Short-lived trace gases during HIPPO

E. Atlas, R. Lueb, K. Smith, X. Zhu, L. Pope (UMiami/RSMAS)
Roger Hendershot (NCAR/ACD)
F. Moore, B. Miller, S. Montzka, J. Elkins, D. Nance, C. Sweeney (NOAA)
S. Wofsy, E. Kort, B. Daube, R. Jimenez, J. Pittman (Harvard)
P. Romashkin (NCAR/RAF)

Trace gases measured in whole air samples during HIPPO

Chlorofluorocarbons	NOAA	UM
CFC-11 (CCl_3F)	✓	✓
CFC-12 (CCl_2F_2)	✓	✓
CFC-13($CClF_3$)	✓	✓
CFC-113 (CCl_2FCClF_2)	✓	✓
CFC-114 ($CClF_2CClF_2$)	✓	✓
CFC-115 (CF_2ClCF_3)	✓	✓
Halons		
CFC-12b1 (Halon 1211,CF_2ClBr)	✓	✓
CFC-13b1 (Halon 1301, CF_3Br)	✓	✓
CFC-114b2 (Halon 2402, $C_2F_4Br_2$)	✓	✓
Hydrochlorofluorocarbons/ Hydrofluorocarbons		
HCFC-22 (CHF_2Cl)	✓	✓
HCFC-141b (CH_3CFCl_2)	✓	✓
HCFC-142b (CH_3CF_2Cl)	✓	✓
HFC-134a ($C_2H_2F_4$)	✓	✓
HFC-124 (C_2HClF_4)	✓	✓
HFC-123 ($C_2HCl_2F_3$)	✗	✓
HFC-125 (C_2HF_5)	✓	✓
HFC-143a ($C_2H_3F_3$)	✓	✓
HFC-23 (CHF_3)	✓	✓
HFC-227ea(C_3HF_7)(1,1,1,2,3,3,3-Heptafluoropropane)	✓	✓
HFC-365mfc ($C_4H_5F_5$) (1,1,1,3,3-pentafluorobutane)	✓	✓

Organic Nitrates	NOAA	UM
Methyl nitrate(CH_3ONO_2)	✗	✓
Ethyl nitrate($C_2H_5ONO_2$)	✗	✓
Propyl nitrates($C_3H_7ONO_2$)	✗	✓
Butyl nitrates ($C_4H_9ONO_2$)	✗	✓
Pentyl nitrates ($C_5H_{11}ONO_2$)	✗	✓
Solvents	✓	✓
Carbon Tetrachloride (CCl_4)	✓	✓
Methyl Chloroform(CH_3CCl_3)	✓	✓
Tetrachloroethylene (C_2Cl_4)	✓	✓
Methylene Chloride (CH_2Cl_2)	✓	✓
Chloroform ($CHCl_3$)	✓	✓
Trichloroethylene(C_2HCl_3)	✗	✓
1,2-Dichloroethane ($C_2H_4Cl_2$)	✗	✓
Methyl Halides and related		
Methyl Bromide(CH_3Br)	✓	✓
Methyl Chloride (CH_3Cl)	✓	✓
Methyl Iodide (CH_3I)	✓	✓
Methylene Bromide(CH_2Br_2)	✓	✓
CHxBryClz	✗	✓
Bromoform ($CHBr_3$)	✓	✓
Perfluorocarbons	✓	✓
Sulfur Hexafluoride (SF6)	✓	✓
PFC-116 (C_2F_6)	✗	✓
PFC-218 (C_3F_8)	✓	✓
PFC-318 (C_4F_8)(perfluorocyclobutane)	✗	✓
Others		
CO_2, H_2, $^{13}CO_2$, ^{18}OCO	✓	✗

Non-Methane Hydrocarbons	NOAA	UM
Ethane (C_2H_6)	✓	✓
Ethyne (C_2H_2)	✓	✓
Propane(C_3H_8)	✓	✓
Isobutane(C_4H_{10})	✗	✓
n-Butane (C_4H_{10})	✓	✓
Isopentane (C_5H_{12})	✓	✓
n-Pentane (C_5H_{12})	✓	✓
Isoprene (C_5H_{10})	✓	✓
Benzene (C_6H_6)	✓	✓
Toluene (C_7H_8)	✗	✓
C2-Benzenes (C_8H_{10})	✗	✓
Other		
Methane (CH_4)	✓	✓
Carbon Monoxide (CO)	✓	✓
Nitrous Oxide (N_2O)	✓	✓
Carbonyl Sulfide (COS)	✓	✓
Dimethyl Sulfide (C_2H_6S)	✗	✓
Carbon disulphide (CS2)	✓	✗
Methyl-t-butyl ether	✗	✓
Methyl Acetate/Ethyl Acetate	✗	✓
Acetonitrile	✗	✓
1,2 Dichlorobenzene	✗	✓

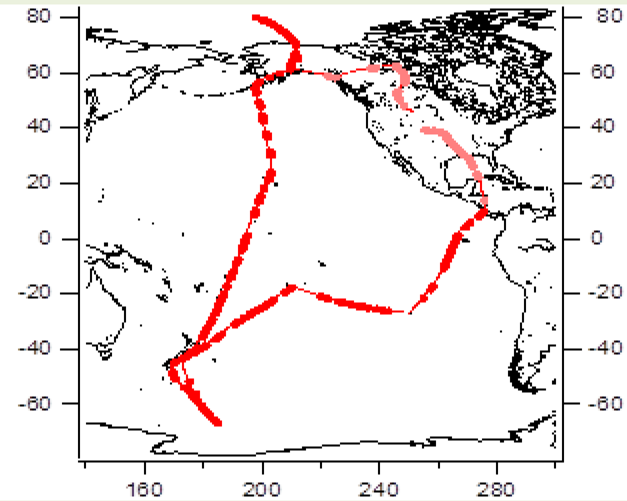
Short-lived gases (days – months)

- Organic halogen sources/distributions
  - Impact on UT/LS chemistry
  - Characterize emission distribution
- Impact of different emission sources on background troposphere
  - Evaluation of sources, transport and chemistry
  - Marine, Biomass/Biofuel burning, Industrial, Continental/Biogenic sources
  - Vertical/latitudinal/seasonal effects

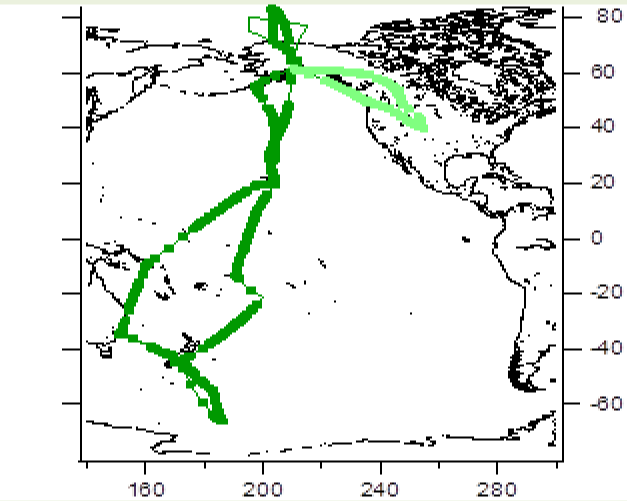
Initial Look

- Comparisons to ground sites
  - NMHC (UC-Irvine (D. Blake); NOAA (D. Helmig))
  - Other gases (AGAGE)
- Seasonal cross-sections
- Organic Bromine/Nitrates
  - Trace gas distributions/emissions
    - TransBrom Cruise (Oct., 2009)
  - Methyl nitrate

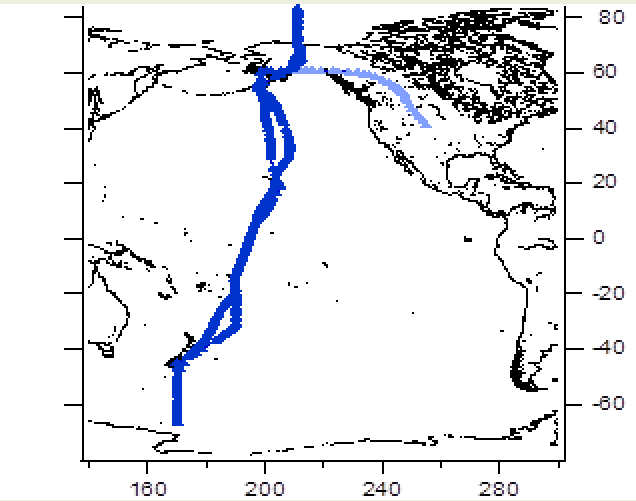
HIPPO FLIGHT TRACKS



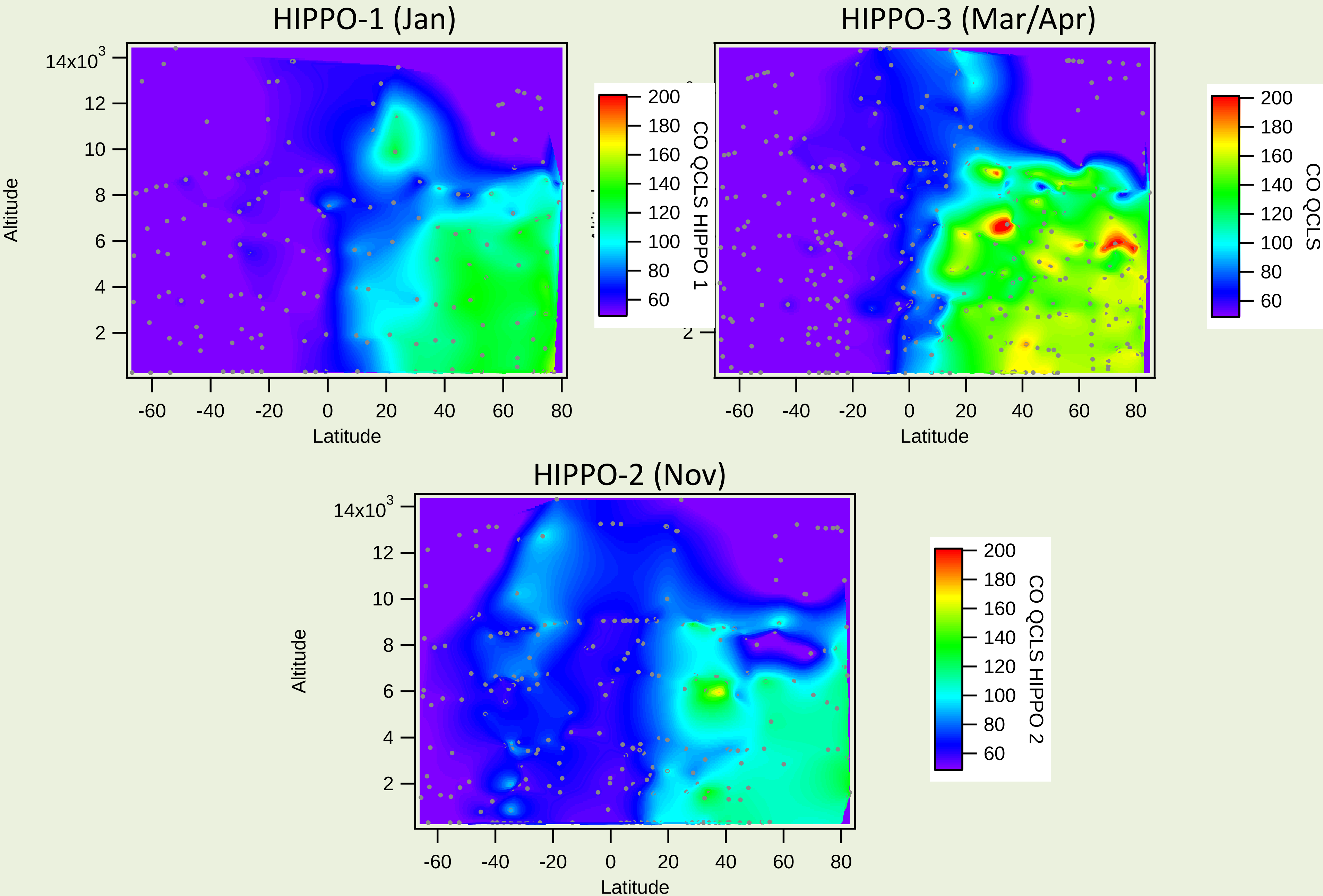
HIPPO – 1 (Jan. 2009)



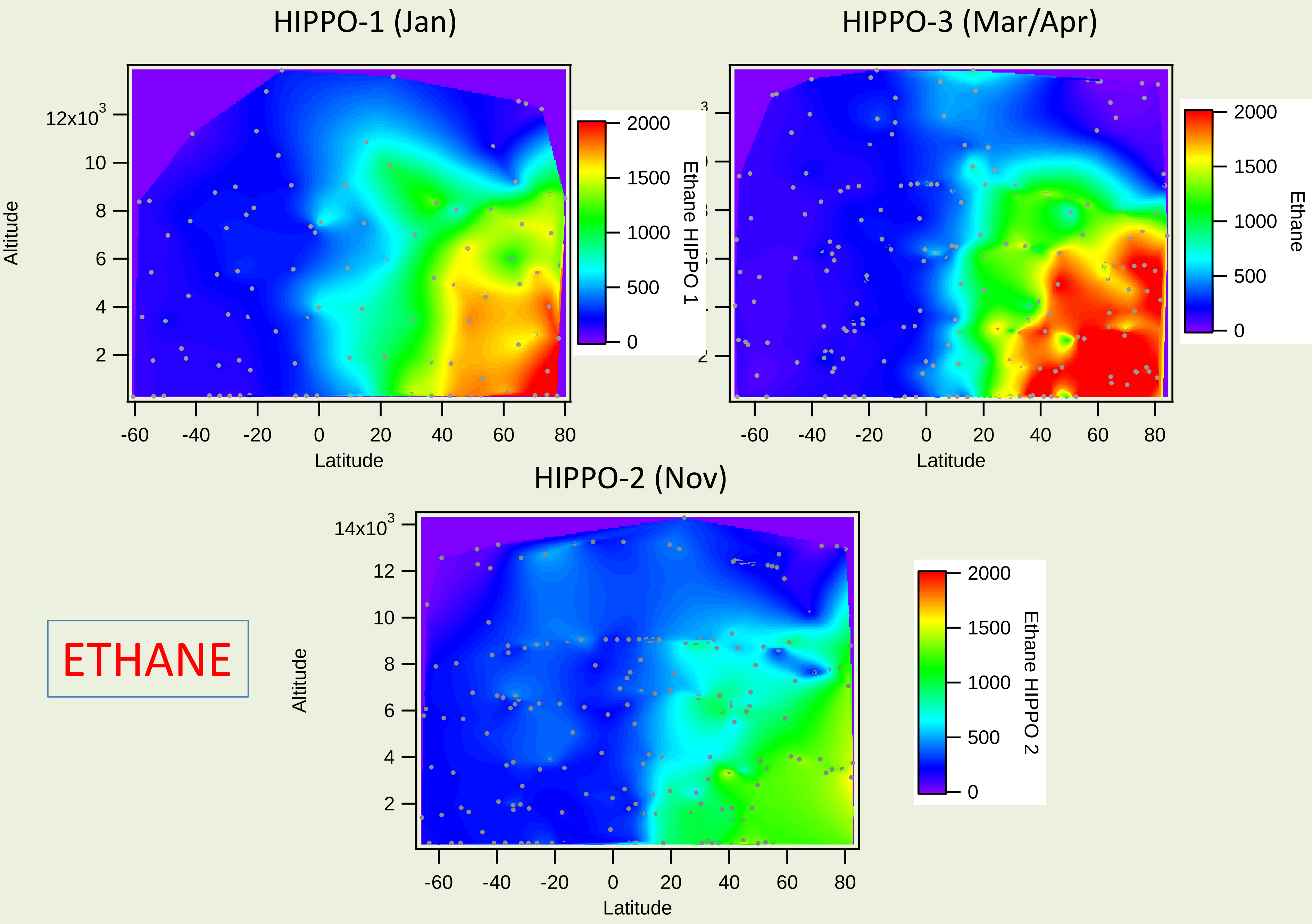
HIPPO – 2 (Nov. 2009)

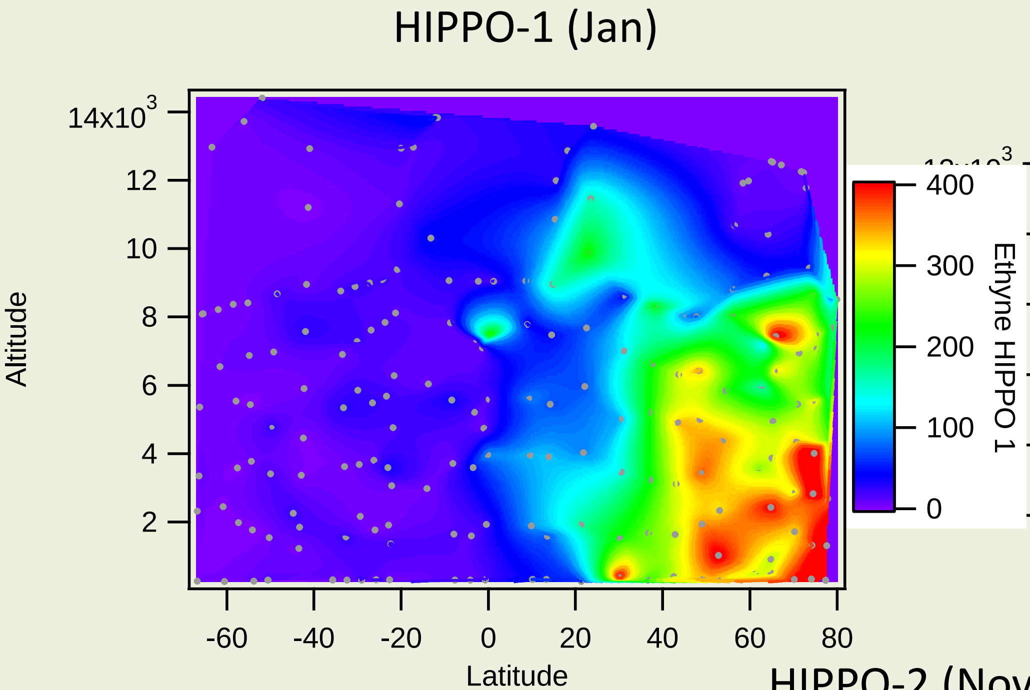


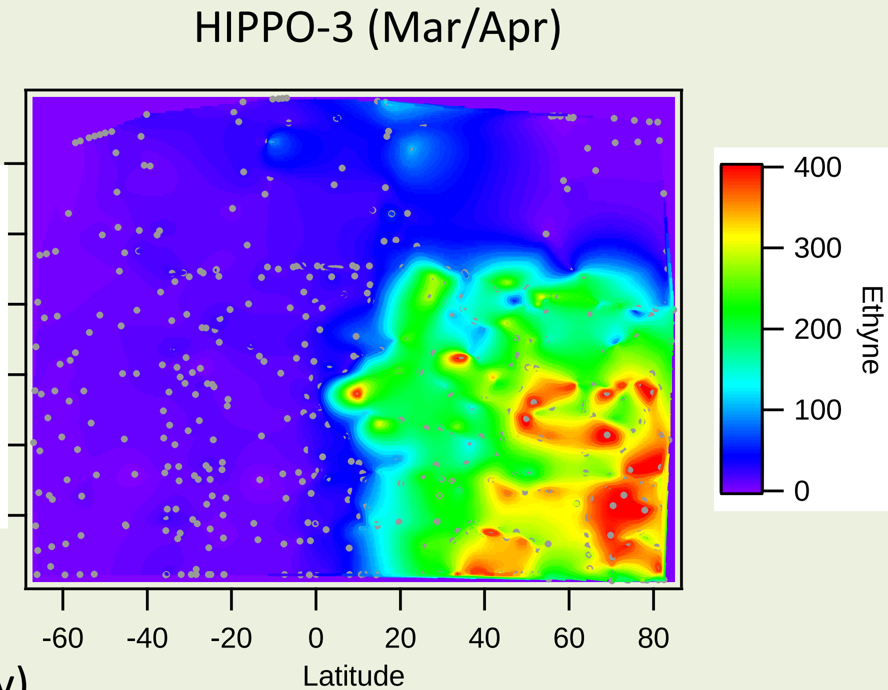
HIPPO –3 (Mar/Apr 2010)



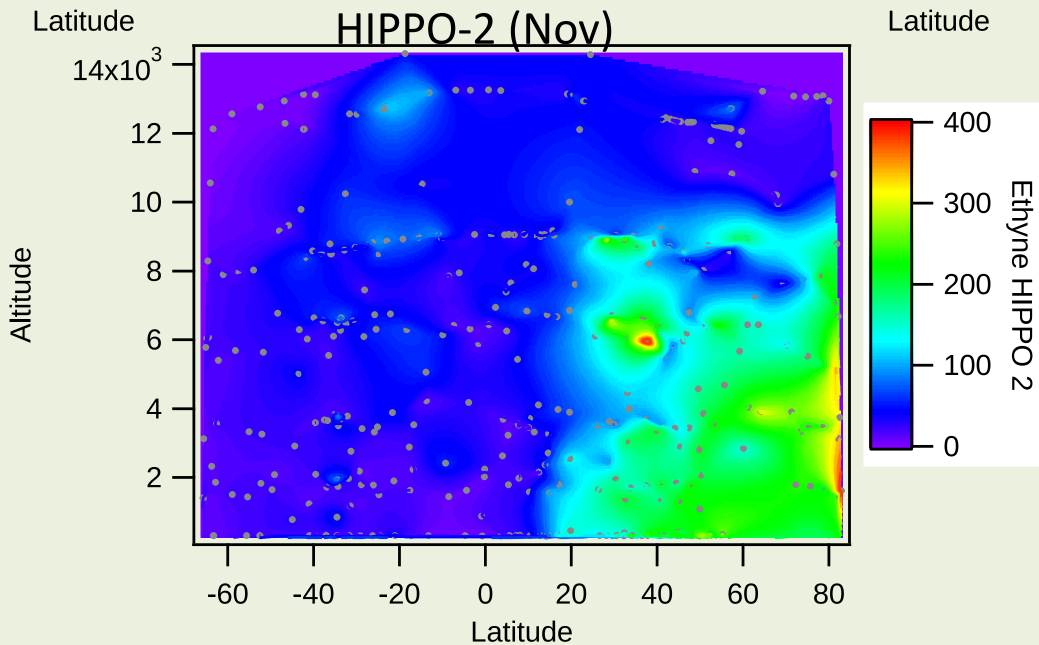
CO (QCLS) Merged to WAS sample times

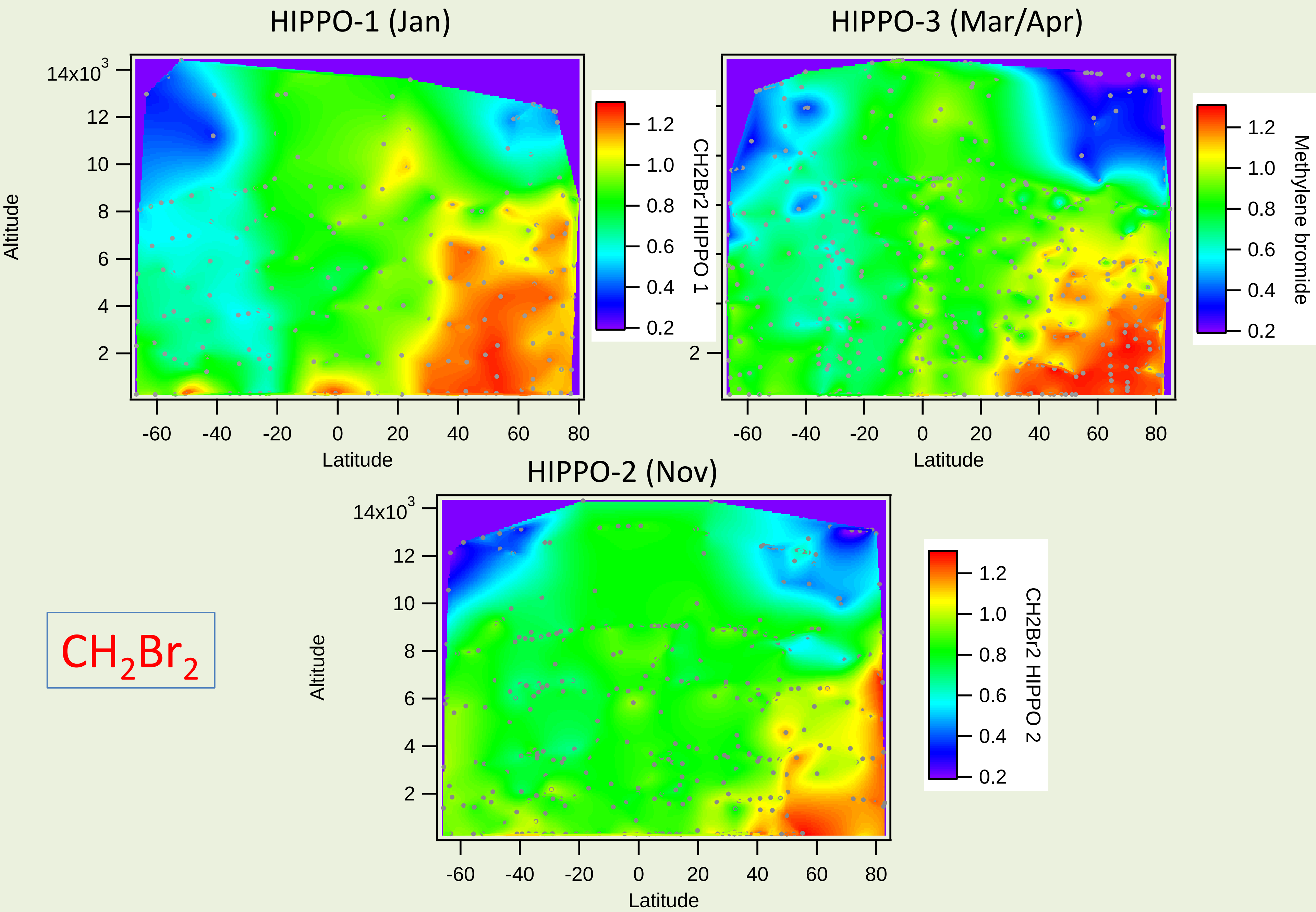

ETHANE
HIPPO-1 (Jan)
12x10^3
10
8
6
4
2
Altitude
-60
-40
-20
0
20
40
60
80
Latitude
2000
1500
1000
500
0
Ethane HIPPO 1
HIPPO-3 (Mar/Apr)
2
Latitude
2000
1500
1000
500
0
Ethane
HIPPO-2 (Nov)
14x10^3
12
10
8
6
4
2
Altitude
-60
-40
-20
0
20
40
60
80
Latitude
2000
1500
1000
500
0
Ethane HIPPO 2


HIPPO-1 (Jan)
14x10^3
12
10
8
6
4
2
Altitude
-60
-40
-20
0
20
40
60
80
Latitude
400
300
200
100
0
Ethyne HIPPO 1


HIPPO-3 (Mar/Apr)
-60
-40
-20
0
20
40
60
80
Latitude
400
300
200
100
0
Ethyne

ETHYNE


HIPPO-2 (Nov)
14x10^3
12
10
8
6
4
2
Altitude
-60
-40
-20
0
20
40
60
80
Latitude
400
300
200
100
0
Ethyne HIPPO 2


HIPPO-1 (Jan)
HIPPO-3 (Mar/Apr)
HIPPO-2 (Nov)
Altitude
Latitude
14x10^3
12
10
8
6
4
2
-60
-40
-20
0
20
40
60
80
1.2
1.0
0.8
0.6
0.4
0.2
CH2Br2 HIPPO 1
Methylene bromide
CH2Br2 HIPPO 2

CH_2Br_2

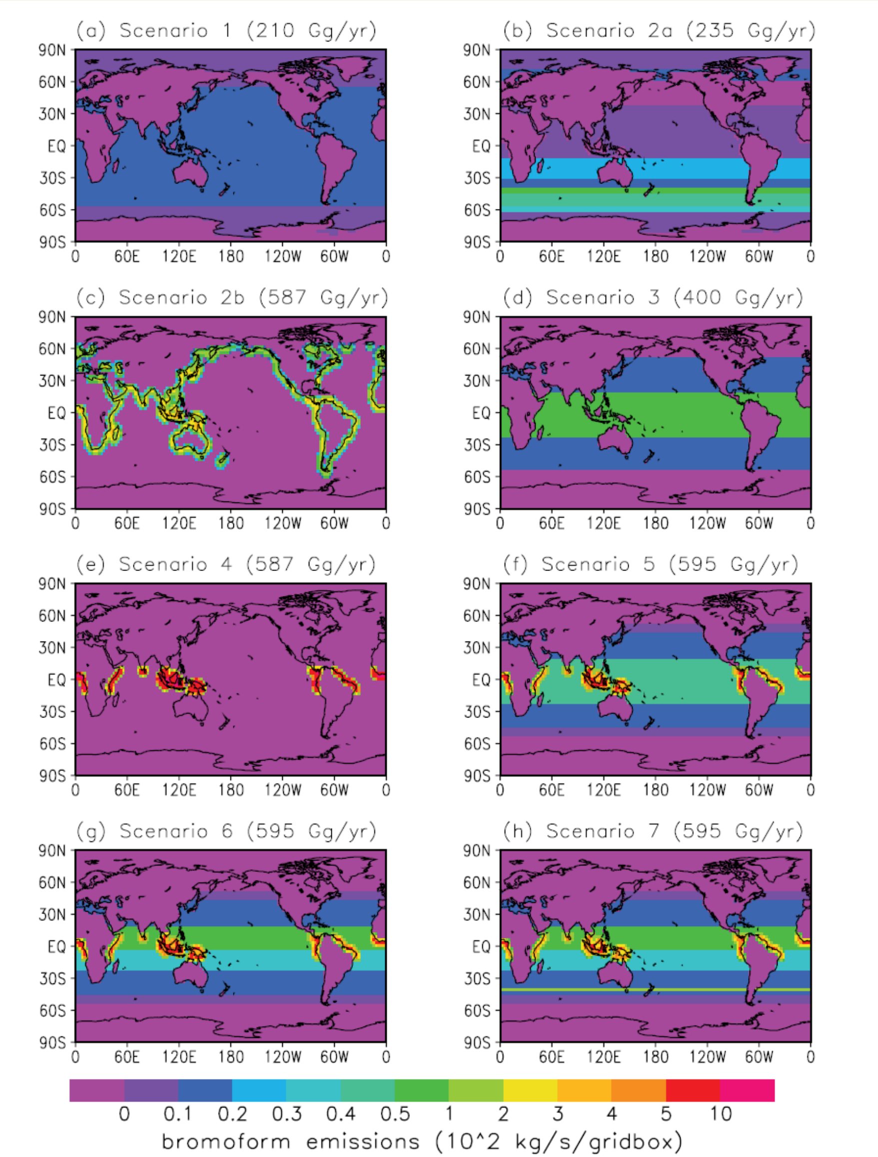
“Reactive Bromine” modeling

- Recent series of modeling papers to better understand role of natural emissions (mostly marine) of bromocarbons
- Major species: Bromoform, Dibromomethane
- Compare multiple airborne and surface measurements vs. emission scenarios (PEM Tropics, TRACE, INTEX, etc.)

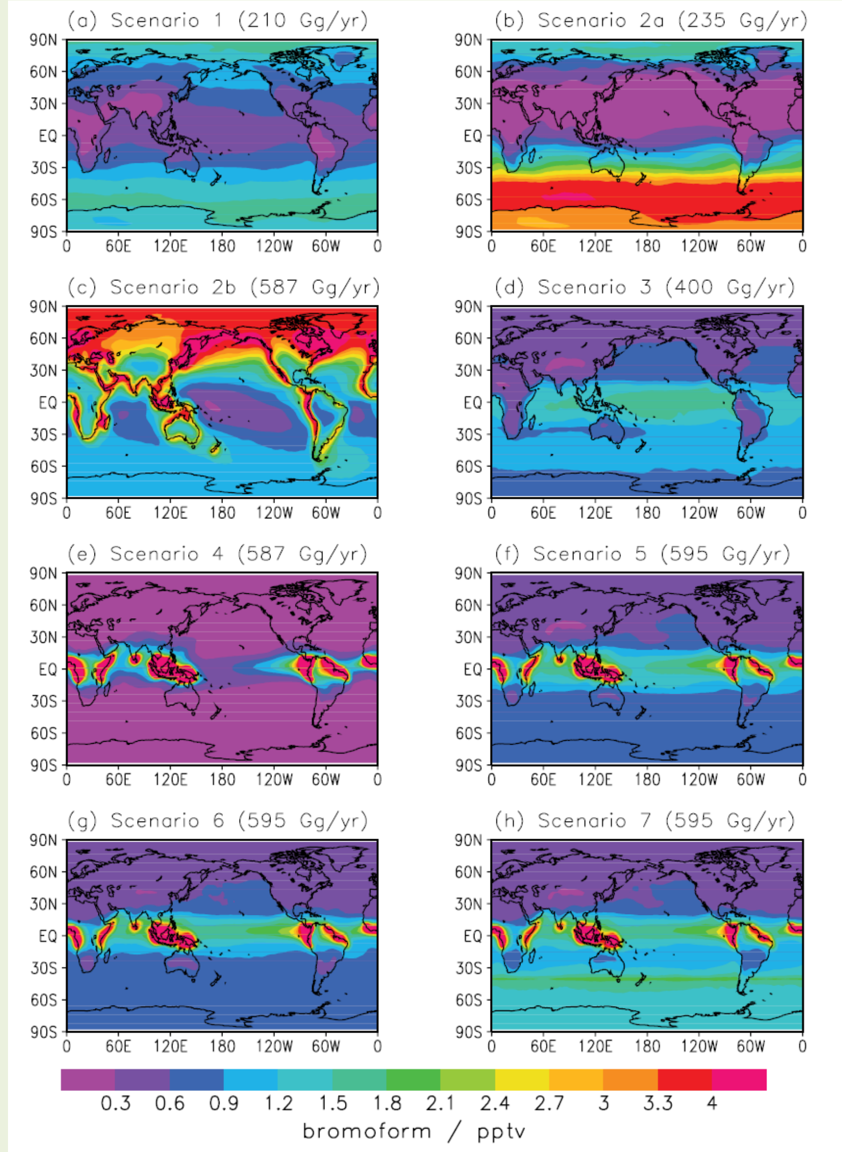
Global modeling of biogenic bromocarbons

N. J. Warwick,[1] J. A. Pyle,[1,2] G. D. Carver,[1,2] X. Yang,[1] N. H. Savage,[1,2] F. M. O'Connor,[3,4] and R. A. Cox[1]

Emission scenarios



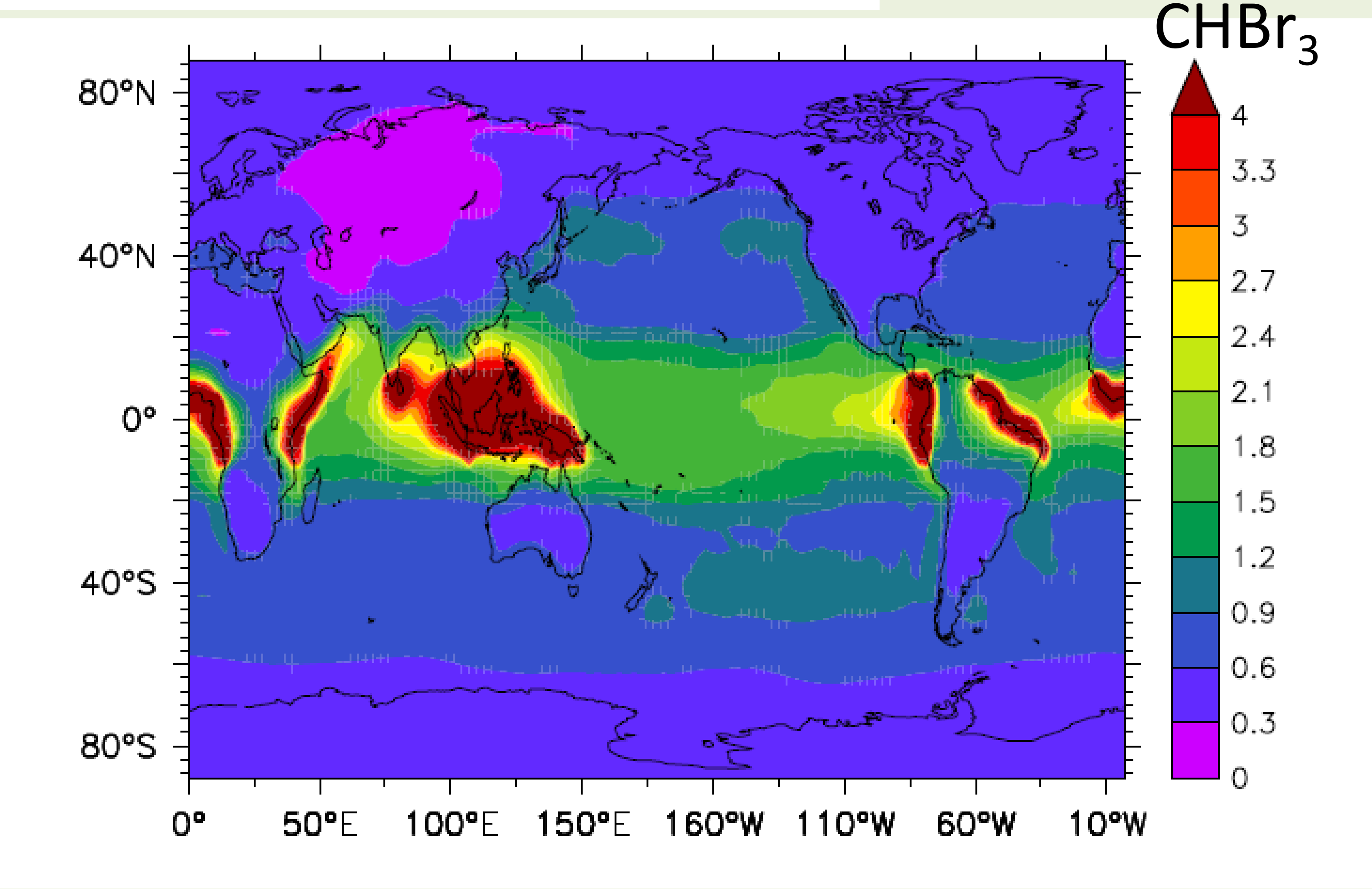
Bromoform concentration



JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 111, D24305, doi:10.1029/2006JD007264, 2006

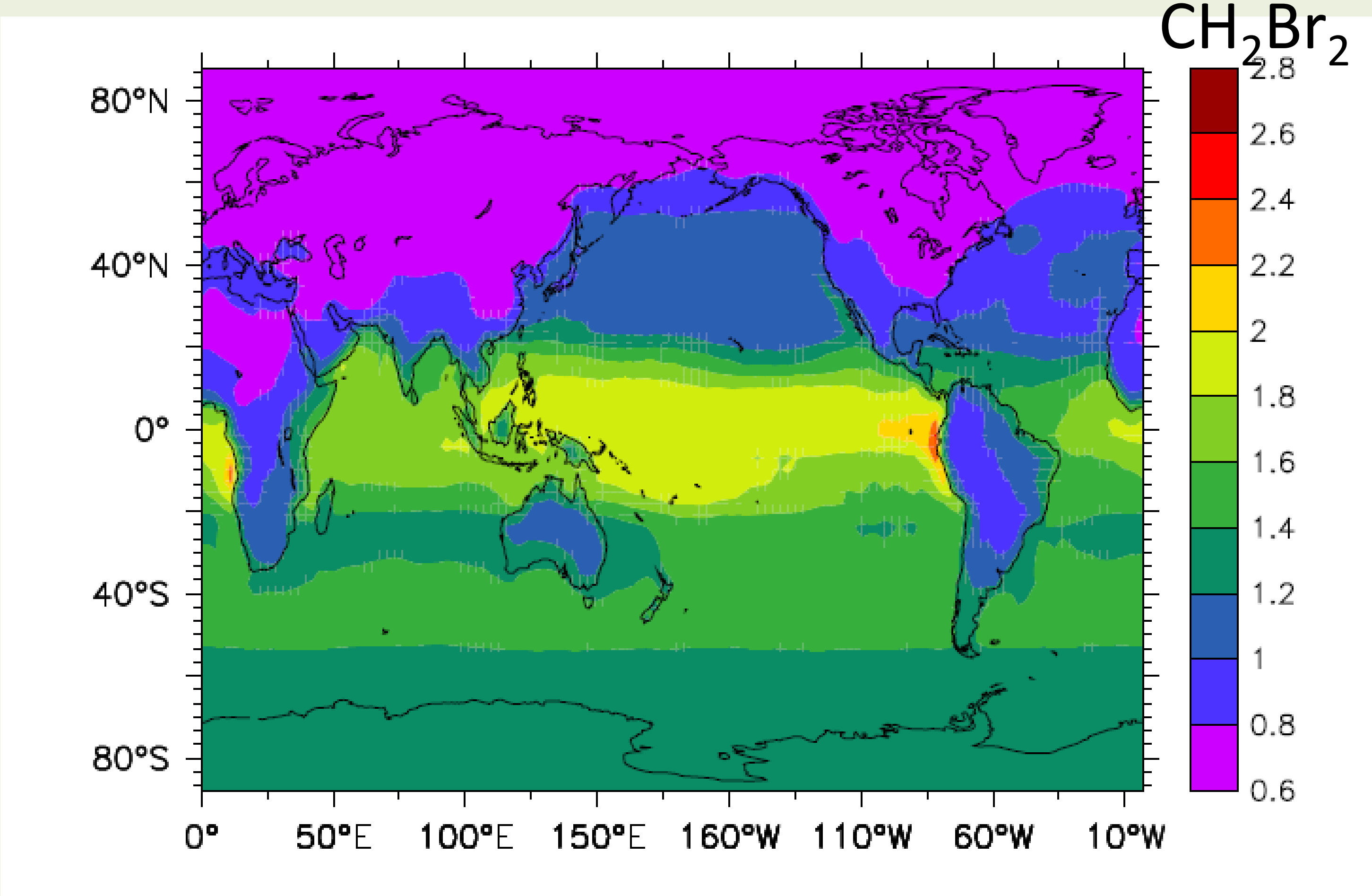
A. Kerkweg et al.: Part 2: Sources of reactive bromine – Bromocarbons

Atmos. Chem. Phys., 8, 5919–5939, 2008



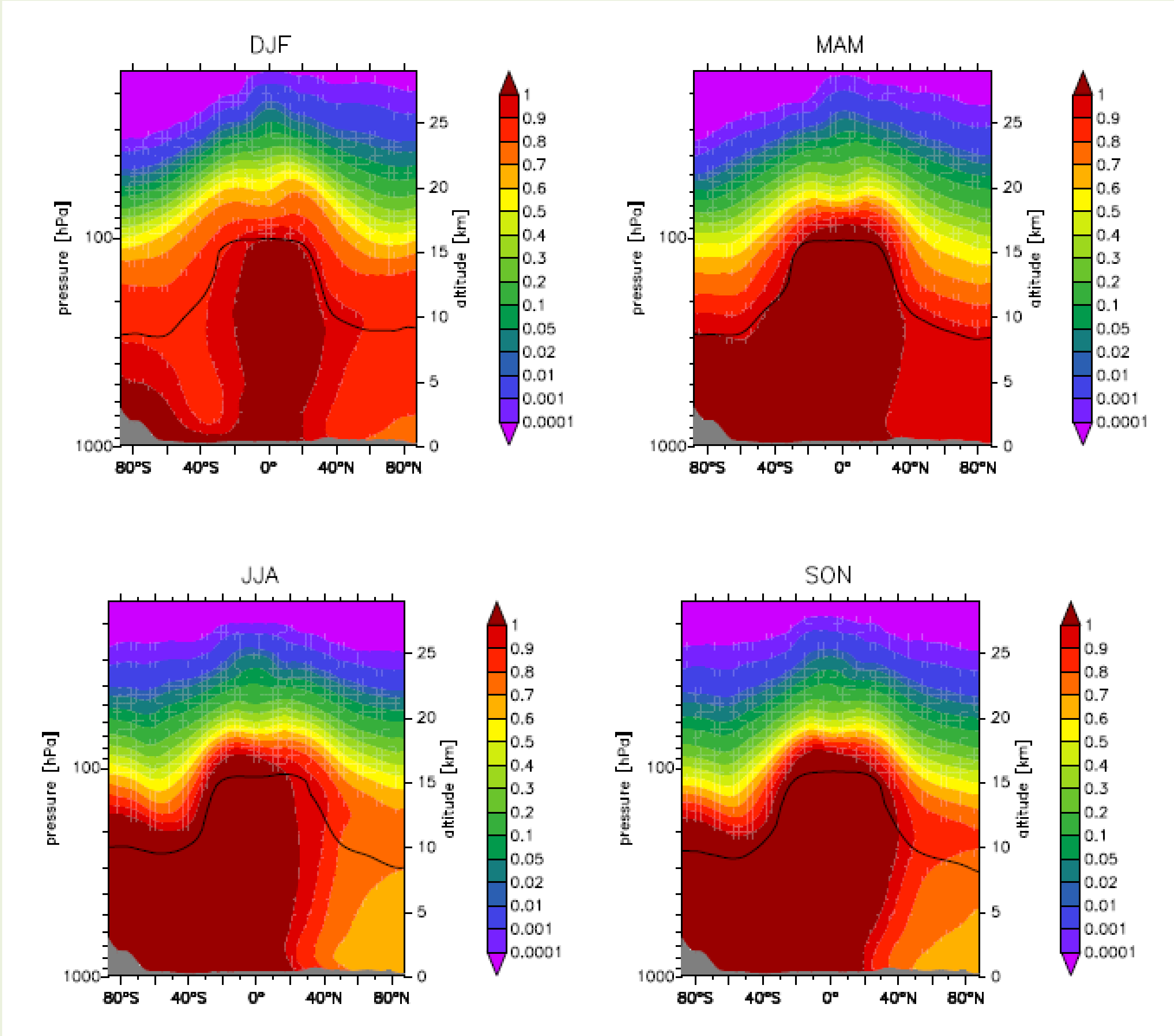
Simulated annually averaged $CHBr_3$ mixing ratio (pmol/mol) in the lowest model layer for the year 2000.

A. Kerkweg et al.: Part 2: Sources of reactive bromine – Bromocarbons

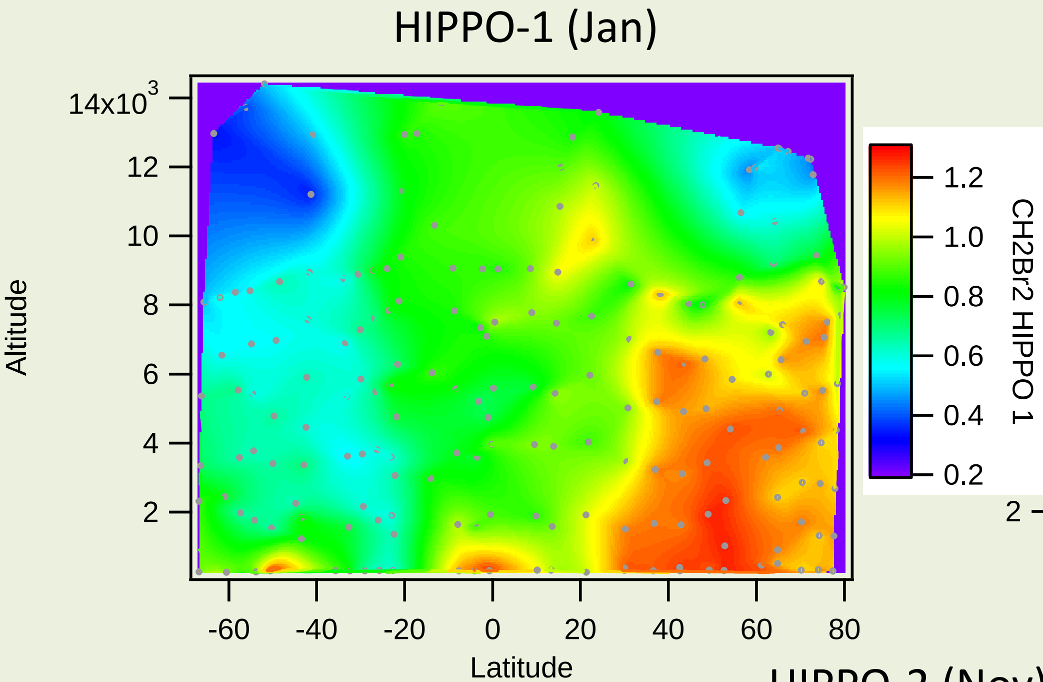


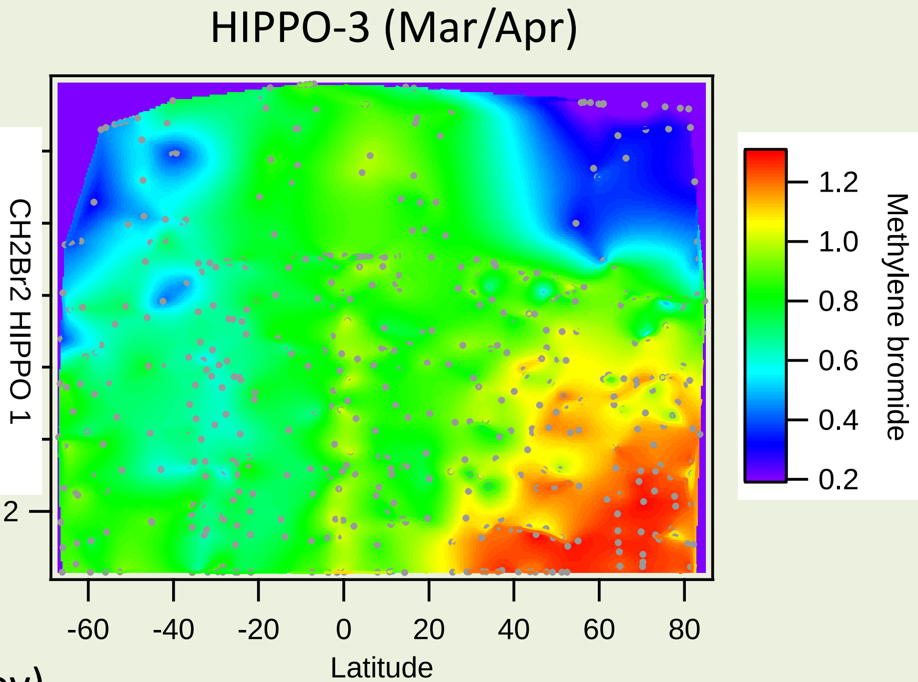
Simulated annual average CH_2Br_2 in pmol/mol in the lowest model layer

CH_2Br_2

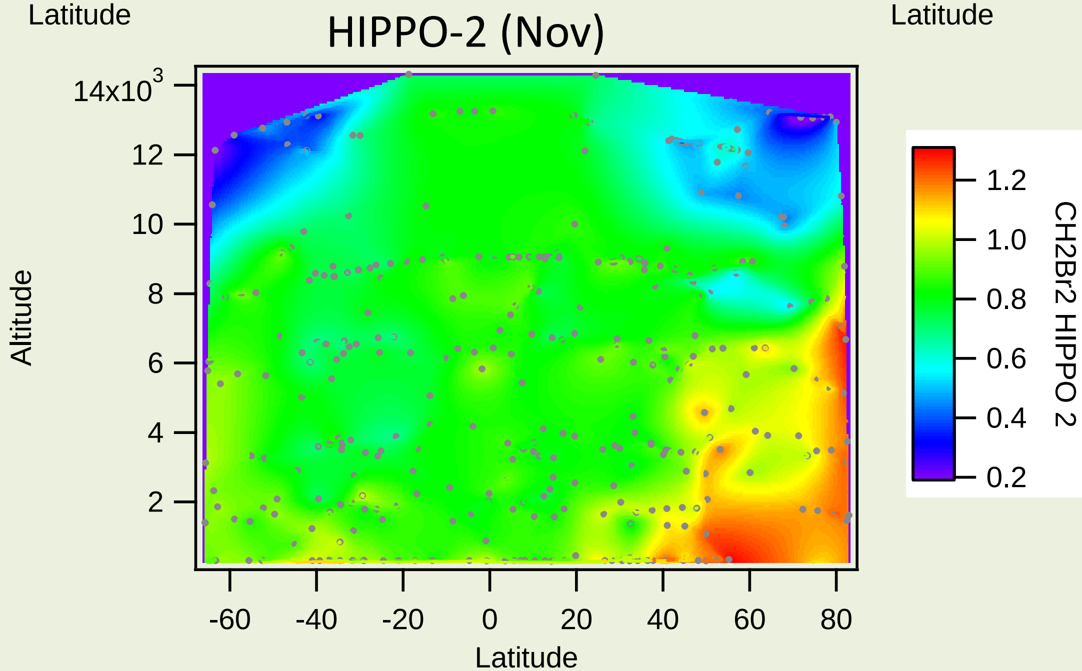


Simulated vertical distribution of CH_2Br_2 in pmol/mol. Shown are seasonal averages; DJF: December 1999, January 2000, February 2000; MAM: March–May 2000; JJA: June–August 2000; SON: September–November 2000.

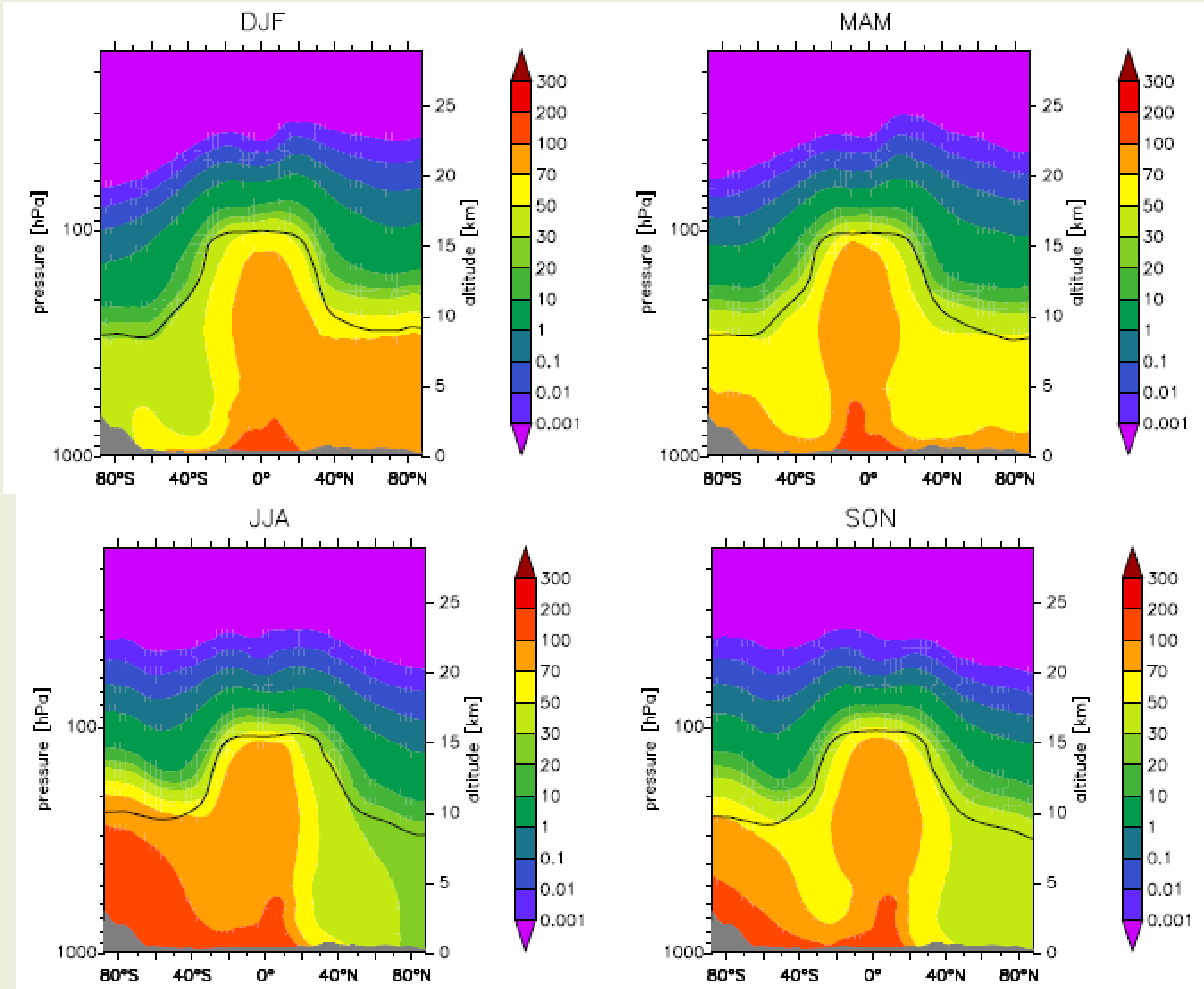

HIPPO-1 (Jan)
Altitude
14x10^3
12
10
8
6
4
2
-60
-40
-20
0
20
40
60
80
Latitude
1.2
1.0
0.8
0.6
0.4
0.2
CH2Br2 HIPPO 1


HIPPO-3 (Mar/Apr)
2
-60
-40
-20
0
20
40
60
80
Latitude
1.2
1.0
0.8
0.6
0.4
0.2
Methylene bromide

CH_2Br_2

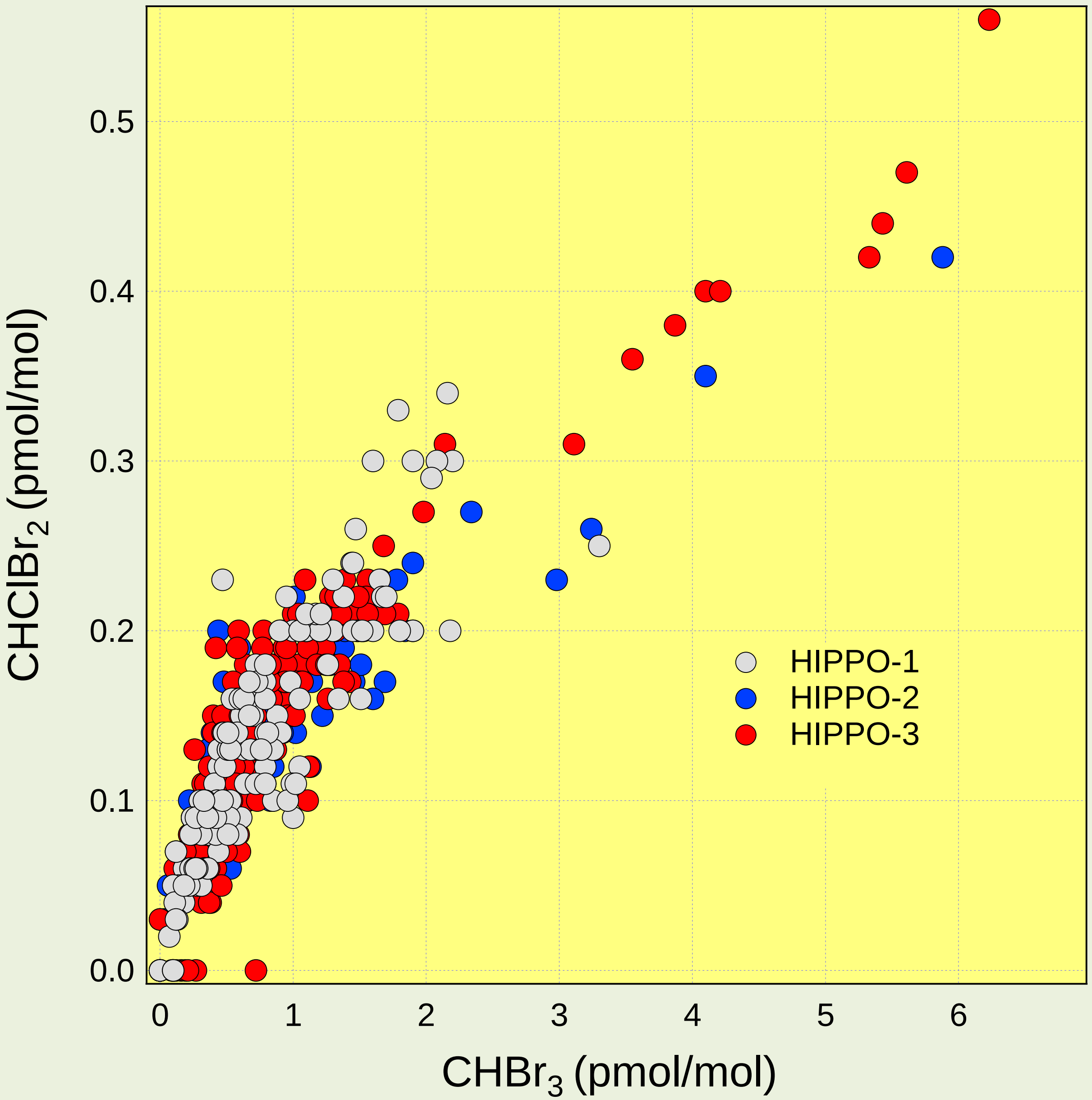

HIPPO-2 (Nov)
Altitude
14x10^3
12
10
8
6
4
2
-60
-40
-20
0
20
40
60
80
Latitude
1.2
1.0
0.8
0.6
0.4
0.2
CH2Br2 HIPPO 2

$CHBr_2Cl$



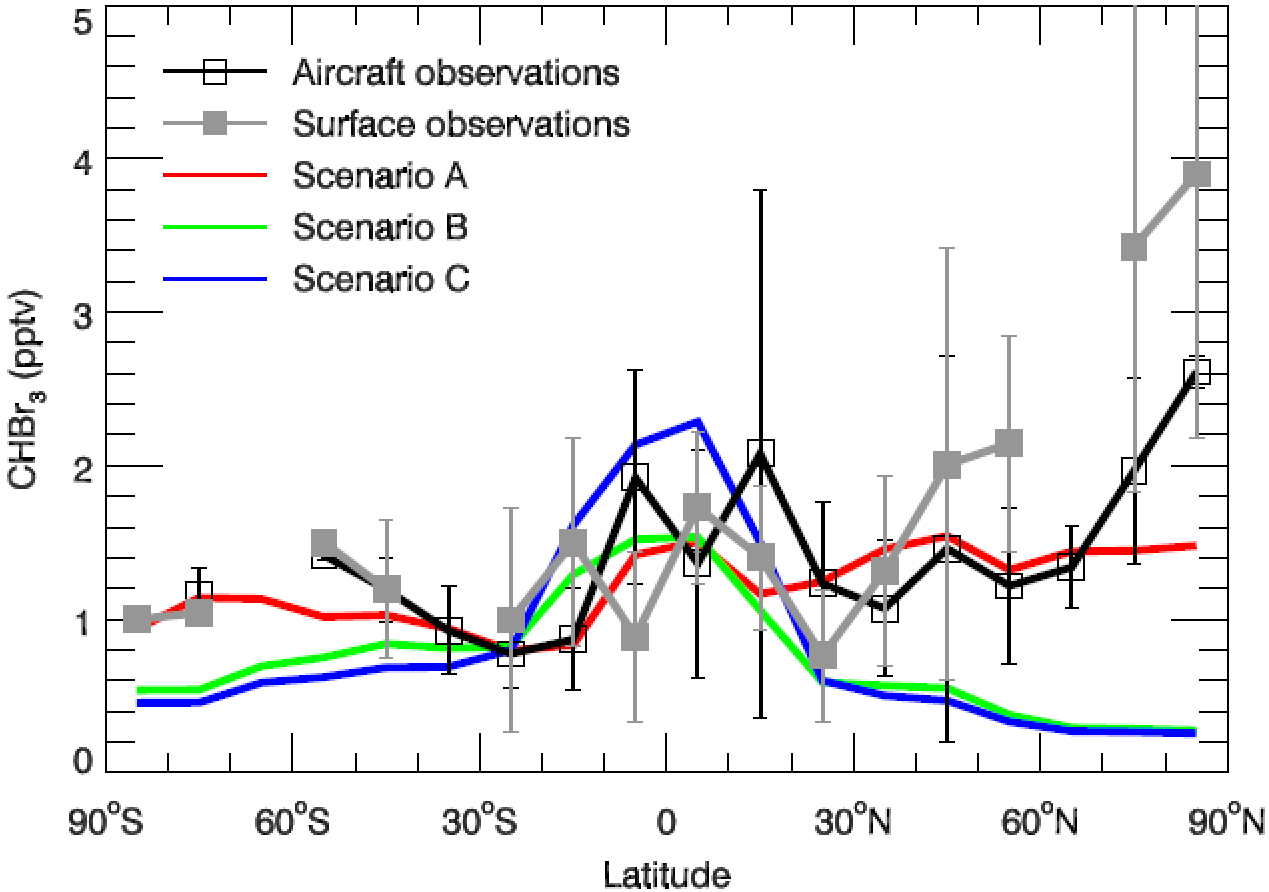
Simulated vertical distribution of $CHBr_2Cl$ in fmol/mol. Shown are seasonal averages; DJF: December 1999, January 2000, February 2000; MAM: March–May 2000; JJA: June–August 2000; SON: September–November 2000.

Bromoform vs. Dibromochloromethane (HIPPO)



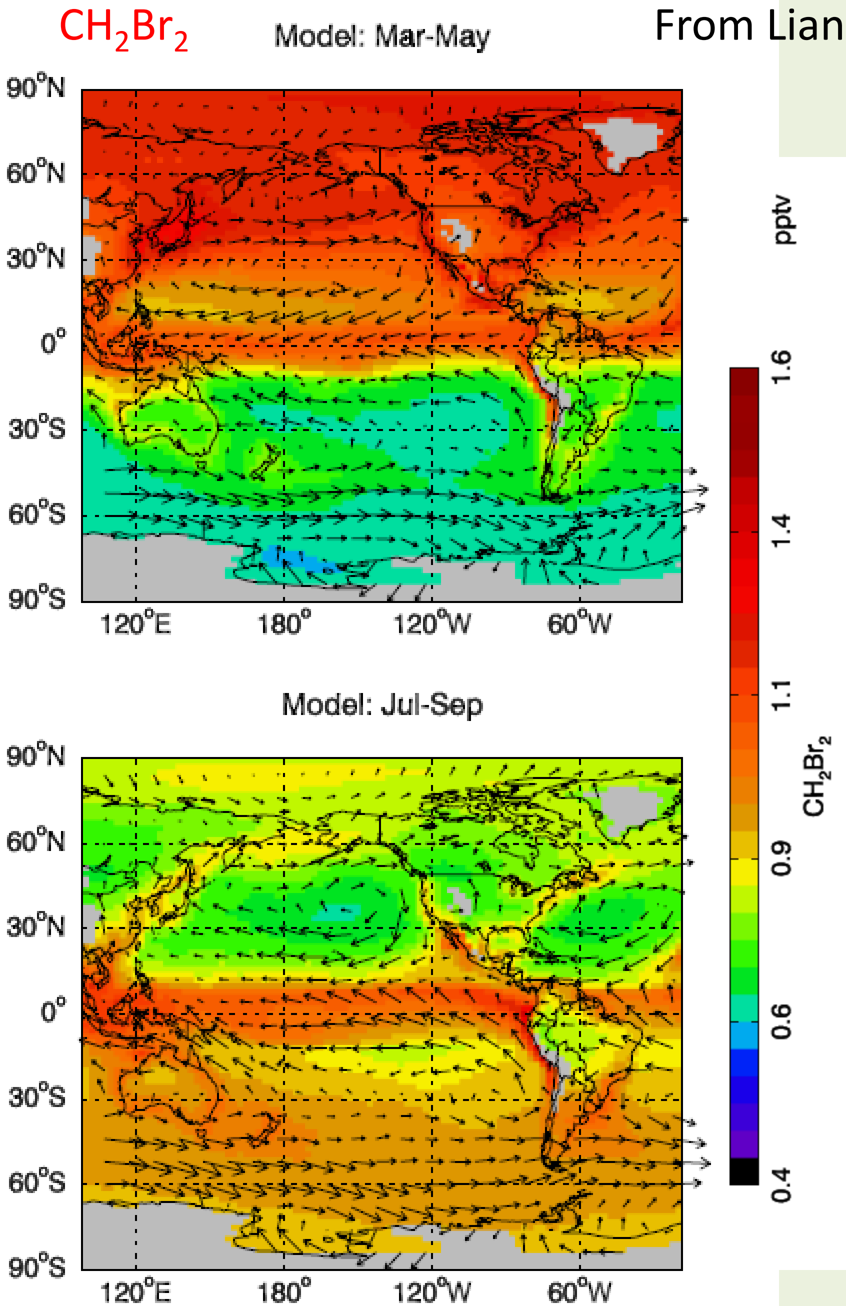
Finding the missing stratospheric Br_y: a global modeling study of $CHBr_3$ and CH_2Br_2

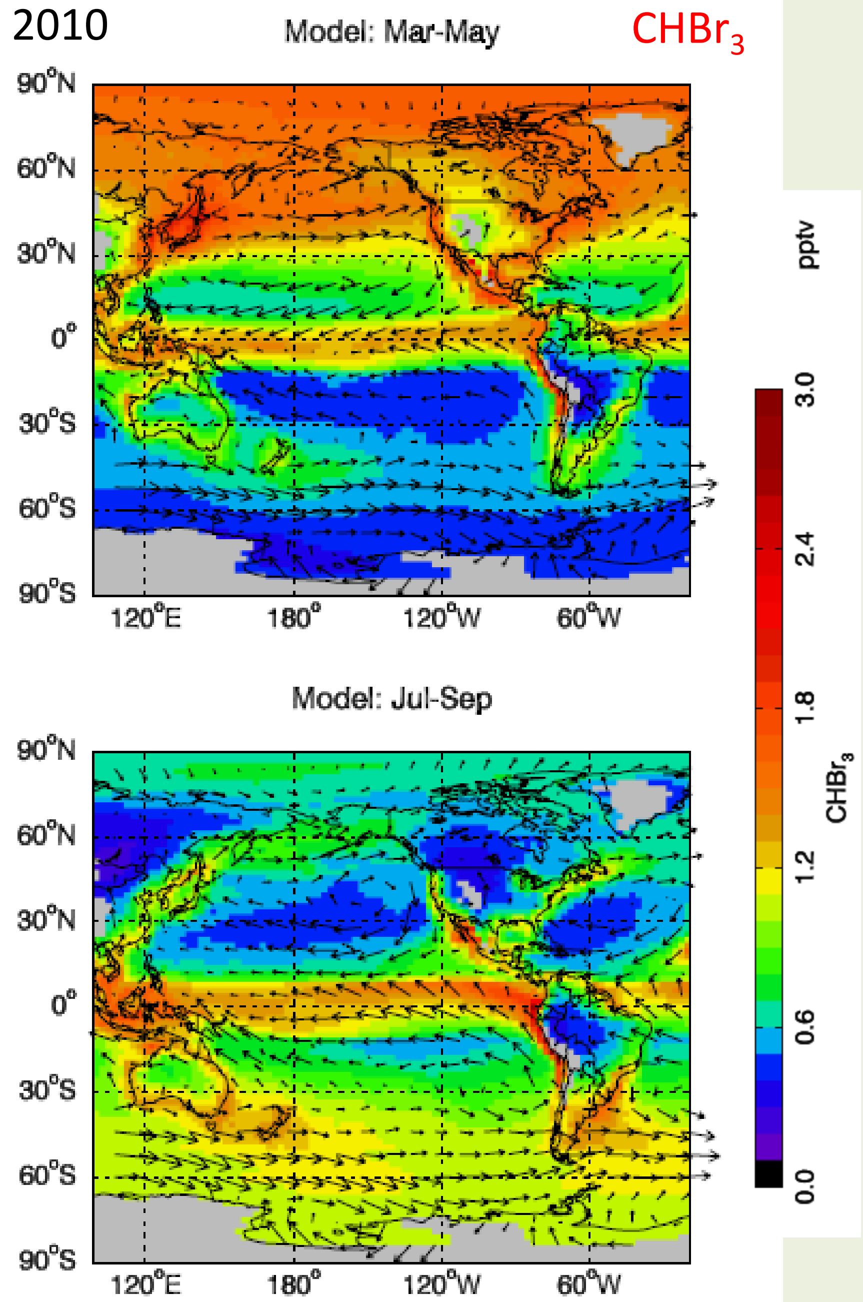
Q. Liang[1,2,*], R. S. Stolarski[1], S. R. Kawa[1], J. E. Nielsen[3,4], A. R. Douglass[1], J. M. Rodriguez[1], D. R. Blake[5], E. L. Atlas[6], and L. E. Ott[3,7]

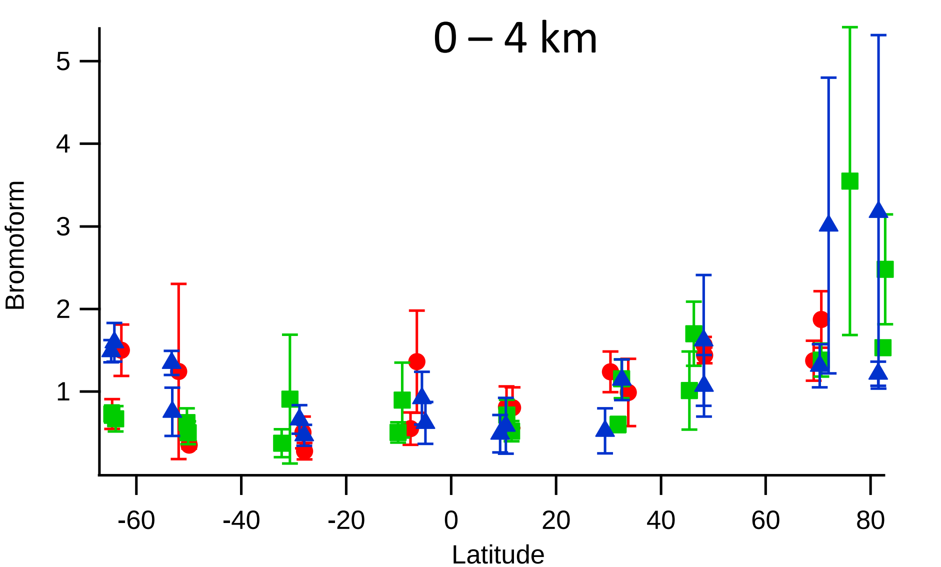


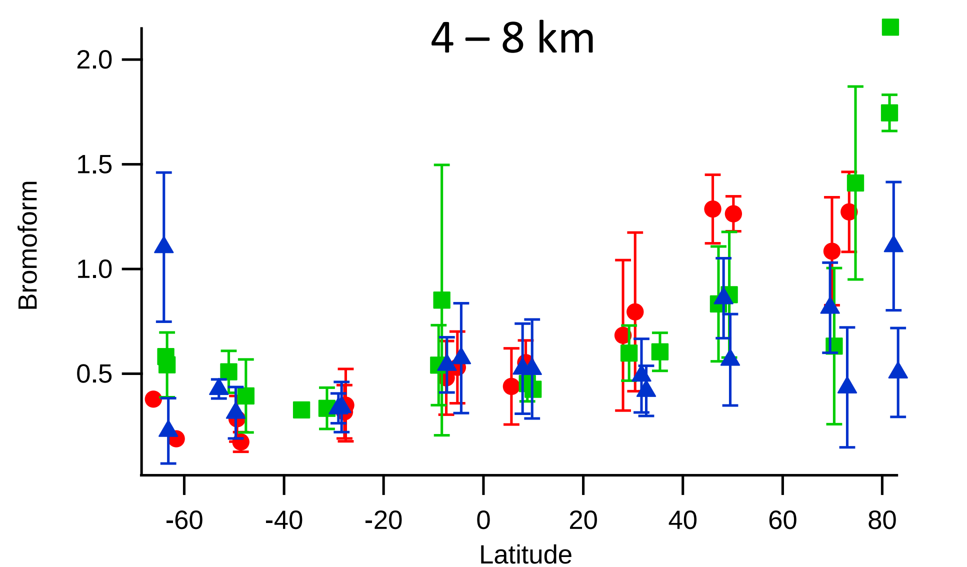
Atmos. Chem. Phys., 10, 2269–2286, 2010

From Liang et al., 2010

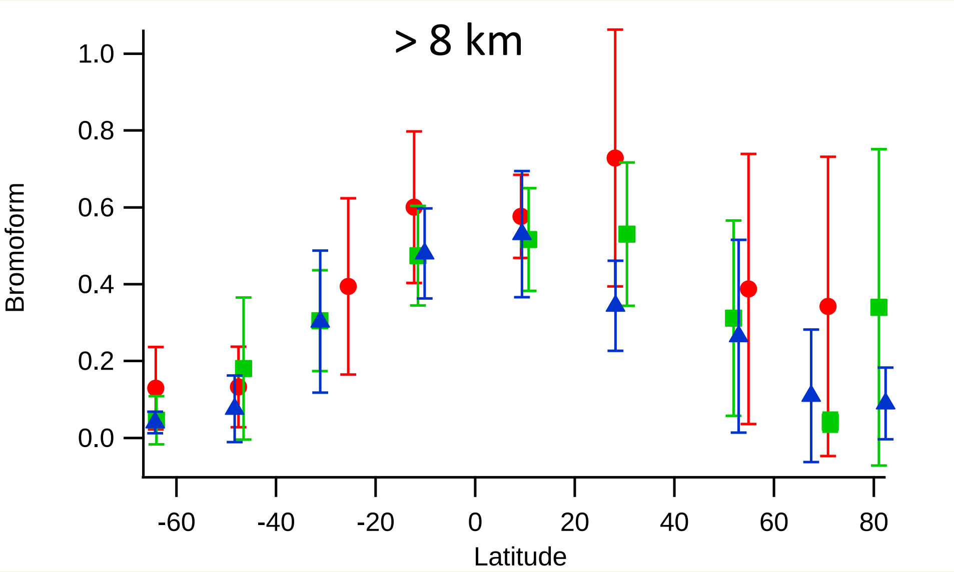






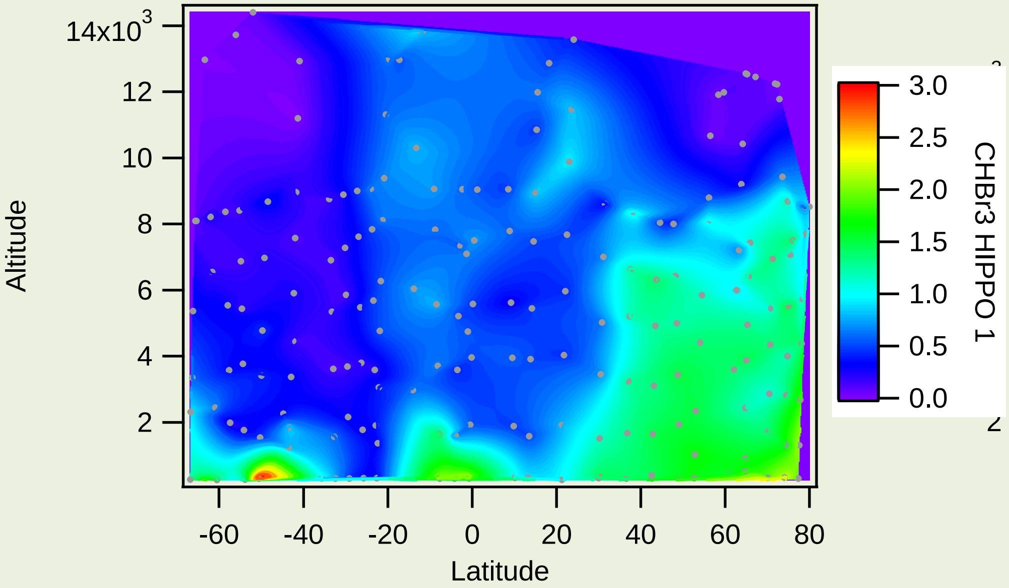


$CHBr_3$

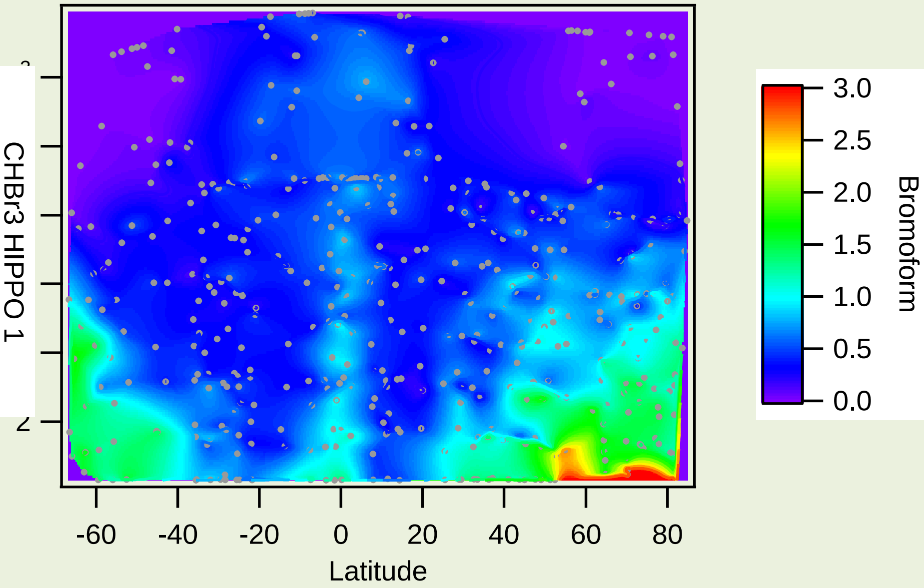


Averages from HIPPO 1 are represented by red circles , HIPPO 2 green squares and HIPPO 3 blue triangles.

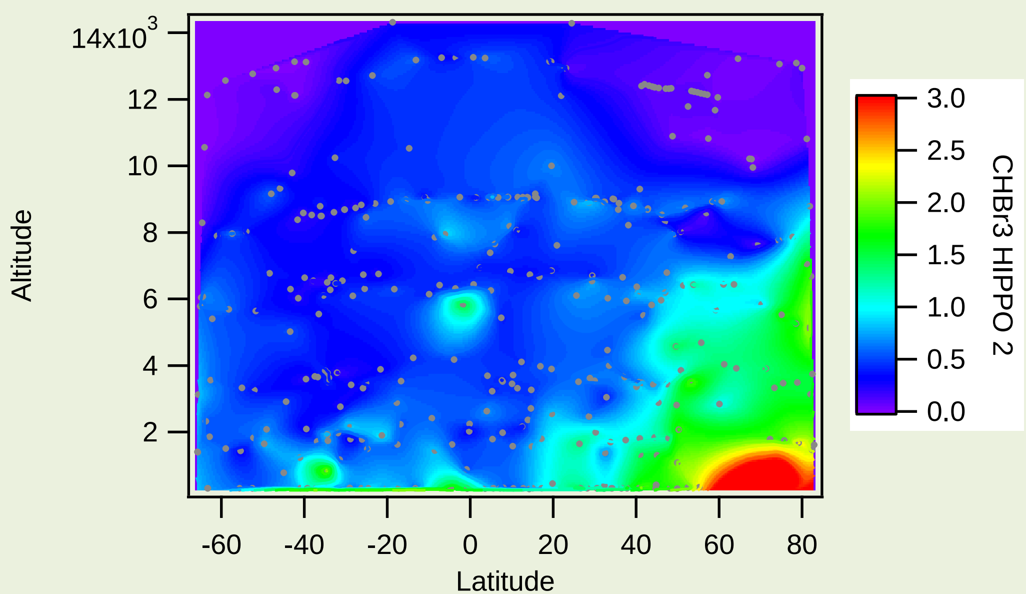
HIPPO-1 (Jan)



HIPPO-3 (Mar/Apr)



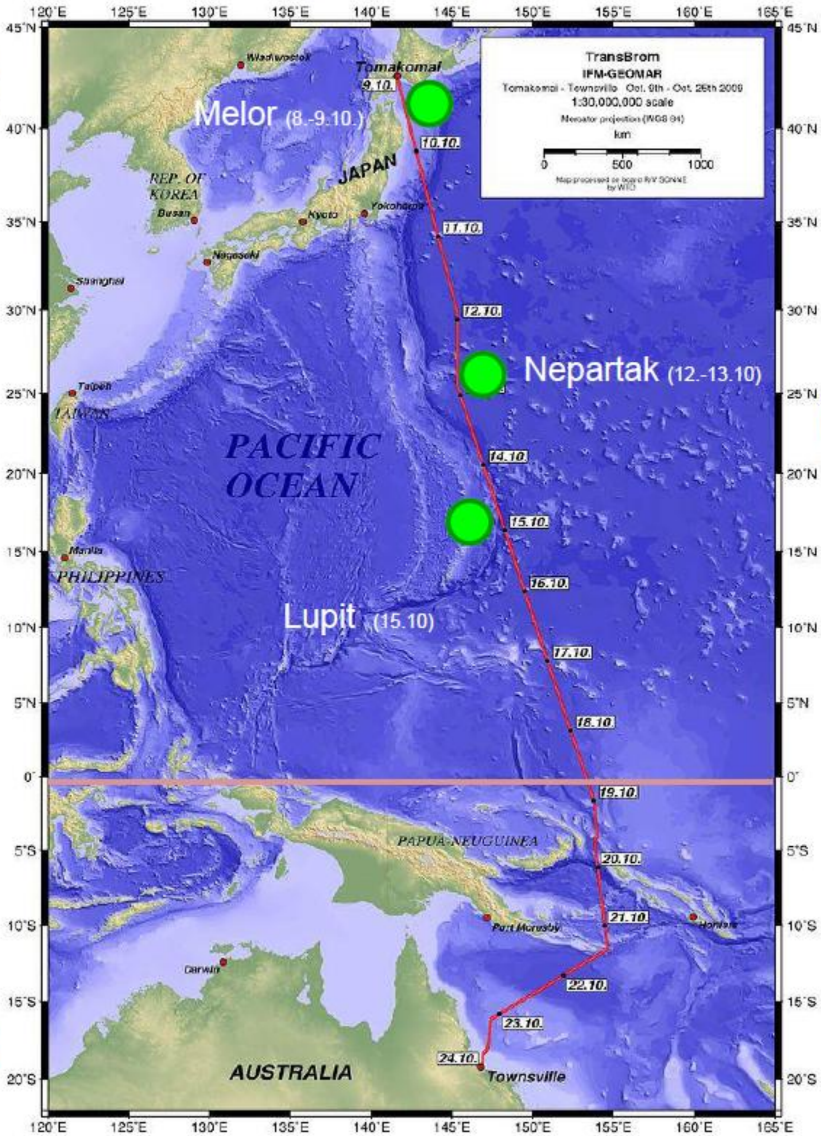
HIPPO-2 (Nov)



$CHBr_3$

145 E

42



19

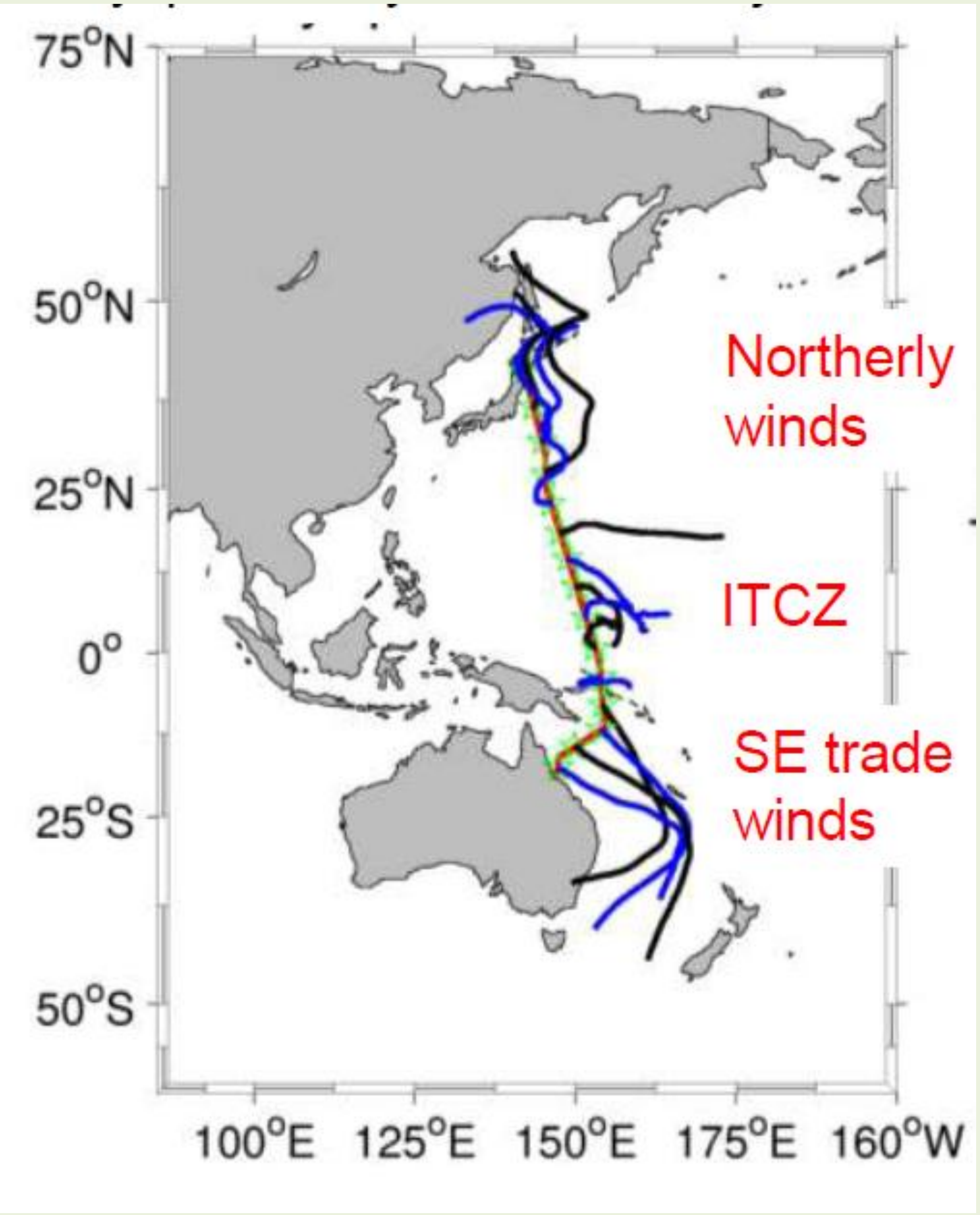
Tomakomai
(Japan, 42 35,4'N/ 141 37,5'E)

60 lat (4000 nm)

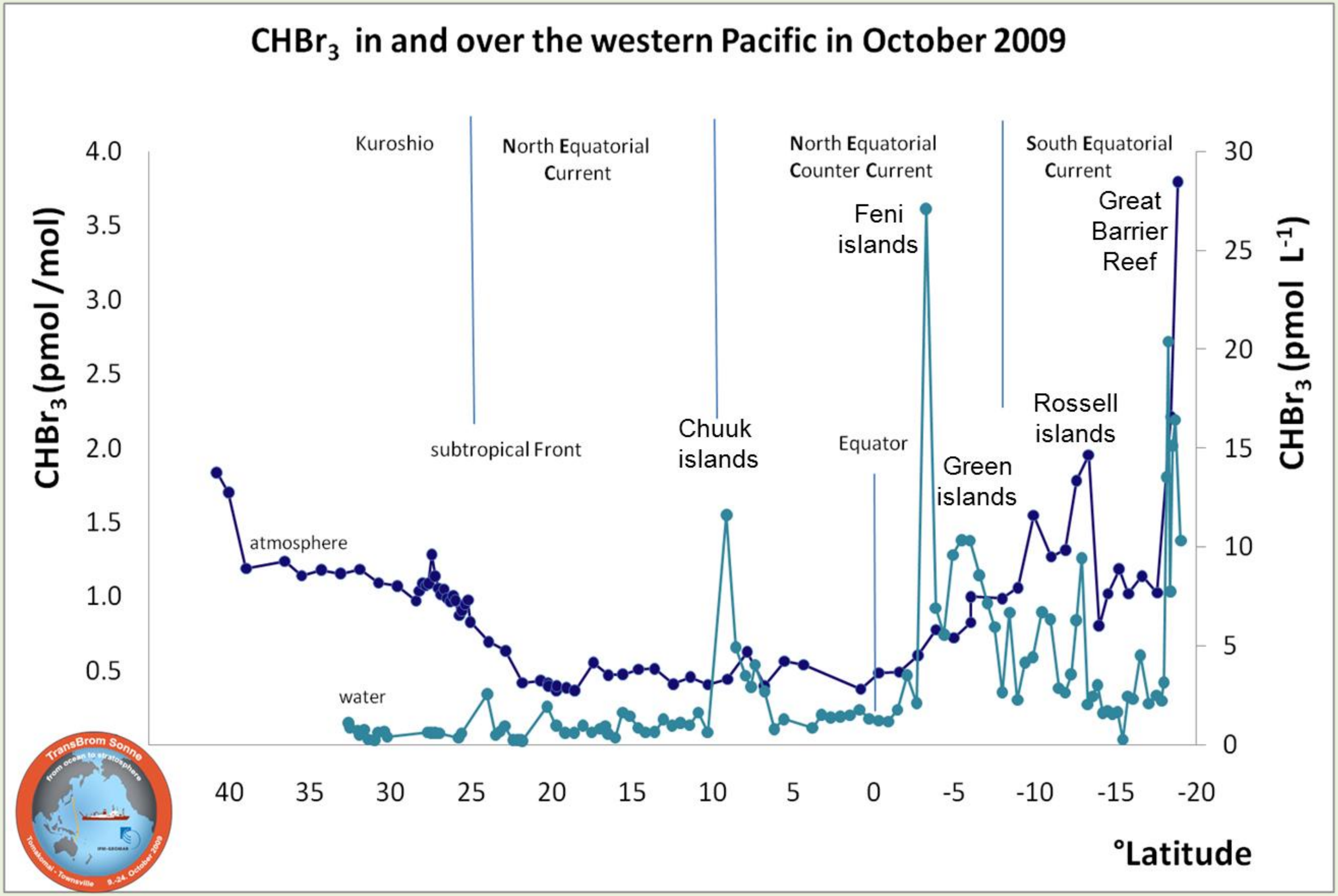
Townsville
(Australia, 19 06,6'S/ 146 50,5'E).

TransBrom Sonne
from ocean to stratosphere
Tomakomai - Townsville 9.-24. October 2009
IFM-GEOMAR

Birgit Quack, Chief Scientist

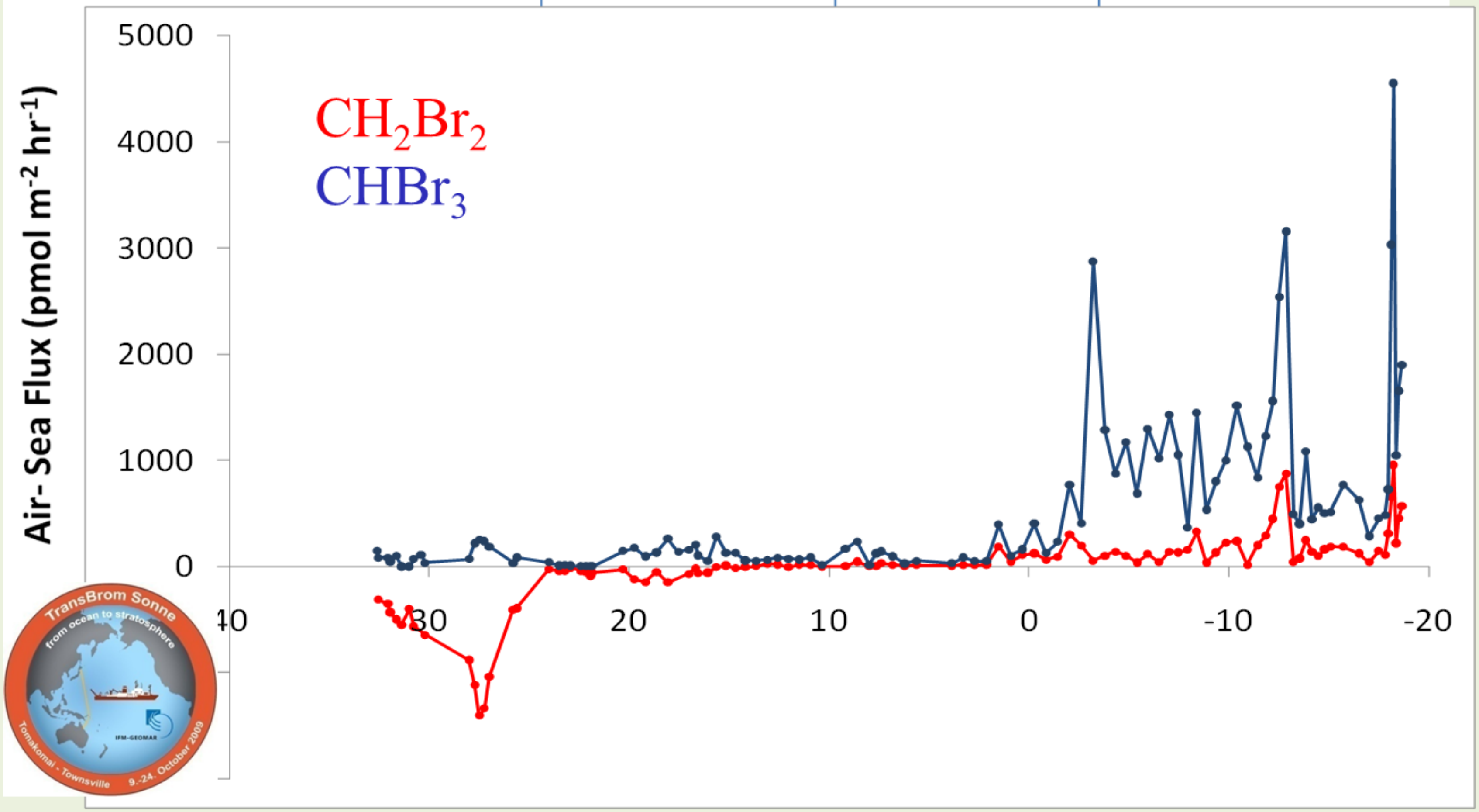


75°N
50°N
25°N
0°
25°S
50°S
100°E
125°E
150°E
175°E
160°W
Northerly winds
ITCZ
SE trade winds

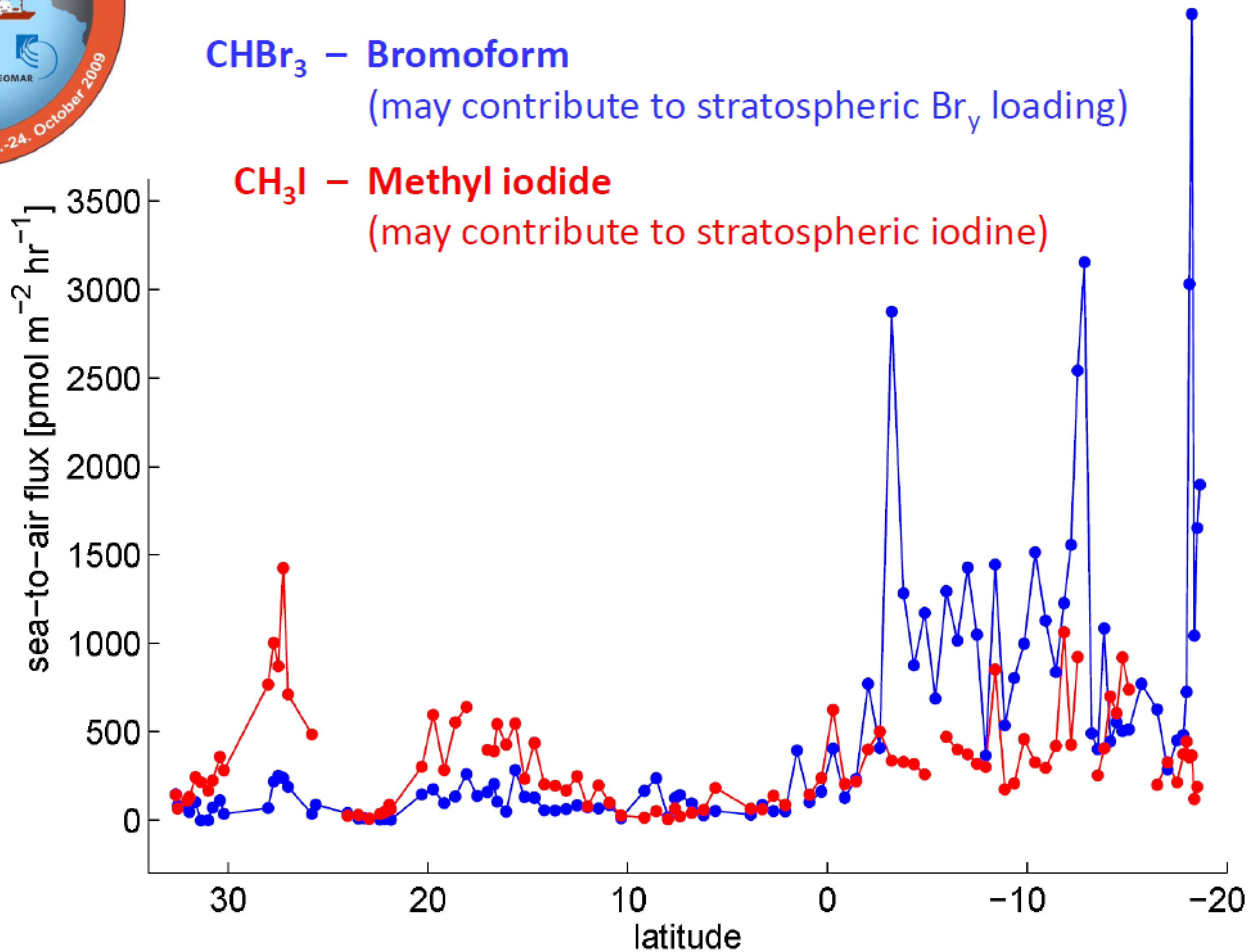


CHBr3 in and over the western Pacific in October 2009
Kuroshio
North Equatorial Current
North Equatorial Counter Current
South Equatorial Current
subtropical Front
Equator
Feni islands
Great Barrier Reef
Chuuk islands
Green islands
Rossell islands
atmosphere
water
CHBr3 (pmol /mol)
CHBr3 (pmol L-1)
°Latitude
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
30
25
20
15
10
5
0
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
TransBrom Sonne
from ocean to stratosphere

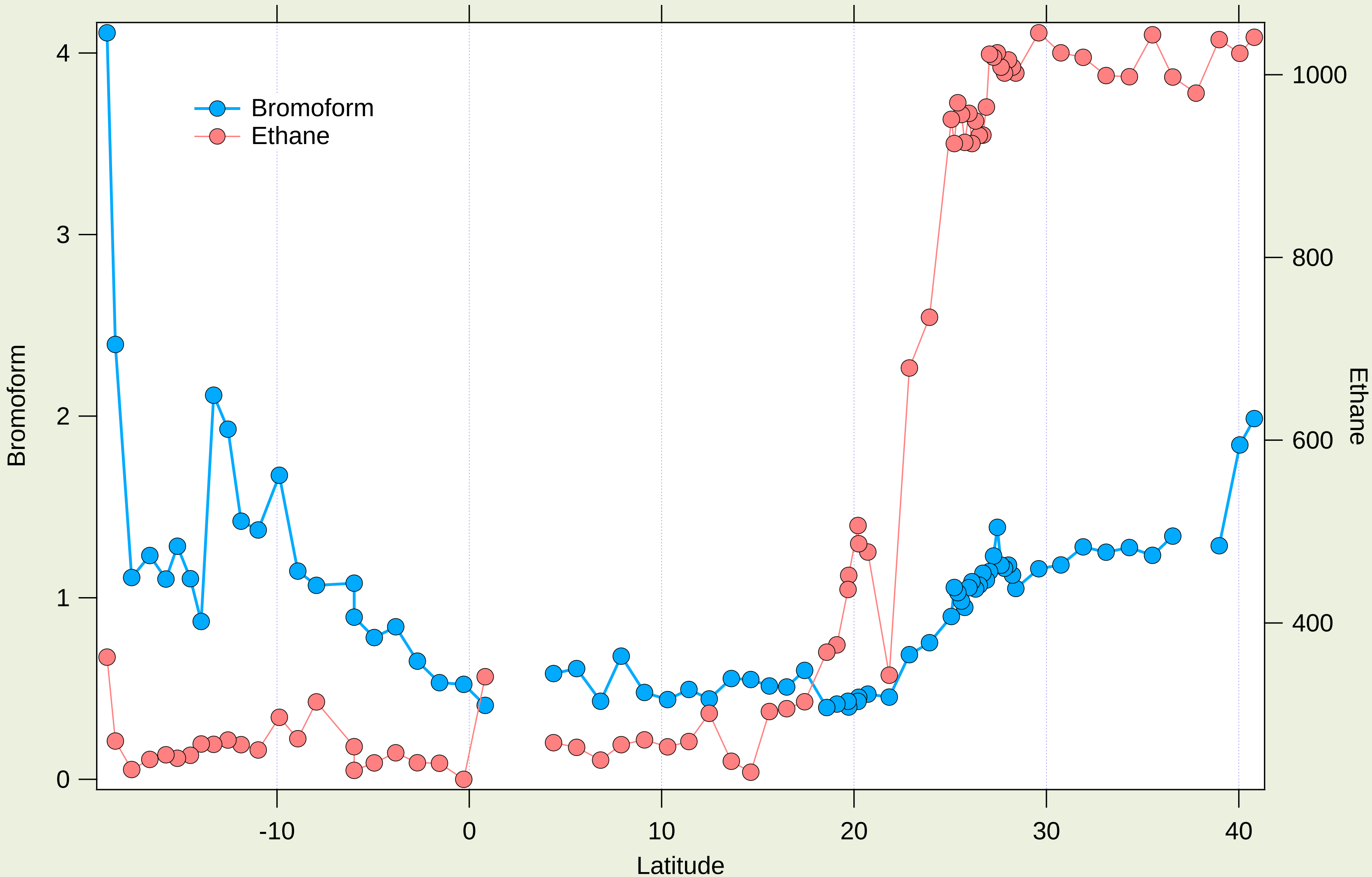
$CHBr_3$ and CH_2Br_2 emissions in the western Pacific in October 2009



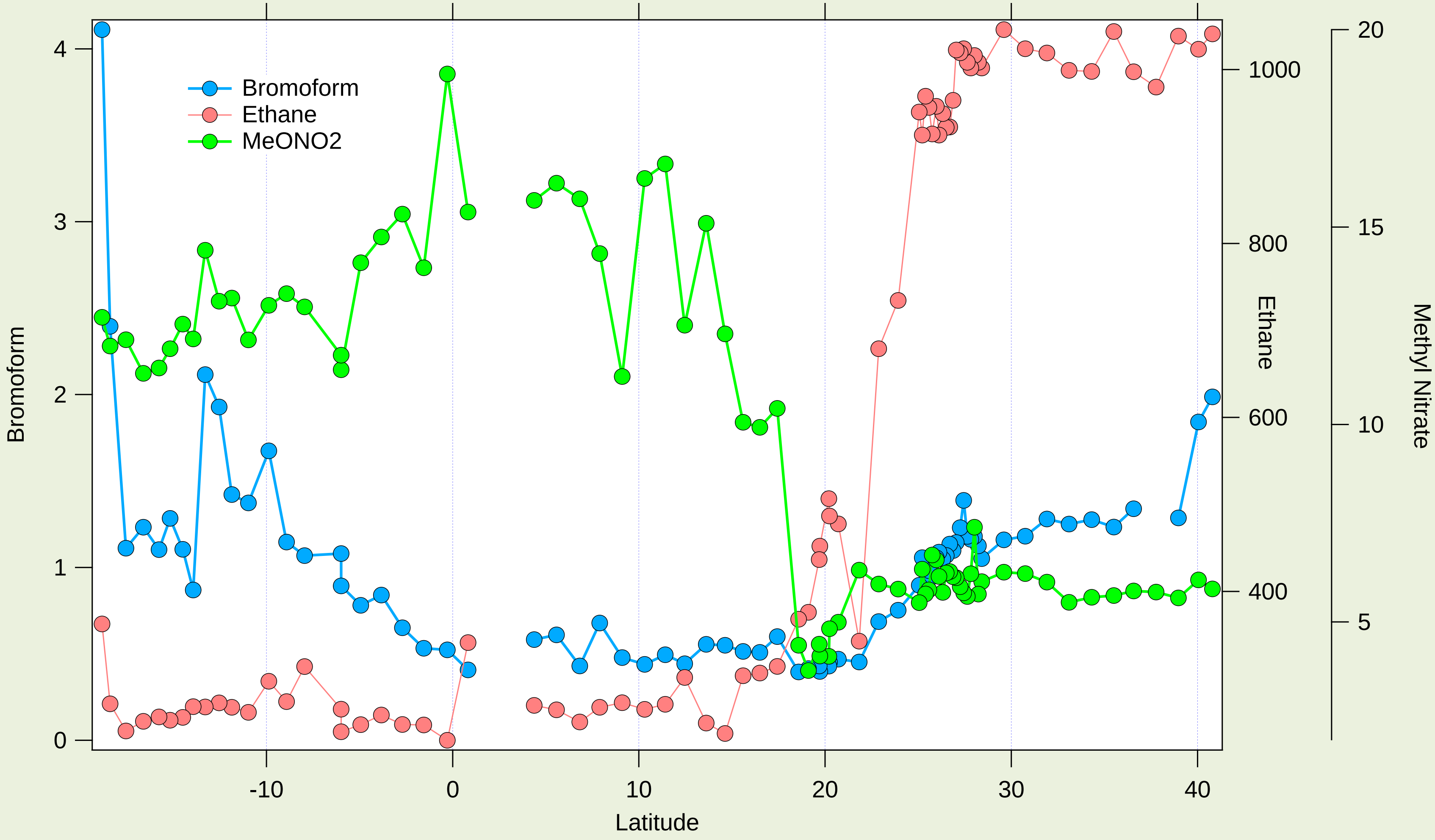
VSLS emissions in the western Pacific in October 2009



Trace gas distribution in Western Pacific during TransBrom cruise, 2009



Trace gas distribution in Western Pacific during TransBrom cruise, 2009



Sources of RONO2

- From Dahl et al. (2003),
  - In seawater, photolysis of nitrite, organic matter

$$NO_2^- \xrightarrow{h\nu, H_2O} NO + OH + OH^-$$

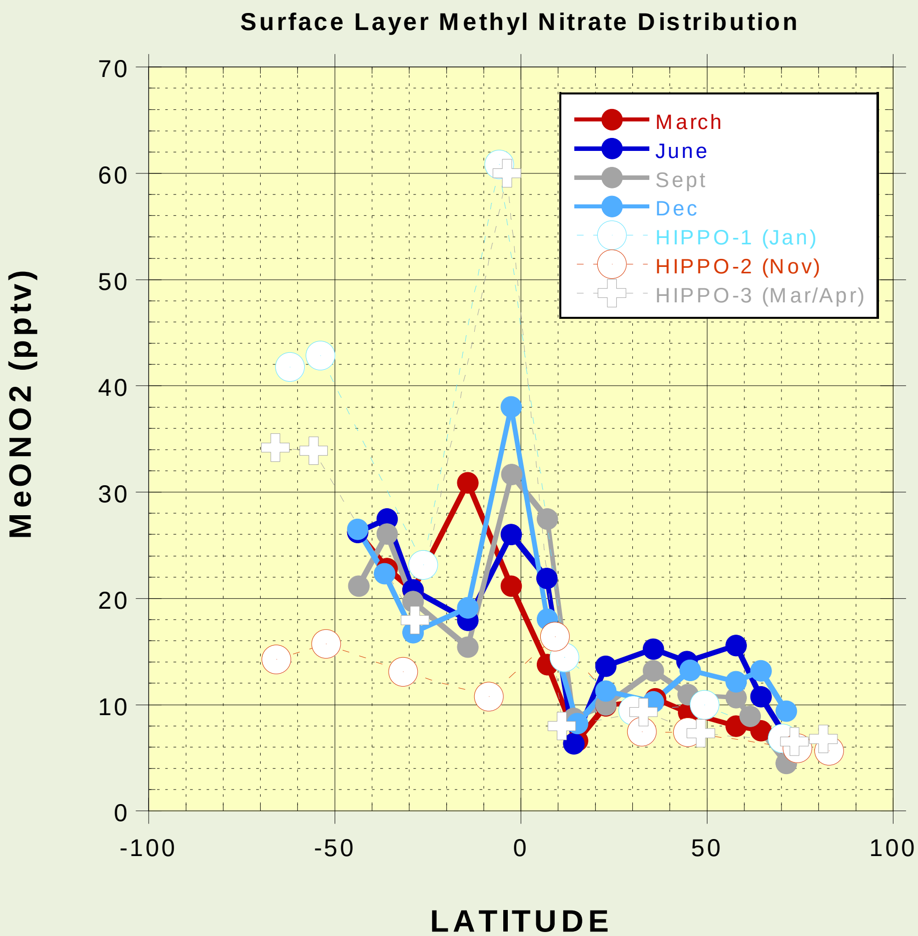
$$CDOM \xrightarrow{h\nu} ROO$$

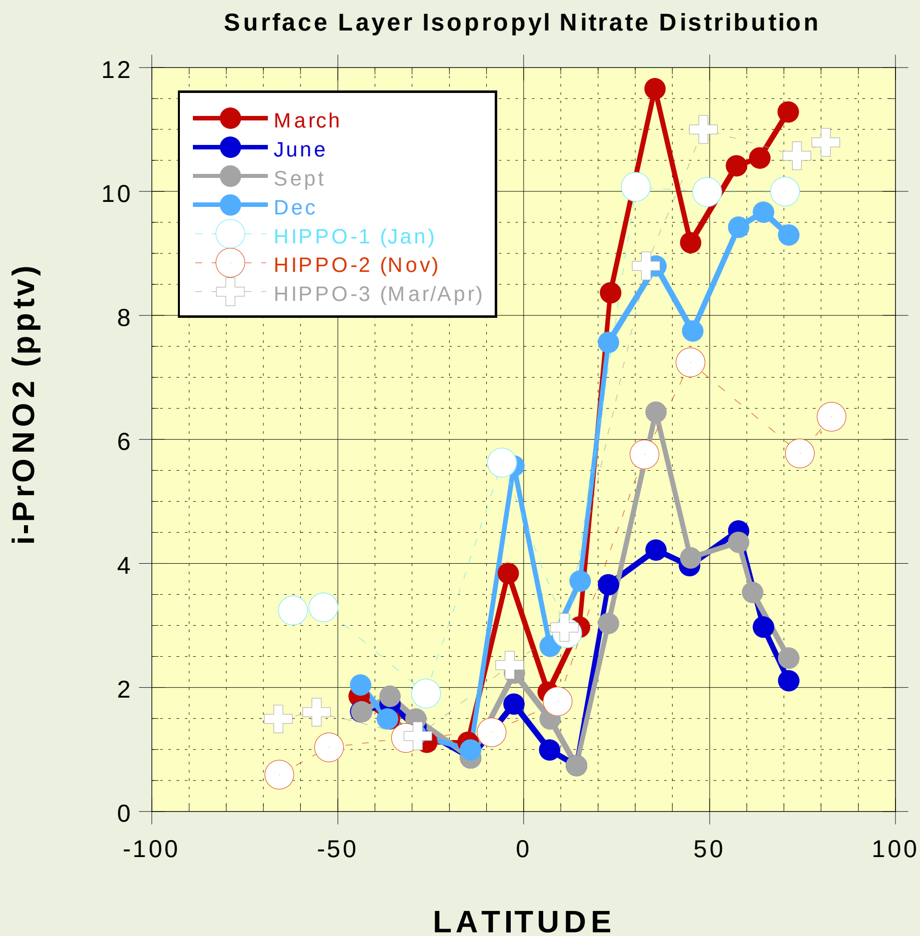
  - Followed by:

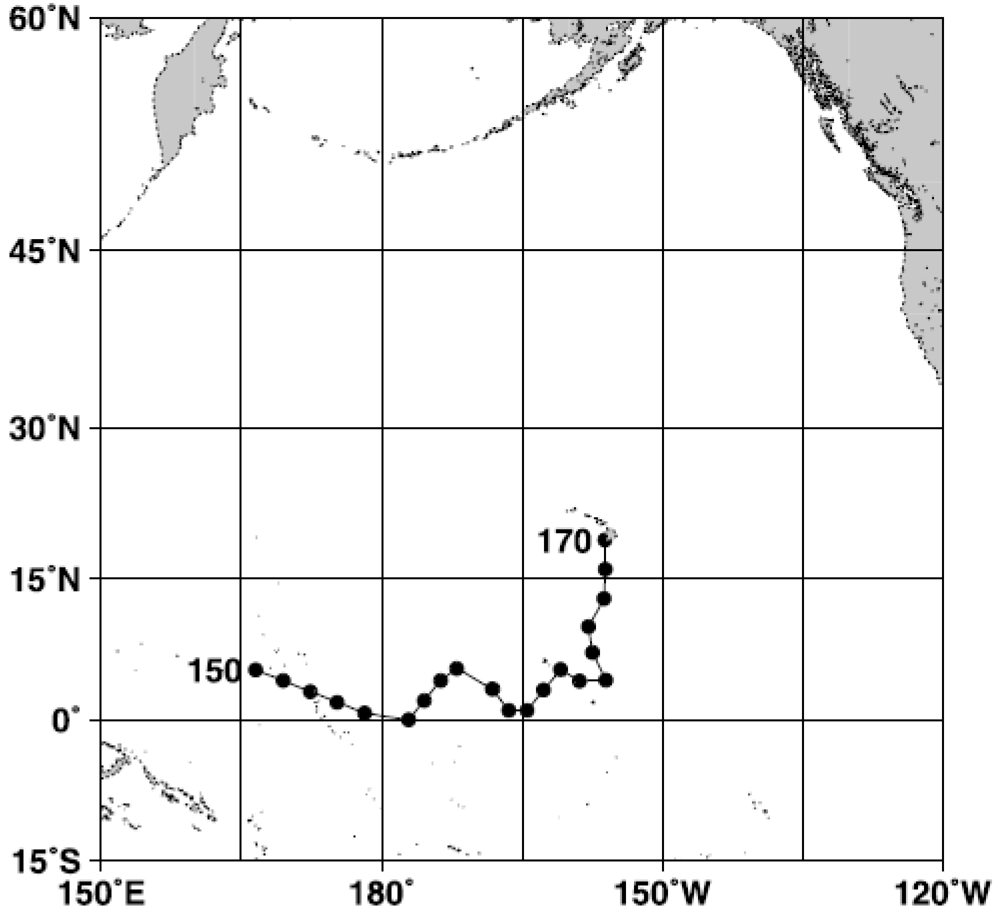
$$ROO + NO \longrightarrow ROONO \longrightarrow RONO_2 \quad \text{or} \quad RO + NO_2$$

  - From seawater: Methyl>Ethyl>Propyl, etc.

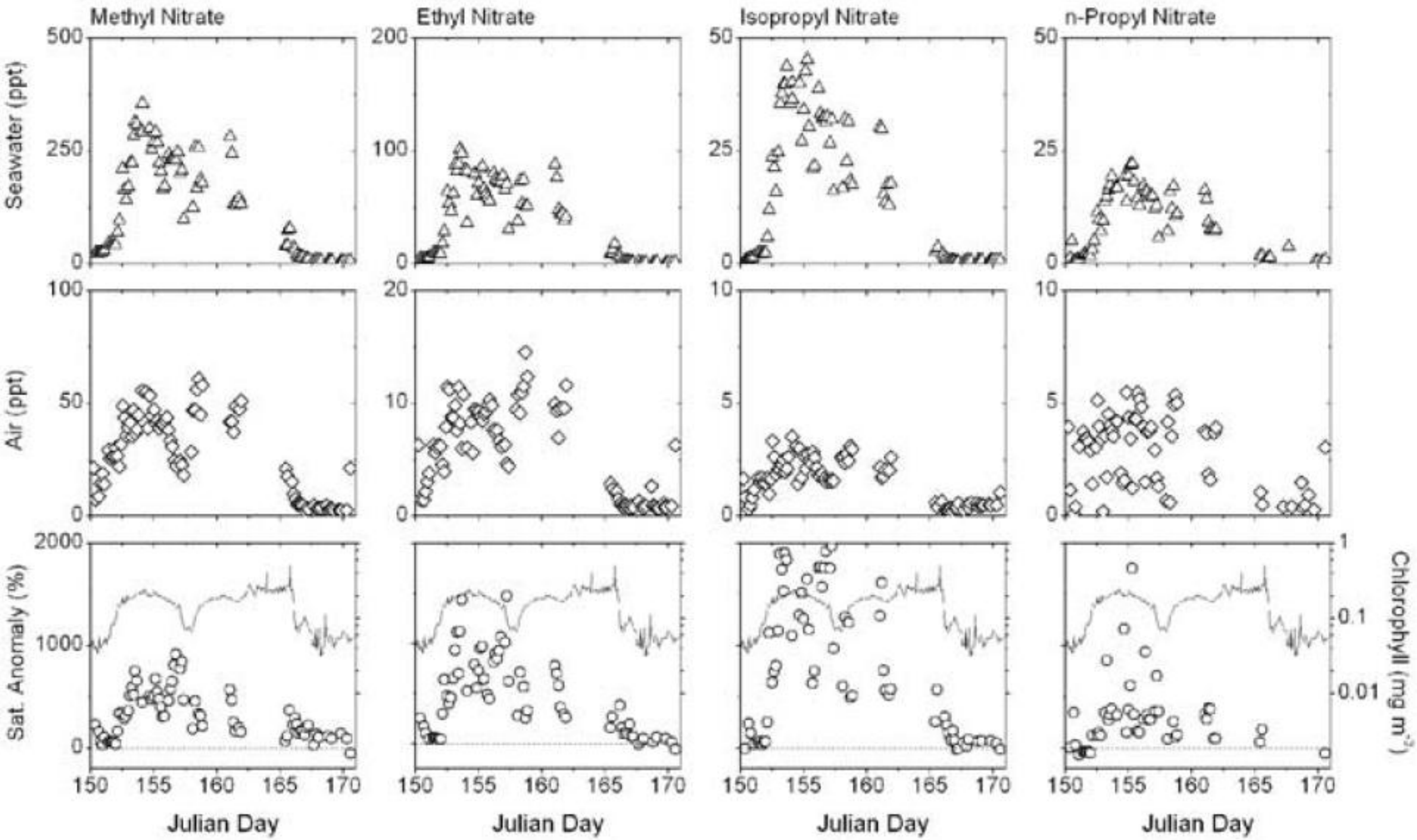
Long term average from UCI Pacific Flask Network vs. HIPPO: RONO2 (Alkyl Nitrates)







GEOPHYSICAL RESEARCH LETTERS, VOL. 32, L20817, doi:10.1029/2005GL023896, 2005

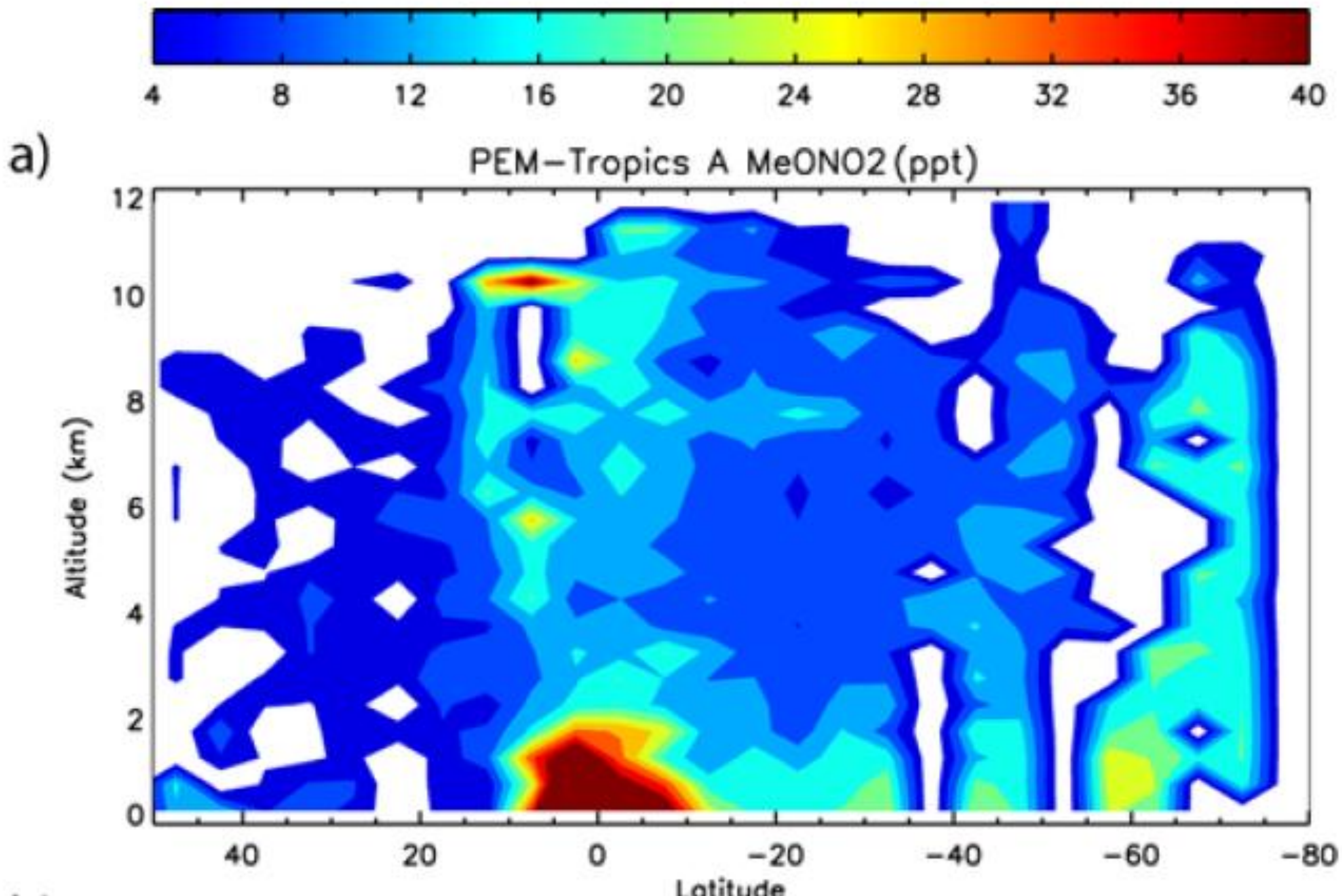


GEOPHYSICAL RESEARCH LETTERS, VOL. 32, L20817, doi:10.1029/2005GL023896, 2005

Oceanic alkyl nitrates as a natural source of tropospheric ozone

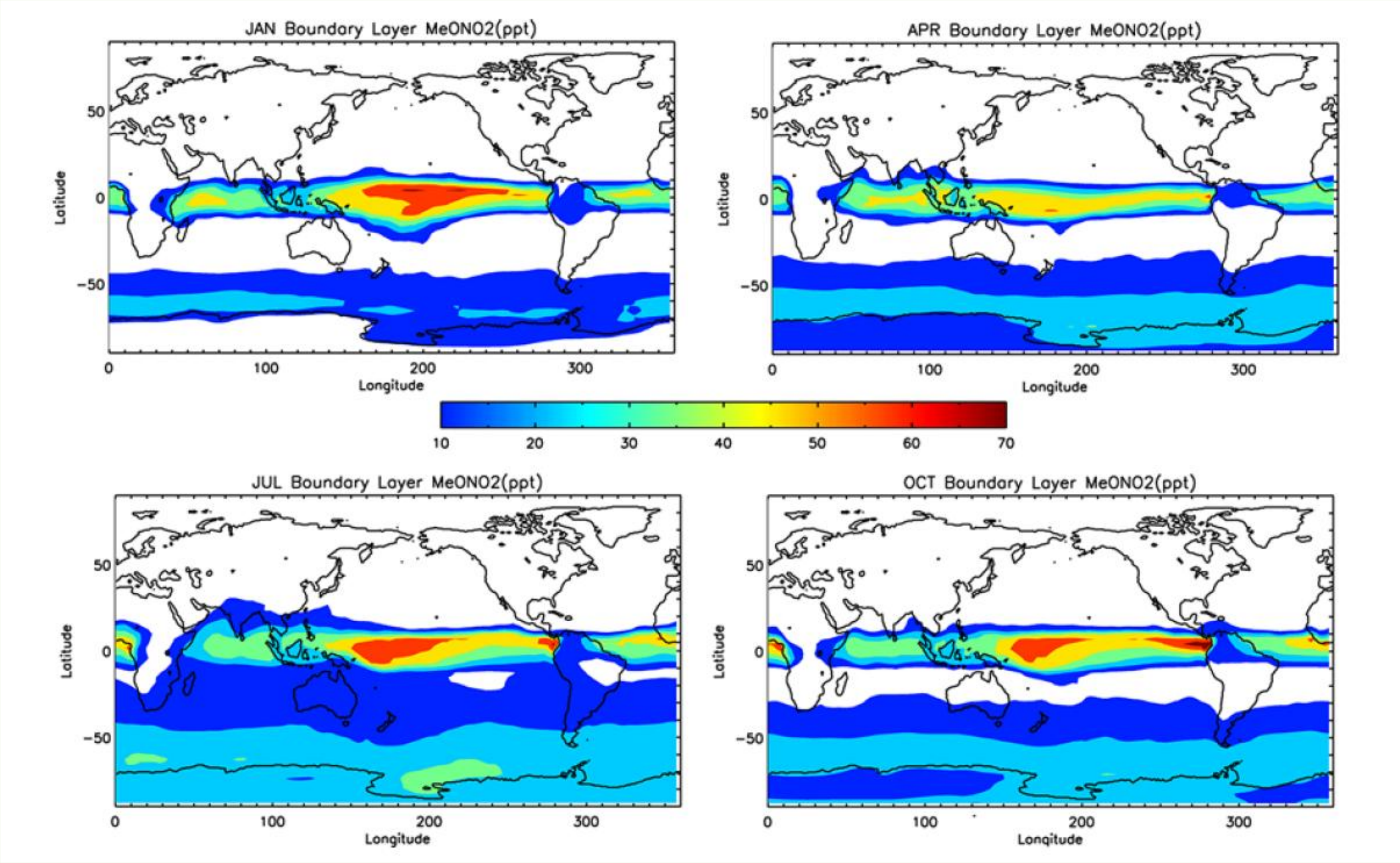
Jessica L. Neu,[1] Michael J. Lawler,[1] Michael J. Prather,[1] and Eric S. Saltzman[1]

GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L13814, doi:10.1029/2008GL034189, 2008



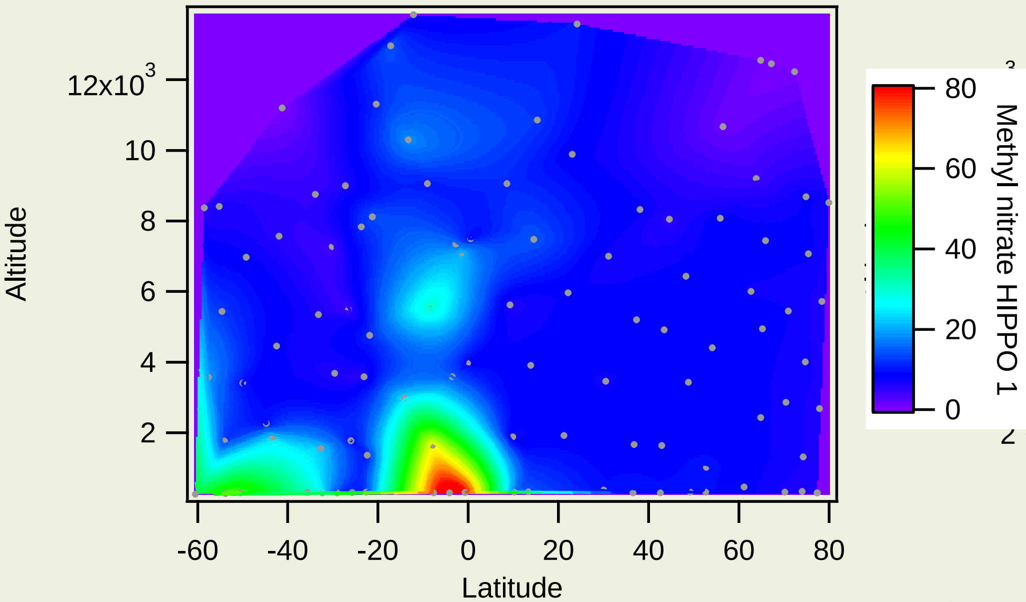
Data from Blake et al.

NEU ET AL.: OCEANIC ALKYL NITRATES

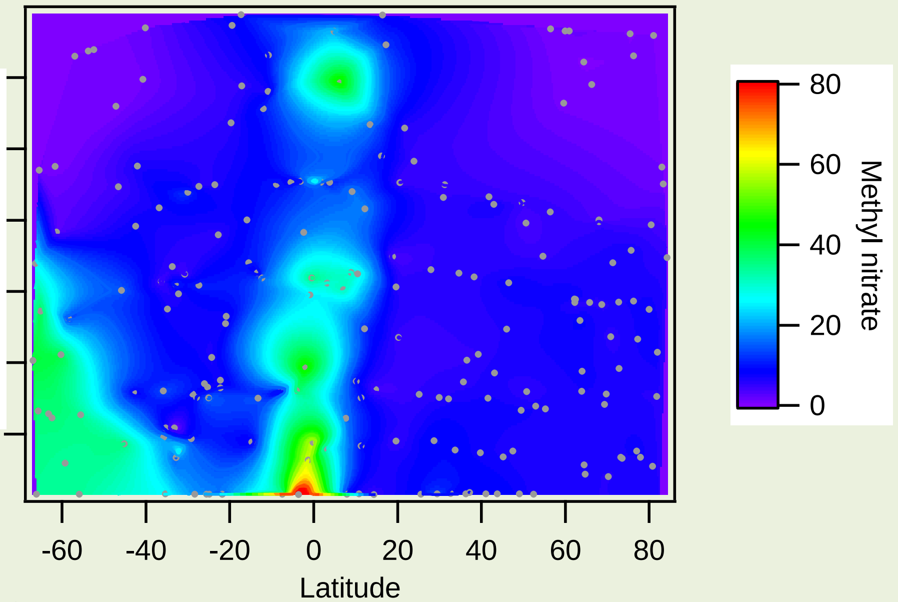


GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L13814, doi:10.1029/2008GL034189, 2008

HIPPO-1 (Jan)

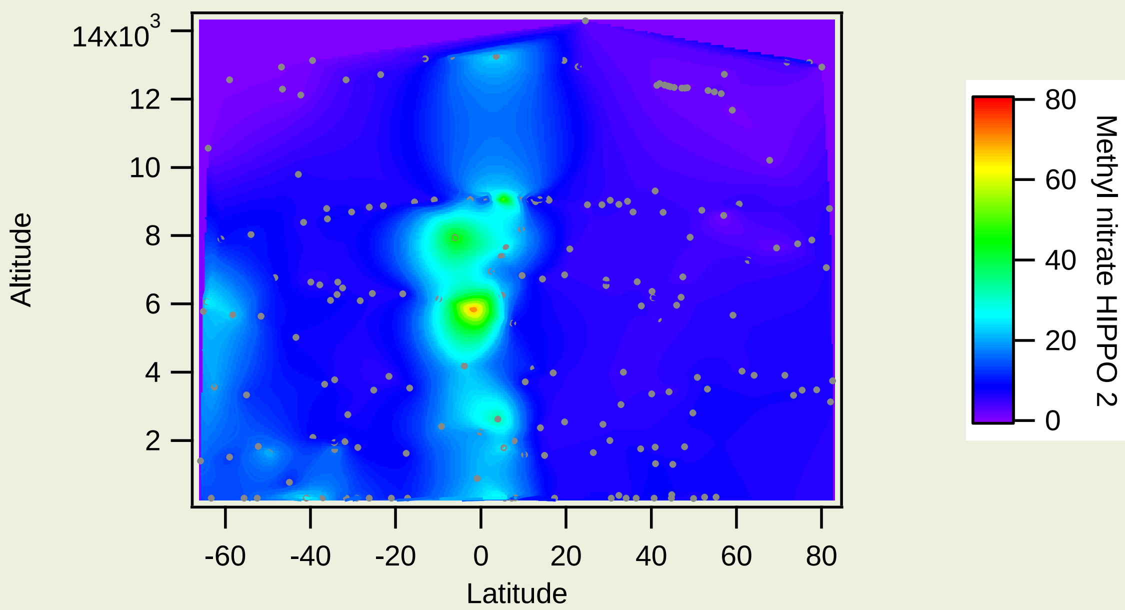


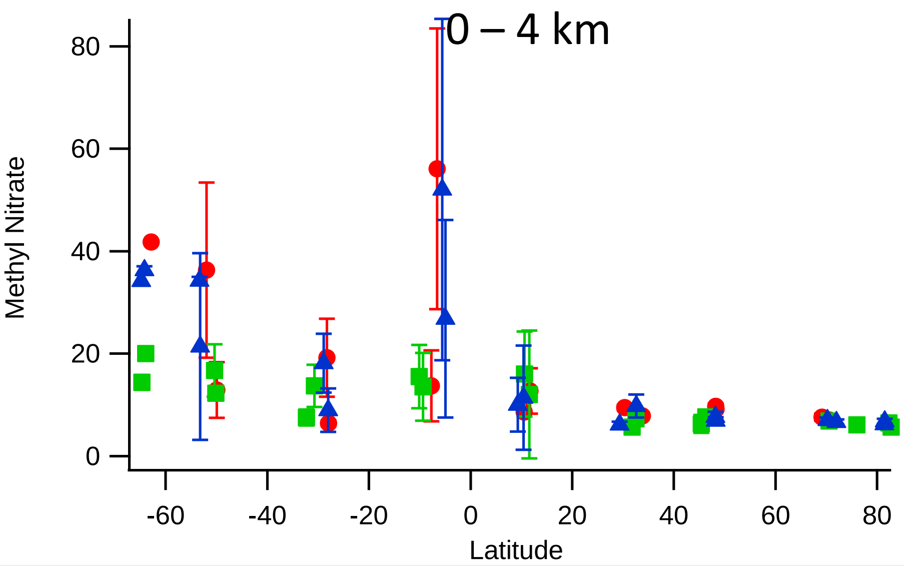
HIPPO-3 (Mar/Apr)

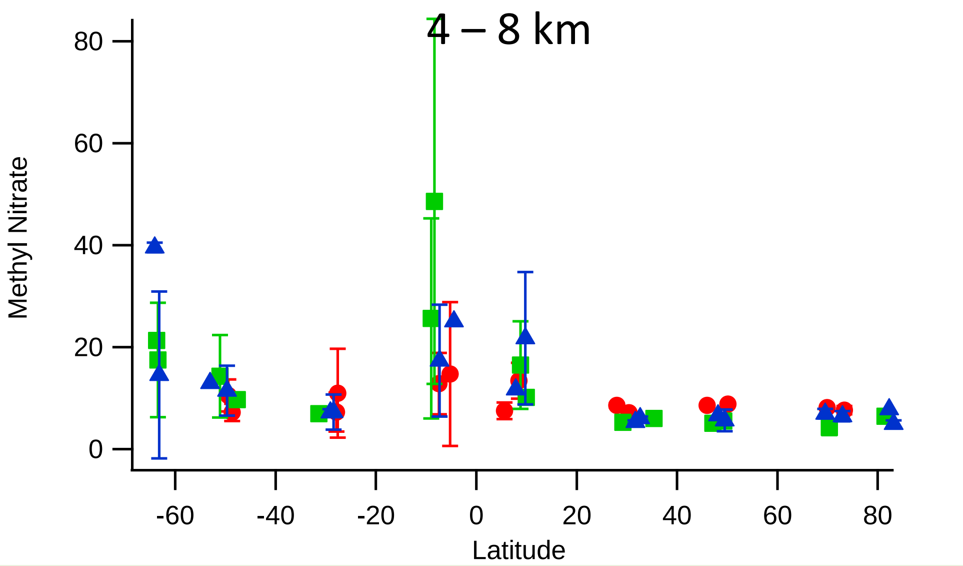


HIPPO-2 (Nov)

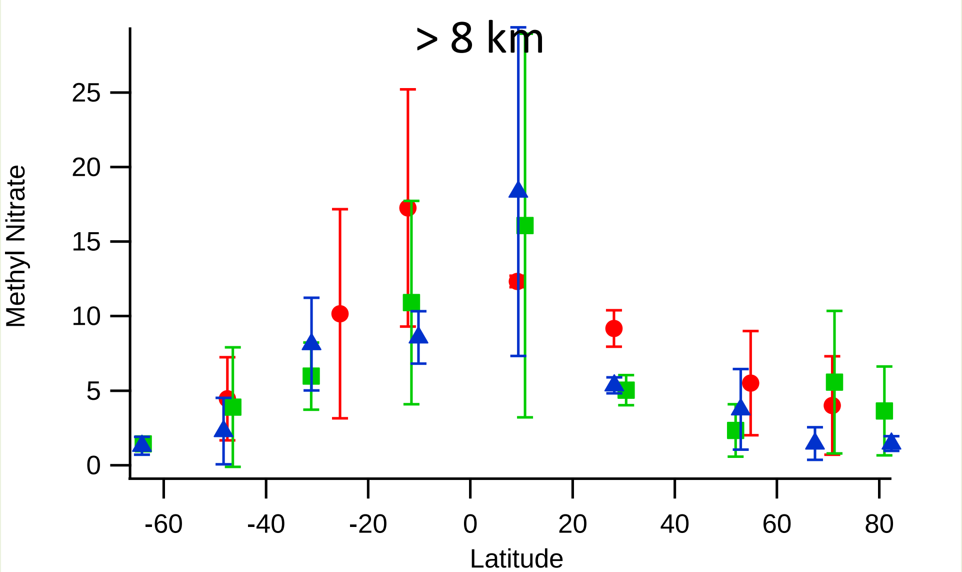
CH_3ONO_2







CH_3ONO_2



Averages from HIPPO 1 are represented by red circles , HIPPO 2 green squares and HIPPO 3 blue triangles.

Summary

- Just a first look at a few gases….
  - Marine emissions/distributions show variations that need further evaluation.
  - Seasonal differences will be telling
  - HIPPO already a significant contribution to defining state of atmosphere for a wide range of gases.
  - Western Pacific transect will be a valuable addition to the suite of measurements.