Diurnal cycle and eddy covariance flux measurements of glyoxal over the tropical Pacific Ocean during TORERO 2012

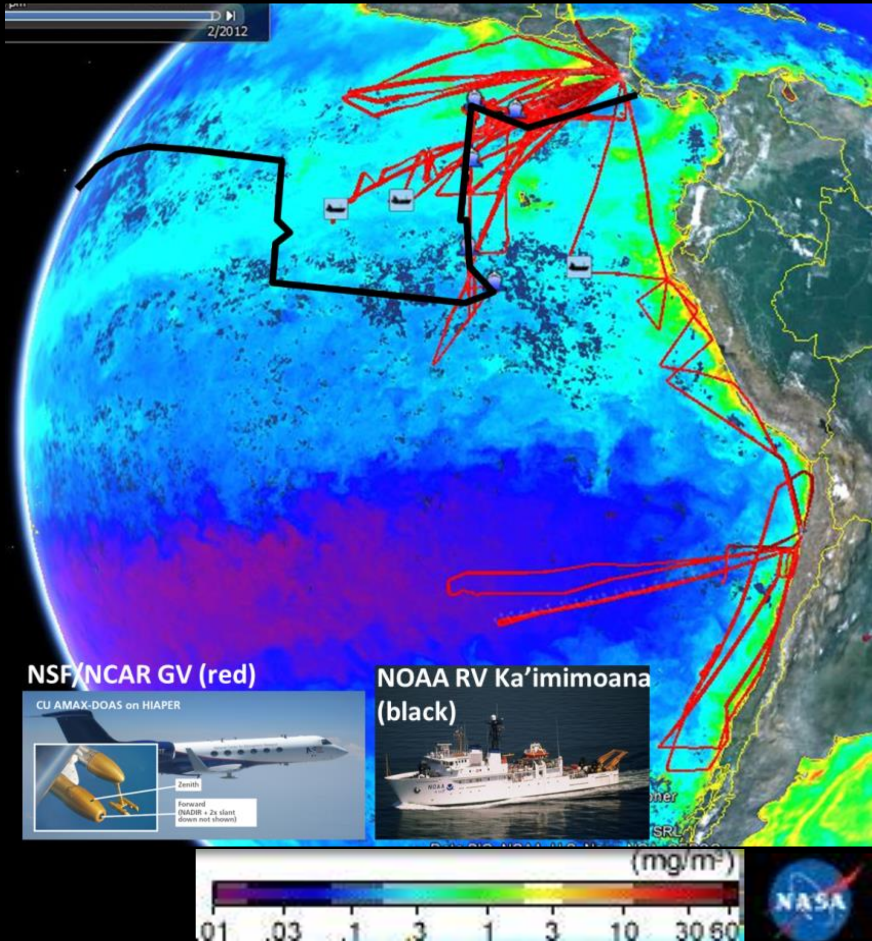
Sean Coburn[1], Barbara Dix[1], Laura Gonzalez[1], Ivan Ortega[1], Roman Sinreich[1], Ryan Thalman[1,#] , Eleanor Waxman[1], Rainer Volkamer[1,2]

[1]Dept. Chemistry and Biochemistry, and [2]CIRES, CU Boulder

[#]Now at Brookhaven National Lab, Long Island, New York

Overview

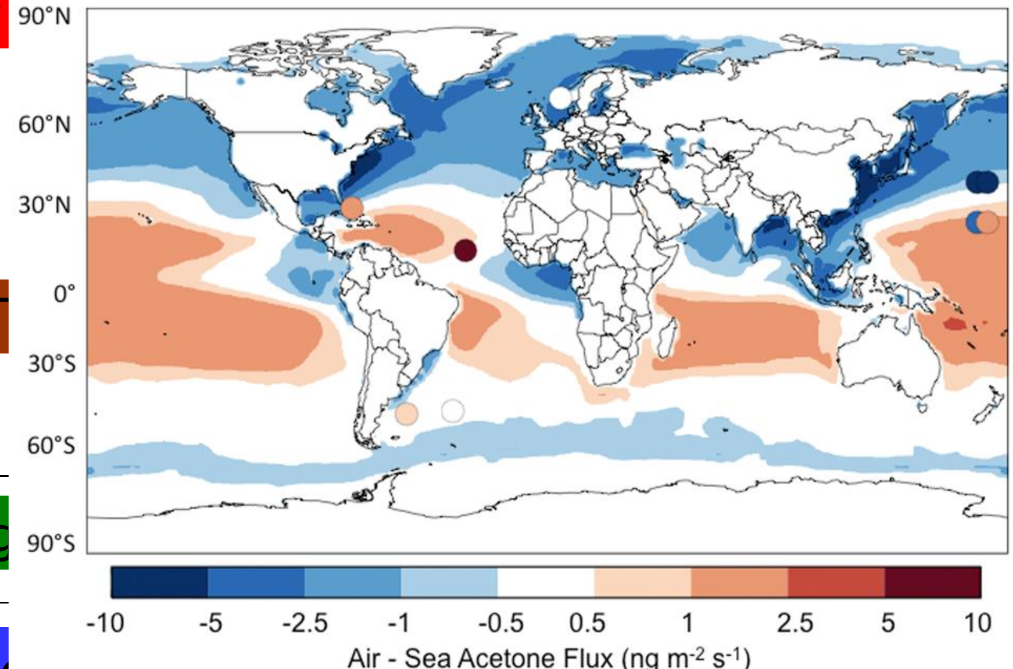
- Introduction/Background
- CU LED-CE-DOAS instrument
- Eddy covariance method
- Results
- Discussion



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:						
DMS	Global sulfur budget Aerosol precursor: atmospheric acidity and cloud nucleation	14-29				
COS	Precursor of stratospheric aerosol	0.30 TgS/yr				
CS_2	COS precursor	0.15 TgS/yr				
NMHC	Tropospheric (photo)chemistry, aerosol precursors and cloud nucleation	1-10 T				
POA	Tropospheric (photo)chemistry, cloud nucleation	3-8 Tg				
Acetaldehyde Acetone		57 Tg ?				

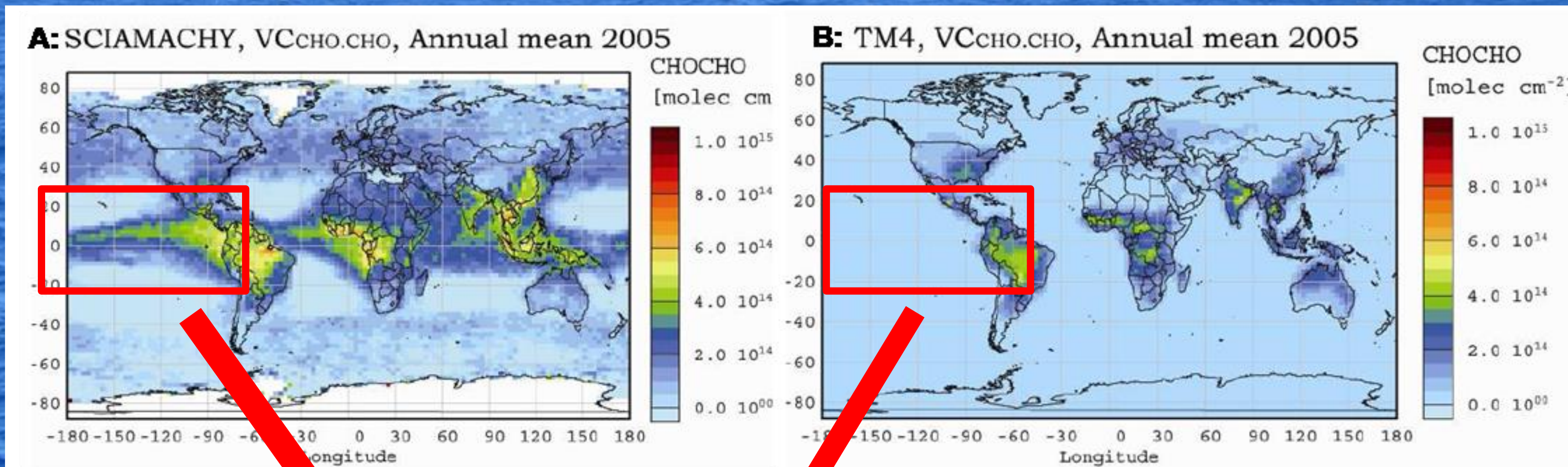
Acetone: GEOS-Chem annual mean

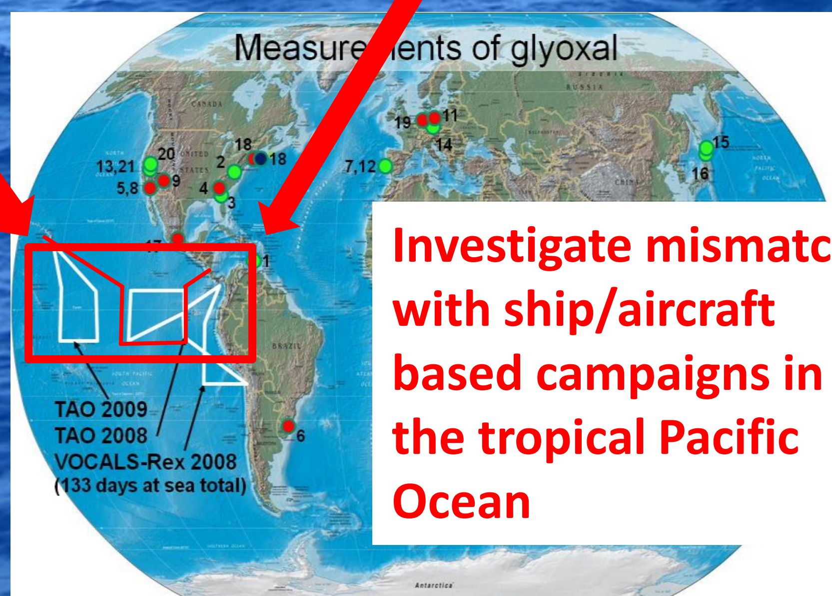


Small global average net flux (~1.2 TgC/yr).
Fischer et al., 2012

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

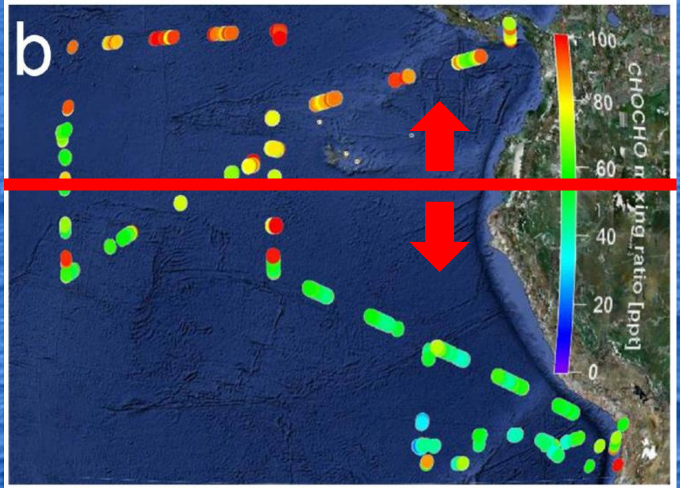
Glyoxal: Over the Ocean





Investigate mismatch with ship/aircraft based campaigns in the tropical Pacific Ocean

Glyoxal: Over the Ocean…cont'd



Sinreich et al, 2010 (ACP)

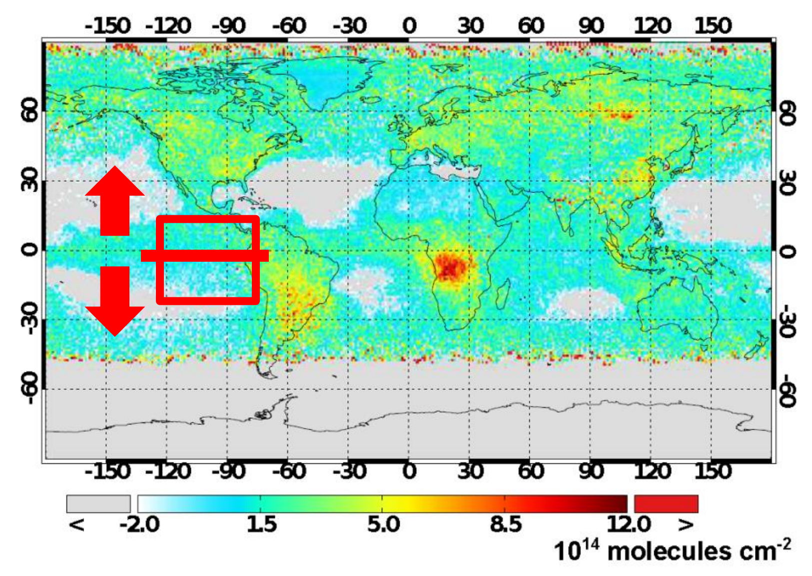
Tropical Pacific Ocean

Sinreich et al, 2010: 40-80 ppt (~63 ppt)

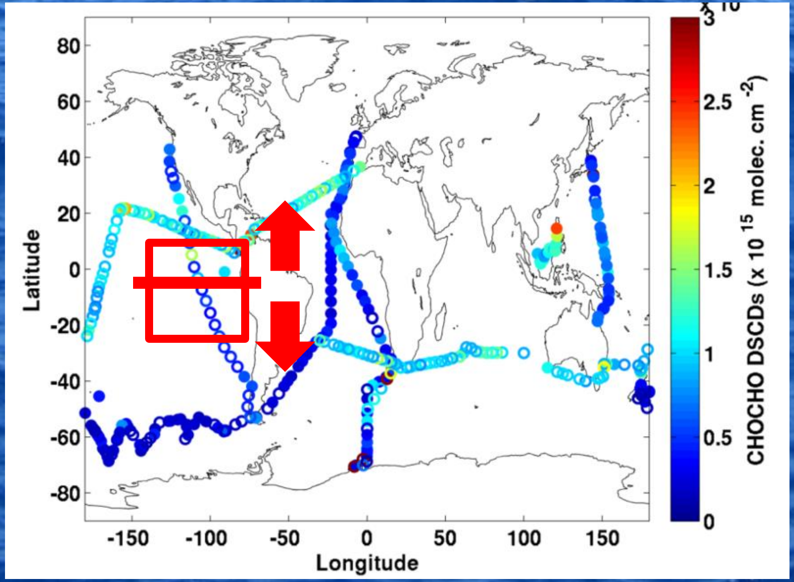
Miller et al, 2014 : 40-90 ppt (~60 ppt)

Mahajan et al, 2014: <40 ppt (~25 ppt)

→ Gradient: North H. > South H.



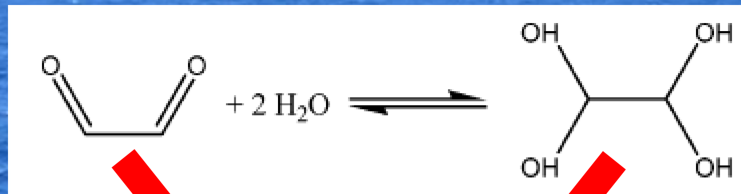
Miller et al, 2014 (AMTD)



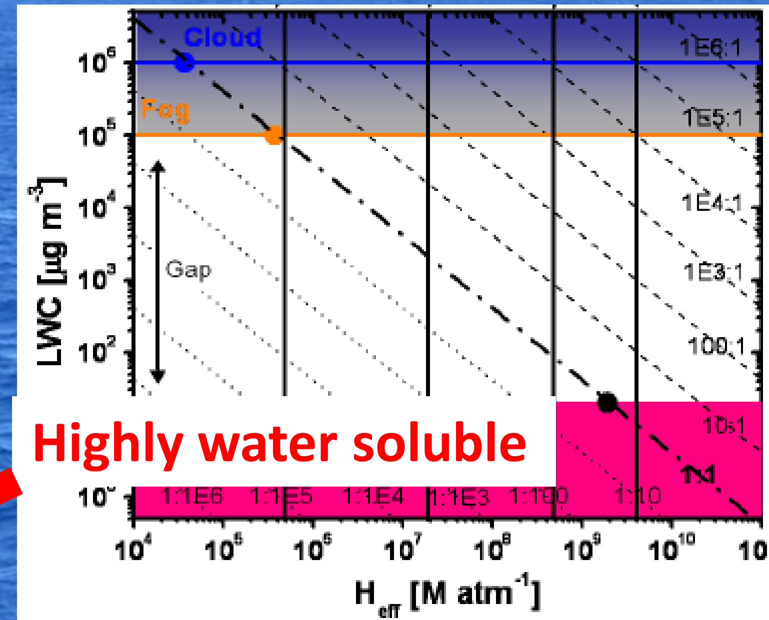
Mahajan et al, 2014 (JGR-A)

Glyoxal: Chemical and Physical Properties

Oxidation of many VOCs →



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	$4x10^5$



Highly water soluble

Atmospheric lifetime: ~ 2.5hrs
- 52% photolysis
- 18% OH
- 22% SOA in
- 8% Dry/wet dep

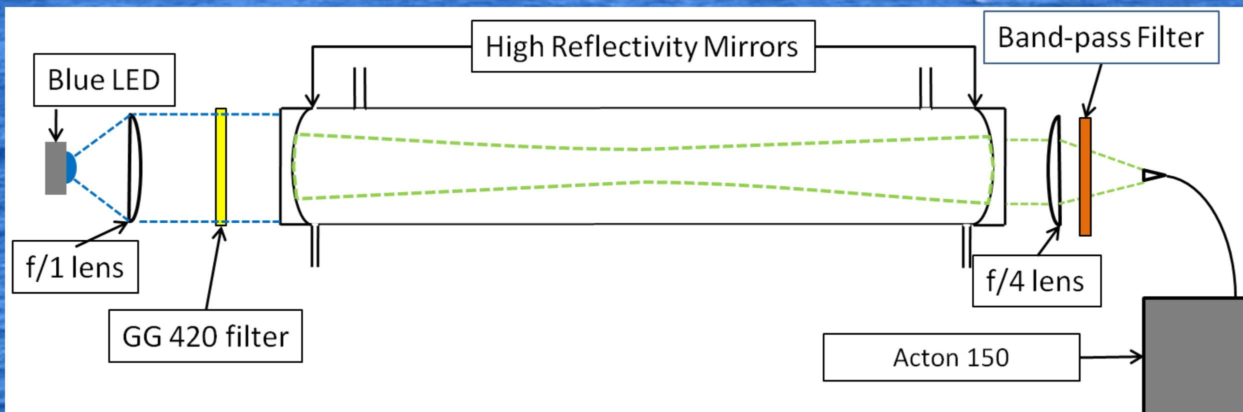
Poster #8:
Eleanor Waxman

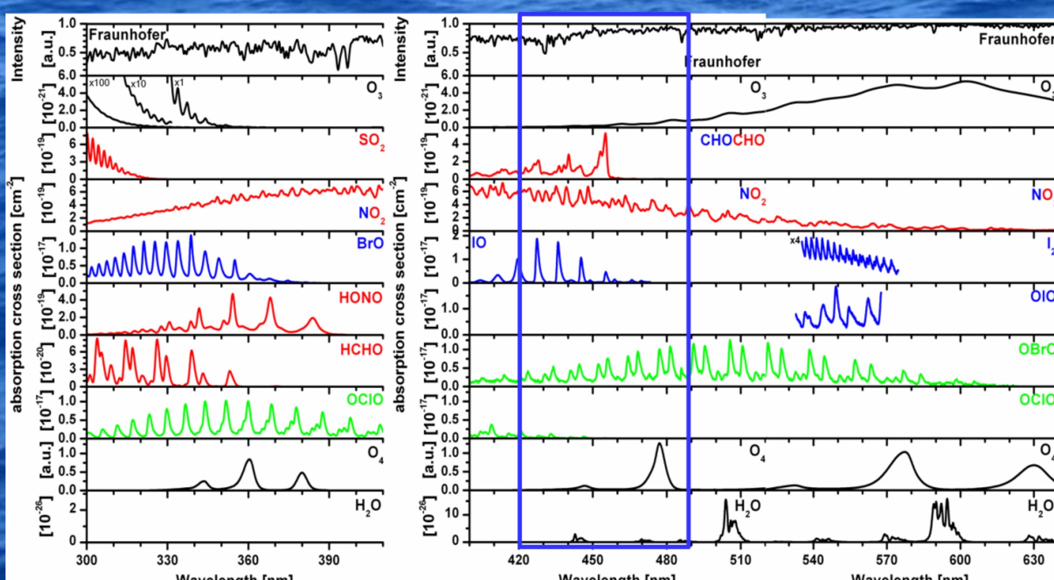
Continental source: ~108 Tg/yr
- 50% unaccounted
- 30% biogenic (i.e. isoprene)
- 14% anthropogenic
- 6% biomass burning

→ Unique properties → Unique indicator for atmospheric processes (VOC sources, oxidation)

Stavrakou et al., 2009 (ACP); Volkamer et al., 2005 (GRL)

Cavity Enhanced DOAS (CE-DOAS)





420-490nm, R(460nm) =0.99997

L_{eff}= 18-20km

ACTON/PIXIS

0.7 nm FWHM

Thalman and Volkamer, 2010 (AMT)

Coburn et al., 2014 (AMTD)

TORERO Activities: RV *Ka'imimoana*

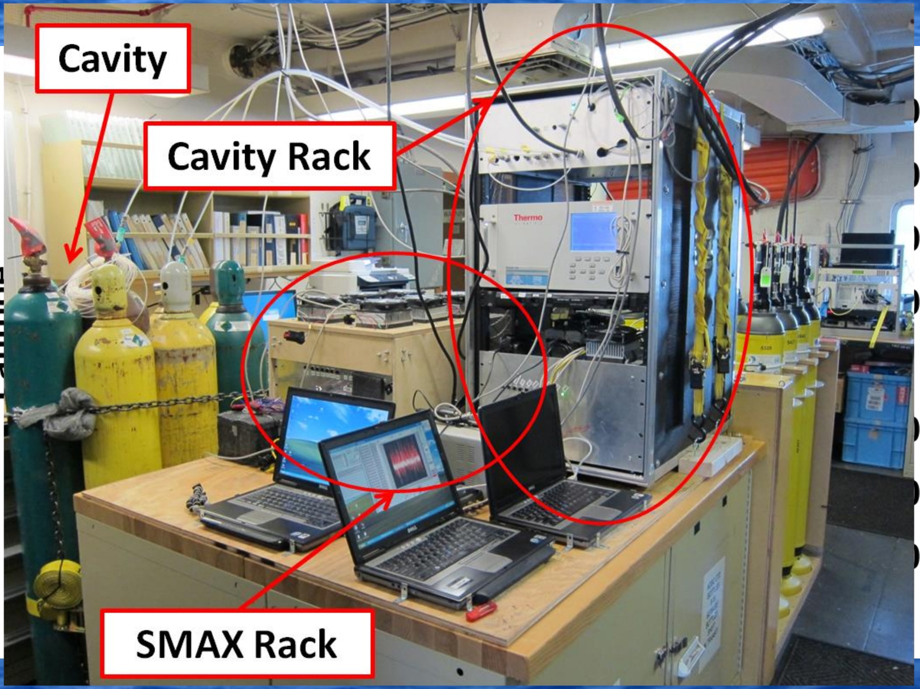
Instrument/Technique	Species Measured	Institution
MAX-DOAS	VOCs, BrO, IO, NO_2	University of Colorado
CE-DOAS	Glyoxal, NO_2	University of Colorado
Air canisters	VOCs	University of Miami
GC-MS (air/water)	VSLH	University of York
Denuders	I_2, inter-halogen species	University of Mainz
Flux tower	CO_2 fluxes	University of Hawaii/NOAA
Aerosol filters	Aerosol chemical speciation	Hokkaido University

TORERO Activities: RV *Ka'imimoana*

Inlets for CE-DOAS, O_3 monitor, GC-MS, Anemometer

Aircraft: NCAR GV

Ship: NOAA *Ka'imimoana*



Eddy Covariance Technique

- Flux is the mean covariance of the vertical wind velocity fluctuations and fluctuations in the physical/chemical parameter of interest

$$F_x = \overline{w'x'}$$

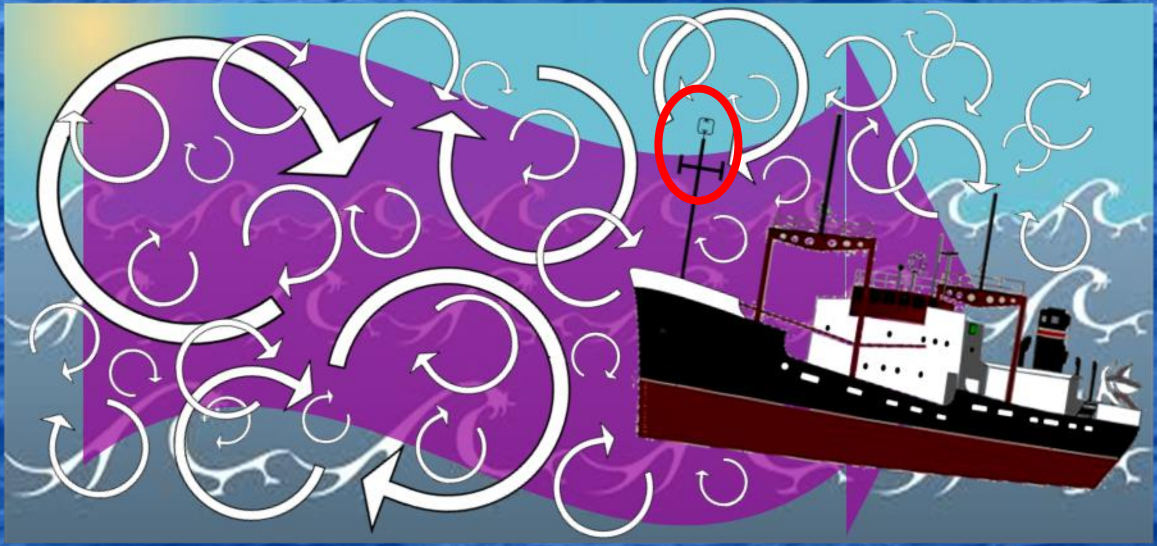
w = vertical wind velocity
x = mixing ratio of analyte

Prime denotes instantaneous deviation from the mean

- Allow to measure vertical gas fluxes in the MBL
  - Facilitate understanding of air-sea exchange of measured species

<u>Requirements:</u>

- Fast measurements
  - Wind velocities
  - Concentration of analyte
- Accurate wind measurements
- Bonus: white noise sensor



Eddy Covariance Technique

vertical wind velocity fluctuations → **Measurements complicated for mobile platforms (ships)** → **Only 7 molecules currently reported**

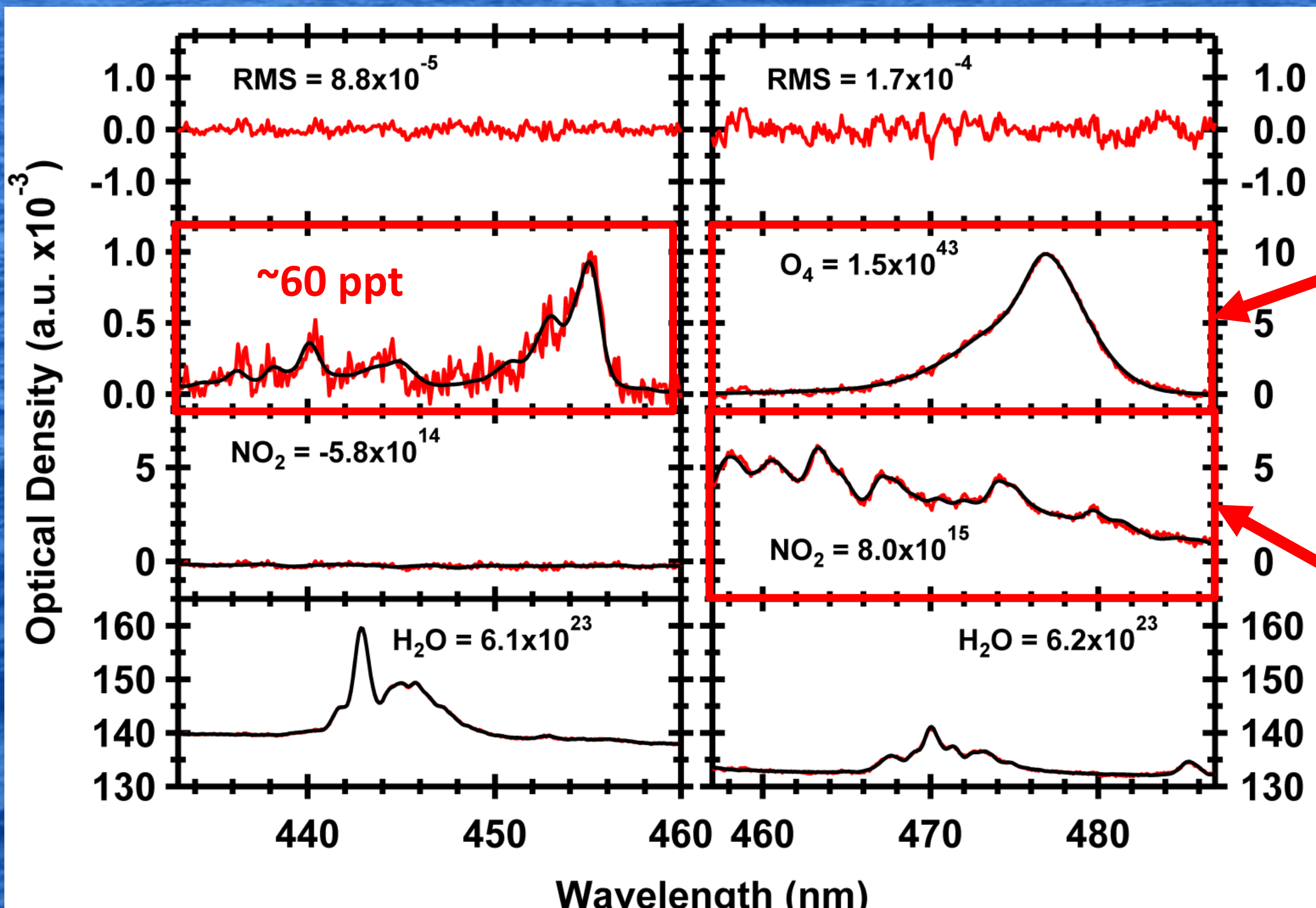
$$F_x = \overline{w'x'}$$

Molecule	MBL Concentration (pptv)	k_H (M/atm)	Lifetime* (days)	Reference flux measurement in MBL
CO_2	380-400 ($x10^6$)	0.035	$>3x10^5$	Fairall et al. 2000
CO	60-150 ($x10^3$)	$1x10^{-3}$	16	Blomquist et al. 2012
Acetone	[illegible]	[illegible]	[illegible]	...et al. 2014
O_3	10...	[illegible]	[illegible]	...et al. 2010
Methanol	[illegible]	[illegible]	[illegible]	...o et al. 2005
DMS	20-1500	0.485	0.8	Hubert et al. 2004
Acetaldehyde	200-300	14.1	0.2	Yang et al. 2014
Glyoxal	25-80	$4.2x10^5$	$9x10^{-2}$	This work

*Lifetimes calculated against reaction with OH (assuming [OH] = $3x10^6$ molec cm^{-3}), and photolysis rates calculated for aerosol free, noon time at equator conditions

Could help inform about sources of marine organic carbon

Trace Gas Measurements



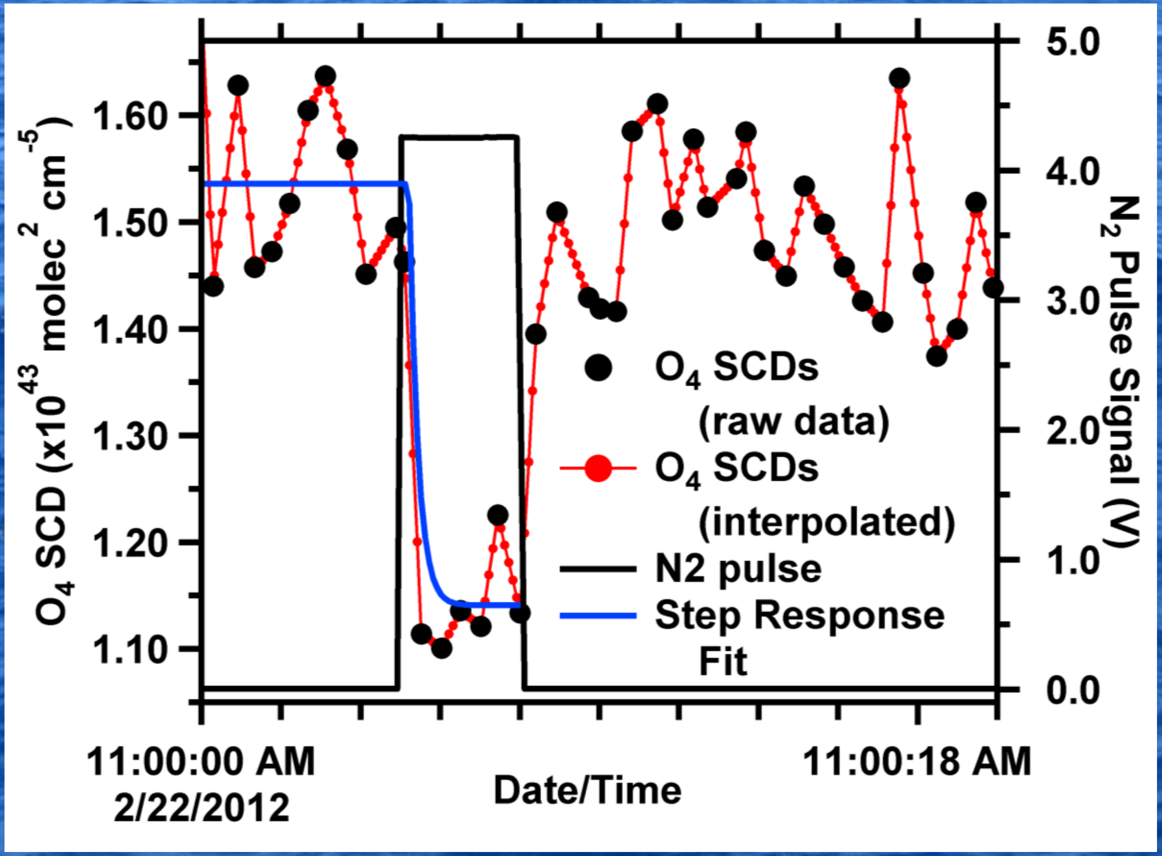
O_4 measurements for instrument characterization

NO_2 measurements for data filtering

Coburn et al., 2014 (AMTD)

Data Processing

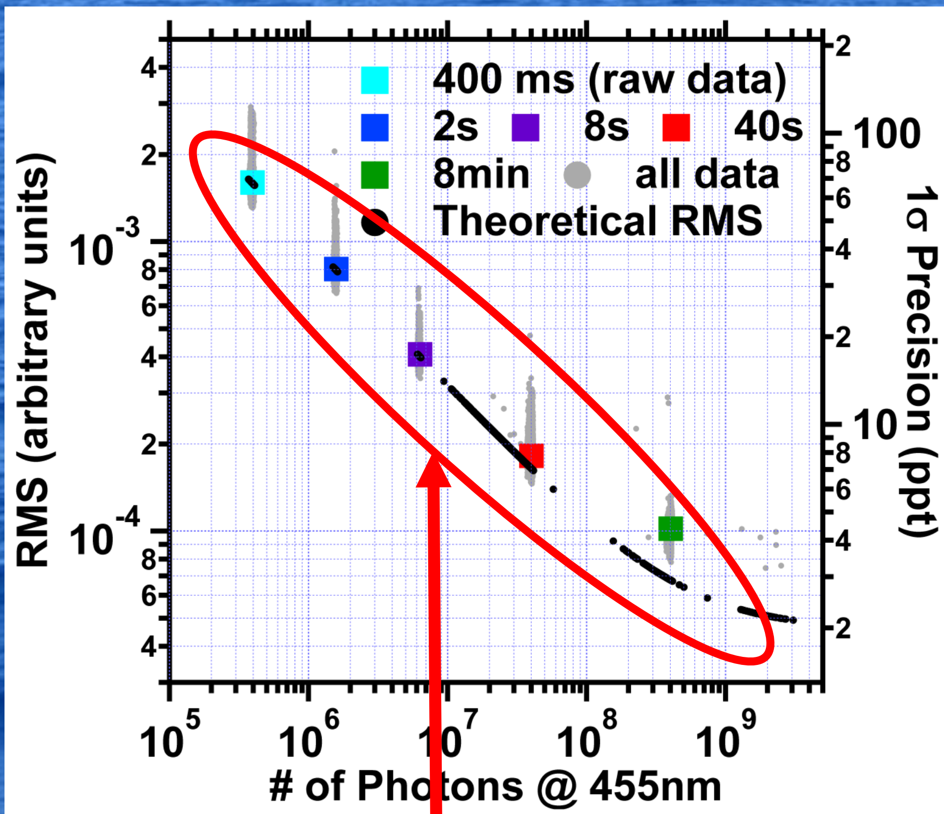
- Measurements of trace gas concentration and vertical wind velocity need to be on same time stamp
- Nitrogen pulse and O_4 signal to perform correction



Bariteau et al., 2014 (AMT)

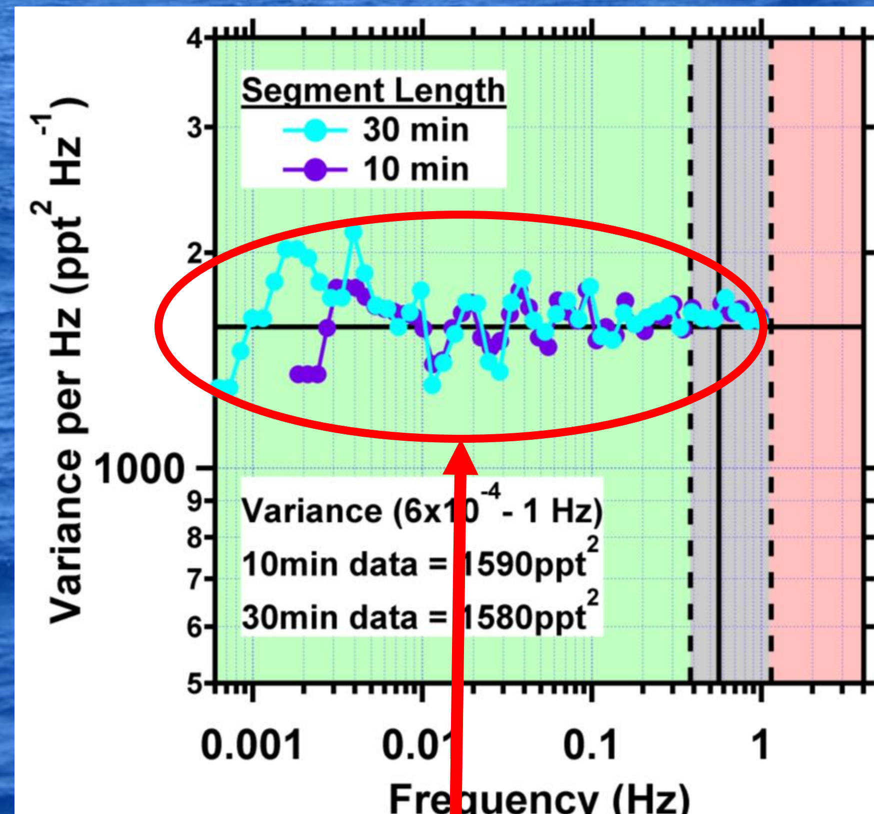
Instrument Performance

Sensitivity



Follows theoretical values

Frequency Response

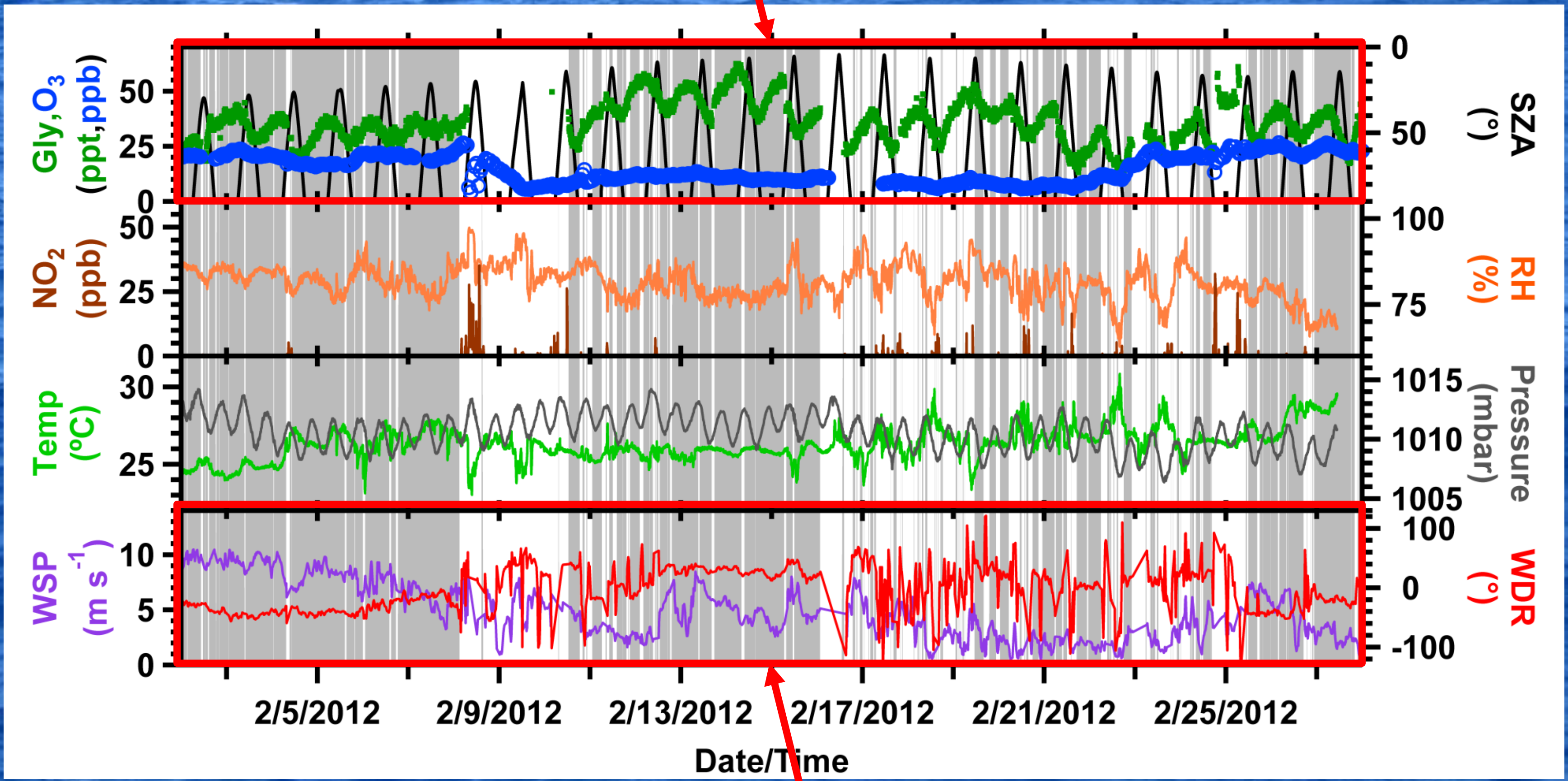


White noise sensor (constant variance per Hz)

Coburn et al., 2014 (AMTD)

Results: Glyoxal Diurnal Measurements

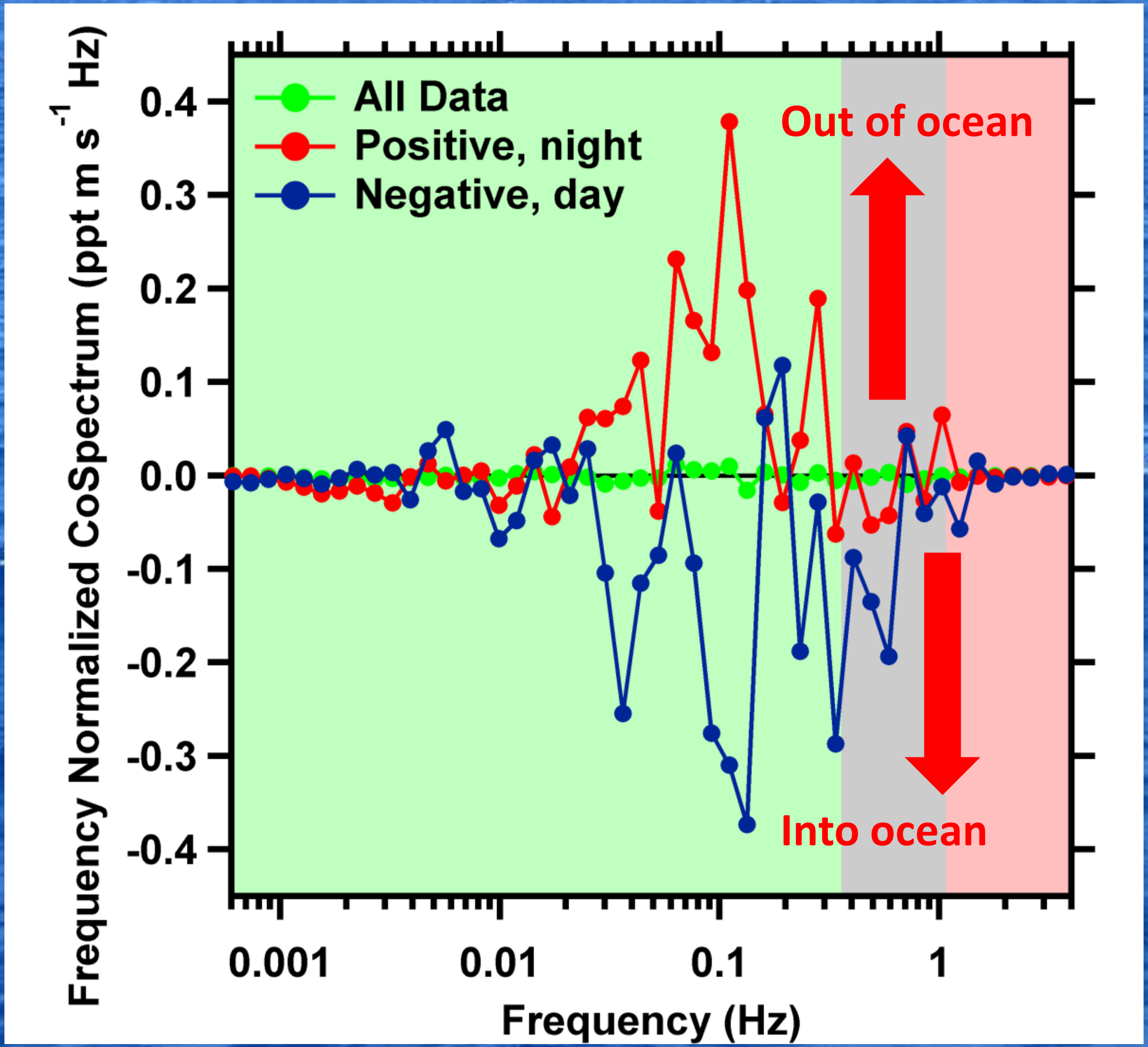
First diurnal cycle measurements of glyoxal over the open ocean



WDR: important for flux filtering

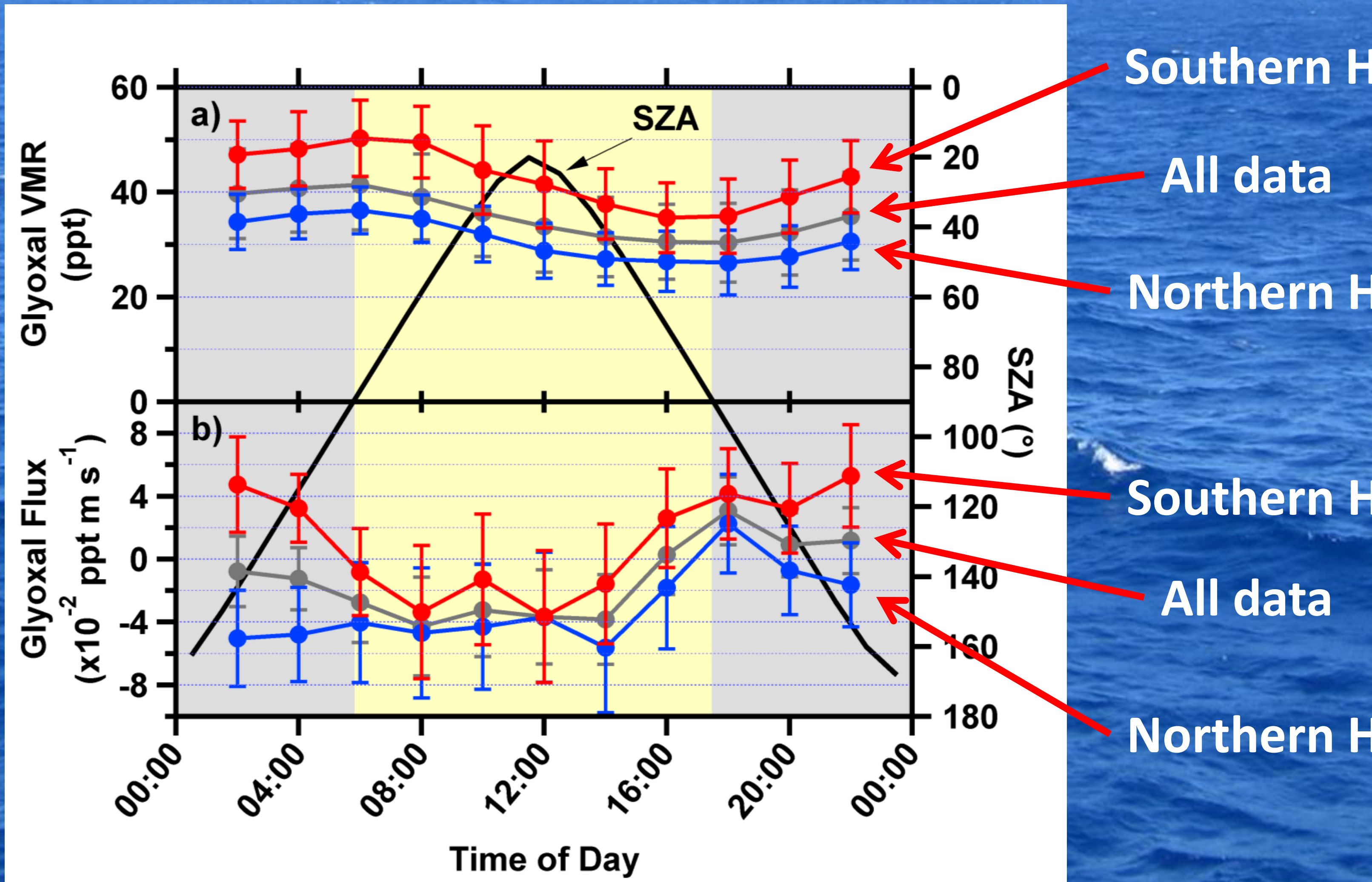
Coburn et al., 2014 (AMTD)

Results: Glyoxal Flux Measurements



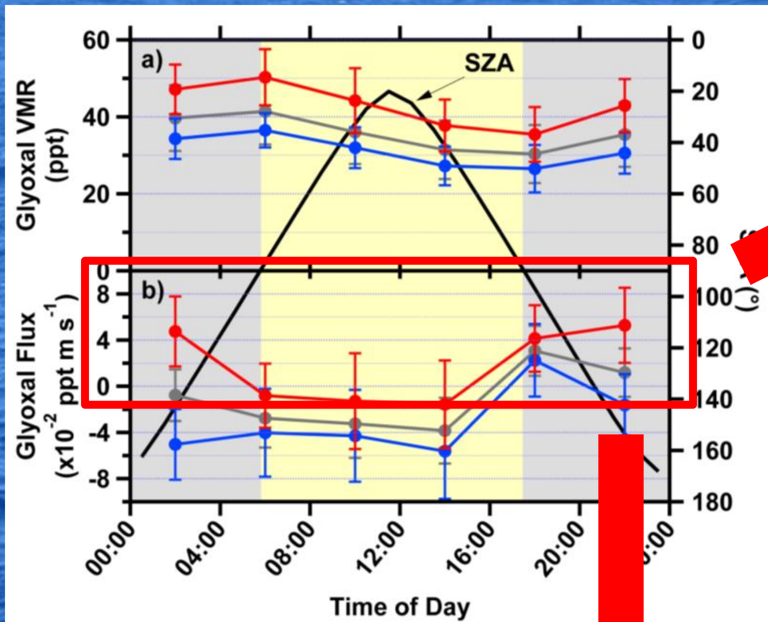
Coburn et al., 2014 (AMTD)

Results: Temporal and Spatial Gradients



Coburn et al., 2014 (AMTD)

Results: Flux Implications



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

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

t = 140 ms (Lifetime against hydroylsis)

L = 0.5-17 µm

Positive ... explai... product...

Posters #5 & #6: Laura Gonzalez

Highest positive flux measured: 5.3×10^{-2} pptv m s^{-1}

- Corresponds to ~4 pptv accumulation of glyoxal in a 500 m high BL over 12 hours
- Only about 30% of the increase observed in the diurnal cycle of the VMRs (~15 pptv)

Coburn et al., 2014 (AMTD); Ervens and Volkamer, 2010 (ACP)

Conclusions

- The Fast-CU-CE-DOAS capable of high frequency measurements
- First measurements of the glyoxal diurnal cycle in the remote MBL
    - Average near surface VMR: ~40 ppt; other measurements: ~60 ppt (Sinreich et al, 2010), ~25 ppt (Mahajan et al, 2014), ~60 ppt (Miller et al, 2014)
- Significant southern/northern hemisphere gradient that is not currently reflected in other measurements – actually opposite of what is reflected in other measurements
- First EC flux measurements of glyoxal: Positive glyoxal flux in SH at night
    - Direct evidence for surface organic micr… laye… e of producing glyoxal
    - Only accounts for ~30% of increase in gly… d
    - Potential source for other VOCs

Guest Speaker:
Sarah Lawson
(CSIRO)

Acknowledgements

- Entire Volkamer Group!
- Byron Blomquist (U of Hawaii) and Chris Fairall (NOAA)
- Captain and crew of RV *Ka'imimoana*

<u>Financial Support</u>

- NASA Earth and Space Science Graduate Fellowship Program
- National Science Foundation award AGS-1104104 (TORERO)

ACP/AMT Special Issue 55: Marine trace gases and aerosols over tropical oceans (Eds. L. Carpenter, M. Uematsu, R. Volkamer)

Coburn et al: Measurements of diurnal variations and EC fluxes of glyoxal in the tropical marine boundary layer: description of the Fast-LED CE-DOAS instrument, AMTD, 7, 6245-6285, 2014.