Methyl Chloride from the Aura Microwave Limb Sounder: Preliminary Validation and Climatology

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1 Abstract

Methyl chloride (CH_3Cl), the largest natural source of stratospheric chlorine, currently accounts for about 16% of chlorine-catalyzed ozone destruction in the stratosphere. Its importance is expected to increase, however, as emission controls alter the relative contributions from natural and anthropogenic halogen sources. Thus a quantitative understanding of the CH_3Cl distribution and variability will be valuable in enhancing our prognostic capability for ozone layer stability. The Aura Microwave Limb Sounder (MLS) measures vertical profiles of temperature, cloud ice, and an extensive suite of trace gases in the middle atmosphere. With the recent release of the version 3 (v3.3) data processing algorithms, Aura MLS now provides the first daily global observations of CH_3Cl. The unprecedented scope of the MLS data set makes it uniquely suited to studying the spatial, seasonal, interannual, and longer-term variations in the distribution of CH_3Cl at the tropopause and in the lower stratosphere. Reprocessing of the MLS data with the v3.3 algorithms is currently underway, with the entire mission data set scheduled for completion by early 2011. We present preliminary validation results to substantiate the quality of the v3.3 MLS CH_3Cl measurements and their utility for scientific studies. A preliminary global climatology of CH_3Cl is also shown.

2 Introduction

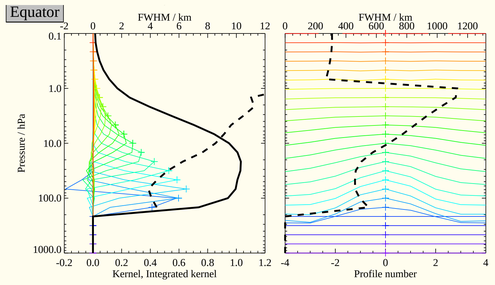
- CH_3Cl (methyl chloride, chloromethane), the largest natural source of stratospheric chlorine, currently accounts for ∼16% of chlorine-catalyzed ozone destruction.
- Unlike most other relatively long-lived ozone-depleting gases, CH_3Cl has both natural and anthropogenic sources of significance.
  - Known sources of emissions are predominantly natural, including tropical / subtropical plants, senescent and dead plant matter, oceans, coastal salt marshes, wood-rotting fungi, freshwater wetlands, rice paddies, etc.
  - Biofuel / biomass burning accounts for nearly 25% of its global source strength.
  - Exclusively anthropogenic activities such as coal combustion, municipal and domestic waste incineration, and industrial processes make minor contributions to the atmospheric flux of CH_3Cl.
- CH_3Cl will likely increase in importance as a source of stratospheric chlorine.
  - Anthropogenic halocarbons are declining in response to regulations mandated by the Montreal Protocol.
  - Biomass burning, about 90% of which is estimated to be human-induced, is expected to increase at the rate of a few percent per year, leading to larger pyrogenic CH_3Cl emissions in the future.
  - Changes in the oxidative capacity of the atmosphere may appreciably alter CH_3Cl abundances.
  - CH_3Cl fluxes from many natural sources vary depending on ambient environmental conditions (e.g., temperature, moisture / humidity, salinity, acidity, the types of organic material present, the length of the growing season, etc.), so changes in global climate and land use patterns may have a substantial impact on the CH_3Cl input to the atmosphere.
- Limited measurements of CH_3Cl have been obtained in the upper troposphere and lower stratosphere through in situ and remote techniques from balloons and aircraft.
- Stratospheric profiles of CH_3Cl have also been measured from space using infrared solar occultation by the Atmospheric Trace Molecule Spectroscopy (ATMOS) Spacelab 3 and space shuttle missions, and by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS).
- But solar occultation data are sparse, especially in the tropics, which are typically only sampled by ACE-FTS during 4–5 months of the year at intermittent intervals.
- The catalog of Aura MLS data products has been expanded in version 3 to include the first daily global observations of CH_3Cl.
- The unprecedented scope of the Aura MLS data set — daily global measurements over (at least) six complete annual cycles, by far the most comprehensive CH_3Cl observational record — makes it uniquely suited to studying the spatial, seasonal, interannual, and longer-term variations in the distribution of CH_3Cl at the tropopause and in the lower stratosphere.

3 Quality of the Aura MLS Version 3 CH_3Cl Measurements: Preliminary Validation Results

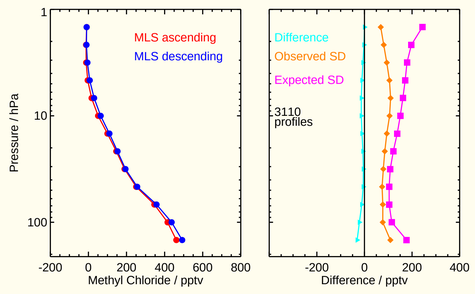
Overview of the Aura MLS CH_3Cl Retrieval

- The version 2 (and earlier) Aura MLS ClO measurements were characterized by a substantial (∼0.1–0.4 ppbv) negative bias at retrieval levels below (i.e., pressures larger than) 22 hPa.
- Contamination from CH_3Cl, which has lines in two wing channels of the 640-GHz band used to measure ClO, is partially responsible for the bias in the previous ClO retrievals.
- Retrieval of CH_3Cl in the version 3 (v3.3) data processing algorithms has largely mitigated the bias in the ClO data and yielded a reliable CH_3Cl product.

Resolution, Precision, and Range



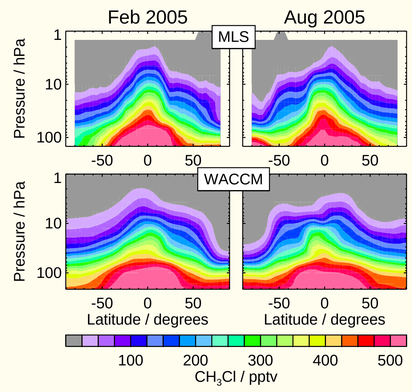
- CH_3Cl measurements are reported at 6 pressure levels per decade change in pressure.
- Smoothing, imposed on the retrieval system in both the vertical and horizontal directions to enhance retrieval stability and precision, degrades the inherent resolution of the measurements.
- Vertical resolution, determined from the full width at half maximum of the rows of the averaging kernel matrix (figure above), is ∼4–6 km in most of the lower stratosphere, degrading to 8–10 km at and above 14 hPa.
- There is overlap in the averaging kernels for the 100 and 147 hPa retrieval surfaces, indicating that the 147 hPa retrieval does not provide completely independent information.
- From the horizontal averaging kernels, the along-track horizontal resolution is determined to be ∼450–600 km below 10 hPa and ∼700–850 km at and above that level.
- The cross-track resolution, set by the width of the field of view of the 640-GHz radiometer, is ∼3 km.
- The along-track separation between adjacent retrieved profiles is 1.5° great circle angle (∼165 km), whereas the longitudinal separation of MLS measurements, set by the Aura orbit, is 10°–20° over low and middle latitudes, with much finer sampling in the polar regions.



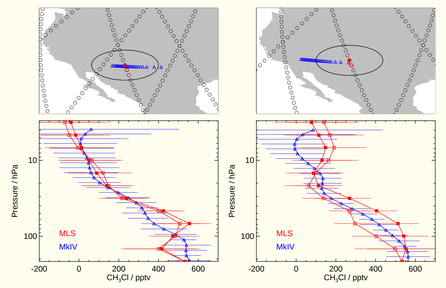
- Precision is estimated empirically by computing the standard deviation of the differences between matched measurement points at the intersections of the ascending (day) and descending (night) sides of the orbit.
- Differences between paired profiles are mostly small (figure above), implying the absence of significant systematic ascending / descending biases.
- Observed scatter, representing the statistical repeatability of the measurements, is 100 pptv or less throughout the vertical domain.
- This estimate reflects the precision of a single profile; precision can usually be improved by averaging, with the precision of an average of N profiles being $1/\sqrt{N}$ times the precision of an individual profile.
- The theoretical precision reported by the Level 2 data processing system exceeds the observationally-determined precision throughout the vertical range, indicating that the smoothing applied to stabilize the retrieval and improve the precision has a nonnegligible influence.
- Although CH_3Cl is retrieved (and reported in the L2GP files) over the range 147 to 0.001 hPa, on the basis of the drop off in precision and resolution, the lack of independent information contributed by the measurements, and the results of simulations using synthetic data as input radiances to test the closure of the retrieval system, the data are not deemed reliable at retrieval levels above (i.e., pressures lower than) 4.6 hPa.
- Despite the overlap in the averaging kernels for the 147 and 100 hPa surfaces, maps at 147 hPa display substantial features not seen at 100 hPa that are believed to represent real atmospheric variations.
- Thus we recommend that the v3.3 CH_3Cl data may be used for scientific studies between 147 and 4.6 hPa.

Accuracy and Comparisons with Correlative Data Sets

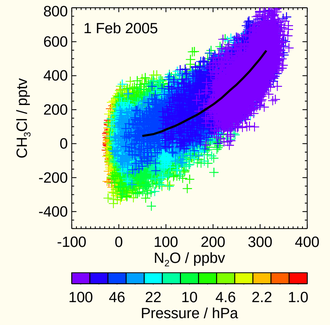
- The impact of various sources of systematic uncertainty has not yet been quantified for CH_3Cl. This work is planned as part of a dedicated validation exercise for the v3.3 CH_3Cl data.



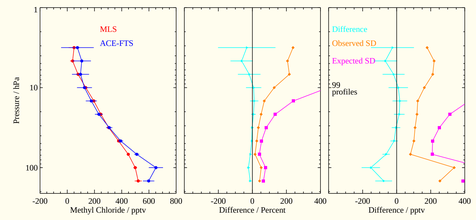
- As a first-order check on the fidelity of the v3.3 CH_3Cl, monthly zonal mean cross sections from MLS are compared to simulated fields from the NCAR WACCM coupled chemistry-climate model (figure above, WACCM data courtesy of D. Kinnison).
- In general the retrievals show excellent agreement with expectation, in terms of both morphology and magnitude.
- Slight differences are seen, however, especially at higher latitudes, where the measured CH_3Cl gradients are somewhat steeper.
- As part of the Aura validation program, measurements from the JPL MkIV solar occultation Fourier Transform Infrared spectrometer [*Toon*, 1991] were obtained near Aura overpasses during balloon campaigns in Ft. Sumner, New Mexico, in September 2004 and 2005.
- Comparisons (figure below) between the balloon measurements and coincident (within ±1° of latitude, ±12° of longitude, and ±12 hours) MLS measurements show good agreement within the MLS uncertainty, although for the 2004 flight both coincident MLS profiles show slightly oscillatory behavior at the lowest levels.



- Whole air samples of a large suite of chlorine-containing organic compounds, including CH_3Cl, were collected between 52°N and 88°N over the 10–21 km altitude range during the Stratospheric Aerosol and Gas Experiment III Ozone Loss and Validation Experiment (SOLVE) campaign in January–March 2000 [*Schauffler et al.*, 2003].
- The SOLVE CH_3Cl data show a very compact correlation with N_2O (black overlay in figure below).
- Although characterized by a far greater degree of scatter due to radiance noise, the MLS data (colored points) display essentially the same CH_3Cl/N_2O relationship as the in situ measurements.

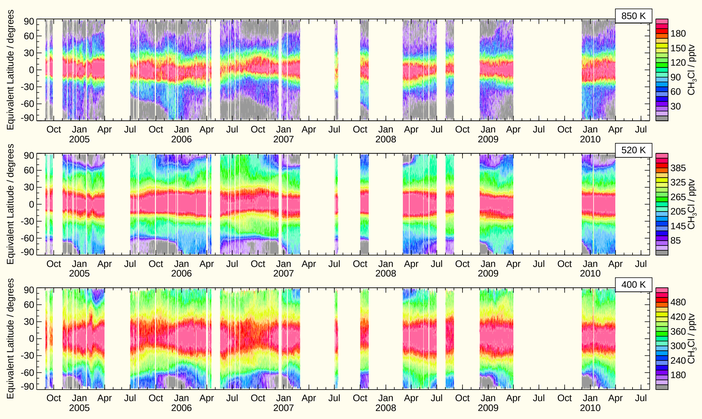


- MLS and ACE-FTS (v3, data courtesy of the ACE Science Team; [*Bernath et al.*, 2005]) CH_3Cl measurements are in very good agreement (within ∼20%) over most of the altitude range (figure below).

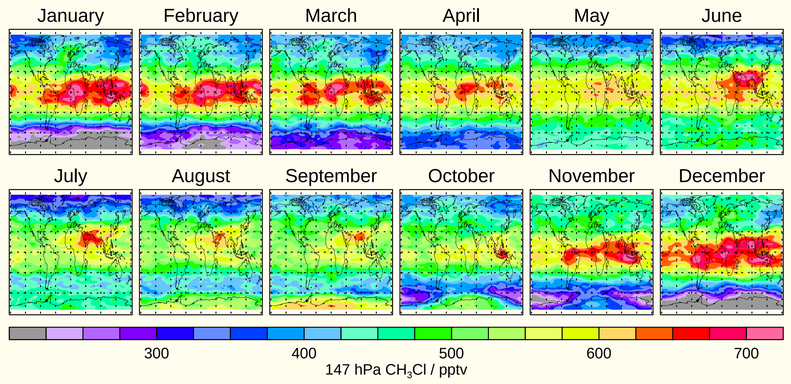


- Though preliminary, these validation results indicate that the v3.3 Aura MLS CH_3Cl measurements are of sufficiently high quality to be useful in scientific studies.

4 Climatology of CH_3Cl at the Tropopause and in the Stratosphere: Spatial and Seasonal Variations



- Time series of MLS CH_3Cl over the Aura mission at 850 K (corresponding approximately to the 10 hPa MLS retrieval surface), 520 K (46 hPa), and 400 K (100 hPa) (figure above; note that large gaps reflect periods for which v3.3 data are not yet available) show substantial temporal variations.
- A distinct minimum in the polar regions in late winter / early spring every year is induced by the action of diabatic descent inside the winter polar vortices in each hemisphere bringing down air poor in CH_3Cl from above.



- Monthly mean maps of MLS CH_3Cl at 147 hPa (for 2006, figure above) show considerable geographical and seasonal variability in the tropical CH_3Cl distribution.
- Factors contributing to this variability include convection (which can inject CH_3Cl from biomass burning into the upper troposphere very rapidly) and the seasonal and spatial patterns of the surface sources.
- Measurements of the distribution of CH_3Cl, a relatively long-lived (1.3 year global lifetime) species of tropospheric origin, are valuable for investigating troposphere-stratosphere exchange processes and their representation in models.

5 Summary and Future Plans

- With the recent release of version 3 data processing algorithms, Aura MLS is providing the first daily global measurements of CH_3Cl.
- The MLS CH_3Cl retrieval is useful for scientific studies over the range 147 to 4.6 hPa, with a single-profile precision of ±100 pptv and a vertical resolution of 4–6 km in the lower stratosphere.
- Increases in CH_3Cl — the predominant natural carrier of chlorine to the stratosphere — in a future warmer climate could potentially offset projected declines in stratospheric chlorine and delay ozone recovery.
- We will use the MLS data to characterize the distribution and variability of CH_3Cl at the tropopause and in the lower stratosphere, establishing a baseline against which the future stratospheric CH_3Cl burden may be assessed.
- Such a comprehensive climatology will provide needed global and seasonal context for sparse aircraft and balloon profiling and will also be of benefit for model initialization and validation.
- We will compare the distribution of CH_3Cl to that of other pollutants measured by MLS, including CO, HCN, and CH_3CN.
- CH_3Cl provides a valuable constraint on transport into the stratosphere and may help to distinguish biomass burning from industrial emissions.
- Model studies are planned to evaluate the relative influence of surface emissions and vertical transport and convection on trace gas distributions at the tropopause and in the lower stratosphere.