Short-lived trace gases during HIPPO

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P. Romashkin (NCAR/RAF)
<table>
<thead>
<tr>
<th>Chlorofluorocarbons</th>
<th>Hydrochlorofluorocarbons/Perfluorocarbons</th>
<th>Organic Nitrates</th>
<th>Non-Methane Hydrocarbons</th>
<th>Other</th>
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</thead>
<tbody>
<tr>
<td>CFC-11 (CCl3F)</td>
<td>HCF-C-22 (CHF2Cl)</td>
<td>Methyl nitrate(CH3ONO2)</td>
<td>Ethane (C2H6)</td>
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<tr>
<td>CFC-12 (CCl2F2)</td>
<td>HCFC-141b (CH3CFCl2)</td>
<td>Ethyl nitrate(C2H5ONO2)</td>
<td>Ethyne (C2H2)</td>
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<tr>
<td>CFC-13 (CCIF3)</td>
<td>HCFC-142b (CH3CF2Cl)</td>
<td>Propyl nitrates(C3H7ONO2)</td>
<td>Propane(C3H8)</td>
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<tr>
<td>CFC-113 (CClFCClF2)</td>
<td>HFC-134a (C2H2F4)</td>
<td>Butyl nitrates (C4H9ONO2)</td>
<td>Isobutane(C4H10)</td>
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<tr>
<td>CFC-114 (CCIF2CCIF2)</td>
<td>HFC-124 (C2HClF4)</td>
<td>Pentyl nitrates (C5H11ONO2)</td>
<td>n-Butane (C4H10)</td>
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<tr>
<td>CFC-115 (CF2ClCF3)</td>
<td>HFC-125 (C2HF3)</td>
<td></td>
<td>Isopentane (C5H12)</td>
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<td>Halons</td>
<td>HFC-123 (C2HCl2F3)</td>
<td>Carbon Tetrachloride (CCl4)</td>
<td>n-Pentane (C5H12)</td>
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<tr>
<td>CFC-12b1 (Halon 1211,CF3Br)</td>
<td>HFC-125 (C2HF3)</td>
<td>Methyl Chloroform(CH3CCl3)</td>
<td>Isoprene (C5H10)</td>
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<tr>
<td>CFC-13b1 (Halon 1301, CF3Br)</td>
<td>HFC-143a (C2HF3)</td>
<td>Tetrachloroethylene (C2Cl4)</td>
<td>Benzene (C6H6)</td>
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<td>CFC-114b2 (Halon 2402, C2F4Br2)</td>
<td>HFC-23 (CHF3)</td>
<td>Methylene Chloride (CH2Cl2)</td>
<td>Toluene (C6H5)</td>
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<tr>
<td>Hydroflurocarbons</td>
<td>HFC-227ea(C2HF7)(1,1,1,2,3,3,3-Hepafluoropropane)</td>
<td>Chloroform (CHCl3)</td>
<td>C2-Benzenes (C6H10)</td>
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<tr>
<td>HCFC-365mfc (C4H3F5)</td>
<td>HFC-365mfc (C4H3F5)</td>
<td>Trichloroethylene(C2HCl3)</td>
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<tr>
<td>Methyl Halides and related</td>
<td>CH2BrClz</td>
<td>1,2-Dichloroethane (C2H4Cl2)</td>
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<tr>
<td>Methyl Bromide(CH3Br)</td>
<td>CHxBrClz</td>
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<tr>
<td>Methyl Chloride (CH3Cl)</td>
<td>CHxBrClz</td>
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<td>Methyl Iodide (CH3I)</td>
<td>CHxBrClz</td>
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<tr>
<td>Methylene Bromide(CH2Br2)</td>
<td>CHxBrClz</td>
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<tr>
<td>CH3Br</td>
<td>CHxBrClz</td>
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<tr>
<td>Bromoform (CHBr3)</td>
<td>CHxBrClz</td>
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<tr>
<td>Perfluorocarbons</td>
<td>PFC-116 (C3F8)</td>
<td>Sulfur Hexafluoride (SF6)</td>
<td>Methyl-t-butyl ether</td>
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<tr>
<td>PFC-218 (C3F8)</td>
<td>PFC-318 (C3F8)(perfluorocyclobutane)</td>
<td>PFC-218 (C3F8)</td>
<td>Methyl Acetate/Ethyl Acetate</td>
<td></td>
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<tr>
<td>Others</td>
<td>CO2, H2, 13CO2, 18OCO</td>
<td></td>
<td>Acetonitrile</td>
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<td></td>
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<td></td>
<td>1,2 Dichlorobenzene</td>
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</tbody>
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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
HIPPO-1 (Jan)

HIPPO-2 (Nov)

HIPPO-3 (Mar/Apr)

ETHANE
HIPPO-1 (Jan)

HIPPO-2 (Nov)

HIPPO-3 (Mar/Apr)

ETHYNE
CH$_2$Br$_2$
“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. Cox1

Emission scenarios

Bromoform concentration

(a) Scenario 1 (210 Gg/yr)
(b) Scenario 2a (235 Gg/yr)
(c) Scenario 2b (587 Gg/yr)
(d) Scenario 3 (400 Gg/yr)
(e) Scenario 4 (587 Gg/yr)
(f) Scenario 5 (595 Gg/yr)
(g) Scenario 6 (595 Gg/yr)
(h) Scenario 7 (595 Gg/yr)

(b) Scenario 1 (210 Gg/yr)
(c) Scenario 2a (235 Gg/yr)
(d) Scenario 3 (400 Gg/yr)
(e) Scenario 2b (587 Gg/yr)
(f) Scenario 5 (595 Gg/yr)
(g) Scenario 6 (595 Gg/yr)
(h) Scenario 7 (595 Gg/yr)

Simulated annually averaged CHBr$_3$ mixing ratio (pmol/mol) in the lowest model layer for the year 2000.
Simulated annual average CH$_2$Br$_2$ in pmol/mol in the lowest model layer
\textbf{CH}_2\textbf{Br}_2
Bromoform vs. Dibromochloromethane (HIPPO)
Finding the missing stratospheric Br\textsubscript{y}: a global modeling study of CHBr\textsubscript{3} and CH\textsubscript{2}Br\textsubscript{2}

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

Atmos. Chem. Phys., 10, 2269–2286, 2010
From Liang et al., 2010

CH₂Br₂

Model: Mar-May

Model: Jul-Sep

CHBr₃
Averages from HIPPO 1 are represented by red circles, HIPPO 2 green squares and HIPPO 3 blue triangles.

$\text{CHBr}_3$
Tomakomai
(Japan, 42 35,4°N/ 141 37,5°E)

60 lat (4000 nm)

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

Birgit Quack, Chief Scientist
CHBr₃ in and over the western Pacific in October 2009

- Kuroshio
- North Equatorial Current
- North Equatorial Counter Current
- Feni islands
- Chuuk islands
- Equator
- Green islands
- Rossell islands
- South Equatorial Current
- Great Barrier Reef

CHBr₃ (pmol/mol) vs Latitude

CHBr₃ (pmol L⁻¹) vs Latitude

atmosphere
water
CHBr\textsubscript{3} and CH\textsubscript{2}Br\textsubscript{2} emissions in the western Pacific in October 2009

Air-Sea Flux (pmol m\textsuperscript{-2} hr\textsuperscript{-1})

CH\textsubscript{2}Br\textsubscript{2}

CHBr\textsubscript{3}
VSLs emissions in the western Pacific in October 2009

$\text{CHBr}_3$ – Bromoform  
(may contribute to stratospheric Br$_y$ loading)

$\text{CH}_3\text{I}$ – Methyl iodide  
(may contribute to stratospheric iodine)
Trace gas distribution in Western Pacific during TransBrom cruise, 2009
Trace gas distribution in Western Pacific during TransBrom cruise, 2009

Bromoform
Ethane
MeONO2

Bromoform
Ethane
MeONO2

Latitudes
Sources of RONO₂

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

\[
\begin{align*}
\text{NO}_2^- & \xrightarrow{\text{hv}, \text{H}_2\text{O}} \text{NO} + \text{OH} + \text{OH}^- \\
\text{CDOM} & \xrightarrow{\text{hv}} \text{ROO}
\end{align*}
\]

  – Followed by:

\[
\text{ROO} + \text{NO} \rightarrow \text{ROONO} \rightarrow \text{RONO}_2 \text{ or } \text{RO} + \text{NO}_2
\]

  – From seawater: Methyl"> Ethyl"> Propyl, etc.
Long term average from UCI Pacific Flask Network vs. HIPPO: RONO2 (Alkyl Nitrates)
DAHL ET AL.: ALKYL NITRATE SATURATION

Oceanic alkyl nitrates as a natural source of tropospheric ozone

Data from Blake et al.
\( CH_3ONO_2 \)
CH$_3$ONO$_2$

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.