In Situ Measurements of Methyl Chloride at the NOAA Baseline Observatories

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The Chromatograph for Atmospheric Trace Species (CATS) program consists of five gas chromatographs deployed at the NOAA baseline observatories. Hourly air samples are analyzed for 14 trace gases including CFCs, chlorinated solvents, HCFCs, N_2O, SF_6, halon-1211, and methyl chloride (CH_3Cl). However, the CH_3Cl data have not been publicly available due to calibration problems. Each field CATS gas chromatograph consumes about two calibration cylinders per year. These cylinders are analyzed in Boulder prior to being sent to a field site and again when the tank is returned from the station. Of the 50 CATS calibration cylinders that have been analyzed twice, all have exhibited increases in CH_3Cl ranging from 6.3 to 174.5 parts-per-trillion (ppt) over their period of use. The CH_3Cl production is most likely a byproduct from the aluminum cylinder passivation treatment known as Aculife (Scott Specialty Gas Company).

Three methods have been used to calculate the CH_3Cl air concentration at the stations using the drifting calibrations cylinders (see figure). The first method uses the average of the original and final CH_3Cl mixing ratios measured in the calibration tanks. The second method assumes that the mixing ratio in the cylinder increases at a constant rate (ppt per unit time). The third method assumes a constant source of CH3Cl within the cylinder (moles per unit time) integrated over the life of the cylinder, and results in mixing ratios that are both pressure and time dependent. All three methods have been compared to the monthly means measured by the ESRL Halocarbons and other Atmospheric Trace Species (HATS) Group flask program and are illustrated for data acquired at Barrow, Alaska (see figure). The differences between the flask and in situ CH_3Cl programs are the smallest when method three is applied to the CATS calibration cylinders (top panel of figure). The average monthly differences are approaching the sum of precisions of the two measurement programs, about ±10 to 15 ppt (error bars in figure). This method is now used to compute CATS CH_3Cl data, now available on the ESRL GMD data server.

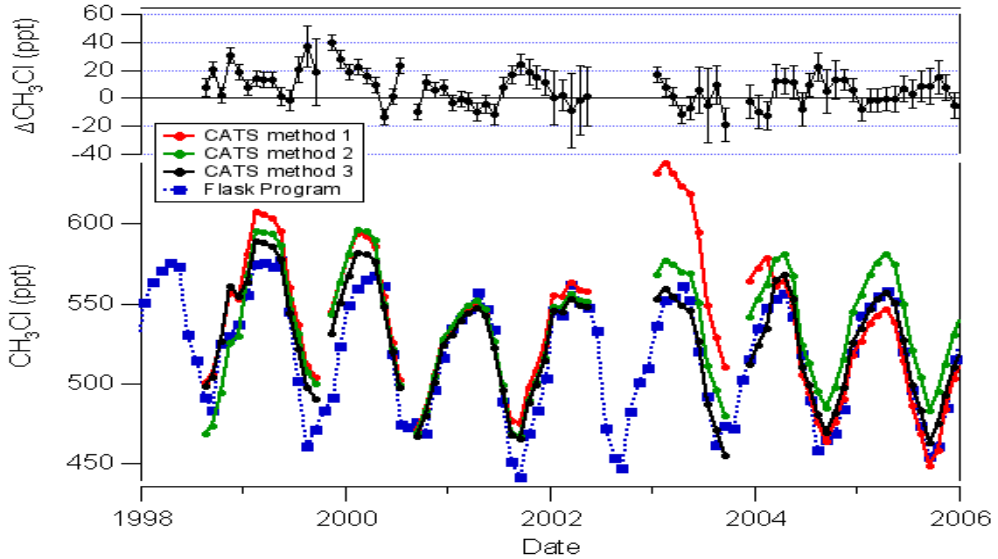

Figure 1. CATS Barrow, Alaska monthly median results from using three different CH_3Cl calibration cylinder drift correction methods. The results are compared to the HATS flask program's monthly means (blue squares). Method 3 drift correction, constant molar production, best matches the flask samples; difference are plotted at the top with error bars calculated from the sum of precisions of the two measurements.