Two Decades of Quasi-Continuous Methane Measurements at Mauna Loa Observatory

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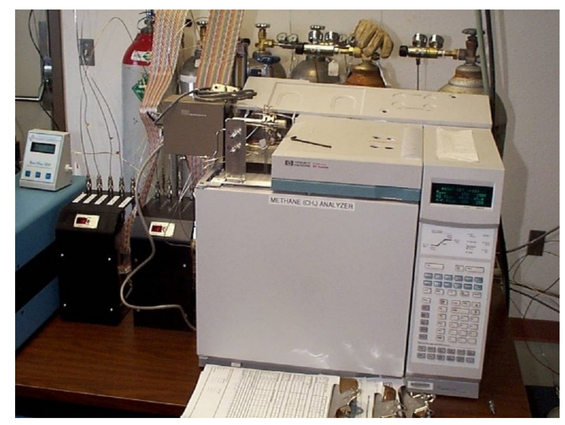
1. Introduction:

Methane (CH_4) plays a crucial role in atmospheric chemistry and climate. CH_4 is the third most important greenhouse gas, and its atmospheric chemistry affects the cleansing capacity of the troposphere. Because it has a short lifetime (~9 yr) and reducing its emissions is cost effective, it is an attractive target for short-term mitigation strategies. Unfortunately, natural and anthropogenic sources of CH_4 are widely dispersed and emission rates are small, so quantifying its budget requires long-term, accurate, high precision measurements, especially if emission reductions are to be verified. Here we demonstrate the feasibility of such long-term measurements from a remote observatory and show some uses of the data in constraining the methane budget.

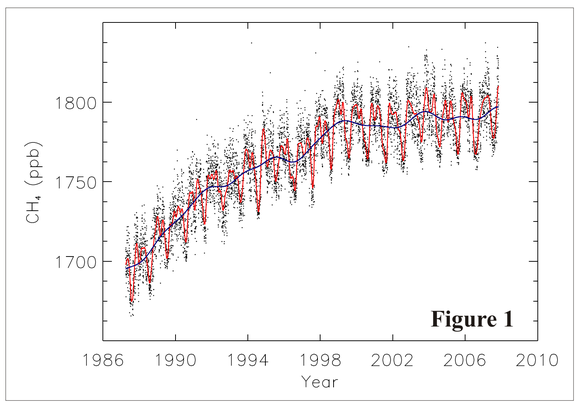
2. Experimental Methods:

The NOAA/ESRL/GMD Carbon Cycle Group has measured atmospheric CH_4 *in situ* at the Mauna Loa Observatory (MLO: 19.54°N, 155.58°W, 3397 masl) since April, 1987. Sample lines run from the ~38 m level on a tower to a gas chromotograph (GC) with flame ionization detection (FID) (photo at right), where the samples are dried with Nafion. Four ambient samples are measured each hour relative to the NOAA2004 CH_4 standard scale (Dlugokencky et al., 2005). Repeatability of the measurements has averaged ~2 ppb. In addition to these *in situ* CH_4 measurements, we also measure CH_4 in discrete samples collected weekly with a portable sampler at MLO.



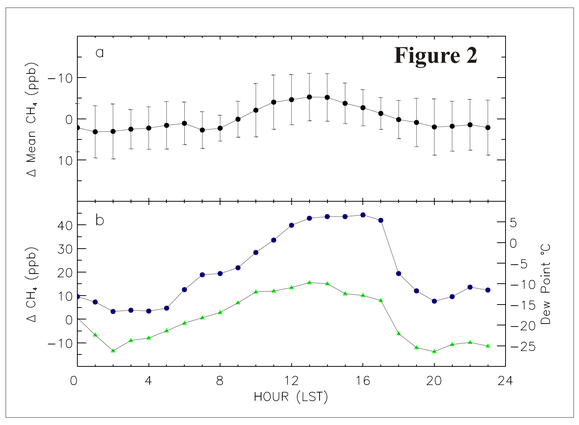
3. Results:

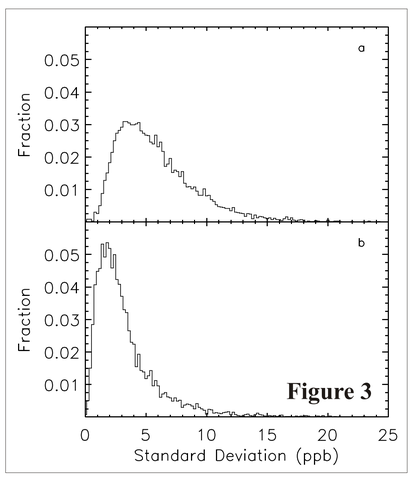
Data



The time-series: MLO daily averaged CH_4 is plotted in Figure 1. The red line is a smooth curve that has been fitted to the data and the blue line represents the de-seasonalized, long-term trend. The average rate of increase in CH_4 at MLO is 4.7 ppb yr^{-1}, but it has decreased from ~15 ppb yr^{-1} at the start to near zero since 2000. Superimposed on the long-term trend is a strong seasonal cycle with minimum values during summer and maximum values during winter and spring.

Diurnal cycle: Daily cycling between distinct flow regimes causes a diurnal cycle in CH_4. Figure 2a: average deviations from the daily mean are plotted for September 2006. Figure 2b: left axis (green triangles), same as Figure 2a but for 5 Sep 2006 and, right axis, dew points for the same day (blue circles). On that day, a diurnal variation in CH_4 of ~35 ppb was accompanied by a significant cycle in dew point.

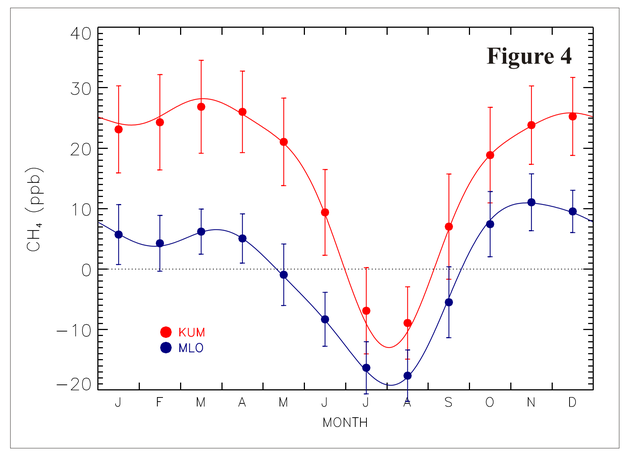




Impact on variability: Distributions of the standard deviations for MLO daily means calculated from hourly averages are plotted in Figure 3a. The long tail is due to natural variability of CH_4, particularly during transitions between upslope and downslope flow. The distribution peaks at ~4 ppb. In Figure 3b, the analysis is restricted to periods of predominant down-slope flow (0000-0700 local time). The peak moves left and improves to ~2 ppb, comparable to the analytical repeatability.

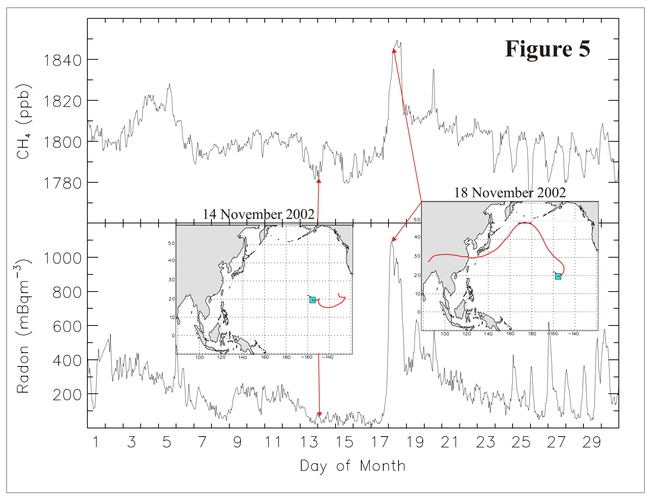
Seasonal Cycle

Vertical gradients: In Figure 4, average CH_4 seasonal cycles for MLO and Cape Kumukahi (KUM: 19.52°N, 154.82°W, 3 masl), adjusted for the mean difference in annual averages, are plotted. CH_4 values at KUM are greater than at MLO (15.7 ± 3.4 ppb), because it is in the marine boundary layer closer to emissions. The vertical gradient varies during a year from ~6 ppb during summer to about ~20 ppb at other times. Though the phases of the seasonal cycles are about the same, the amplitude of the seasonal cycle at KUM is about 40% larger than the cycle at MLO. Seasonal cycles constrain annual variations in rates of emissions and reaction with hydroxyl radical (OH).

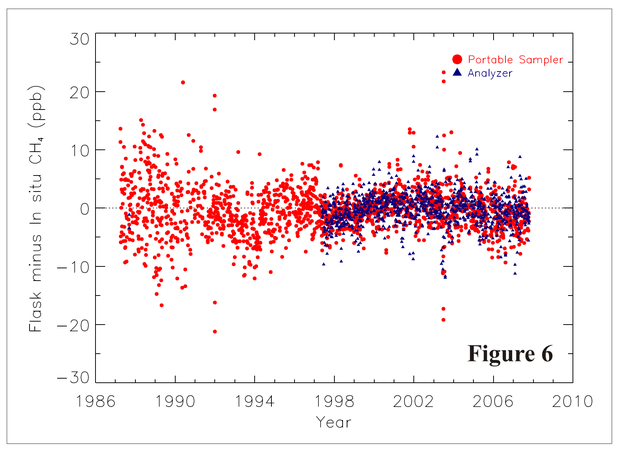


Impact of Long-Range Transport

In Figure 5, CH_4 and radon hourly averages are plotted for November 2002. Ten-day back trajectories demonstrate the influence of air mass origin on CH_4 observed at MLO. Air originating from the tropical Pacific (14 Nov 2002) has relatively low CH_4. Because the ocean is only a weak source of radon and its lifetime is relatively short (~3.6 days), radon values are also low. Air masses originating in Asia, where there are strong emissions of both CH_4 and radon, show relatively high values of both (18 Nov 2002).

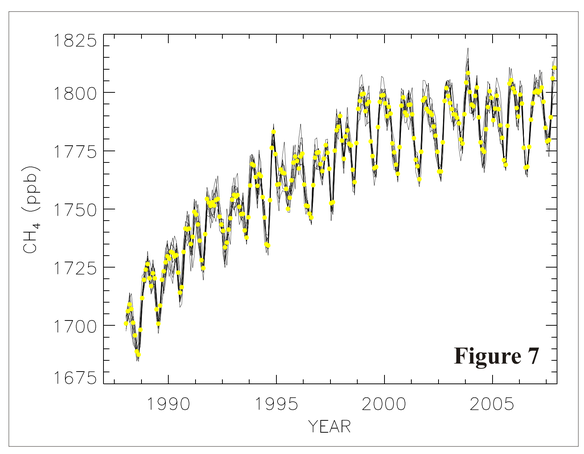


Quality Control on Flask Data



Internal consistency: In Figure 6, differences between discrete flask samples and hourly averaged *in situ* data are plotted (red = portable sampler, blue = GC in-take line). The mean difference is 0.3±3.7 ppb (*in situ* larger).

Estimating uncertainties: In Figure 7, *in situ* monthly mean CH_4 mixing ratios are plotted as yellow circles. The lines are monthly means from 10 pseudo discrete sample records, where each one was determined by randomly selecting hourly averages, one per week, to mimic discrete sample records. The range of CH_4 values at each month is an indication of the uncertainty in monthly means calculated from discrete sample records. Standard deviations in monthly means calculated from 100 pseudo records ranged from 3 to 10 ppb with a typical value of ~ 5 ppb.



4. Conclusions:

We have demonstrated the feasibility of making climate-quality *in situ* CH_4 measurements from a remote observatory. These measurements, and those from the NOAA cooperative air sampling network, are vital to our current understanding of the CH_4 budget. To improve our understanding of this budget and position ourselves for verification of emission reductions, we need to increase the number of *in situ* measurement sites, especially in regions close to emissions. Establishing measurements in the Yukon Basin and Siberia are of extreme importance because of the potential for melting permafrost to increase CH_4 emissions. We will begin measurements at two Siberian sites in 2008. In addition, we hope to add *in situ* CH_4 measurements to daily flask samples collected as part of the CCG Tall Towers program to better quantify North American CH_4 emissions.

5. Acknowledgments:

We would like to thank the MLO staff for all their efforts in collecting weekly samples and maintaining the measurement apparatus, Kirk Thoning for developing data acquisition and system control software, and Andrew Crotwell for continuing over sight and improvements of the analytical system.