Growth in stratospheric loading of very short-lived substances and their impact on ozone and climate

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--Ozone Layer-- halogen-driven ozone loss

Troposphere

HCFCs, CFCs, and Halons

Stratosphere

“Very Short-lived Substances (VSLS)”
Lifetimes < 6 months

CH₂Br₂
CH₂I₂

CHBr₃

CH₃I

CH₂Cl₂
C₂Cl₄

Anthropogenic VSLS (mostly Cl-containing)

Halocarbons from the biosphere

Seaweed
Phytoplankton

Long-lived, anthropogenic

Lifetimes < 6 months

12 km
More bromine in stratosphere that can be explained by long-lived gases alone.

Oceanic VSLS estimated to supply 6 (3-8) ppt of bromine in the stratosphere.

~20 to 30% of the TOTAL bromine in the stratosphere.

Contribution from long-lived gases.

M. Dorf, K. Pfeilsticker et al. in WMO (2014)
Key Questions

1. What is the impact of VSLS on ozone in the lower stratosphere?
   → Which VSLS (natural vs anthropogenic) influence ozone most?

2. What are the radiative implications?

3. Has VSLS-driven ozone loss changed over time?
   → Contribution to the radiative forcing of strat. ozone

4. Is the stratospheric loading of anthropogenic VSLS changing?
Global Model Simulations

VSLS Tracers**
Mixing ratio boundary condition

Natural
CHBr₃
CH₂Br₂
CHBr₂Cl
CH₂BrCl
CHBrCl₂
CH₃I

Anthrop.
CHCl₃
CH₂Cl₂
C₂Cl₄
C₂H₄Cl₂
C₂HCl₃

\[ \Delta O_3 \text{ from VSLS [2011]} \]

\[ \Delta O_3 \text{ from VSLS [pre-industrial]} \]

Radiative transfer model

** VSLS in red were scaled to give lower, best estimate & upper limit of stratospheric loading from WMO (2014)
** Time-independent Br and I; trends considered for chlorine.
ΔO₃ column due to VSLS [2011]

i.e., the presence or absence of all VSLS in the 2011 atmosphere

Largest impact at mid to high latitudes

ClO + BrO ---- Cl + Br + O₂
Cl + O₃ ---- ClO + O₂
Br + O₃ ---- BrO + O₂
Net: 2O₃ ---- 3O₂
ΔO₃ column due to VSLS [2011]

i.e., the presence or absence of all VSLS in the 2011 atmosphere

Largest impact at mid to high latitudes

VSLS reduce O₃ column up to ~6% or ~15 Dobson Units

Uncertainty due to poor constraint on stratospheric loading of VSLS

ClO + BrO ---- Cl + Br + O₂
Cl + O₃ ---- ClO + O₂
Br + O₃ ---- BrO + O₂
Net: 2O₃ ---- 3O₂
Altitude-resolved $\Delta O_3$ due to VSLS

In the LS, 86% of $\Delta O_3$ due to Br, 11% due to Cl, & 3% due to iodine.
Altitude-resolved $\Delta O_3$ due to VSLS

$\Delta O_3$ from all VSLS

In the LS, 86% of $\Delta O_3$ due to Br, 11% due to Cl, & 3% due to iodine.

$\Delta O_3$ from long-lived gases (CFCs etc.)

Per molecule, O$_3$ perturbations in UTLS cause larger radiative effects.
Radiative Effect (RE) of \( O_3 \) loss

**Long-lived ODSs**

RE of \(-0.17\) Wm\(^{-2}\)

Caused by >3000 ppt equivalent Cl

**Bromine VSLS**

RE of \(-0.07\) Wm\(^{-2}\)

Caused by (just) several hundred ppt equivalent Cl

Normalised, \( O_3 \) Radiative Effect due to VSLS is 4x larger than that from long-lived gases
Is there a trend in VSLS-driven O₃ loss?

Yes. For two reasons...

[Reason 1:] Increase in stratospheric chlorine (from long-lived ODSs) has enhanced natural VSLS-driven O₃ loss through coupled Br-Cl cycles.

Stratospheric O₃ Radiative Forcing calculations should consider VSLS.
Trend in VSLS-driven $O_3$ loss?

[Reason 2.] Some anthropogenic VSLS are increasing throughout the global atmosphere:

Overall, estimated contribution of $-0.02\pm0.01\,\text{Wm}^{-2}$ from VSLS (Cl and Br) to stratospheric $O_3$ RF since pre-industrial (bromine accounts for 75% of this RF)
Recent growth in strat. Cl-VSLS

TOMCAT tropospheric model—transporting gases to the stratosphere:
Organic chlorine at 15 km, 20°N to 20°S latitude

\[ \text{Sum Cl} = (2 \times \text{CH}_2\text{Cl}_2) + (3 \times \text{CHCl}_3) + (2 \times \text{C}_2\text{Cl}_4) \]

Model at 15 km: 87 ppt Cl (2013)

Model uses surface observations of \( \text{CH}_2\text{Cl}_2 \), and \( \text{C}_2\text{Cl}_4 \) (NOAA) and \( \text{CHCl}_3 \) (AGAGE) as boundary condition.
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Model at 15 km: 87 ppt Cl (2013)
ATTREX at 15km: 91 ppt Cl (2013)

Model uses surface observations of \( \text{CH}_2\text{Cl}_2 \), and \( \text{C}_2\text{Cl}_4 \) (NOAA) and \( \text{CHCl}_3 \) (AGAGE) as boundary condition.

ATTREX data from E. Atlas

![Graph showing the total organic chlorine at 15 km from VSLS from 2005 to 2013](graph.png)
Modelled trend in $\text{Cl}_y^{\text{VSLS}}$

TOMCAT tropospheric model— Including product gases in total Cl amounts

EXP2: CH$_2$Cl$_2$, CHCl$_3$ and C$_2$Cl$_4$ only
EXP3: Sensitivity inc. C$_2$H$_4$Cl$_2$ and C$_2$HCl$_3$ in addition

Product gas injection increases the total by ~18 ppt at 15 km in tropics
Modelled trend in Cl$_y^{VSLS}$

TOMCAT tropospheric model— Including product gases in total Cl amounts

EXP2:

CH$_2$Cl$_2$, CHCl$_3$ and C$_2$Cl$_4$ only

EXP3:

Sensitivity inc. C$_2$H$_4$Cl$_2$ and C$_2$HCl$_3$ in addition

3.7 ppt Cl/yr

at 15 km in tropics

Product gas injection increases the total by ~18 ppt

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Summary

• **Significant impact of VSLS on LS O\(_3\)**
  → \(\Delta O_3\) of \(~8-12\%\) *(for an atmosphere without VSLS)*
  → \(O_3\) change is mostly from *natural* Br-containing VSLS

• **VSLS-driven O\(_3\) loss is efficient at influencing climate**
  → **Radiative effect** of -0.1 Wm\(^{-2}\) *(stratosphere in 2011)*
  → 4x more efficient than CFCs at influencing climate
  → Small contribution (-0.02 Wm\(^{-2}\)) to strat. \(O_3\) R. Forcing

• **Stratospheric Cl from anthropogenic VSLS increasing**
  → Growth of 3.7 ppt Cl/yr *(2005-2013)* *(vs. -13.4 ppt/yr from LL ODS)*
  → \(CH_2Cl_2\) not controlled by Montreal Protocol
For further details..


Misc Slides
Radiative effect of VSLS O$_3$ loss

RE of up to -0.30 Wm$^{-2}$

Global mean RE -0.1 Wm$^{-2}$

Q. Has VSLS-O$_3$ loss changed in time?

Radiative forcing?
Uncertainty in CHBr$_3$ emissions

Large uncertainty in distribution and magnitude of emissions

Factor of 3 uncertainty in total global CHBr$_3$ emission

Hossaini et al. (2013, ACP)
Uncertainty in CH$_2$Br$_2$ emissions

Large uncertainty in distribution and magnitude of emissions

Factor of 2 uncertainty in total global CH$_2$Br$_2$ emission

Hossaini et al. (2013, ACP)
Altitude-resolved $\Delta O_3$ due to VSLS

Natural bromine VSLS are the most important for stratospheric $O_3$.

Relative contribution to LS $O_3$ loss from VSLS:
- Bromine (86%)
- Chlorine (11%)
- Iodine (3%)

Chlorine-containing VSLS are of mostly anthropogenic origin.
Trend in VSLS-driven $O_3$ loss?

Enhanced VSLS-driven $O_3$ loss post volcanic eruptions.

Ozone change due to VSLS 1979–2013

$\Delta O_3 = -9$ (−5 to −12)%

Best estimate

Range due to uncertainty in VSLS loading

Impact of bromine /SLS

Enhanced VSLS-driven $O_3$ loss post volcanic eruptions
New ozone-destroying gases on the rise

Doyle Rice, USA TODAY  12:38 p.m. EST February 16, 2015

In humanity’s ongoing experiment with the Earth’s atmosphere, scientists Monday warned of a growing threat from new man-made gases that are chewing away at the ozone layer.

(Photo: AP)
Vertical distribution of $O_x$ catalytic loss cycles

- HO$_x$ cycles
- ClO$_x$ cycles
- NO$_x$ cycles
- HO$_x$ cycles

Graph showing pressure (hPa) on the y-axis and $O_x$ loss rate (molecules/cm$^3$/s) on the x-axis, with various lines indicating production, total loss, and different chemical cycles.
Fig. 1. Radiative forcing sensitivity of global surface temperature to changes in vertical ozone distribution. The heavy solid line is a least squares fit to one-dimensional model radiative-convective equilibrium results computed for 10 Dobson unit ozone increments added to each atmospheric layer. Ozone increases in region I (below \(~30\) km) and ozone decreases in region II (above \(~30\) km) warm the surface temperature. No feedback effects are included in the radiative forcing.
“O₃ increments added near the tropopause produce the largest increase in surface temperature.

Because the greenhouse blanketing produced by a given atmospheric O₃ increment is directly proportional to the temperature contrast between the radiation absorbed and radiation emitted by the O₃ increment; since this temperature contrast is greatest for O₃ increments added near the tropopause, the RF efficiency on a per molecular basis is also greatest for O₃ changes near the tropopause.”

Lacis et al. [1990, JGR]