Air mass source regions and their influence on the distribution of organic and inorganic bromine species

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Abstract

Brominated very short-lived substances (VSLS), along with their degradation products (e.g. BrO, Br_y ^{inorg}), contribute significantly to stratospheric bromine that ultimately leads to ozone depletion. However, the accurate estimate of the stratospheric bromine budget remains uncertain due to the limited understanding of tropospheric processes, and the spare observations of organic and inorganic brominated species.

Short-lived brominated gases, and/or their breakdown products, could be delivered from the marine boundary layer to the lower stratosphere via deep convection, but their temporal and spatial distribution vary significantly. These changes in their distribution are attributable to the several factors, including the geographical location of the source, the transport dynamics and history of air masses.

In this presentation, we examine the vertical distribution of organic brominated species (CH_3Br, Halons, and VSLS) and the VSLS degradation products (BrO and Br_y ^{inorg}) measured simultaneously, and for the first time, by two instruments deployed during NASA ATTREX campaign (GWAS and Mini-DOAS). We focused on measurements taken during ascending profiles (from ~14 to 19 Km) where observations from both instruments overlapped. 10-day diabatic back trajectories (from selected points along the flight tracks) are used to investigate the impact of the air masses source regions on the distribution of organic and inorganic brominated species, and on the estimation of the total bromine in the Tropical Tropopause Layer.

Sampling and Analysis

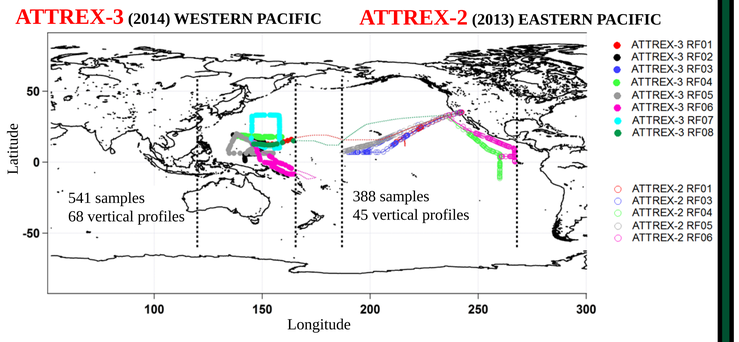

Figure 1: GWAS sampling location and area of study during ATTREX campaign

Table 1: Partial list of target gases measured by GWAS during ATTREX

Longer Lived Species	Yrs	S	Shorter Lived Species	Yrs	S	Shorter Lived Species	Yrs	S
Chlorofluorocarbons			**Solvents**			**Organic nitrates**		
CFC-11	50	A	Methylene Chloride	0.3	A	Methyl nitrate	0.08	A/N
CFC-12	102	A	Chloroform	0.4	A/N	Ethyl nitrate	0.04	A/N
CFC-113	85	A	Tetrachloroethylene	0.3	A	Propyl nitrate	0.03	A/N
Halons			Trichloroethylene	0.02	A			
Halon 1211	20	A				**Non- Methane Halocarbons**		
Halon 2402	20	A	**Methyl Halides**			Ethane (C2H6)	0.2	A
Hydro(chloro)fluorocarbons			Bromoform	0.1	N	Ethyne	0.06	A/B
HCFC_141b	9.4	A	Methyl Bromide	0.8	A/N/B	Propane	0.04	A
HCFC-22	13	A	Methylene Bromide	0.4	N	Benzene	0.04	A/B
HCFC_142b	19.5	A	Methyl Iodide	0.01	N			
Solvent			CHxBryClz	0.1	N			
Carbon Tetrachloride	40	A						
Methyl chloroform	4.8	A	**Others**					
Other			1,2 dichloro ethane	0.3	A			
Methyl Chloride	1.5	N/B	Chlorobenzene	0.05	A			
Carbonyl Sulfide (COS)	30	N/A/B						

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

Table 2: Target species measured by Mini-DOAS during ATTREX

Fit Ranges wavelength:	
BrO & O_3:	346 – 360.5 nm
NO_2:	425 – 446.8 nm
O_2:	346 – 355 nm
	437.2 – 485.5 nm

For more details please attend to: K. Pfeilsticker talk: "Measurement and simulation of CH4, O3, NO2, BrO, and major brominated source gases during the NASA-ATTREX Global Hawk deployments in 2013: Implications for the photochemistry and total amount of bromine in the TTL and stratosphere"
Tuesday July 21, 2015 at 17:20

Br_y and Br_{Org} approximations used by Mini-DOAS

$$[BrO] = \frac{\alpha_{BrO}}{\alpha_{O3}} \times \frac{DSCD_{BrO}}{DSCD_{O3}} \times [O_3]_{in-situ}$$

RT Model Calculations — DOAS — NOAA

DSCD= differential *slant column density*

$$[Br_{tot}] = [Br_{org}] + \left.\frac{[Br_y]}{[BrO]}\right|_{calc} [BrO]$$

Br_y = Br + BrO + $BrONO_2$ + BrCl + HOBr + HBr

Br_{org}= CH_3Br + CH_2BrCl + 2 x CH_2Br_2 + $CHBrCl_2$ + 2 x $CHBr_2Cl$ + 3 x $CHBr_3$ + halons

GWAS Correlations of Natural and Anthropogenic Species over the Pacific

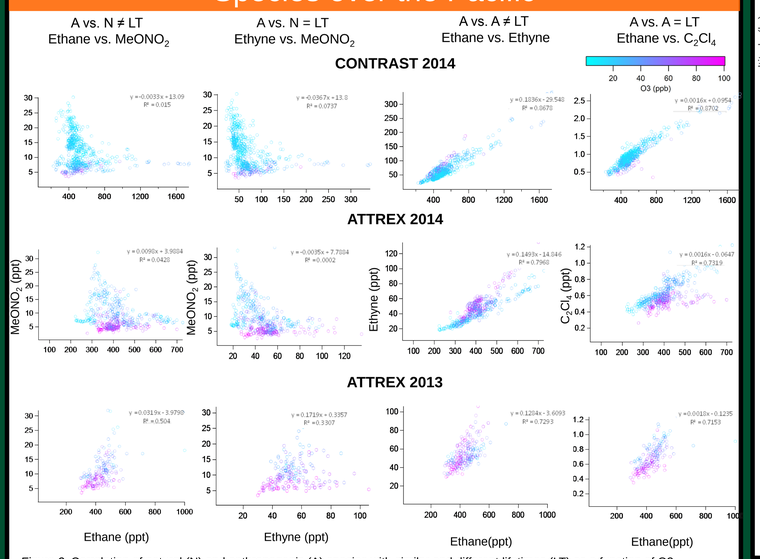

Figure 2: Correlation of natural (N) and anthropogenic (A) species with similar and different lifetimes (LT) as a function of O3 concentrations. The correlations indicate potential impacts in TTL composition from biomass burning (high ethyne:ethane), tropical convection (high MeONO2, low NMHC); and N. mid-latitudes (intrusions of high NMHC and C_2Cl_4)

We gratefully acknowledge UCATS, NOAA and HAIS Fast O_3 teams for providing O_3 data

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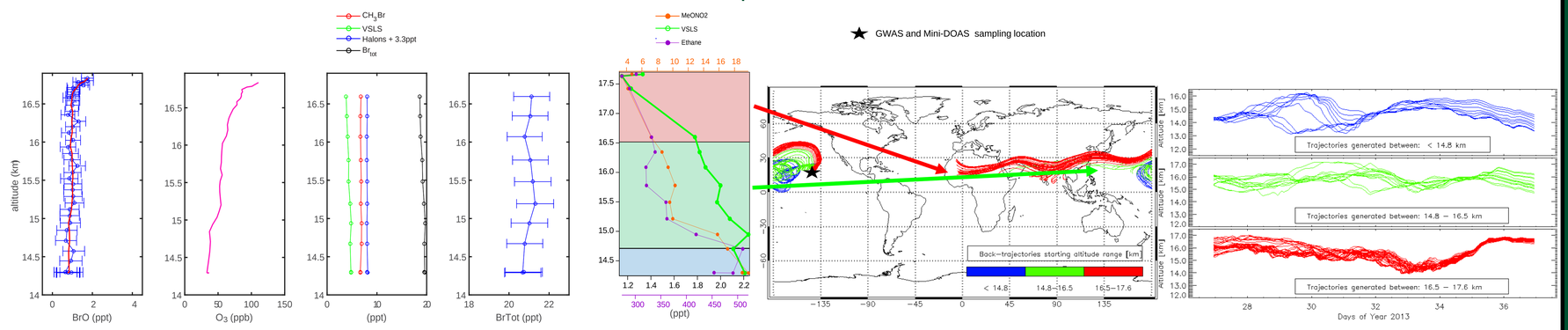
Vertical profiles and back trajectories analysis

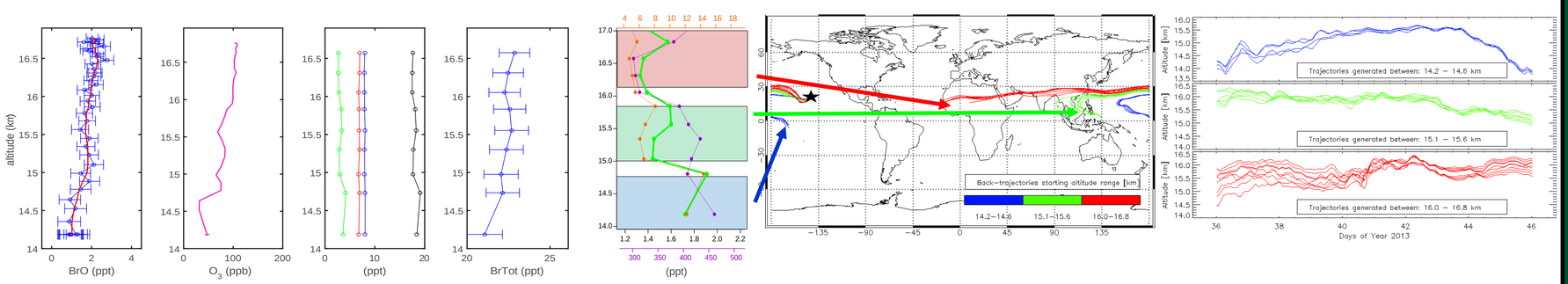
Figure 3: Vertical profile of organic and inorganic bromine species, and 10 days back trajectories. Changes of VSLS mixing ratios greater than 0.1 ppt defined the structures. Structures are color coded by the altitude range at which the back trajectory analysis starts. The color-coded arrows show the location of the air masses 10 days prior to sampling. O_3 profiles are used to identify tropospheric or stratospheric conditions. Ethane and Methyl Nitrate are used as tracers of natural and anthropogenic origin respectively.

ATTREX 2013 RF01 Profile # 1: Vertical profile with No Structure



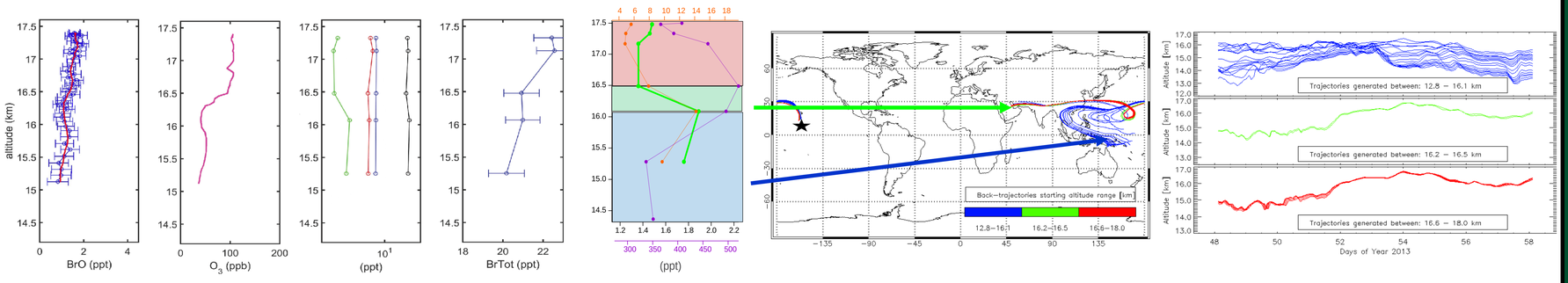
Vertical profile of BrO, CH_3Br and Halons are constant along the range of altitudes. VSLS as well as Br total mixing ratios decrease as altitude increase. The back trajectory analysis show that the air masses for samples taken above 14.8 Km were over Africa 10 days prior to sampling. Some air masses between 14.8 and 16.5 km were over the Pacific 10 days prior to sample, which agrees with a decrease of Ethane mixing ratios. O_3 mixing ratios indicate tropospheric conditions.

ATTREX 2013 RF03 Profile # 1: Vertical profile with Structure



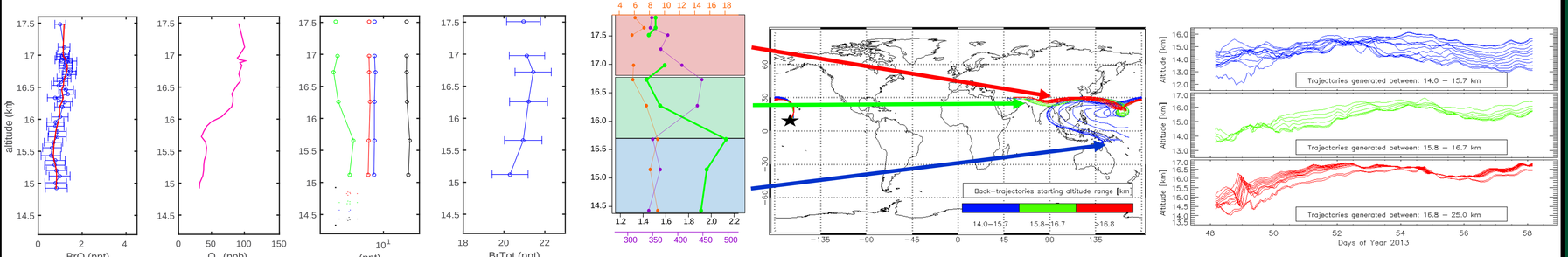
Vertical profile of VSLS, BrO and Br Total show some variability as altitude increase. The back trajectory analysis show that the air masses for samples taken below 14.6 Km were over the Pacific 10 days prior to sampling. This also agrees with an increase of $MeONO_2$ and a decrease of Ethane mixing ratios. Some air masses between 15.1 and 15.6 km were over the coast of Asia passing over Thailand 10 days prior to sample and agree with a decrease of $MeONO_2$ and an increase of Ethane mixing ratios. O_3 mixing ratios as well as the altitude vs days figure indicated that the air masses where below the stratosphere.

ATTREX 2013 RF05 Profile # 2: Vertical profile with structure (stratospheric influence)



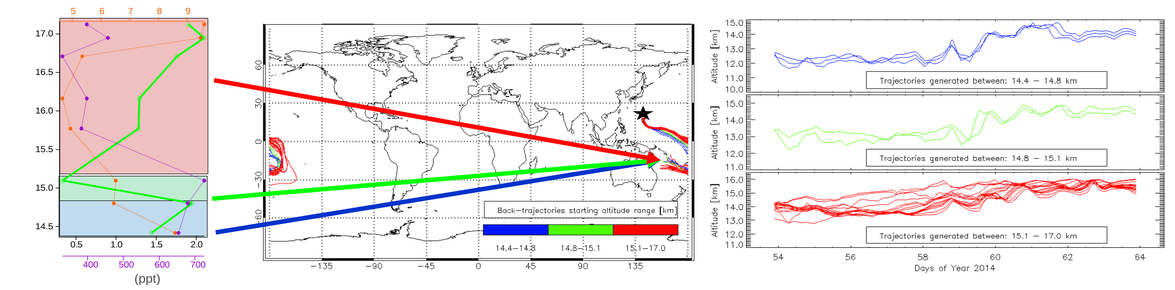
Vertical profile of VSLS, BrO and Br-Total show some variability as altitude increase. The back trajectory analysis show that the air masses for samples taken below 16.1 Km were over the Maritime Continent 10 days prior to sampling. This influence appears to be related to an increase of $MeONO_2$ and a decrease of Ethane mixing ratios. Air masses above 16.2 km were over South Asia10 days prior to sample and are associated with a decrease of $MeONO_2$ and an increase of Ethane mixing ratios. O_3 mixing ratios as well as the altitude vs days figure indicated that the air masses were influenced by mixing with the lower stratosphere. In contrast, Br-Total tends to show a rather monotonic increase with altitude, from 20 – 22 ppt Br.

ATTREX 2013 RF05 Profile # 3: Vertical profile with structure (stratospheric influence)



Similar to previous plot. Ethane is less enhanced in the mid-level (15.5 – 16.5 km) altitude range compared to the first profile. Br-Total remains similar to that in the first profile shown above.

ATTREX 2014 RF04 Profile # 6: Vertical profile during strong convective event (Tropical Storm FAXAI)



The vertical profile of VSLS and $MeONO_2$ show an increase of mixing ratios as a consequence of the fast uplift. Back trajectory analysis show that all air masses where over the Western Pacific 10 days prior to sample, but the composition was strongly influenced by the strong convection associated with Faxai. Impact on the Br budget is still to be determined.

10-day diabatic back trajectories are from selected points along the flight tracks of ATTREX. 6-hourly ERA-Interim analyses (.75 by .75 degree resolution) were used, along with heating rates depending on longitude, latitude, and altitude (constant in time, based on CALIPSO/CLOUDSAT data) Vertical resolution is approximately 1 km near the tropical tropopause. The approach divided each flight into 1 hour segments, and initialize the back trajectories for that segment at a single time.
Notice that these back trajectory maps use pressure-altitude instead of GPS.

Summary

Source regions of air masses could influence the amount of total Br, and the distribution of its components, affecting the accurate estimation of the stratospheric bromine budget. Air masses originated over the ocean agree with the enhancement of VSL source gases even in a small range of altitude. Further studies of the history of air masses and convective event over the Pacific region are necessary.

This study is work in progress. Back trajectory analyses starting at specific GWAS locations will provide more precise information. Similarly, the use of other natural and anthropogenic tracers could be useful for a detailed study.