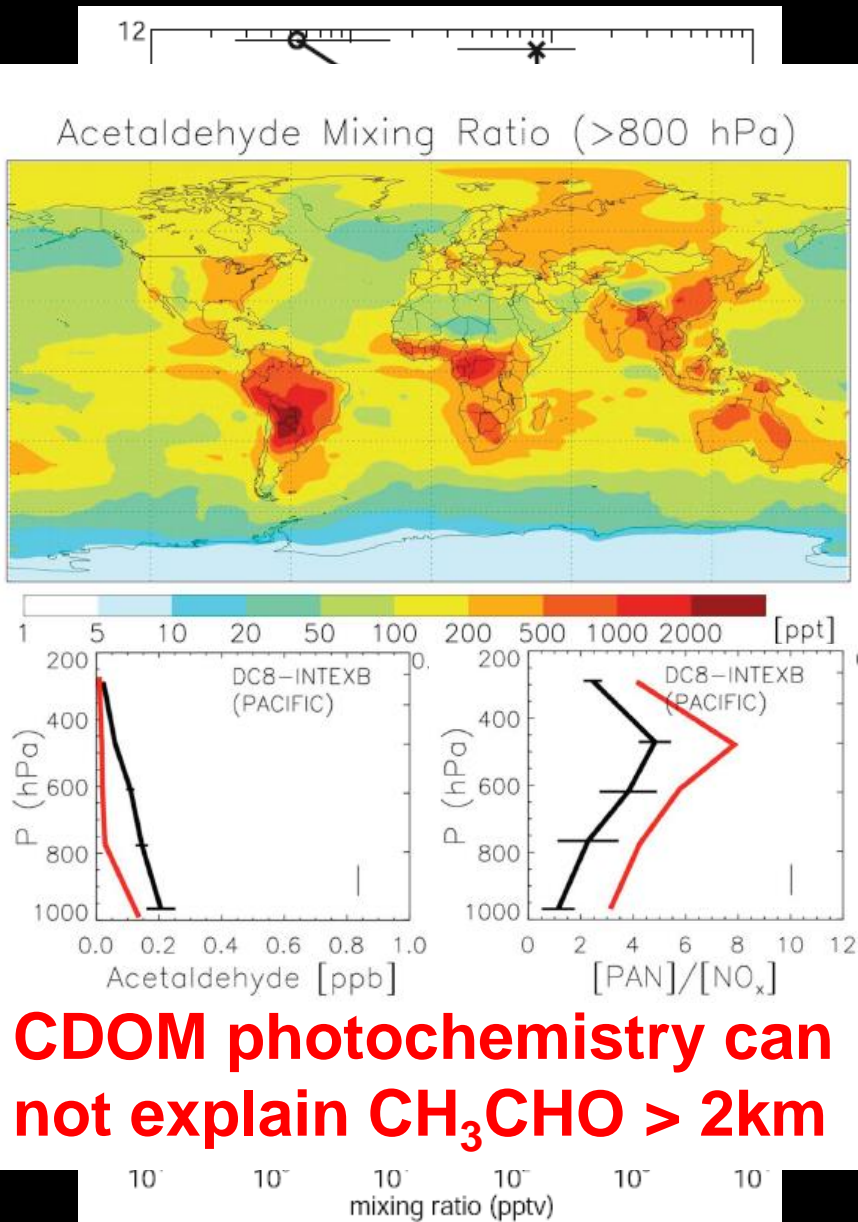
David J. Kieber\*†, Julie McDaniel\*†  
& Kenneth Mopper\*‡

\* Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, Florida 33149, USA

DISSOLVED organic carbon (DOC) in sea water represents one of the largest reservoirs of carbon on the earth<sup>1</sup>. The main fraction of this DOC is generally believed to be composed of old<sup>2</sup>, biologically refractory material<sup>3</sup> such as humic substances, for which the removal mechanisms remain largely unknown. One potentially important removal process in the ocean that has not been investigated is the photochemical breakdown of this DOC in the photic zone to form biologically labile organic products. Here we show that biological uptake of pyruvate is highly correlated to its rate of photochemical production in sea water ( $r = 0.964$ ), and that the photochemical precursor(s) of pyruvate is from the fraction of DOC having a nominal molecular weight of 500. This is the first evidence that photochemical breakdown of high-molecular-weight marine DOC, which is presumably biologically refractory, results in the production of a compound that is used by plankton as a substrate. Our results have important implications for the oceanic carbon cycle, particularly with respect to planktonic-food-web dynamics and the global carbon budget.

NATURE · VOL 341 · 19 OCTOBER 1989

# Short lived OVOC in the FT ?



**CDOM photochemistry can not explain CH<sub>3</sub>CHO > 2km**

**Singh et al., 2001, Nature**

A large ocean source of acetaldehyde?

**Staudt et al., 2003 JGR; Singh et al., 2004, JGR**

Observations in the tropical FT are not consistent with PAN: NO<sub>x</sub> ratios

**Kwan et al., 2006, GRL**

OA volatilization: A source for acetaldehyde in the FT? (Thornberry and Abbatt, 2003; Molina et al., 2004)

**Millet et al., 2009, ACP**

No compelling need for a missing OVOC source in the FT

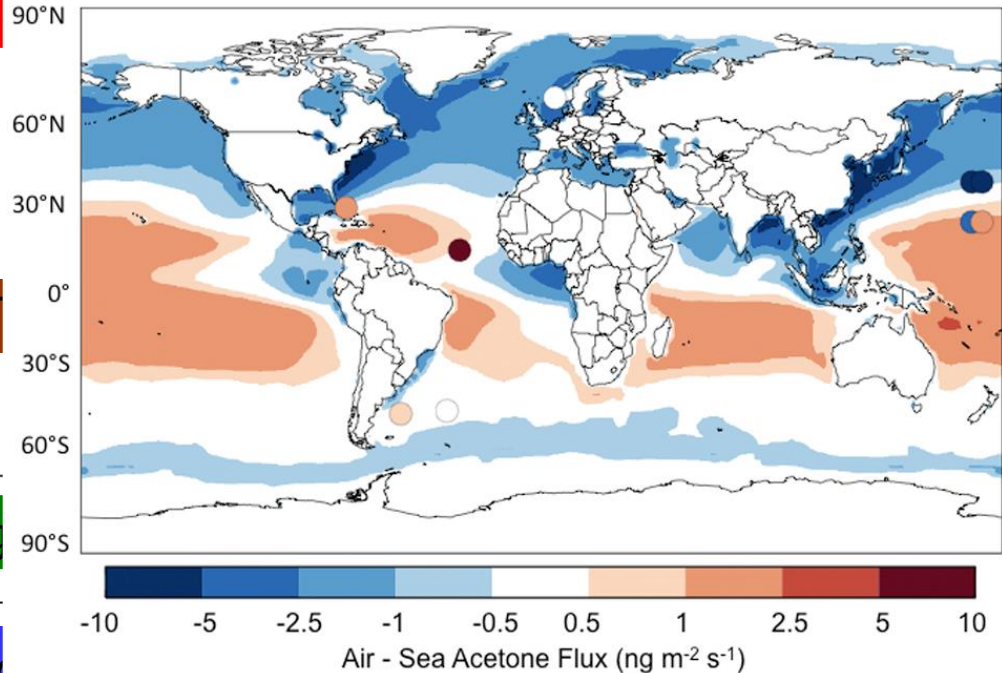
Quantitative evaluation of the model is complicated by known measurement artifacts in clean air

# Organic carbon flux from the ocean

## OCEANIC EMISSION

COMPOUND	ROLE IN ATMOSPHERE	MASS FLUX	C FLUX	% OF TOTAL EMISSIONS	OTHER SOURCES	TOKEN REFERENCES
Sulfur volatiles:						
<b>DMS</b>	Global sulfur budget Aerosol precursor: atmospheric acidity and cloud nucleation	<b>14-29</b>				
COS	Precursor of stratospheric aerosol	0.30 TgS/yr				
CS <sub>2</sub>	COS precursor	0.15 TgS/yr				
<b>NMHC</b>	Tropospheric (photo)chemistry, aerosol precursors and cloud nucleation	<b>1-10</b>				
<b>POA</b>	Tropospheric (photo)chemistry, cloud nucleation	<b>3-8 Tg</b>				
<b>Acetaldehyde</b>		<b>57 Tg</b>				
<b>Acetone</b>		<b>?</b>				

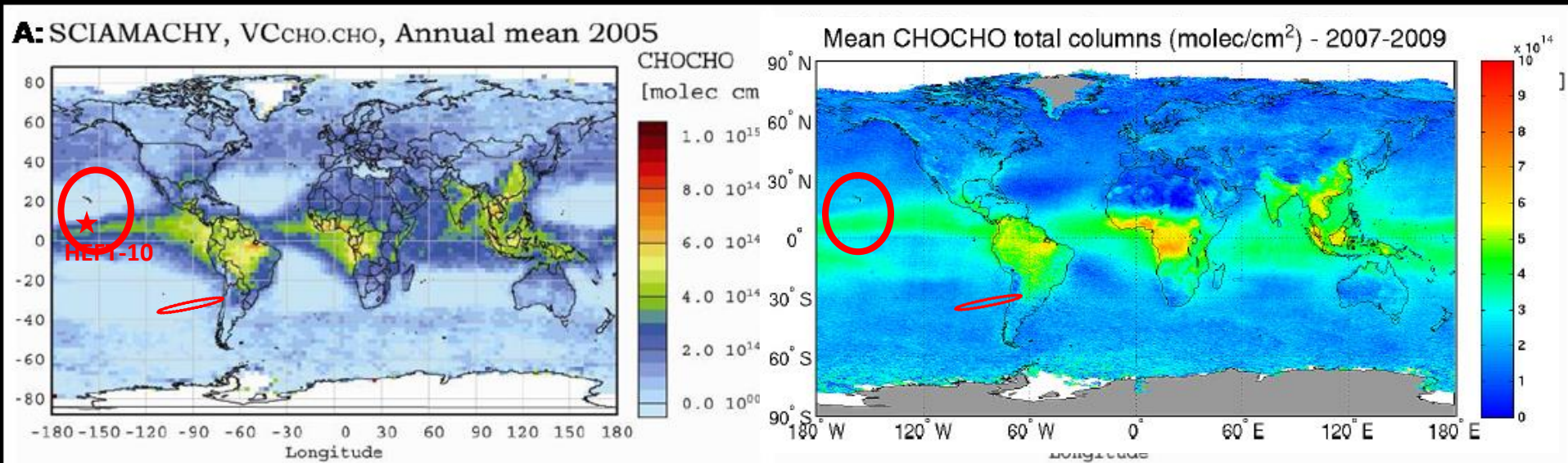
## Acetone: GEOS-Chem annual mean



Small global average net flux ( $\sim 1.2 \text{ TgC/yr}$ ).  
Fischer et al., 2012

- Ocean:  $\sim 7 \times 10^5 \text{ TgC DOM}$  (about equal to atm.  $\text{CO}_2$  mass)

# Satellites show widespread glyoxal over oceans, but disagree over the remote ocean



Wittrock et al., 2006; Myriokefalitakis et al., 2008; Sinreich et al., 2010; Lerot et al., 2010

## Atmospheric models do not predict any glyoxal over oceans

**Continental source: ~45 TgC/yr**

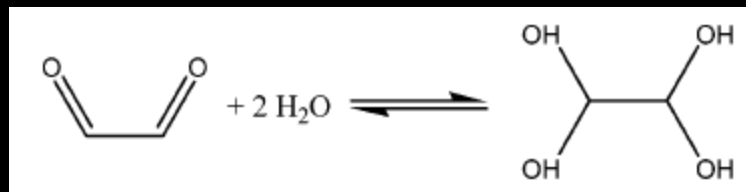
- 50% unaccounted
- 30% biogenic (i.e. isoprene)
- 14% anthropogenic
- 6% biomass burning

**Atmospheric lifetime: ~ 2.5hrs**

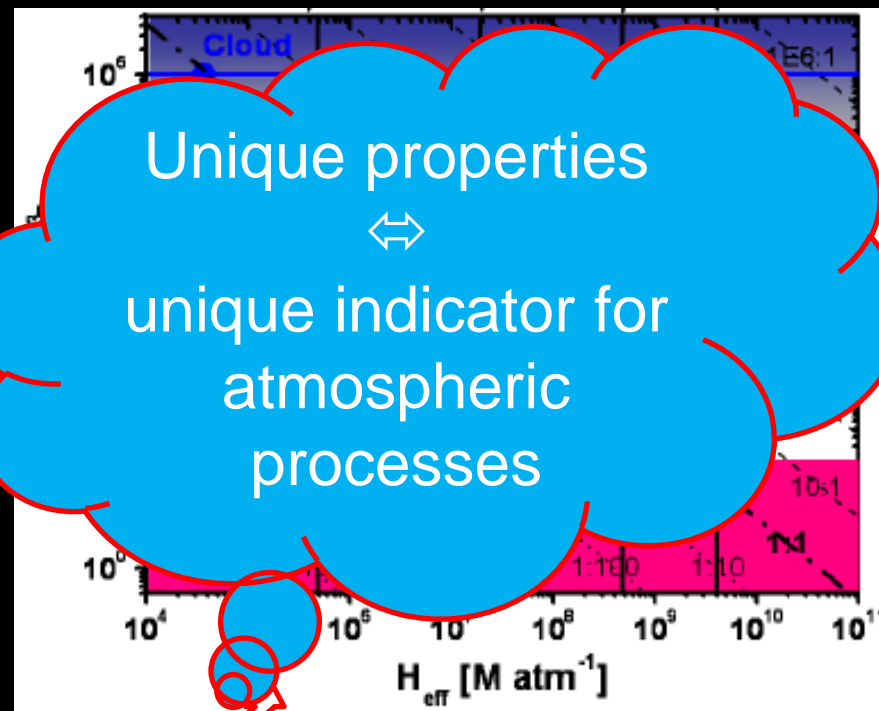
- 52% photolysis
- 18% OH
- 22% SOA in clouds/aerosols?
- 8% Dry/wet deposition

Stavrakou et al., 2009

# Glyoxal: physical and chemical properties



O/C [au/au]	1	2
$P^0$ [atm]	0.3	$\sim 10^{-6}$
$C^*$ [ $\mu\text{g m}^{-3}$ ]	$\sim 10^9$	$\sim 10^4$
$H_{\text{eff}}$ [ $\text{M atm}^{-1}$ ]	$\sim 5$	$4 \times 10^5$



Volkamer et al., 2009; Kampf et al., 2013

**Continental source:  $\sim 45 \text{ TgC/yr}$**

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

**Atmospheric lifetime:  $\sim 2.5 \text{ hrs}$**

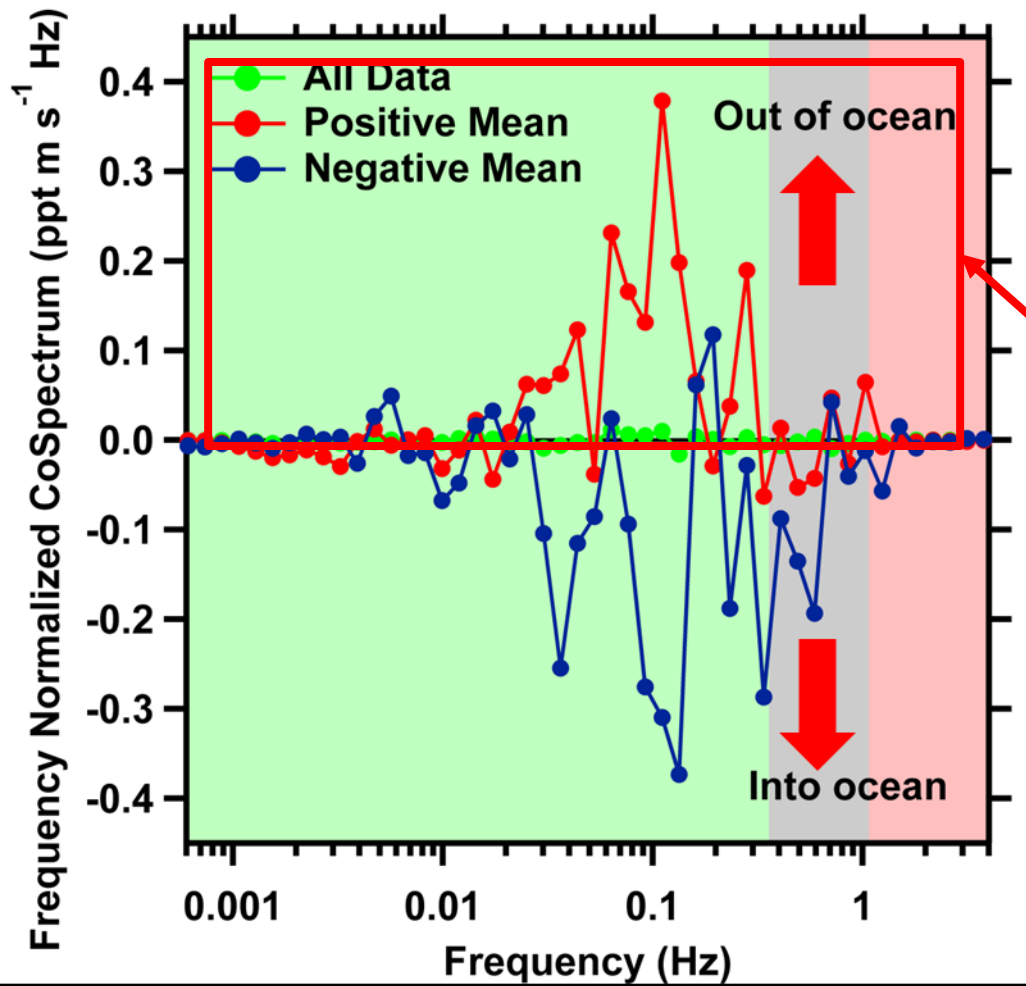
- 52% photolysis
- 18% OH
- 22% SOA in clouds/aerosols?
- 8% Dry/wet deposition

Stavrakou et al., 2009



1. Marine organic carbon at interfaces is a source for OVOC in the tropical FT
2. Short-lived OVOC are widespread in the tropical FT and modify  $\text{HO}_x$ ,  $\text{BrO}_x$ ,  $\text{ClO}_x$
3. Marine VOC emissions are insufficient to explain the observed OVOC levels
4. The OVOC source mechanism involves a heterogeneous photochemical alkene source

# Glyoxal EC Flux Measurements



Positive flux of glyoxal

→ Organic surface microlayer (SML)

$$L = (2Dt)^{1/2}$$

$$D = (0.001-1) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

t = 140 ms (Lifetime against hydrolysis)

$$L = 0.5-17 \text{ } \mu\text{m}$$



# Glyoxal: Indicator for **surface** DOC oxidation

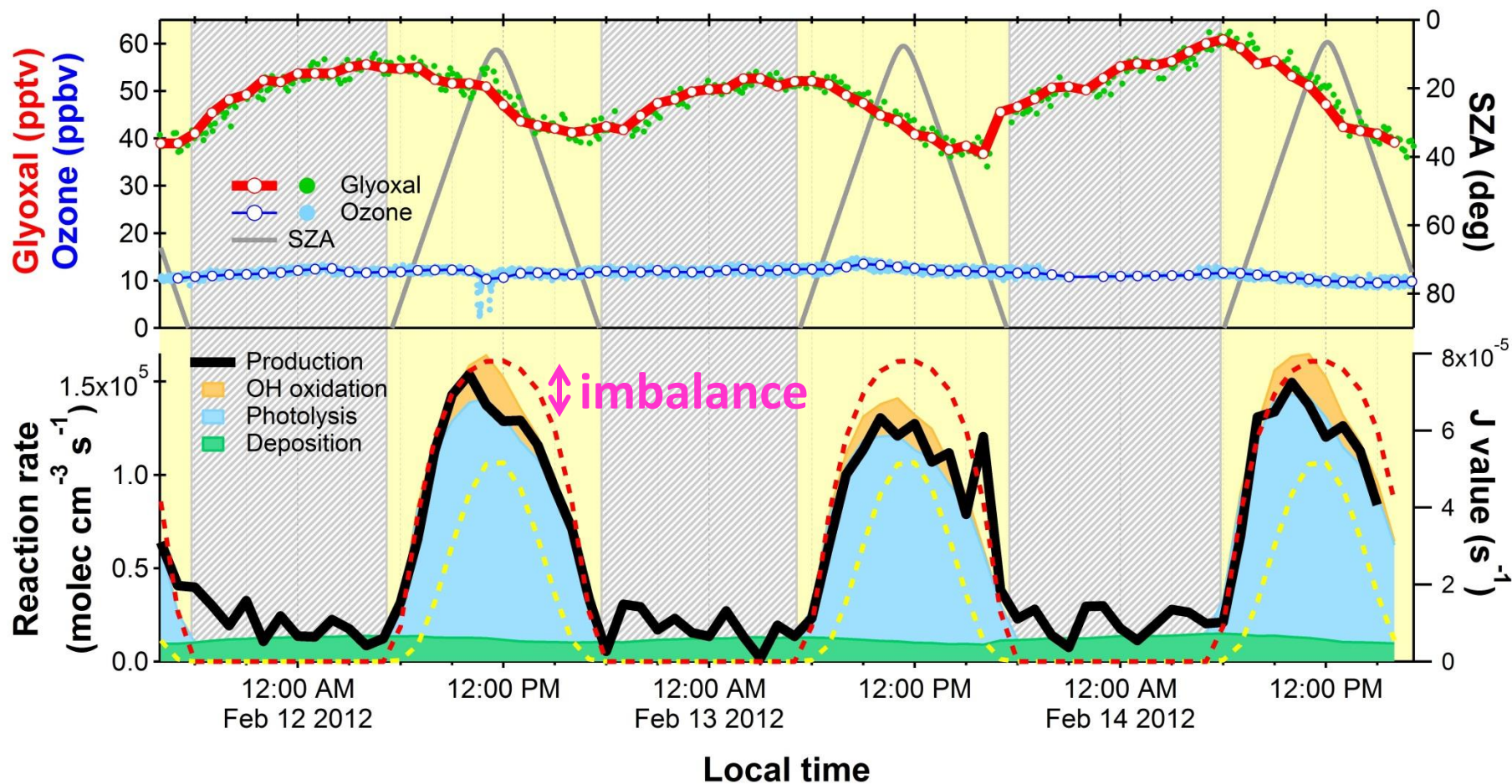
- Vertical diffusivity in the thermocline:  
 $0.15 \text{ cm}^2 \text{ s}^{-1}$  (Ledwell et al.)
- Hydration rate:  
 $k_{\text{hydr}} = 7 \text{ s}^{-1}$  (Creighton et al., 1988)
- Diffusion length scale:  $\sim 1 \text{ mm}$

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 ?

# Diurnal cycle carries mechanistic information

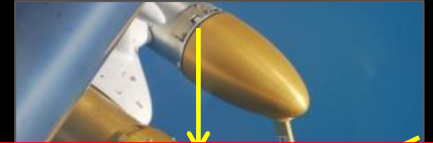


- Night time increase: O<sub>3</sub> reaction ⇒ **alkene precursor**
- Daytime rate ≫ nighttime rate ⇒ **Photochemical mechanism**

# CU-AMAX-DOAS instrument aboard NSF/NCAR GV

University of Colorado Airborne Multi-AXis  
Differential Optical Absorption Spectroscopy

Telescope pylon

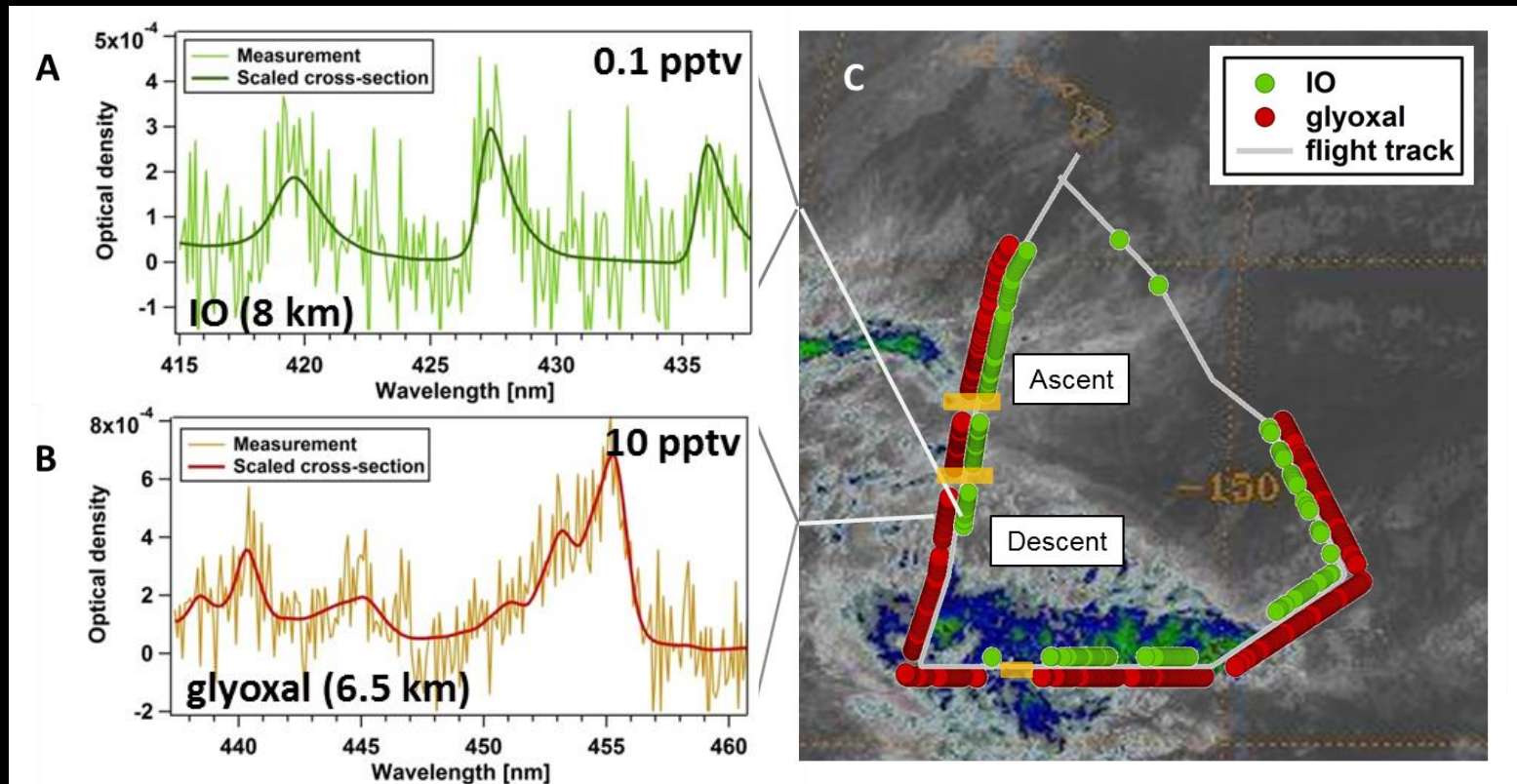


Forward, zenith, nadir      slant forward/backward      power supply      PC104      MMQ (INS/GPS) + inclinometer      temp. controllers      opt. converter



Volkamer et al., SPIE 2009  
Baidar et al., AMT 2013

# CU AMAX-DOAS on NSF/NCAR GV (HEFT-10)



- Heterogeneous recycling of iodine is needed to explain vertical profile  
Elevated IO in a decoupled MBL is incompatible with iodine lifetime
- Iodine is responsible for ~10% of ozone loss rate in the FT

# Trace Organic Gas Analyzer (TOGA)

VOCs: NMHCs (C3-C10), OVOCs (C2-C9), HVOCs

High selectivity GC/MS

2 minute continuous analyses of **50** VOCs

Semi-autonomous operation up to 50,000 ft

TORERO, DC3

TOGA on GV aircraft



**Eric Apel**  
**Alan Hills**  
**Becky Hornbrook**  
**Dan Riemer (U Miami)**

**TORERO – Maiden  
Science Mission**



Instrument designed to have very low limits of detection (low – sub pptv)

# CU AMAX - DOAS

**Volkamer group**

Parameters measured by CU AMAX-DOAS	Detection limit* / Accuracy
BrO	0.3 ppt **
IO	0.05 ppt
HCHO	100 ppt
CHOCHO	3 ppt
H <sub>2</sub> O	5 ppm (590nm)
NO <sub>2</sub>	10 ppt
OCIO	0.7 ppt
HONO	12 ppt
Aerosol extinction from O <sub>4</sub> at 360, 477, and 577nm	0.01 - 0.03 km <sup>-1</sup>

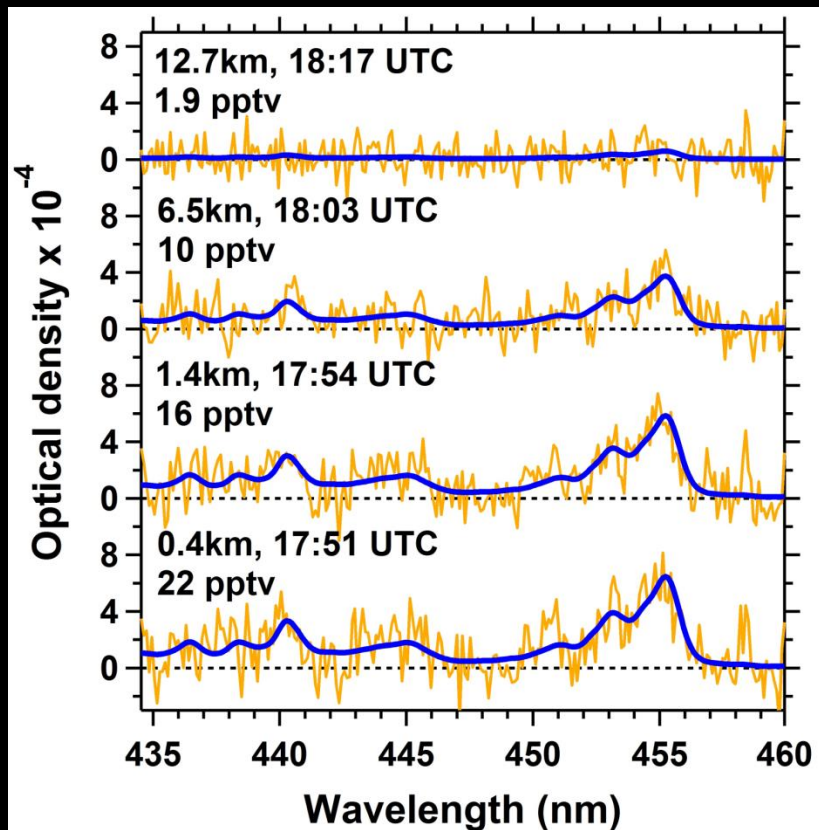
Profile Scan: 0.5 - 2 min, Vertical Resolution ~ few 100 m



# Optical spectroscopy & Chromatography

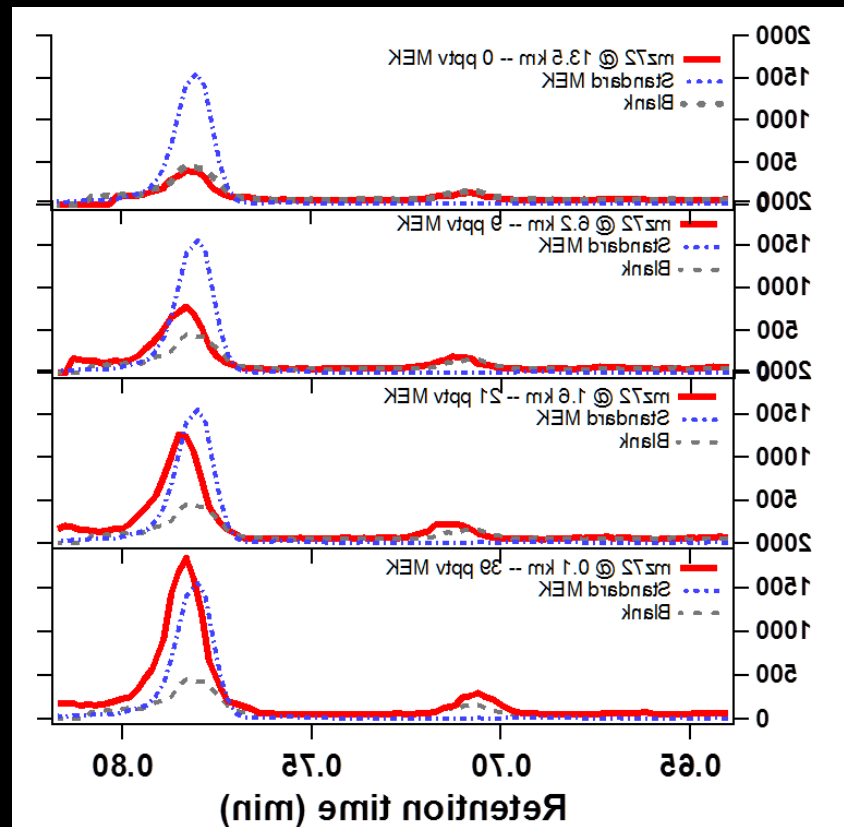
## CU AMAX-DOAS

spectral proof (*remote sensing*)



## TOGA

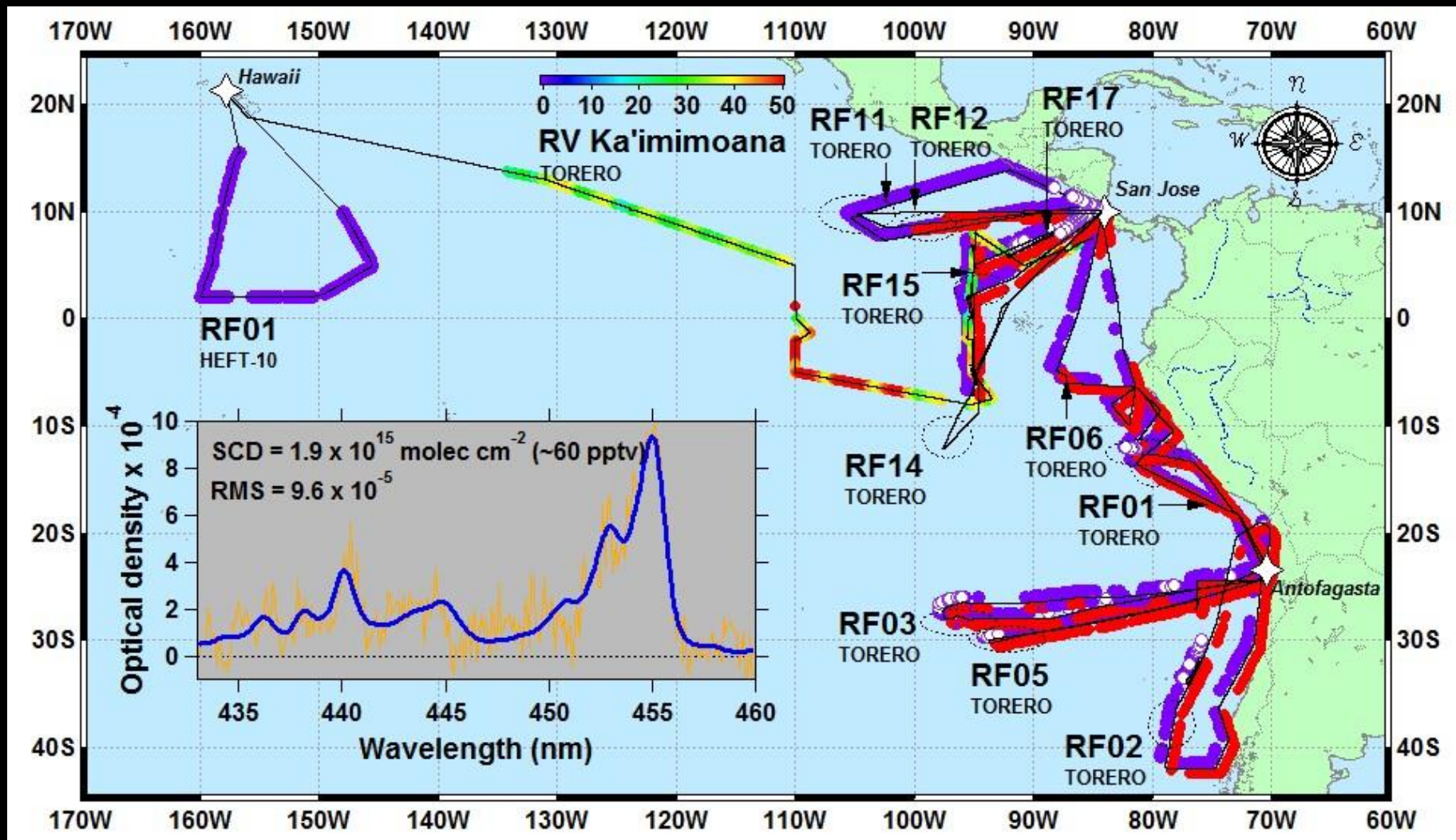
*in-situ* Gas-Chromatography/MS



**Consistent evidence from optical (absorption) spectroscopy and mass spectrometric techniques establishes the presence of OVOC in the tropical FT**



# OVOC measurements in the tropical troposphere



- Glyoxal and MEK are widespread in the tropical FT
- Spectral proof from *in-situ* LED-CE-DOAS (KA-12-01)

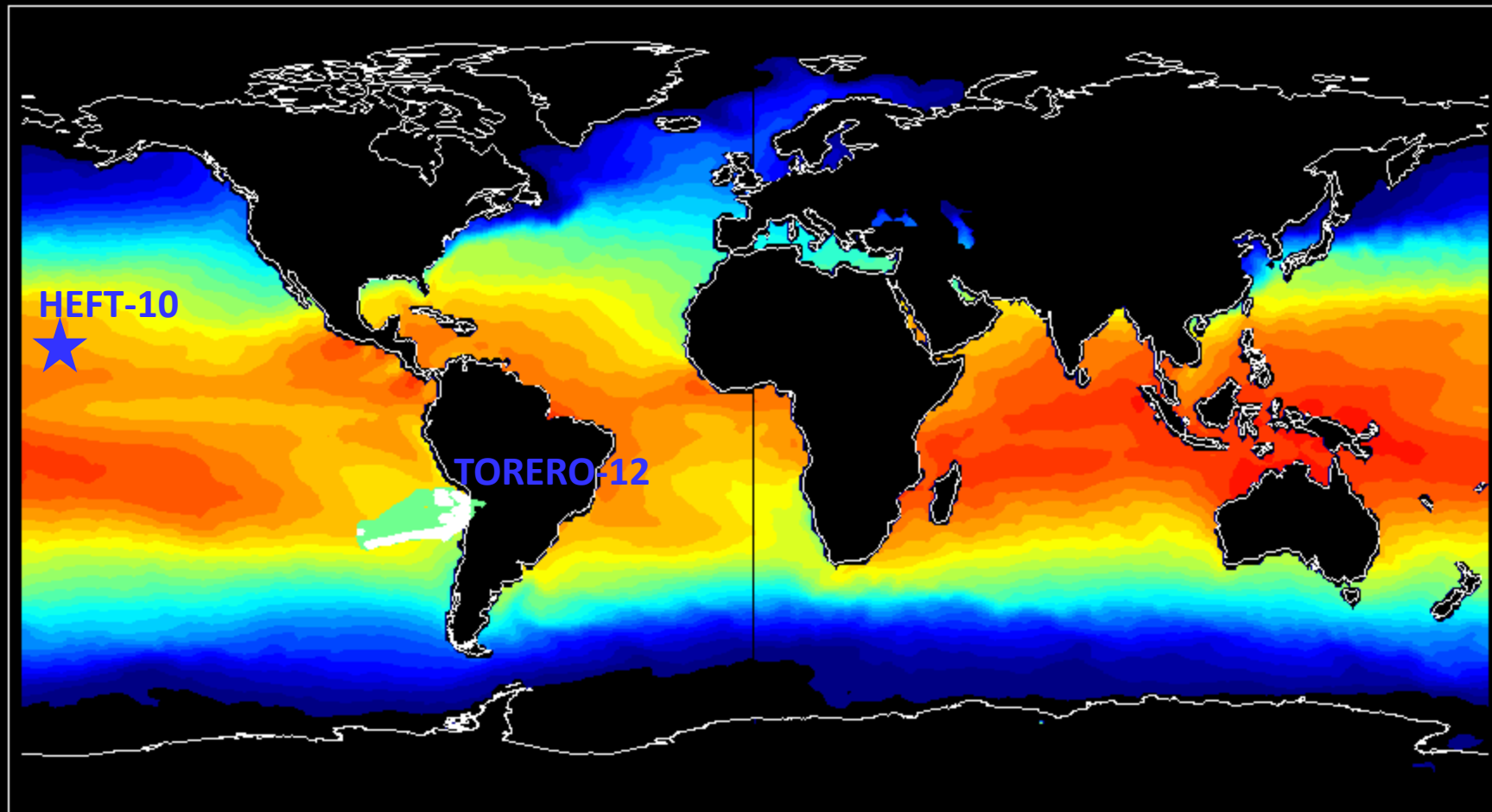
# RF05 (29 Jan 2012) – 7 day back trajectories

uwhyb\_2012013000\_torero\_7\_day\_1x1\_curtain.traj  
2012012912

Marine Boundary Layer Trajectories (white)

Free Trop Trajectories (green)

Stratospheric Trajectories (blue)



HEFT-10

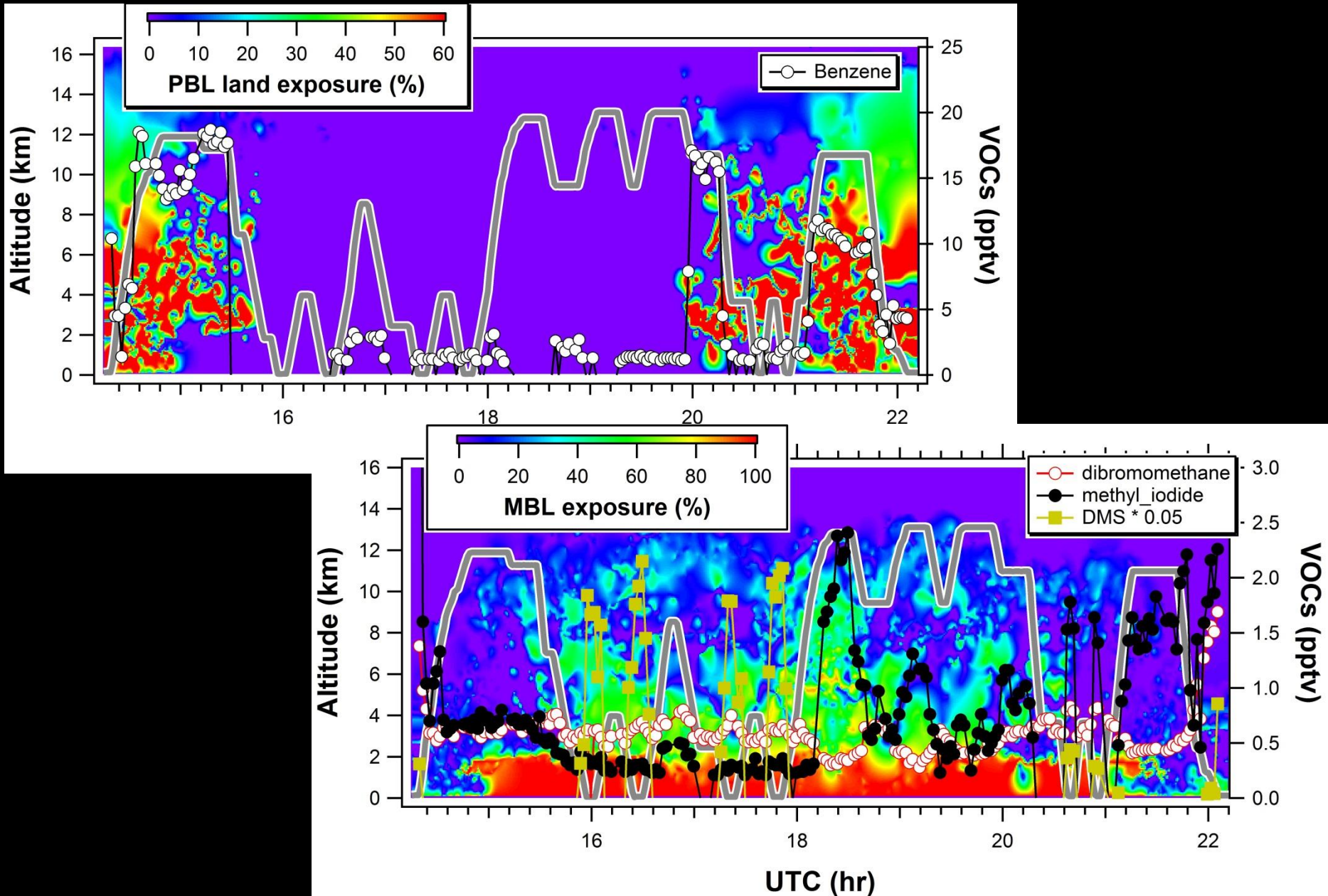


TORERO-12



Brad Pierce, RAQMS model

# TOGA: DMS, benzene, CH<sub>3</sub>I, CH<sub>2</sub>Br<sub>2</sub>

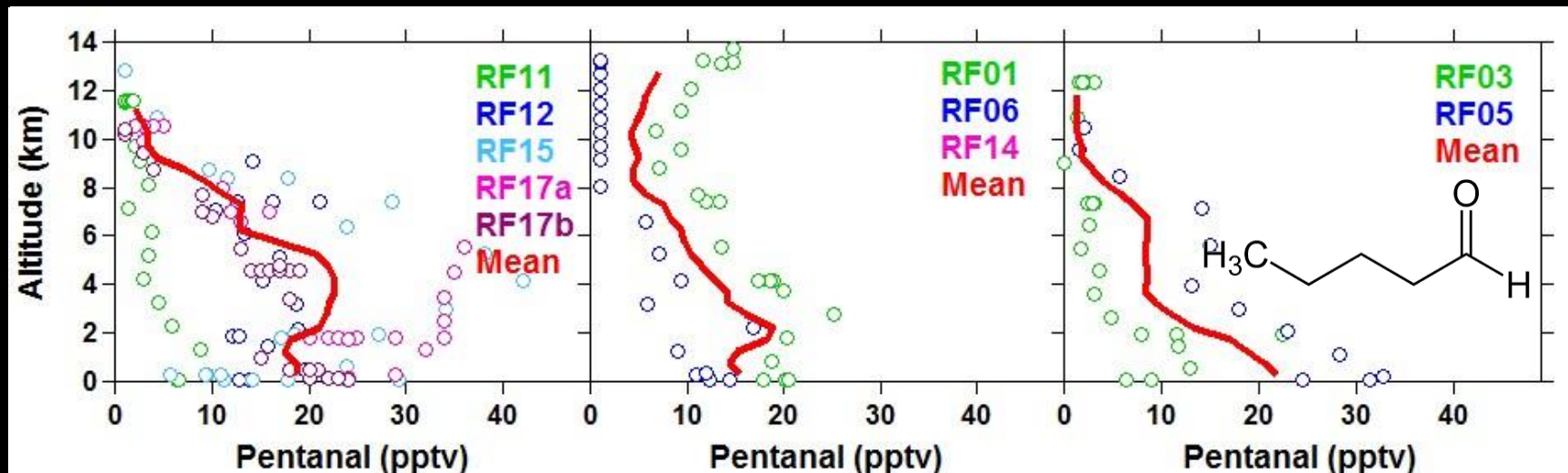
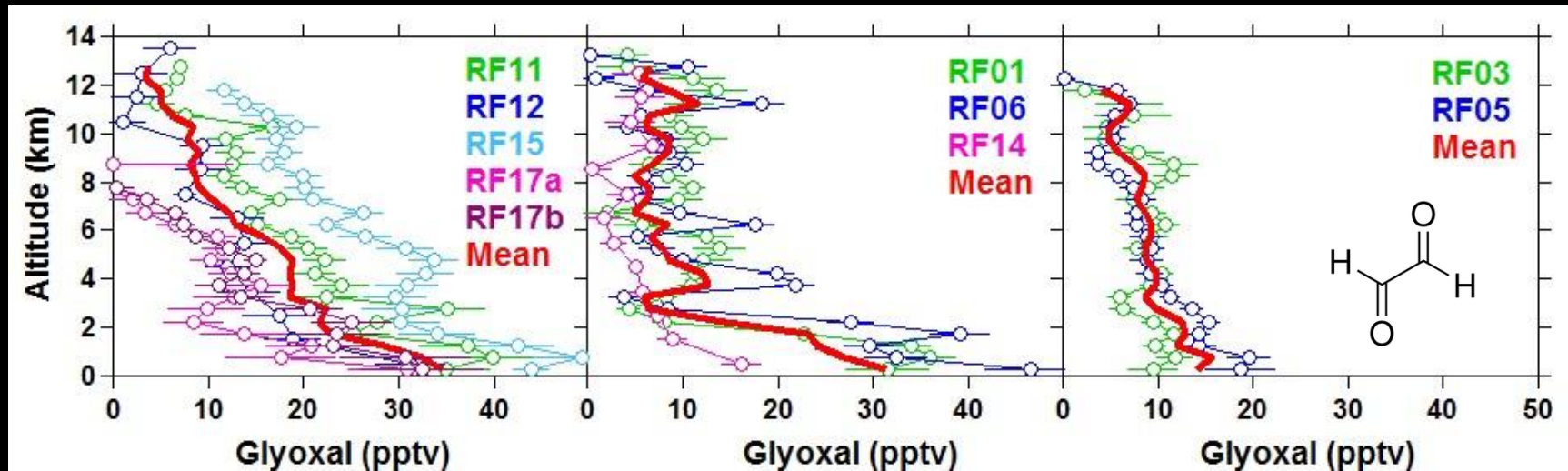


# Vertical profiles of diverse OVOC

NH tropics

SH tropics

SH oligotrophic ocean



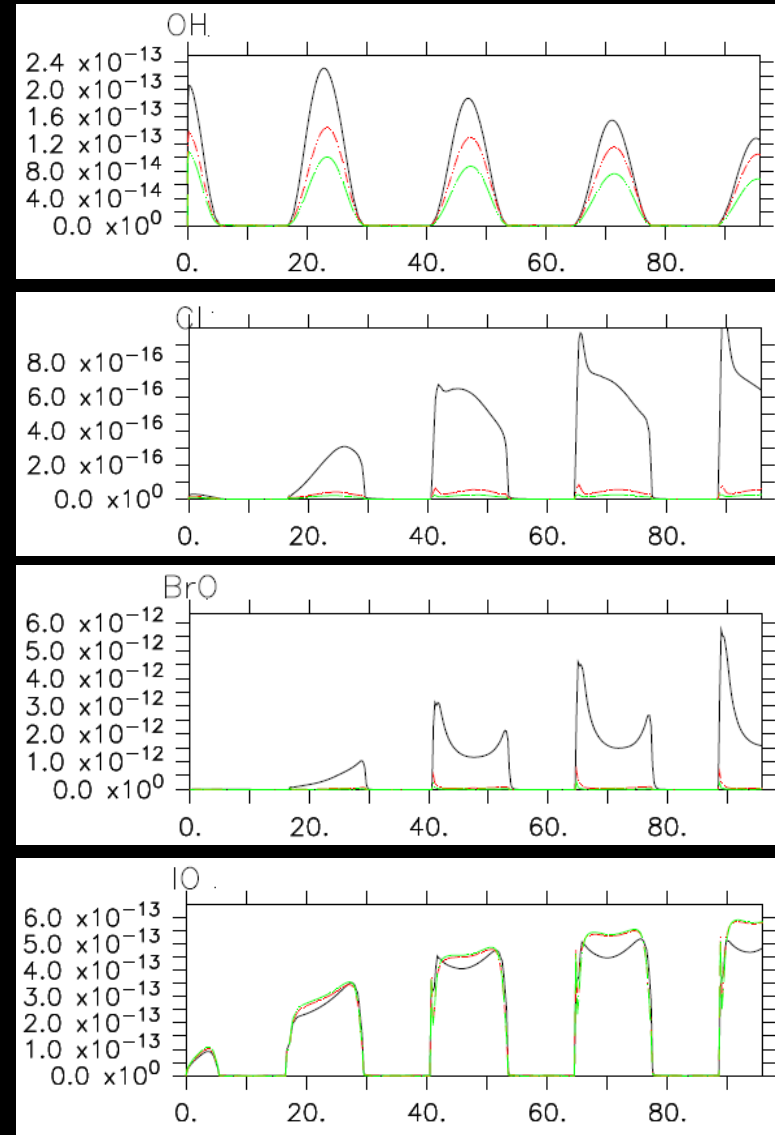
- OVOC: aliphatic aldehydes, ketones,  $\alpha$ -dicarbonyl (glyoxal)

# Reaction of Organics with halogen atoms

- Cl:  $10^{-13} < k_{\text{VOC}} < 10^{-10} \text{ cm}^3/\text{mol/s}$ 
  - $\tau_{\text{Cl}} < 0.2 \text{ sec}$  (capped by  $\text{CH}_4$ )
- Br:  $10^{-12} < k_{\text{OVOC}} < 10^{-11} \text{ cm}^3/\text{mol/s}$ 
  - $\tau_{\text{Br}} < 4 \text{ sec}$  (RCHO  $\sim 0.8 \text{ ppb}$ )
- I: organic sink is inefficient (endothermic, but indirect effects might exist through coupling with Cl and Br chemistry)

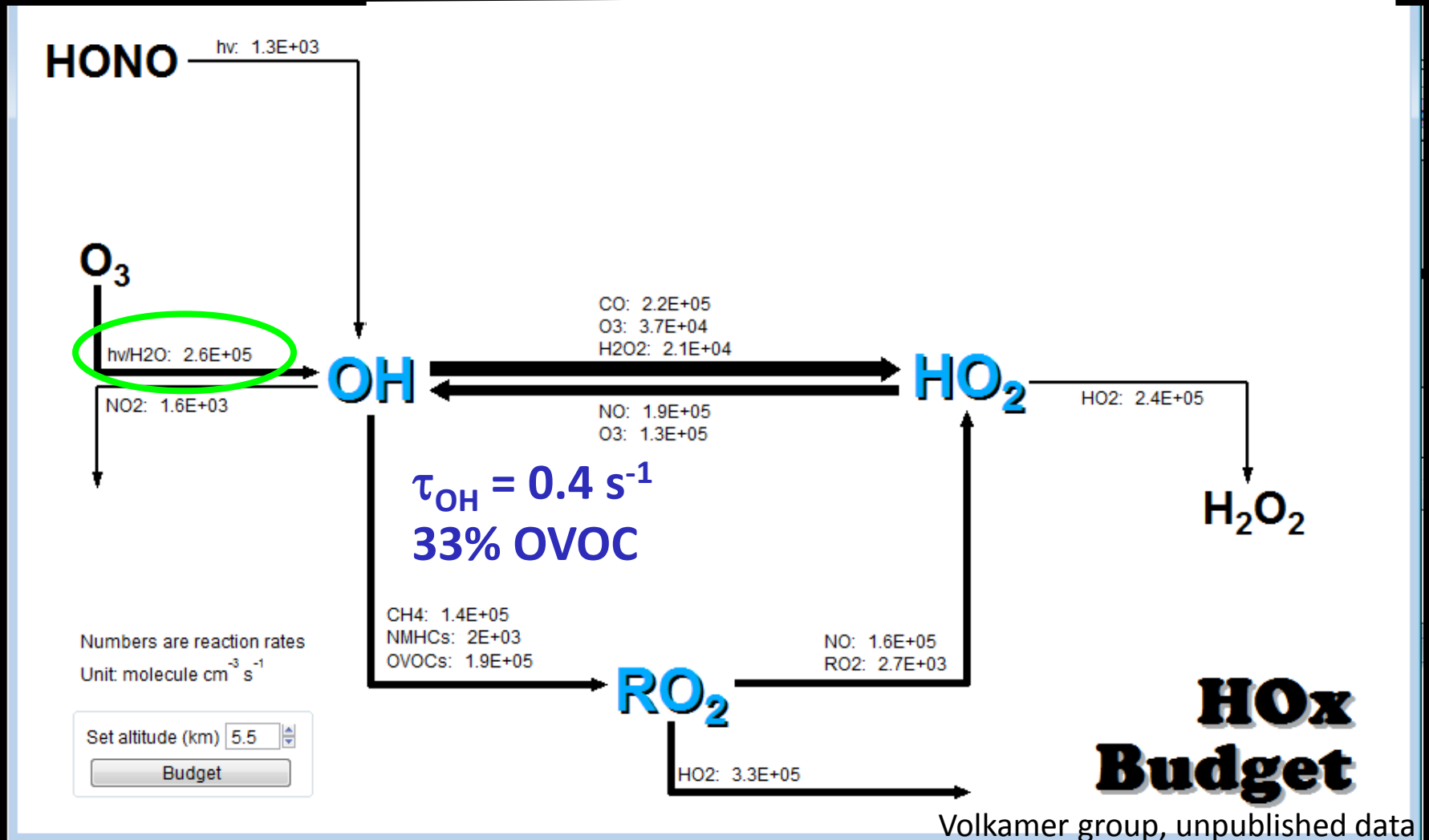
# OVOC impact on oxidative capacity in MBL

- Black: base case
- Red: +0.8 ppb HCHO
- Green: +1.8 ppb ALD2
  
- OH: strong reduction
- Cl: strong reduction
- Br: strong reduction
- I: insensitive

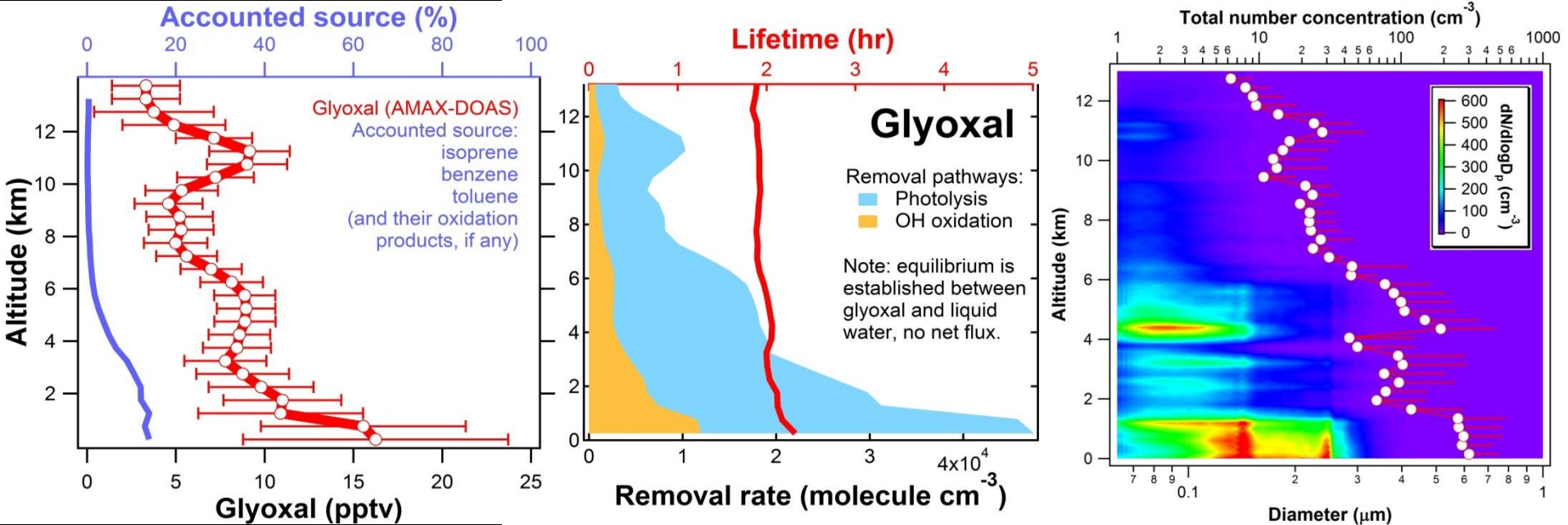


⇒ OVOC are efficient sinks for OH, Cl and Br

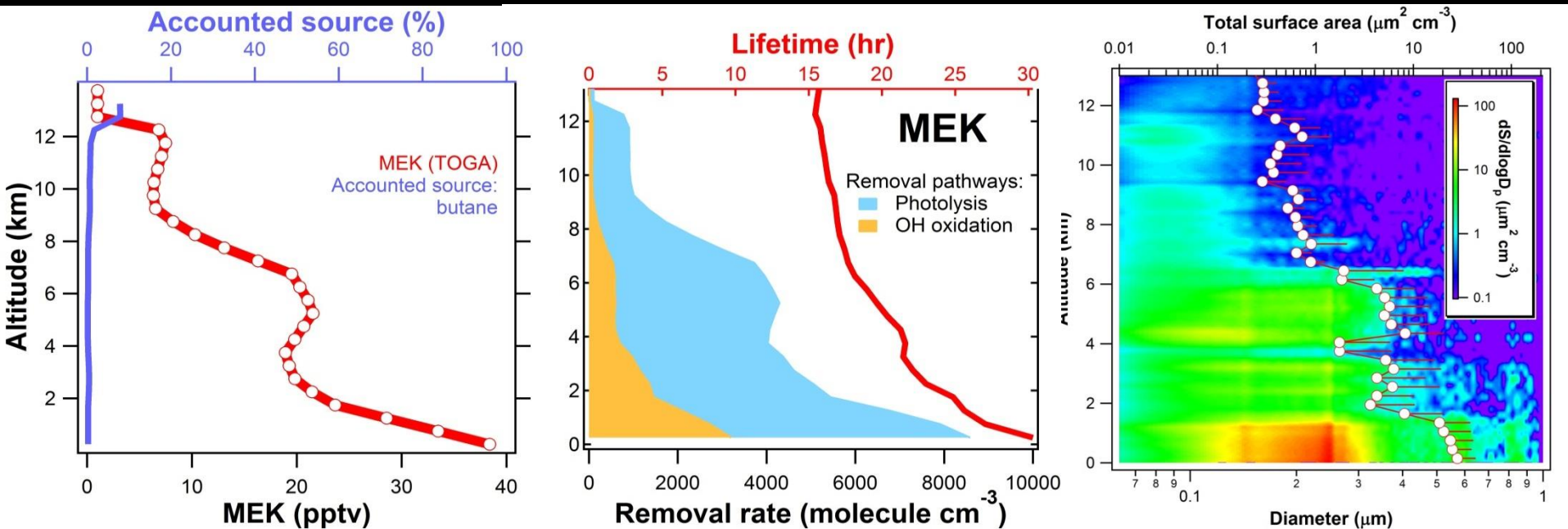
# OVOC impact on HO<sub>x</sub> in FT



RF05 @ 5.5km: OVOC determine ~33% of the OH sink, and ~70% of the recycling flux of OH from HO<sub>2</sub> → net OH source in FT

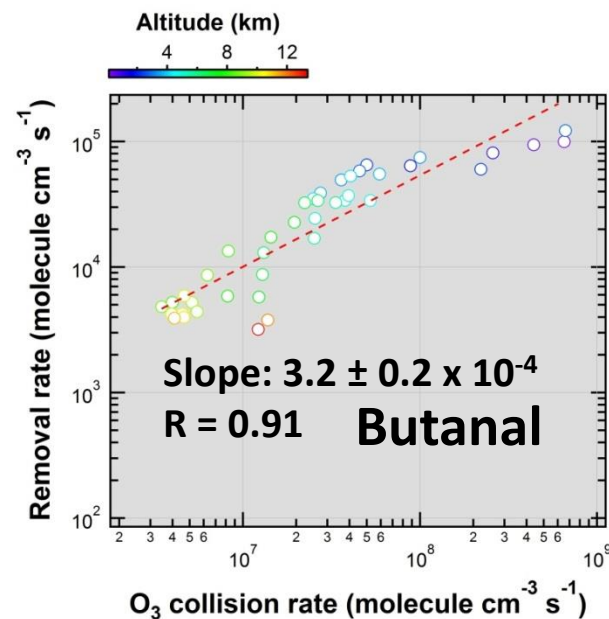
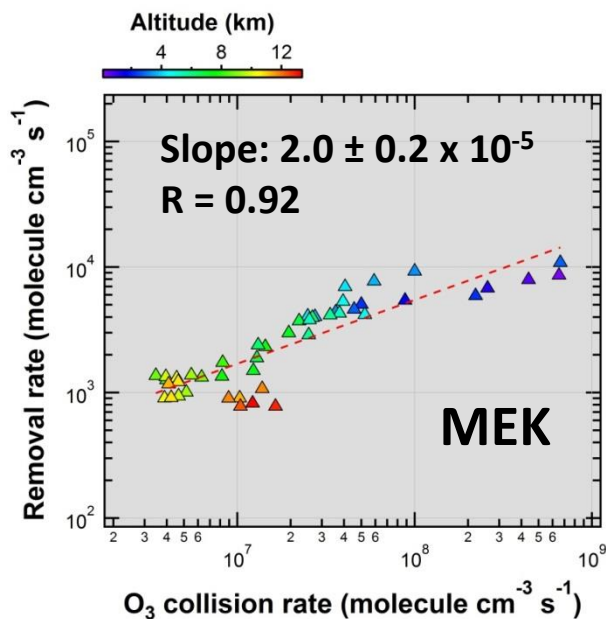
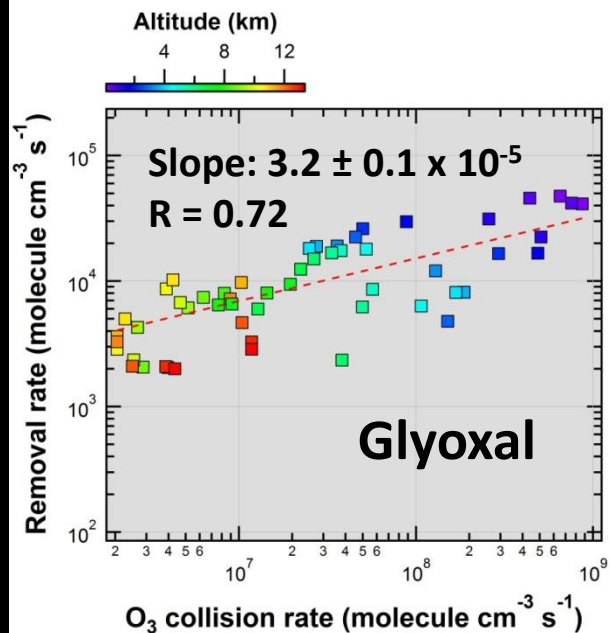


**Steady state assumption: Production rate = loss rate**

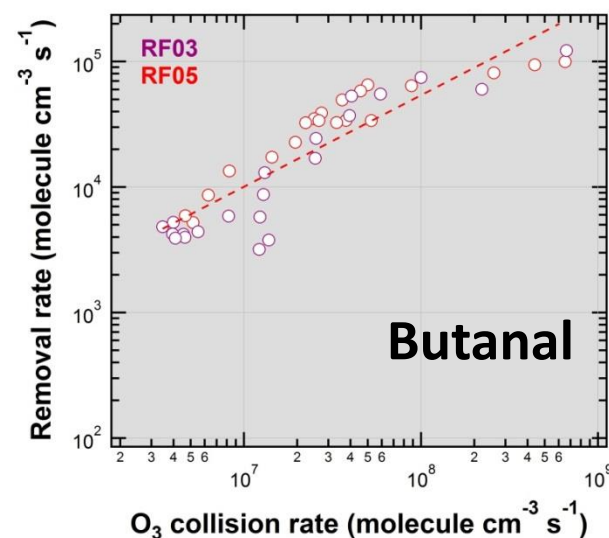
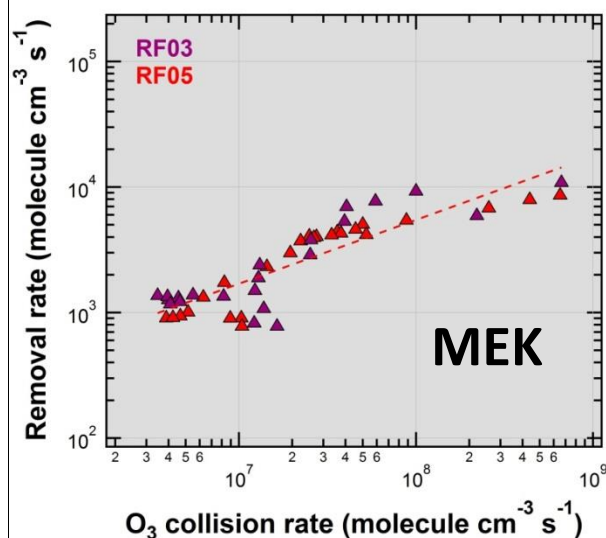
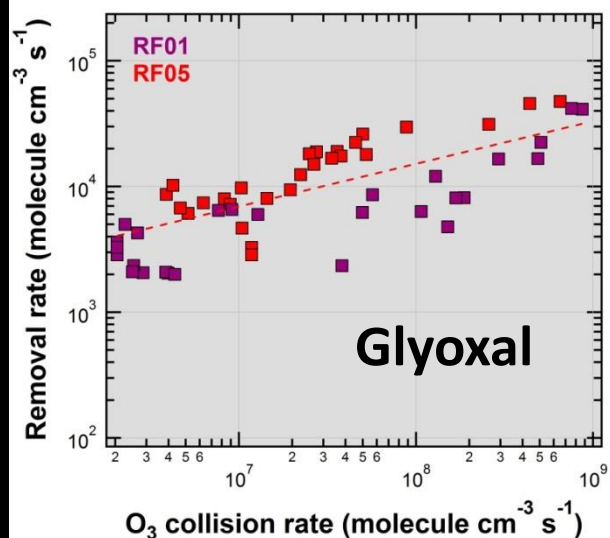




# OVOC profiles are described by variations in aerosol surface area



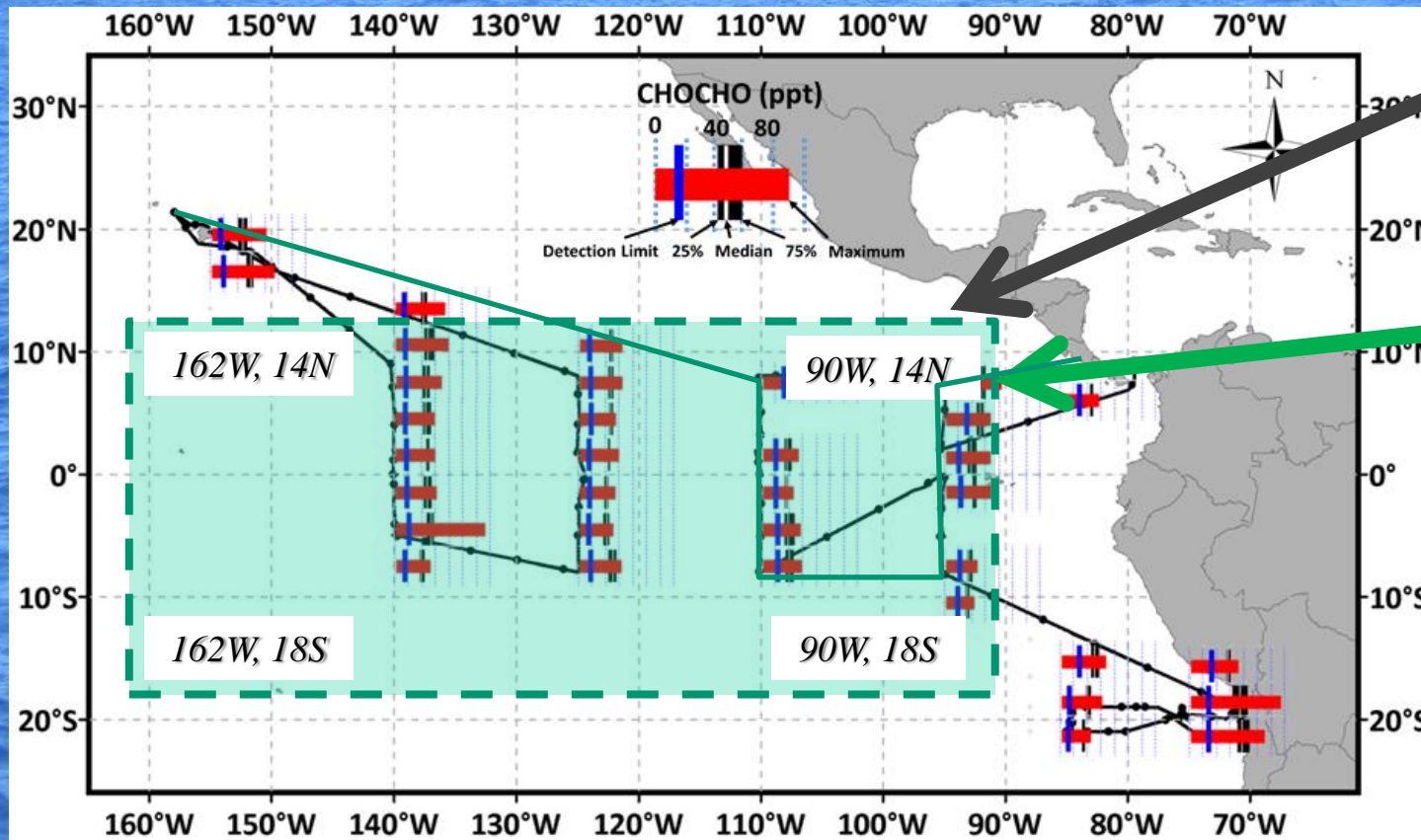
If OH collision rate is calculated  $\rightarrow$  the slope is  $\gg 1$  (non-physical)



# Organic carbon flux of glyoxal



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



**SMAX-DOAS  
Measurements**

**TM4ECPL  
Budget  
Analysis**

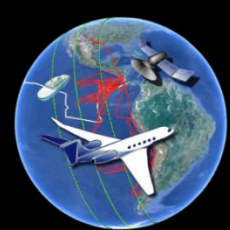
**14-31 TgC  
Glyoxal  
(lower limit)**

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

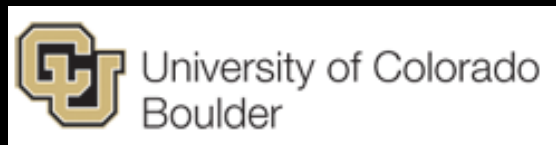
# Organic carbon flux from the ocean

COMPOUND	ROLE IN ATMOSPHERE	OCEANIC EMISSION			OTHER SOURCES	TOKEN REFERENCES
		MASS FLUX	C FLUX	% OF TOTAL EMISSIONS		
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
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	3-8/50 TgC/yr		minor?	Plants, soils, industrial, combustion	Spracklen et al. 2008, Roelofs 2008, Gantt et al. 2009
Acetaldehyde Acetone Glyoxal MEK, Butanal		57 TgC/yr ~1-5 TgC/yr ~30-55 TgC/yr ~100TgC/yr			CDOM  Alkene/OA	Zhou and Mopper, 1990 Kieber et al., 1990 Millet et al., 2009  This work
					<b>(lower limit)</b>	

Ocean:  $\sim 7 \times 10^5$  TgC DOM (about equal to atm. CO<sub>2</sub> mass)



# Conclusions



- Heterogeneous recycling of iodine → Dix et al., 2013, PNAS
- Glyoxal, MEK, Butanal and other OVOCs are observed in the FT  
→ consistent evidence from both optical spectroscopic and mass spectrometric techniques.
- An organic carbon source is missing in models and measurements (OVOC only indicate the intermediate oxidation state).
- Novel chemistry of organic carbon at interfaces, possibly involves a photochemical source of alkenes
- **These OVOC significantly influence oxidative capacity in FT:**
  - source for  $\text{HO}_2$
  - sink for  $\text{OH}$ ,  $\text{BrO}_x$ ,  $\text{ClO}_x$
  - **Coupling of the organic carbon cycle and halogens**



**Funding:** NSF-CAREER, NSF-TORERO, EPRI, NASA, DoE

**Acknowledgements:** NCAR/EOL and RAF, entire TORERO team



2<sup>nd</sup> TORERO Science Team meeting  
CU Boulder, 23-25 July 2012

# Relevance of atmospheric chemistry for Climate

Halogens and organic carbon are relevant components of the atmosphere-climate system, because...

- influences 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
- Can modify the number, size (CCN), and optical properties of aerosols → **aerosol direct and indirect aerosol effect on climate**

# Differential Optical Absorption Spectroscopy (DOAS)

Lambert

In Theory:

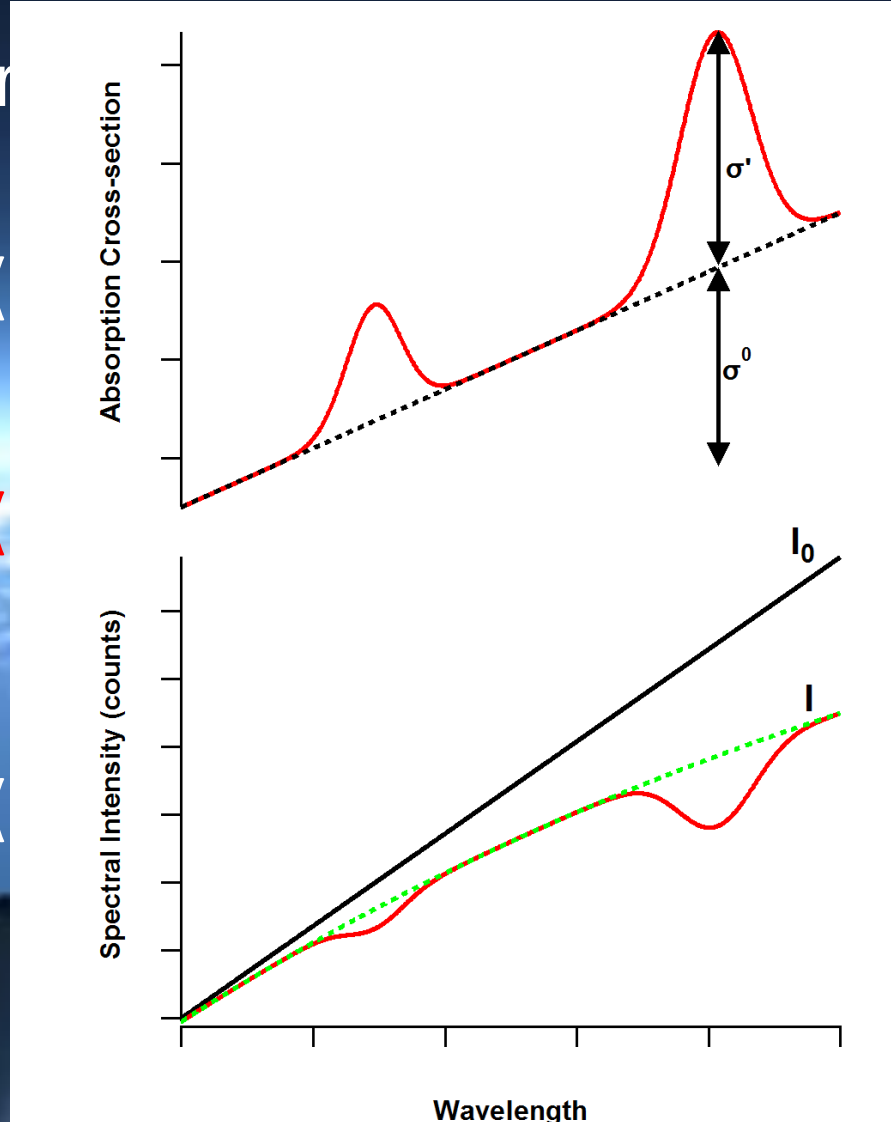
$$I(\lambda) = I_0(\lambda) \cdot e^{-\sigma(\lambda) \cdot L}$$

In reality:

$$I(\lambda) = I_0(\lambda) \cdot e^{-\sigma(\lambda) \cdot L} \cdot T(\lambda)$$

The DOAS

$$I(\lambda) = I_0(\lambda) \cdot e^{-\sigma(\lambda) \cdot L} \cdot T(\lambda)$$



scattering  $\sim \lambda^{-(1...3)}$

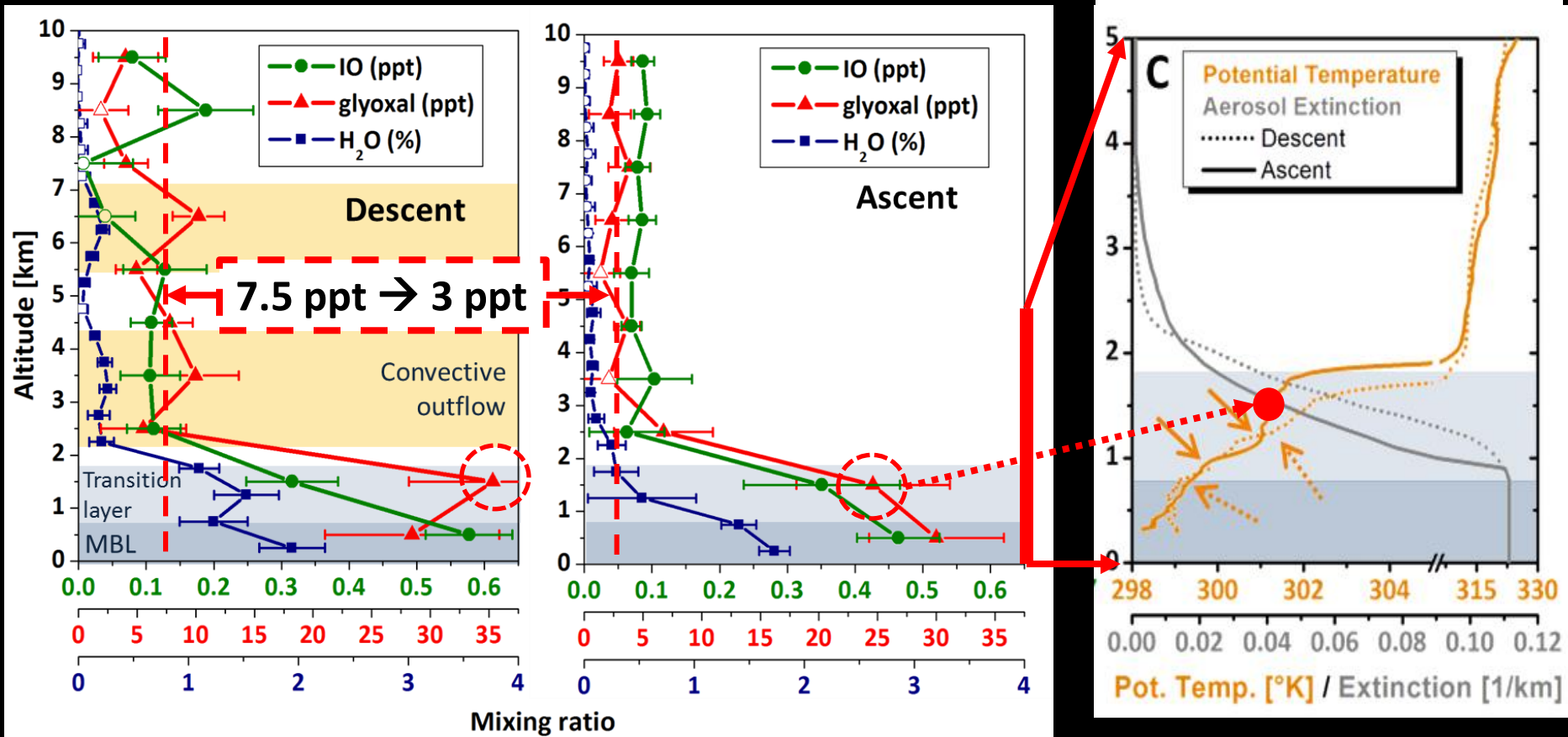
$$I_0 \cdot T(\lambda)$$

$$I_0(\lambda) \cdot e^{-\sigma(\lambda) \cdot L} \cdot T(\lambda)$$

extinction

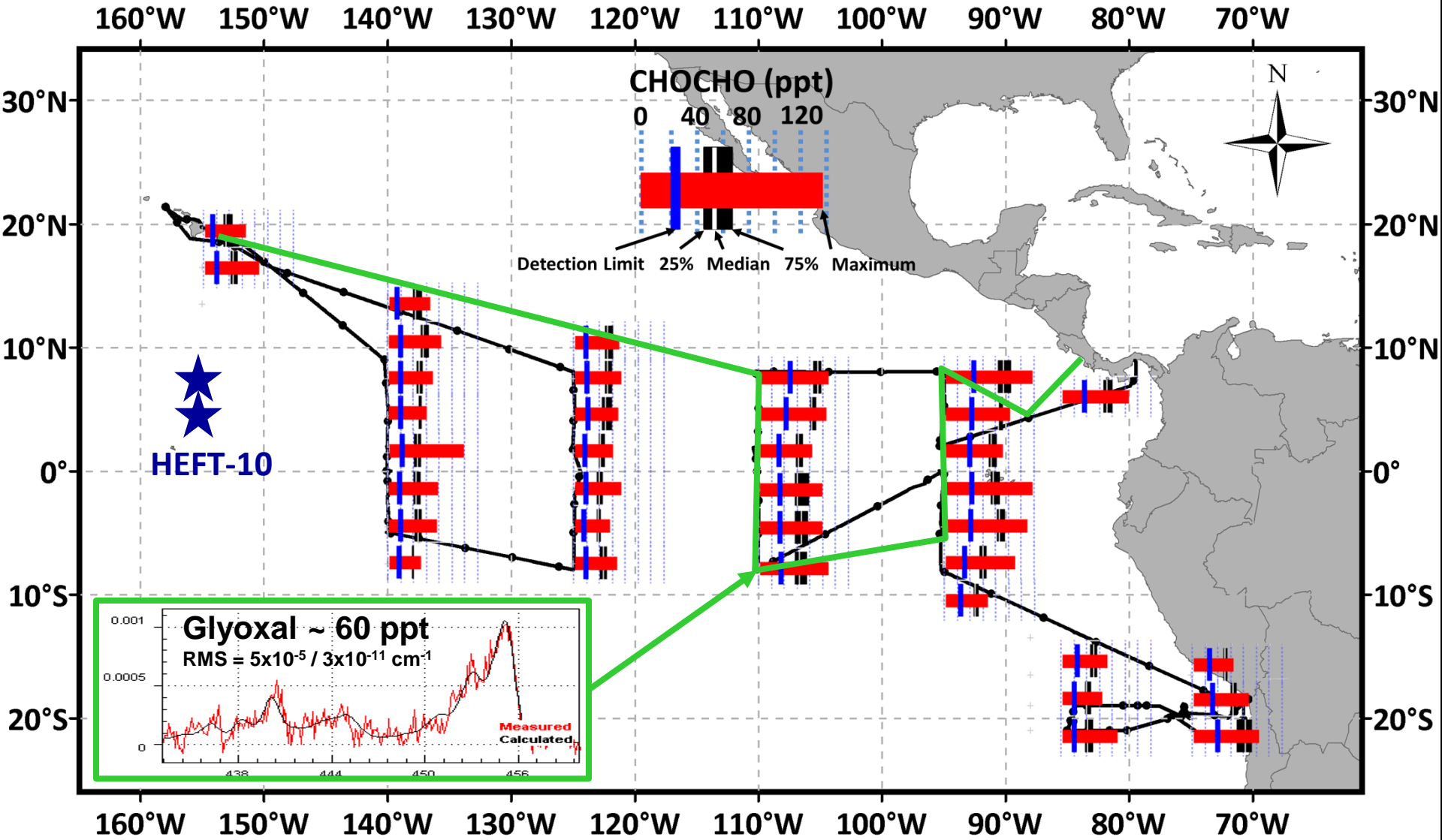
high-pass filtering

# HEFT-10: Iodine oxide, glyoxal and H<sub>2</sub>O



- First glyoxal vertical profiles in the tropical free troposphere
- Glyoxal in a decoupled MBL and in FT are incompatible with its lifetime?  
In contrast to IO, **Glyoxal decreases in aged FT air (60% over 6-7 days)**  
**What is the precursor?**



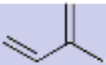

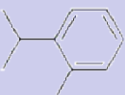
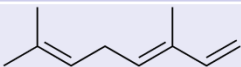
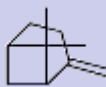
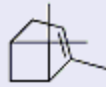


*in-situ* CE-DOAS: **Glyoxal spectral proof** of presence over SH mesotrophic ocean!  
 5 cruises: RB-08-06/07 (VOCALS-Rex), RB-08-08, KA-09-03, KA-12-01 (167 d.a.s.)  
 HEFT-10 flight RF01 → Consistency in MBL: *in-situ* and *remote sensing* instruments

# Reaction of Organics with halogen atoms

- Cl:  $10^{-13} < k_{\text{VOC}} < 10^{-10} \text{ cm}^3/\text{mol/s}$ 
    - $\tau_{\text{Cl}} < 0.2 \text{ sec}$  (capped by  $\text{CH}_4$ )
  - Br:  $10^{-12} < k_{\text{OVOC}} < 10^{-11} \text{ cm}^3/\text{mol/s}$ 
    - $\tau_{\text{Br}} < 4 \text{ sec}$  (RCHO  $\sim 0.8 \text{ ppb}$ )
  - 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

# 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

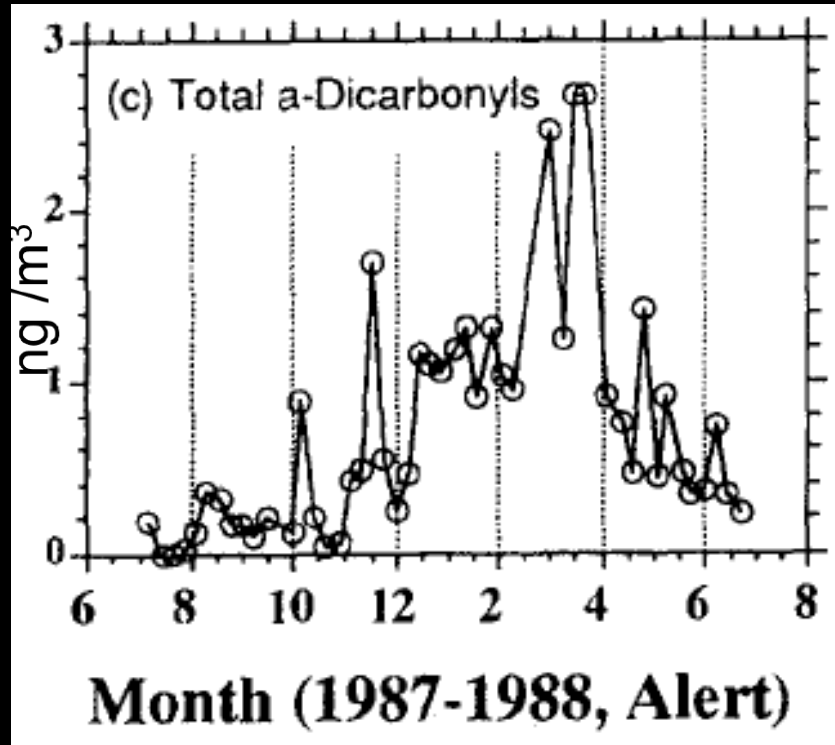
**$\Sigma$  Glyoxal = 2-7 ppt**

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 must be a heterogeneous process !**

\* b-pinene yield: 100%; o/p-cymene yield: taken as o/p-xylene; limonene yield: unpublished data; assuming  $[\text{OH}] = 3 \cdot 10^6 \text{ molec/cm}^3$  and a glyoxal lifetime of 1.5 hrs

# Glyoxal in particles: Field evidence

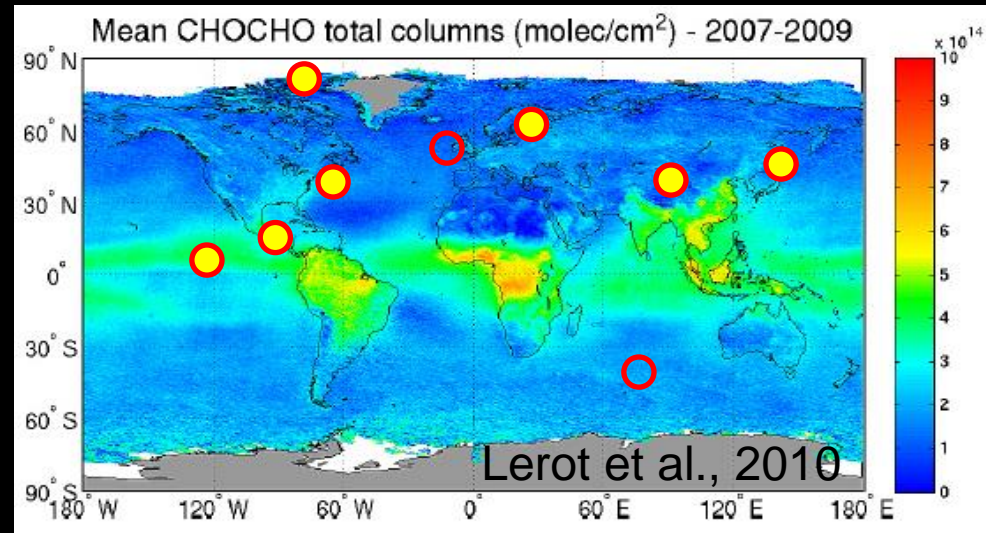


## Arctic aerosol: Alert

Peak in early spring

Few weeks earlier than diacids

3-4 times more GLY than MGLY



**Glyoxal is a ubiquitous product of anthropogenic and biogenic/marine precursors, and found in aerosols**

## Marine aerosol: Hokkaido Island

GLYg = 42 ng /m<sup>3</sup> (18 ppt)

$P / (P + G) = 0.46$

Alert: Kawamura et al., 1996

Mexico City: Volkamer et al., 2007

Continental (Tibet): Meng et al., 2013

Marine: Matsunaga and Kawamura, 2004

Biogenic (Hyytiälä): Kampf et al., 2012

Southern Hemisph.: Rinaldi et al., 2011

# Organic carbon flux from the ocean

COMPOUND	ROLE IN ATMOSPHERE	OCEANIC EMISSION			OTHER SOURCES	TOKEN REFERENCES
		MASS FLUX	C FLUX	% OF TOTAL EMISSIONS		
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
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	3-8/50 TgC/yr		minor?	Plants, soils, industrial, combustion	Spracklen et al. 2008, Roelofs 2008, Gantt et al. 2009
Acetaldehyde Acetone Glyoxal MEK, Butanal		57 TgC/yr ~1-5 TgC/yr >30-55 TgC/yr >100TgC/yr			CDOM  Alkene/OA	Zhou and Mopper, 1990 Kieber et al., 1990 Millet et al., 2009  This work

**(lower limit)**

Ocean:  $\sim 7 \times 10^5$  TgC DOM (about equal to atm. CO<sub>2</sub> mass)

# Conclusions (TORERO hypothesis #1)

**TORERO hypothesis #1: Glyoxal over oceans is a smoking gun for other oxygenated VOC, and 'missing' sources from ocean biology.**

## **Confirmed**

- *Glyoxal, MEK, Butanal are observed in the FT → consistent evidence from both optical spectroscopic and mass spectrometric techniques.*
- *OVOC are observed over the least productive (oligotrophic) ocean, and over much of the tropical air column (not in stratosphere)*
- *Previously unrecognized chemistry of marine organic carbon at interfaces likely involves a heterogeneous photochemical alkene source.*

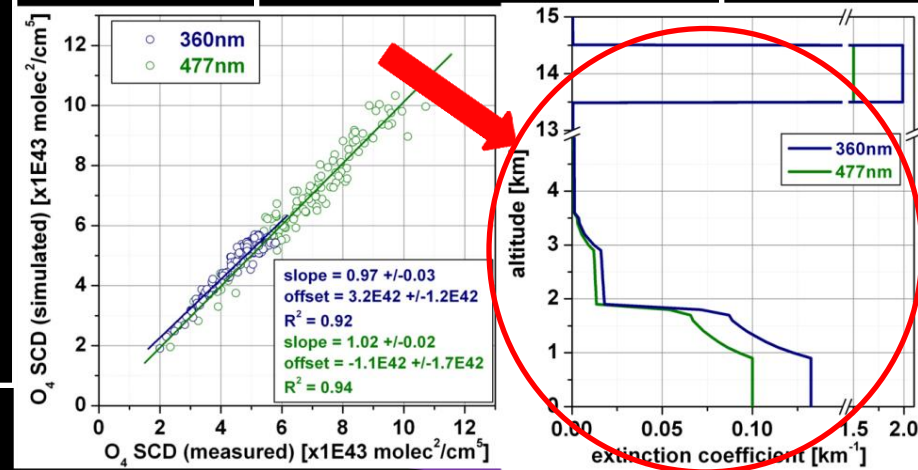
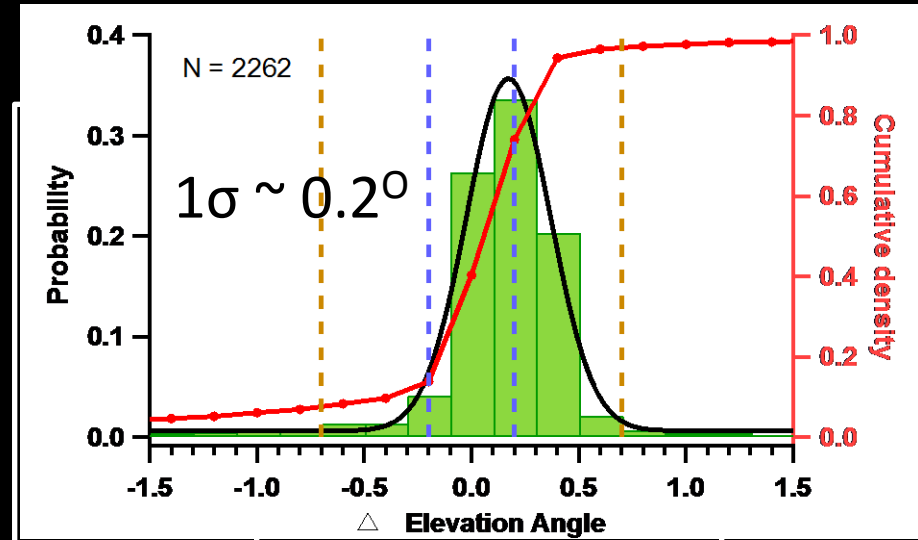
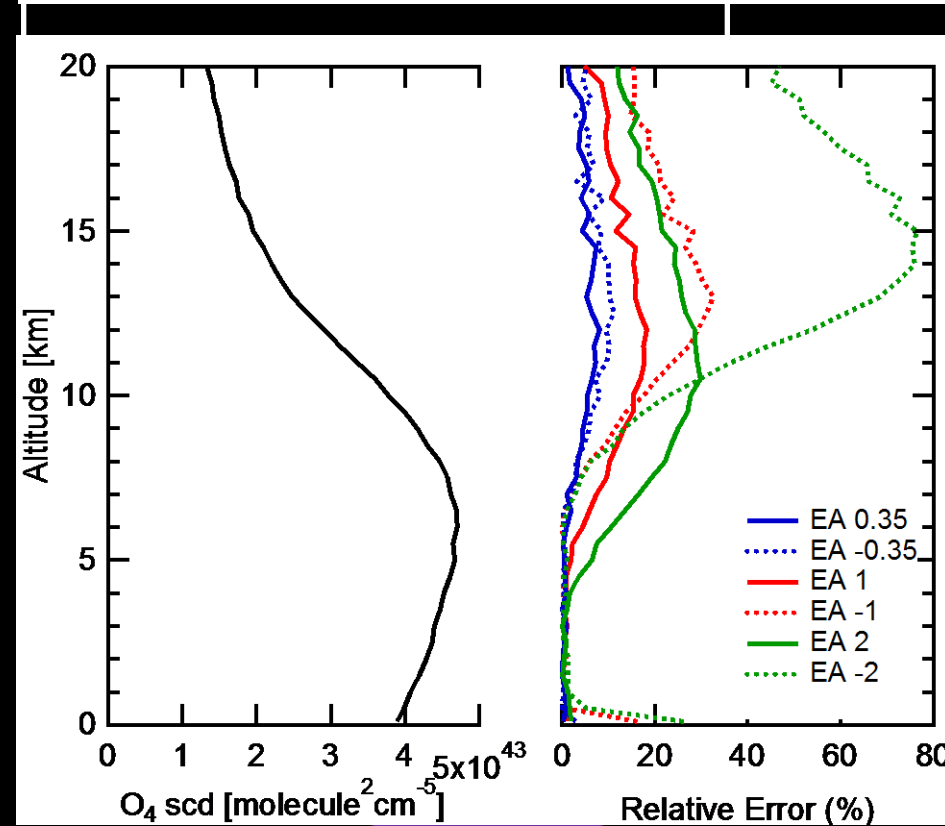
***Biological link ? – Maybe, but glyoxal is found over oligotrophic ocean! More widespread than Chl-a suggests – physics, chemistry, biology?***

**Funding: NSF-CAREER, NSF-AGS (TORERO)**



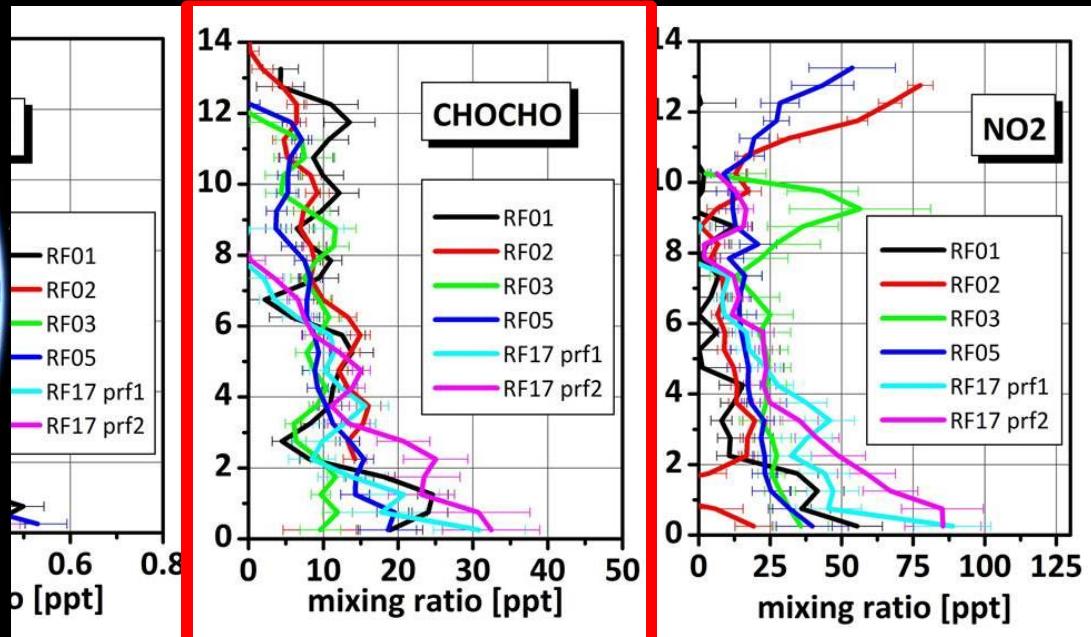
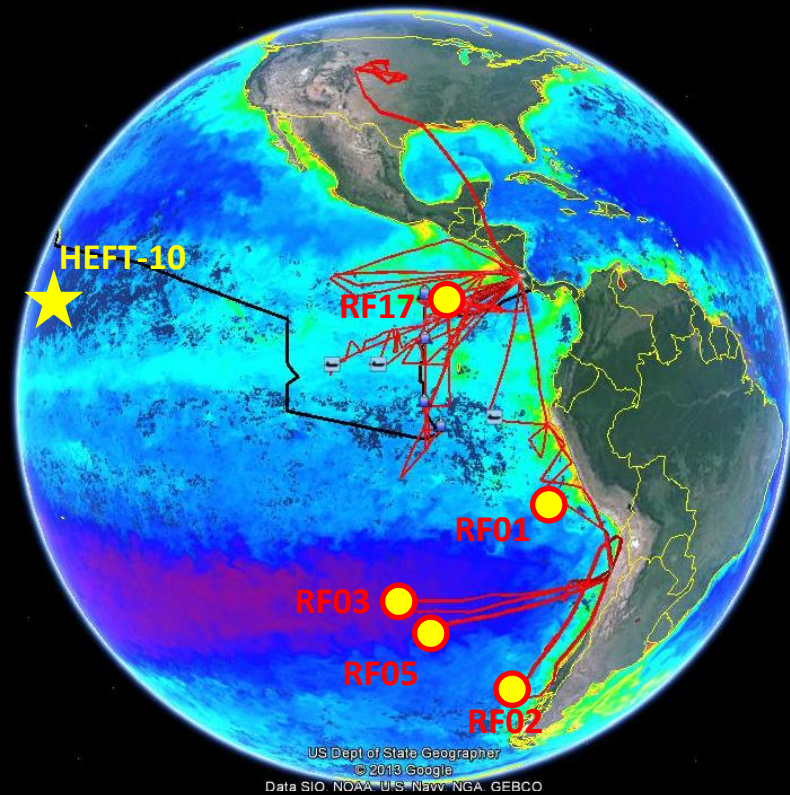
# Vertical profiles: Non-linear Optimal Estimation

Technological innovation:  
Motion stabilization & low RMS



⇒ Trace gases and aerosol extinction profiles

# Widespread BrO, IO, glyoxal, and NO<sub>2</sub> in the FT



- MBL: 10-35 ppt glyoxal (Eastern Pacific Ocean)
- FT: 5-15 ppt (Eastern) and 3-7 ppt (Central Pacific – HEFT-10)
- Stratosphere: no signal detectable
- Glyoxal is part of a biogeochemical cycle



Marine organic carbon at interfaces is distributed throughout the entire tropospheric air column

Are OVOCs boiling off organic aerosols as the result of heterogeneous oxidation?

Thornberry and Abbatt, 2003; Molina et al., 2004

Further mechanistic insights from *in-situ* fast **CE-DOAS** measurements

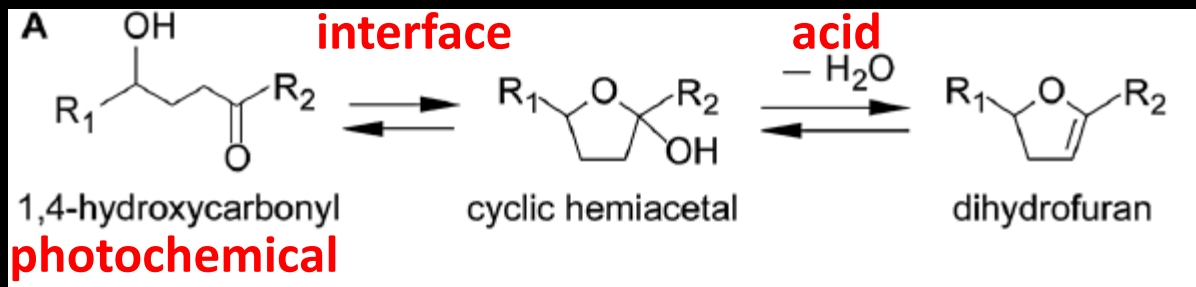
Diurnal Cycle, Eddy Covariance Fluxes

# What field data tells us about the mechanism

- Dark source:  $O_3$  reaction => alkene precursor
- Daytime source ~ 6x larger than nighttime source
  - Photochemistry involved (forms OVOC or its precursor)
- Aerosol surface area variations drive the variability in the OVOC production rate vertical profile
  - Mechanism involves an interface !
- OVOC precursor: aerosol or gas-phase?
  - OVOC precursor: lifetime > 4 days
  - 200nm particle:  $\gamma_{O_3} \sim 10^{-6} \rightarrow$  lifetime  $\tau_{OA} \sim 1.5$  d
  - OVOC source:  $2 \times 10^{-5} < \gamma_{O_3} < 2 \times 10^{-4} \rightarrow$  lifetime  $\tau_{OA} \ll 1$  d
  - POA source 7-50 TgC/yr  $\leftrightarrow$  30-55 TgC/yr glyoxal (MBL only)
    - The glyoxal source is comparable or larger than the marine POA source

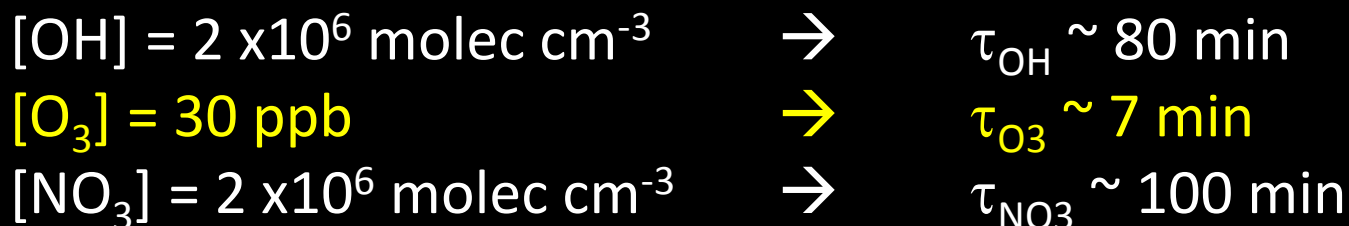
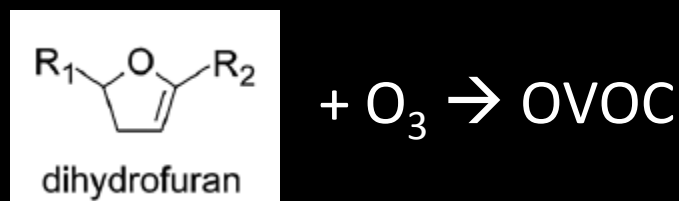
Marine POA oxidation may account for some OVOC, but what about partitioning of the gas-phase pool?

# Heterogeneous photochemical alkene source



Ziemann and Atkinson, 2013

Alkane + OH  $\rightarrow$   $\rightarrow$  surfaces  $\rightarrow$   $\rightarrow$  Alkene



Atkinson et al., 2008; Lim and Ziemann, 2009