Methyl chloride as a tracer of tropical tropospheric air in the lowermost stratosphere inferred from IAGOS-CARIBIC passenger aircraft measurements

ABSTRACT

Methyl chloride (CH$_3$Cl) is a predominantly natural tracer gas which provides ozone-depleting chlorine to the stratosphere. Nitrous oxide (N$_2$O) is the third most important greenhouse gas that also plays a dominant role in stratospheric ozone depletion. In this study, we present variations of N$_2$O and CH$_3$Cl in the lower stratosphere (LMS) observed by the IAGOS-CARIBIC passenger aircraft observatory. CH$_3$Cl undergoes clear seasonal variations in the LMS with a minimum in spring, the seasonal amplitude being pronounced going deeper in the LMS. Significant correlations between N$_2$O and CH$_3$Cl are found in the LMS from winter to early summer due to mixing between LMS and upper tropospheric air. This correlation disappears in late summer to autumn. Using the CH$_3$Cl-N$_2$O correlation slope, we estimate the stratospheric lifetime of CH$_3$Cl to be 35±7 years. We also examine the partitioning of stratospheric air, tropical tropospheric air and extratropical tropospheric air in the LMS based on a mass balance approach using N$_2$O and CH$_3$Cl. This analysis clearly indicates efficient inflow of tropical tropospheric air into the LMS in summer and demonstrates the usefulness of CH$_3$Cl as a unique tracer of tropical tropospheric air.

1. The IAGOS-CARIBIC flying observatory and CH$_3$Cl & N$_2$O data

- IAGOS-CARIBIC uses a 1:4-1 air freight container with a variety of instruments onboard a Lufthansa Airbus A340-600 aircraft and has conducted almost monthly observation flights to various destinations from Germany (http://caribic-atmospheric.com).
- Two types of whole air samplers collect 116 samples in the UT/LMS (9–12 km altitude) during each series of consecutive flights since May 2005.
- CH$_3$Cl mixing ratio is measured using GC-MS at UEA since 2005 and using GC-FID at MPIC since 2008 (Umezawa et al. 2014). The dataset is adjusted to the NOAA CH$_3$Cl scale (Montzka et al. 2011).
- N$_2$O mixing ratio is measured using GC-ECID at MPIC (Schuck et al. 2009) on the NOAA 2006 scale (Hall et al. 2007).
- In this study, N$_2$O data are expressed as ANO, deviations from the long-term trend observed at MLO (data provided by NOAA/GMD) (Umezawa et al. 2014).

2. Background and concept

CH$_3$Cl is a potentially useful tracer of tropical air in the LMS. It shows a clear gradient across the tropopause and decreases going deeper in the LMS, which is expanded in the entire LMS in autumn. Namely, high fraction of stratospheric overworld, (2) from CARIBIC measurements (Umezawa et al. 2014) for the tropical troposphere and (3) from NOAA/GMD data at MLD (Montzka et al. 2011) for the extra-tropical troposphere. CH$_3$Cl in the LMS is almost uniform below the tropopause, shows a clear gradient across the tropopause and decreases going deeper in the troposphere. CH$_3$Cl decreases similarly in the stratosphere, but characteristic is the latitudinal distribution peaking in the tropical troposphere. Arrows indicate exchange of air that may be detectable in each gas.

3. Time series of CARIBIC N$_2$O and CH$_3$Cl data

Number of air samples collected by CARIBIC for the period 2008–2012 in 5° grids. Hereafter CARIBIC N$_2$O data are expressed as ΔN$_2$O = N$_2$Oobs - N$_2$O trend/σtrend. Both N$_2$O and CH$_3$Cl shows curtain-like seasonal pattern in the LMS, while the tropospheric variation are different.

4. Seasonal and vertical variations of N$_2$O and CH$_3$Cl in the LMS

- N$_2$O undergoes a seasonal variation with a minimum in spring in the LMS and the amplitude increase going deeper in the stratosphere.
- CH$_3$Cl shows a seasonal variation similar in phase to that of N$_2$O in the LMS, while the seasonal cycle in the UT is different (a minimum in late summer).
- Vertical gradients of AN$_2$O and CH$_3$Cl vary with season: largest in spring and smallest in autumn.

5. Scatterplots between N$_2$O and CH$_3$Cl

Scatterplots of CH$_3$Cl as a function of AN$_2$O for different seasons (DJF, MAM, JJA and SON). Geometric mean regression lines for the stratospheric AN$_2$O data are shown. Grid colors indicate number of data. The horizontal line shows the N$_2$O-based tropopause.

6. Estimate of stratospheric lifetime of CH$_3$Cl

The stratospheric lifetime of two long-lived trace gases are related as follows (Plumb and Keis, 1992):

$$\tau_{strat} = \omega_{strat} \times \sigma_{strat} \times \sigma_{trop} \times \sigma_{obs} \times \sigma_{temp} \times \sigma_{alt} \times \sigma_{lat} \times \sigma_{seasonal}$$

7. Partitioning LMS air into stratospheric and tropical/extra-tropical tropospheric air

- We utilize N$_2$O and CH$_3$Cl to partition air of different origins: (1) the stratospheric overworld, (2) the tropical upper troposphere and (3) the extra-tropical tropical surface air.

$$\Delta N_2O = \omega_{strat} \times \sigma_{strat} \times \sigma_{trop} \times \sigma_{obs} \times \sigma_{temp} \times \sigma_{alt} \times \sigma_{lat} \times \sigma_{seasonal}$$

$$\Delta CH_3Cl = \omega_{strat} \times \sigma_{strat} \times \sigma_{trop} \times \sigma_{obs} \times \sigma_{temp} \times \sigma_{alt} \times \sigma_{lat} \times \sigma_{seasonal}$$

- The boundary values are given (1) from literature (Bönisch et al. 2009, Engel et al. 2002) for the stratospheric overworld, (2) from CARIBIC measurements (Umezawa et al. 2014) for the tropical upper troposphere and (3) from NOAA/GMD data at MLD (Montzka et al. 2011) for the extra-tropical tropospheric air.

- The AN$_2$O contours are parallel to the PV isolines year round. The AN$_2$O contours also follow the PV isolines in spring, but in summer, a high tropical tongue extends across the tropopause, which is expanded in the entire LMS in autumn. Namely, high fraction of tropospheric air is dominated by flushing of the LMS by the tropical tropospheric air.

Potential temperature-equivalent latitude cross sections of (from left to right) N$_2$O, CH$_3$Cl, fraction of tropospheric air based on N$_2$O, fraction of tropical tropospheric air and ratio of N$_2$O to CH$_3$Cl for different seasons. Black lines PV isolines (PV = 2, 4, 6 and 8 PVU) indicating dynamical tropopause.