Very-Short Lived (VSL) Halogen Chemistry in CAM-CHEM:

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VSL Halogen Scientific Questions

- What is the Role that VSL organic bromine and iodine species have on the ozone budget in the tropical lower troposphere?
- What are the climatic impacts of VSL halogens?

Paper submitted to Nature Geosciences

- What is the impact of VSL halogens on CH₄ lifetimes through amplification of OH?
- Can observation of VSL halogens help constrain transport pathways into the tropical UTLS in a 3D CCM?
- What impact does VSL substances have on model derived ozone trends?

Tropospheric Halogen Chemistry



Subset of the VSL Halogenated Substances currently being added the CAM-CHEM mechanism (~20 SG)

Source Gas	Formula	Local Lifetime (days)	Main Loss processes	WAS
Bromochloromethane	CH ₂ BrCl	150	ОН	\checkmark
Trichloromethane (chloroform)	CHCl₃	150	OH	\checkmark
Methylene chloride	CH ₂ Cl ₂	140	OH	\checkmark
Dibromomethane	CH ₂ Br ₂	120	ОН	\checkmark
Bromodichloromethane	CHBrCl ₂	78	OH, hv	\checkmark
Dibromochloromethane	CHBr ₂ CI	69	hv, OH	\checkmark
Tribromomethane (bromoform)	CHBr ₃	26	hv	\checkmark
Methyl iodide	CH ₃ I	7	hv	\checkmark
Trifluoroiodomethane	CF₃I	4	hv	-

Tropospheric Halogen Chemistry



Modeling the Troposphere with VSL Halogens

- Need a model with representation of Tropospheric O₃ chemistry (e.g., NMHCs; Emissions, etc...).
- Need a model that includes a VSL organic and inorganic mechanism.
 - Organic species: Adds ~18
 - Inorganic species: Adds ~20
 - Photolysis Rxns: Adds ~23
 - Sulfate Het. Rxns: Adds ~5
 - Sea Salt Aer. Rxns: Adds ~9
- Emissions Observations suggest that the biogenic production seems to come from seaweed, phytoplankton, algae etcs... [we use Chlorophyll-A obs from SeaWIFS]

Emissions of VSL Halogens

Emissions – Observations suggest that the biogenic production seems to come from seaweed, phytoplankton, algae etcs... [we use Chlorophyll-A obs from SeaWIFS]





Organic Halogens



Comparison of modeled average vertical profiles of organic halogens with aircraft observations from the missions PEM-Tropics A, PEM-Tropics B and TRACE-P. Model results are averaged within the geographical region of each campaign, only considering latitudes between 30° N - 30° S and matching

Organic Halogens



IO and BrO at Cape Verde



Read et al., Nature, 2008
Cape Verde [16.85N, 24.87W]
DOAS measurements.

Halogen Odd-Oxygen Loss [Surface]





Top: Surface ozone loss (in 10⁵ molec cm⁻³ s⁻¹) resulting from including tropospheric halogen chemistry in CAM-CHEM.

Left: Annual average of diurnal ozone loss observed and simulated by CAM-CHEM at Cape Verde. Model IO and BrO distributions are also shown.

Odd Oxygen Loss Partitioning

Percentage of the annual average chemical ozone loss due to halogens in the tropical troposphere. The primary odd-oxygen loss catalytic cycle is:

 $I + O_3 => IO + O_2$ Br + O_3 => BrO + O_2 IO + BrO=> I + Br + O_2

Net: $20_3 => 30_2$



Odd Oxygen Loss Partitioning

16.9° N, 24° W



Tropical Ozone comparisons from Sondes [Surface]



Tropospheric Column Ozone Difference (%)



Next Step

NASA Roses 10 A.14 – was funded!

- 50% Kinnison
- 50% Post Doc.

Model Development....

- Include emissions for mid-latitudes.
- Include emission processes for the polar regions.

Science questions

- Understanding transport pathways of VSL into the LS.
- What is the impact of VSL halogens on CH₄ lifetime through amplification of OH?
- What impact does VSL substances have on model derived Ozone trends?

The End!