The contribution of Very Short-Lived Substances (VSLS) to the stratospheric halogen loading

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Scientific objectives&questions

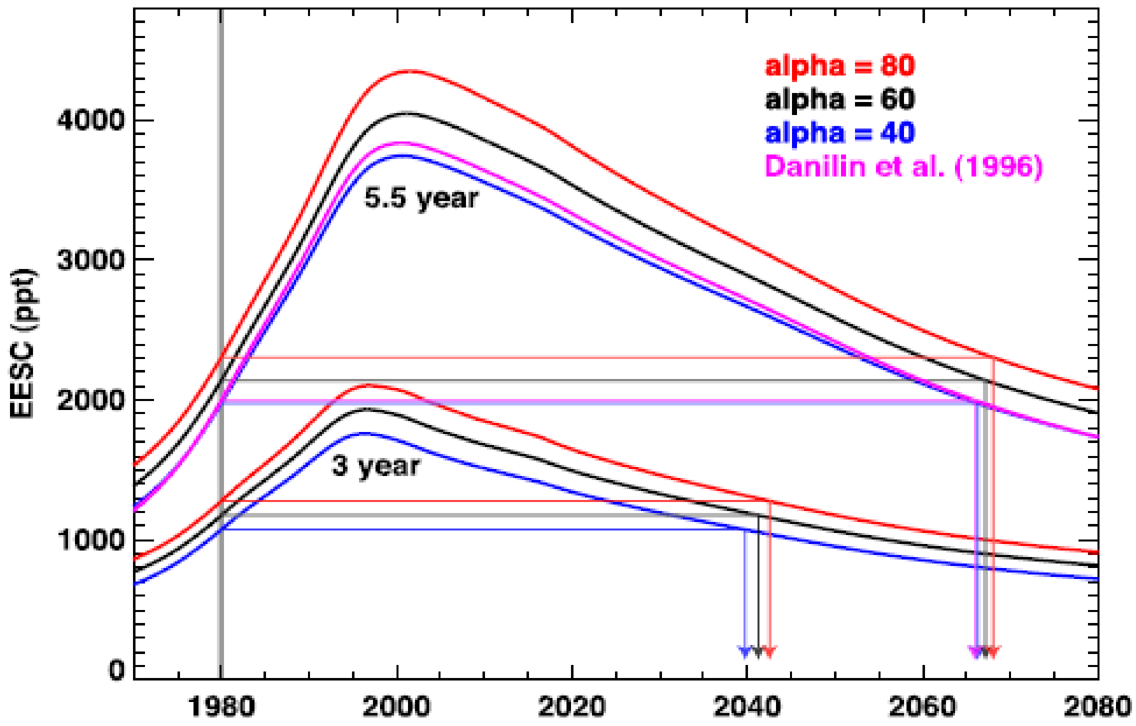
1. Contribution of halogenated molecules (SG and PG[i]), in particular of VSLS to the stratospheric halogen burden (see also WMO-UNEP 2006) (today's focus !)

2. Role of organics halogens in the pristine tropical marine boundary layer (PBL) for the
   - photochemistry of ozone
   - particle formation
   - ....

[(i)] WMO-2007 notation:
SG: source gases (CFC, HCFC, halons, CH3Br, CH3I, CHBr3, CBr2Cl2, …
PG: products gases (HCl, IO, BrO, ….
VSLS: very short lived species (lifetimes < 6 months)

Equivalent Effective Stratospheric Chlorine (EESC)

EESC calculations (e.g., Newman et al., 2007) usually ignore the contribution of VSLS to the total stratospheric halogen load under the assumption that their emission, atmospheric transport and lifetime will not change (compared to 1980) in a changing climate !



The upper and lower groups of curves are for a 5.5 and 3-yr mean age, respectively. The red, black, and blue curves are for α = 40, 60, and 80, respectively (Newman et al., ACPD, 2007). For updated α-calculations see e.g., Sinnhuber et al., ACPD 2006.

Some questions concerning VSLS

Q1: Is the assumption justified that in a changing climate the

- **emissions**
- **lifetimes**
- **atmospheric transport**

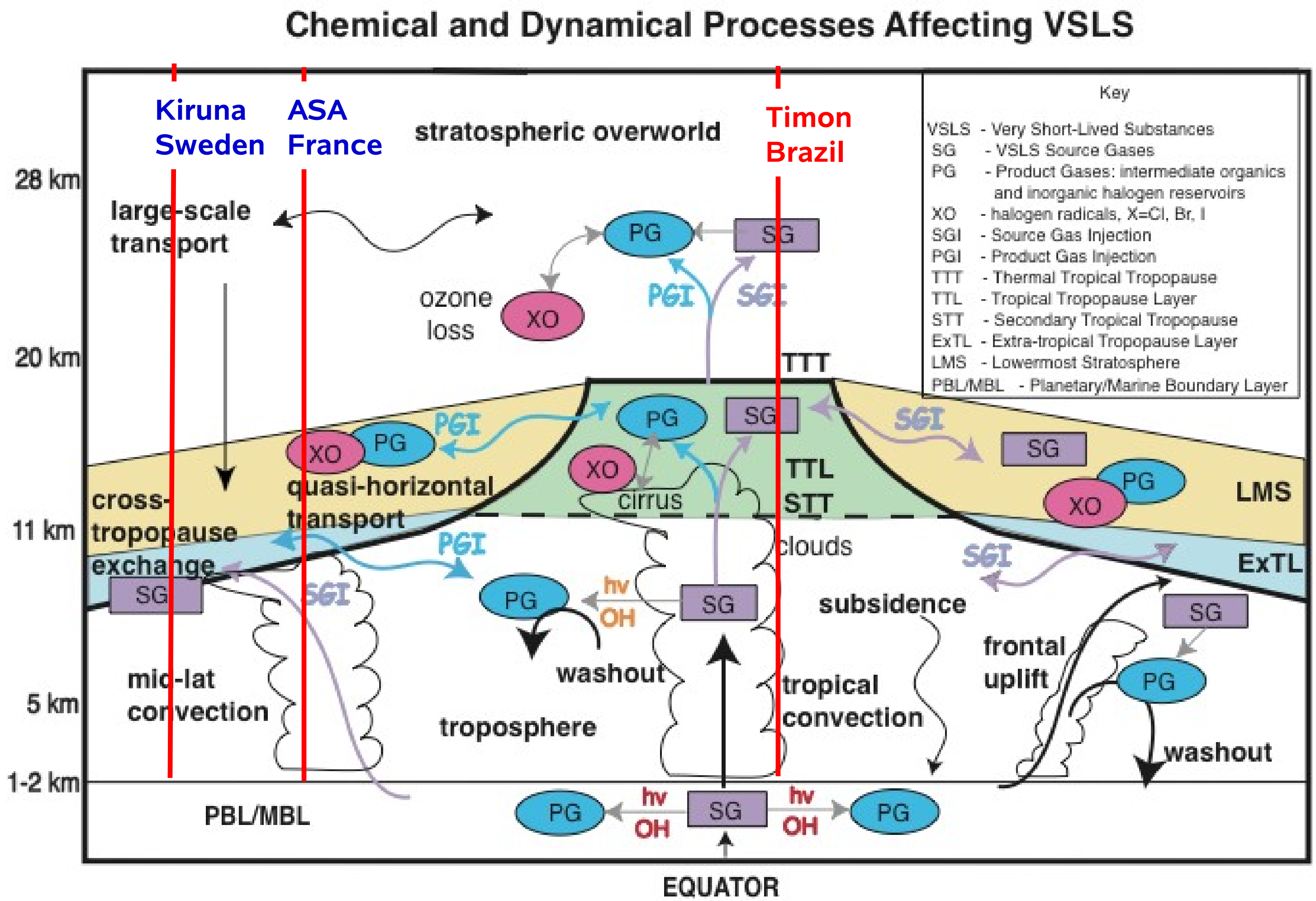
of the VSLS (and PG) will change (e.g., Salawitch 2005) ?

→ Actually we do not know the answer (still there are good pros and cons) !

Q2: What is the present contribution of VSLS to the stratospheric halogen load ? (today‘s objective)

Q3: (most important for SPARC): How will this potential change affect stratospheric ozone ?

The role of VSLS in stratospheric ozone and climate



[Fig. 2.1.3, WMO-2007]

VSL SGs from UNEP-WMO 2006

Species	Reported Tropospheric Mixing Ratio [a]	Reported 10-km Tropical Mixing Ratio [a]	Estimated Tropical [MBL] Mixing Ratio and Range	Estimated Tropical [UT] Mixing Ratio and Range	Estimated Ratio of Tropical [UT]/[MBL]	Atmospheric Source
CH_2BrCl			**0.47 (0.38-0.59)[c]**	**0.32 (0.26-0.35)[c]**	**0.7**	N
CH_2Br_2	0.8-3.4	0.6-0.9	**1.1 (0.7-1.5)[b,c,f]**	**0.9 (0.7-1.0)[b,c,e]**	**0.8**	N
$CHBr_2Cl$	0.1-0.5	0.04-0.11	**0.30 (0.06-0.76)[b,g,i]**	**0.08 (0.03-0.12)[b,c]**	**0.3**	N(A)
$CHBrCl_2$	0.12-0.6	0.04-0.11	**0.33 (0.14-0.91)[b,c,g,j]**	**0.12 (0.05-0.15)[b,c]**	**0.4**	N(A)
$CHBr_3$	0.6-3.0	0.4-0.6	**1.6 (0.5-2.4)[b,c,f,g]**	**0.37 (0.13-0.7)[b,c,e]**	**0.2**	N(A)
CH_3I	0.1-2.0	0.05-0.2	**0.8 (0.3-1.9)[b,c,f]**	**0.08 (0.02-0.18)[b,c]**	**0.1**	N N
CH_2ClI			**0.35[g]**			N
CH_2Cl_2			**17.5 (9-39)[b,c,f]**	**13.2 (9-19)[b,c,e]**	**0.75**	AN
$CHCl_3$	NH, 10-15 **12.4 (9.8-14.5)[k]** SH, 5-7 **8.0 (6.5-9.1)[k]**	3.1 ±0.7	**7.8 (5.2-13.3)[b,c,f,k]**	**6.0 (4.8-7.5)[b,c,e]**	**0.78**	A(N)
C_2HCl_3	NH, 1-5 SH, 0.01-0.1	0-0.1	**0.5 (0.05-2)[b,c,d]**	**0.14 (0.02-0.3)[b,c,d,e]**	**0.3**	AN
C_2Cl_4	NH, 5-15 **5.3 (3.3-7.3)[k]** SH, 0.7-1.5 **1.5 (1.1-1.6)[k]**	1-3	**1.8 (1.2-3.8)[b,c,f,k]**	**1.3 (0.9-1.6)[b,c,e]**	**0.7**	A
C_2H_5Cl	**NH, 2.6[l]** **SH, 1.6[l]**		**5.0 (2.7-5.9)[d]**	**1.5 (1.0-1.8)[d]**	**0.3**	AN
CH_2ClCH_2Cl	NH, 20-40 SH, 5-7	14.9 ±1.1	**3.7 (0.7-14.5)[b,c,h]**	**1.8 (0.7-3.3)[b,c,e,h]**	**0.5**	A
$COCl_2$				**22.5 (20-25)[m]**		PG
Total Cl			**81 (75-99)[n]**	**55 (52-60)[n,o]**		
Total Br			**8.4 (6.9-9.6)[n]**	**3.5 (3.1-4.0)[n]**		
Total I			**1.2 (0.7-2.3)[n]**	**0.08 (0.02-0.18)[n]**		

e.g., Pfeilsticker et al., 2000, Dorf et al., 2006
Bösch et al., 2003

Methods to identify the contribution of VSLS to stratospheric halogens

Global measurements: Global (mostly surface) measurements are of limited value to answer Q1 and Q2, since the concentration of VSLS (and PG) may strongly vary with location, time,……… !

Local measurements (today):

- at stratospheric entry level, i.e by simultaneously probing of SG and PG around the TTL/LS as a function of height, time, …
- in the middle upper stratosphere of all relevant PGs and air mass age

used data: ‚in-situ‘ balloons

- whole-air samples from Uni. Frankfurt
- HCl, $ClONO_2$ from CNRS and MIPAS-B
- BrO, IO and OIO measurements from IUP-HD

taken in the tropical TTL/LS and middle stratosphere in June 2005.

Cl_y: Profile sounding of chlorinated SGs in the tropical pipe

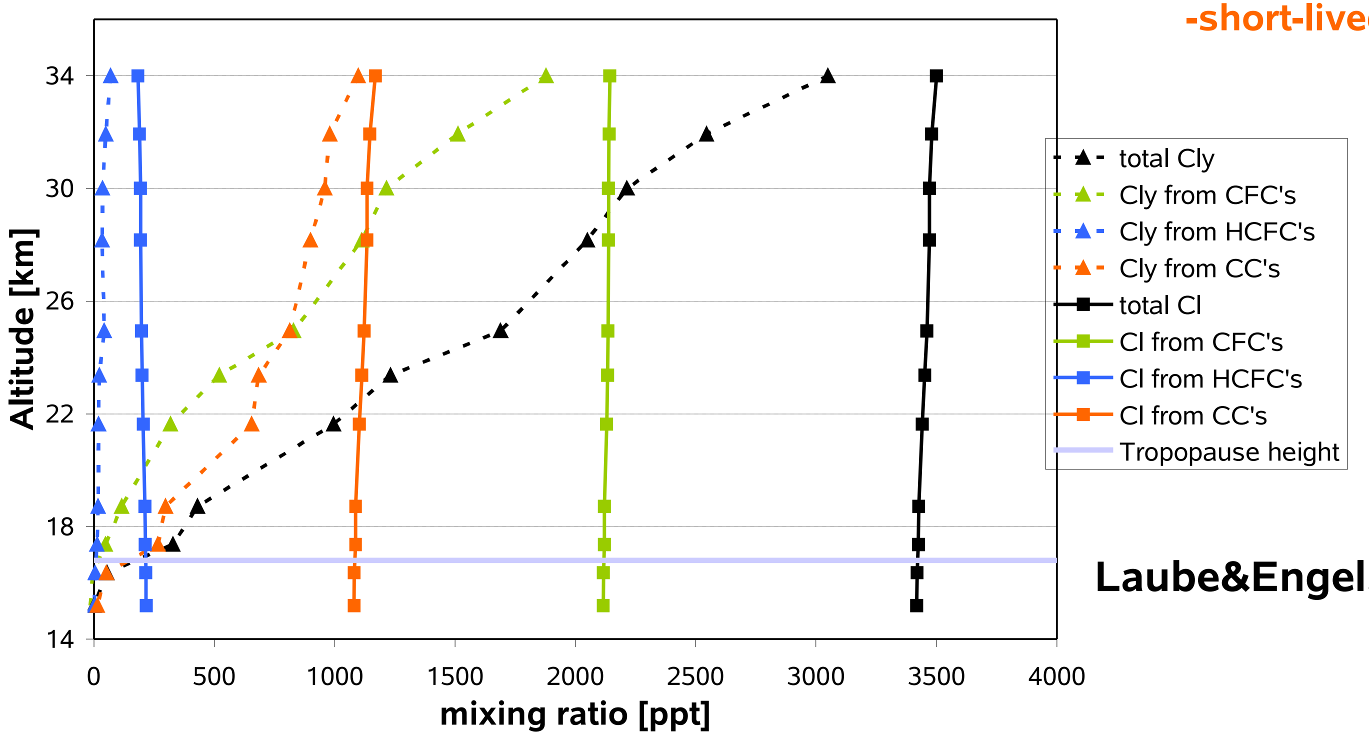
(North Eastern Brazil in 2005)

in 34 km altitude:
(4.3 years old air)

inorganic Chlorine
Cly: 3048 ppt

total available chlorine
3500 ppt

Contribution from
-long-lived CC's: 1097.7 ppt
-short-lived CC's: 34.5 ppt



Laube&Engel, Uni. Frankfurt

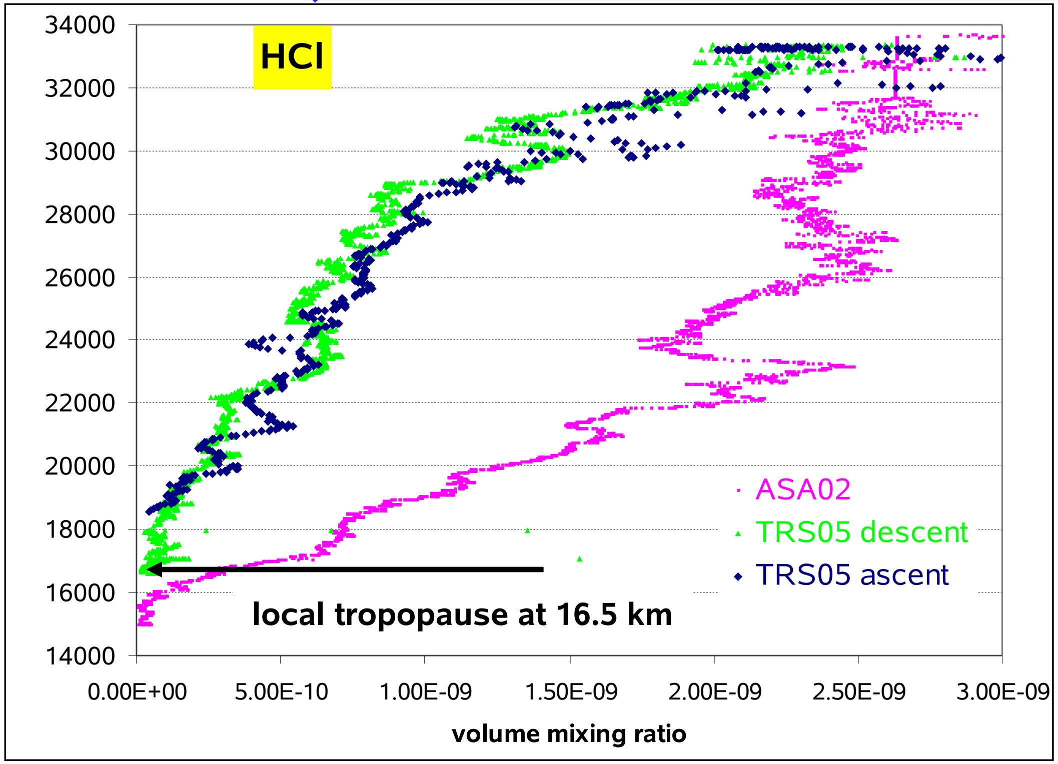
Key results (chlorinated SGs at 30 km in 4 year old air):

2. **Total chlorine: 3500 ppt**
3. **Inorganic chlorine: 3048 ppt**

→ Contribution from VSLS: 34.5 ppt (mainly from CC i.e chlorinated carbons), or ~ 1 %

Cl_y: Profile sounding of (one) chlorinated PG in the tropical pipe

(North Eastern Brazil in June 2005)



unpublished data from Catoire et al., CNRS

Key result: PGs at the tropical tropopause:

2. [HCl] = ~ 50 ppt !
3. [$ClONO_2$] < 20 ppt at 18.5 km (G. Wetzel, IMK, Karlsruhe)
4. [ClO_x] < several 10 ppt ? (F. Stroh pers. communication !)

→ Contribution from chlorinated PGs: < 100 ppt, or 3 – 4%

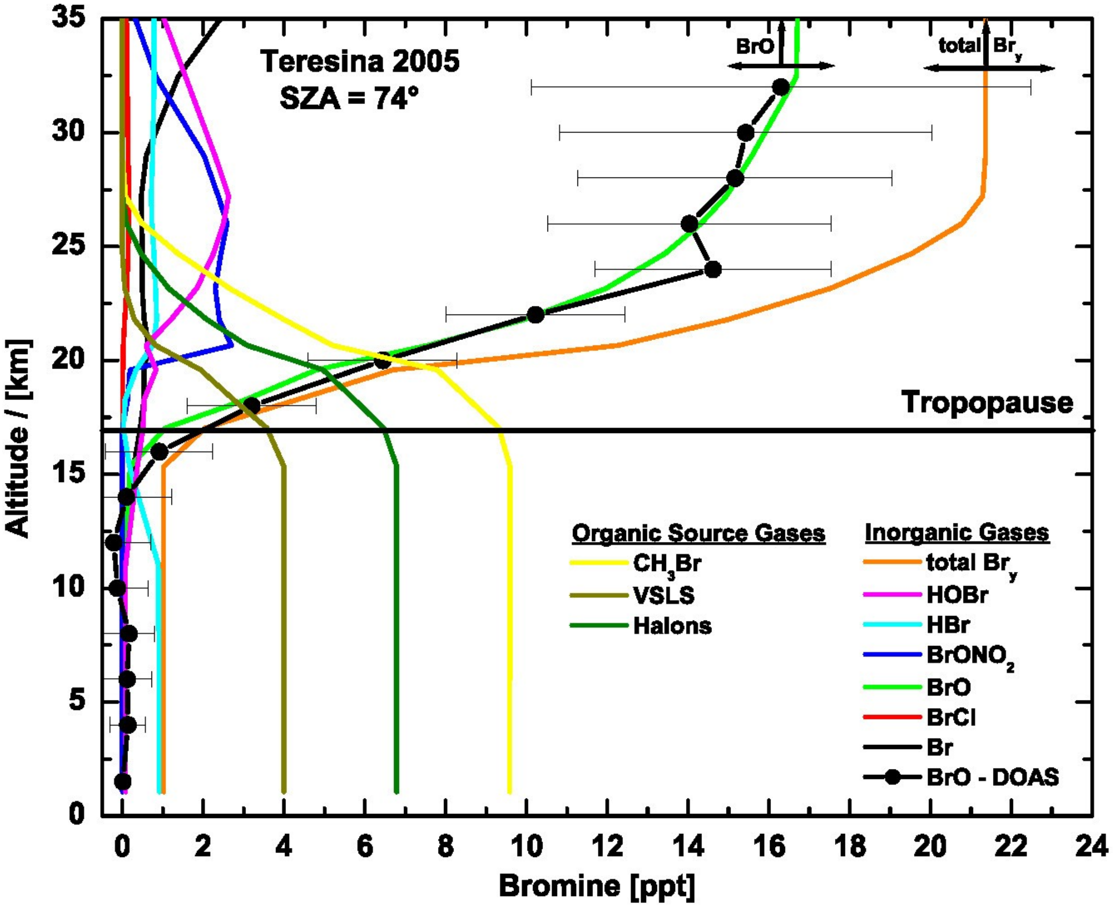
Conclusion on chlorine (present stratospheric level 3450 ppt)

- Concentration of VSLS (which are mainly of anthropogenic origin) in the tropical UT/LS were ~ 35 ppt (UNEP WMO-2006: TTL 75 – 99 ppt)

- PG injection (mainly HCl and ClO) was 50 – 100 ppt (e.g., Catoire et al., for the Teresina 2005 sounding, and F. Stroh et al., from SCOUT-O3 data)

→ **Present contribution of chlorinated PG+VSLS are likely about 100 – 150 ppt, or 3 – 4 % to total stratospheric chlorine (in agreement with WMO-2006) !**

Bromine: Br_y by BrO profiling through the tropical pipe



DOAS BrO profiling in the tropics on June 17, 2005 indicates:

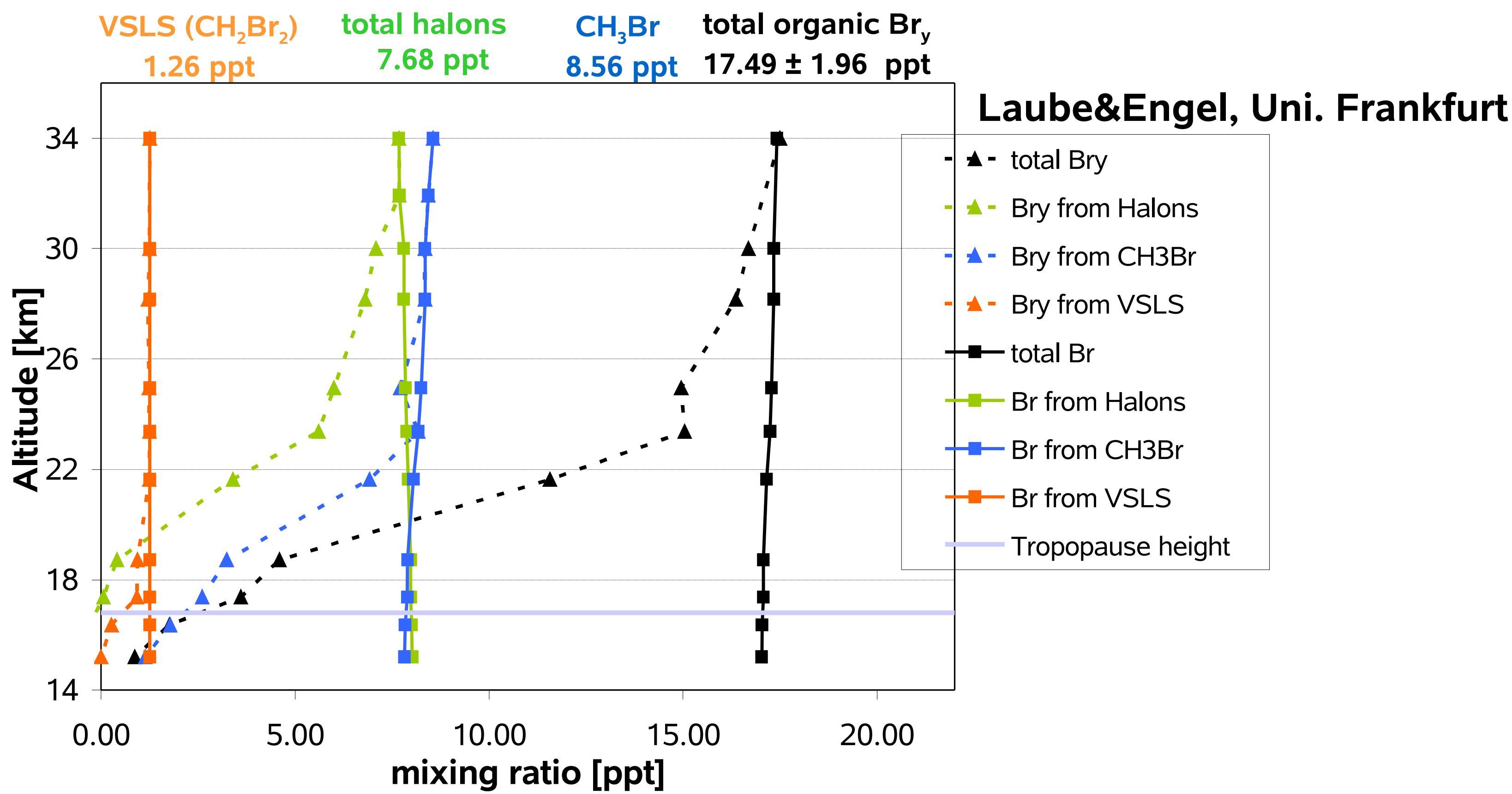
- BrO in the tropical troposphere between 0-0.5 ppt
- non-zero amounts of Br_Y at the tropopause
- rapid release of Br_Y above the tropopause
- good agreement with updated CTM SLIMCAT runs

Dorf et al., 2006a+b

Key results (PG for 4 year old LS air):

→ $[Br_y]$ = 21.5 ±2.5 ppt in 4 year old air !

Br_y: Profile sounding of brominated SGs in the tropical pipe (North Eastern Brazil)



Key results (brominated SGs for 4.3 year old air):

1. $[CH_3Br]$ = 856 ppt, [Halons] = 7.68 ppt, [VSLS] = 1.26 ppt

→ $[Br_y]$ = 17.5 ± 2 ppt in 4.3 year old air !

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Key result: Br_y budget for ~ 4 year old air (Teresina 2005)

CH_3Br	8.56 ppt
halons	7.68 ppt
VSLS (predom. CH_2Br_2)	~ 1.6 ppt
Σ source gas (SG) injection	17.5 ± 2 ppt
total inorganic bromine	21.5 ± 2.5 ppt
→ PG injection	4.0 ± 2.5 ppt; Teresina, 2005 3.1-2.9/+3.5 ppt; Kiruna 1999 (Pfeilsticker et al., 2000)

Bromine: UNEP-WMO's VSLS + PG contribution to stratospheric Br_y

Table 2-8. Contribution to stratospheric Br_y^{VSLS}.

Data Source	Br_y^{VSLS} Central Value (ppt)	Br_y^{VSLS} Range (ppt)	Reference
Ground-based BrO 11 sites, 78°S-79°N	5	1-9 [a]	Sinnhuber et al. (2002)
Ground-based BrO Lauder, New Zealand, 45°S	6	3-9	Schofield et al. (2004)
Ground-based BrO Arrival Heights, Antarctica, 78°S	6	3-9	Schofield et al. (2006)
DOAS Balloon BrO Profiles 5°S-68°N, 0-35 km	4.1	1.6-6.6	Dorf, 2005
Aircraft & Balloon BrO Profiles, 22°S-35°N, 17-32 km and GOME Satellite Column BrO, 60°S-60°N	7	4-10 [a]	Salawitch et al. (2005)
SCIAMACHY Satellite BrO Profiles 80°S-80°N, 15-28 km	8.4	6.4-10.4	Sioris et al. (2006)
SCIAMACHY Satellite BrO Profiles 80°S-80°N, 15-28 km	3	0-6	Sinnhuber et al. (2005)
SCIAMACHY Satellite BrO Profiles 80°S-80°N, 15-28 km	3.5	0-7.5	Sheode et al. (2006)
MLS Satellite BrO Profiles 55°S-55°N, 30-42 km	3.0	0-8.5	Livesey et al. (2006)
Ensemble	**5 (3-8)** [b]		

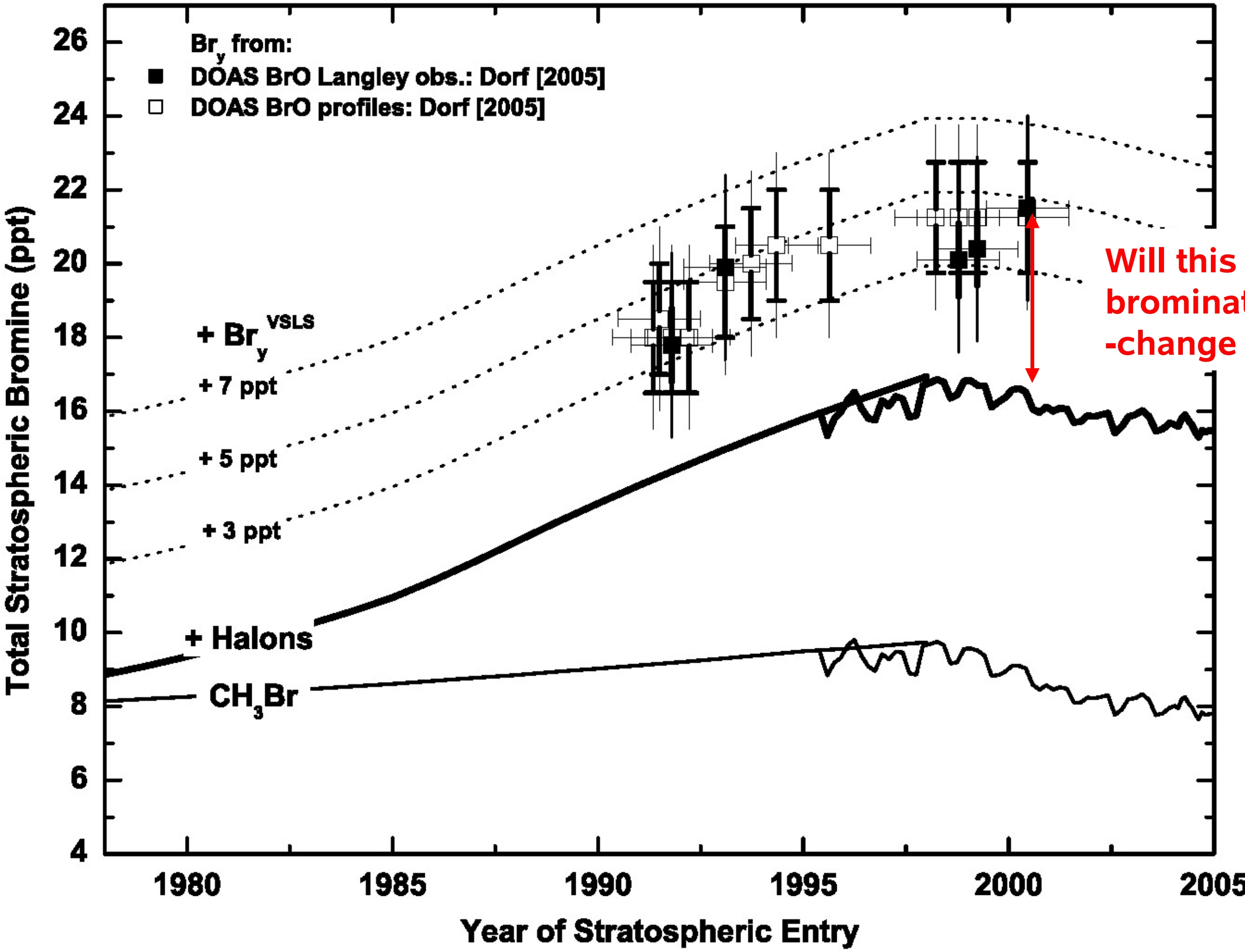
DOAS, Differential Optical Absorption Spectroscopy; GOME, Global Ozone Monitoring Experiment; SCIAMACHY, Scanning Imaging Absorption Spectrometer for Atmospheric Cartography; MLS, Microwave Limb Sounder.

[a] Range estimated by this Assessment, based on the uncertainty in stratospheric Br_y inferred from BrO that was stated in the reference.

[b] Average and range of the central values of the 8 estimates of Br_y^{VSLS}.

UNEP-WMO 2006, Table 2.8

Trend in total stratospheric bromine



[Dorf et al., GRL, 2006

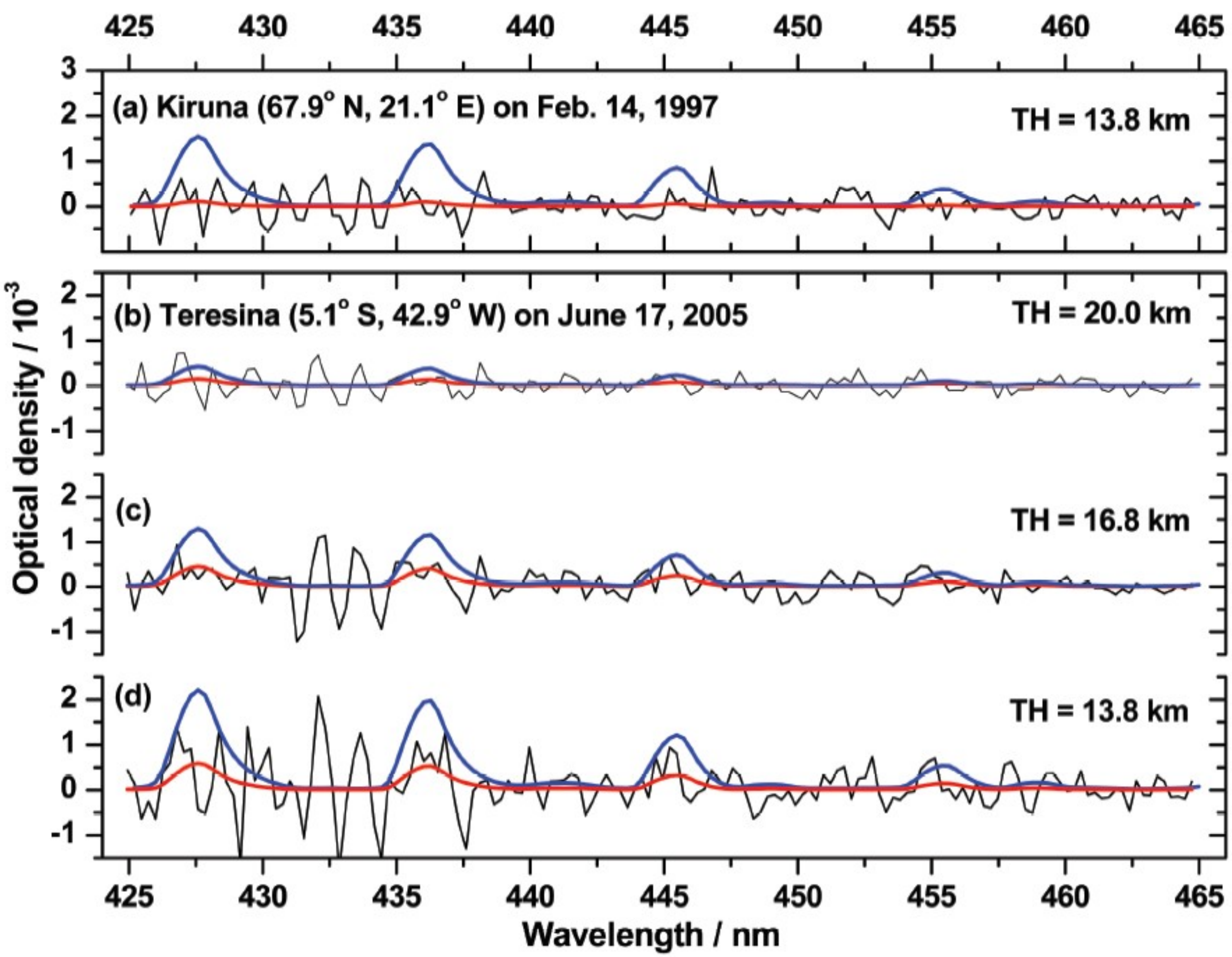
Conclusion on bromine (present stratospheric level ~ 21 ppt)

- **VSLS (which are mainly of natural origin) were 1.3 ppt in the tropical UT/LS in June (UNEP-WMO: range 3.1 – 4.0 ppt)**

- **PG injection (mainly HBr, BrO, Br) is < 2 ±2.5 ppt (in good agreement with the FZ-J BrO results)**

→ PG + VSLS contribution 4.0±2.5 ppt (UNEP-WMO 2006: range 3 - 8 ppt) or 25 % of the total stratospheric bromine !

Iodine: UT/LS Iodine



Butz, 2006 & WMO-2007

Conclusion on iodine (present stratospheric level < 0.1 ppt)

- VSLS i.e., CH_3I were ~ 0.3 ppt in the tropical UT/LS (UNEP-WMO: range 0.02 – 0.18 ppt)

- IO was ≤ 0.3 ppt in the tropical UT/LS (in reasonable agreement with UNEP-WMO 2006 and Bösch et al., 2003)

→ Iodine is not (yet or never ?) important for stratospheric ozone

→ An efficient loss mechanism must exist for iodine in the troposphere which is particularly efficient in the UT/TTL !

Overall Summary & Conclusion

VSLS and PGs contribute to total stratospheric

2. **Chlorine: ~100 – 150 ppt or 3 – 4 %**
3. **Bromine: 5 ppt (range 2 – 8 ppt) or 25 %**
4. **Iodine: < 0.1 ppt but 100 %**

In this context, the most important question is today:

Will these numbers change in a changing climate.....

and if yes, why ?

(i.e. due to emissions, transport&lifetime, ...)