

An aerial view of Earth from space, showing the curvature of the planet and the atmosphere. Several aircraft are visible in the sky, and a large satellite is in orbit. The sun is visible on the right side of the frame, creating a bright glow.

Very Short-Lived Halocarbons into CAM-Chem

Don Wuebbles

Department of Atmospheric Sciences
University of Illinois
Urbana, Illinois 61801

June 19, 2007

Halogens and Tropospheric Chemistry

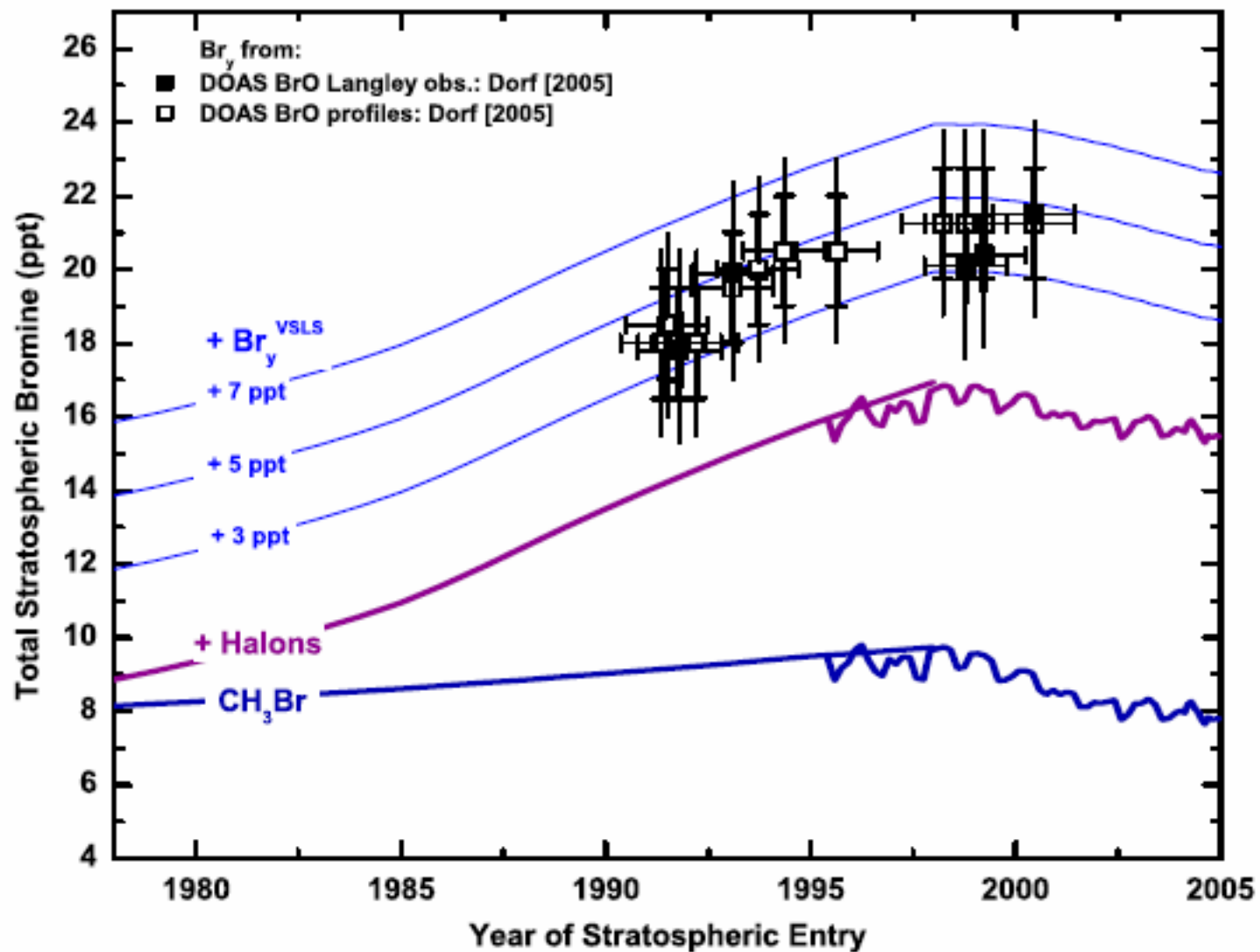
Boundary Layer

- Effects on ozone (above snow, over salt lakes)
- Br, Cl interactions over marine areas
- Effects on DMS chemistry (von Glasow, 2004)

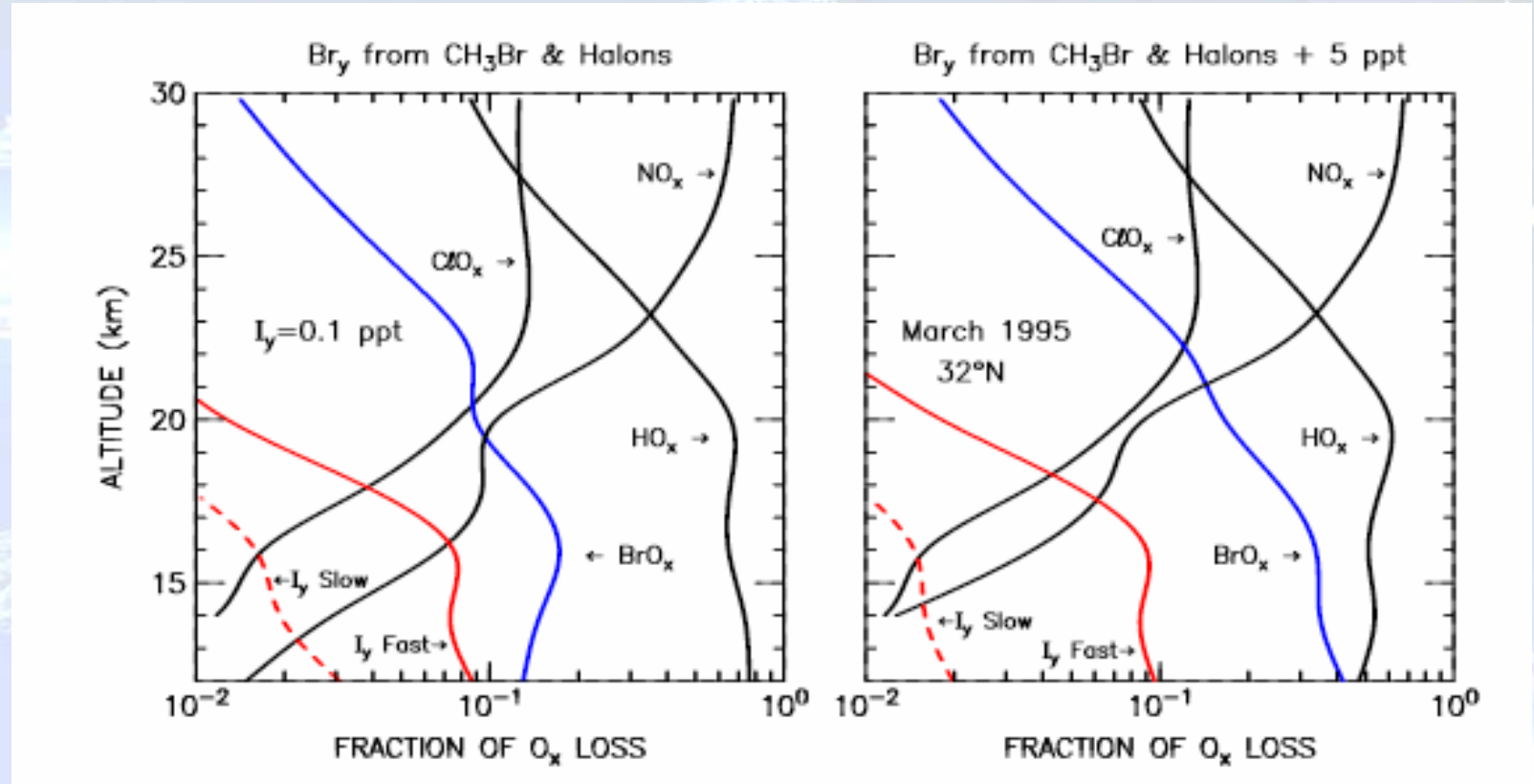
Free Troposphere

- Cl is ~10% initiation of methane oxidation
- BrONO₂ important to HNO₃ production in lower troposphere (as much as 30%)
- Partitioning of OH and HO₂
- Partitioning of NO and NO₂

VSL Halocarbons & Stratospheric Br_y



VSL Halocarbons Affect Stratospheric O_x



VSL Halocarbons Affect Troposphere and Stratospheric Chemistry

Chemical and Dynamical Processes Affecting VSLs

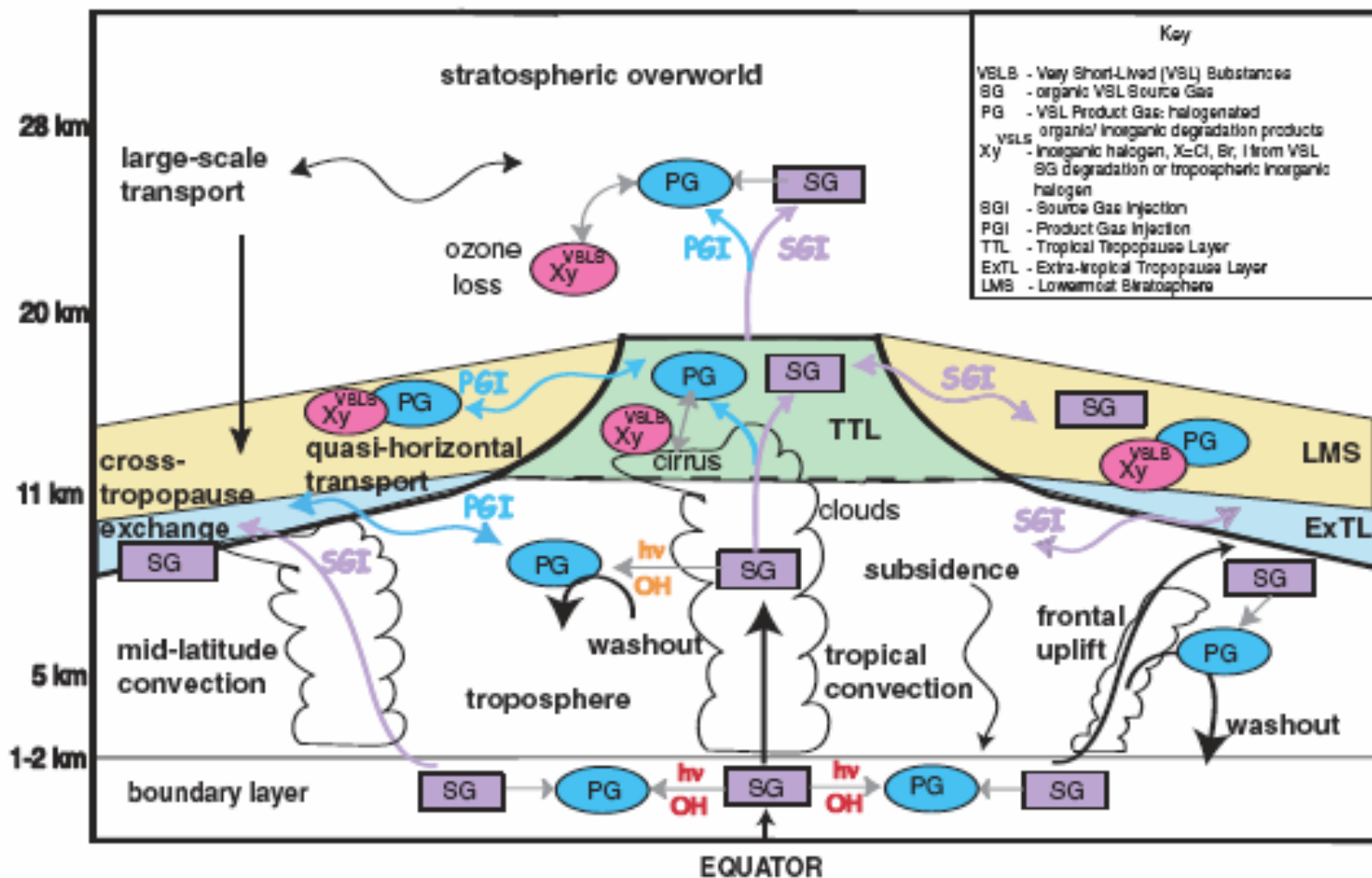


Table 2-3. Estimated local lifetimes, burdens, removal rates, and sources for some halogenated VSLS.
 New information since WMO (2003) is indicated in boldface.

Compound	Local Lifetime (days)	Estimated Burden (Gg)	Estimated Removal Rate (Gg yr ⁻¹)	Estimated Source from Inventory or Estimate of Biogeochemical Cycle (Gg yr ⁻¹)
CH ₂ BrCl	150 ^a	1.2 (Br), 0.5 (Cl) ^l	2.9 (Br), 1.3 (Cl) ^c	
CH ₂ Br ₂	120 ^a	18-22 (Br) ^b 19 (Br) ^l	55-67 (Br) ^c 58 (Br) ^f	
CHBrCl ₂	78 ^a	1.3-1.5 (Br) ^b 1.2-1.3 (Cl)	6.1-7.0 (Br) ^f 5.4-6.2 (Cl)	17 (Cl) open ocean ^{15a} 19 (Br) open ocean ^{15a}
CHBr ₂ Cl	69 ^a	1.2 (Br), 1.1 (Cl) ^l 0.8-2.2 (Br), 0.2-0.5 (Cl) ^b	5.5 (Br), 4.9 (Cl) ^c 4.2-12 (Br), 0.9-2.7 (Cl) ^f	5 (Cl) open ocean ^{15a} 23 (Br) open ocean ^{15a}
CHBr ₃	26 ^a	2.3 (Br), 0.5 (Cl) ^l 11-18 (Br) ^b 14 (Br) ^l	12 (Br), 2.7 (Cl) ^f 150-250 (Br) ^c 200 (Br) ^c 285 ^{2, d}	209 (47-370) (Br) ³ 800 (240-1760) (Br) ⁹ 28 (20-112) (Br) industry ⁹
CH ₃ I	5 ^e 6 ^f	1.7-2.2 (I) ^b 4.8 (I) ^f	120-160 (I) ^f 214 (I) ^f	90-450 (I) ⁴ 272 (I) total ¹⁰ 191 (I) net ocean (incl. 66 anthropogenic) ¹⁰ 180 (I) open ocean ^{15a}
C ₂ H ₅ I	4 ^a	0.5 (I)	46 (I) ^c	
CH ₂ ClI	0.1 ^a			95 (I) open ocean ^{15a} 27 (Cl) open ocean ^{15a}
CH ₂ Cl ₂	140 ^a 180 ^{6, c}	83-250 (Cl) ^b 250 (Cl) ^f	220-650 (Cl) ^f 650 (Cl) ^f 500 (Cl) ^{6, d}	487 (Cl) industrial ⁵ 160 (Cl) ocean 49 (Cl) biomass burning ¹⁶ⁱ
CHCl ₃	150 ^a 183 ^{7e}	66-130 (Cl) ^b 210 (Cl) ⁷	160-320 (Cl) ^f 511 (Cl) ^c 470 (350-600) ^{7, e} 412 (Cl) ^{6, d}	564 (Cl) ⁶ 588 (392-784) (Cl) ¹¹ 320 (240-400) (Cl) seawater ¹¹ 196 (107-285) (Cl) soil ¹¹
C ₂ HCl ₃	4.6 ^a 5.5 ^{6e}	3.1 (Cl) ^b 5.30 (Cl) ⁶	260 (Cl) ^f 440 (Cl) ^f 350 (Cl) ^{6, e}	95 (Cl) industry ⁵ 20 (Cl) ocean ⁶ 3 (Cl) fossil fuel ⁶
C ₂ Cl ₄	99 ^a 133 ^{6e}	17-85 (Cl) ^b 160 (Cl) ^f	63-310 (Cl) ^c 590 (Cl) ^f 440 (Cl) ^{6, e}	313 (Cl) industry ⁵ 16 (Cl) ocean ⁶ 2 (Cl) fossil fuel ⁶
C ₂ H ₂ Cl	~30 ¹³ ~24 ¹⁴	14 (Cl) ¹³ 4.6-7.3 (Cl) ¹⁴	165 (Cl) ^c 70-110 (Cl) ^c	222 (210-235) (Cl) ^{12g}
CH ₂ ClCH ₂ Cl	70 ^a	5-26 (Cl) ^b	26-130 (Cl) ^c	700 ⁸



QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.



Table 2-2. Reported mixing ratios of VSL source gases in the troposphere (global and hemispheric values), at 10 km in the tropics, and best estimates from this Assessment of median mixing ratios in the tropical marine boundary layer [MBL] (<1 km), and tropical upper troposphere [UT]. All mixing ratio values are in parts per trillion (ppt). New information since WMO (2003) is indicated in boldface.

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]
CH₂BrCl			0.47 (0.38-0.59)^c	0.32 (0.26-0.35)^c	0.7
CH ₂ Br 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
CHBr ₂ Cl	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
CHBrCl ₂	0.12-0.6	0.04-0.11	0.33 (0.14-0.91)^{b,c,g,i}	0.12 (0.05-0.15)^{b,c}	0.4
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
CH ₃ I	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
CH₂ClI			0.35^g		
CH ₂ Cl ₂			17.5 (9-39) ^{b,c,f}	13.2 (9-19) ^{b,c,e}	0.75
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
C ₂ HCl 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
C ₂ Cl 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,l,k}	1.3 (0.9-1.6) ^{b,c,e}	0.7
C ₂ H ₂ Cl	NH, 2.6 ^l SH, 1.6 ^l		5.0 (2.7-5.9) ^d	1.5 (1.0-1.8) ^d	0.3
CH ₂ ClCH ₂ Cl	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
COCl ₂				22.5 (20-25) ^m	
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	