# TTL/LS halogens

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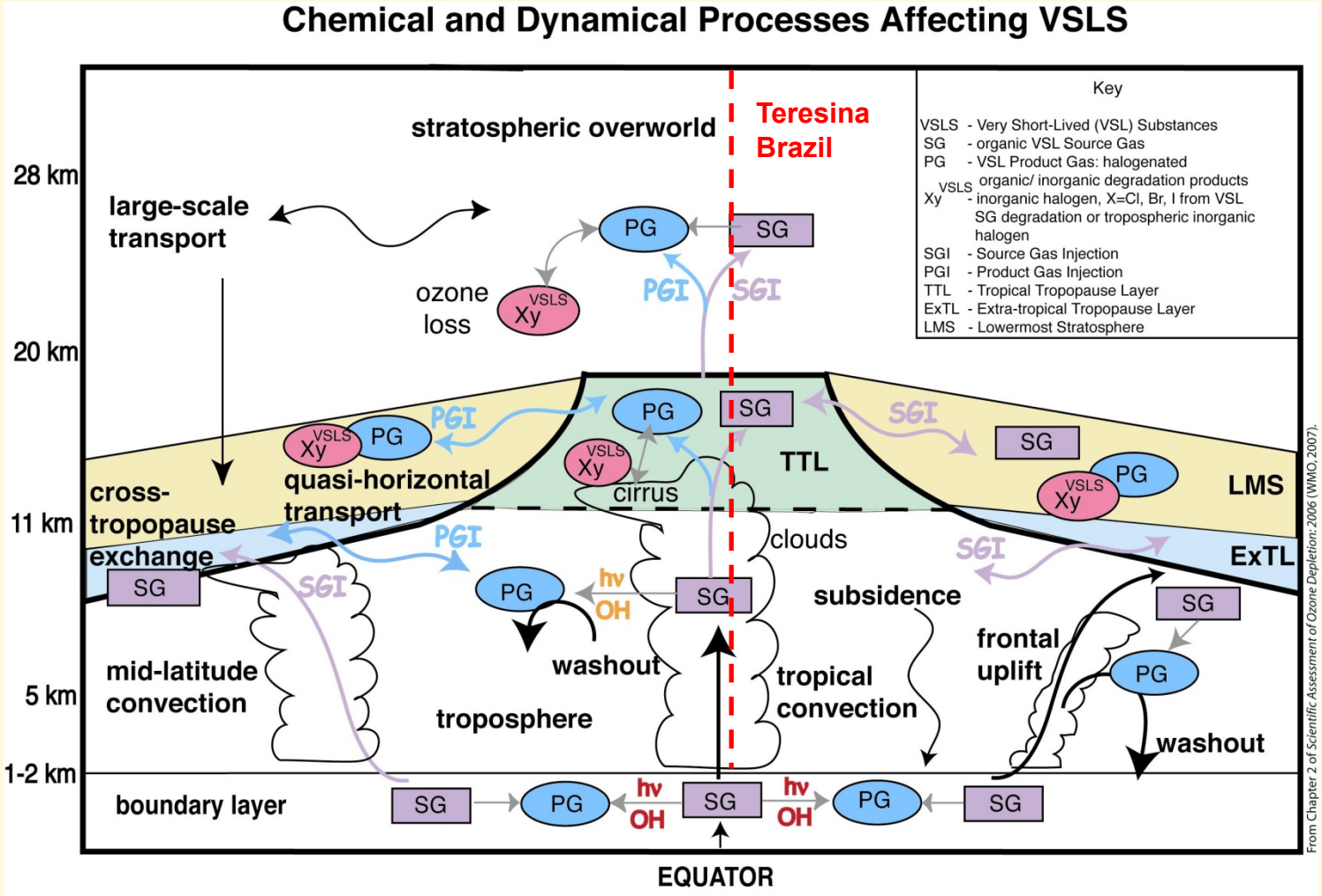
# Overview

1. Introduction
2. Organic and inorganic bromine and iodine in the MBL of the Pacific; some prelimary results of the TransBrom and the EU-SHIVA projects
3. Balloon-borne measurements of organic and inorganic
   - bromine &
   - iodine

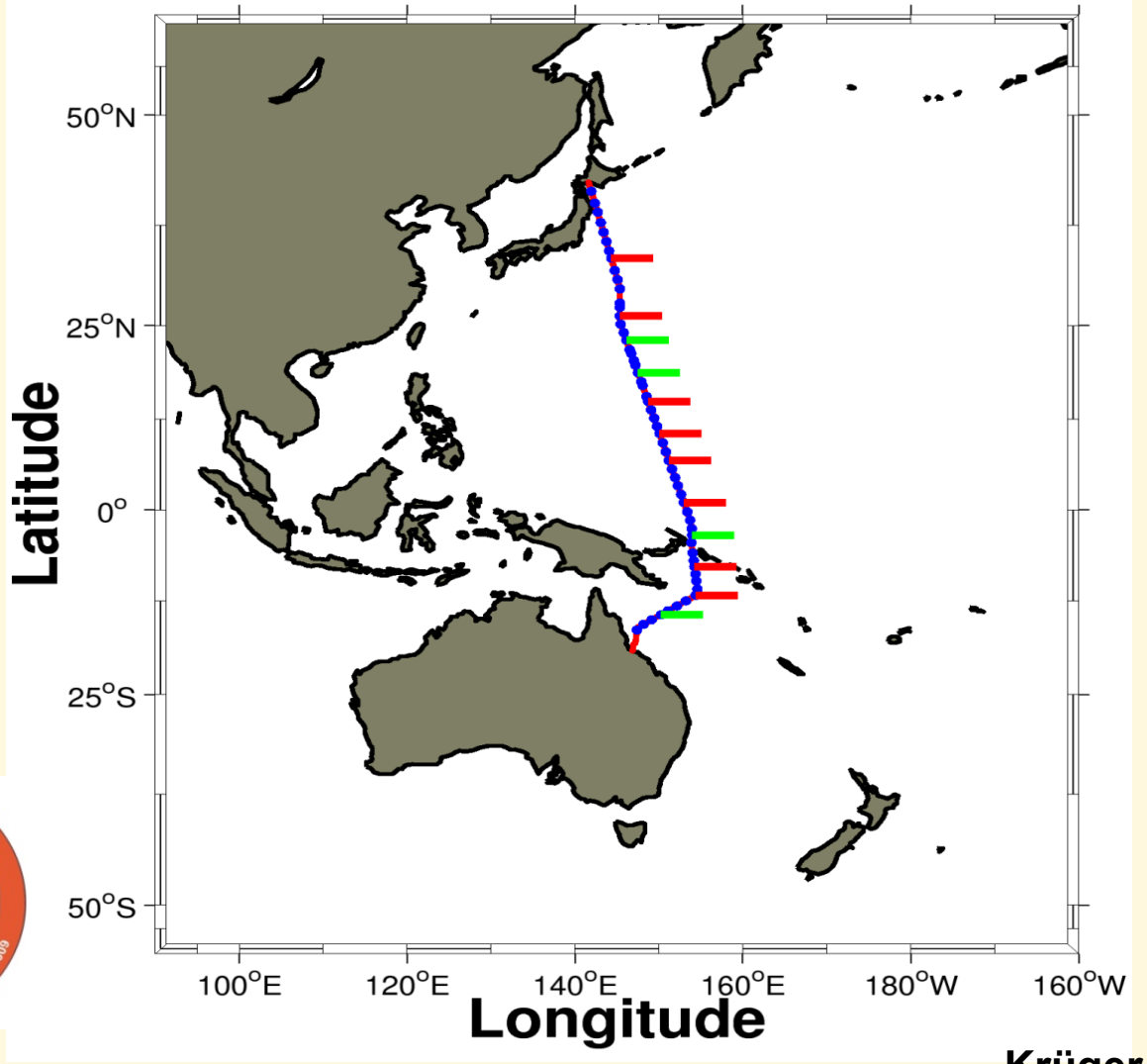
   in the TTL/LS
4. Conclusions
5. Annex: Some more scientific objectives related to the GH miniDOAS measurements

# The role of halogens in stratospheric ozone and climate




(Fig.2-1, WMO-2006)

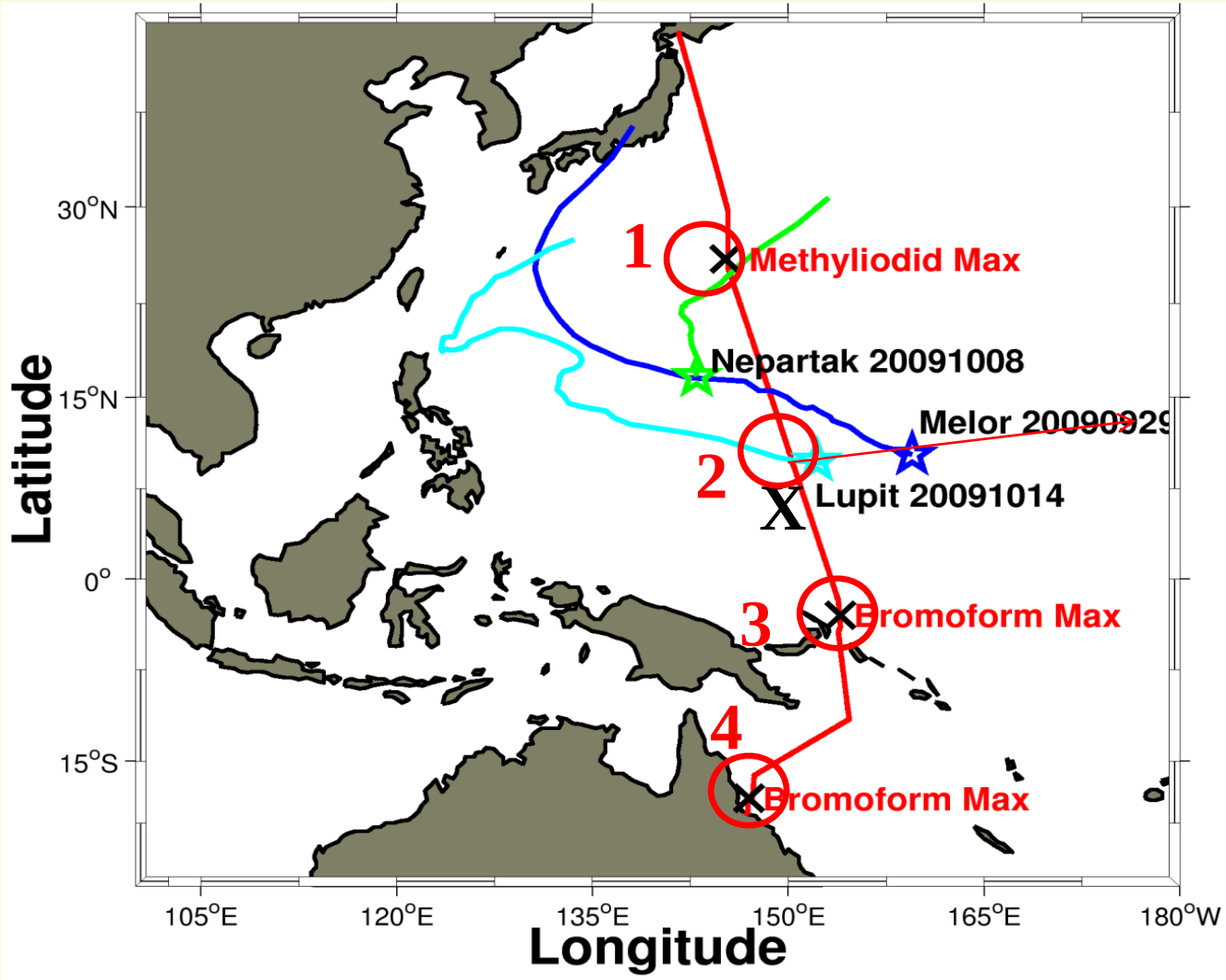
# TransBrom RV SONNE measurements




--Ship track
VSLS (3 to 6 hrly)
GRAW radiosonde (6 hrly)
__Ozone+radio sonde
__COBALD+ozone+radio sonde

Krüger and Quack et al. (priv. comm.)

# Points of interest for the TRANSBrom RV Sonne Cruise in fall 2009




Krüger and Quack et al. (priv. comm.)

# Transport simulations with FLEXPART

- **FLEXPART is a Lagrangian particle dispersion model that simulates the long-range and mesoscale transport, diffusion, dry and wet deposition, and radioactive decay of tracers (*Stohl et al.,* 2005).**

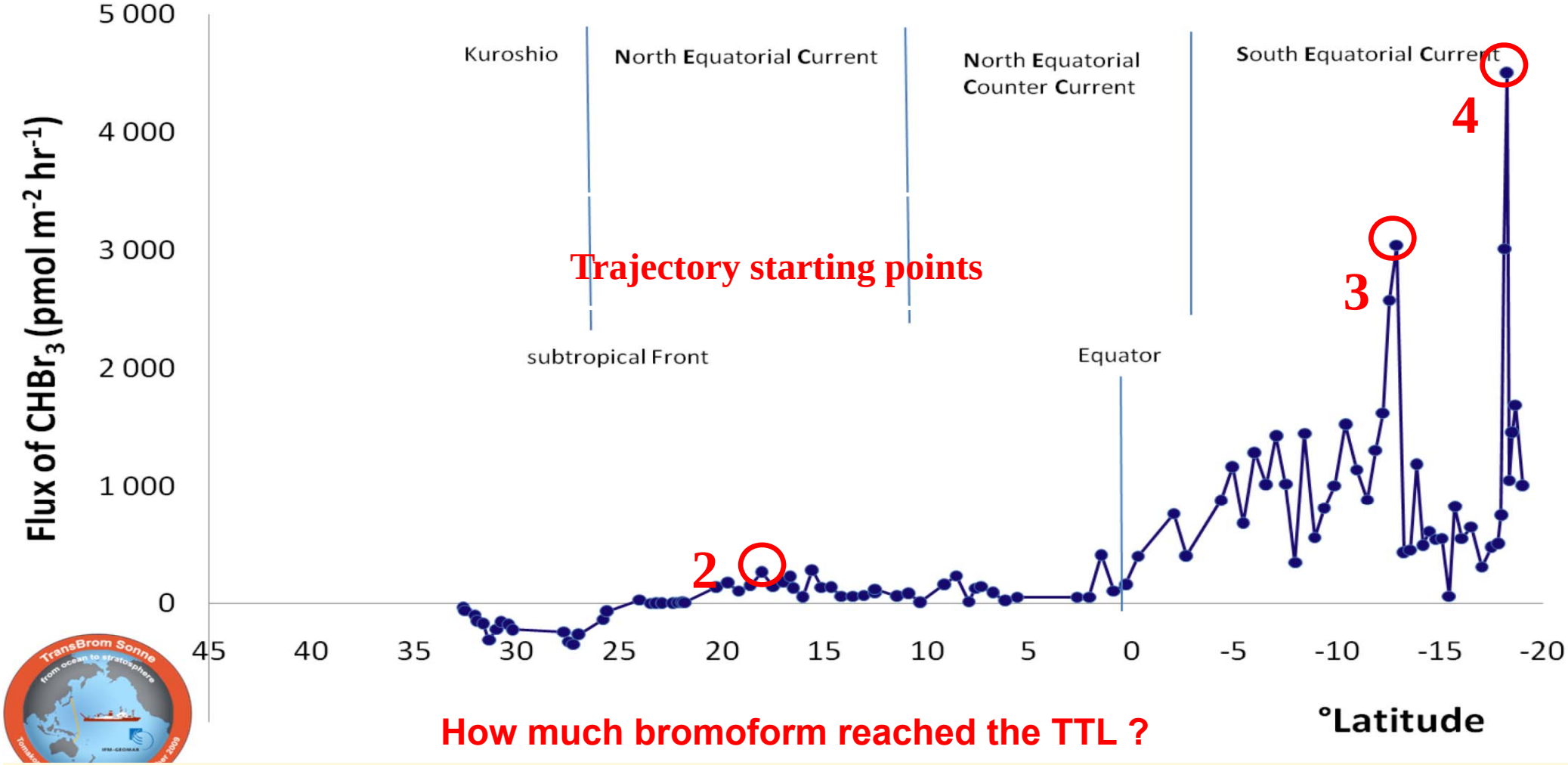
- **FLEXPART is an off-line model using meterological fields from the ECMWF numerical weather prediction model (here ERA-INTERIM: u, v, w, T, q, convective and large scale precipitation ... )**

- **FLEXPART uses the convective parameterization scheme from Emanuel and Zivkovic-Rothman (1999).**

- **FLEXPART is used forward in time to compute trajectories of a large number of particles to describe the transport and diffusion of methyliodid and bromoform in the atmosphere.**

**Tegtmeier et al., (priv. comm.)**

# $CHBr_3$ emissions in the Western Pacific in Oct. 2009




**How much bromoform reached the TTL ?**

**Quack et al., (priv. comm.)**

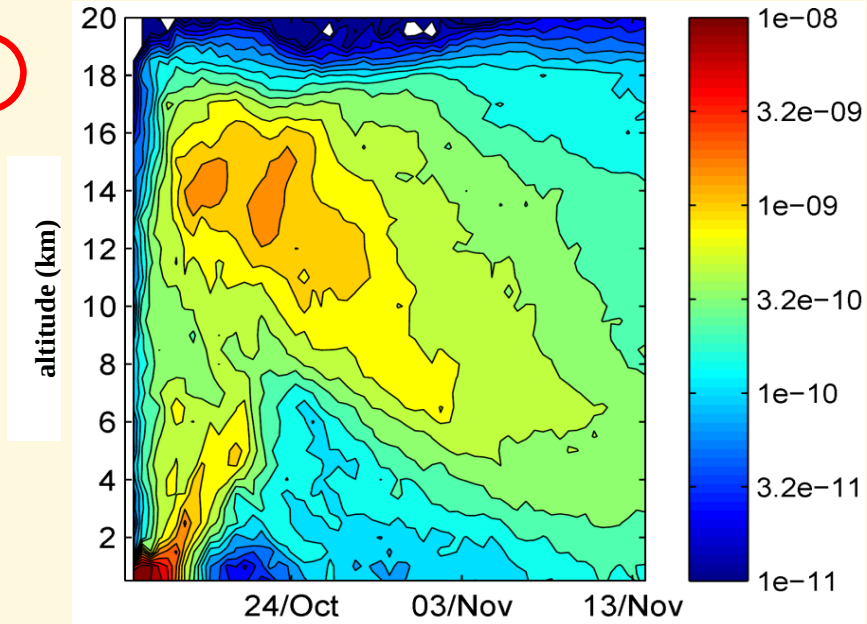
# Simulated Bromoform transport

**FLEXPART transport simulation based on emitted CHBr3 :**
**2) 285 pmol m-2 hr-1**
**3) 3000 pmol m-2 hr-1**
**4) 4000 pmol m-2 hr-1**

**Figure shows for every time step bromoform [kg] as a function of altitude.**

**Tegtmeier et al., priv. com.**

②

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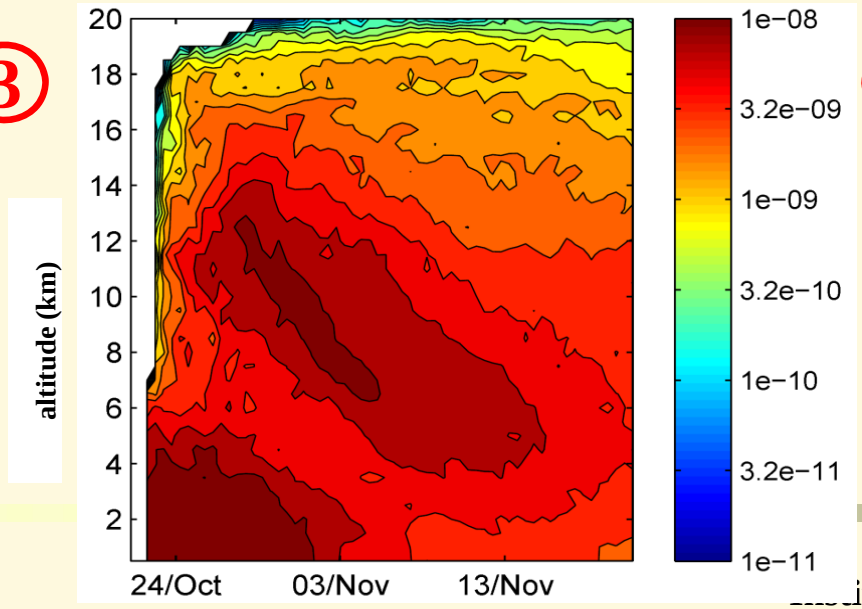


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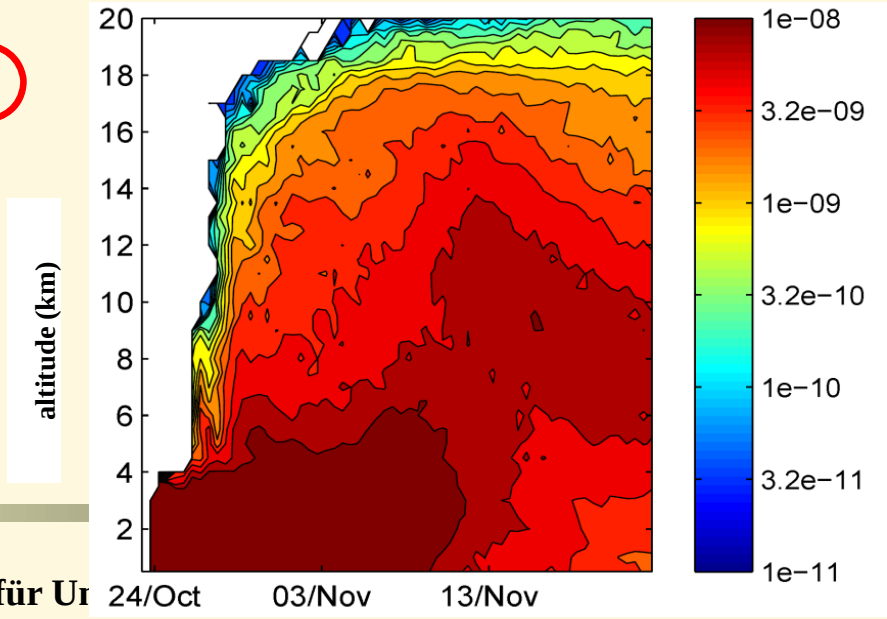
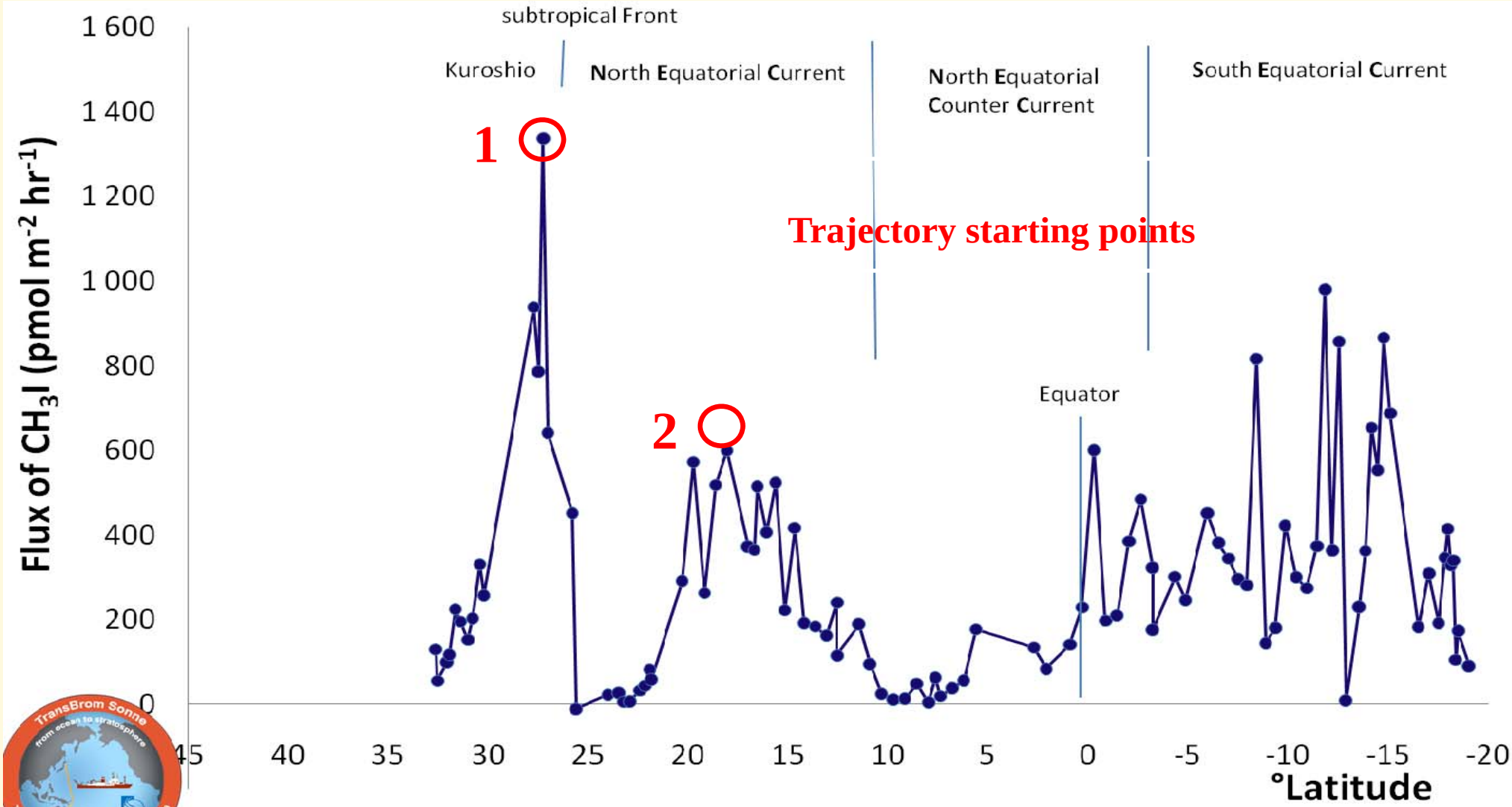


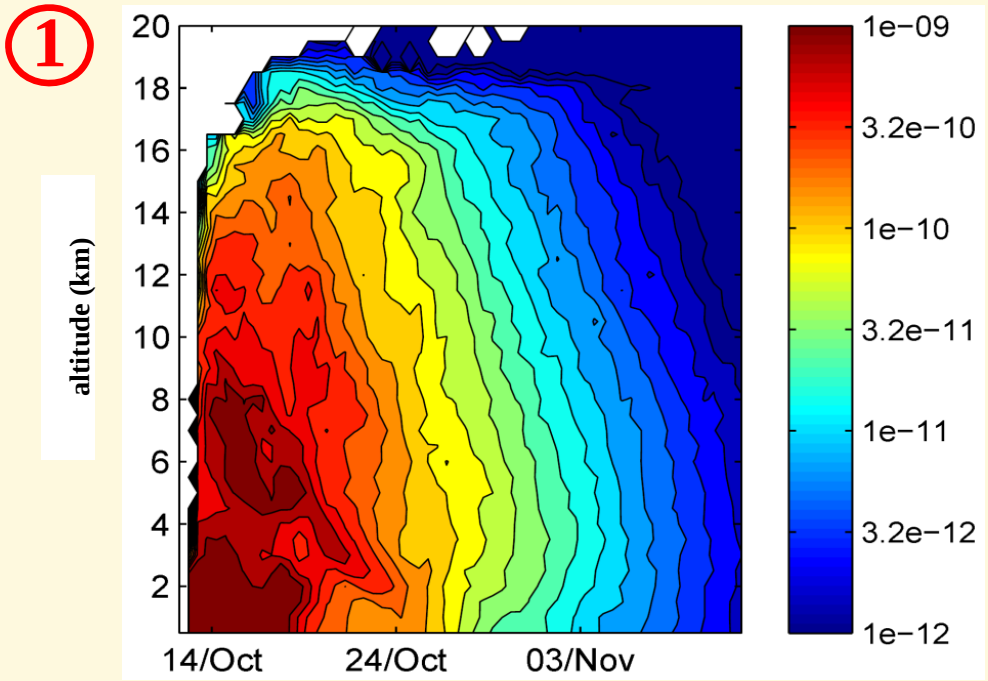
# $CH_3I$ emissions in the Western Pacific in Oct. 2009

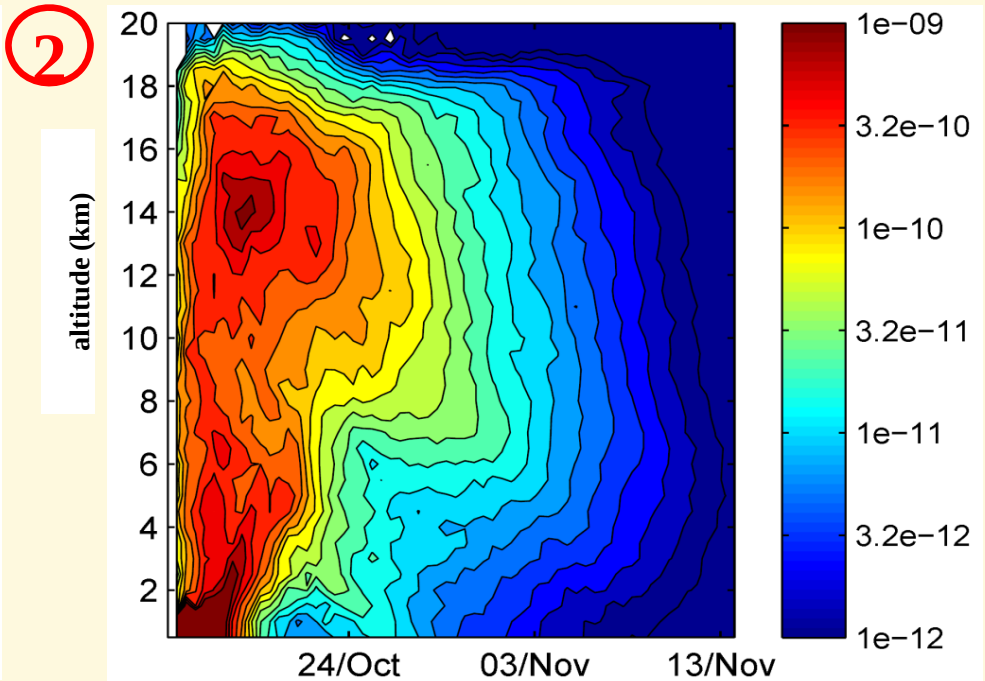



**Can Methyliodid reach the TTL ?**

**Quack et al., (priv. comm.)**

# Simulated Methyliodid transport



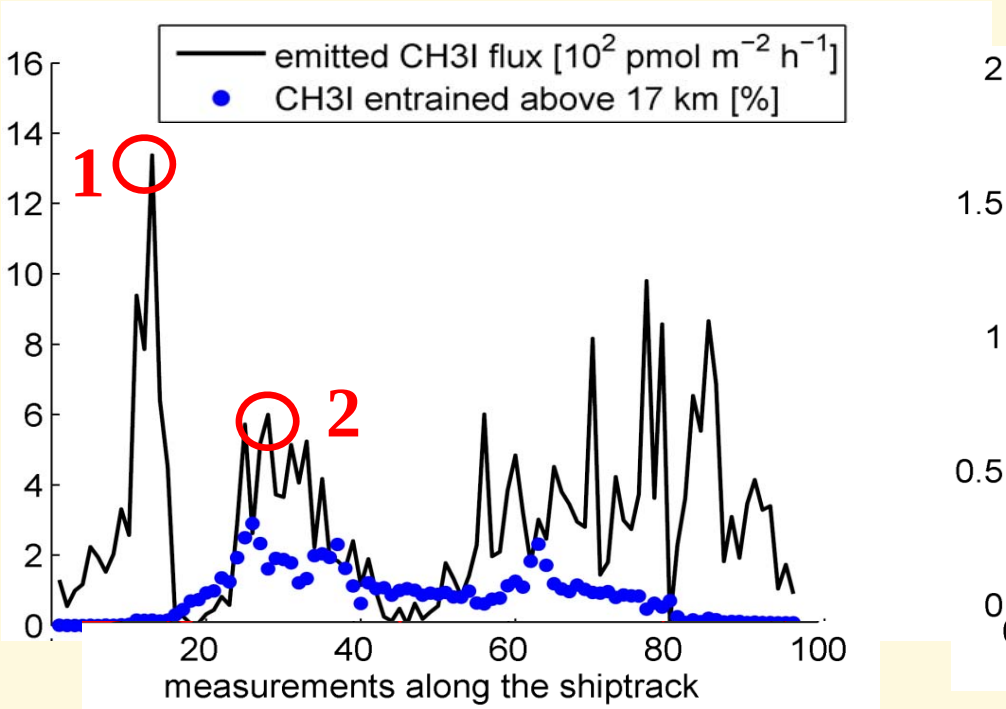



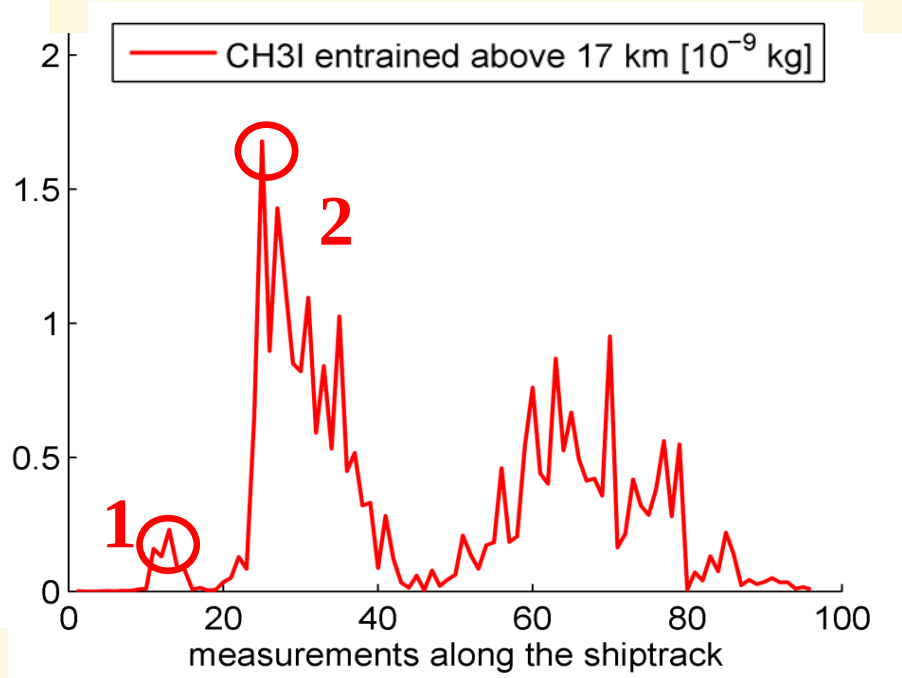

**FLEXPART transport simulation based on emitted $CH_3I$ :**
**1) 1300 pmol m-2 hr-1 and 2) 600 pmol m-2 hr-1**

**Figure shows for every time step methyliodid [kg] as a function of altitude.**

**Tegtmeier et al., (priv. comm.)**

# Simulated Methyliodid transport to the TTL



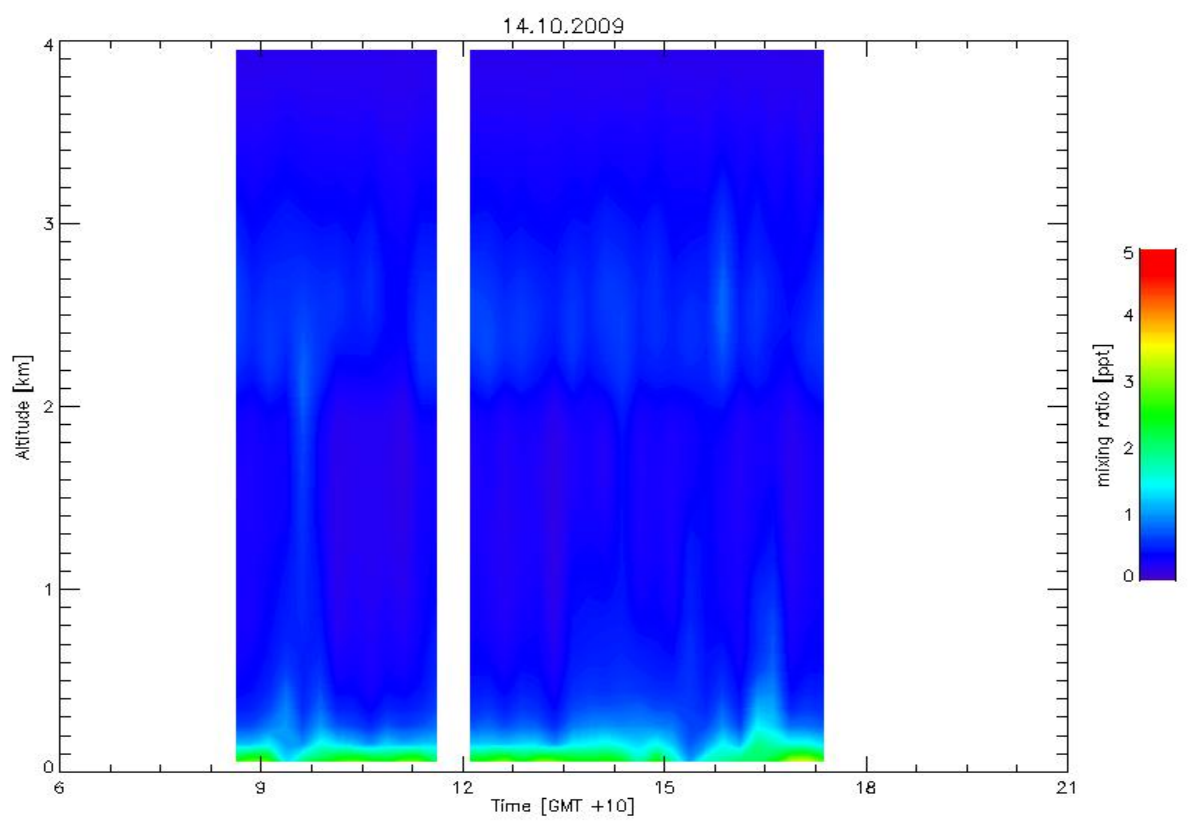

**Although emission was a stronger at event (1) the methyliodid transported into the stratosphere is larger for event (2).**

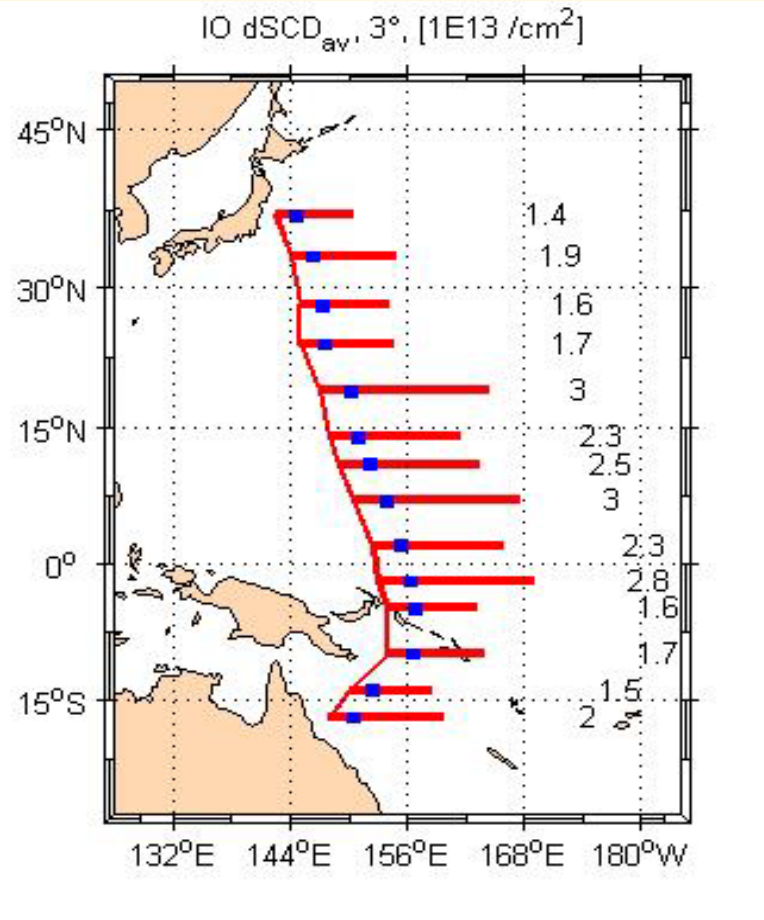
**Tegtmeier et al., (priv. comm.)**

# Iodine sources in the Pacific Ocean

## DOAS data were taken during the Transbrom cruise in fall 2009

**IO in the Pacific MBL, Oct. 14, 2009**




**Katja Grossmann (priv. comm.)**

# TTL/LS bromine and the stratospheric bromine budget

**Two methods are available based on measurements:**

**1.) Measuring stratospheric BrO and accounting for the BrO / $Br_y$ ratio by photochemical modelling:**

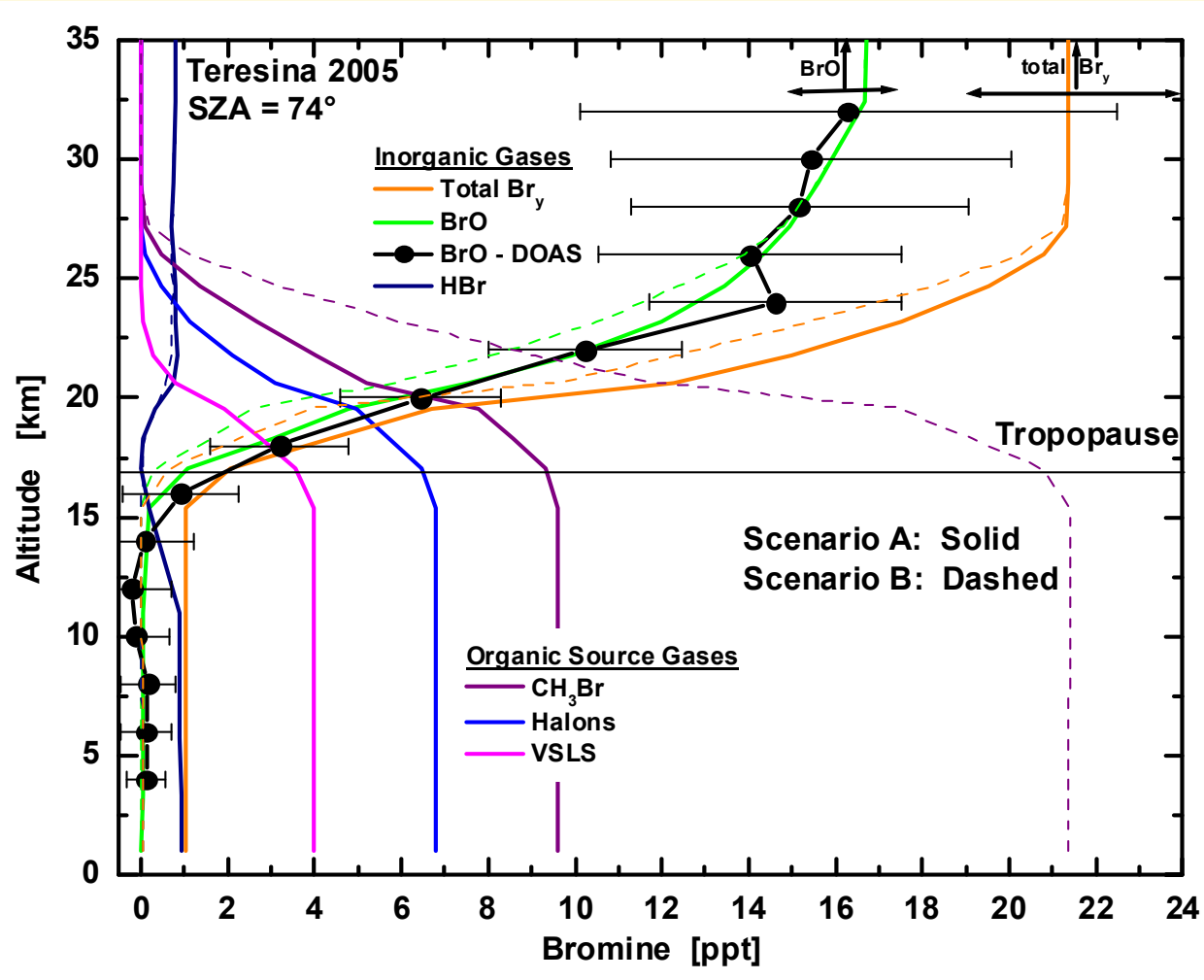
- **Comparison of measured vs modelled stratospheric BrO profiles**
- **Langley regression of measured BrO vs total air mass at balloon float**

**2.) Summing up all source gases (SG) [*e.g., Wamsley et al., 1998; Pfeilsticker et al., 2000; Montzka et al., 2003*, .....]:**

- **CH3Br (~ 8.5 ppt)**
- **Halons (~ 7 ppt), i.e., CBrClF2 (H1211), CBrF3 (H1301), CBrF2CBrF2 (H2402), and CBr2F2 (H1202)**
- **VSLS (~ 2 ppt), i.e CHBr3, CH2BrCl, CH2Br2, CHBrCl2, CHBr2Cl,...**

**Problem: Product gas (PG) injection is not well known at stratospheric entry level i.e., Br tied in aerosols and / or inorganic bromine gases**

# DOAS - BrO profiling in the tropics




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

- **BrO in the troposphere < 1 pptv**
- **Non-zero amounts of $Br_Y$ at the tropopause [BrO] ~ (2.0 ± 1.5) ppt**
- **Rapid release of $Br_Y$ above the tropopause**
- **Good agreement with updated <u>SLIMCAT</u> runs**

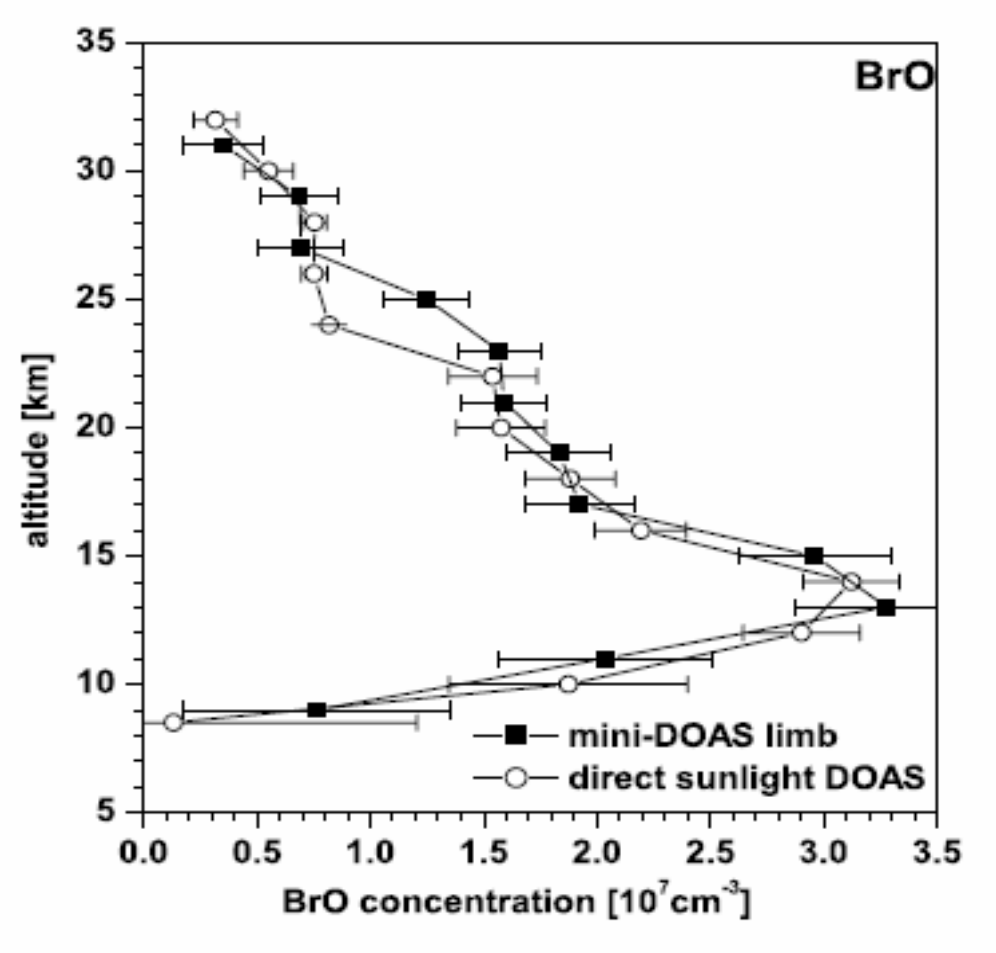
**→ [VSLS] + [PG] = 5 ppt**

**→ [$Br_y$] = (21 ± 2.5) ppt**

**for June 2005**

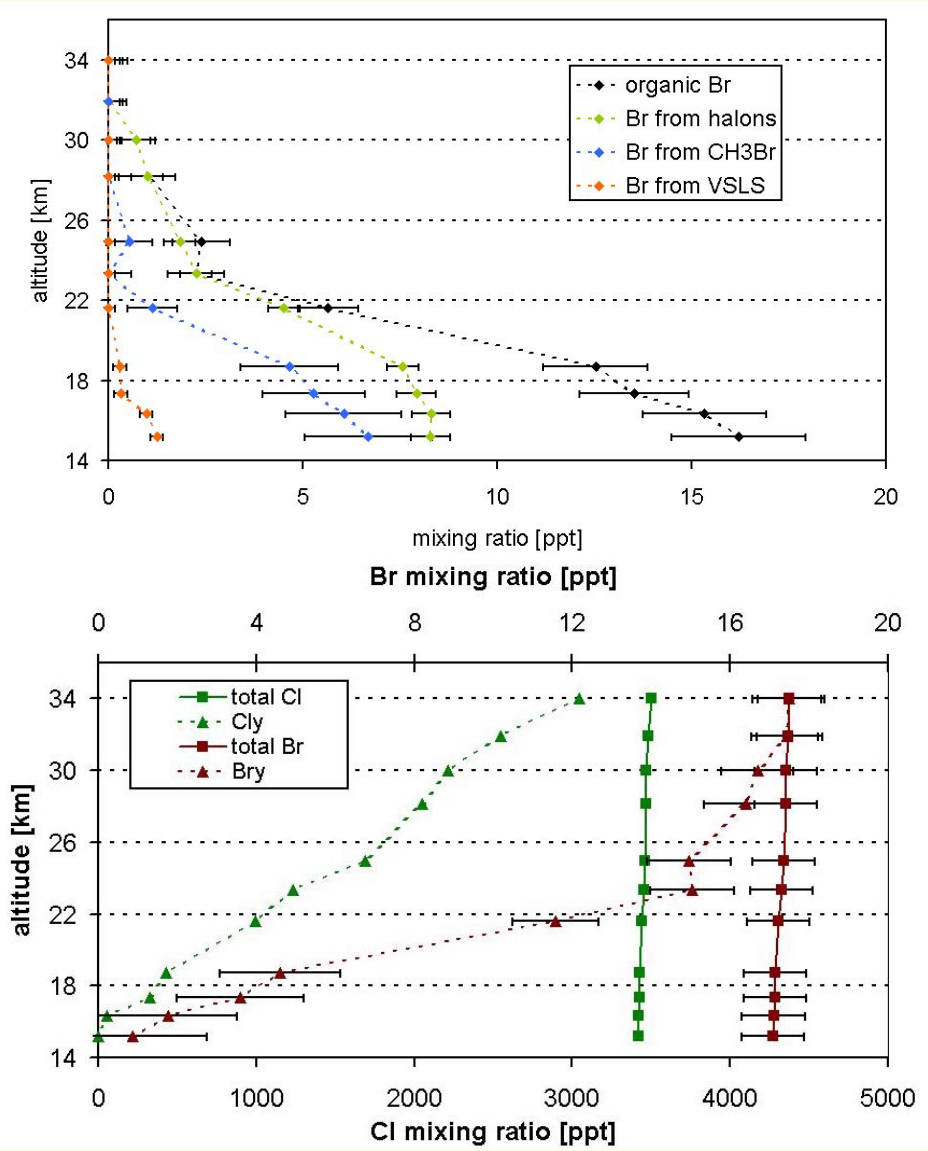
**(air mass age ~ 4 yrs)**

# Comparison of direct sun and Limb BrO measurements




(Weidner et al., 2005)

# $Br_y$ inferred from bromo-organic source gases

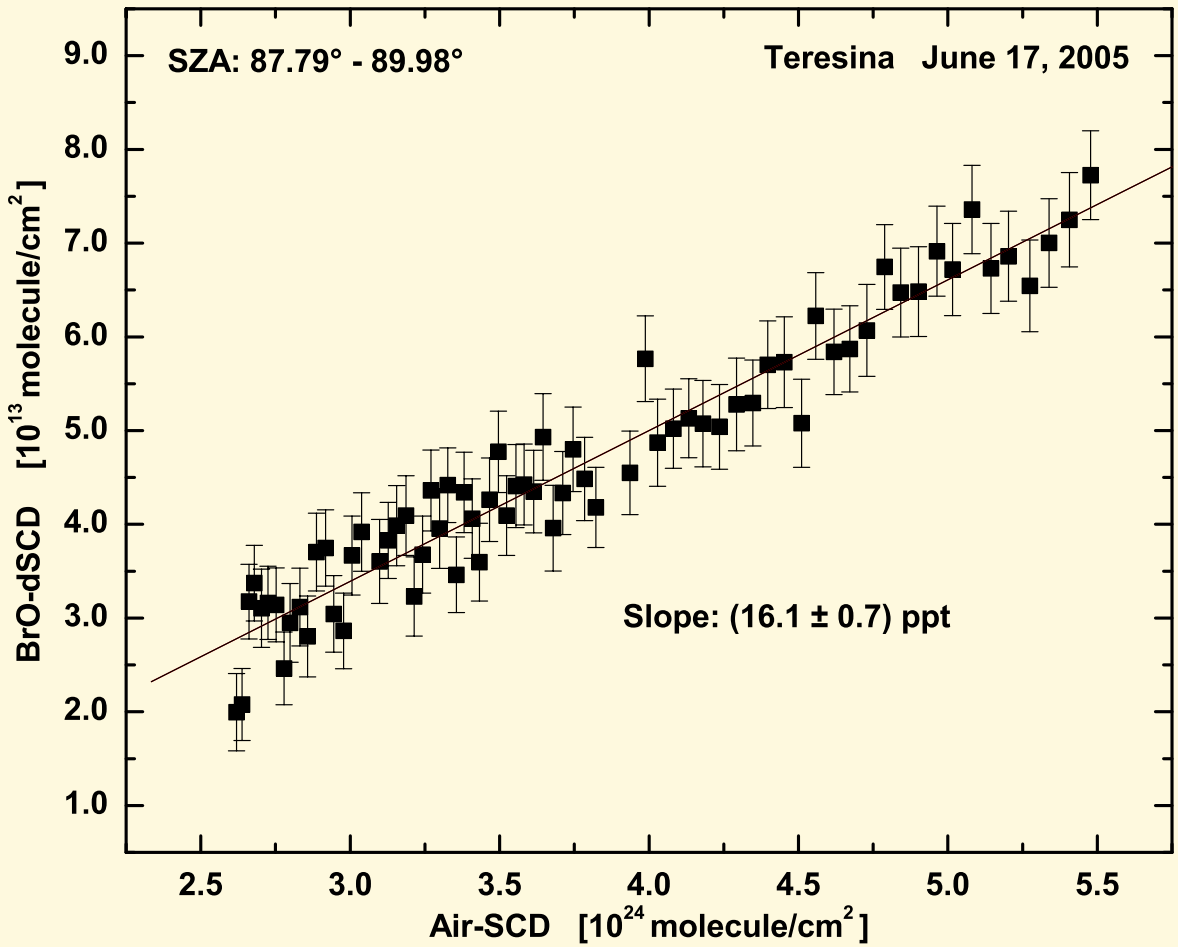



**Tropical whole-air sampler source-gas observations on June 8, 2005 indicate:**

- **$Br_y$ = ( 17.5 ± 0.4) ppt**
- **1.25 ppt of stratospheric bromine due to VSLS emissions (e.g., mostly due to $CH_2Br_2$, and to a lesser extend by $CHBr_3$)**

**(Laube et al., ACP, 2008)**

# Total stratospheric bromine: Langley regression of measured BrO vs total air mass




**Tropical DOAS BrO float observations on June 17, 2005 indicate:**

- **$[BrO]_{> 34\ km}$ = (16.1±0.7) ppt**
- **During daytime, $Br_y$ chemistry above balloon float altitude (> 34 km) is dominated ( > 90 %) by**

$$BrO + h \cdot v \rightarrow Br + O$$

$$Br + O_3 \rightarrow BrO + O_2$$

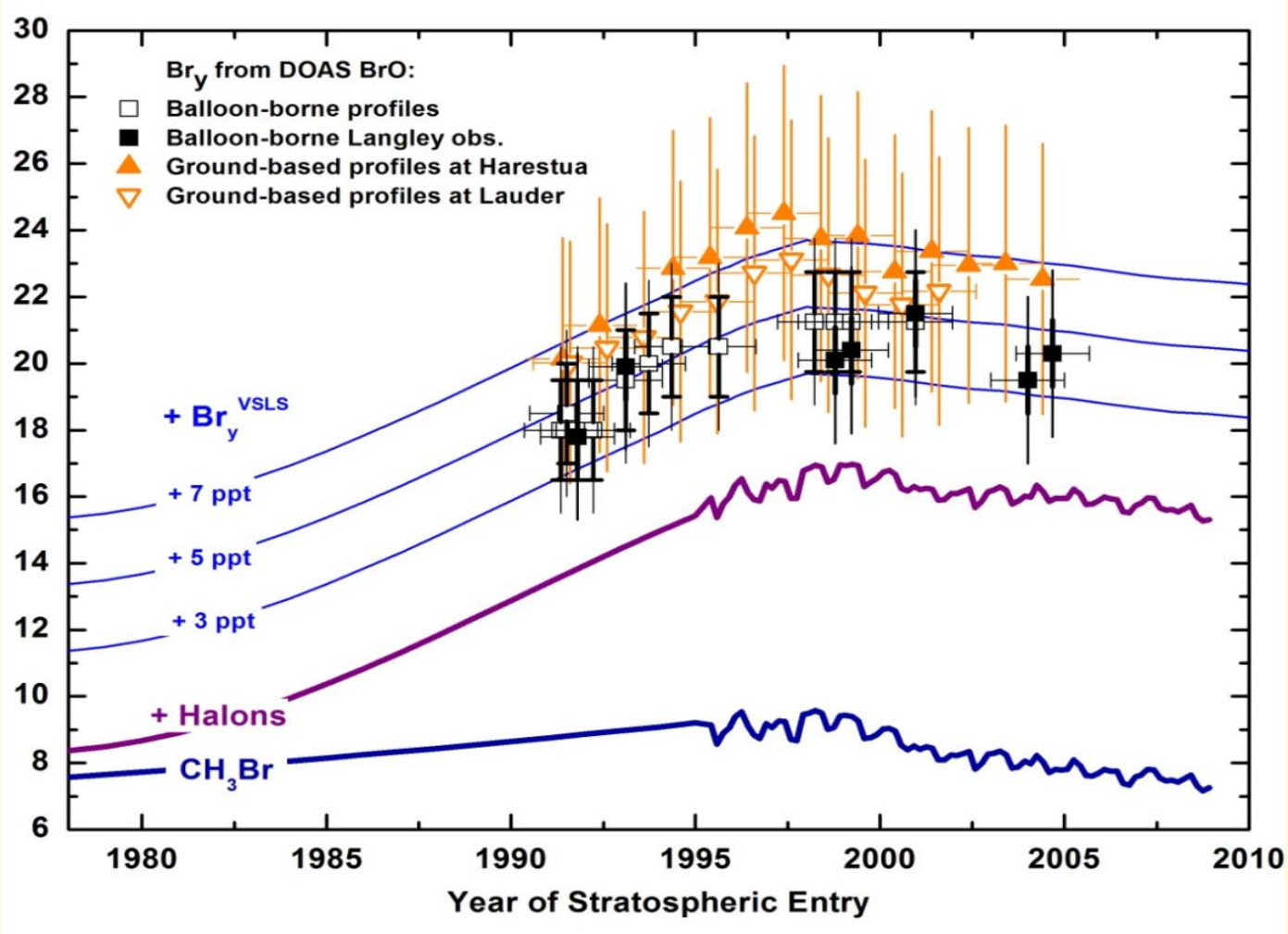
**Accordingly, [BrO] / $[Br_y]$ = 0.75 (*SLIMCAT*)**

**→ $[Br_y]$ = (21.5 ± 2.5) ppt**

**→ [VSLS] + [PG] = ~ 5.2 ppt**

**for June, 2005 (air mass age ~ 4 yrs)**

# Trend in total stratospheric bromine




(Dorf et al., 2006 and Hendrick et al., 2008 with recent updates)

# Estimated contribution of VSLS and PGs, from SG and $Br_y$ measurements

| | Kiruna 1999 | Teresina 2005 |
|---|---|---|
| Air-mass age at balloon-float (years) | $6.0 \pm 1$ | $4.5 \pm 1$ |
| $CH_3Br$ (ppt) [a] | 9.3 | 8.8 |
| Halons (ppt) [a] | 5.8 | 7.5 |
| $Br_y$ from BrO, $Br_y^{BrO}$ (ppt) | $19.9 \pm 2.5$ [b] | $21.5 \pm 2.5$ |
| Inferred VSLS + PG injection, i.e. $Br_y^{BrO}$ - ($CH_3Br$ + halons) (ppt) | 4.7 | 5.2 |
| $Br_y$ from SG measurements, $Br_y^{SG}$ (ppt) | 18.4 (-1.5 / +1.8) | $17.5 \pm 0.9$ |
| Measured VSL - SGs at stratospheric entry level (ppt) | $2.6 \pm 0.6$ | $1.25 \pm 0.16$ |
| Potential maximum PG injection assuming a locally balanced bromine-budget, [c] i.e. $Br_y^{BrO}$ - ($CH_3Br$ + halons + measured VSLS) (ppt) | $2.1 \pm 2.6$ | $4.0 \pm 2.5$ |

[a] Surface $CH_3Br$ and halon data are from *Montzka et al.* [2003]. We assume no tropospheric loss of $CH_3Br$.
[b] Value based on the Langley method as compared to the SCD-/profile comparison of *Pfeilsticker et al.* [2000].
[c] This is more likely true for the tropics, where most of the upward flux into the stratosphere occurs, than for high-latitudes.

**(from Dorf et al., 2008)**

**Discrepancy between organic and inorganic bromine is due to ?:**

- **PG injection**
- **Calibration uncertainties**
- **Additional brominated organic substances**
- **Regionality: Observed TTL region does not represent global VSLS mean entrance mixing ratios to stratosphere**
- **....**

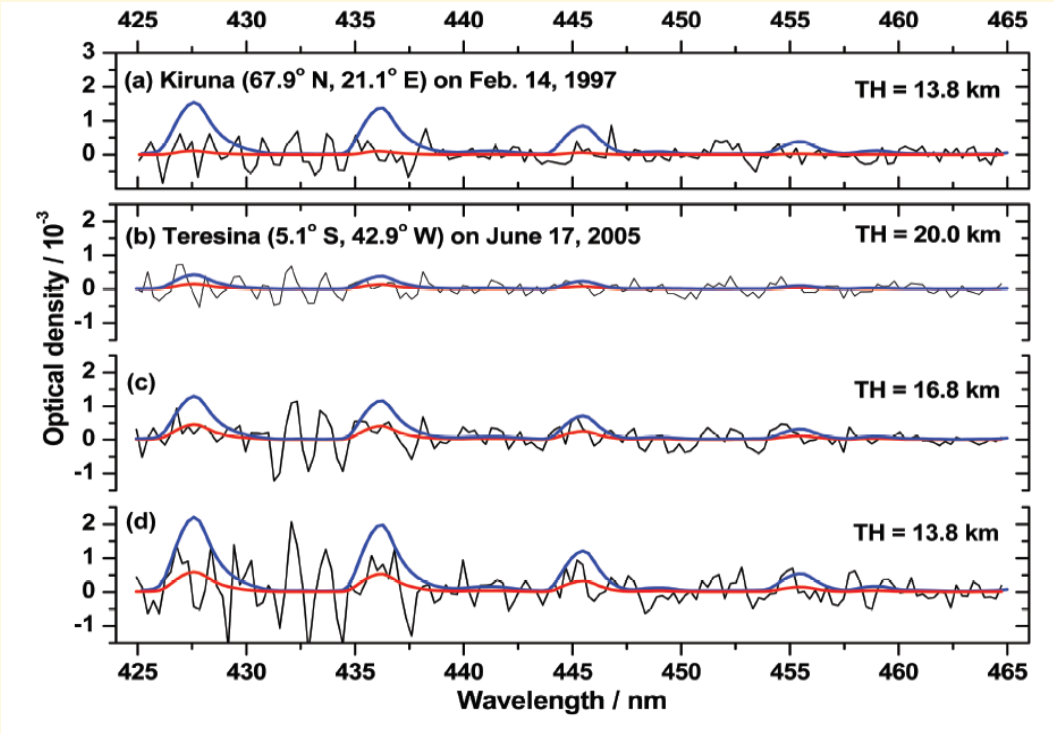
# Iodine in the TTL/LS

**What is with iodine?**

# Iodine: UT/LS Iodine

**Past studies (e.g. Davis et al., 1996; Yano et al. 2003) indicated that in the tropical UT/LS, concentrations of iodinated VSLS (e.g., $CH_3I$, .. ) are ~ 0.3 ppt (UNEP-WMO: range 0.02 – 0.18 ppt).**

**Spectroscopic detection of IO and OIO**

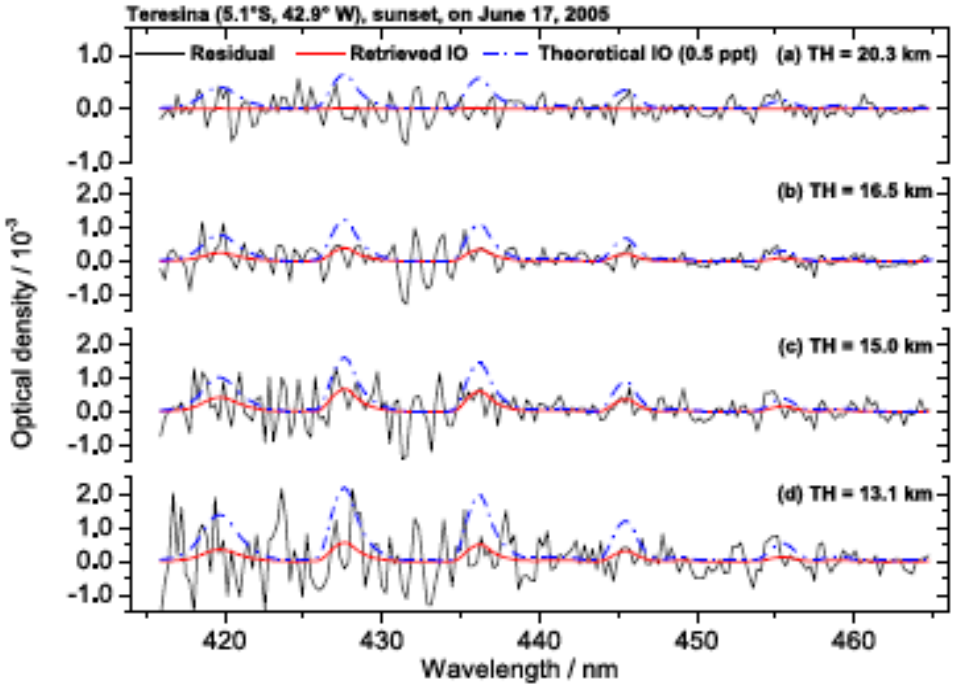


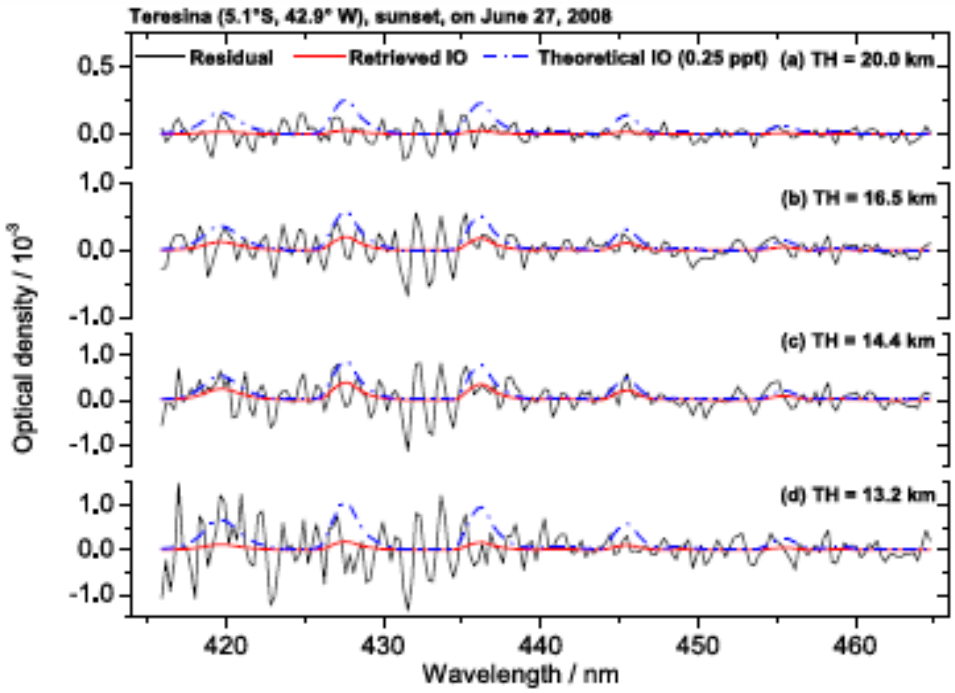

**but spectroscopic studies of our group indicated IO was ≤ 0.3 ppt in the mid- and high latitude UT/LS (Bösch et al., 2003) which is in reasonable agreement with conclusions drawn on stratospheric iodine by UNEP-WMO 2006.**

# Iodine: TTL/LS Iodine

**In June 2005 and 2008, we probed the tropical TTL/LS (over north eastern Brazil) e.g. for IO and OIO by means of balloon-borne solar occultation spectroscopy (Butz et al., ACP, 2009).**

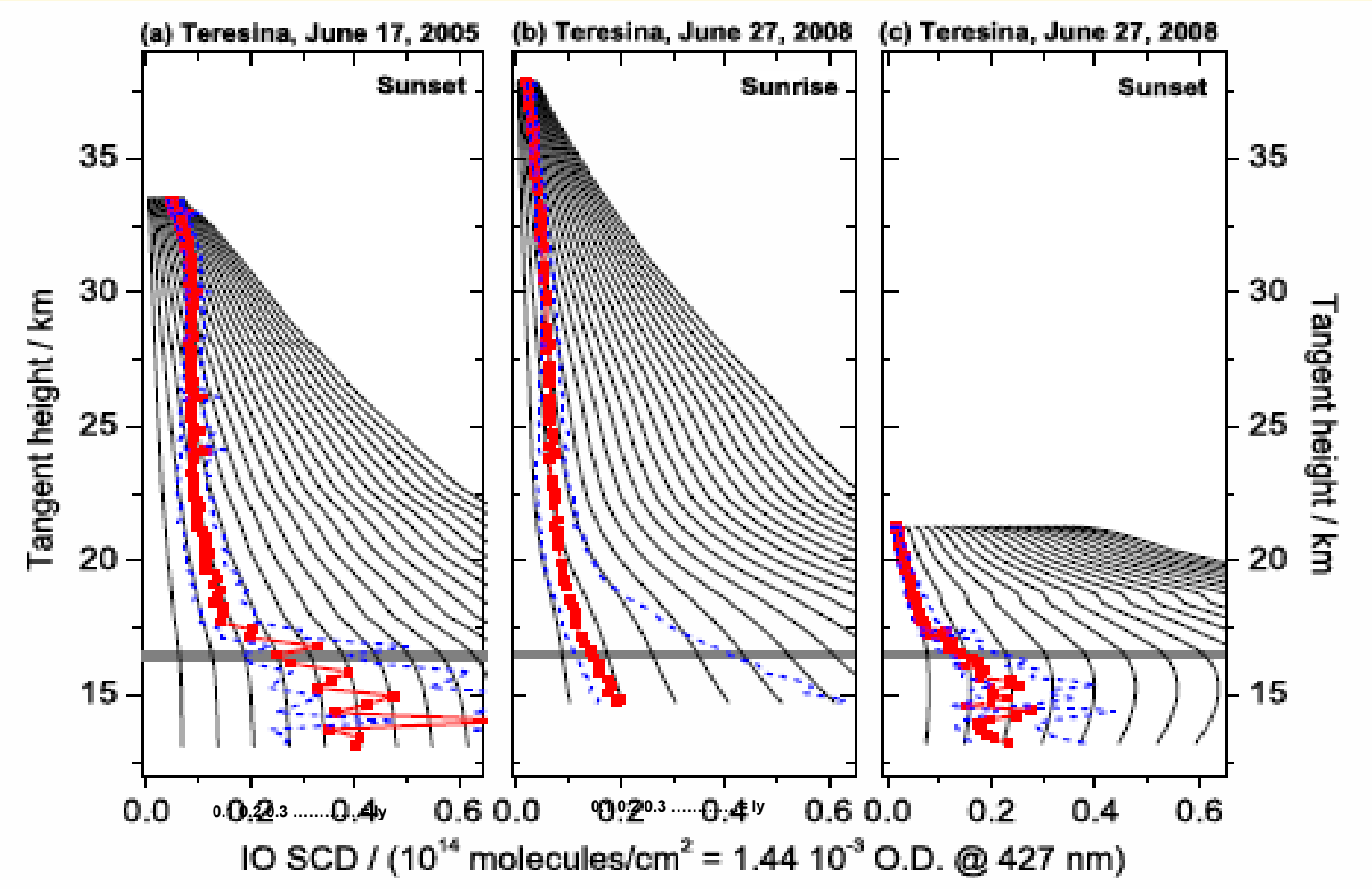
## Spectroscopic detection of IO and OIO by solar ocultation




**Butz et al., ACP, 2009.**

# Iodine: TTL/LS Iodine upper limits




(Butz et al., ACP, 2009)

# Conclusion:

(1) In the tropical TTL/LS, detected IO and OIO are < 0.1 ppt.

(2) Photochemical modelling assisting the observations suggests $I_y$ smaller than
- 0.09 to 0.16 (+0.10/−0.04) ppt in the tropical LS (21.0 km to 16.5 km) and
- 0.17 to 0.35 (+0.20/−0.08) ppt TTL (16.5 km to 13.5 km).

→ Iodine plays a minor role in UT/TTL and LS ozone

More iodine measurements will be performed in the Western Pacific during EU-SHIVA

# Overall Summary & Conclusion

**VSLS and PGs contribute to total stratospheric**

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

**In this context, most important questions are today:**

**(1) What is the amount and fraction of brominated and iodinated SGs and PGs entering the tropical stratosphere**

**(2) What are the most dominating source regions, atmospheric transport and transformation processes for SGs and PGs**

**(3) Will the above given numbers change in a changing climate.....**

- **and if yes, why ?**
- **(i.e. due to emissions, transport&lifetime, or other factors .....)**

# Some more scientific objectives related to the GH miniDOAS measurements

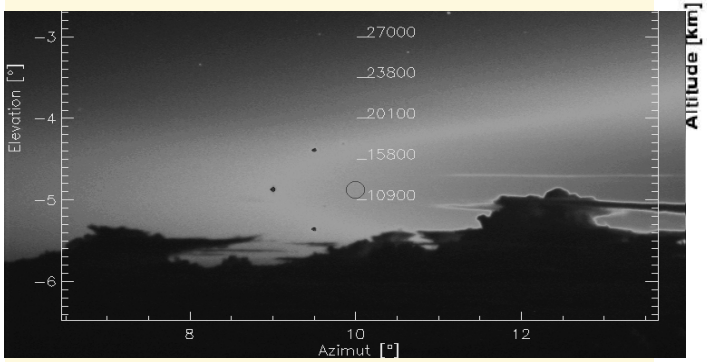
1.) To monitor the amount of BrO and IO in the tropical TTL/LS
→ to investigate the impact of bromine and iodine for the TTL/LS photochemistry
→ to assess the total amount of stratospheric bromine and iodine

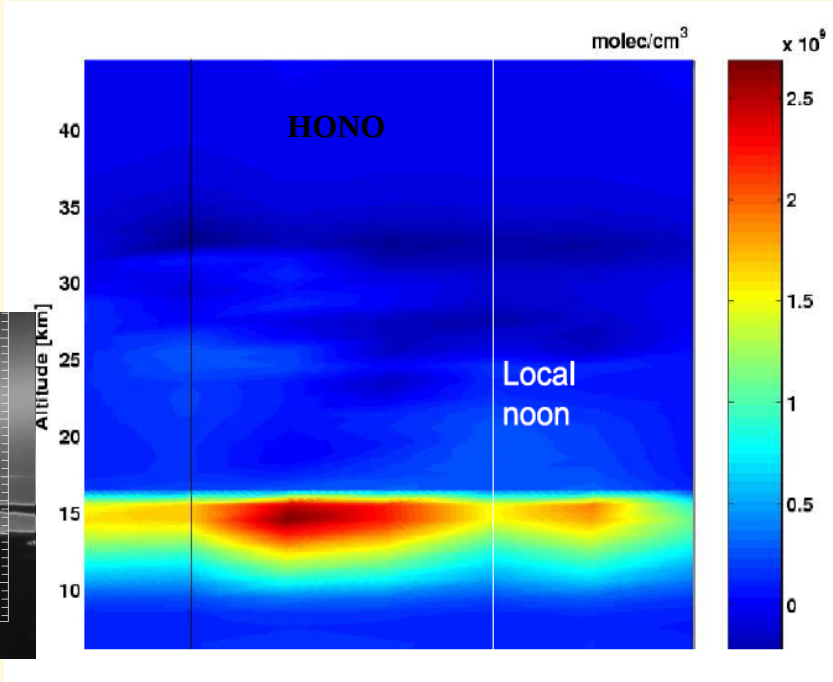
2.) To investigate the formation of NOx and HOx in deep convection
→ to assess the oxidation potential of the TTL/LS

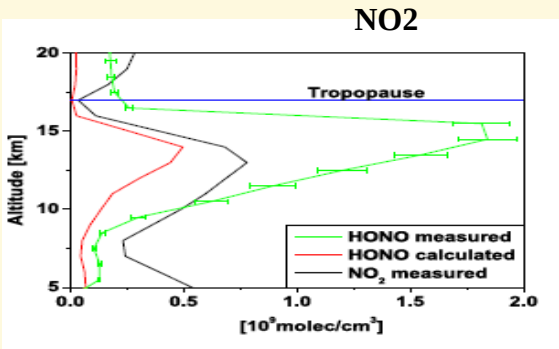
3.) To monitor the occurrence of subvisible clouds and aerosols
→ to assess the impact of these particles in support of hetereogeneous reactions and radiative impact

# Example 2: TTL/LS NOx and HOx photochemistry & deep convection

**Thunderstorm related observations of NO2 and HONO in the tropical TTL (aboard the MIPAS-B gondola over north-eastern Brazil on June 13, 2005)**




**Observed NO2 (black), calculated HONO, which is used as a priori for the inversion (red) and retrieved HONO (green), height of the tropopause (blue).**