Iodine Detection in the Lower Stratosphere

Prof. Rainer Volkamer

Theodore K. Koenig, Alfonso Saiz-Lopez, Pedro Campuzano-Jost, Benjamin A. Nault, Jose L. Jimenez

Solomon et al. 1994 JGR: “We speculate that iodine chemistry… may also be a factor in determining the widespread current depletion of lower stratospheric ozone.”

Br atoms in the stratosphere have ~60 times the O₃ destruction impact of Cl

I atoms less certain but estimated at ~600 times the impact of Cl

Atmospheric iodine
WMO 2014, 2018
First detection of IO in TTL
Recent aircraft campaigns

Source: NASA/GSFC
Atmospheric Chemistry of Iodine

**Source**
- Organic VSL\(_y\)
  - CH\(_3\)I (6.8%), CH\(_2\)I\(_2\) (2.8%), CH\(_2\)I\(_x\) (6%)
- Inorganic I\(_y\)
  - HOI (76%), I\(_2\) (8.4%)

**Total source:**
- Inorganic I\(_y\) (~85%), VSL\(_y\) (~15%)

**Global flux**
- Organic: 0.6 Tg I yr\(^{-1}\)
- Inorganic: 3.23 Tg I yr\(^{-1}\)
- Total source: 3.83 Tg I yr\(^{-1}\)

**Lifetime**
- mins - days
- seconds - mins

**Release atomic I**

**Stratospheric O\(_3\) (Cl,Br)**
- RF\(_{St-O3}\) ~ 0.05 W m\(^{-2}\)
- Iodine?

**Tropospheric O\(_3\)**
- Loss rate: 748 Tg O\(_x\) yr\(^{-1}\)
- O\(_3\) burden: -9%
  - HOI photolysis (78%)
  - OIO photolysis (21%)

**New particle formation**

**Stratospheric O\(_3\) (Cl,Br)**
- RF\(_{St-O3}\) ~ 0.05 W m\(^{-2}\)
- Iodine?

**Tropospheric O\(_3\)**
- Loss rate: 748 Tg O\(_x\) yr\(^{-1}\)
- O\(_3\) burden: -9%
  - HOI photolysis (78%)
  - OIO photolysis (21%)

**Halogens lower RFTO\(_3\)**
- 0.030 W m\(^{-2}\) (I)
- 0.087 W m\(^{-2}\) (Cl, Br, I)

**Additional reactions**
- I\(_y\), I\(_y\), HOI, HI, IONO\(_2\), I\(_x\)O\(_y\)
- Ice-uptake and heterogeneous recycling
- Washout and scavenging
- Sea-salt aerosol
- Heterogeneous recycling and deposition

**Sherwen et al. 2016; 2017**

**Saiz-Lopez et al. 2015**
WMO perspective on iodine in the LS

- **Iodine Oxide (IO):** <0.1 ppt, twilight conditions
  (Butz et al. 2009; Boesch et al. 2003; Pundt et al. 1998; Wennberg et al. 1997)

- **Methyl iodide (CH₃I):** <0.05 ppt
  (Tegtmeier et al. 2013; Saiz Lopez et al. 2015)

- **Particle Iodine** has qualitatively been detected in LS aerosols, but not yet been quantified
  (Murphy and Thomson, 2000; Murphy et al. 2006, 2014)

### WMO 2018: Revised Iᵥ estimate

<table>
<thead>
<tr>
<th>Halogen</th>
<th>Xᵥ (pptv)</th>
<th>O₃ eff. (a.u.)</th>
<th>Xᵥ * O₃ eff. (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>115</td>
<td>1</td>
<td>115</td>
</tr>
<tr>
<td>Bromine</td>
<td>5</td>
<td>60</td>
<td>300</td>
</tr>
<tr>
<td>Iodine₉₉</td>
<td>&lt;0.15</td>
<td>600</td>
<td>&lt;90</td>
</tr>
<tr>
<td>Iodine₉₉</td>
<td>0 - 0.8</td>
<td>600</td>
<td>0 - 540</td>
</tr>
</tbody>
</table>

Volkamer et al., 2015; Saiz-Lopez et al. 2015
First IO detection in daytime TTL (Volkamer et al. 2015)

- Volkamer et al., 2015 AMT
- Wang et al., 2015 PNAS
- Saiz-Lopez et al., 2015 GRL
- Sherwen et al., 2016 ACP
- Schmidt et al., 2016 JGR
- Dix et al., 2016 AMT
- Koenig et al., 2017 ACP
- Wales et al., 2018 JGR
- Badia et al., 2019 ACP
- Zhu et al., 2019 ACP

Telescope pylon
0.13-0.15 pptv IO in the Tropical Transition Layer (both hemispheres)

“Our understanding of the chemical processes involving halogens and organic carbon species in the tropics seems incomplete.”

Volkamer et al. 2015 AMT

Wang et al. 2015 PNAS

Dix et al. 2016 AMT
Stratospheric I$_y$ injection inferred from TTL-IO

Daytime TTL-IO suggests 0.25 to 0.70 pptv I$_y$ are injected into the LS.

Previous measurements had found <0.1 pptv IO at twilight in the LS (Butz et al. 2009; Wennberg et al. 1997).

There is no previous daytime detection of IO in the LS.
CONTRAST RF15: Bromine injection to the stratosphere

We have re-visited this case study to measure iodine oxide radicals

Koenig et al., 2017
Wales et al., 2018

Bry injection = 5 ± 2 pptv WMO 2018
~5 pptv WMO 2014 (confirmed)

SGI = ~3 pptv Bry based on VSL_{Br} observations
PGI = 2-4 pptv Bry inferred from BrO observations

Good consistency for Bry in LS, incl. several recent aircraft datasets (i.e., TORERO, CONTRAST, ATTREX)
CONTRAST RF15: Jet crossing into NH mid latitude LS

$I_{y, \text{gas}}$ decreases from $\sim0.6$ pptv in UT to $\sim0.1$ pptv in LS

0.055 pptv IO in the daytime LS is compatible with previous upper limits (twilight)
Iodine in the UTLS — a global perspective

First IO detection in daytime LS.
First quantitative $l_{y,\text{part}}$ detection in the UTLS.
Heterogeneous $O_3$ loss due to the $I^- + O_3$ reaction

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>$I_{y,\text{gas}}$ (ppt)</th>
<th>$I_{y,\text{part}}$ (ppt)</th>
<th>$I^-/I_{y,\text{part}}$ (%)</th>
<th>$[I^-]$ (mmol/kg)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.7</td>
<td>0.64</td>
<td>0.13</td>
<td>50</td>
<td>14.7</td>
<td>9.2e-6</td>
</tr>
<tr>
<td>13.7</td>
<td>0.25</td>
<td>0.52</td>
<td>30</td>
<td>10.7</td>
<td>5.7e-6</td>
</tr>
<tr>
<td>15.5</td>
<td>0.09</td>
<td>0.68</td>
<td>12</td>
<td>9.19</td>
<td>4.9e-6</td>
</tr>
</tbody>
</table>

$I_{y,\text{gas}} = f(H_2O/O_3)$

$I_{y,\text{part}} = f(I^-, IO_3^-)$ lab calib.

![Graph](image1)

![Graph](image2)
Measurements support $I_y$ injection >0.6 pptv; rapid conversion to $I_{y,part}$ (Compare WMO 2018: 0 – 0.8 pptv $I_y$), but $I_{y,gas}$ remains detectable

$O_3$ loss: $I_{y,part}$ is competitive with $I_{y,gas}$. $I_y$ is comparable to $Br_y$, $Cl_y$
Conclusions

• TORERO: First IO detection in the daytime TTL (Volkamer et al., 2015) suggested 0.25 to 0.70 pptv I\textsubscript{y} are injected into the LS (Saiz Lopez et. al 2015). Revised WMO2018 estimate of 0 to 0.8 pptv I\textsubscript{y} injection to LS inferred from TTL.

• CONTRAST: First IO detection in the daytime LS. The values are low (0.06 pptv IO) and compatible with previous IO upper limits measured at twilight.

• ATom-1 & ATom-2: First quantification of aerosol iodine in the LS. The fraction I\textsuperscript{-}/I\textsubscript{y,part} decreases in the LS, but is non-zero, suggesting heterogeneous re-cycling.

• Our measurements support 0.76 ± 0.15 pptv I\textsubscript{y} are injected into the LS

<table>
<thead>
<tr>
<th>Halogen</th>
<th>$X_{y}$ (pptv)</th>
<th>O\textsubscript{3} eff. (a.u.)</th>
<th>$X_{y}$ * O\textsubscript{3} eff. (a.u.)</th>
<th>O\textsubscript{3} loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>115</td>
<td>1</td>
<td>115</td>
<td>16%</td>
</tr>
<tr>
<td>Bromine</td>
<td>5</td>
<td>60</td>
<td>300</td>
<td>43%</td>
</tr>
<tr>
<td>Iodine</td>
<td>0 - 0.8</td>
<td>~600</td>
<td>0 - 540</td>
<td></td>
</tr>
<tr>
<td>Total I\textsubscript{y}</td>
<td>0.76</td>
<td>375</td>
<td>285</td>
<td>41%</td>
</tr>
<tr>
<td>- Gas</td>
<td>0.11</td>
<td>960</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>- Particle</td>
<td>0.65</td>
<td>280</td>
<td>180</td>
<td></td>
</tr>
</tbody>
</table>

- LS-O\textsubscript{3} loss: Br ~ I >> Cl
- Gas-phase more efficient than particulate iodine at destroying O\textsubscript{3}
- Heterogeneous O\textsubscript{3} loss dominates over gas-phase, and is responsible for >60% of iodine O\textsubscript{3} loss in LS.

Acknowledgements: NSF AGS 1620530, 1261740, 1104104
NASA doi: 10.3334/ORNLDAAC/1581
TORERO, CONTRAST, Atom-1, Atom-2 science teams