Chemical Forecasting will be beneficial for the successful achievement of numerous objectives:

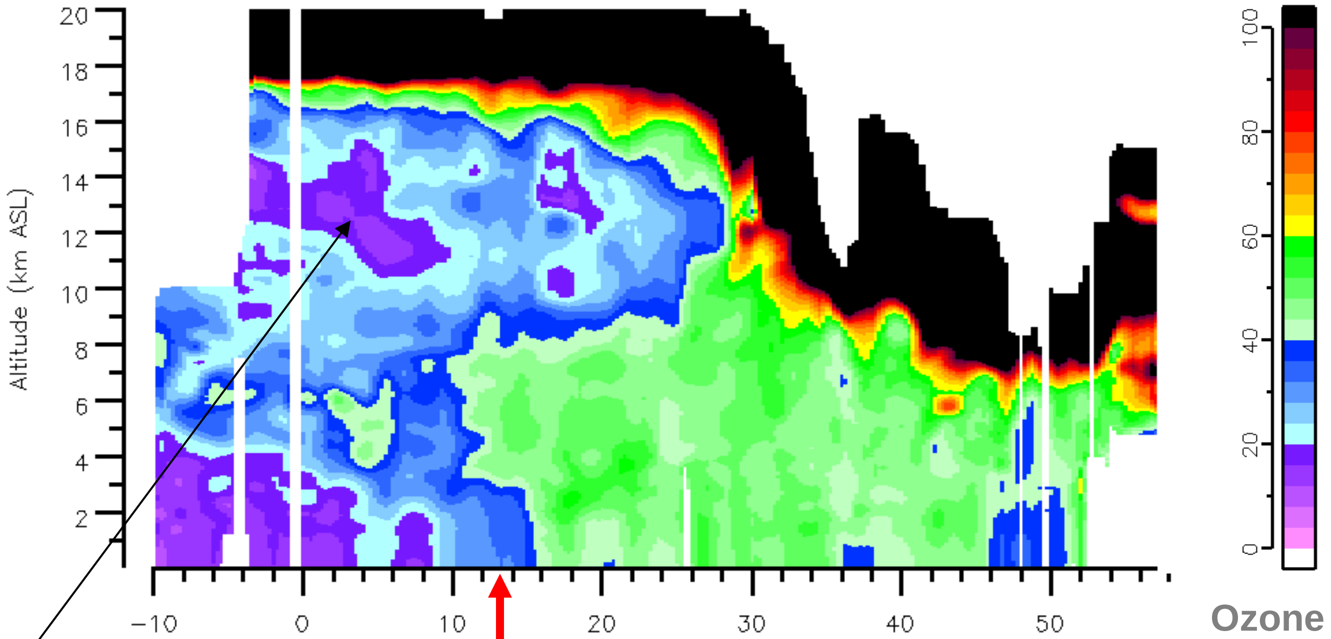
1) Abundance of VSLs normally removed by reaction w/ OH at level of main convective outflow
2) Bromine budget: PGI & SGI
3) Provide measurements for assessing OH fields within CCMs, such as O_3, H_2O, CH_4, CO, isoprene, formaldehdye, radiative flux in UV/Vis, etc
4) Provide observational constraint on transport pathways from the ocean surface to the stratosphere, via ***coordinated flights*** with CAST and ATTREX

Chemical Forecasts and Field Modeling

Ross Salawitch, Dan Anderson, Elliot Atlas, John Bergman,
Rafael Fernandez-Cullen, Tom Hanisco, Neil Harris,
Cameron Homeyer, Shawn Honomichl, Doug Kinnison,
Jean-Francois Lamarque, Qing Liang, Julie Nicely,
Laura Pan, Alfonso Saiz-Lopez, Simone Tilmes, Glenn Wolfe
and many others ☺

22 Oct 2013

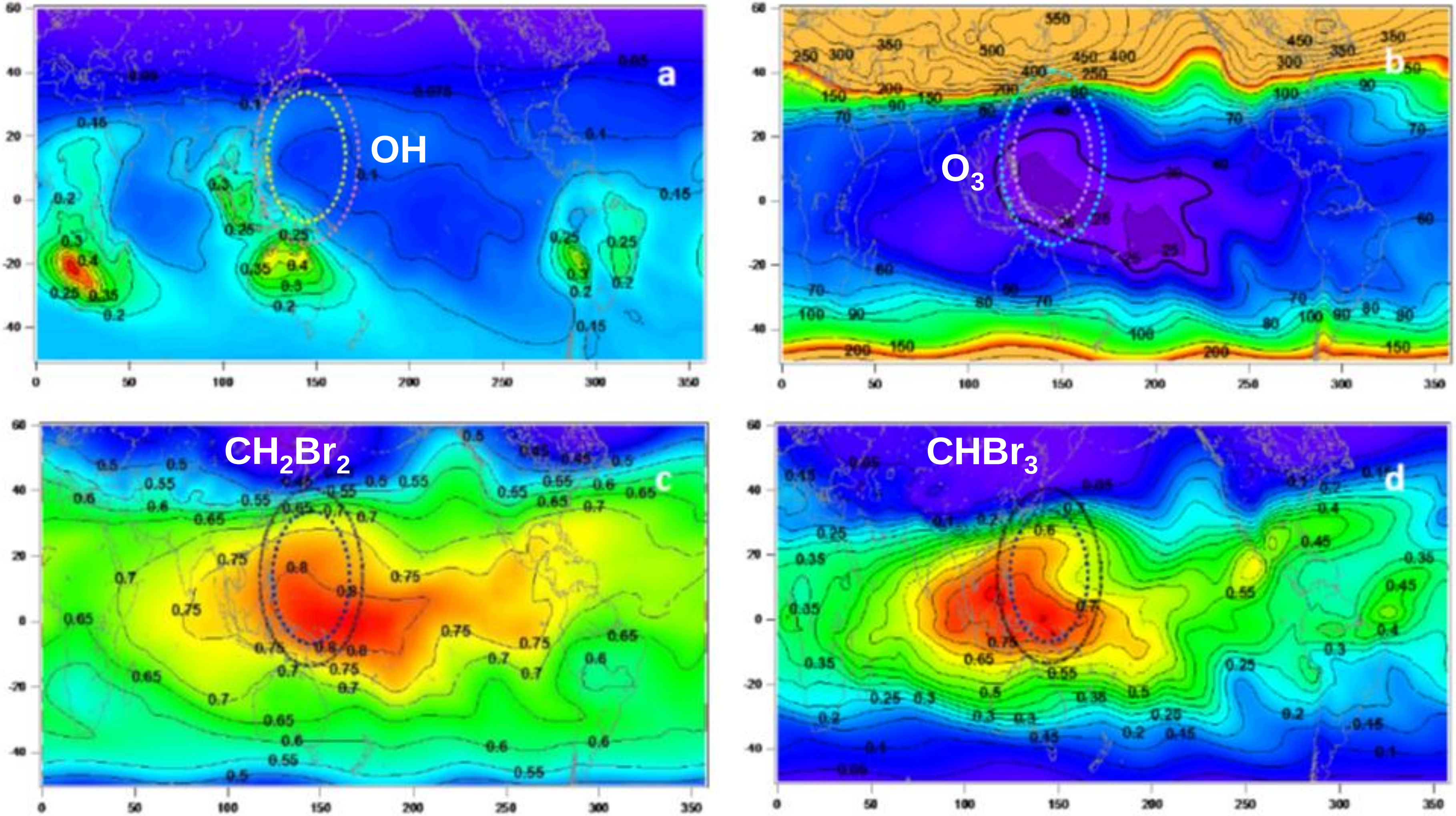
PEM WEST O_3, Western Pacific: Feb 1994, along ~140°E



We'd like forecasts of these low O_3 airmass

Guam

Crawford et al., 1997, Newell et al., 1997



As well as fields such as OH, CH_2Br_2, and $CHBr_3$

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

Source: Doug Kinnison

NCAR CESM CAM-CHEM

- Global Chemistry-Climate Model
- 1.9° (lat) x 2.5° (lon) horizontal resolution
- 26 vertical levels (surface to ~ 4 hPa)

Lamarque et al., *Geosci. Mod. Dev.*, 2012

Tropospheric Halogen Chemistry

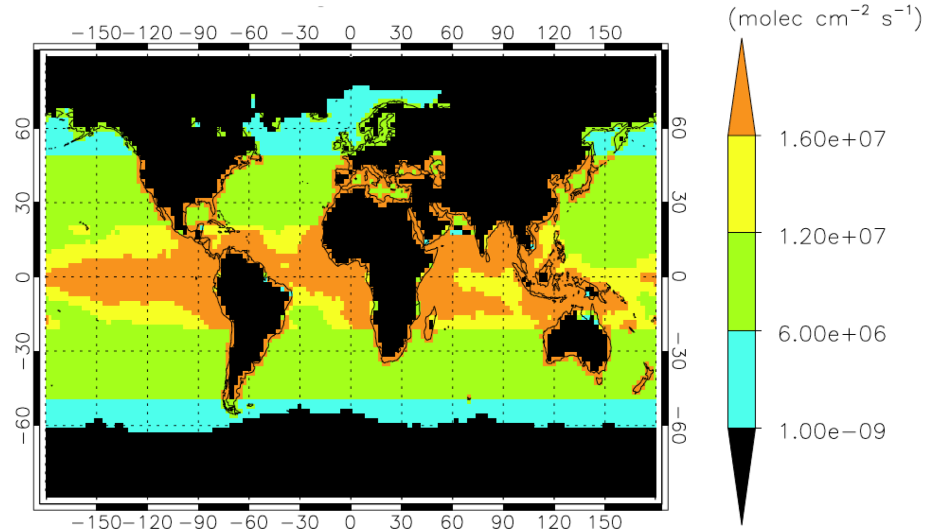
Halogenated sources from the ocean.

- Emissions following Chl-a over tropics
- Catalytic release from sea-salt
- Do NOT have polar emission processes

Chemical Processes

- Photochemistry (Cl, Br, and I)
- Dry / wet deposition
- 9 Additional vsl Organic species included.
- 160 species, 427 reactions

$CHBr_3$ Flux in CAM-Chem



Source gas	Global annual flux (Gg yr^{-1})		Lifetime (this study)
	This study	Literature	
$CHBr_3$	533	400[a], 595[b], 448[d]	17 days
CH_2Br_2	67.3	113[c], 62[d]	130 days
CH_2BrCl	10.0	6.8[c]	145 days
$CHBr_2Cl$	19.7	23[c]	56 days
$CHBrCl_2$	22.6	16[c]	46 days
CH_3Br*	climatology	131[c]	1.6 yr[g]
CH_3I**	303	304[e]	5 days
CH_2ICl	234	236[f]	8 h
CH_2IBr	87.3	87[f]	2.5 h
CH_2I_2	116	116[f]	7 min

Total Bromine: 632 Gg Br yr^{-1}
Total Iodine: 600 Gg I yr^{-1}

Ordoñez et al., ACP, 2012

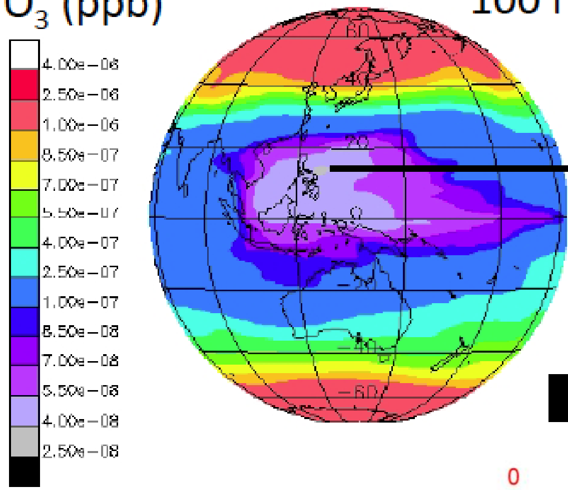
CONTRAST

Guam, Jan–Feb 2014

Source: Doug Kinnison

O_3 (ppb)

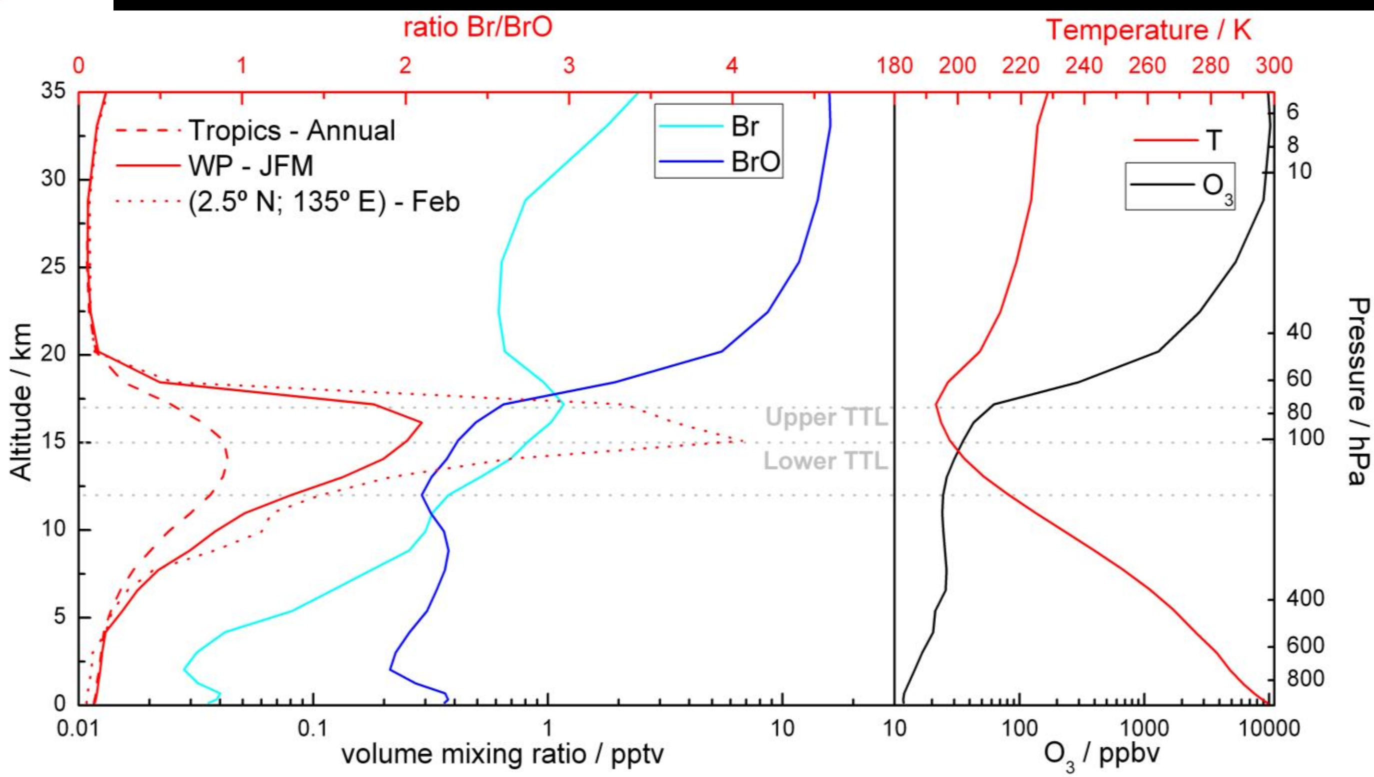
100 hPa, DJF



For the range of Temp in the TTL:

O_3 threshold below which Br>BrO is ~60 ppbv

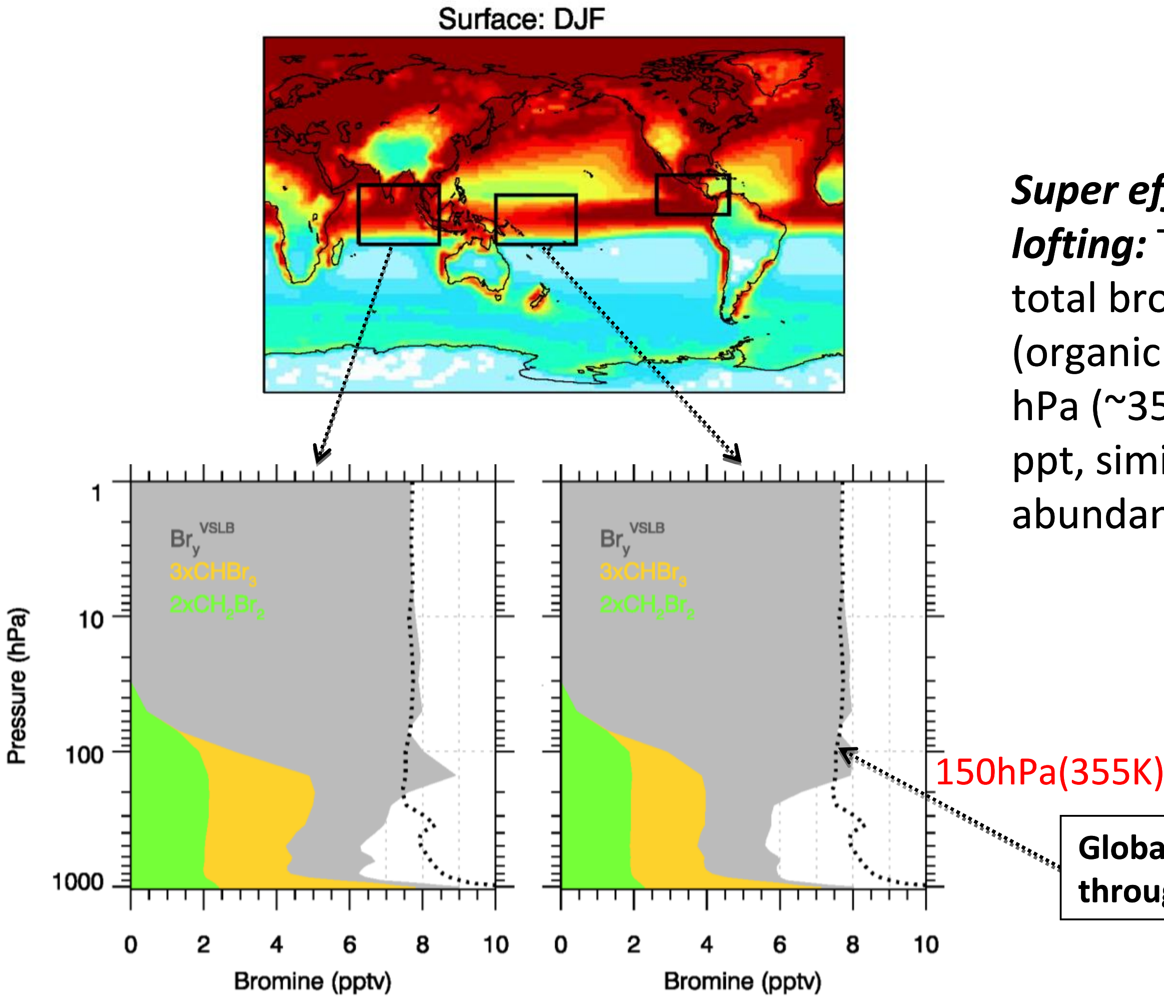
[redacted]



Source: Qing Liang

Prior obs & modeling: SGI (source gas injection) of Br_y is probably 5 to 7 ppt

Prior obs & modeling: PGI (product gas injection) of Br_y highly uncertain: depends on efficiency of aerosol uptake and washout versus het chem release of labile bromine and strength of convection (Q. Liang talk)

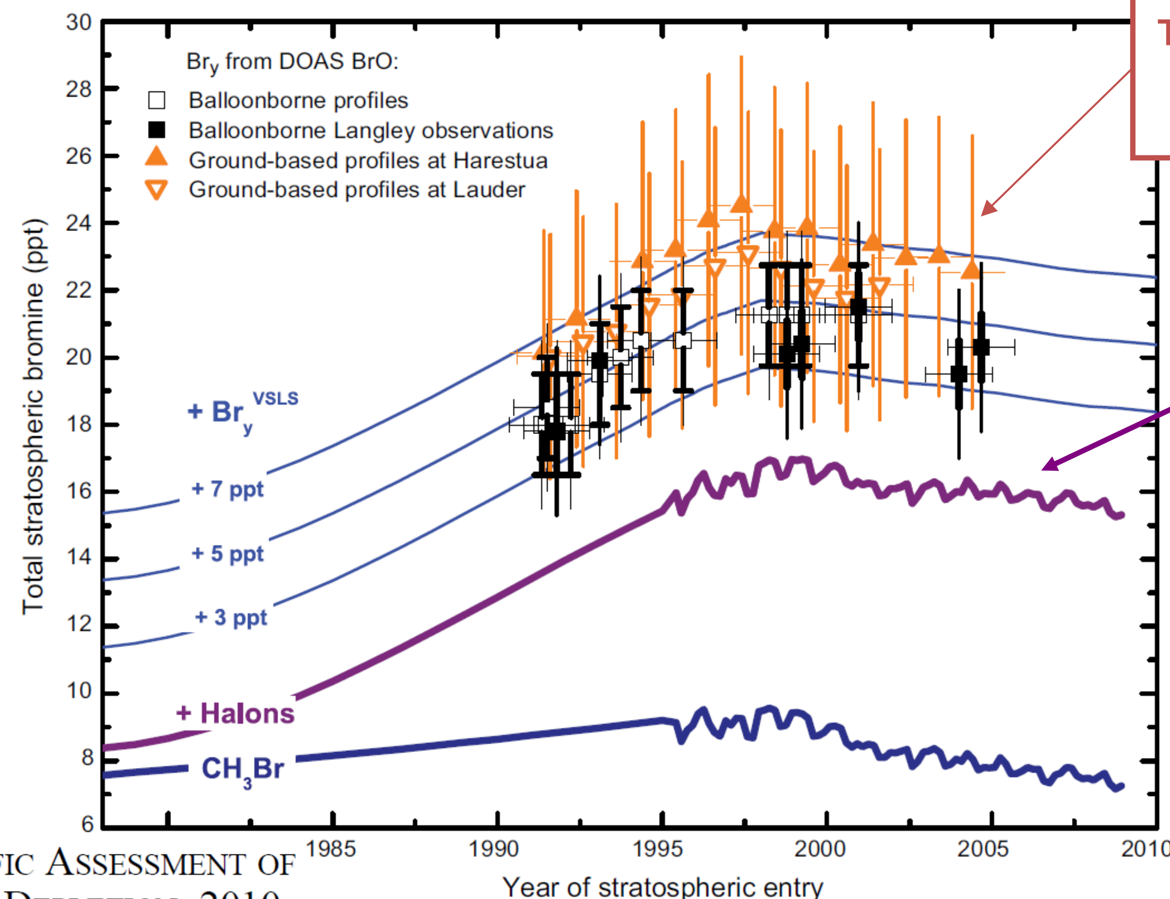


Super efficient convective lofting: The mixing ratio of total bromine from VSLB (organic + inorganic) at 150 hPa (~355K) is about 8.0 - 8.5 ppt, similar to the surface abundance.

Global Mean Br_y^{VSLB} ~ 7.7 ppt throughout stratosphere.

Prior obs & modeling: SGI (source gas injection) of Br_y is probably 5 to 7 ppt

Prior obs & modeling: PGI (product gas injection) of Br_y highly uncertain: depends on efficiency of aerosol uptake and washout versus het chem release of labile bromine and strength of convection (Q. Liang talk)



Data points:
Total Product Gas Abundance Based on BrO in the Upper Stratosphere

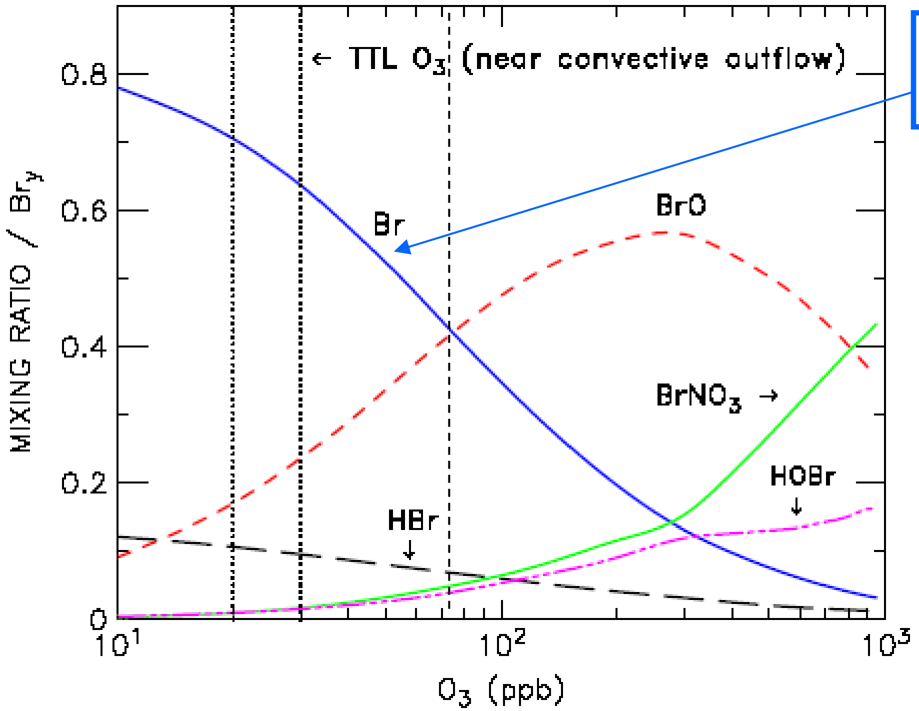
Total Long Lived Source Gas Abundance, Surface Observations (!)

Figure 1-21

SCIENTIFIC ASSESSMENT OF OZONE DEPLETION: 2010

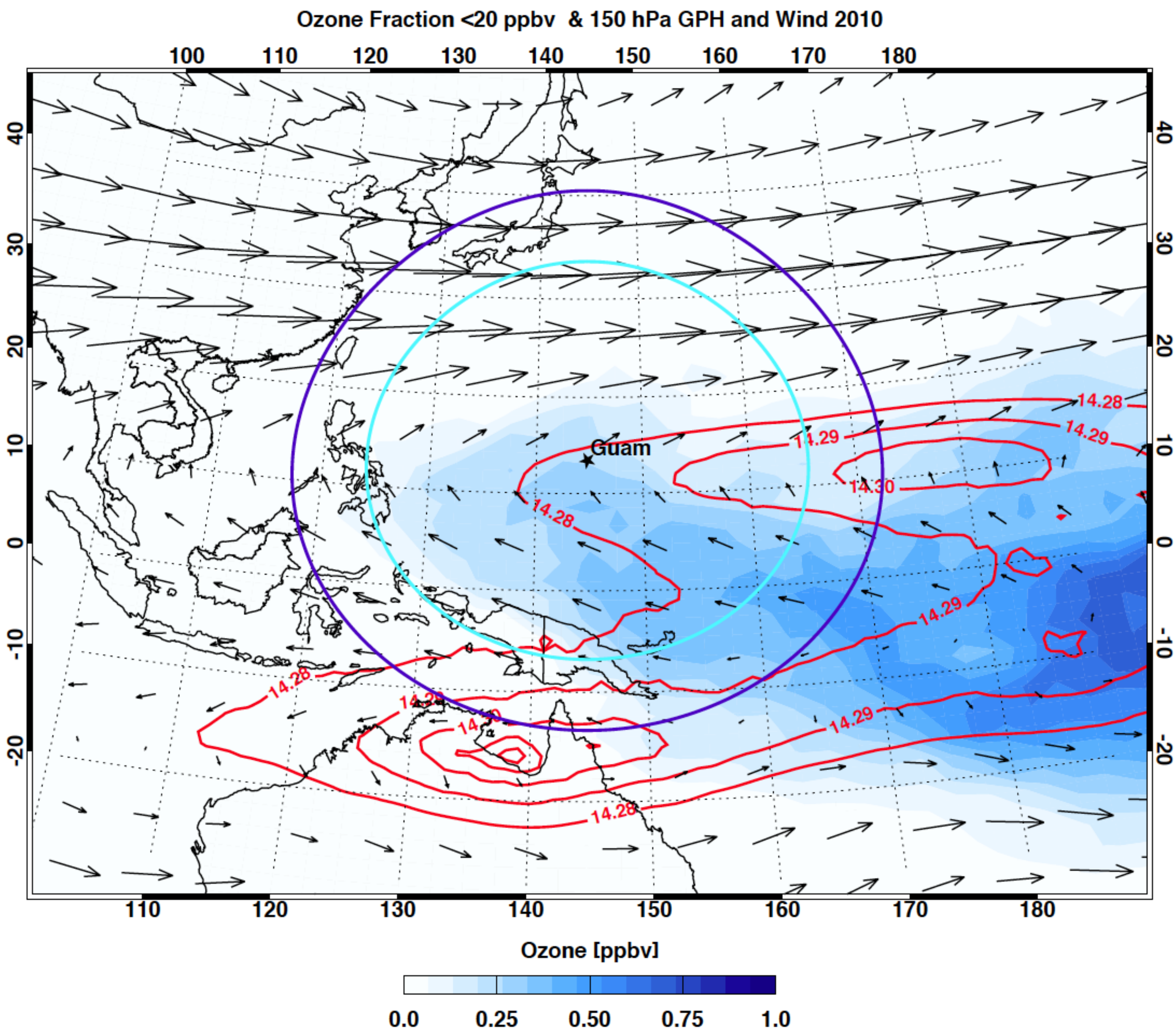
Prior obs & modeling: SGI (source gas injection) of Br_y is probably 5 to 7 ppt

Prior obs & modeling: PGI (product gas injection) of Br_y highly uncertain: depends on efficiency of aerosol uptake and washout versus het chem release of labile bromine and strength of convection (Q. Liang talk)



Br + HCHO is route out of Br-reservoir for low O_3 conditions

Source: Doug Kinnison & Shawn Honomichl



The Plan:

- NCAR CESM CAM-CHEM forecast simulations to occur in Boulder
- 3 day forecasts will be available every ~24 hrs using GEOS5 met fields
- forecasting will begin with ferry flights
- domain-wide plots to be generated via script
- curtain plots along candidate flight trajectories possible: probably implemented by folks in Guam providing ASCII file with flight coordinates to server in Boulder, with plots generated in Boulder
- at this time we are not planning to transfer model files to Guam
- besides O_3, we intend to examine fields of:
  - H_2O, CH_4, CO
  - 10 VSLs listed on slide 5 plus a few select ratios
  - OH, HO_2, HCHO, NO, NO_2, BrO, Br/BrO, IO (daytime active species)
  - HBr, HOBr, $BrNO_3$, BrCl (dawn/dusk flights)

All numbers units of days

		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	50	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 *<u>OH loss will decline</u>*

A forecast of ratio of halocarbons lost mainly by photolysis to other halocarbons lost mainly by reaction with OH may be helpful for diagnosing the "OH hole"

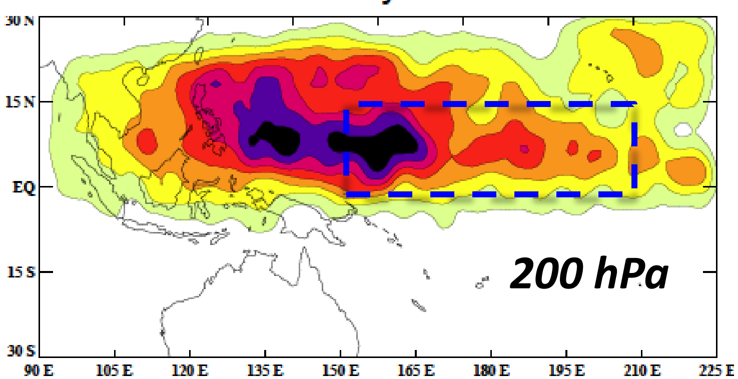
Action Item: Kinnison & Salawitch to assess what ratios to be cataloged

Source: John Bergman & Laura Pan

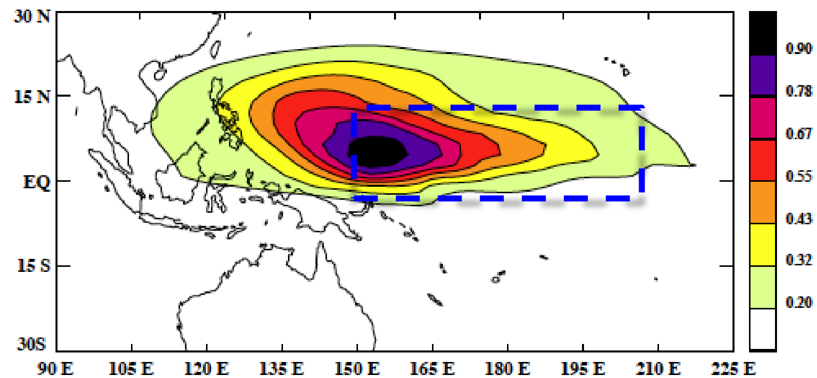
Convective influence from both trajectory models and SD-CAM

NW Pacific

ECMWF trajectories



SD-CAM Tracers



Access to MBL origin plots (John Bergman's product) will be extremely helpful for flight planning as well as near real time data interpretation

A chemical modeler's / co-mission scientist wish list ☺

Class 1	**O_3**
Class 2	**CO, H_2O & CH_4** **CH_2Br_2, $CHBr_3$, CH_3I, etc** **NO_x, OH, HO_2, HCHO**
Class 3	**BrO, BrO/Br_y, IO : daytime flights** **HBr, HOBr, $BrNO_3$, BrCl : dawn/dusk flights** **Non-methane precursors of HO_x & HCHO (H_2O_2, acetone, isoprene, ethane, etc)**

Class 1 ⇨ as many vetted models as possible

Class 2 ⇨ multiple models very helpful

Class 3 ⇨ at least one model

Near Real Time TOMCAT/SLIMCAT Model Simulations

Hannah Mantle, Ryan Hossaini, Martyn Chipperfield

University of Leeds, UK

- Forced by ECMWF operational analyses. Available within 1 day of analysis time.
- Model resolution up to e.g. 1^o x 1^o.
- Run could include 'full ' chemistry (stratosphere/troposphere).
- Can include tracers for different emission fields (e.g. 4 different $CHBr_3$ emission datasets).
- Can provide sample at stations and along flight tracks for 'first look' comparisons.

Can set up web page. See example from SHIVA campaign:
www.see.leeds.ac.uk/slimcat
http://homepages.see.leeds.ac.uk/~earrh/SHIVA_SITE/

Other possible sources of forecast information:

MACC: Monitoring atmospheric composition and climate

http://www.gmes-atmosphere.eu

Standard products: O_3, CO, NO_x, HCHO, and SO_2

Surface, 850, 500, 300, and 30 hPa

Field campaign support available upon request

http://www.gmes-atmosphere.eu/services/aqac/campaign_support

D-AQ: Total AOD, Dust, Sea-Salt, Sulphate, Black Carbon, Organic Matter

TRAQA: Dust, Black Carbon, tagged CO (South Asia, W. Europe, E. Europe N. Africa, Europe Biomass-burning)

MOZART−4 MOPITT

http://www.acd.ucar.edu/acresp/forecast

Standard products: O_3, CO, tagged CO, NO_x, and PAN

Surface, 4 km, 10 km, and column

CO tags: fires, NA, Europe, India, E. Asia

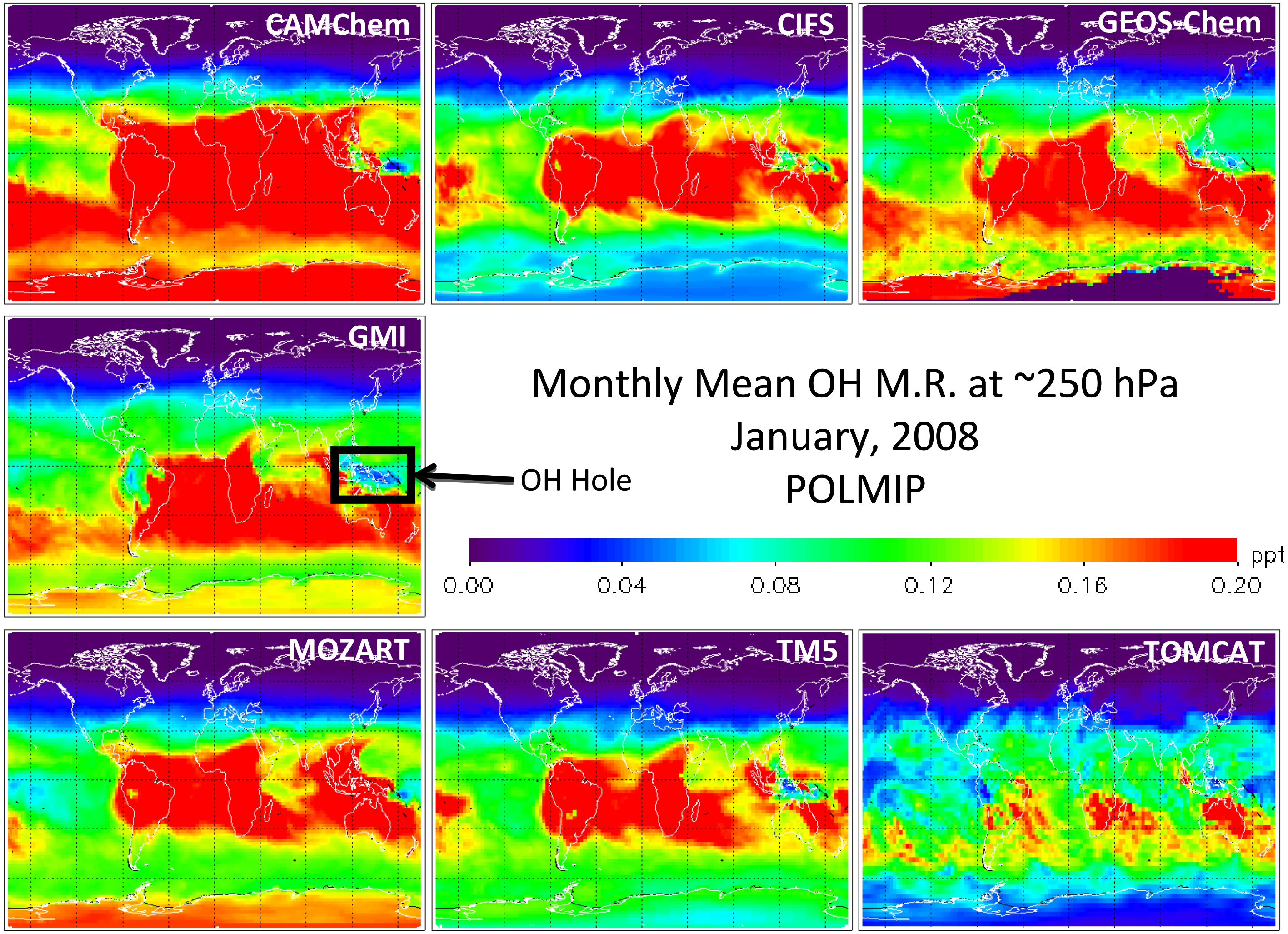
Output routinely provided on line

Tool developed for air pollution applications; the higher in altitude the more the product is influenced by climatology

CONTRAST

Guam, Jan–Feb 2014

Source: Julie Nicely



Julie Nicely's analysis of CTM fields of OH

Fields of forecast OH at different flight levels would be interesting to examine, both for flight planning and data analysis

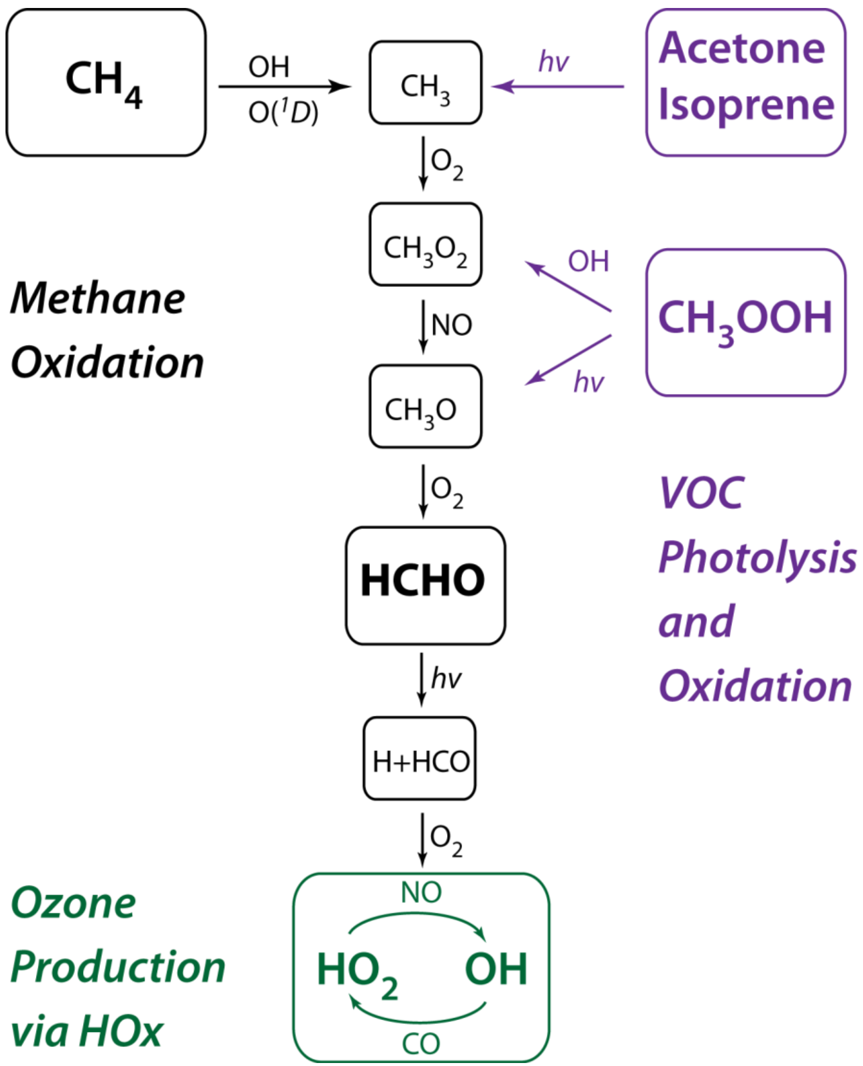
Source: Julie Nicely

Box model constraints	Box model output
p	OH and HO_2
T	H_2O_2
Overhead O_3 Column	NO_2
O_3	HCHO
CO	Acetone
H_2O	Acetaldehyde
NO	Methanol
CH_4	Ethanol
C_2H_6	Methyl vinyl ketone
C_3H_8	Methacrolein
Isoprene	Methyl butenol
$J(O^1D)$	Propanal
$J(NO_2)$	Butanal
Aerosol Surface Area Density	…

*Blue: measured on GV

Note: box model amenable to quantification of $O(^1D)+H_2O$ vs CH_4 oxidation source of HO_x

Source: Tom Hanisco and Glenn Wolfe



Comparison of modeled and measured HCHO may provide empirical constraint on role of non-methane hydrocarbon sources of HOx

Source: Tom Hanisco and Glenn Wolfe

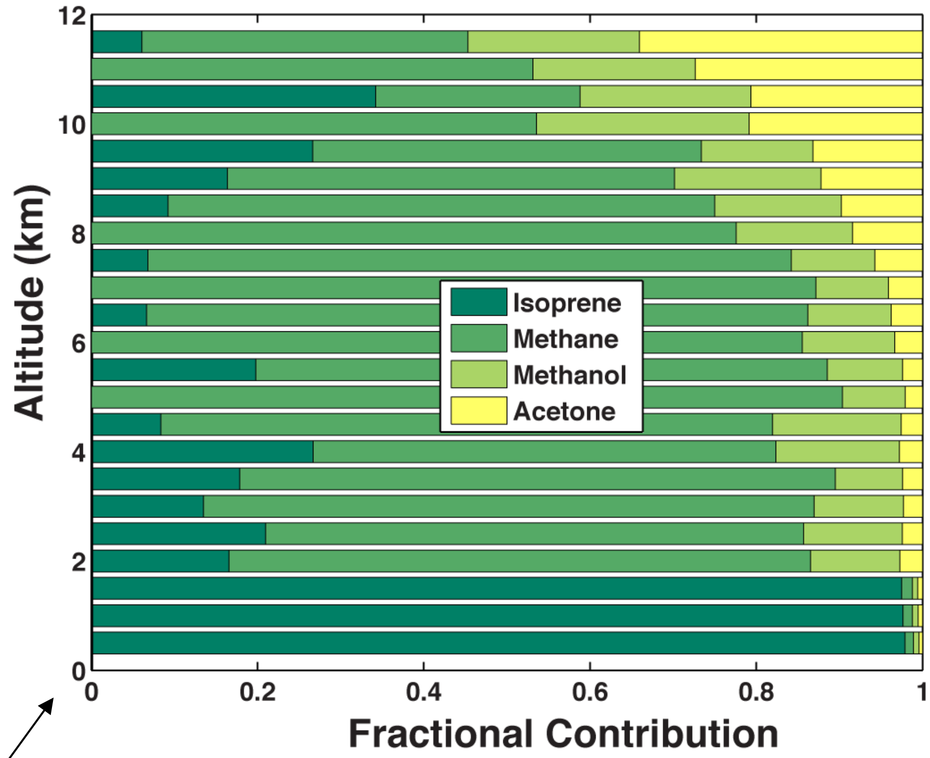
Small amounts of labile sources lead to large HCHO production.

We are sensitive to **recent** convection.

We are also susceptible to biases in source terms:

- Isoprene noise
- Acetone (VOC) offset

Can we identify loss via
Br + HCHO –> HBr + HCO ?



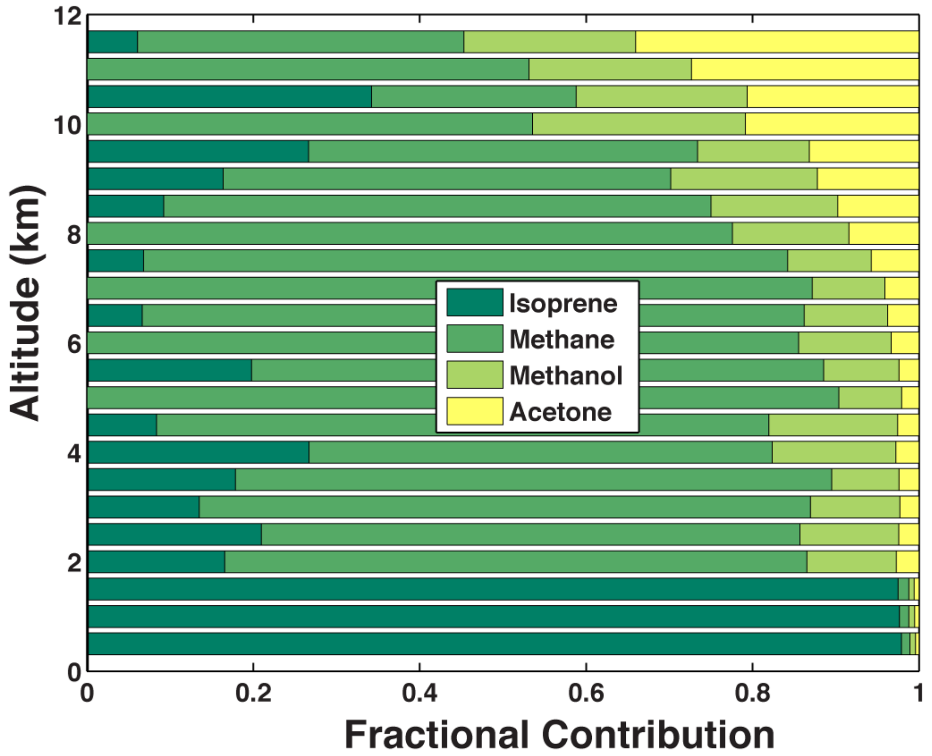
Access to plots such as this, in the field, will be helpful as a "reality check" on the global models

Source: Tom Hanisco and Glenn Wolfe

Small amounts of labile sources lead to large HCHO production.

We are sensitive to **recent** convection.

We are also susceptible to biases in source terms:
- Isoprene noise
- Acetone (VOC) offset



Can we identify loss via
Br + HCHO –> HBr + HCO ?

Would be fantastic to have an empirical, near real time estimate of [Br] based on observations of HCHO, J_{HCHO}, and the total sources of HCHO … would only be "believable" if we see unmistakable drawn down of HCHO in the presence of low O_3 and a chemical scale analysis shows loss of HCHO via rxn w/ Br occurs at comparable rate to loss by photolysis

The Plan:

- Julie & Tim will be conducting box model simulations along the GV flight track in the field, with a focus on OH
- Glen & Dan will also be conducting box model simulations along the GV track in the field, with a focus on HCHO
- box modeling by others encouraged, either during or after deployment!
- box modeling requires a suite of GV measurements as inputs
- in my prior life as stratospheric modeler, we could used tracer/tracer relations to fill in gaps until data became available
- data gaps not easily filled in the tropical troposphere: *modelers must clearly communicate to instrument team which observations are needed as input to various box models*

Concluding Thoughts

1) Mission success contingent on chemical forecasting & near real time box modeling
2) Of course post-mission modeling is also a key component of mission success ☺
3) Coordination of CONTRAST chemical forecasting with CAST and ATTREX in everyone's best interest
4) If I have overlooked or mis-represented a component of chemical forecasting or near real time box modeling, please let me know !