



Geographical Distribution of Brominated Organic Trace Gases in the UT/LS region of the Pacific

Maria Navarro¹, E. Atlas¹, A. Saiz-Lopez³, X. Rodriguez-Lloveras³, R. Lueb¹, R. Hendershot², S. Gabbard², D. Kinnison², JF. Lamarque², S. Tilmes², C. Cuevas³, S. Schauffler², V. Donets¹, X. Zhu¹, L. Pope¹

- 1) Division of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida, USA
- 2) Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA
- 3) Atmospheric Chemistry and Climate Group, Institute of Physical Chemistry Rocasolano, CSIC, Madrid, Spain

OBJECTIVES

I- Characterize variability and distribution of organic bromine species in the UT/LS of the Eastern and Western Pacific.

II- Determine the amount of total very short lived brominated species ($VSL_{Br} = VSL_{org} + Br_y$) that enters the stratosphere.

- Examine the amount of inorganic bromine present at the Tropical Tropopause and the partitioning of these species from modeling results.

III- Examine the inter-hemispheric distribution of VSL_{org} .

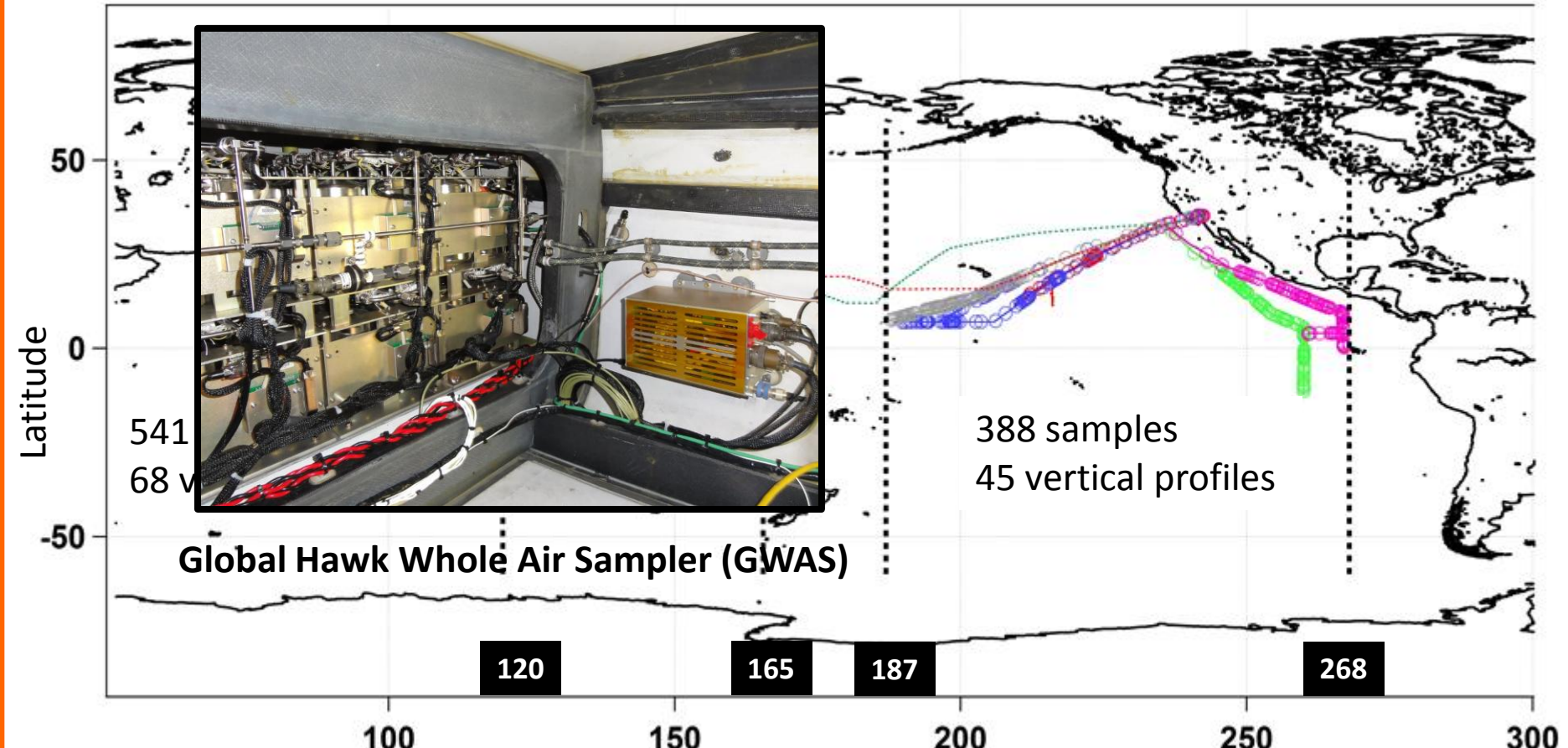
MOTIVATION

- One of ATTREX questions: *“What is the vertical distribution of BrO and short lived halogen compounds in the TTL and how does it vary seasonally and geographically?”*
- Uncertainties on the amount of VSL_{Br} reaching the stratosphere (2-8 ppt according to WMO-2014)

ATTREX locations and area of study

ATTREX-3 (2014) WESTERN PACIFIC

ATTREX-2 (2013) EASTERN PACIFIC



- ATTREX-3 RF01
- ATTREX-3 RF02
- ATTREX-3 RF03
- ATTREX-3 RF04
- ATTREX-3 RF05
- ATTREX-3 RF06
- ATTREX-3 RF07
- ATTREX-3 RF08

- ATTREX-2 RF01
- ATTREX-2 RF03
- ATTREX-2 RF04
- ATTREX-2 RF05
- ATTREX-2 RF06

Trace Gas Species from GWAS

Longer Lived Species

		Yrs	S
Halons			
Halon 1211	CBrClF ₂	20	A
Halon 2402	C ₂ Br ₂ F ₄	20	A
Halon 1301	CBrF ₃		
Chlorofluorocarbons			
CFC-11		50	A
CFC-12		102	A
CFC-113		85	A
Hydrochlorofluoroarbons/ Hydrofluorocarbons			
HCFC_141b		9.4	A
HCFC-22		13	A
HCFC_142b		19.5	A
Solvent			
Carbon Tetrachloride		40	A
Methyl chloroform		4.8	A
Other			
Carbonyl Sulfide (COS)		30	N/A/B
Methyl Chloride		1.5	N/B

Shorter Lived Species

		Yrs	S
Methyl Halides			
Bromoform	CHBr ₃	0.4	N
Methyl Bromide	CH ₃ Br	0.8	N/B
Methylene Bromide	CH ₂ Br ₂	0.4	N
Methyl Iodide		0.01	N
CHxBryClz		0.1	N
Solvents			
Minor VSLBr			
Methylene Chloride	CH ₂ Cl ₂	0.3	A
Chloroform	CHCl ₃	0.4	A/N
Tetrachloroethylene	C ₂ Cl ₄	0.3	A
Trichloroethylene	C ₂ HCl ₃	0.02	A

Shorter Lived Species

Organic nitrates		
Methyl nitrate	0.08	A/N
Ethyl nitrate	0.04	A/N
Propyl nitrate	0.03	A/N
Non- Methane Halocarbons		
Ethane (C ₂ H ₆)	0.2	A
Ethyne	0.06	A/B
CH ₃ BrCl	0.04	A
CH ₂ BrCl	0.04	A/B
Others		
1,2 dichloro ethane	0.3	A
Chlorobenzene	0.05	A

Sources

A= antropogenic/industrial
 N= natural/marine
 B=Biomass burning

CAM-Chem

- Community Atmosphere Model (CAM V.5) (*details in: Lamarque et al., Geosci. Mod. Dev., 2012, Ordoñez et al., ACP, 2012 and Saiz-Lopez et al., ACP, 2012*)
- Simulations with **specific meteorological fields**
- Vertical resolution: 56 levels (surface to ~ 993 hPa)
- Spatial resolution 1° x 1°
- Temporal resolution: 30 min
- Tropospheric Halogen Chemistry

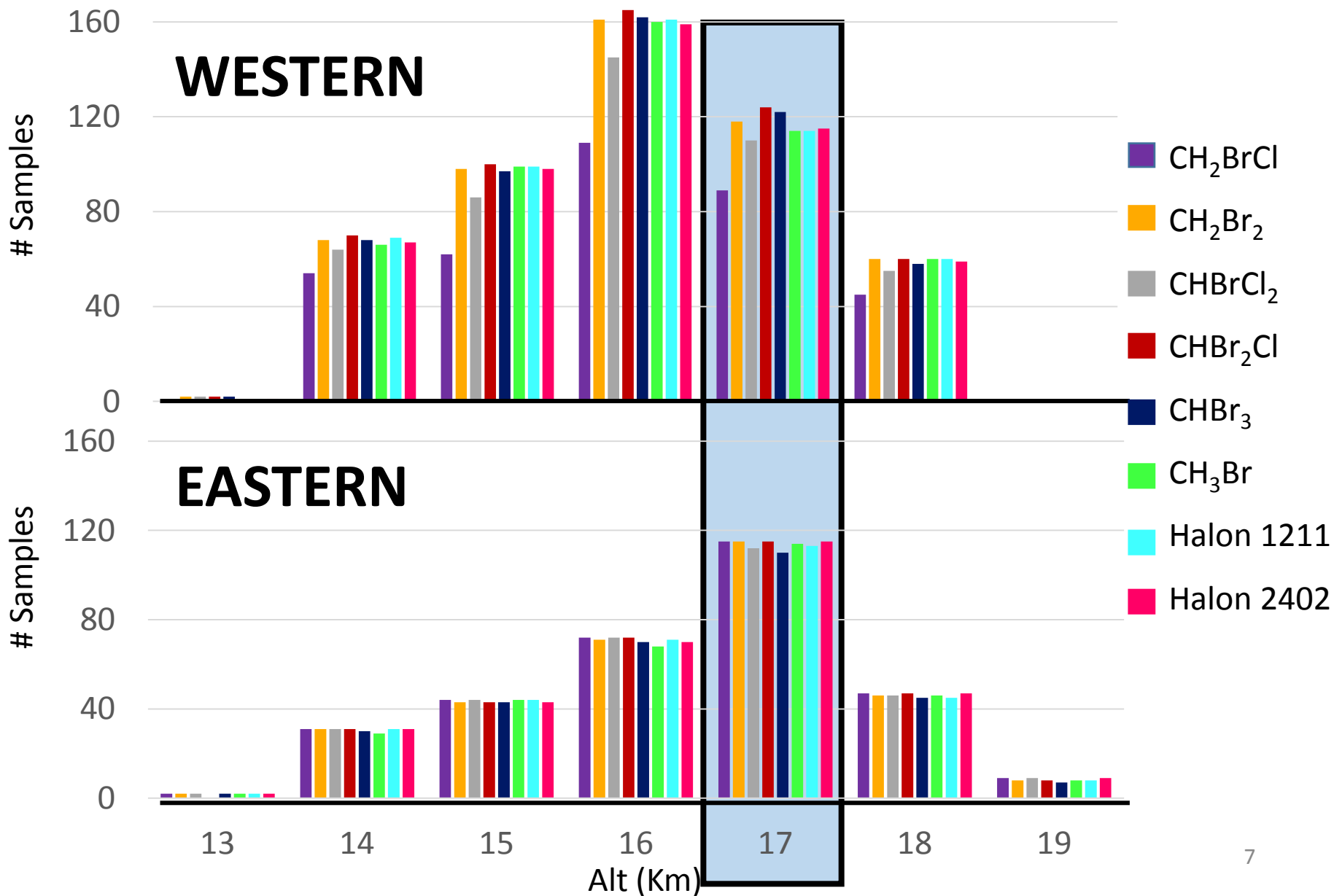
Chemical Processes

- . Halogen gas phase photochemistry (Cl, Br, and I)
- . Dry / wet deposition
- . Heterogeneous chemistry on sea-salt aerosols and ice particles
- . 9 additional VSL halocarbon species included.

Halogenated VSL sources from the ocean

- . Emissions following Chl-a over tropics (SeaWIFS)
- . Geographical and temporal distribution of VSL sources

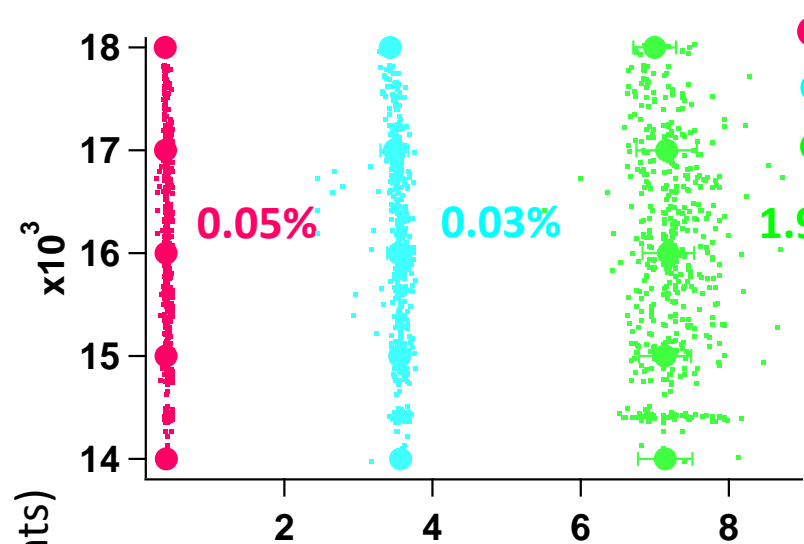
Sampling Density of Organic Br Species



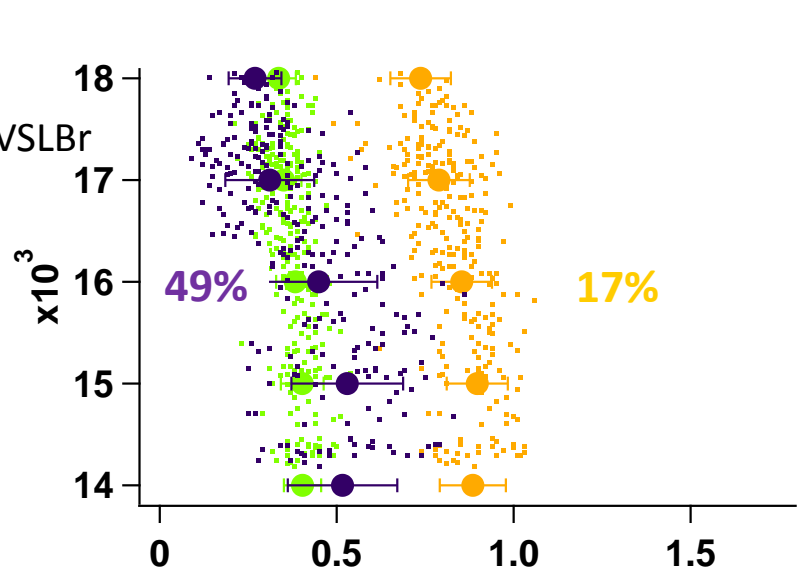
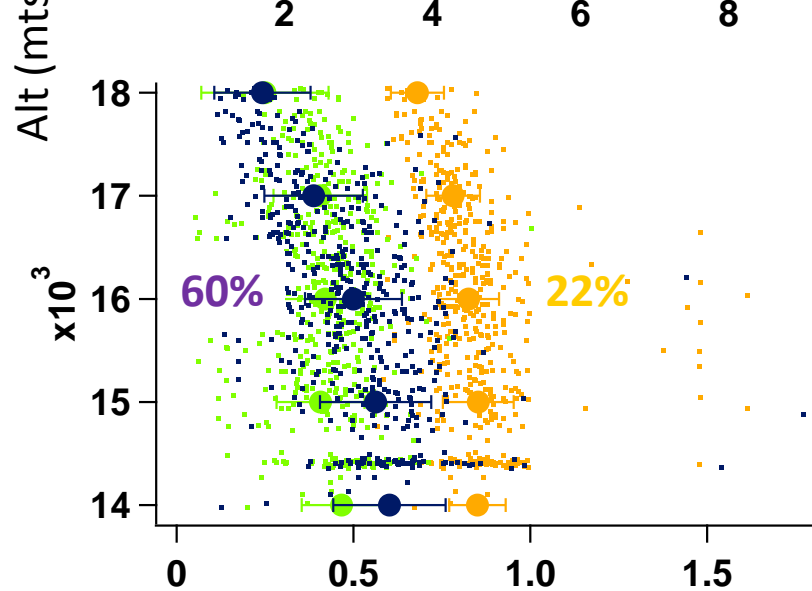
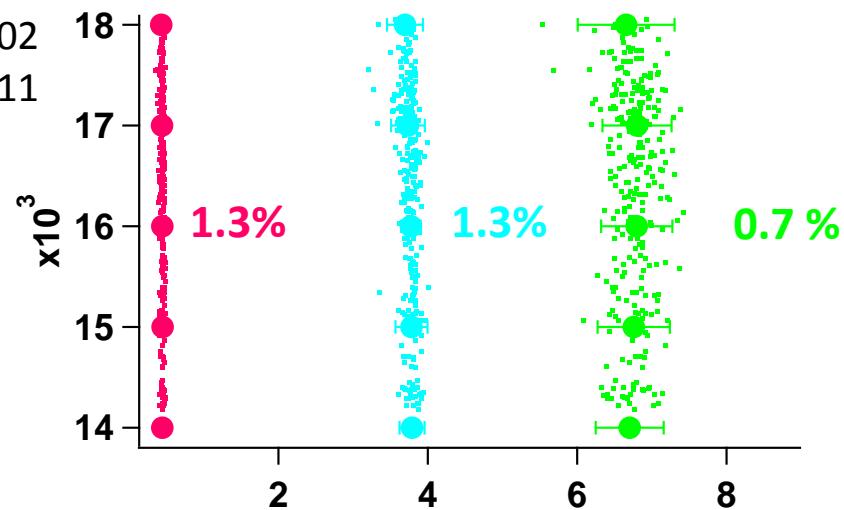
I- Variability and Distribution of GWAS Organic Bromine Species

Variability and Distribution of GWAS Organic Bromine Species

WESTERN PACIFIC



EASTERN PACIFIC



- CHBr₃
- CH₂Br₂
- Minor VSLBr

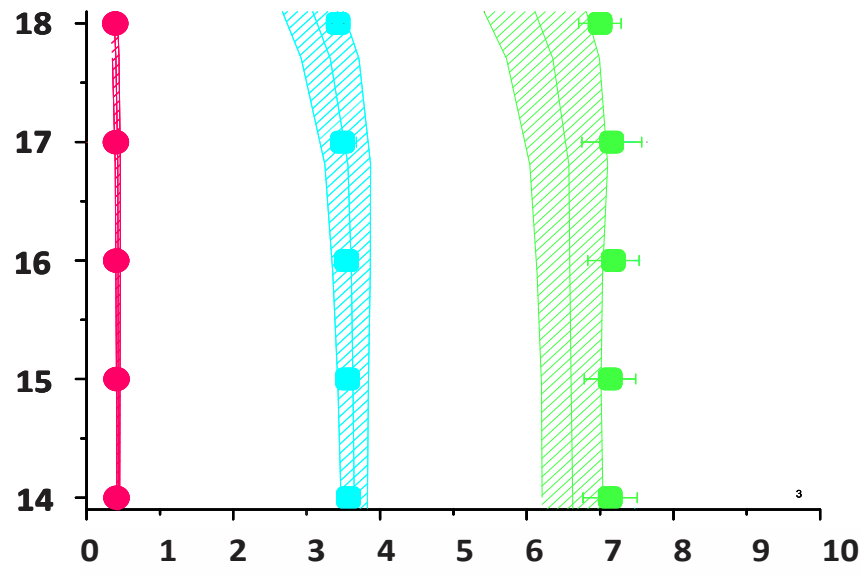
Minor VSL = CH₂BrCl + CHBr₂Cl + CHBrCl₂

Mixing ratios (pmol/mol)

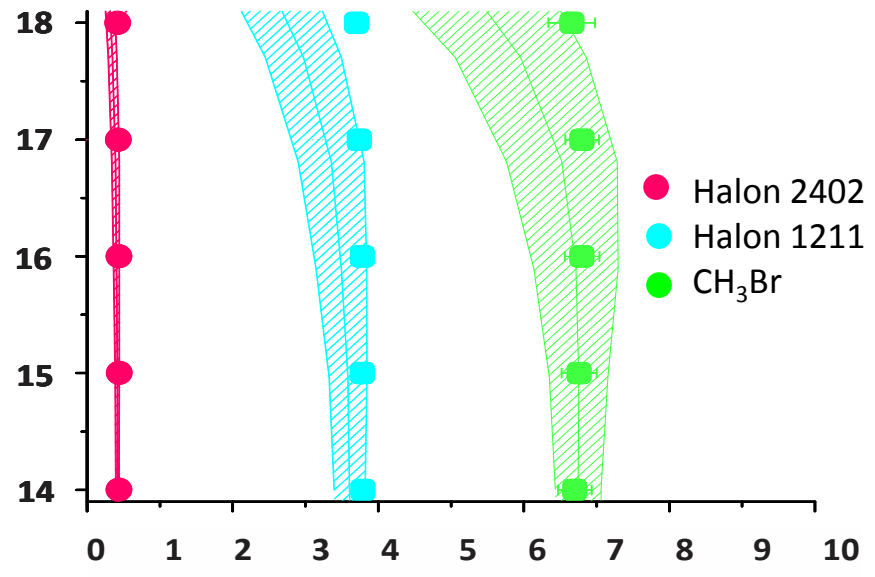
○ Bin 1Km Alt
Error = 1sd

CAM-Chem: Variability and Distribution of Organic Bromine Species

WESTERN PACIFIC

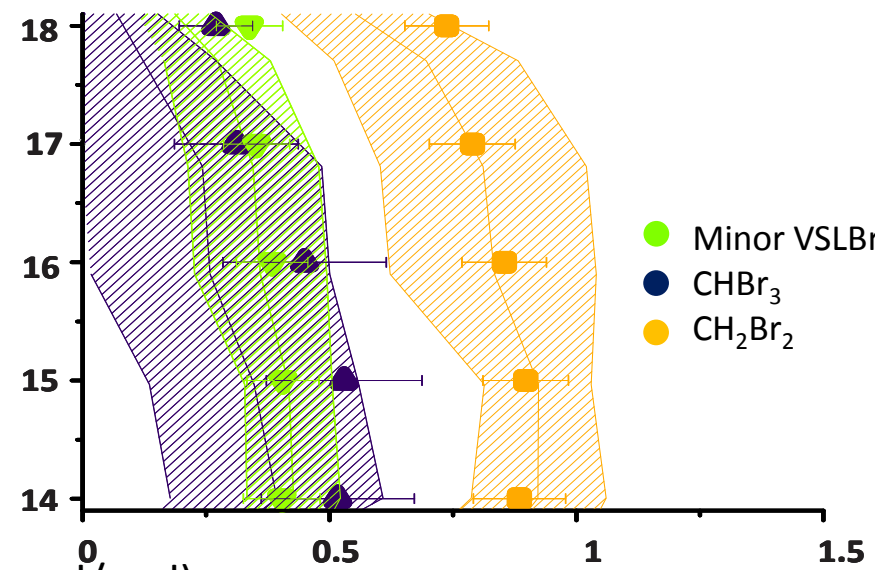
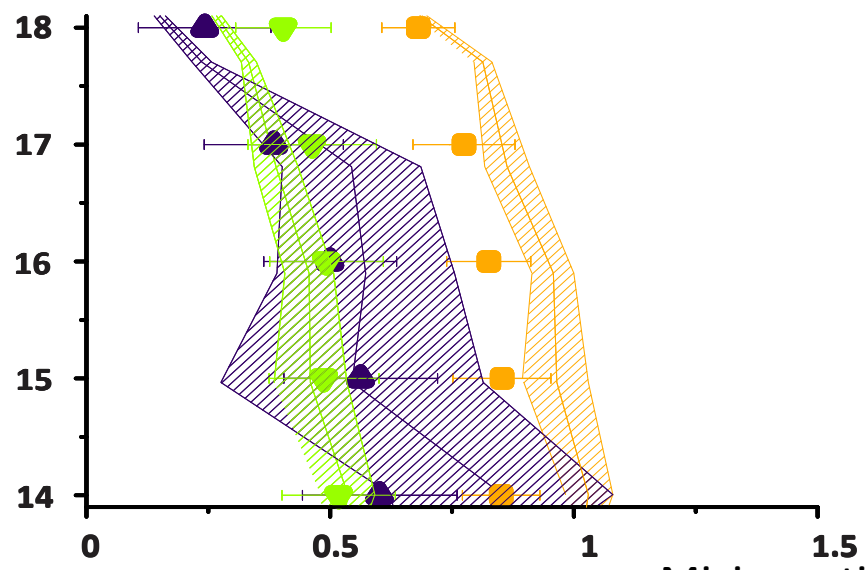


EASTERN PACIFIC



- Halon 2402
- Halon 1211
- CH₃Br

Alt (Km)



- Minor VSLBr
- CHBr₃
- CH₂Br₂

○ Bin 1Km Alt

Mixing ratios (pmol/mol)

Error model and measurements =1sd

Organic Bromine Species by Groups

TOTAL HALONS = HALON 1211+ HALON 2402+ HALON 1301

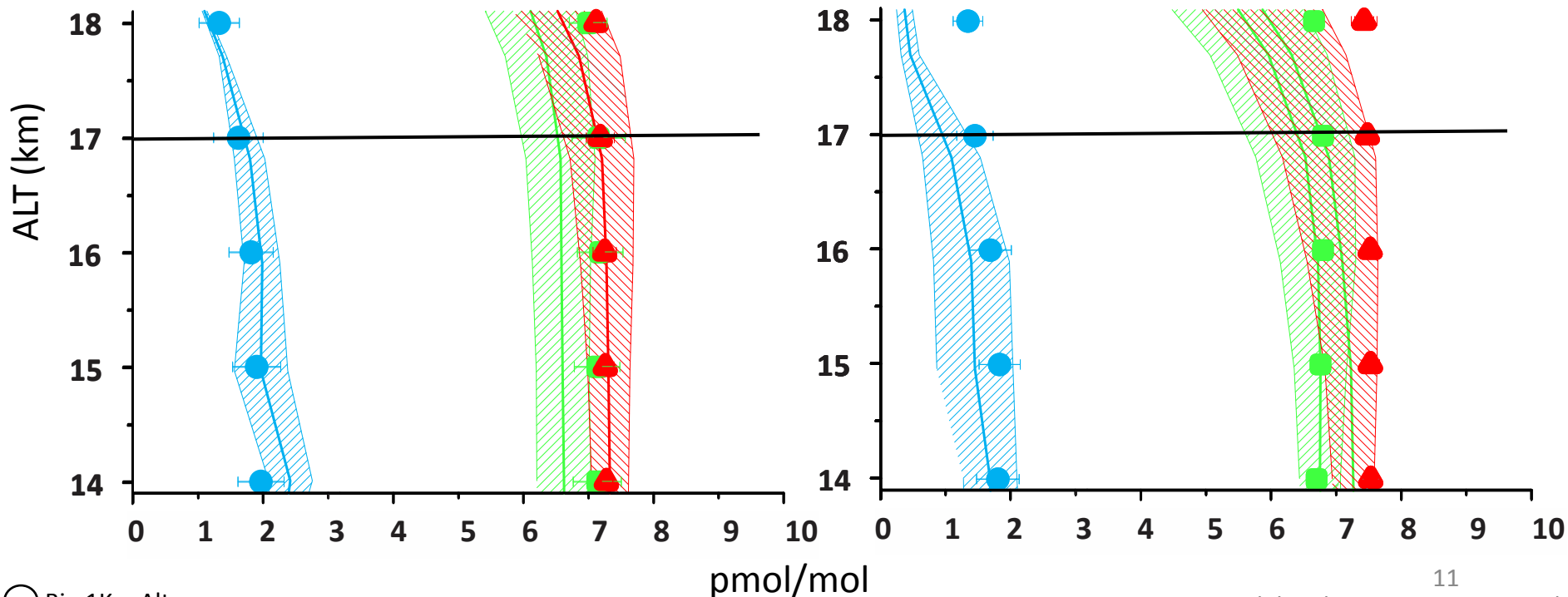
CH₃Br = CH₃Br

VERY SHORT LIVED Br (VSL_{org}) = CHBr₃+ CH₂Br₂ + CHBrCl₂+ CHBr₂Cl + CH₂BrCl

WESTERN PACIFIC

EASTERN PACIFIC

- VSL_{org}
- CH₃Br
- Total Halons



II- VSL_{org} and Br_y at the Tropical Tropopause

Organic Bromine Budget at the Tropopause (17Km)

ORGANIC BROMINE BUDGET

TOTAL HALONS = HALON 1211+ (2*HALON 2402)+ HALON 1301

CH3Br = CH₃Br

VERY SHORT LIVED Br (VSL_{org}) = (3* CHBr₃)+ (2* CH₂Br₂) + CHBrCl₂+ (2*CHBr₂Cl)+ CH₂BrCl

VERY SHORT LIVED Br (VSL_{org}) = (3* CHBr₃)+ (2* CH₂Br₂) + **Minor VSLBr**

@ 17Km	Western (pmol Br/mol)	Eastern (pmol Br/mol)
Halons	7.59 ± 0.19	7.92 ± 0.11
CH ₃ Br	7.16 ± 0.41	6.80 ± 0.23
VSL _{org}	3.27 ± 0.49	2.96 ± 0.42
Total Org Br Budget	18.02 ± 0.66	17.68 ± 0.49

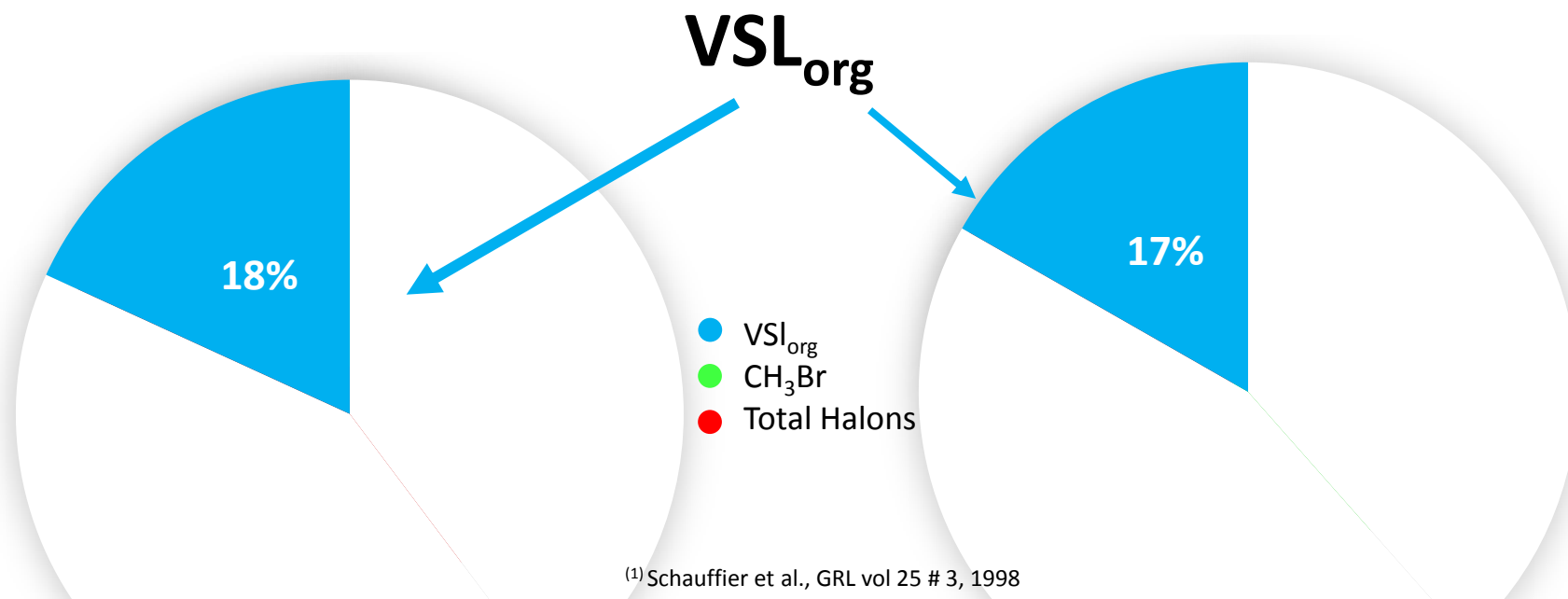
Organic Bromine Budget at the Tropopause (17Km)

WESTERN PACIFIC

EASTERN PACIFIC

Br org budget = 18.02 ± 0.66 pmol Br/mol

Br org budget = 17.68 ± 0.49 pmol Br/mol



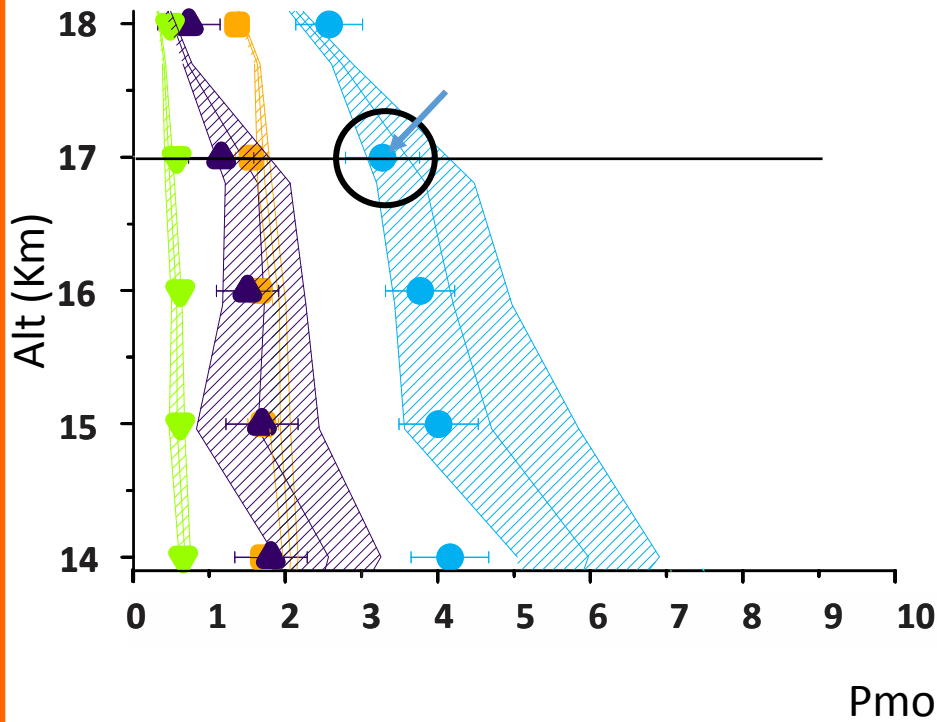
⁽¹⁾Schauffier et al., GRL vol 25 # 3, 1998

@ 17Km	STRAT 1996 ⁽¹⁾ (%)
Halons	38
CH ₃ Br	55
VSL _{org}	6.8
Total Org Br Budget (ppt)	17.4 ± 0.9

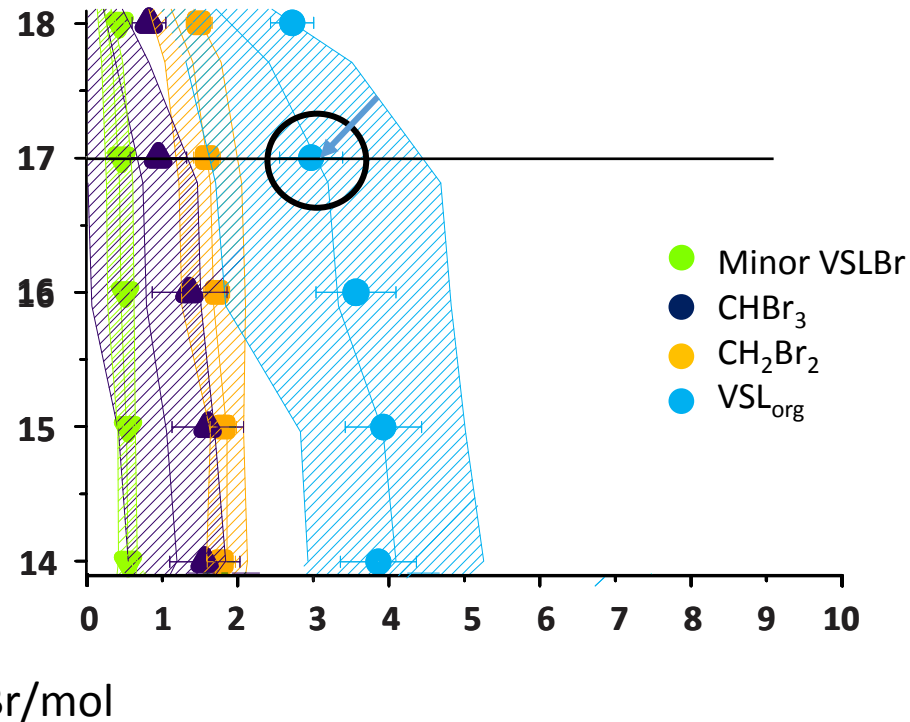
@ 17Km	CRA-VE 2006 (%)
Halons	47
CH ₃ Br	45
VSL _{org}	8
Total Org Br Budget (ppt)	17.5 ± 0.6

VSL_{org} in the Pacific Tropical Tropopause

WESTERN PACIFIC



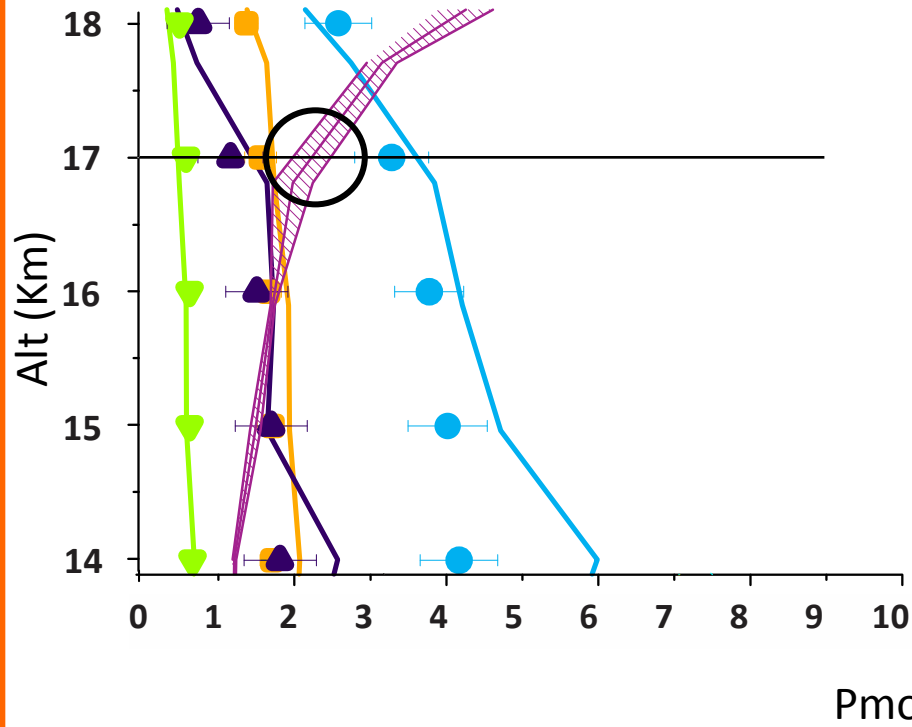
EASTERN PACIFIC



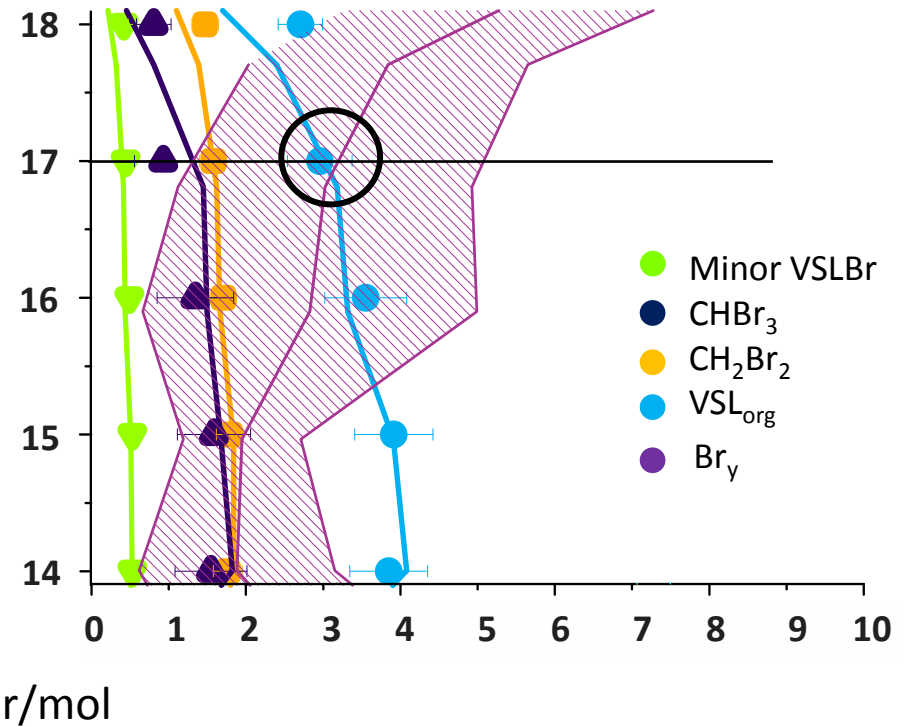
VSL _{Org} @ 17Km	WESTERN PACIFIC	EASTERN PACIFIC
GWAS measurements	3.27 ± 0.47	2.96 ± 0.42
CAM-Chem	3.84 ± 0.64	3.18 ± 1.49 ¹⁵

Inorganic Bromine in the Pacific Tropical Tropopause

WESTERN PACIFIC



EASTERN PACIFIC



$$\text{Br}_y = \text{Br} + \text{BrO} + \text{HOBr} + \text{BONO}_2 + \text{HBr} + \text{BrCl} + 2\text{Br}_2 + \text{BrNO}_2 + \text{IBr}$$

Br_y @ 17Km

WESTERN PACIFIC

EASTERN PACIFIC

CAM-Chem

1.97 ± 0.21

3.02 ± 1.90₁₆

VSL_{org} and Inorganic Bromine in the Tropopause

VSL_{org}

VSL _{org} @ 17Km	WESTERN PACIFIC (ppt)	EASTERN PACIFIC (ppt)
GWAS measurements	3.27 ± 0.47	2.96 ± 0.42
CAM-Chem	3.84 ± 0.64	3.18 ± 1.49

Br_y

Br _y @ 17Km	WESTERN PACIFIC (ppt)	EASTERN PACIFIC (ppt)
CAM-Chem	1.97 ± 0.21	3.02 ± 1.90

Bromine Fraction in the Pacific Tropical Tropopause

WESTERN PACIFIC

EASTERN PACIFIC

$$\frac{Br_y}{VSL_{org}}$$

$$\frac{1.97 \pm 0.21}{3.84 \pm 0.64} = 0.51 \pm 0.04$$

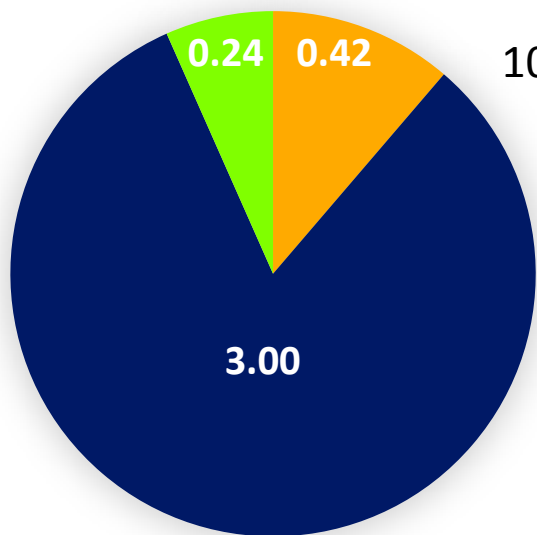
$$\frac{3.02 \pm 1.90}{3.18 \pm 1.49} = 0.95 \pm 0.32$$

Why do we have

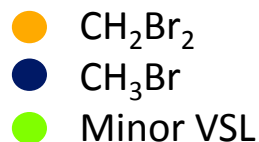
- Abundance of Br_y is $\frac{1}{2}$ of the abundance of VSL_{org} in Western Pacific
- Abundance of Br_y is similar to abundance of VSL_{org} in Eastern Pacific
 - **Different Br_y mixing ratios**
- **Since VSL_{org} mixing ratio is similar in both region, Br_y mixing ratio in the Eastern Pacific is similar to Br_y in the Western Pacific**

VSL_{org} Emission fluxes

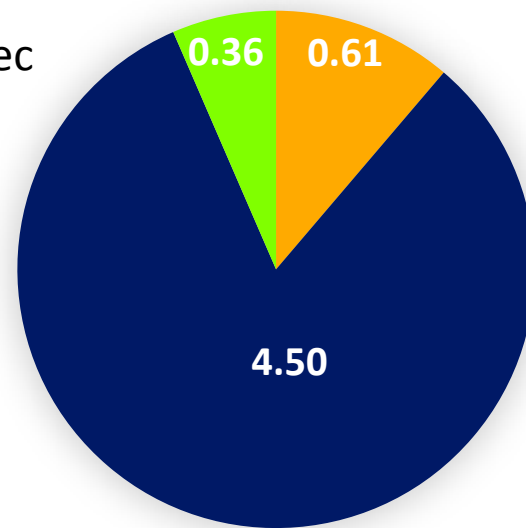
WESTERN PACIFIC



10e⁺⁰⁷ molecule/cm²/sec



EASTERN PACIFIC



Total VSL _{org} Emission	WESTERN PACIFIC (10e ⁺⁰⁷ molecule/cm ² /sec)	EASTERN PACIFIC (10e ⁺⁰⁷ molecule/cm ² /sec)
CAM-Chem	3.7	5.5

In less convective area (LIKE THE EASTERN PACIFIC)

- ***VSL_{org} have time to react → more Br_y production***
- ***Higher VSL_{org} emission → compensate the loss due to rxn***

Injection of Total VSL Brominated Species ($VSL_{Br} = VSL_{org} + Br_y$)

WESTERN PACIFIC

EASTERN PACIFIC

$$VSL_{Br} = VSL_{org} + Br_y$$

$$(3.84 \pm 0.64) + (1.97 \pm 0.21)$$

$$(3.18 \pm 1.49) + (3.02 \pm 1.90)$$

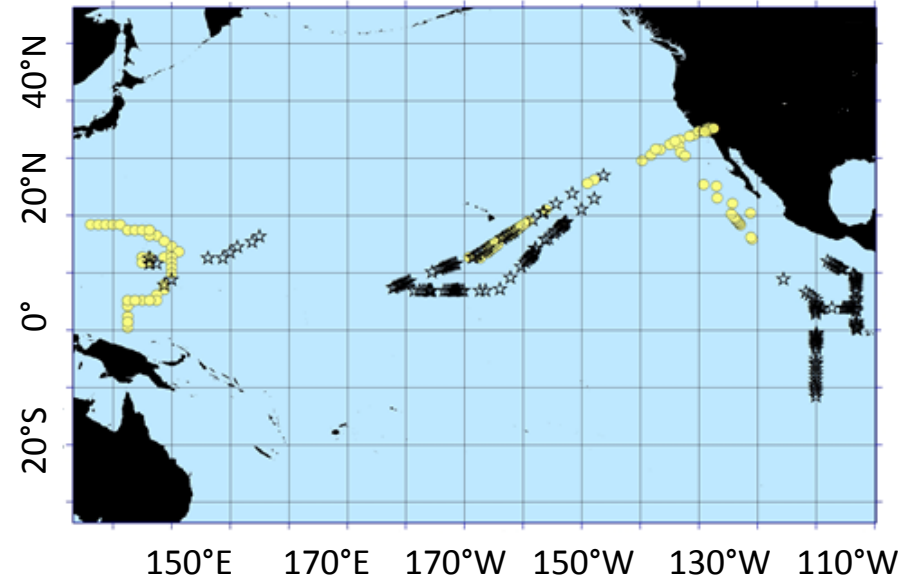
5.81 ± 0.67 ppt

6.20 ± 2.41 ppt

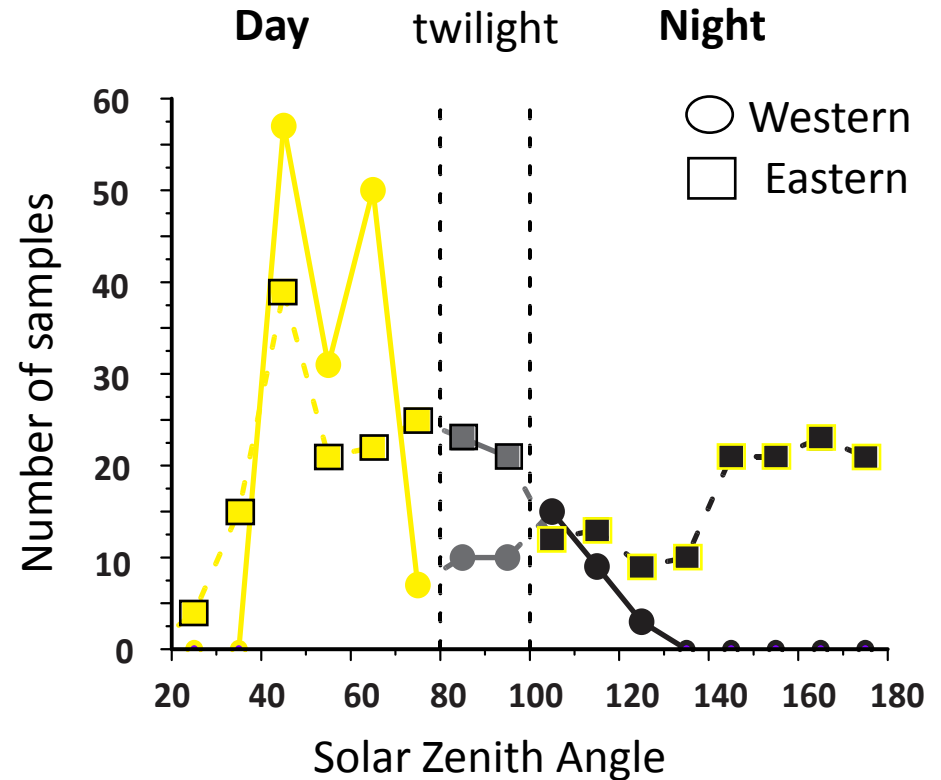
VSLBr (ppt)	WESTERN	EASTERN
ATTREX	5.81 (5.14-6.48)	6.20 (3.79-8.61)
WMO (2014)	~ 5 (2-8)	
ATTREX ESTIMATED	~ 6 (4-9) ← NARROW RANGE	



- Inorganic Bromine Partitioning in the Pacific Tropical Tropopause

Sampling density and geographical distribution day and night



No twilight samples ($80 < \text{TAS} < 100$)



		Western Pacific	Eastern Pacific
day		146	81
night		28	210

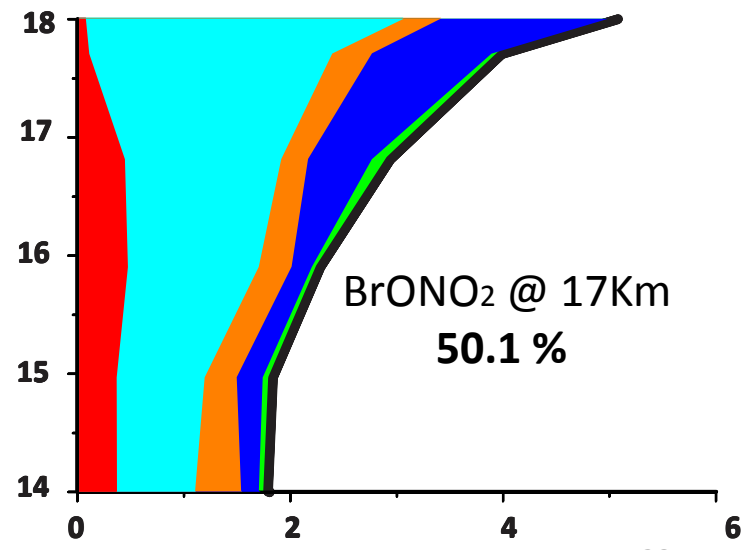
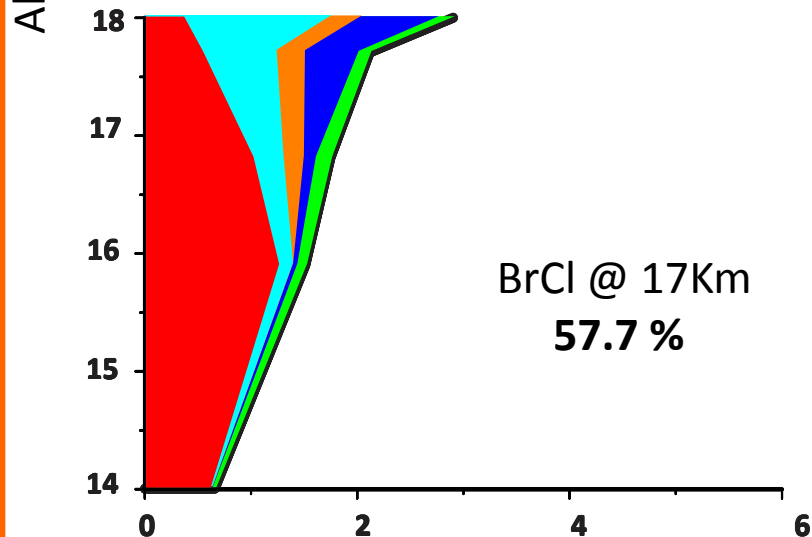
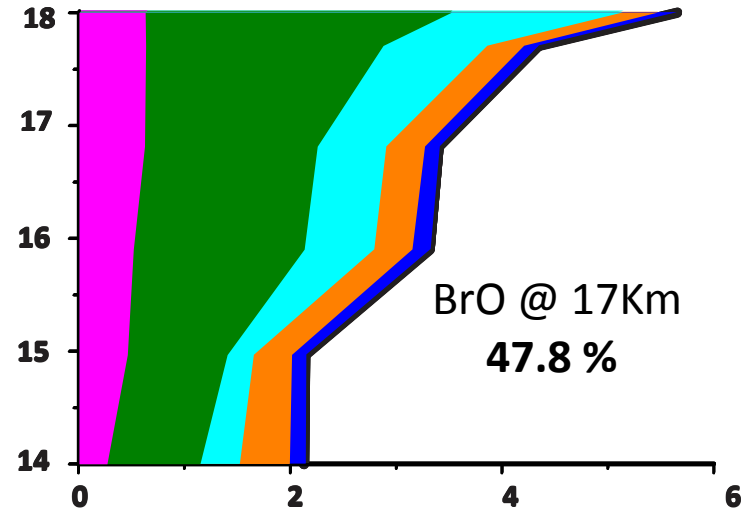
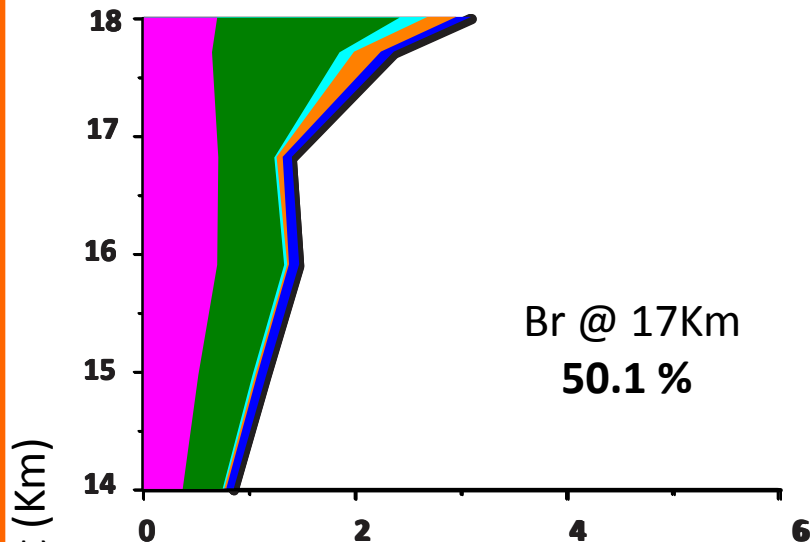
Br_y partitioning in the Pacific Tropical Tropopause

WESTERN PACIFIC

EASTERN PACIFIC

DAY

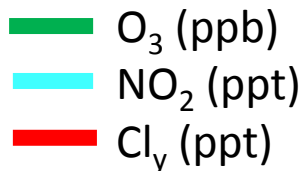
NIGHT



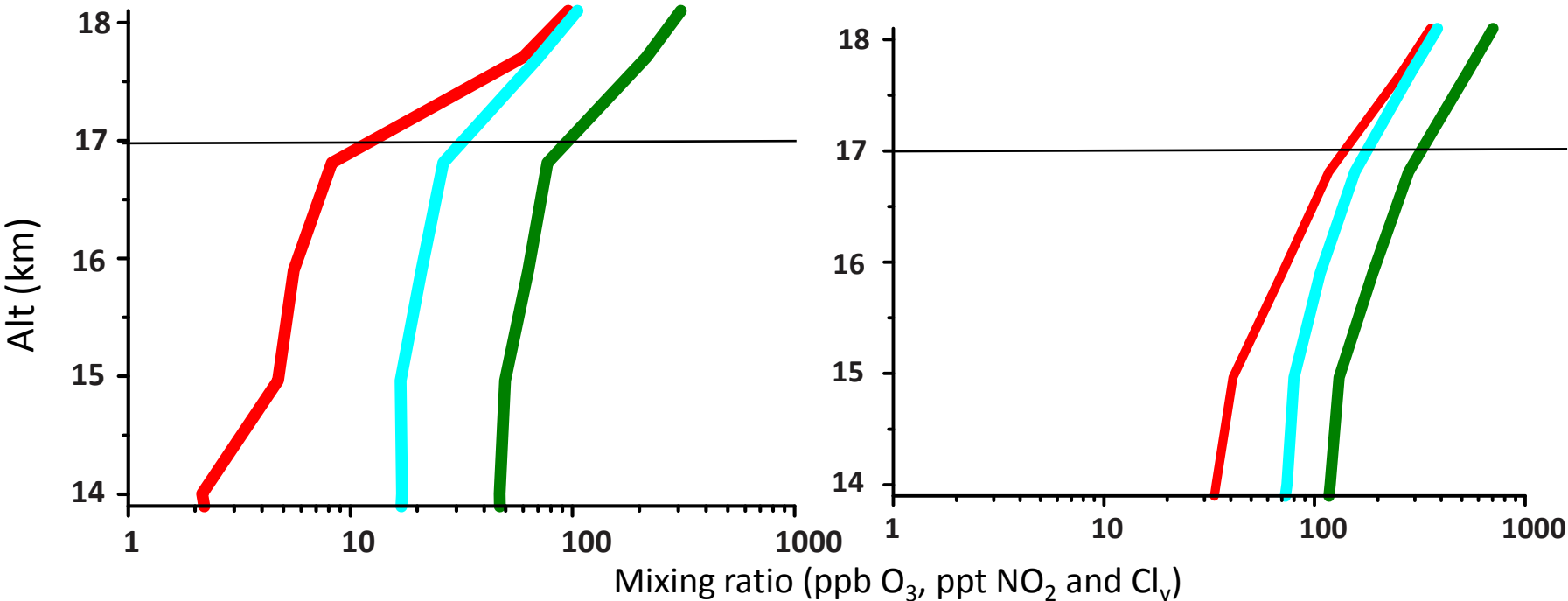
Br IBr BrCl BrO HOBr BrONO₂ HBr BrNO₂ + Br₂ Mixing ratio (ppt)

Modeled O₃-NO₂ and Cl_y mixing ratios

WESTERN PACIFIC



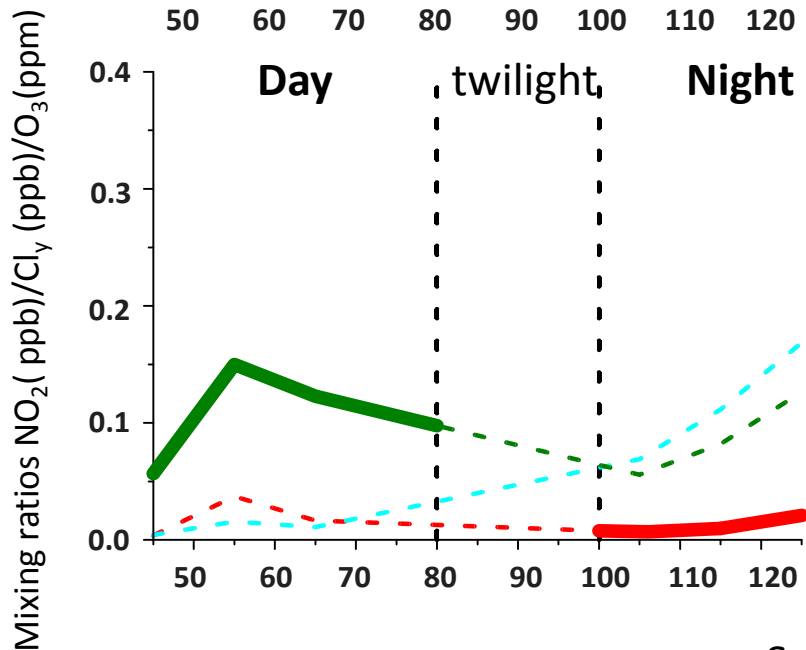
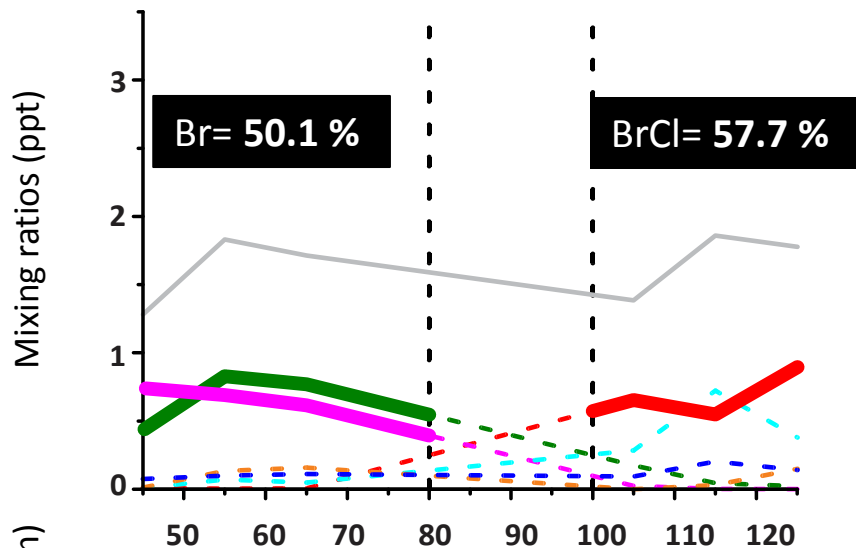
EASTERN PACIFIC



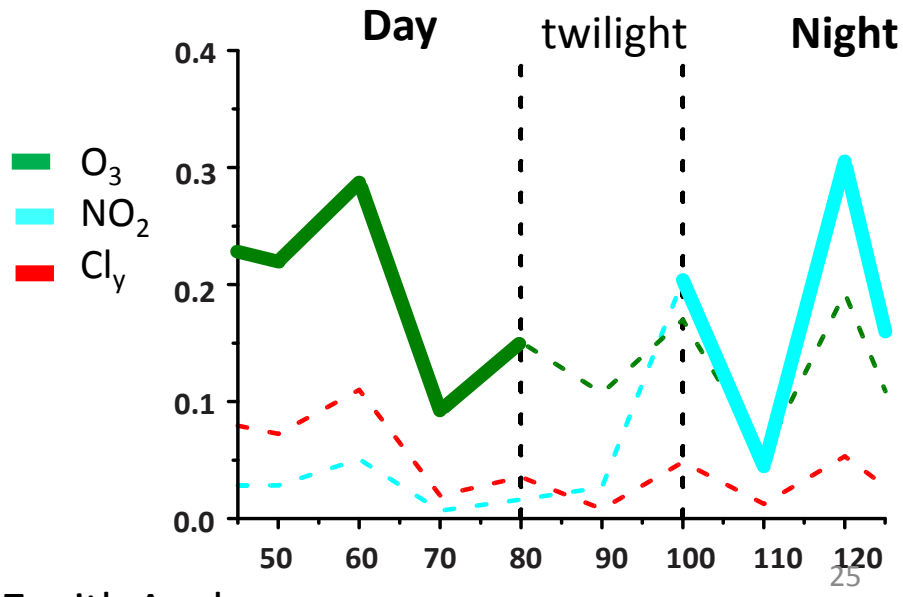
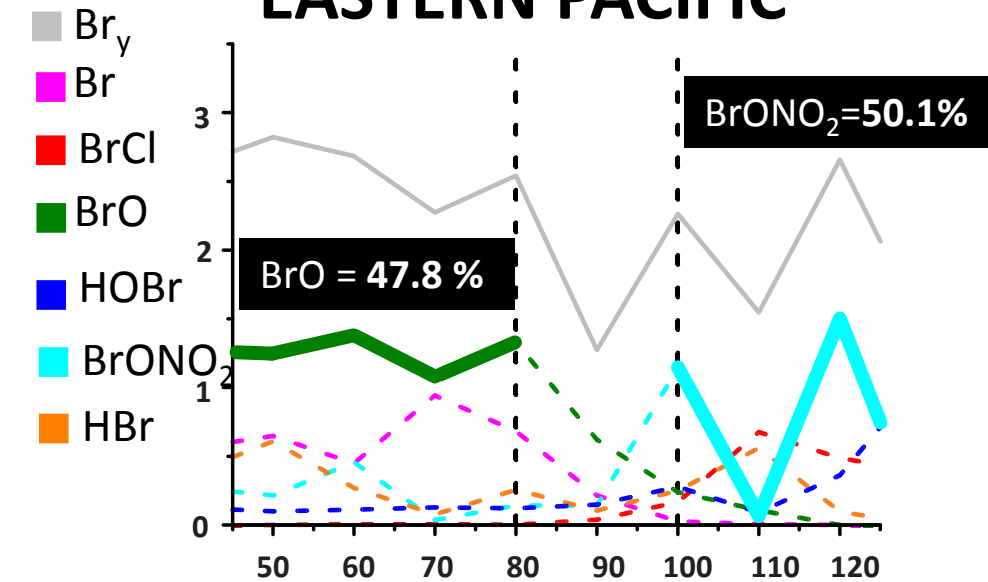
Mixing ratios @ 17 km	Western Pacific	Eastern Pacific
O ₃ (ppb)	77.08	280.27
NO ₂ (ppt)	26.22	155.64
Cl _y (ppt)	8.26	117.06

Br_y partitioning in the tropical tropopause

WESTERN PACIFIC



EASTERN PACIFIC



Solar Zenith Angle

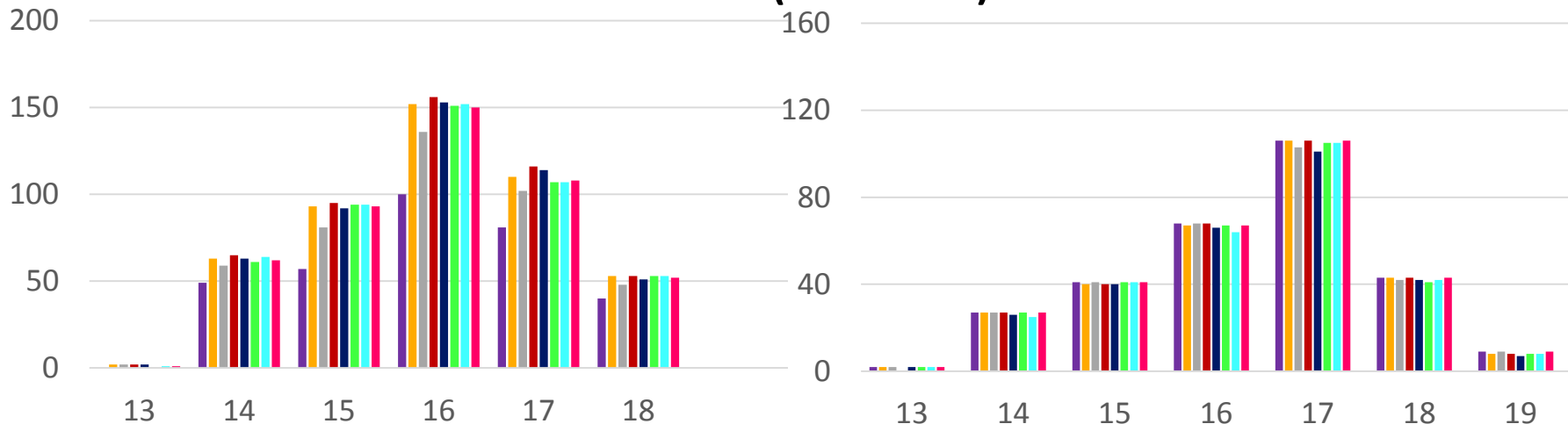
III- Inter-hemispheric behavior of VSLBr

Inter-hemispheric sampling density

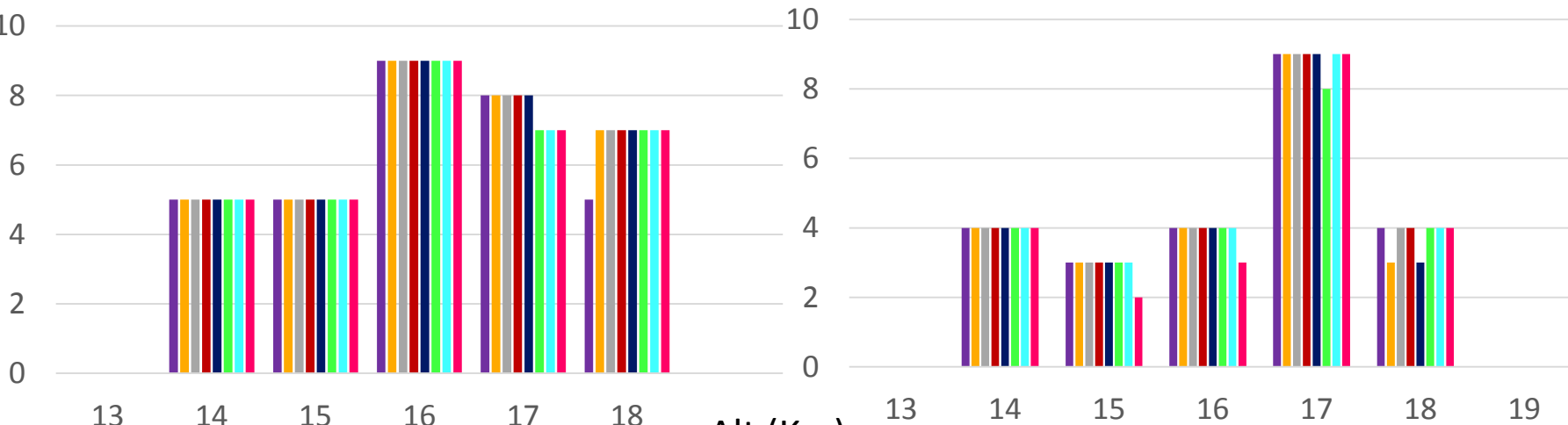
WESTERN PACIFIC

EASTERN PACIFIC

NORTH (0 to 36 °N)



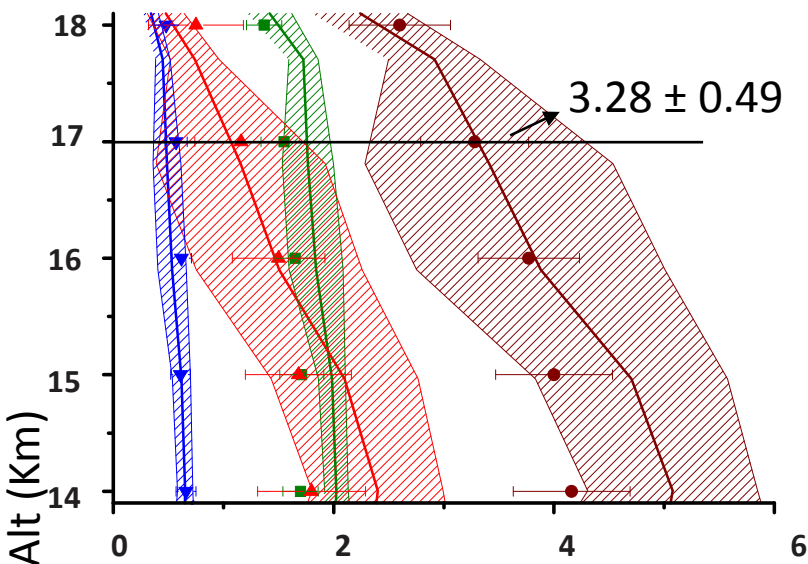
SOUTH (0 to 11° S)



■ CH₂BrCl
 ■ CH₂Br₂
■ CHBrCl₂
■ CHBr₂Cl
 ■ CHBr₃
■ CH₃Br
 ■ Halon 1211
 ■ Halon 2402

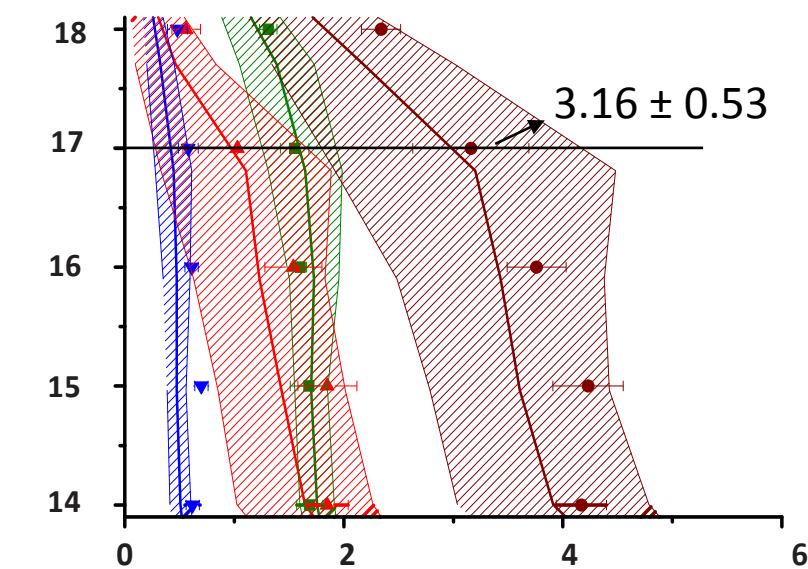
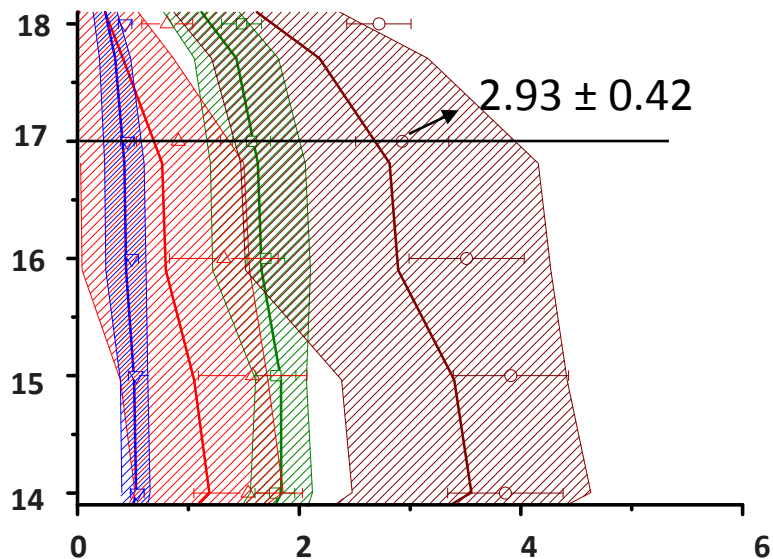
Inter-hemispheric VSLBr distribution from GWAS and CAM-Chem

WESTERN PACIFIC

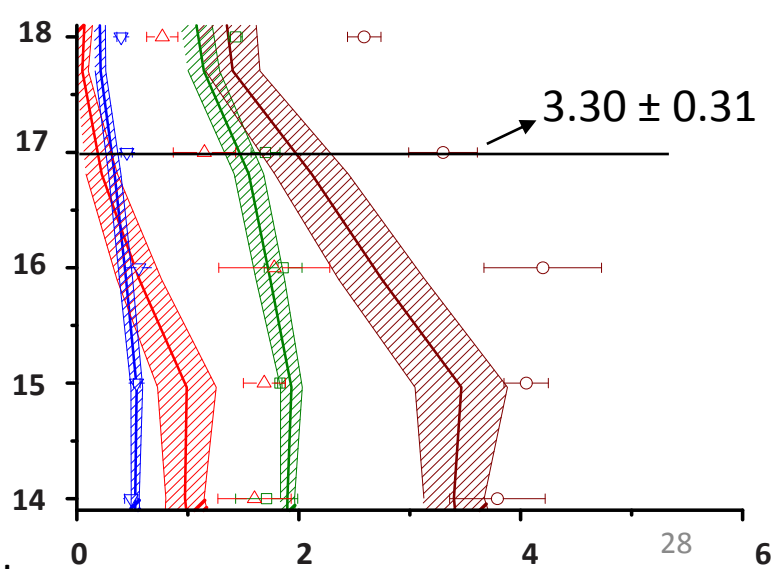


NORTH

EASTERN PACIFIC



SOUTH



- Minor VSLBr
- CHBr_3
- CH_2Br_2
- VSL_{org}

Pmol Br/mol

Summary

- The Total Organic Bromine budget is approximately the same at 17 km ($\Theta \sim 370\text{K}$) in the Eastern and Western Pacific (~ 18 ppt)
- In the less convective region (Eastern Pacific) VSL_{org} could have more time to react and produce ~ 1.5 times more Br_y than in the most convective region (Western Pacific)
- Higher emissions of VSL_{org} in Eastern Pacific could compensate the losses due to reaction, and keep a similar amount of VSL_{org} in both regions of the Pacific (~ 3.8 ppt)
- The amount of VSLBr that reaches the stratosphere (17 Km) of the Eastern and Western Pacific is similar (~ 6 (4-9 ppt)). The range observed in this study is significantly narrower than the one proposed by WMO 2014, particularly at the lower level.
- Partition of Br_y species is different in the Eastern and Western Pacific. According to our model, during the day, Br is the dominant species in the Western Pacific, while BrO dominates the Eastern Pacific. However, during the night, BrCl dominates in the West and BrONO_2 dominates in the East.
- We don't have enough samples from ATTREX to identify a significant interhemispheric difference in organic bromine.



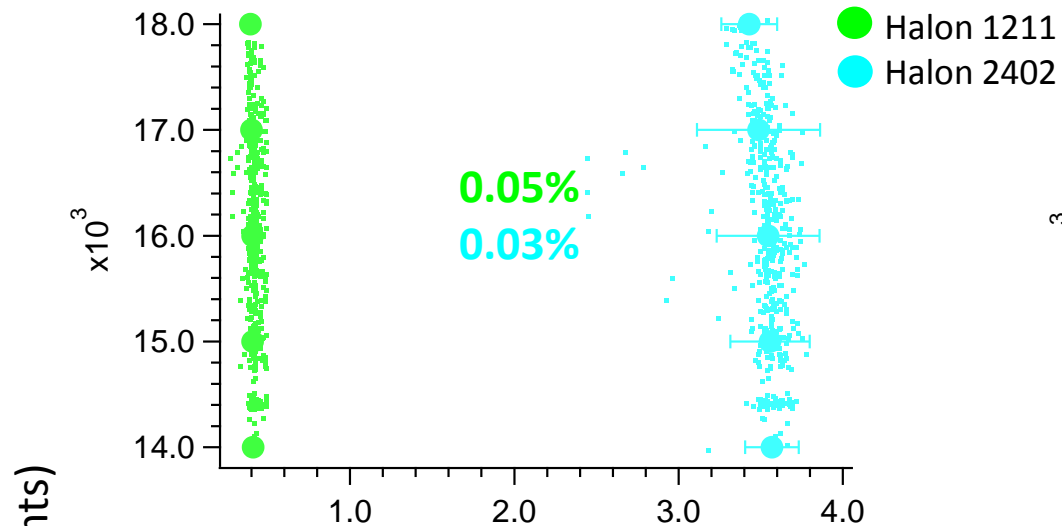
Thank you and Questions



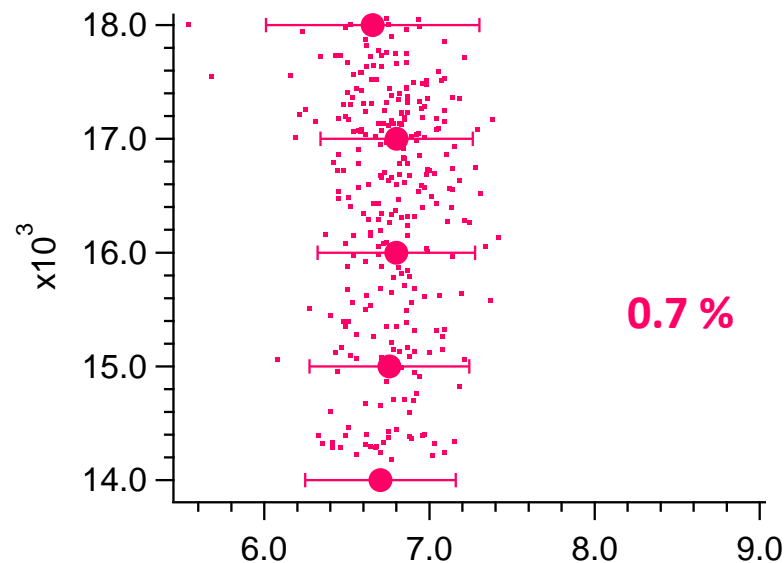
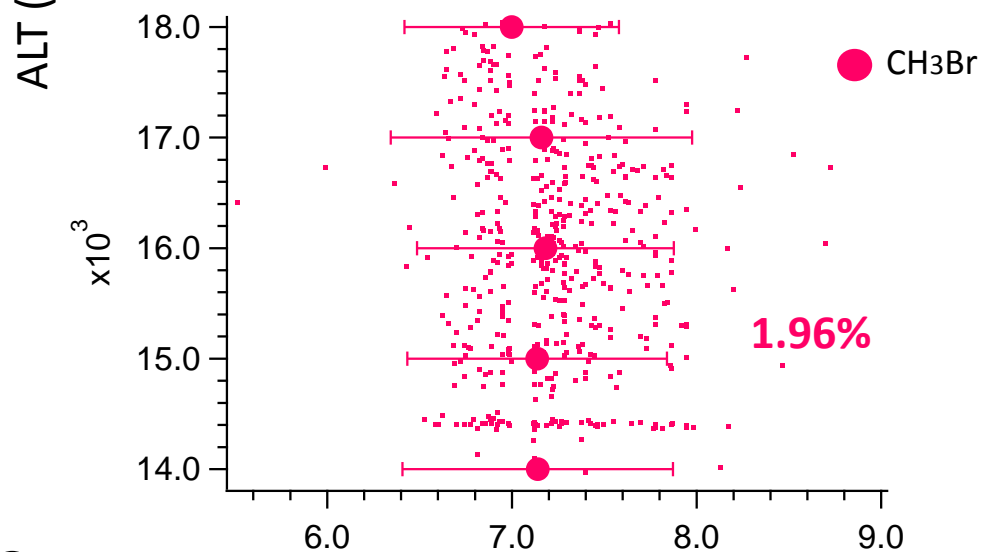
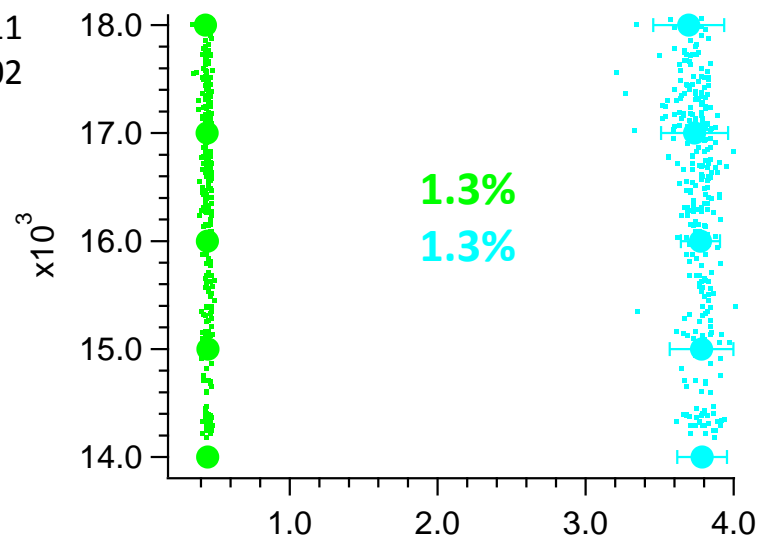
EXTRA SLIDES

Variability and Distribution of GWAS organic bromine species

WESTERN PACIFIC



EASTERN PACIFIC



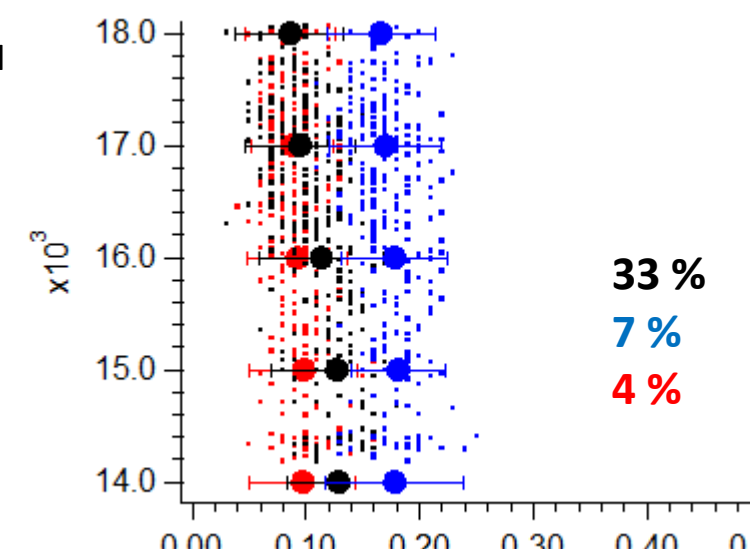
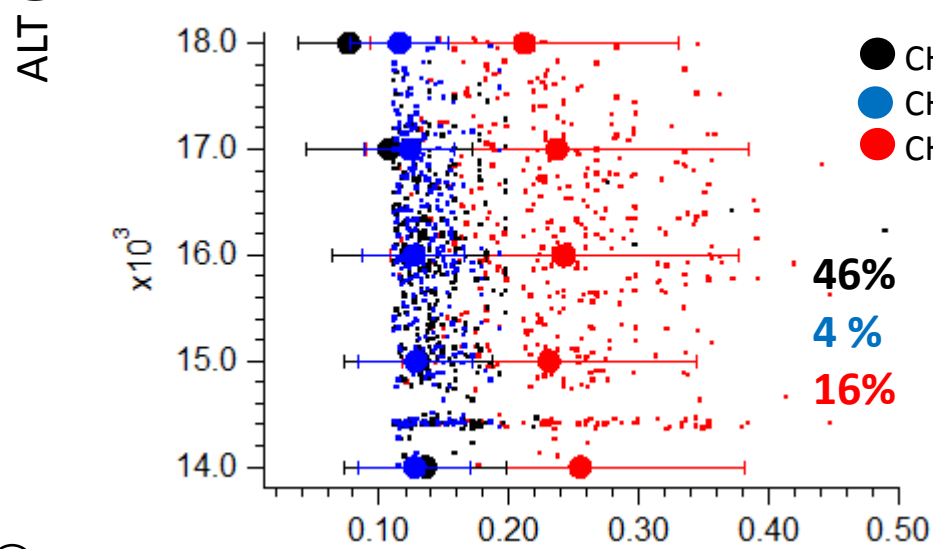
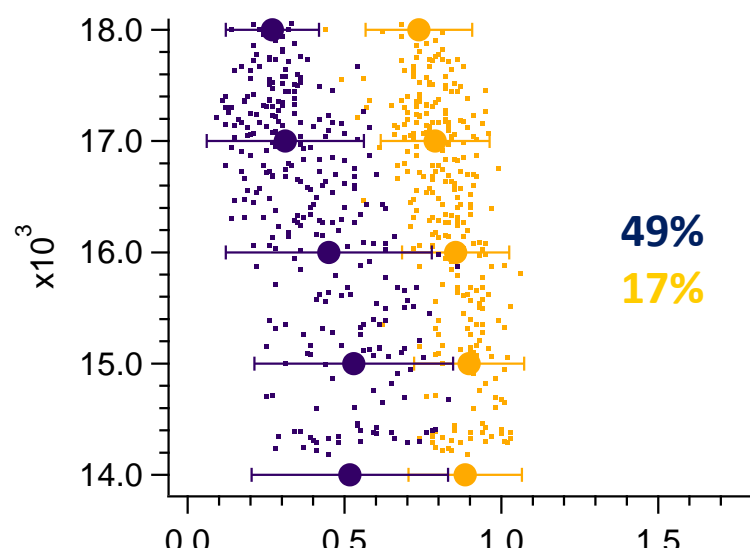
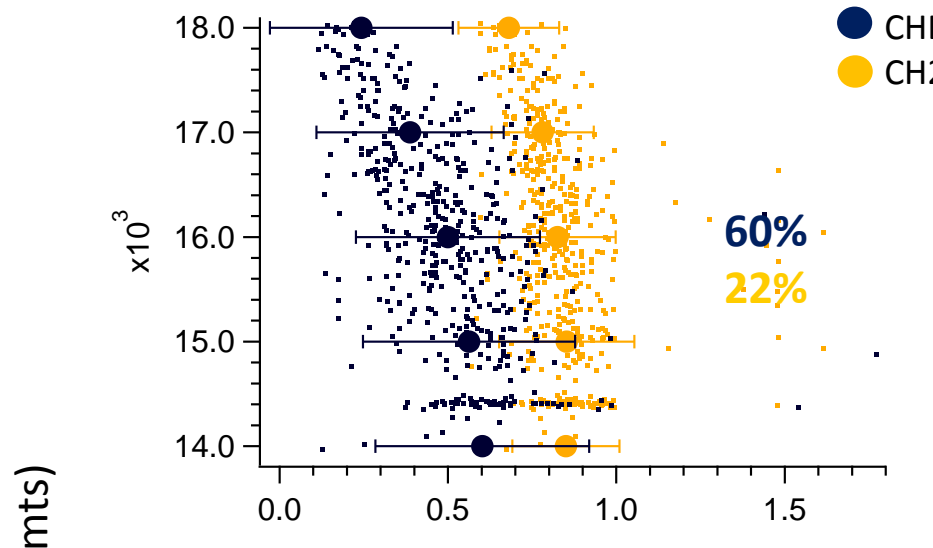
○ Bin 1Km Alt
Error =1sd

Mixing ratios (pmol/mol)

Variability and Distribution of GWAS organic bromine species

WESTERN PACIFIC

EASTERN PACIFIC



○ Bin 1Km Alt
Error =1sd

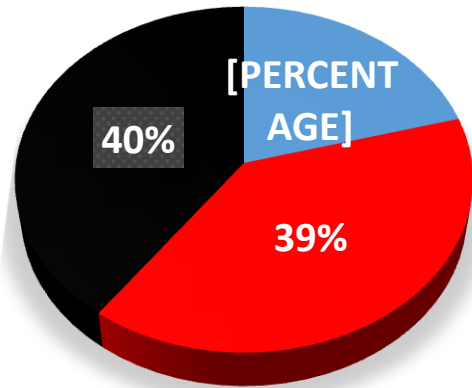
Mixing ratios (pmol/mol)

Organic Bromine Budget in TTL (15-17Km)

WESTERN PACIFIC

Minor VSLBr ATTREX 3

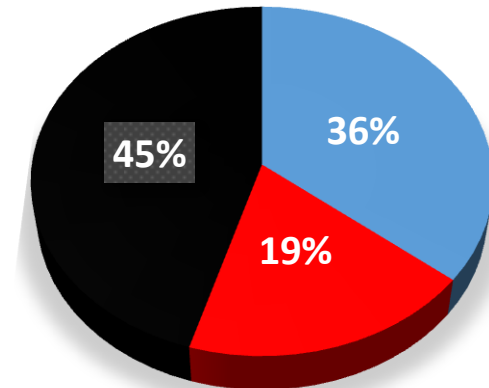
days



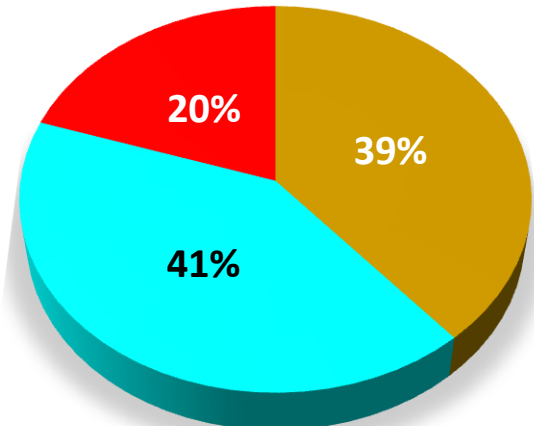
CHBrCl ₂	46
CHBr ₂ Cl	56
CH ₂ BrCl	145

EASTERN PACIFIC

Minor VSLBr ATTREX 2

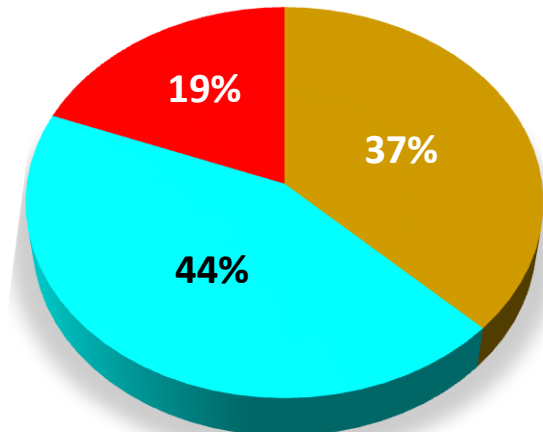


Org Br Budget ATTREX 3



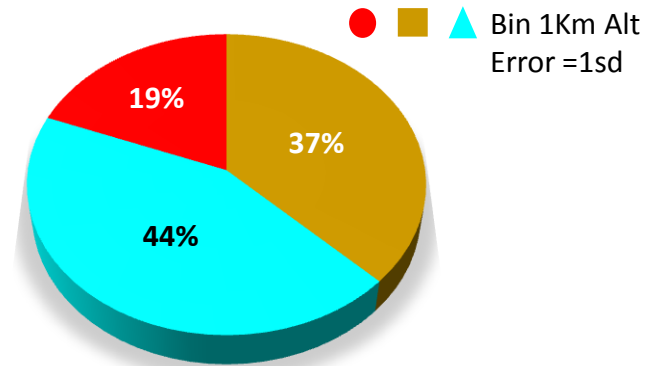
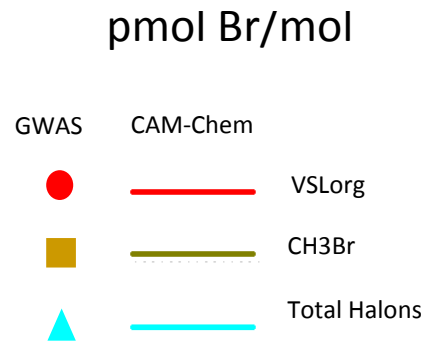
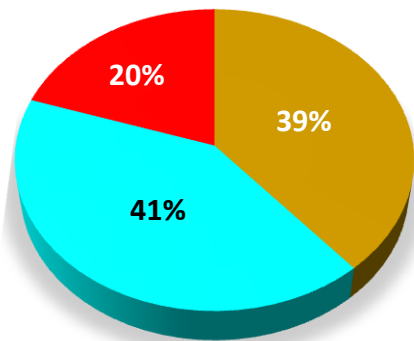
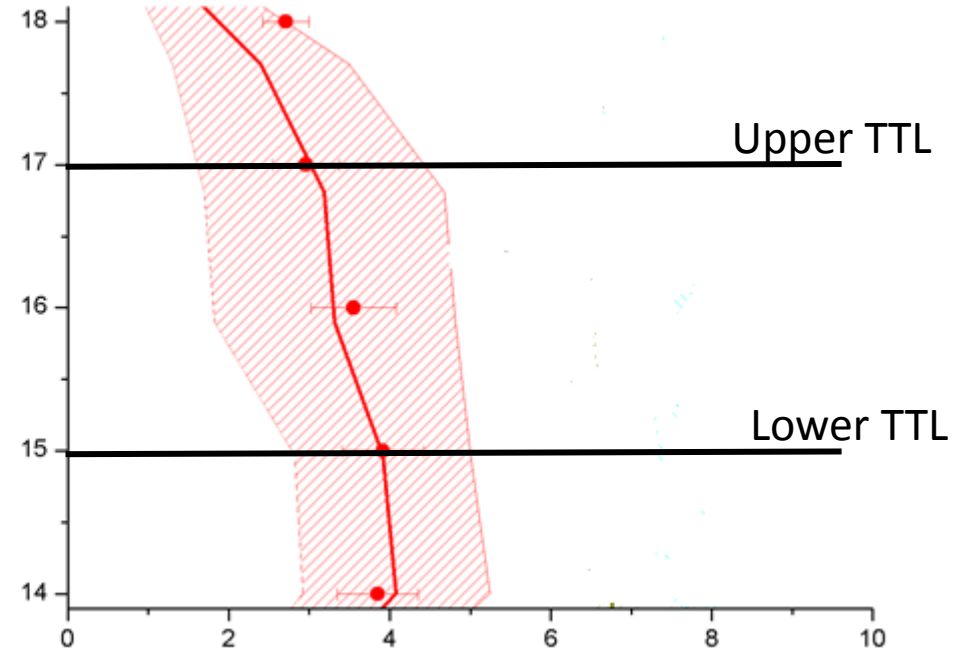
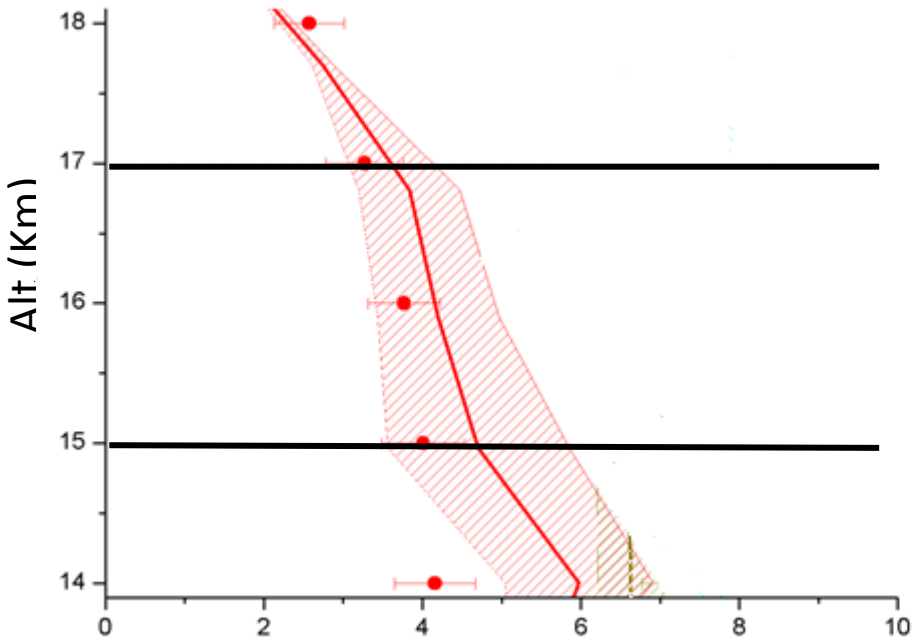
CH ₃ Br	
Total Halon	
VSLorg	

Organic Br Budget ATTREX 2



$$\text{VERY SHORT LIVED Br (VSLorg)} = (3 * \text{CHBr}_3) + (2 * \text{CH}_2\text{Br}_2) + \text{Minor VSLBr}$$

Organic Bromine Budget in TTL (15-17Km)



Average Br org = $18.48 \pm x.xx$ pmol Br/mol

Average Br org = $18.19 \pm x.xx$ pmol Br/mol