Reactive gas studies during ORCAS

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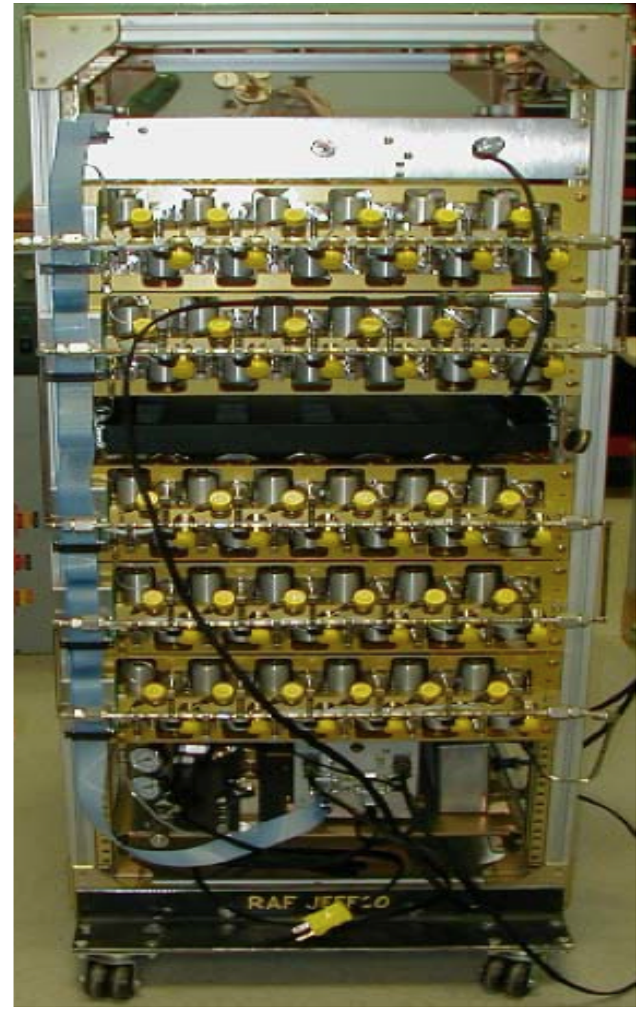
Scientific Motivations

- Emissions from productive Southern Ocean can have regional and global (?) impacts.
  - Reactive halocarbons and hydrocarbons
    - Oxidative processes / ozone depletion (tropospheric and stratospheric)
    - Aerosol formation
  - Organic nitrates
    - Marine origin/source of NOx
  - Sulfur species
    - DMS and aerosol formation
- Distributions and fluxes poorly characterized/or conflicting conclusions
  - Complex source/sink relationships
  - Mechanisms of production/loss also complex/variable
  - Limited information on links to biogeochemical processes
    - Pigments
    - Species dependence

HAIS Advanced Whole Air Sampler (AWAS)

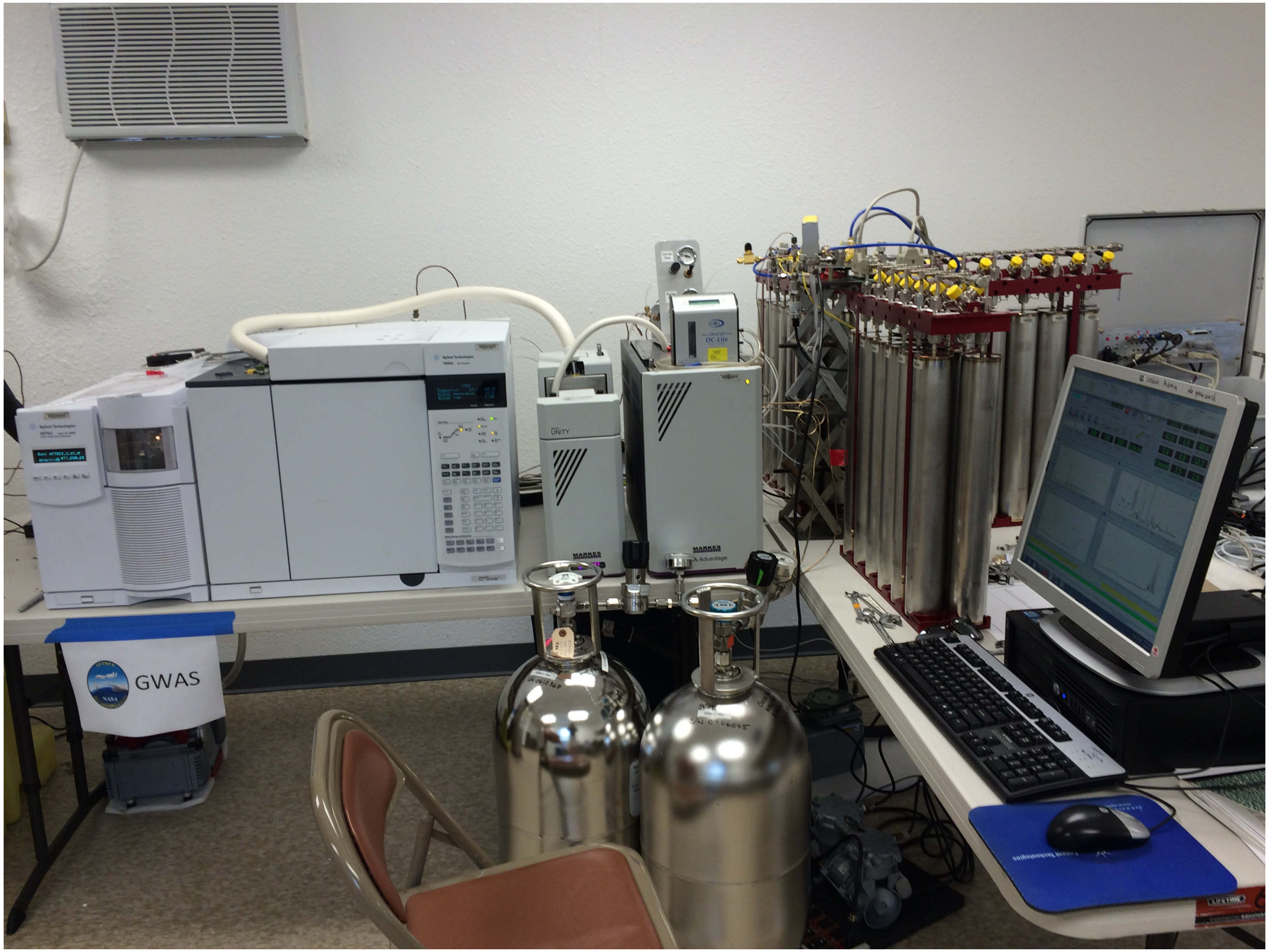
- **60 total sample canisters: 5 modules with 12 canisters/module**
- **Each canister is ~ 1.1 liters and the interior surface is electropolished stainless steel**
- **4 stage metal bellows pump**
- **Each sample pressurized to ~40 psi**
- **Sample fill time dependent on altitude. Range is 5 sec. in the boundary layer to 50+ sec at 49Kft**
- **A broad suite of trace gases are measured in each sample in the laboratory using multiple GC systems**
- **High sensitivity: detection limits of ppt to sub-ppt**
- **Altitude: surface - 50,000 feet**

Modules ready for installation.



HAIS Advanced Whole Air Sampler (AWAS) during laboratory tests. Bottom rack holds pump, electronics, and pneumatics for sample valves.

AWAS semi-automated field analytical system



HAIS Trace Organic Gas Analyzer (TOGA)

- Fast online GC/MS VOC measurement
- Up to 70 different VOCs measured
- High sensitivity: detection limits of NMHCs & OVOCs to ppt, many halocarbons to sub-ppt
- 35-sec integrated measurements every 2 min
- 14.5 cc sample volume up to 40Kft; pressure dependent lower volume above 40Kft
- Altitude: surface - 50,000 feet

TOGA installed on GV

TOGA inlet on GV

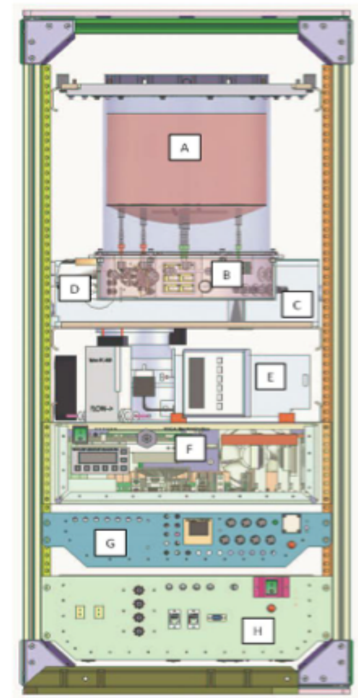


Figure 1. Diagram of the HIAPER/TOGA showing the major instrument components: (A) LN_2 dewar, (B) Heated space holding cryogenic enrichment traps and switching valves, (C) Mass spectrometer vacuum chamber, (D) Gas chromatograph, (E) Mass spectrometer, (F) Electronics box, (G) Zero air generator/dilution system, (H) Power box and UPS.

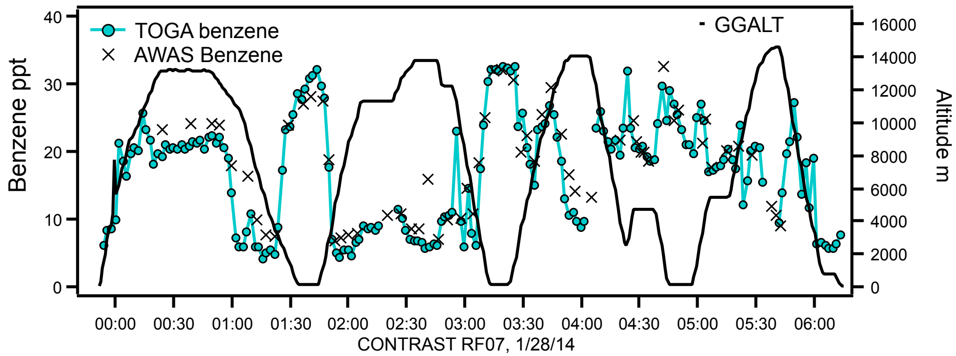
AWAS & TOGA provide complementary measurements of wide range of reactive gases

- **Halocarbons:**
  - Short-lived bromine and iodine compounds
    - Impact on ozone/oxidant chemistry & aerosol formation
  - CFC/HCFC/Halons (long-lived – Stratospheric trend)
  - Solvents (ocean sink?)
- **Non-methane hydrocarbons**
  - Reactive hydrocarbons (alkenes/isoprene)
    - Ocean emissions/impact on oxidation
    - Continental sources
- **Organic nitrates**
  - Ocean sources
    - Photochemical processes/bacterial influence?
    - Major NOy species
- **Sulfur species**
  - Mainly DMS (short-lived ocean emission)
- **Oxygenated VOC**
  - Oxidation products of other reactive HC
  - Ocean emissions/deposition?
- **Source tracers (various)**
  - Biomass burning (nitriles/halocarbons)
  - Combustion sources (light NMHC)
  - Anthropogenic (halocarbons/NMHC)

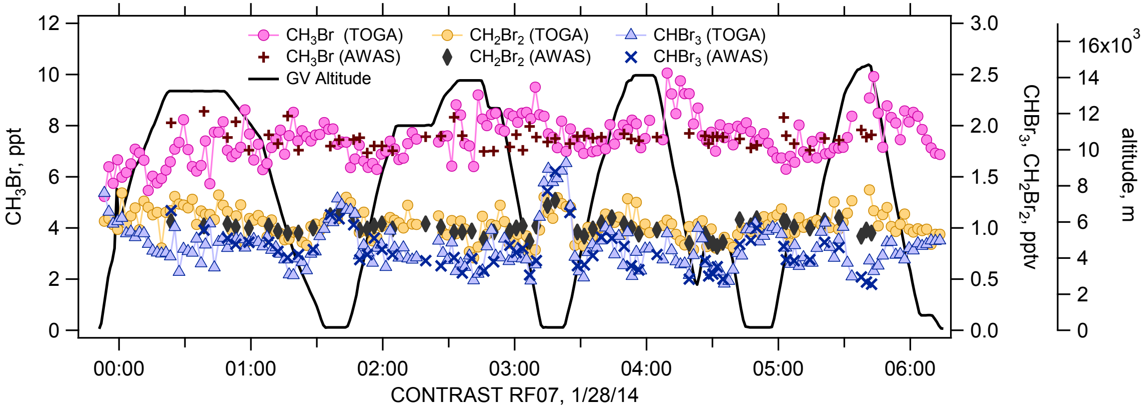
	Lifetime	Source	AWAS	TOGA
Oxygenates				
Formaldehyde (CH2O)	1 day	A/N/B		✔
Acetaldehyde	1 day	A/N/B		✔
Propanal	1 day	A/B		✔
Butanal	0.5 day	A/B		✔
Acrolein	1 day	A/B		✔
Methacrolein	0.5 day	N		✔
Methyl Vinyl Ketone	1 day	N		✔
Methyl Butenol	0.5 day	N		✔
Methanol	~20 days	A/N/B		✔
Ethanol	~4 days	A/N/B		✔
Acetone	~15 days	A/N/B		✔
Butanone	3 days	N/A/B		✔
Methyl t-Butyl Ether	3 days	A		✔
Methyl Halides and related				
Methyl Bromide(CH3Br)	0.8 yrs	A/N/B	✔	✔
Methyl Chloride (CH3Cl)	1.5 yrs	N/B	✔	✔
Methyl Iodide (CH3I)	~4 days	N	✔	✔
Methylene Bromide(CH2Br2)	145 days	N	✔	✔
Bromoform (CHBr3)	~22 days	N	✔	✔
CHxBryClz	50-165 days	N	✔	✔
Chloroiodomethane	hrs	N	✔	✔
Diiodomethane	mins	N	✔	✔
Solvents				
Carbon Tetrachloride (CCl4)	40 yrs	A	✔	✔
Methyl Chloroform(CH3CCl3)	4.8 yrs	A	✔	
Tetrachloroethylene (C2Cl4)	0.3 yrs	A	✔	✔
Methylene Chloride (CH2Cl2)	0.3 yrs	A	✔	✔
Chloroform (CHCl3)	0.4 yrs	A	✔	✔
Trichloroethylene (C2HCl3)	~7 days	A	✔	
1,2 Dichloroethane (C2H4Cl2)	0.25 yrs	A	✔	
Chlorobenzene	~20 days	A	✔	✔
Other				
Methane (CH4)	9 yrs	A/N	✔	
Dimethyl Sulfide (C2H6S)	< 4 days	N	✔	✔
Carbonyl Sulfide (COS)	30 yrs	N/A/B	✔	
Hydrogen Cyanide (HCN)	1 yr	B		✔
Acetonitrile (CH3CN)	2 yrs	B		✔
Chlorofluorocarbons				
CFC-11 (CCl3F)	50 yrs	A	✔	✔
CFC-12 (CCl2F2)	102 yrs	A	✔	
CFC-113 (CCl2FCClF2)	85 yrs	A	✔	
CFC-114 (CClF2CClF2)	300 yrs	A	✔	✔

	Lifetime	Source	AWAS	TOGA
Organic Nitrates				
Methyl nitrate(CH3ONO2)	~30 days	A/N	✔	✔
Ethyl nitrate(C2H5ONO2)	~15 days	A/N	✔	✔
Propyl nitrates(C3H7ONO2)	~11 days	A/N	✔	✔
Butyl nitrates (C4H9ONO2)	~7 days	A	✔	
Non-Methane Hydrocarbons				
Ethane (C2H6)	~73 days	A	✔	
Ethene (ethylene; C2H4)	~2 days	A/N	✔	
Ethyne (acetylene; C2H2)	~22 days	A/B	✔	
Propane(C3H8)	~15 days	A	✔	✔
Isobutane(C4H10)	~ 7 days	A	✔	✔
n-Butane (C4H10)	~ 7 days	A	✔	✔
Butene	hrs	A		✔
Isobutene	hrs	A		✔
Isopentane (C5H12)	~4 days	A	✔	✔
n-Pentane (C5H12)	~4 days	A	✔	✔
n-Hexane	~3 days	A		✔
n-Heptane	~3 days	A		✔
Isoprene (C5H10)	hrs	N	✔	✔
Benzene (C6H6)	~15 days	A/B	✔	✔
Toluene (C7H8)	~3 days	A	✔	✔
Xylene	~36 days	A		✔
Trimethylbenzene	hrs	A		✔
Ethyl Benzene	~2.2 days	A		✔
a-Pinene	hrs	N		✔
b-Pinene	hrs	N		✔
Limonene	hrs	N		✔
Camphene	hrs	N		✔
Myrcene	hrs	N		✔
Halons				
CFC-12b1 (Halon 1211,CF2ClBr)	20 yrs	A	✔	
CFC-13b1 (Halon 1301, CF3Br)	65 yrs	A	✔	
CFC-114b2 (Halon 2402, C2F4Br2)	20 yrs	A	✔	
Hydrochlorofluorocarbons/ Hydrofluorocarbons				
HCFC-22 (CHF2Cl)	13 yrs	A	✔	
HCFC-141b (CH3CFCl2)	9.4 yrs	A	✔	
HCFC-142b (CH3CF2Cl)	19.5 yrs	A	✔	
HFC-134a (C2H2F4)	14 yrs	A	✔	
HFC-152a (F2HC-CH3)	1.5 yrs	A	✔	
HCFC-124 (C2HF4Cl)	5.9 yrs	A	✔	
HCFC-21 (CHFCl2)	2 yrs	A	✔	

AWAS/TOGA from CONTRAST



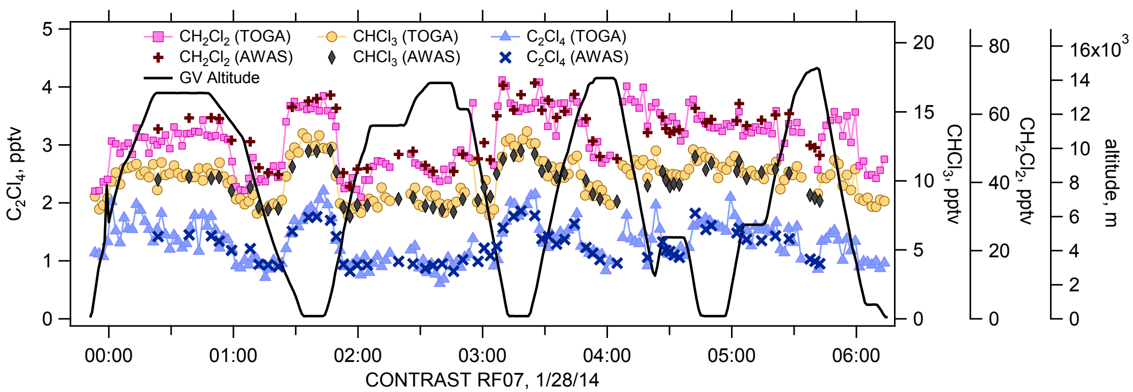
Benzene



Methyl bromide

Dibromomethane

Bromoform

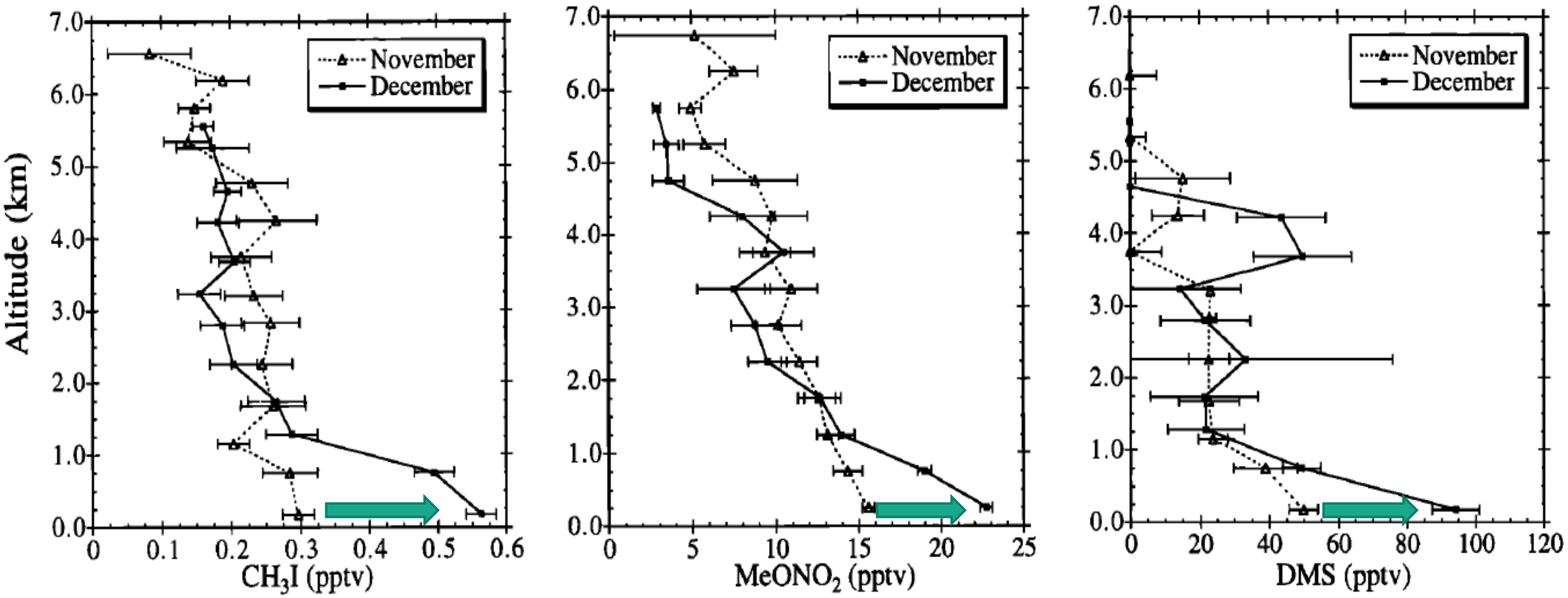


Dichloromethane

Chloroform

Perchlorethylene

Background: Few Airborne Studies



ACE-1 (Blake et al.): Seasonal increase in marine emissions from Nov – Dec (mostly lowest 2 km): Halocarbons, MeONO2, DMS

PEM-Tropics: $RONO_2$ high in tropics <u>and</u> Southern Ocean atmosphere

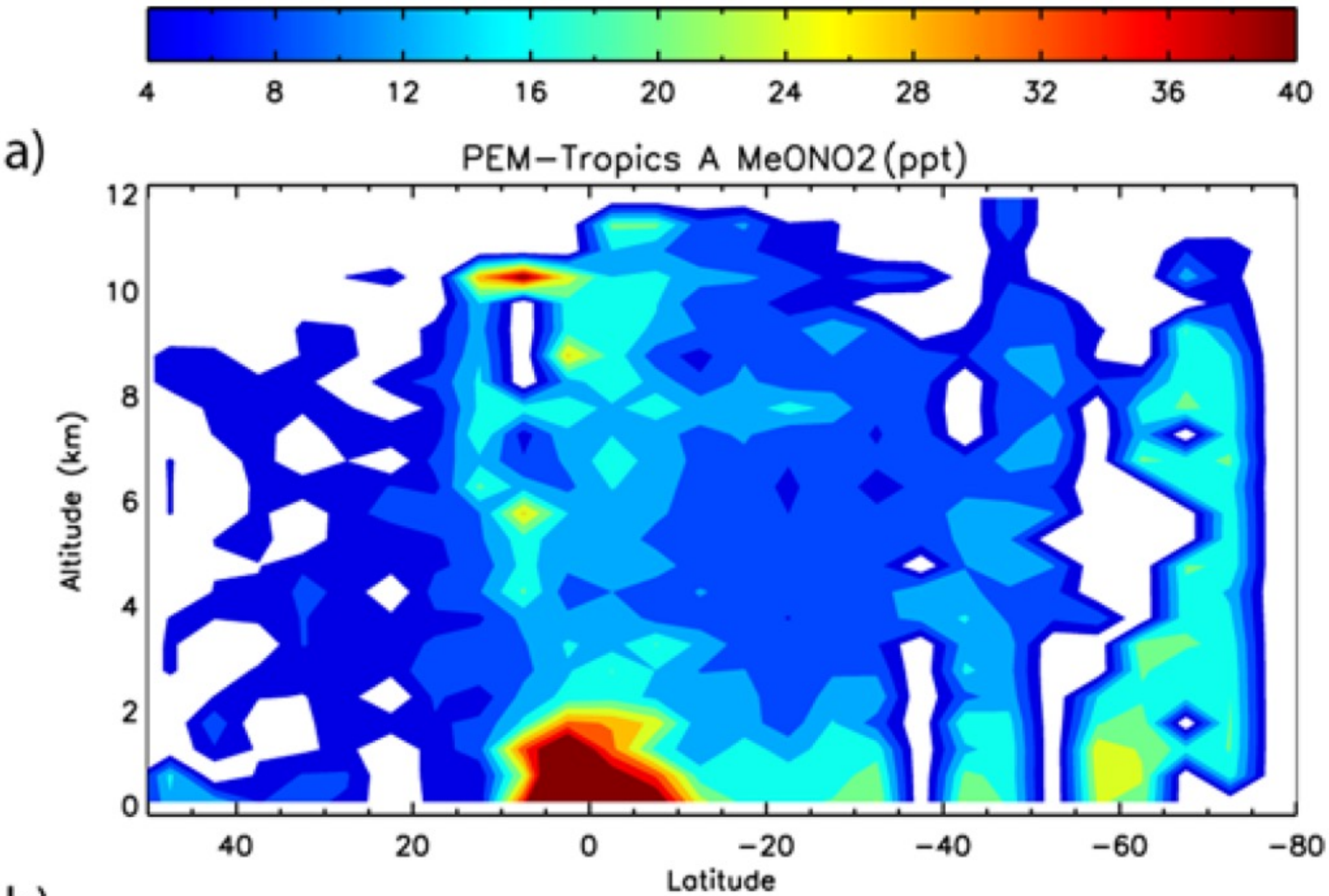
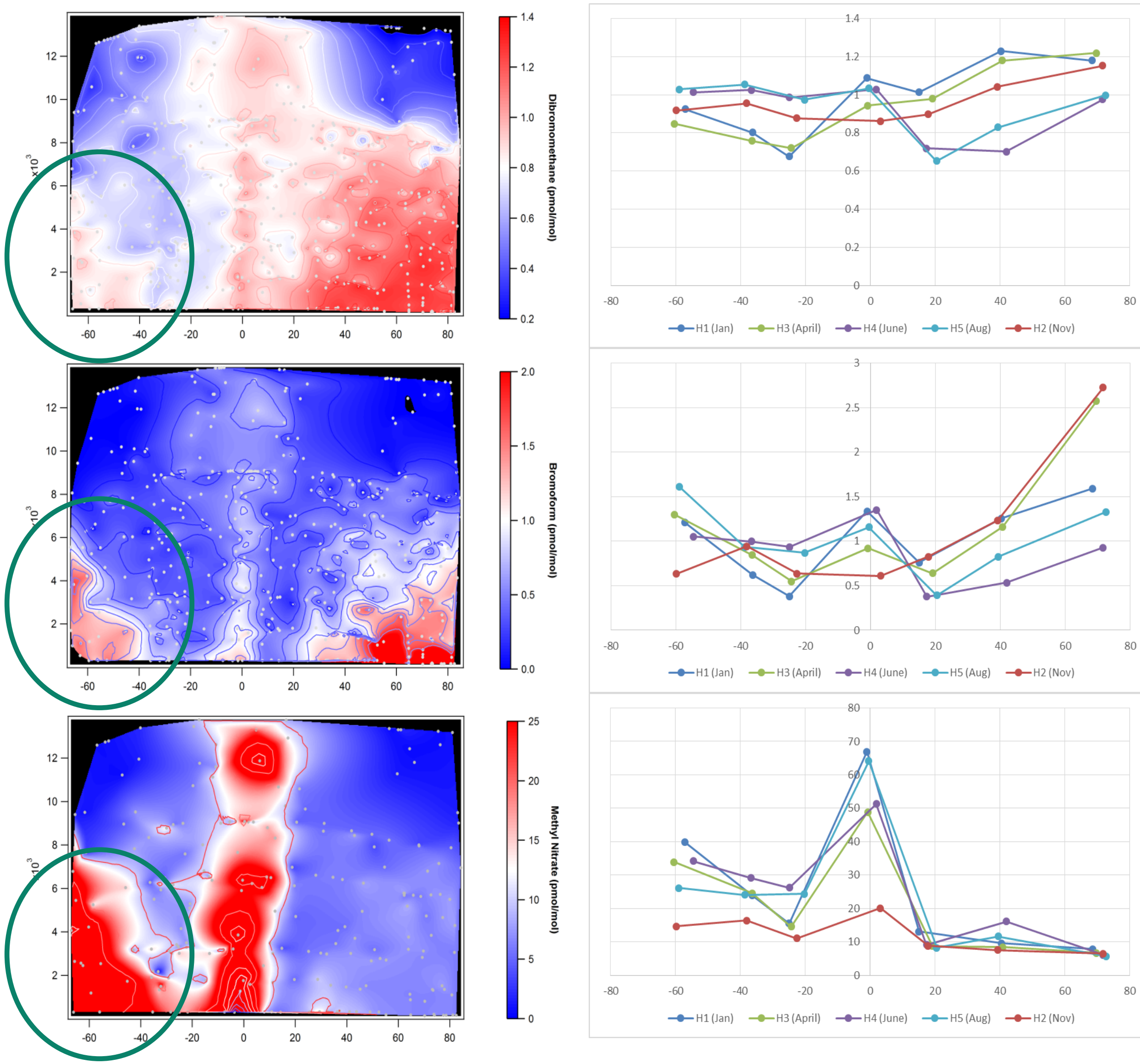


Figure from Neu et al., GRL, 2008.

HIPPO mission: Seasonality and large scale distributions

(example from HIPPO-3; March/April 2010)



Dibromomethane
CH_2Br_2

Bromoform
$CHBr_3$

Methyl nitrate
CH_3ONO_2

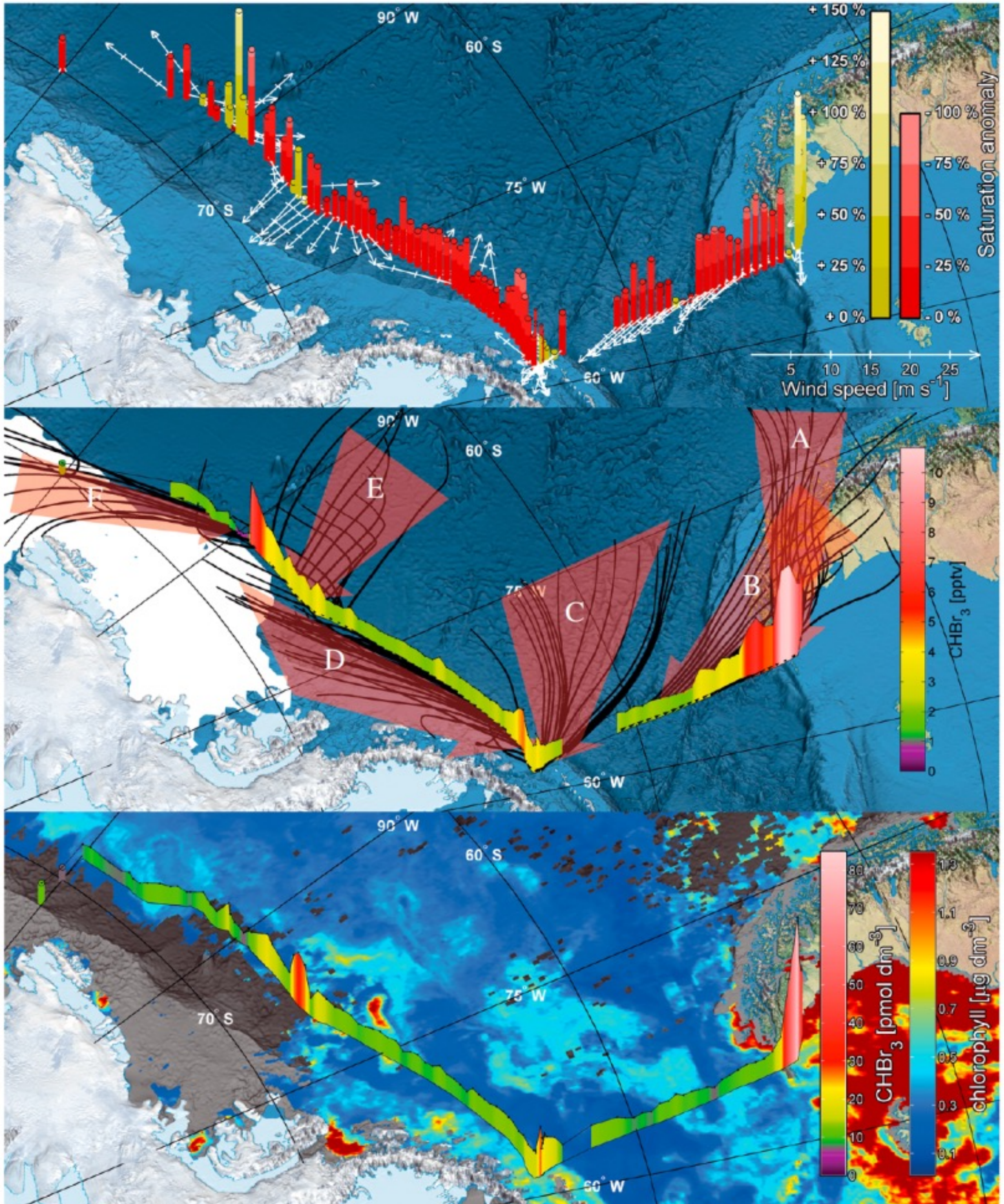
Boundary Layer/Ocean Studies

- Numerous cruises + Antarctic station studies
- Some of the main factors on reactive gas distributions (focus on halocarbons):
  - Ice algae and melting sea ice sources
  - Plankton size/species distributions
  - Coastal vs offshore differences
  - Variable relationship to primary productivity and associated factors
    - Pigments, etc.
  - Bacterial modification
  - Halogen specific effects
  - Role of transport

Uncertain and variable fluxes (nmol m^{-2} day^{-1})

LOCATION/SEASON	CH_3I	CH_2ClI	$CHBr_3$	CH_2Br_2	Reference
40 – 52 S., Atlantic, Sept. – Feb.	6 (0 – 20)	-1 (-3 – 5)	-40 (-56 - -7)	--	Chuck et al., 2005
Southern Ocean Feb-April	17 (0.4 – 9.8)		5.4 (-7.6 – 32)	7.5 (-3.4 – 24)	Butler et al.,2007
70 – 72 S, Coast Dec/Jan			32.3 (1 – 100)		Carpenter et al., 2007
Ryder Bay, 67 S Ice-free conditions			107 (-13 – 353) Bloom 34 (-49 – 227) non bloom		Hughes et al., 2012
Ross Sea/Amundsen Sea; Dec/Jan		SA*: -6 – 1200% (source)	SA*: -83 – 11% (sink)		Mattson et al., 2012
Sea Ice Dec/Jan		SA*: 91 – 22000% (source)	SA*: -61 – 97% (source and sink)		Mattson et al., 2012
Drake Passage; Dec/Jan.			-16 (-48 – 2)		Mattson et al., 2013
Antarctic Sea Ice edge, Dec., Jan			-10 (-72 – 24)		Mattson et al., 2013.
Southern Ocean (combined data) Dec/Jan.			-8 (-20 – 1)		Mattson et al., 2013
Marguerite Bay, Summer season			84 (-13 – 275)	21 (2-70)	Hughes et al., 2009
Southern Ocean (model),DJF			~ 7 (median)		Stemmler et al., 2014
Southern Ocean (model), Annual	~4.8 (est)		~-4.8 (est.)	4.8 (est.)	Ziska et al., 2013.

Bromoform in air and water: role of transport

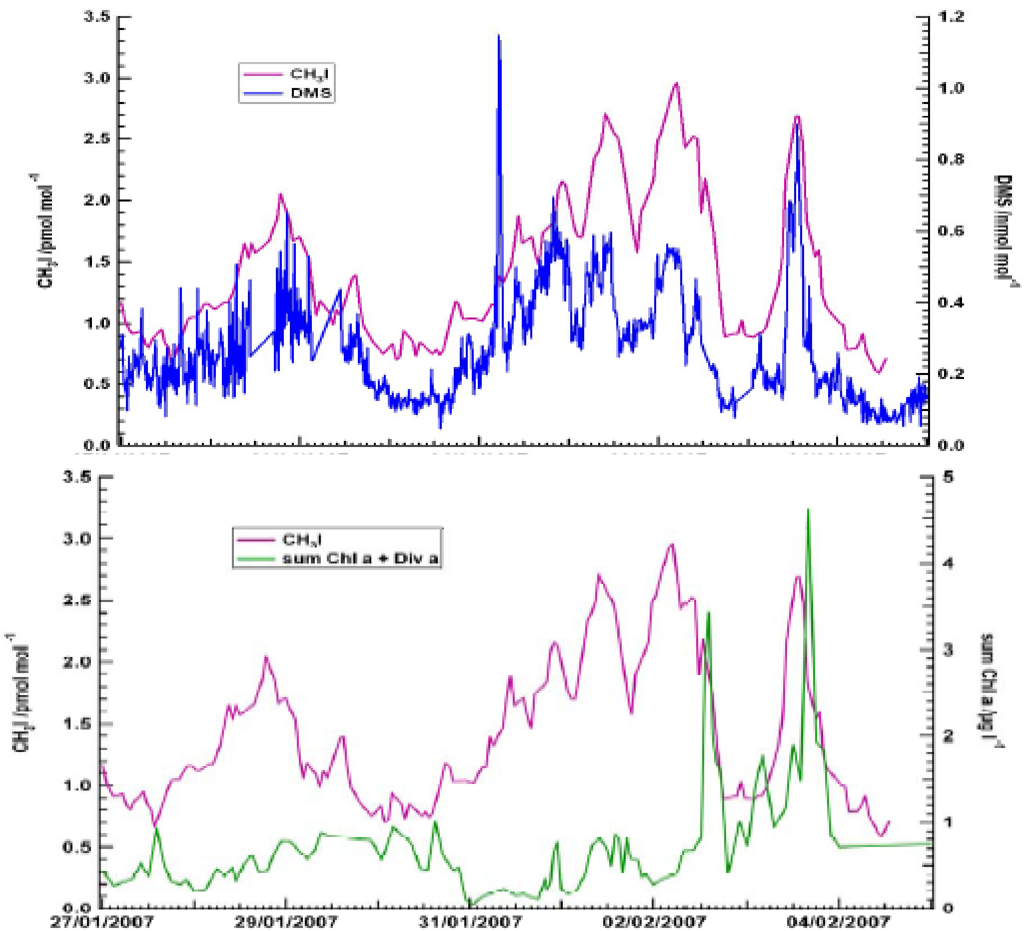


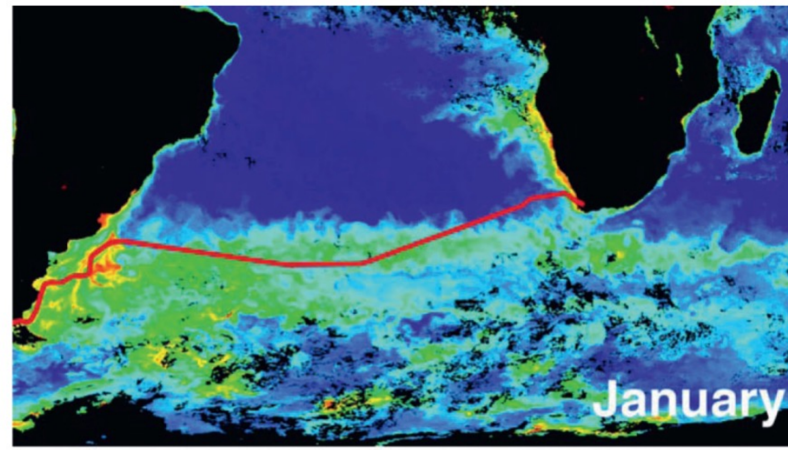
Bromoform saturation anomalies. Yellow = supersat'd; Red = undersat'd

Air concentrations and back trajectories; White indicates sea-ice extent

Water concentrations and average monthly Chl a (December)

OOMPH cruise: DMS, CH3I and Chl*a*





Time series along cruise track (to Argentina): Good correlation between gases in atmosphere, but little consistent correlation to Chl a. Improved correlation considering back trajectories over productive areas (from retrospective satellite obs.)

Proposed main objectives

- 1) Define the chemical distributions of reactive trace gases as a function of altitude and geographical location around the Southern Ocean;
- 2) Evaluate the chemical emissions from different potential source regions during the Austral Summer;
- 3) Evaluate procedures to combine observations and modeling to constrain the magnitude and direction of trace gas fluxes in the Southern Ocean during the peak time of biological productivity;
- 4) Examine potential application of remote sensing data to more accurately characterize trace gas fluxes and extrapolate to other ocean regions.

Questions related to main ORCAS objectives:

- What are the vertical distributions and geographical variations of halocarbon and other reactive gases around the Southern Ocean?
- Can the combination of aircraft profiles and Lagrangian transport models effectively quantify the fluxes of halocarbons and other reactive gases from different regions over the Southern Ocean?
- What is the relationship of halocarbon fluxes and distributions to those of CO_2 and O_2?
- What are the trace gas signatures of sources from coastal Antarctica vs Southern Ocean?
- What are the relative importance of emissions of halocarbons near the retreating ice edge versus the nearshore and open ocean environments vs the Argentine Basin?

Questions related to main ORCAS objectives:

- Can quantitative relationships be established between halocarbon fluxes and observations of ocean hyperspectral features?
- What are the main source regions of organic nitrates in the Southern Ocean atmosphere and how are they related to reactive halocarbons or other biogeochemical variables?
- Are the observations of reactive gases consistent with existing model formulations (e.g. CAM-CHEM, etc.)?
- Can the relationships developed for trace gas emissions be translated/extrapolated to other productive ocean regions?