Trace gas studies in the UT/LS from recent airborne campaigns

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- POSIDON, CONTRAST, ATTREX Science Teams

Motivations

- What controls the chemical composition of the UT/LS region?
  - Defines chemical composition of air entering the lower stratosphere
  - Role of reactive organic compounds
    - Short-lived halocarbons and hydrocarbons
    - Sulfur species: OCS, DMS, other
  - What are transport pathways and time scales?
    - Local convection vs. long-range transport
  - What are source regions and emissions?
    - Use of chemical signatures to define source types
    - What is magnitude of human influence?

Observations of chemical composition of the UT/LS

- Satellite remote sensing
  - Large-scale, limited vertical resolution, few species
- In-situ observations
  - Balloon sondes
    - High vertical resolution
    - Water vapor, ozone, temperature, aerosol mass/number
    - Limited chemistry
  - Airborne platforms
    - Few aircraft reach >12 km
    - Large, complex payloads: radiation, aerosol, chemistry
    - Suitable for process and survey studies

Selected trace gases measured by Whole Air Sampler (WAS)

Longer Lived Species

Chlorofluorocarbons	Yrs	S
CFC-11	50	A
CFC-12	102	A
CFC-113	85	A
Halons		
Halon 1211	20	A
Halon 2402	20	A
Hydro(chloro)fluorocarbons		
HCFC_141b	9.4	A
HCFC-22	13	A
HCFC_142b	19.5	A
Solvent		
Carbon Tetrachloride	40	A
Methyl chloroform	4.8	A
Other		
Methyl Chloride	1.5	N/B
Carbonyl Sulfide (COS)	30	N/A/B

Shorter Lived Species

Solvents	Yrs	S
Methylene Chloride	0.3	A
Chloroform	0.4	A/N
Tetrachloroethylene	0.3	A
Trichloroethylene	0.02	A
Methyl Halides		
Bromoform	0.1	N
Methyl Bromide	0.8	A/N/B
Methylene Bromide	0.4	N
Methyl Iodide	0.01	N
CHxBryClz	0.1	N
Others		
1,2 dichloro ethane	0.3	A
Chlorobenzene	0.05	A

Shorter Lived Species

Organic nitrates	Yrs	S
Methyl nitrate	0.08	A/N
Ethyl nitrate	0.04	A/N
Propyl nitrate	0.03	A/N
Non- Methane Halocarbons		
Ethane (C2H6)	0.2	A
Ethyne	0.06	A/B
Propane	0.04	A
Benzene	0.04	A/B

Sources

A= antropogenic/industrial

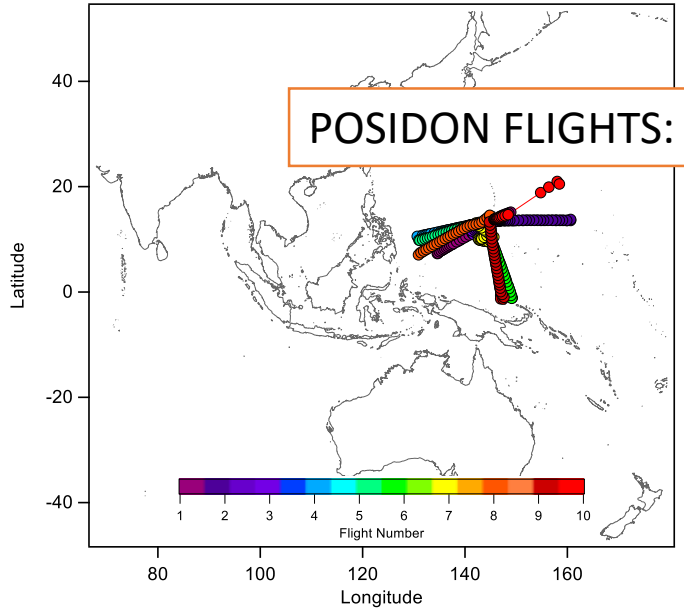
N= natural/marine

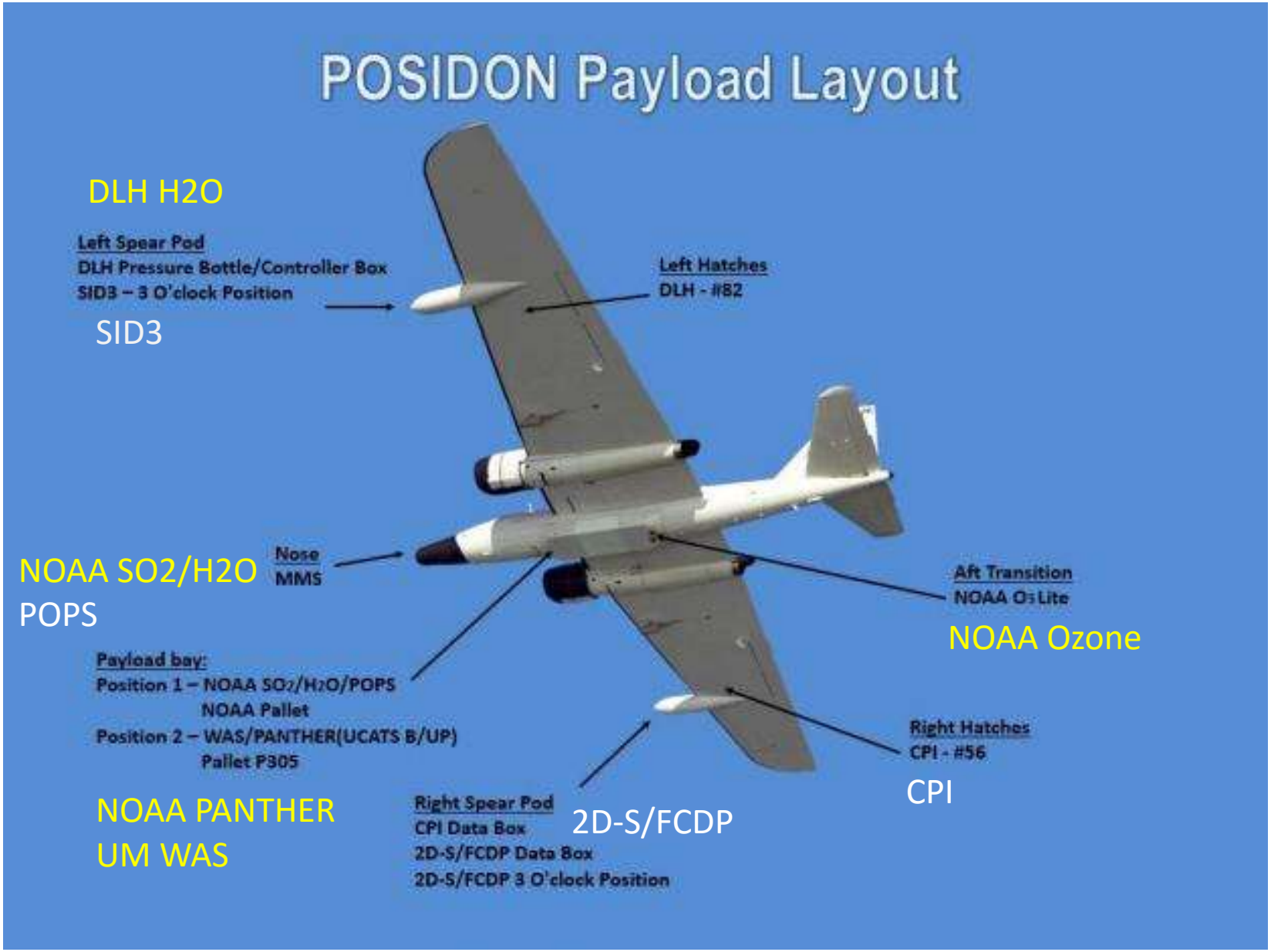
B=Biomass burning

- Organic Halogen (long-lived)
  - → CH_3Br, CH_3Cl
    - → Natural emissions (land and ocean); biomass/biofuel burning
  - → CFCs, HCFCs
    - → Anthropogenic emissions, regional sources, hot spots
- Organic Halogen (VSLS)
  - → Br: $CHBr_3$, CH_2Br_2, $CHBrCl_2$, $CHBr_2Cl$, CH_2BrCl, + ?
    - → Marine biogenic emissions; weeks to months
  - → I: CH_3I
    - → Marine biogenic emission; days
  - → Cl: CH_2Cl_2, C_2Cl_4
    - → NH anthropogenic emission; months (changing emissions)
- Organic Nitrates
  - → Methyl nitrate (CH_3ONO_2)
    - → Equatorial marine photochemical/biochemical emission; weeks
- Hydrocarbons
  - → C2: Ethane (C_2H_6), Ethyne (C_2H_2)
    - → NH anthropogenic emission; biomass burning; weeks (ethyne), months (ethane)


Pacific Oxidants, Sulfur, Ice, Dehydration, and cONvection Experiment
NASA
POSIDON
Guam, October 2016
NOAA • CIRES • University of Miami • University of Hertfordshire • SPEC, Inc. • NASA

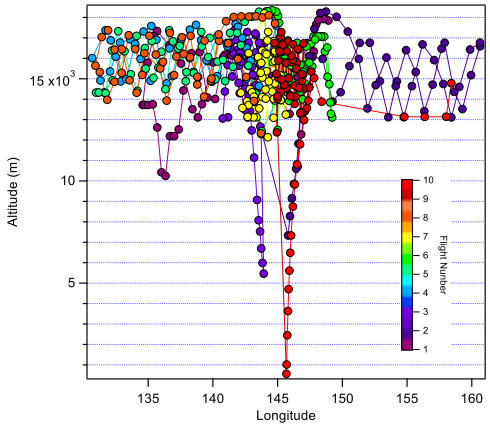
POSIDON FLIGHTS: WAS sample locations

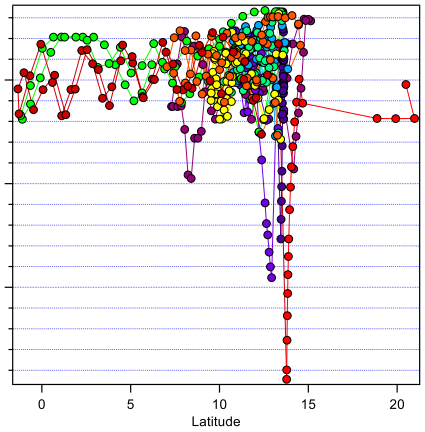



POSIDON Payload Layout
DLH H2O
Left Spear Pod
DLH Pressure Bottle/Controller Box
SID3 – 3 O'clock Position
SID3
Left Hatches
DLH - #82
NOAA SO2/H2O
POPS
Nose
MMS
Aft Transition
NOAA O3 Lite
NOAA Ozone
Payload bay:
Position 1 – NOAA SO2/H2O/POPS
NOAA Pallet
Position 2 – WAS/PANTHER(UCATS B/UP)
Pallet P305
NOAA PANTHER
UM WAS
Right Hatches
CPI - #56
CPI
Right Spear Pod
CPI Data Box
2D-S/FCDP Data Box
2D-S/FCDP 3 O'clock Position
2D-S/FCDP

WB-57 and WAS in Guam

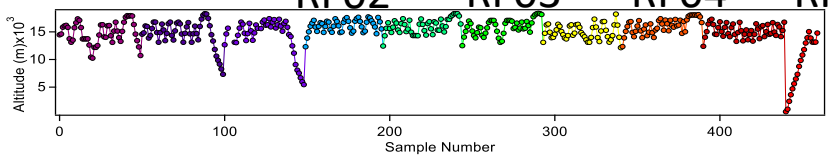
POSIDON FLIGHTS: WAS sample locations





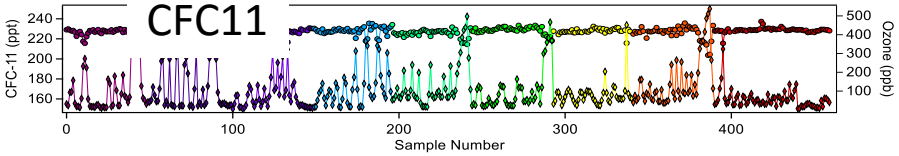
Long-lived halocarbons & ozone

RF01 RF02 RF03 RF04 RF05 RF06 RF07 RF08 RF09 RF10

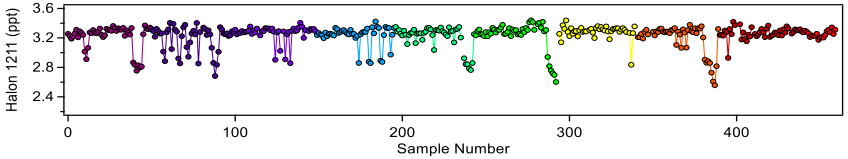


altitude

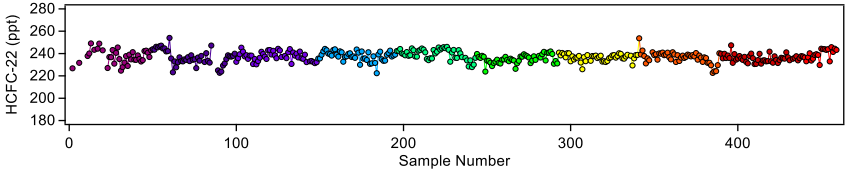
CFC11



Ozone

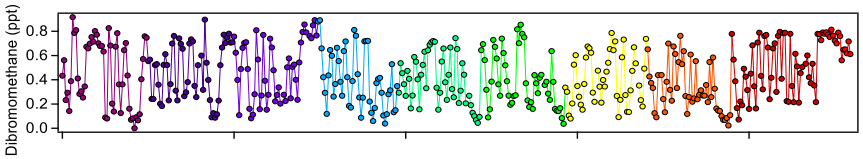


Halon 1211

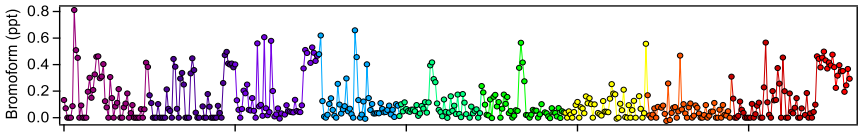


HCFC-22

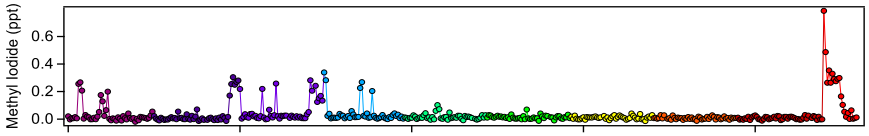
Marine emissions (VSLS)



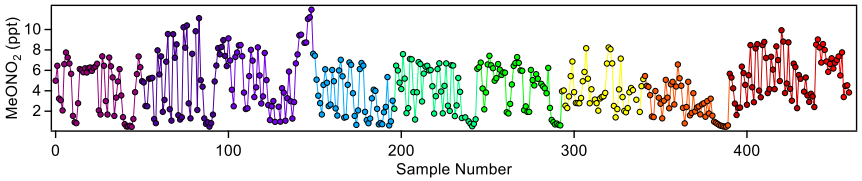
CH_2Br_2



$CHBr_3$



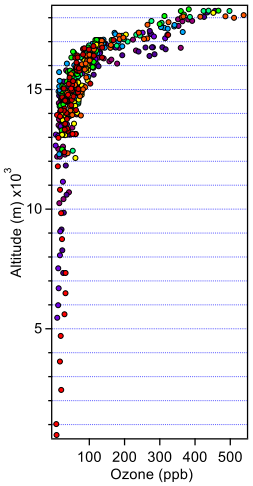
CH_3I



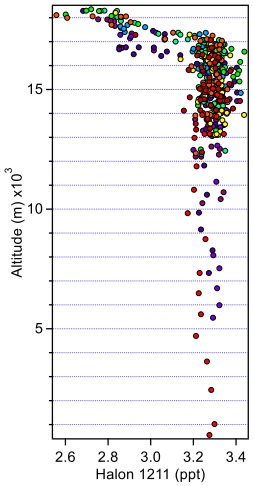
Methyl nitrate

Vertical profiles

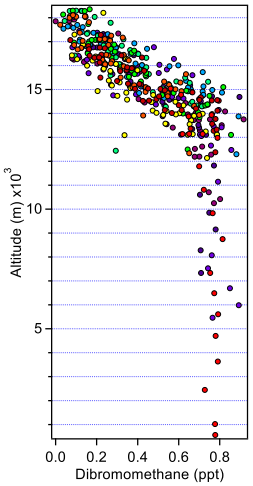
Ozone



Halon 1211

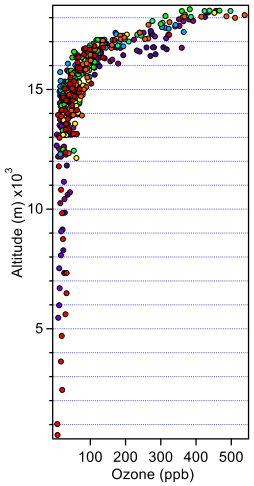


Dibromomethane

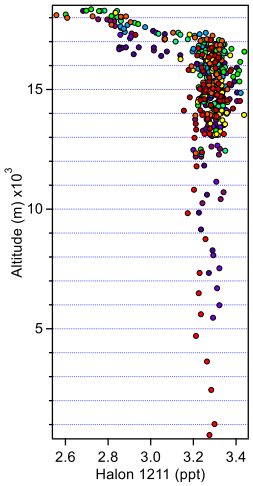


Vertical profiles

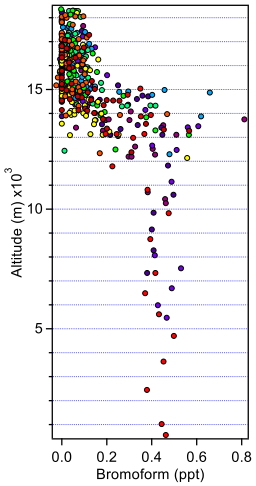
Ozone



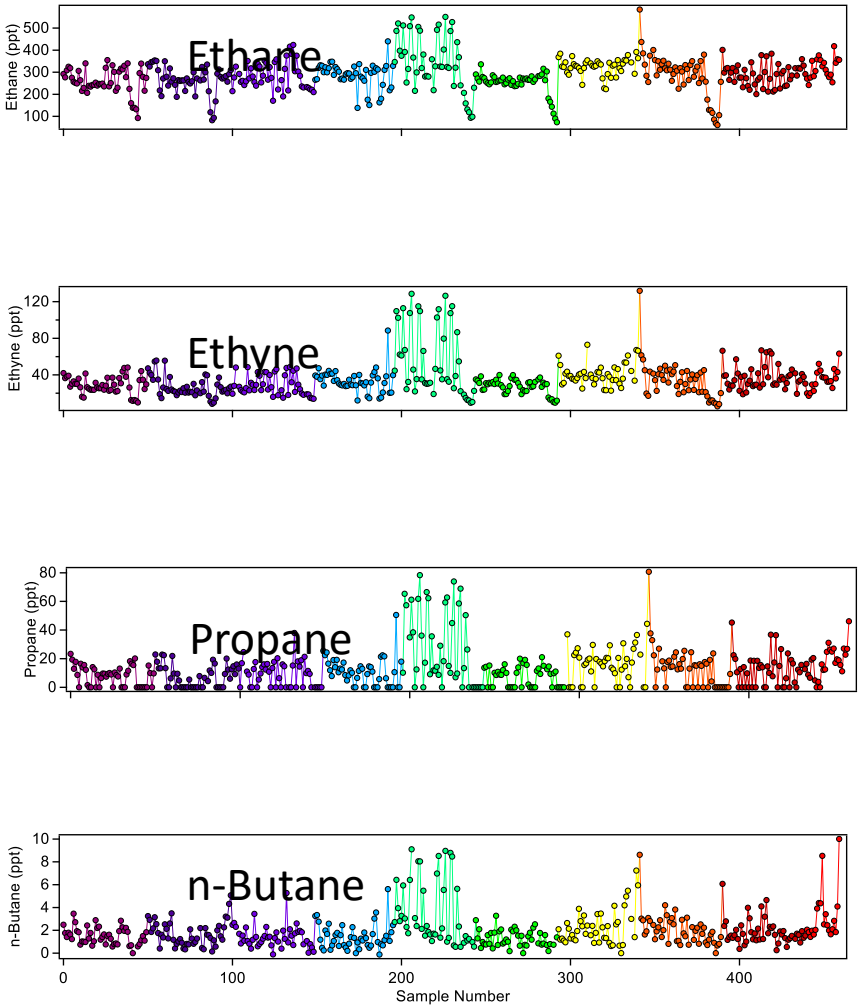
Halon 1211



Bromoform

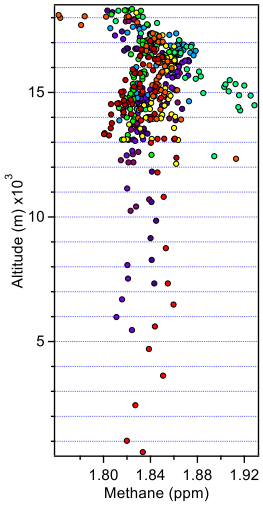


Non-methane hydrocarbons

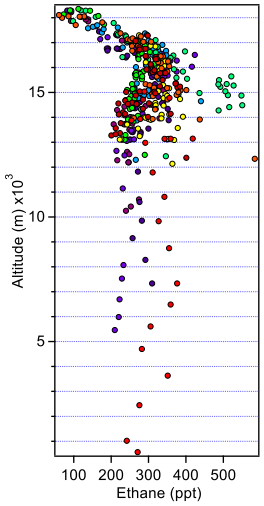


Vertical profiles – Hydrocarbons

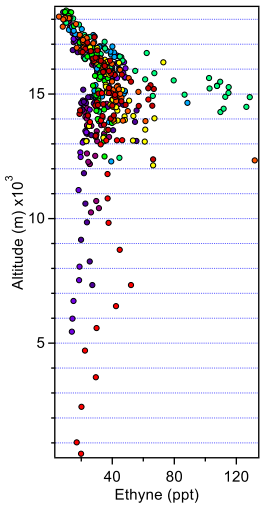
Methane



Ethane

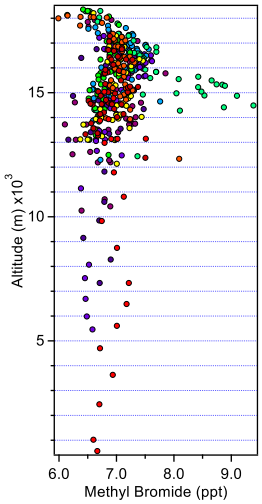


Ethyne

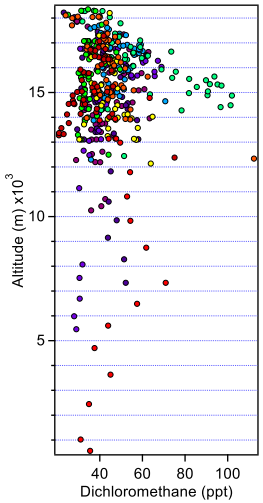


Vertical profiles – Halocarbons

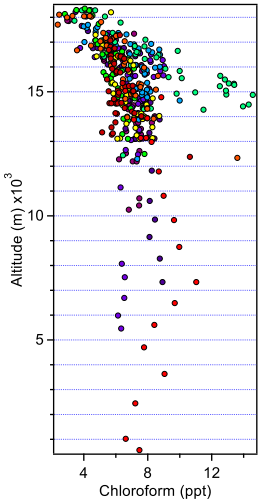
Methyl Bromide



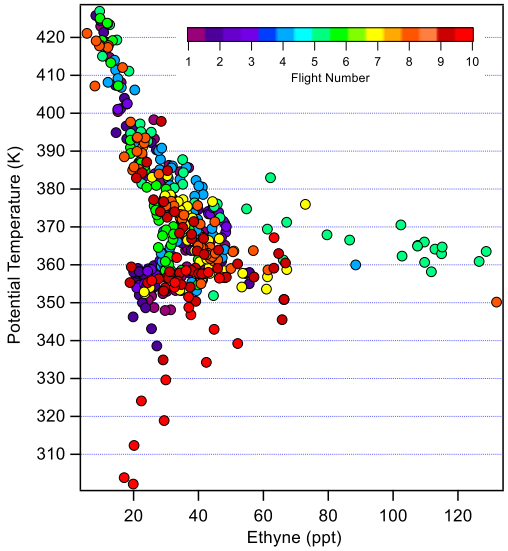
Dichloromethane



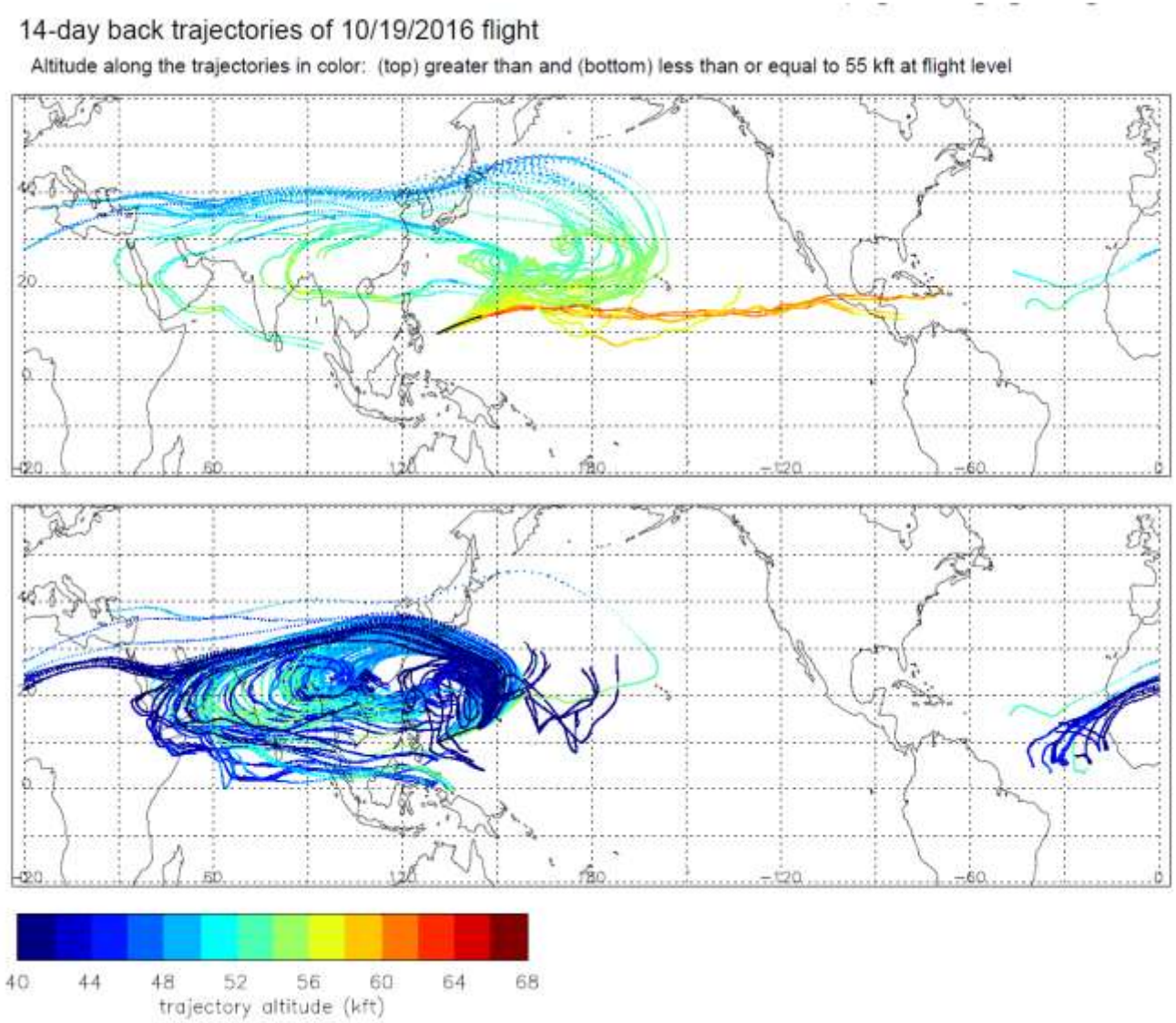
Chloroform



Ethyne vs Potential Temperature



RF05- 14-day back trajectories

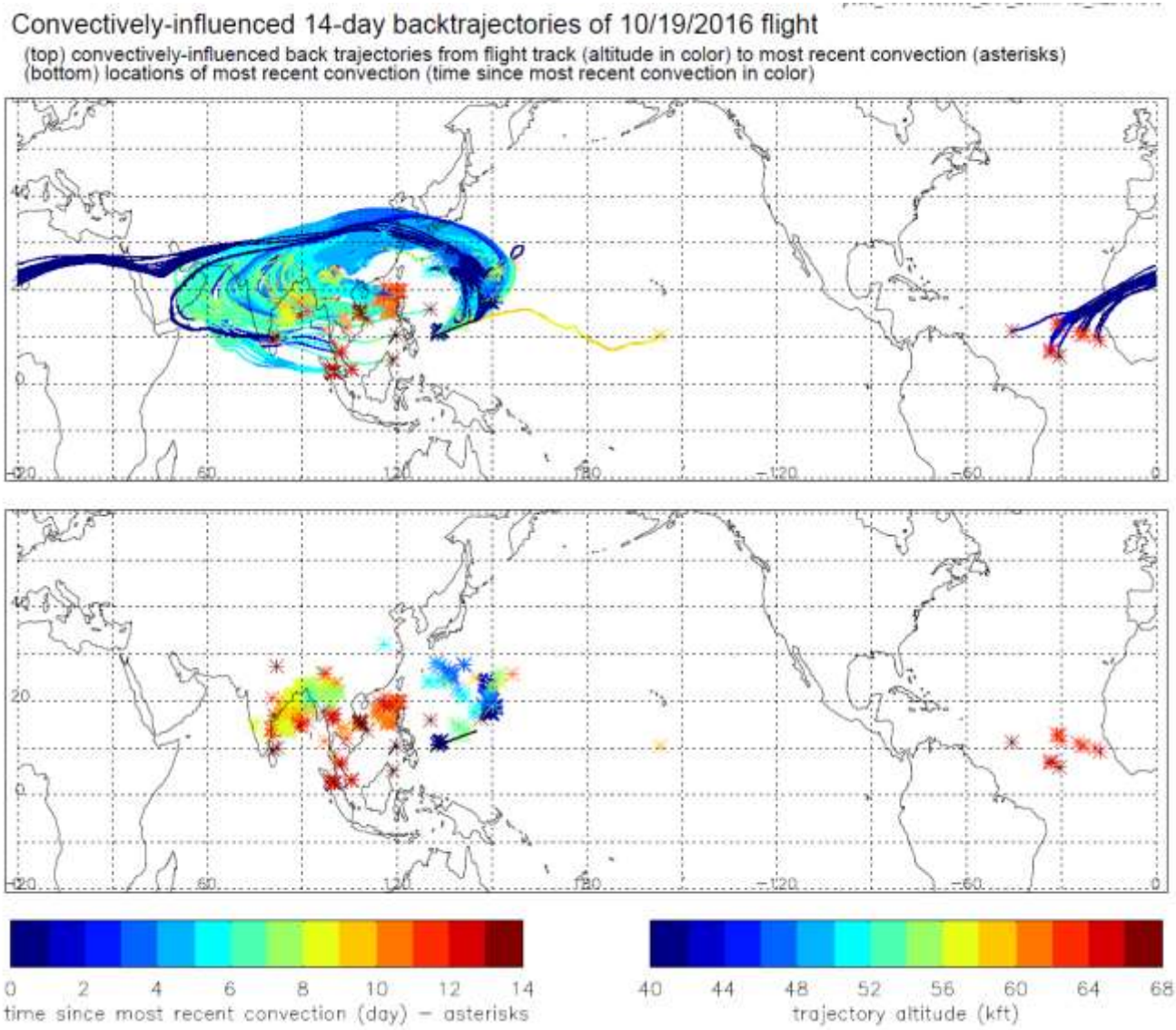


Flight Altitude

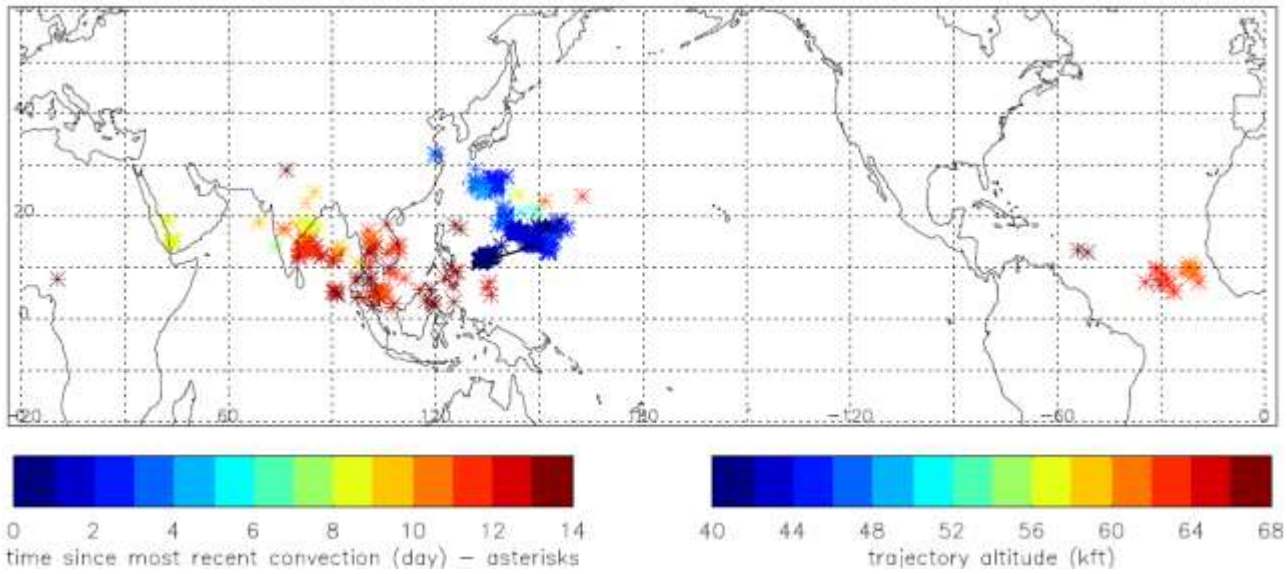
> 55 Kft

<= 55 Kft

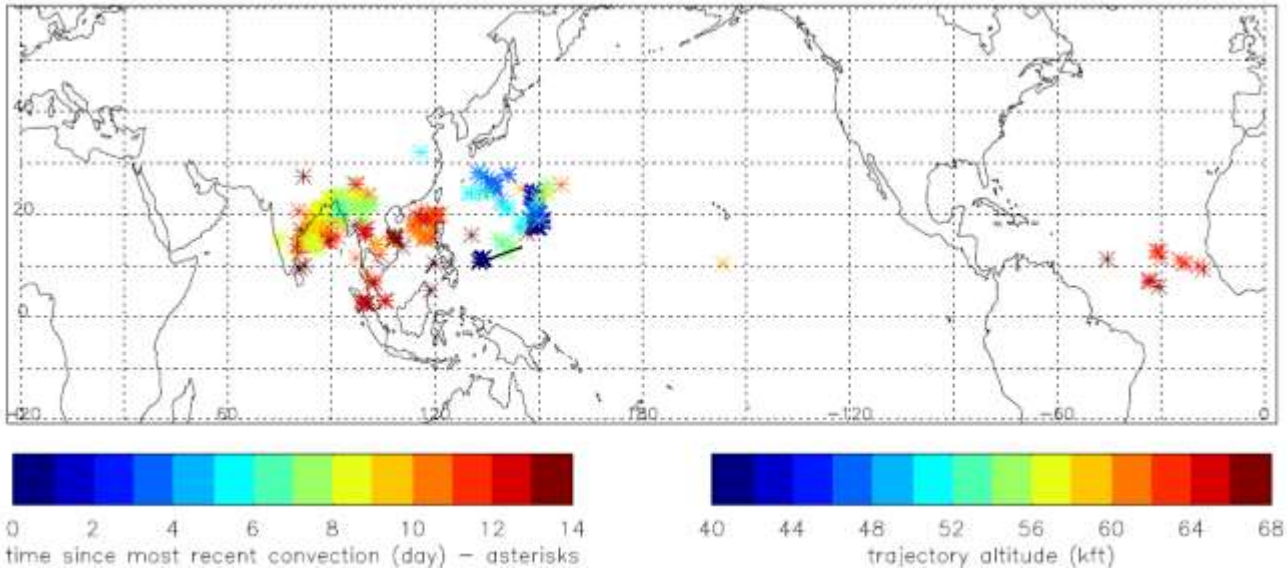
RF05- Convective Influence



Convective Influence: RF04 and RF05

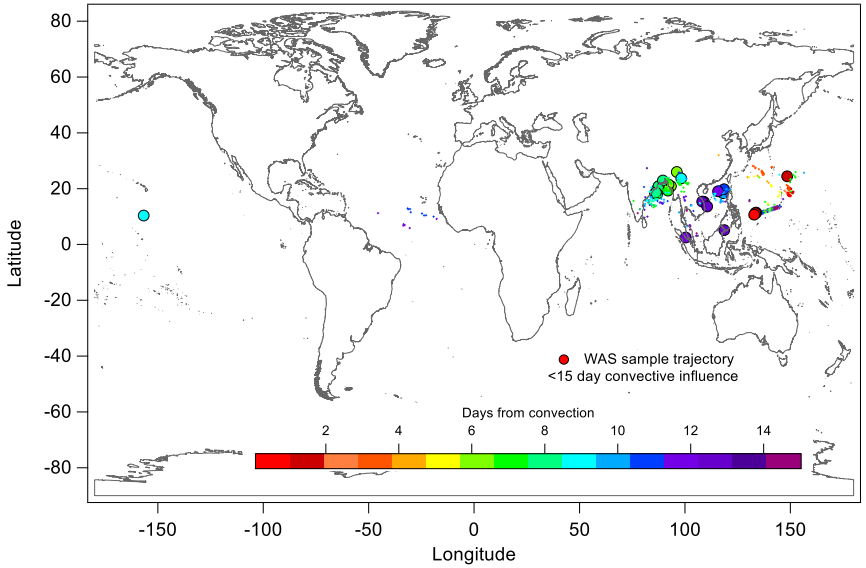


RF04
18 October 2016

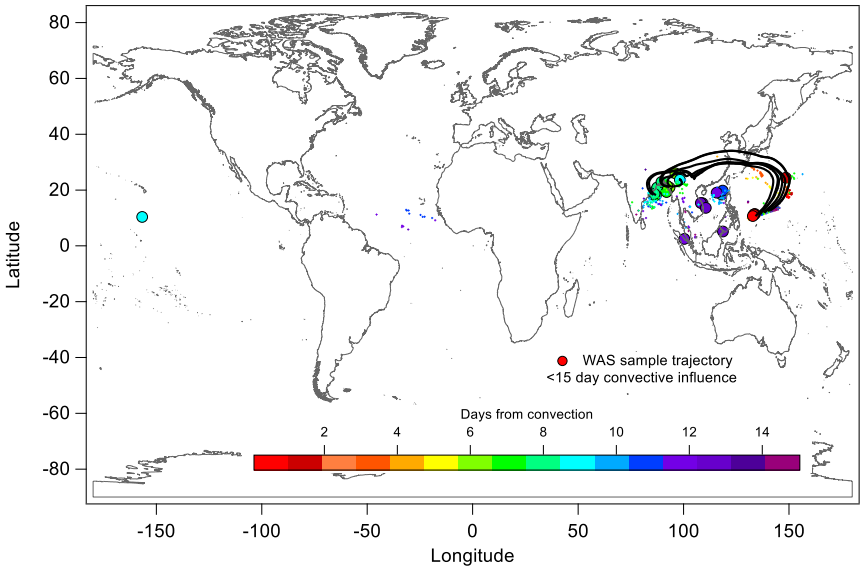


RF05
19 October 2016

RF05- WAS samples with convective influence <15 days



RF05 - Samples ~14 – 15 km



RF05 trace gas enhancements

Compound	Units	Background	Plume	Delta	% over background
Methane	ppb	1840	1925	85	5%
Ethane	ppt	310	530	220	71%
Ethyne	ppt	40	120	80	200%
Propane	ppt	10	65	55	550%
n-Butane	ppt	1	9	8	800%
Methyl Chloride	ppt	550	640	90	16%
Methyl Bromide	ppt	7	9.1	2.1	30%
Dichloromethane	ppt	45	102	57	127%
Chloroform	ppt	7	14	7	100%
Perchlorethylene	ppt	0.6	0.8	0.2	33%

NMHC enhancements in Asian Monsoon Outflow (Baker et al., 2011, ACP)

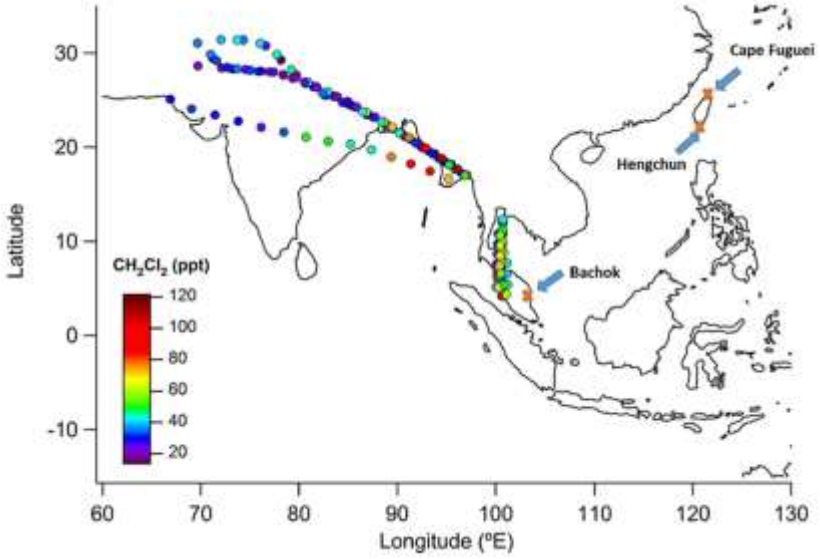
	June	July	August	September
Ethane	115.4 (23%)	64.5 (13%)	16.3 (3%)	−48.6 (−10%)
Propane	29.4 (71%)	16.1 (39%)	15.3 (37%)	6.6 (16%)
i-Butane	4.6 (127%)	2.6 (72%)	3.5 (96%)	2.8 (75%)
n-Butane	5.2 (89%)	3.7 (64%)	3.5 (60%)	2.3 (39%)
i-Pentane	0.1 (2%)	1.6 (49%)	0.4 (12%)	0.3 (8%)
n-Pentane	0.4 (19%)	0.8 (34%)	0.9 (37%)	0.9 (37%)
Ethyne	28.9 (45%)	53.3 (83%)	56.8 (89%)	25.4 (40%)
Benzene	12.7 (145%)	14.7 (168%)	13.5 (154%)	8.7 (99%)

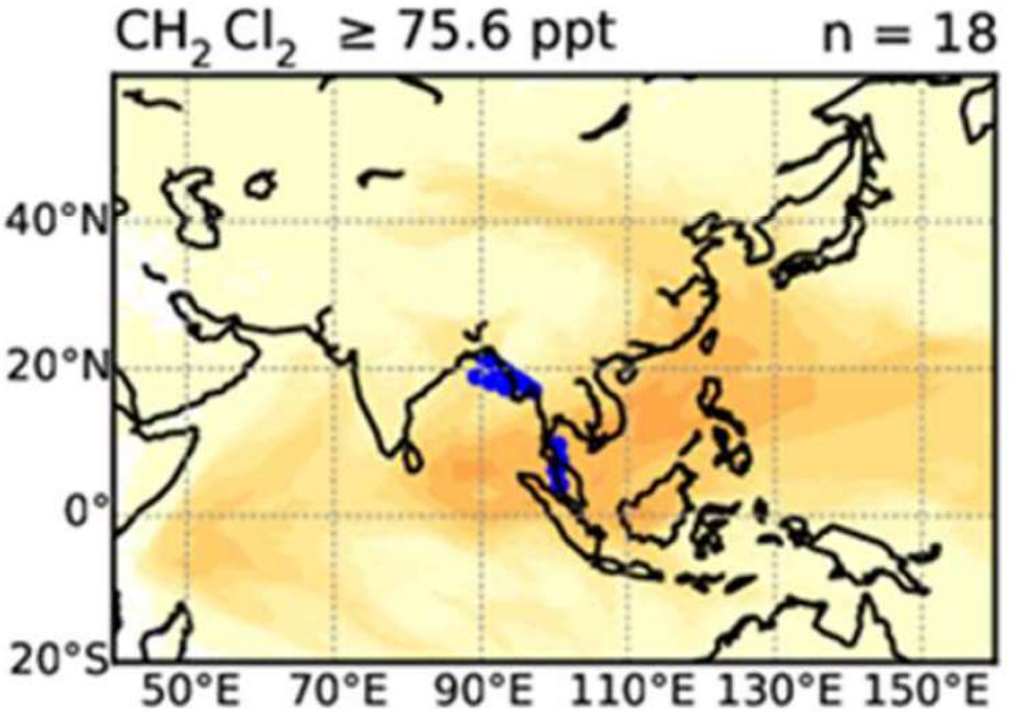
Halocarbon Observations: Surface[1] and Airborne[2]

[1]Barletta et al., 2006 (45 Chinese cities)
[2] Umezawa et al.,2014 (CARIBIC, 2005-2011)

Compound	Units	Background	Average	Delta	% over background
Methyl Chloride	ppt	535	952	417	78%
Methyl Bromide	ppt	8.4	13	4.6	55%
Dichloromethane	ppt	28	226	198	707%
Chloroform	ppt	9	48	39	433%
Perchlorethylene	ppt	5	129	124	2480%
from CARIBIC					
Methyl Chloride	ppt	550	650	100	18%
SON, South Asia (20N)					

Recent report of elevated halocarbons from SE Asia (Oram et al., 2017, ACPD)





Summary

- Trace gas composition of the tropical UT/LS was measured near Guam during October, 2016.
  - Extends available measurements through tropopause region.
- Local/regional convection transported reactive marine emissions to the UT
- One episode of significant pollutant transport was identified at 14 – 16 km (360 – 370 K)
- Chemical “fingerprint” and back trajectory/convective influence analysis suggests mix of urban/biofuel/biomass sources near east Indian coast
  - No enhancements of HCFCs observed.
  - Need further review and update of emission distributions

ACAM papers welcome!

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