Photochemical Hypotheses for Halogen Chemistry during CONTRAST

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21 Oct 2013

Objectives

1. **Quantify role of halogens (bromine, iodine, and chlorine) in the the photochemical of tropospheric ozone**

2a. Quantify delivery of halogens to the LMS via VSL halocarbons

- ⇨ **Primary focus bromine but iodine & chlorine will also be observed**

2b. Close the bromine budget by assessing balance of loss of organics with appearance of inorganics

3. Conduct dawn / dusk flights to:

- ⇨ **Quantify role of VSL chlorocarbons via obs of nighttime BrCl**
- ⇨ **Provide sensitivity to inorganic bromine under low O_3 conditions via obs of nightime BrCl & HOBr**
- ⇨ **Test coupling of BrO & $BrONO_2$ via obs. of BrO, NO_2, etc vs SZA**

1. Role of halogens in the photochemical of tropospheric ozone

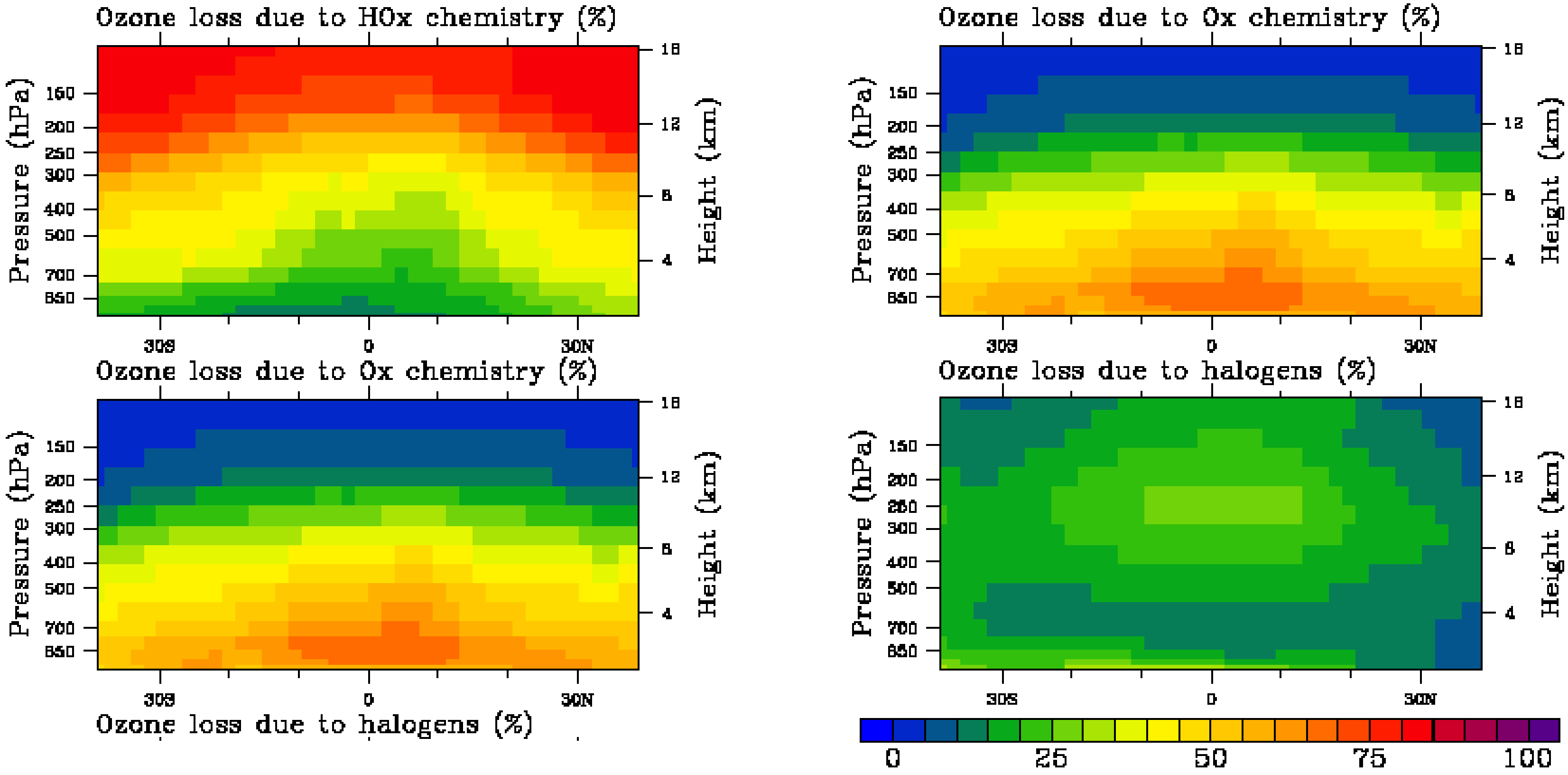


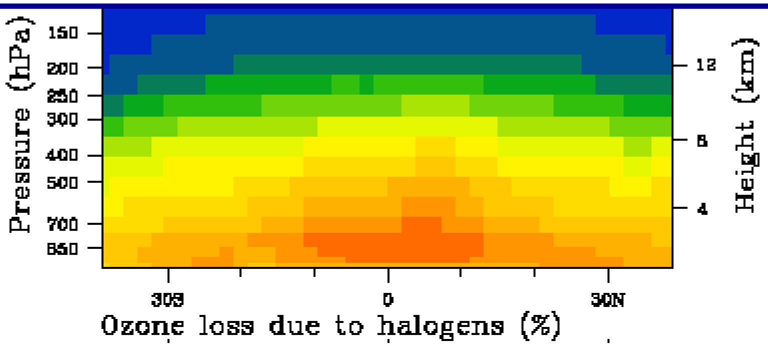
Fig. 6. Percentage of the annually integrated chemical ozone loss from HO_X, O_X and halogen photochemistry as simulated by CAM-Chem.

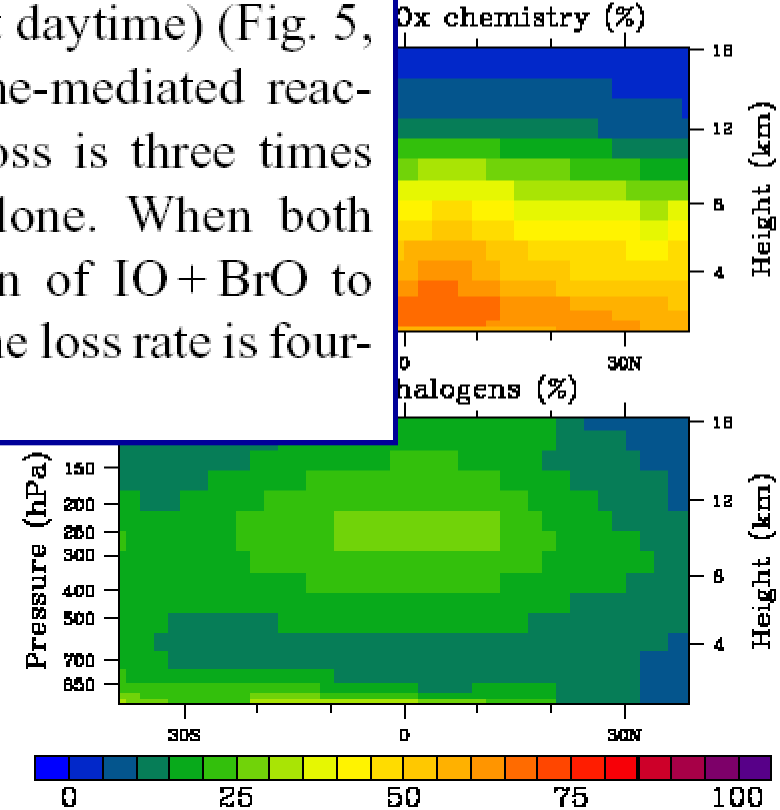
Saiz-Lopez et al., ACP, 2012

Key obs: IO, BrO
BrCl to constrain ClO
H_2O, CH_4, CO, VOCs etc used to constrain HO_2
Halocarbons

> In the TMBL (20° S–20° N), the annually integrated rate of surface ozone loss due to halogen chemistry is ∼6 × 10^5 molecule cm^{-3} s^{-1} (∼0.15 ppbv h^{-1} at daytime) (Fig. 5, left). The integrated contribution of iodine-mediated reactions to the total rate of surface ozone loss is three times larger than that of bromine chemistry alone. When both chemistries are combined via the reaction of IO + BrO to Br + OIO (75 %) and Br + I (25 %), the ozone loss rate is fourfold that of bromine chemistry alone.

eric ozone





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Key obs: IO, BrO
BrCl to constrain ClO
H_2O, CH_4, CO, VOCs etc used to constrain HO_2
Halocarbons such as CH_3I, CH_2I_2, CH_2IBr, and CH_2ICL

2a. Quantify delivery of halogens to the LMS via VSL halocarbons

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Table 1-9. Summary of source gas (SG) and product gas (PG) observations and modeling results to constrain input of halogens from VSLS into the stratosphere. Note that only observations of chlorine-containing PGs exist; estimates of PG amounts for bromine are based solely on modeling studies and only upper limits of iodine-containing PGs are available. For bromine and iodine only ranges can be estimated from this. Details on the way that these numbers have been derived can be found in the Sections 1.3.3.1 (SG), 1.3.3.2 (PG) and 1.3.3.3 (total). All values are given in ppt.

Halogen or Compound	Measured TTL to CPT Abundance (ppt Cl, Br, or I)	"Best Estimate" TTL Abundance (ppt Cl, Br, or I)	"Best Estimate" Contribution from VSLS (ppt Cl, Br, or I)
Chlorine			
VSL SGs	26–80 [a, b]	55 (38–80) [c]	55 (38–80)
HCl PG	0–40 [d]	20 (0–40)	10 (0–20)
$COCl_2$ PG	31 ± 22 to 36 ± 26 [e]	32 (± 22)	16 (0–32)
Total chlorine	25–170 [f]		80 (40–130) [f]
Bromine			
VSL SGs	0.7–6.5 [a, b]	2.7 (1.4–4.6) [a, c]	0.7–3.4 [a, g]
PG sum			0.4–4.2 [h]
Total bromine			1–8 [i, f]
Iodine			
CH_3I SG	< 0.05 [a]	< 0.05 [a]	< 0.05 [a]
IO, OIO PG	< 0.1 [j]	< 0.1 [j]	< 0.1 [j]
Total iodine			< 0.15 [k]

WMO / UNEP 2010 Ozone Assessment Report (Green Book)

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We'd like to help reduce this large range of uncertainty

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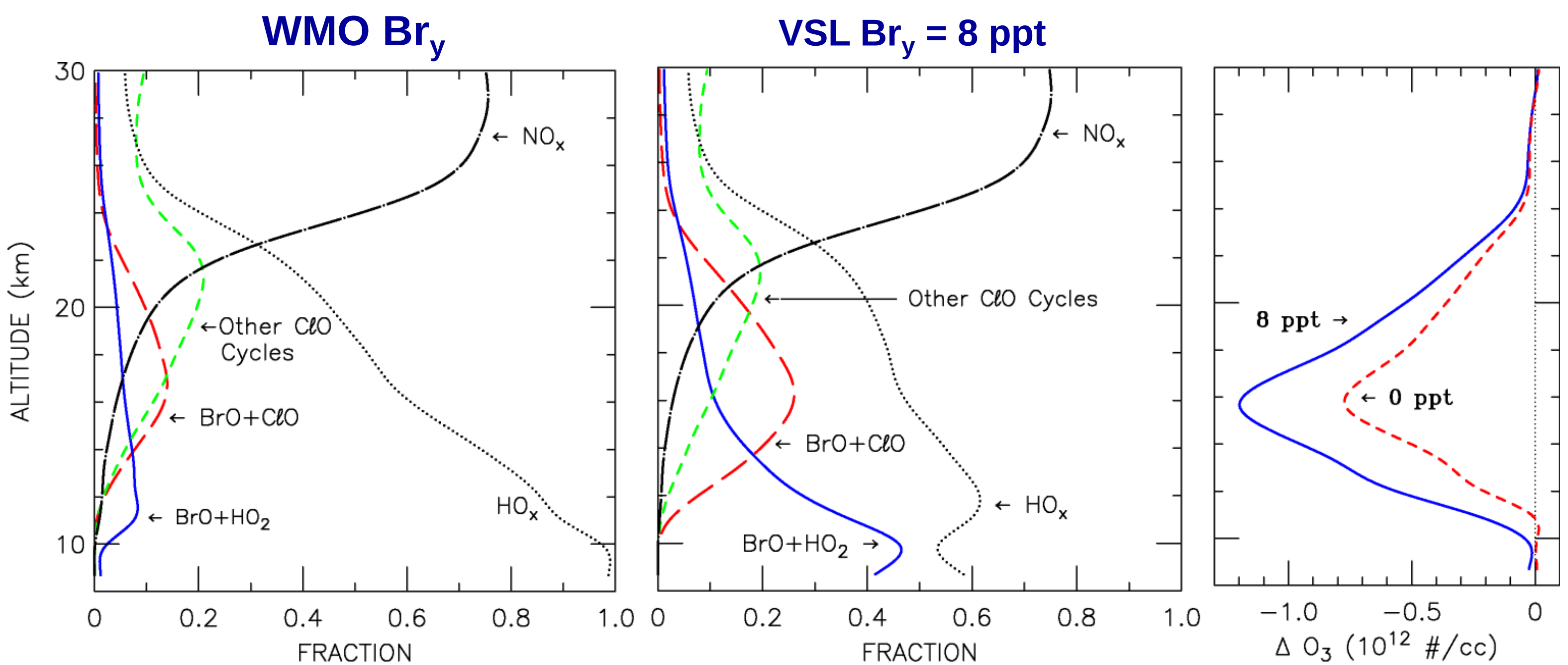

Salawitch et al., GRL, 2005

Bromine supplied by VSL bromocarbons leads to:

- Enhanced ozone depletion due mainly to BrO+ClO cycle
- $BrO+HO_2$ catalytic cycle becomes very significant sink below 16 km

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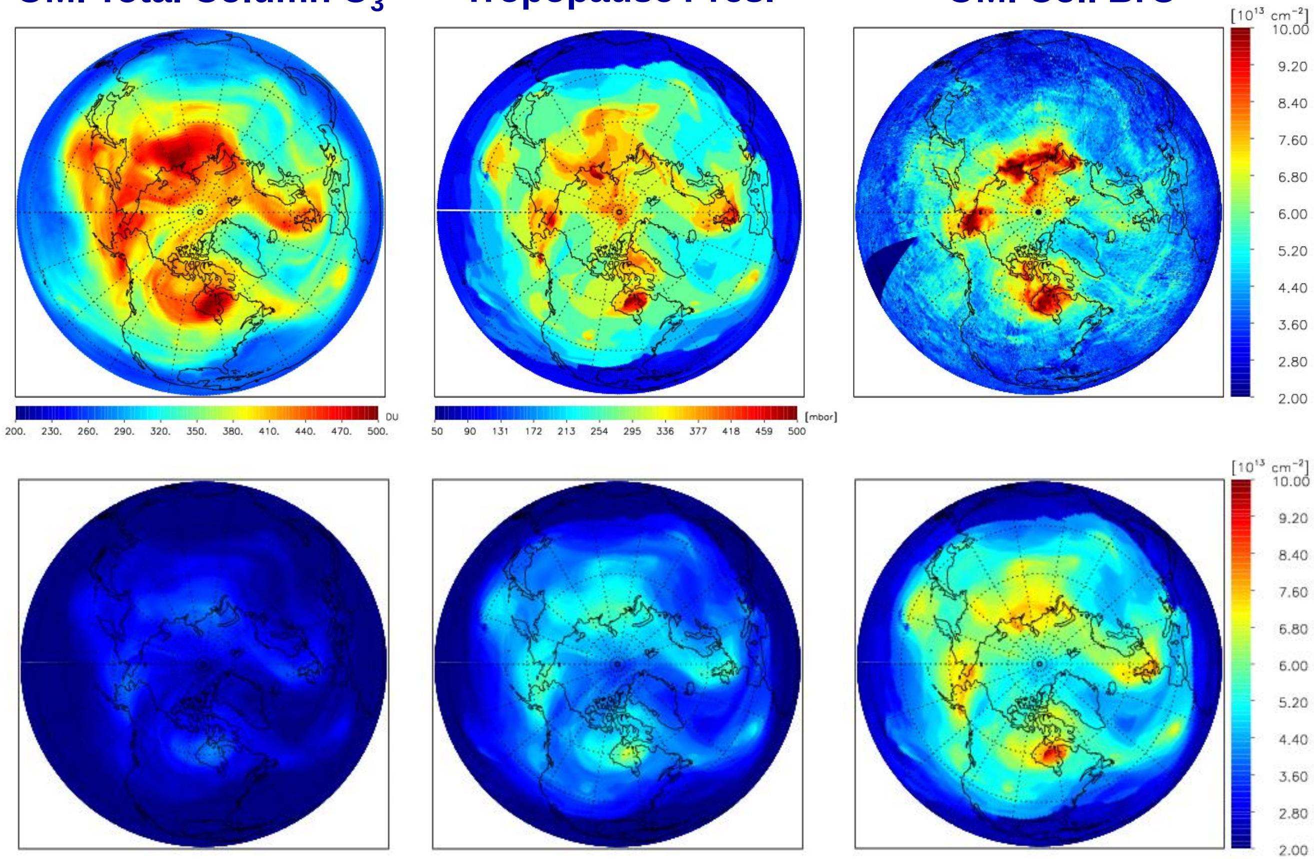
OMI Total Column O_3 **Tropopause Pres.** **OMI Col. BrO**



Model Stratospheric Column BrO

VSL=0 ppt **VSL=5 ppt** **VSL=10 ppt**

Salawitch et al., GRL, 2010

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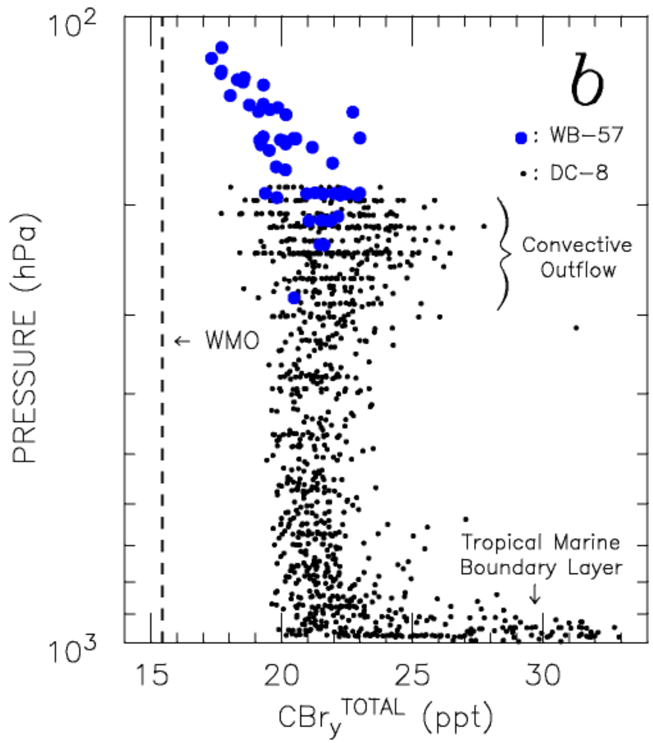
Prior obs: PGI (product gas injection) of Br_y could be 5 to 7 ppt

⇨ **these obs obtained over Costa Rica; PGI could be a lot larger in TWP**



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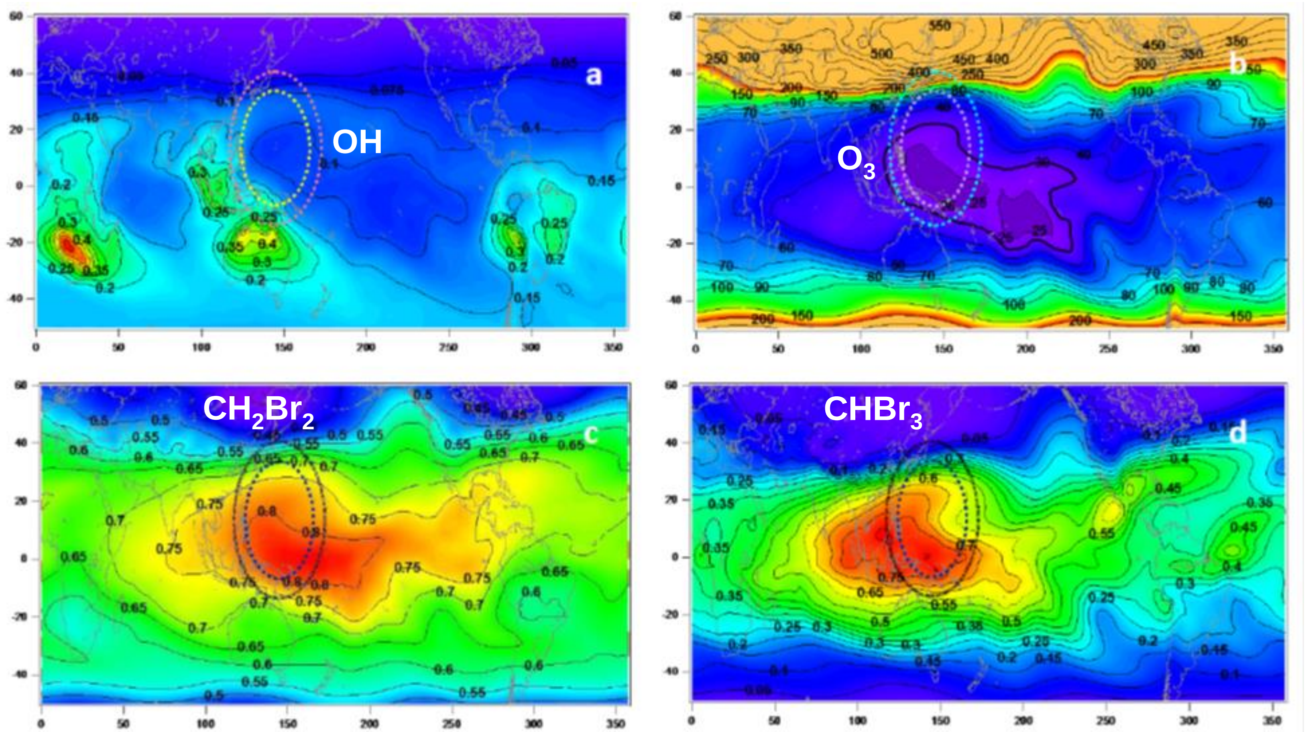

Calculated distributions, CAM-CHEM, for January at 200 hPa.
Concentric ovals indicate range of GV aircraft for a 6 hr flight and 8 hr flight, respectively.

2a. Quantify delivery of halogens to the LMS via VSL halocarbons

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We expect to quantify effect of "OH hole" on halocarbons even though OH will not be observed

		τ_{OH} (275 K, 5 km)	τ_J	τ_{Total}
$CHBr_3$	Bromoform	100	36	26
CH_2Br_2	Dibromomethane	120	5000	120
CH_2BrCl	Bromochloromethane	150	15000	150
C_3H_7Br	n-propyl bromide	13	>1200	13
$CHBr_2Cl$	Dibromochloromethane	120	161	69
$C_2H_4Br_2$	Ethylene dibromide	58	–	58

Expect to see [$CHBr_3$]/[CH_2Br_2], [$CHBr_3$]/[CH_2BrCl], & [$CHBr_3$]/[C_2H_7Br] drop in air masses recently lofted from MBL to region of low O_3 (and presumably low OH) because photolytic loss will continue while *OH loss will decline*:

we can (and will) calculate OH based on obs O_3, H_2O, CH_4, etc but developing an empirical means to infer ambient OH will be an important compliment to modeled OH

2a. Quantify delivery of halogens to the LMS via VSL halocarbons

2b. Close the bromine budget

Prior theory: SGI (source gas injection) of Br_y highly uncertain: depends on efficiency of aerosol uptake and washout versus het chem release of labile bromine

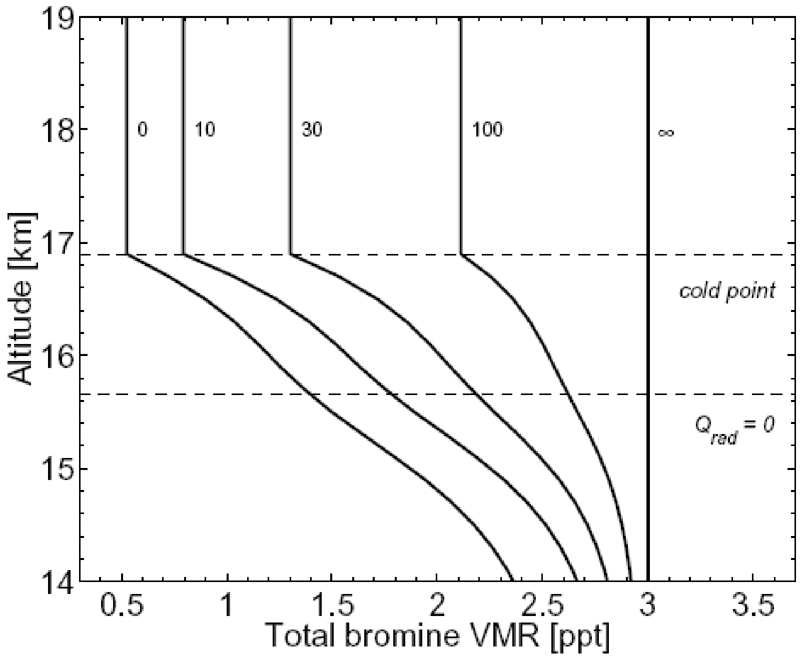


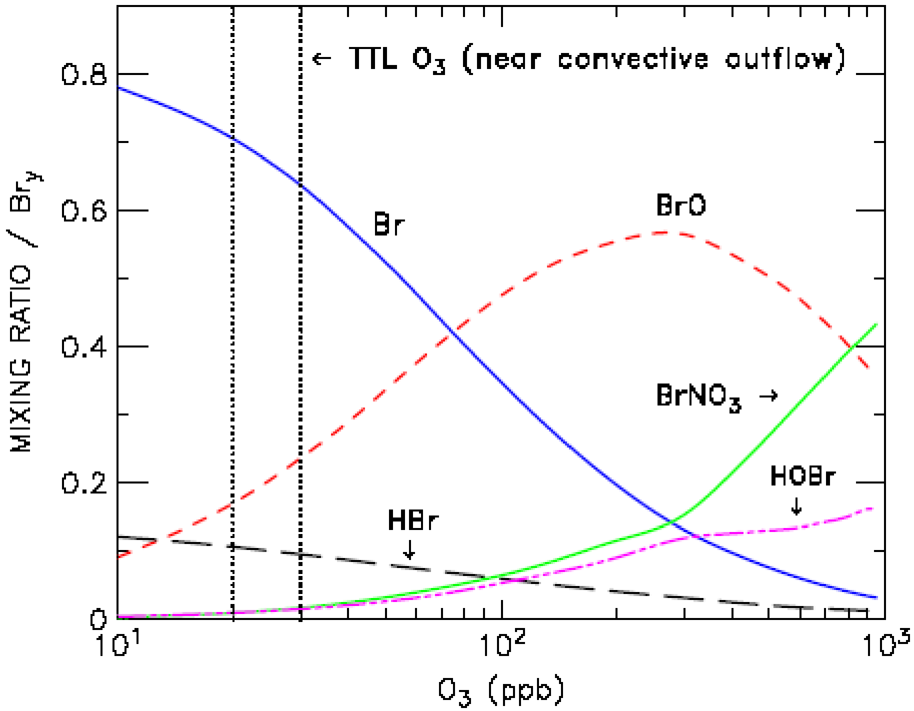
Fig. 5. Calculated total bromine released from bromoform (defined as $Br_y + 3 \times CHBr_3$) for different washout rates of Br_y (numbers in the figure give τ_w in days, the lifetime of Br_y due to washout). The calculations assume 1 pptv of bromoform in the boundary layer and no detrainment of Br_y from convection (see text for discussion).

SInnhuber and Folkins, ACP, 2006

2a. Quantify delivery of halogens to the LMS via VSL halocarbons

2b. Close the bromine budget

Huge challenge: Br_y partitions to Br under low O_3 during daytime



Br*: experimental method for quantifying atomic Br by exposing air to propene (C_3H_6) and NO, which produces stable bromine compounds that can be analyzed by the WAS

e.g., Impey et al., JGR, 1997

Br + HCHO is route out of Br-reservoir

Daytime:

Key obs: CBr_y species, BrO, Br*, O_3, HCHO

Key sampling strategies: target specific O_3 mixing ratios

conduct nighttime flights to target HOBr, BrCl, & Br_2

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If ~100 ppt of chlorine gets through, this is very important for lowerstratospheric O_3

WMO / UNEP 2010 Ozone Assessment Report (Green Book)

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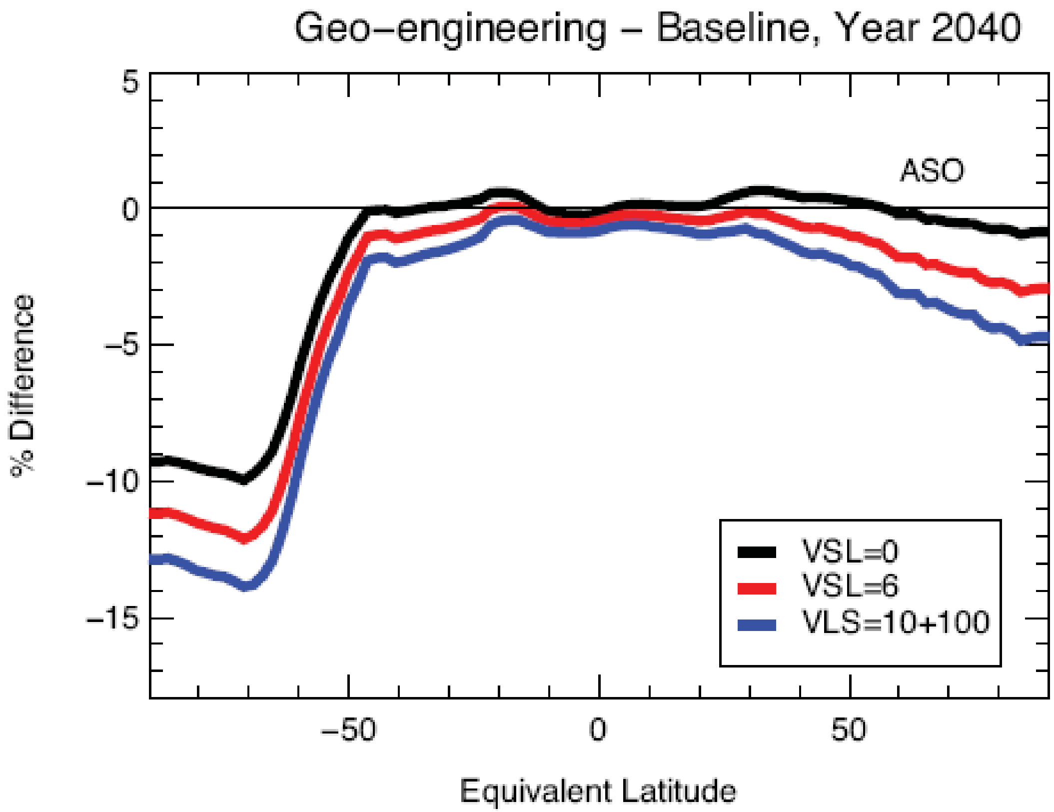

Fig. 2. Relative difference of column ozone between geo-engineering and baseline model results for four seasons (different panels). All calculations are for year 2040. Different values of VSL halogens are considered: Br_y^{VSL} and Cl_y^{VSL} both $= 0$ (black), $Br_y^{VSL} = 6$ ppt and $Cl_y^{VSL} = 0$ (red), and $Br_y^{VSL} = 10$ ppt and $Cl_y^{VSL} = 100$ ppt (blue). Results are shown as a function of equivalent latitude.

Tilmes et al., ACP, 2012

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CONTRAST will observed a comprehensive suite of VSL chlorocarbons plus BrCl

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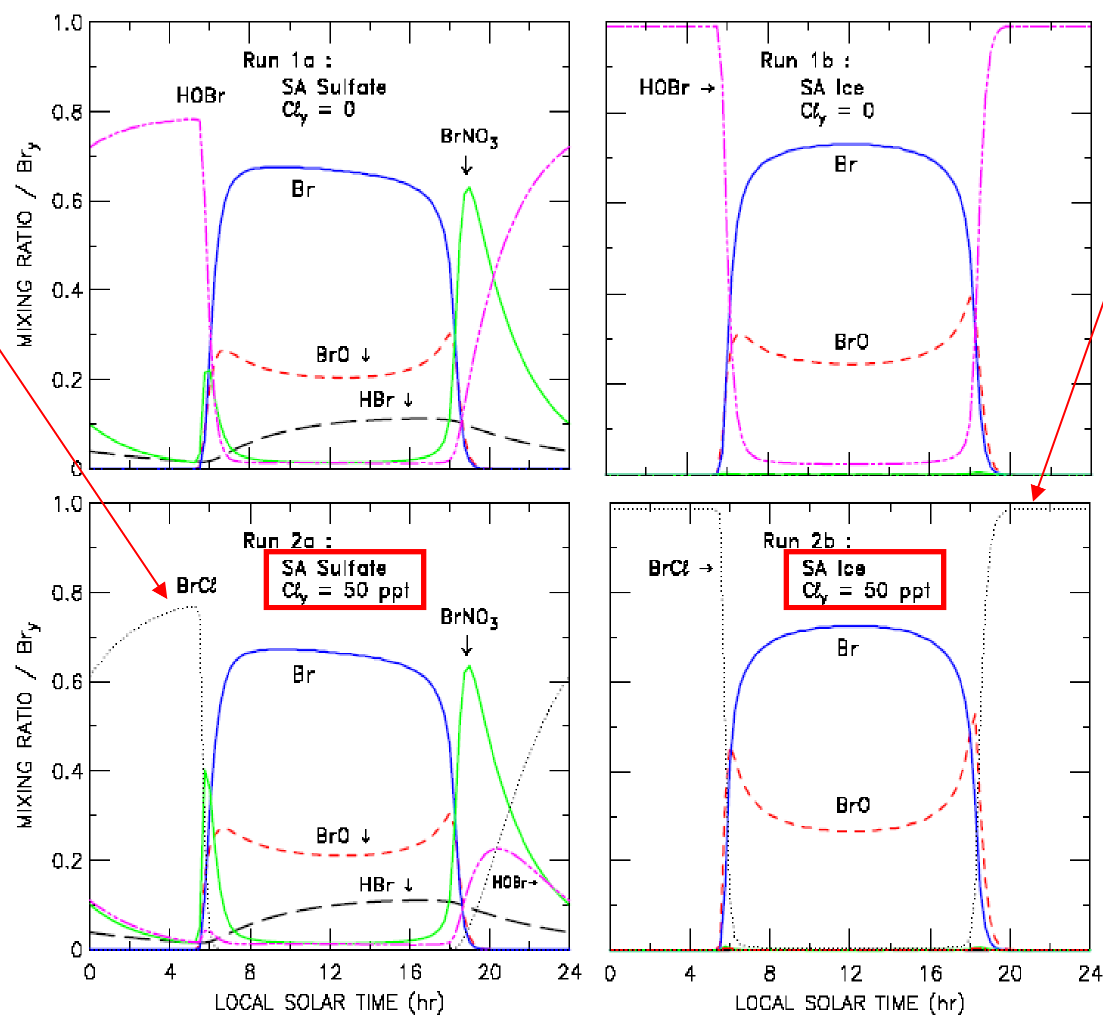
CONTRAST

Guam, Jan–Feb 2014

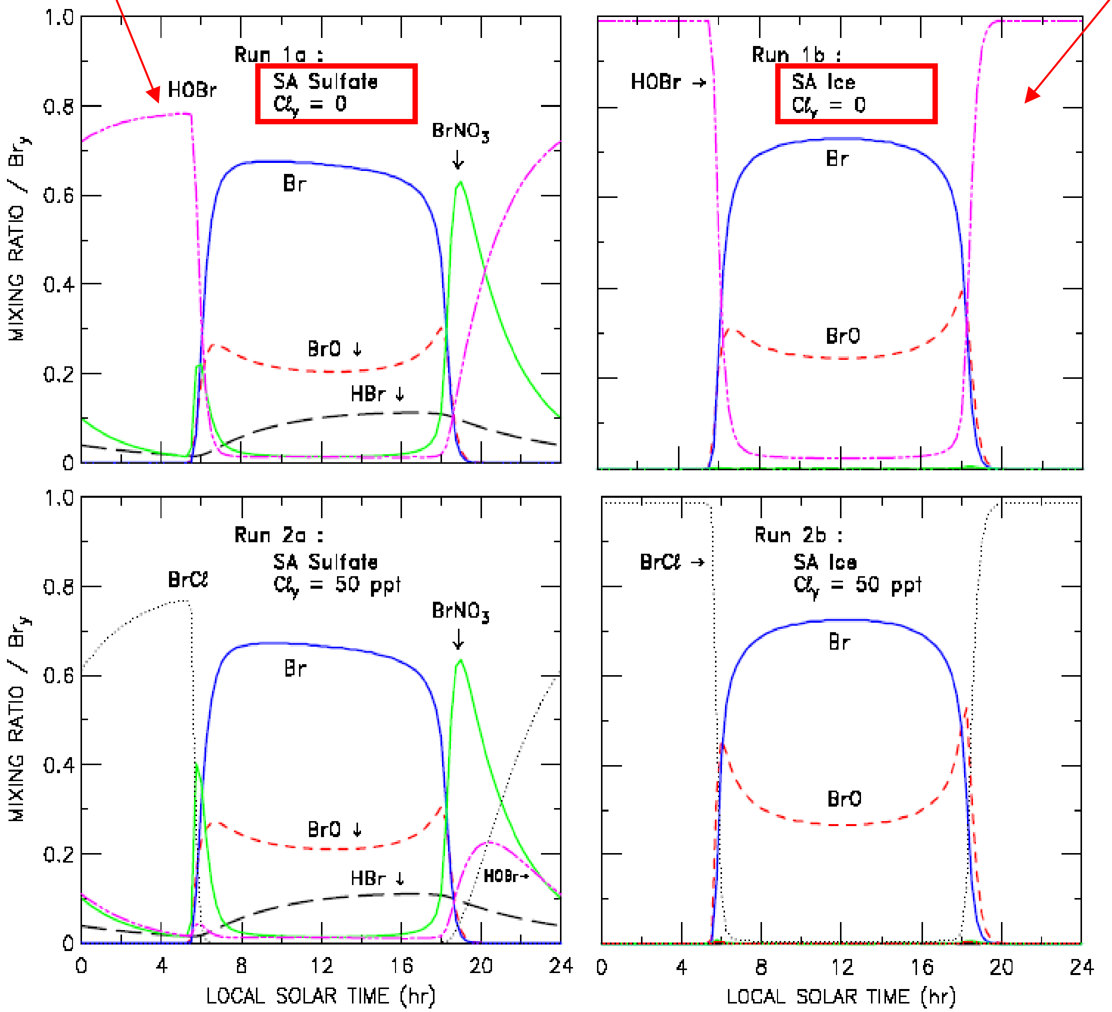
3. Dawn dusk flights

BrCl expected to be primary nighttime reservoir of Br_y in presence of 50 to 100 ppt of Cl_y



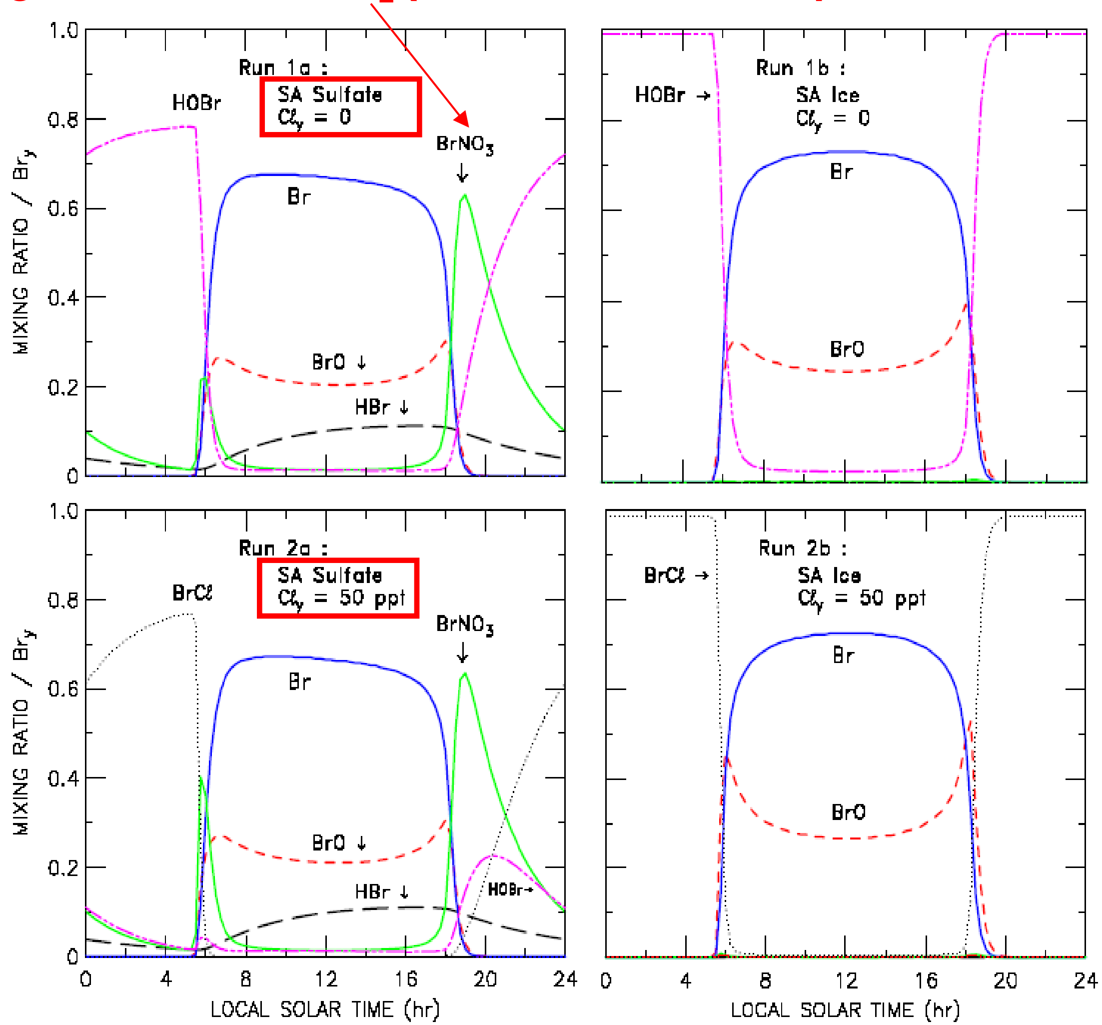
3. Dawn dusk flights

Ability to measure HOBr could be useful for constraining Br_y (but only if Cl_y << 50 ppt)



3. Dawn dusk flights

d(BrO)/dt & d(NO_2)/dt across evening terminator will provide constraint on the partitioning of BrO & $BrONO_2$ (unless ice drives rapid formation of HOBr)



3. Dawn dusk flights

d(BrO)/dt & d(NO_2)/dt across evening terminator will provide constraint on the partitioning of BrO & $BrONO_2$ (unless ice drives rapid formation of HOBr)

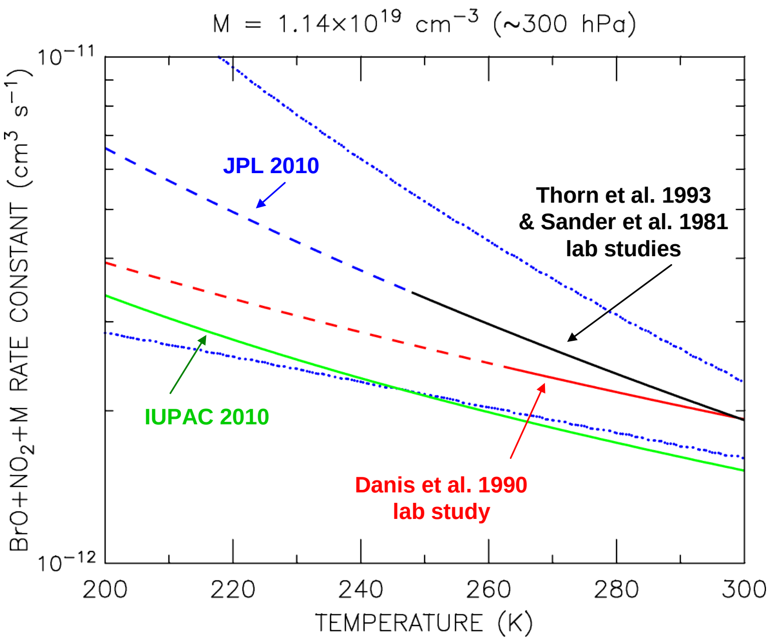
Kreycy et al., ACP, 2013:

> **Abstract.** We report on time-dependent O_3, NO_2 and BrO profiles measured by limb observations of scattered skylight in the stratosphere over Kiruna (67.9° N, 22.1° E) on 7 and 8 September 2009 during the autumn circulation turn-over. The observations are complemented by simultaneous direct solar occultation measurements around sunset and sunrise performed aboard the same stratospheric balloon payload. Supporting radiative transfer and photochemical modelling indicate that the measurements can be used to constrain the ratio $J(BrONO_2)/k_{BrO+NO_2}$, for which at $T = 220 \pm 5$ K an overall 1.7(+0.4 − 0.2) larger ratio is found than recommended by the most recent Jet Propulsion Laboratory (JPL) compilation (Sander et al., 2011).

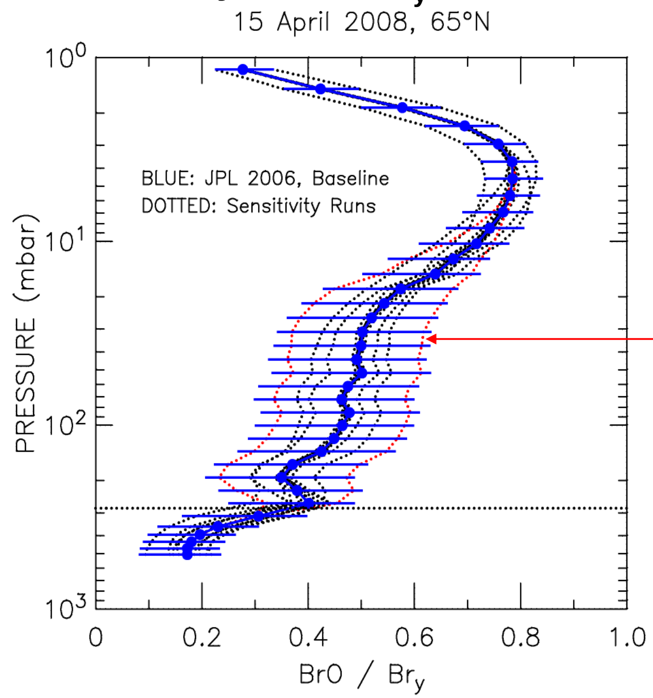
3. Dawn dusk flights

d(BrO)/dt & d(NO_2)/dt across evening terminator will provide constraint on the partitioning of BrO & $BrONO_2$ (unless ice drives rapid formation of HOBr)

$k_{BrO+NO2+M}$ is also uncertain



Uncertainty in $k_{BrO+NO2+M}$ largest contribution t uncertainty in BrO/Br_y



Reactions considered:

- $Br+HO_2$
- $Br+O_3$
- BrO+NO
- $BrO+NO_2$
- $Br+H_2CO$
- J_{BrNO3}
- J_{HOBr}

3. Dawn dusk flights

d(BrO)/dt & d(NO_2)/dt across evening terminator will provide constraint on the partitioning of BrO & $BrONO_2$ (unless ice drives rapid formation of HOBr)

Sunset measurements of BrO, NO_2, & O_3, if executed properly, could add to the long legacy of evaluating atmospheric photochemical mechanisms:

- Salawitch et al. (GRL, 1994) for $J_{O3 \rightarrow O(1D)}$
- Stimple et al. (JGR, 1994) for J_{ClONO2}
- Lary et al. (JGR, 1996) for J_{HOBr}
- Gao et al. (JGR, 2001) for J_{NO2}
- Salawitch et al. (GRL, 2002) for near-IR photolysis of HO_2NO_2
- Stimpfle et al. (JGR, 2003) for J_{ClOOCl}

IT TAKES A VILLAGE

CONTRAST GV Payload

Observation	Instrument	Investigator	Meas. Synergy
O_3	Fast O_3	Weinheimer, Campos, Flocke	GH, BAe
H_2O Vapor	VCSEL	RAF	GH, BAe
CO	ACD (VUV)	Campos	GH, BAe
CH_4	ACD (Picarro)	Flocke	GH, BAe
CO_2	ACD (Picarro)	Flocke	GH, BAe
NO, NO_2	ACD (Chemiluminescence)	Weinheimer, Campos, Flocke	BAe
BrO, HOBr, BrCl, Br_2 (in situ)	CIMS	Huey	BAe
BrO, IO, H_2CO (remote)	CU-AMAX (DOAS)	Volkamer	GH
NMHC, short lived tracers, HCFCs, halocarbons	AWAS	Atlas	GH, BAe
VOCs, NMHCs, OVOCs, halocarbons, etc #	TOGA	Apel, Riemer	None
Aerosol (number, size, distribution)	UHSAS	RAF or Dave Rodgers	None
Cloud detection (in situ)	CDP, 2D-C	RAF or Al Cooper	GH (remote)
Microwave Temperature Profiler	MTP	Haggerty	GH
Radiation (UV/VIS)	HARP	Hall	GH, BAe

TOGA is capable of measuring:

Hydrocarbons: Propane, 1-Butene, i-Butene, Butane, i-Butane, Benzene, Tolouene, Ethyl Benzene, t-2-Butene, c-2-Butene, Pentane, 1,3-Butadiene, Limonene, **Isoprene**, t-2-Pentene, c-2-Pentene, i-Pentane, o-Xylene, m/p-Xylene, 1,3,5-Trimethylbenzene, 1,2,4-Trimethylbenzene, α-Pinene, β-Pinene, Camphene, Myrcene

Oxygenates: Acetaldehyde, Propanal, Butanal, Pentanal, Methacrolein, Methyl Vinyl Ketone, Methyl Butenol, Methanol, Ethanol, Acetone, Butanone, 2-Pentanone, 3-Pentanone, Methyl t-Butyl Ether

Halocarbons: $CHCl_3$, CH_2Cl_2, CH_3Cl, CH_3Br, CH_2Cl_4, C_2Cl_4, CCl_4, CFC-113, HCFC-141b, HCFC-134a, $C_2H_4Cl_2$, CH_3I

N & S compounds: CH_3CN, DMS

CAST BAe-146 Payload

Parameter	Instrument	Performance	Institution
Ozone	TE49C	1 minute integration time, 1ppb detection limit (dl)	FAAM
Water vapour	General Eastern 1011 & Buck CR2		FAAM
Carbon Monoxide	Aerolaser 5002	1 minute integration time, 2 ppb dl	FAAM
Nitrogen oxides	Air Quality Designs	1 Hz, dl is 10 pptv for NO and 20 pptv for NO_2	FAAM + York
VSL Halocarbons: $CHBr_3$, CH_2Br_2, $CHBr_2Cl$, CH_3I, CH_2BrCl, $CHBrCl_2$, C_2H_5I, CH_2ICl, CH_2IBr, CH_2I_2, CH_2Cl_2, $CHCl_3$	In situ Agilent GC-MS with Markes dual TD	3-4 min sampling *in situ*, 2-3 min via WAS bottles < 0.01-0.05 ppt dl.	York
Whole Air Samples NMHC (C_1-C_6), small OVOCs, DMS	Perkin Elmer GC-FID (WAS bottles, ~2-3 min sampling)	2-3 min sampling. 2.5, 1 pptv dl for C_2-C_4 and >C_4 respectively	York
CO_2, CH_4	Los Gatos	5 sec integration precision $\pm\sigma$ CH_4, 1.0 ppb; CO_2, 200 ppb. Max rate 10 Hz.	FAAM + Manchester
N_2O, H_2O	Aerodyne QCLAS	N_2O precision @ 1 Hz $\pm 1\sigma$, 0.2 ppbv. Max sampling rate 20 Hz.	Manchester
BrO	CIMS	2.6 pptv $\pm 3\sigma$ @ 4 s integration	Manchester
Black Carbon	SP2	Black carbon mass size distribution, 1 Hz	Manchester

ATTREX GH Payload

Acronym	Weight (lb)	Power (W)	Measurement	Sampling Rate	Precision	Accuracy
CPL	366		Aerosol/Cloud Backscatter	1 Hz	10-15% backscatter	15-25% extinction
O_3	40	200	O_3	2 Hz	1.5×10^{10} molecules cm^{-3}	5% + precision
AWAS	200	300	~60 tracers with lifetimes of 1 week to years	80 samples per flight	Various, typically 1-10%	Various, typically 2-20%
UCATS	60	250 (450)[a]	O_3	10 s	> 1 ppb or 2%	> 2 ppb or 3%
			H_2O	1 s	2-3%	3-5%
			CH_4	140 s	0.4-0.8%	1%
			N_2O	70 s	0.2-0.5%	1%
			CO	140 s	2-5%	1%
			H_2	140 s	2-3%	1%
			CFC-11*	70 s	0.3-0.6%	1%
			CFC-12*	70 s	0.3-0.6%	1%
			Halon-1211*	70 s	0.5-0.8%	1%
			SF_6	70 s	0.2-0.5%	1%
PCRS	45	370	CO_2	5 s	200 ppbv	150 ppbv
			CO	5 min	3 ppbv	15 ppbv
			CH_4	5 s	2 ppbv	1 ppbv
ULH	24	260	H_2O vapor	1-40 Hz	> 0.05 ppmv or 1%	10%
DLH	50	280	H_2O vapor	100 Hz	1% or 50 ppbv	10%
Hawkeye	135	3200	Ice crystal size distributions, habits	1 Hz	20%	50%
SSFR	40		Radiative Fluxes	20 Hz	0.1%	3%
MMS	65	135	Temperature	20 Hz	0.01 K	0.3 K
			Pressure	20 Hz	0.1 mbar	0.3 mbar
			Horizontal wind	20 Hz	0.01 m/s	1 m/s
			Vertical wind	20 Hz	0.01 m/s	0.1 m/s
MTP	24	51	Temperature Profile	1 prof/15 s	<1 K	<0.05 K
Mini-DOAS	33	28	BrO	50 s	0.9 pptv	8%
			O_3		80 ppbv	2%
			NO_2		20 pptv	5%
			OClO		4.5 pptv	12%
			IO		0.4 pptv	25%
			OIO		0.4 pptv	55%