Measurements of bromine oxide, iodine oxide and oxygenated hydrocarbons in the tropical free troposphere from research aircraft and mountaintops

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TORERO – Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated voc

NSF/NCAR GV (17 flights)
RV Ka (cruise KA-12-01)
• BrO and IO vertical profiles
• Very short lived OVOC (few hours)
  Glyoxal, MEK, Butanal

MLO (since Jan 2014)
Halogen chemistry is crucial because halogens destroy tropospheric ozone, and thus OH radicals play a significant role in the atmospheric chemistry. OH radicals are formed through the photodissociation of ozone (O$_3$) by UV radiation ($h\nu$). 

In the stratosphere, ozone is destroyed by reactions with halogen compounds, such as chlorine (Cl) and bromine (Br), to form hydroxyl (OH) radicals. These radicals are important because they can react with various chemical species, including 

- Oxidation of SO$_2$ to SO$_3$ and H$_2$SO$_4$.
- Formation of H$_2$O$_2$ from H$_2$O.
- Formation of organic peroxides (ROOH) from VOCs.
- Formation of higher oxygenates from CO.

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In the surface region, OH radicals are formed through the photodissociation of ozone by UV radiation ($h\nu$). OH radicals can then react with various chemical species, including 

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Oxidation of long-lived gases by OH is mostly in tropics

Latitude [°]

monthly methane oxidation (GEOS-Chem)

Kevin Wecht, Harvard

TORERO
Jan/Feb 2012
Latitude range

$10^8$ kg CH$_4$ month$^{-1}$

January
July

Annual

RF02  RF01  RF05
BrO comparison: GOME-2 with GEOS-Chem, p-TOMCAT

Satellite: \(1-3 \times 10^{13} \text{ molec cm}^{-2}\)
(Chance et al., 1998; Wagner et al., 2001; Richter et al., 2002; Van Roozendael et al., 2002; Theys et al., 2011)

Ground: \(1-3 \times 10^{13} \text{ molec cm}^{-2}\)
(Hendrick et al., 2007; Theys et al., 2007; Coburn et al., 2011; Coburn et al., 2014, in prep.)

Balloon: \(0.2-0.3 \times 10^{13} \text{ molec cm}^{-2}\)
(Pundt et al., 2002; Schofield et al., 2004, 2006; Dorf et al., 2008)

Models: \(0.2-1.0 \times 10^{13} \text{ molec cm}^{-2}\)
(Saiz Lopez et al., 2012; Parrella et al., 2012)
—in the tropics

Halogens deplete the \(O_3\) column by \(~10\%\) in the tropics (Saiz-Lopez et al., 2012)
\(~0.2-0.5\) ppt \(\text{BrO}\), and \(<0.1\) ppt \(\text{IO}\)  
Parrella et al. [2012]

Theys et al. [2011]
CU-AMAX-DOAS instrument aboard NSF/NCAR GV

University of Colorado Airborne Multi-AXis Differential Optical Absorption Spectroscopy

Volkamer et al., SPIE 2009
Baidar et al., AMT 2013
Sinreich et al., 2010, ACP
Coburn et al., 2011, AMT
Baidar et al., 2013, AMT
Dix et al., 2013, PNAS
Oetjen et al., 2013, JGR
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)

CU AMAX - DOAS

Volkamer group

<table>
<thead>
<tr>
<th>Parameters measured by CU AMAX-DOAS</th>
<th>Detection limit* / Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrO</td>
<td>0.3 ppt **</td>
</tr>
<tr>
<td>IO</td>
<td>0.05 ppt</td>
</tr>
<tr>
<td>HCHO</td>
<td>100 ppt</td>
</tr>
<tr>
<td>CHOCHO</td>
<td>3 ppt</td>
</tr>
<tr>
<td>H₂O</td>
<td>5 ppm (590nm)</td>
</tr>
<tr>
<td>NO₂</td>
<td>10 ppt</td>
</tr>
<tr>
<td>OClO</td>
<td>0.7 ppt</td>
</tr>
<tr>
<td>HONO</td>
<td>12 ppt</td>
</tr>
<tr>
<td>Aerosol extinction from O₄ at 360, 477, and 577nm</td>
<td>0.01 - 0.03 km⁻¹</td>
</tr>
</tbody>
</table>

* 30 sec; ** 60 sec integration time

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

TORERO – Maiden Science Mission

Gulfstream G-V

Zenith
Forward
NADIR + 2x slant down (not shown)
BrO and IO detection SH tropical troposphere

- **NH/SH tropics:** \((1.5 \pm 0.3) \times 10^{13}\) molec cm\(^{-2}\)
- **SH sub-tropics:** \((1.7 \pm 0.3) \times 10^{13}\) molec cm\(^{-2}\)
- **SH mid-latitudes:** \((1.0 \pm 0.3) \times 10^{13}\) molec cm\(^{-2}\)
Vertical profiles & comparison with models

- GEOS-Chem: underestimates BrO by a factor 2-4
- Box-model (organohalogenes, aerosol SA) -> even less BrO
Interim Conclusions

- **Ours are the first limb-observations of BrO and IO in the tropics**

- **BrO is detected regularly above 2-4 km; BrO and IO are abundant throughout the air column**
  - Consistent with the GOME-2 satellite, ground-based MAX-DOAS data (Theys et al., 2011)
  - \(\sim\)8 times higher than direct-sun profiles (Dorf et al.)
  - \(\sim\)2-4 times more than predicted by models

- **Measurements support \(\sim\)10-15 pptv Br\(_{y}\) in the tropical UTLS (\(\sim\)5-6 pptv Br\(_{y}\) unaccounted ?)**
Mauna Loa Observatory, Hawaii

CU-MAX-DOAS

Spectrometers

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<tr>
<td>BrO</td>
<td>0.3 ppt</td>
<td>• 60s integration time</td>
</tr>
<tr>
<td>IO</td>
<td>0.05 ppt</td>
<td>• Full scan: 27 min</td>
</tr>
<tr>
<td>HCHO</td>
<td>100 ppt</td>
<td>• Footprint: 20-80km depending on aerosol load and wavelength</td>
</tr>
<tr>
<td>CHOCHO</td>
<td>3 ppt</td>
<td>• Vertical profiles: ~3DoF</td>
</tr>
<tr>
<td>NO₂</td>
<td>10 ppt</td>
<td></td>
</tr>
<tr>
<td>Extinction</td>
<td>0.01-0.03 km⁻¹</td>
<td></td>
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<tr>
<td>(360, 477, and 560nm)</td>
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Widespread BrO, IO, glyoxal, and NO$_2$ in the FT

- Oligotrophic ocean: ~ 15 pptv (10-20 pptv)
- Mesotrophic ocean: ~ 28 pptv (20-35 pptv)
- FT: 5-15 ppt (Eastern) and 3-10 ppt (Central Pacific – HEFT-10)
- Stratosphere: < 3 pptv – no signal is detectable
- Glyoxal is widespread, possibly ubiquitous → a biogeochemical cycle
**OVOC profiles**

**Lifetime**

**Aerosols**

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**Acme source (%)**

Glyoxal (AMAX-DOAS)

*Accounted source:
isoprene
benzene
toluene
(and their oxidation products, if any)*

**Lifetime (hr)**

Glyoxal

*Removal pathways:
Photolysis
OH oxidation*

*Note: equilibrium is established between glyoxal and liquid water, no net flux.*

**Total number concentration (cm$^{-3}$)**

**Acme source (%)**

MEK (TOGA)

*Accounted source:
butane*

**Lifetime (hr)**

MEK

*Removal pathways:
Photolysis
OH oxidation*

**Total surface area (μm$^2$ cm$^{-3}$)**
Conclusions

- The TORERO mission was very successful – strong focus on technological innovation
  - first limb-observations of BrO and IO in the tropics
  - ~10-15 pptv Br$_y$ in the tropical UTLS
  - What is the Br$_y$ content in the lower stratosphere, and how much stratospheric Br$_y$ reaches the UTLS?

- OVOC are widespread over oceans in the FT
  - Detected by multiple techniques (DOAS, GC-MS)
  - Unaccounted ocean source of marine organic carbon (can NOT be explained from isoprene, monoterpenes)
  - Most of the OVOC column resides in the FT
  - implications for aerosols, oxidative capacity?

Funding: NSF-CAREER award, NSF-AGS (TORERO)

Acknowledgements: NCAR/EOL and RAF, TORERO team
Glyoxal in particles: Field evidence

Glyoxal is a ubiquitous product of anthropogenic and biogenic/marine precursors, and found in aerosols

Arctic aerosol: Alert
Peak in early spring
Few weeks earlier than diacids
3-4 times more GLY than MGLY

Alert: Kawamura et al., 1996
Mexico City: Volkamer et al., 2007
Continental (Tibet): Meng et al., 2013

Marine aerosol: Hokkaido Island

GLYg = 42 ng /m³ (18 ppt)
P / (P + G) = 0.46

Marine: Matsunaga and Kawamura, 2004
Biogenic (Hyytiälä): Kampf et al., 2012
Southern Hemisph.: Rinaldi et al., 2011