

# Tropical Ocean Troposphere Exchange of Reactive halogen species and Oxygenated voc - TORERO

Rainer Volkamer (PI)

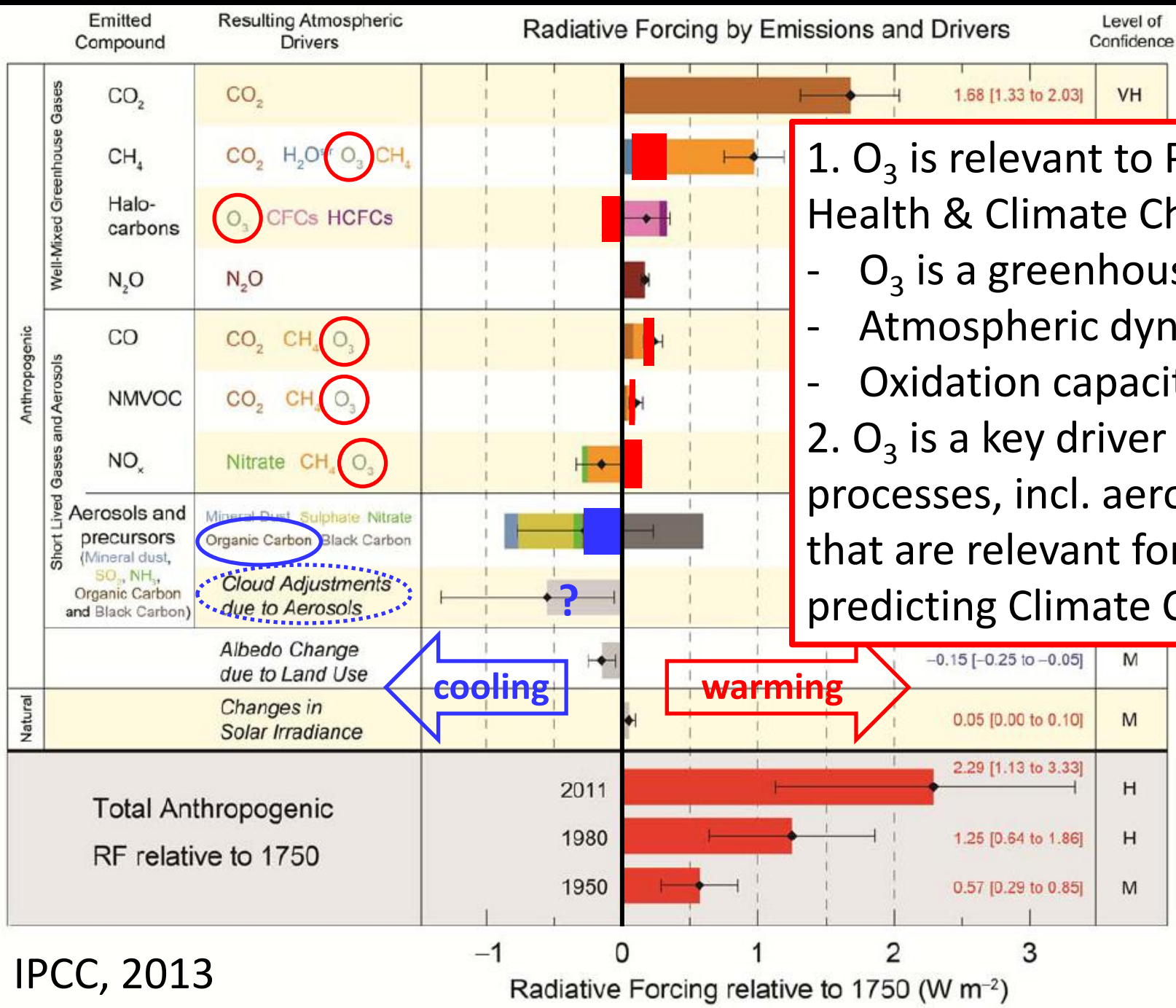
Department of Chemistry and Biochemistry & CIRES

Ocean emissions impact the lifetime of climate active gases in the upper atmosphere

- Scientific questions
- Focus: Technology Innovation

A US contribution to IGBP-SOLAS 'Surface Ocean Lower Atmosphere Study'





1. O<sub>3</sub> is relevant to Public Health & Climate Change:

- O<sub>3</sub> is a greenhouse gas
- Atmospheric dynamics
- Oxidation capacity

2. O<sub>3</sub> is a key driver to many processes, incl. aerosols, that are relevant for predicting Climate Change

cooling

warming



Most of the Earth's surface looks like this!





# Most of the Earth's surface looks like this!

**Hypothesis #1: Marine sources of halogens affect the lifetime of climate active gases ( $O_3$ ,  $CH_4$ , DMS) and oxidize atmospheric mercury over much of the tropical air column.**

*How abundant are halogen oxide radicals (BrO, IO)?*

*Do we understand their sources?*

**Hypothesis #2: Glyoxal over oceans is a smoking gun for other oxygenated VOC and 'missing' sources from ocean biology.**

*Where does it come from, and what comes with it?*

*What do 4D measurements reveal about the source mechanism?*



# Most of the Earth's surface looks like this!

**Hypothesis #3: Is atmospheric oxidation of elemental mercury by bromine in the tropical free troposphere a primary driver for the bioaccumulation of mercury in fish?**

*Where does mercury get oxidized in the atmosphere?*

*What is the lifetime of gaseous elementary mercury?*

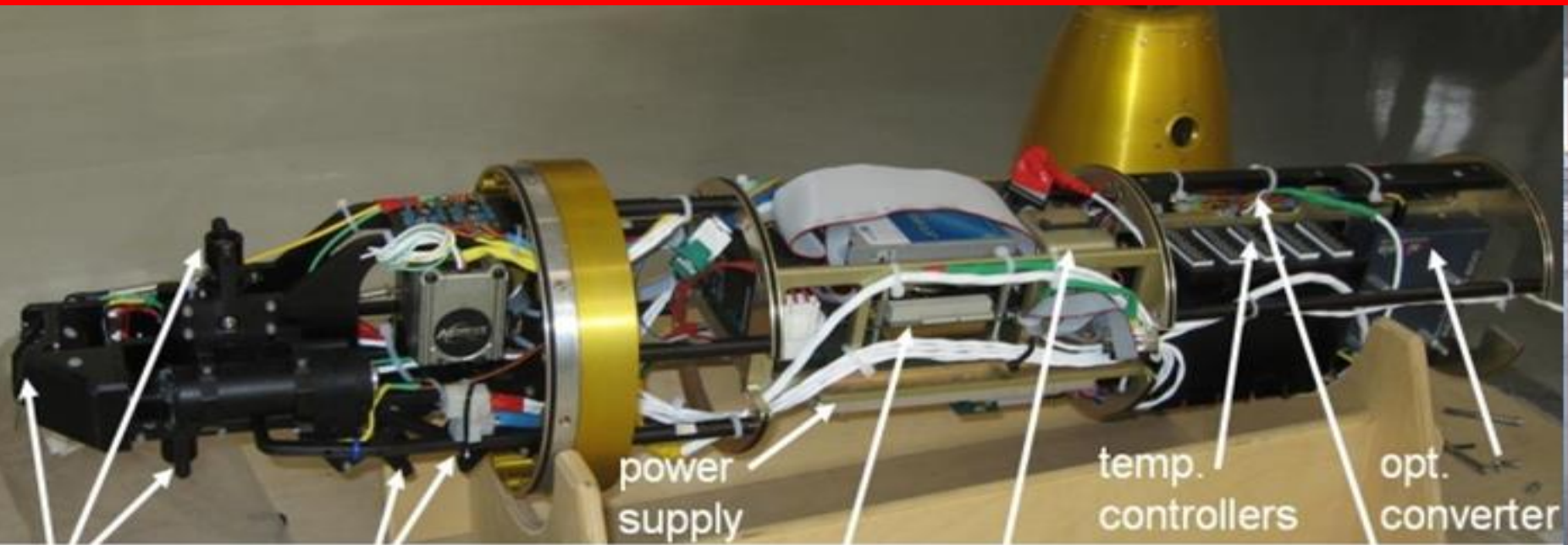
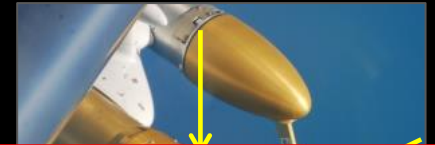
*Do we understand vertical profiles of Gaseous Oxidized Mercury?*

**Topic #4: Gain a wider perspective on the chemistry and climate effects of O<sub>3</sub> and water vapor changes in the tropical FT (and lower stratosphere)**

# 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

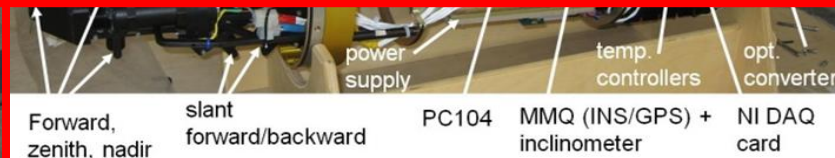
power  
supply

PC104

MMQ (INS/GPS) +  
inclinometer

temp.  
controllers

opt.  
converter



Forward,  
zenith, nadir

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



# 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



Gulfstream G-V

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

# Remote Sensing

Instrument	Species / Parameters	Detection limit / Accuracy / Comment	Time / Space resolution	PI / Institution
CU AMAX-DOAS	IO BrO OCIO NO <sub>2</sub> 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 <sub>O<sub>3</sub></sub> , J <sub>NO<sub>2</sub></sub> , J <sub>OVOC</sub> , J <sub>RX</sub> , J <sub>IxOy</sub> 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 <sup>-9</sup> m <sup>-1</sup> sr <sup>-1</sup> ~ 1% 2x10 <sup>-8</sup> cm <sup>-1</sup>	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)



# In-situ instruments

TOGA-HIAPER	Alkylhalides (incl. $\text{CH}_2\text{X}_2$ , $\text{CH}_2\text{XY}$ , $\text{CH}_3\text{X}$ , $\text{C}_3\text{H}_7\text{X}$ ) VOC (incl. DMS, $\text{C}_5\text{H}_8$ , monoterpenes) OVOC (incl. $\text{CH}_3\text{CHO}$ , DMSO, $\text{C}_2\text{H}_5\text{OH}$ , 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)
$\text{O}_3$	$\text{O}_3$	$1.5 \times 10^{10}$ molec $\text{cm}^{-3}$	1 sec	Ru-Shaun Gao (NOAA/ESRL)
VCSEL	Water vapor	< 1 ppm	0.04 sec	Stuart Beaton (NCAR/RAF)
Hygrometers	Water vapor	$\pm 0.1^\circ\text{C}$	10 - 120 sec	EOL facility instrument
CO	CO	2 ppb	3 sec	Frank Flocke (NCAR/ACD)
CN / NMASS	Aerosol number (nucleation mode)	$0.2 \# \text{cm}^{-3}$ (integral # / 6 and 15 nm cutoff)	1 sec	Dave Rogers (NCAR/RAF) Chuck Brock (NOAA/ESRL)
UHSAS	Aerosol size distribution	$1 \text{cm}^{-3}$ (60-1000 nm)	1 sec	EOL facility instrument
Cloud droplet probes	Cloud droplet size distribution	2-50 $\mu\text{m}$	1 sec	EOL facility instrument
Cloud 2-D imaging spectrometers	Distinguish ice and water droplets / Cloud droplet size distribution	18-640 $\mu\text{m}$ 25-1600 $\mu\text{m}$	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 $\text{O}_3$ 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)