5.8 Methane and Carbon Dioxide Continuous Measurements at Izana GAW Station (Spain)

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5.8.1 Introduction

Izaña Observatory is located at 2360 m above see level, on Tenerife (Canary Islands). Carbon dioxide and methane atmospheric mixing ratios have been continuously measured at Izaña since June 1984. During nighttime (20GMT-08GMT), in situ measurements are representative of free troposphere background conditions. This is due to the following facts: a) usually a strong subtropical temperature inversion layer is located at a lower altitude than Izana station; b) Izana station is located on the top of a crest, so during the night period downslope wind produces (by mass conservation) the arrival of free troposphere air to Izana.

In this paragraph, the content of this report is outlined. Measurement instruments and methods are summarized in section 2. In April 2005, we have started to rebuid (and improve) in Fortran 90 a numerical code for processing raw data to mixing ratios, and analysing them. A preliminary version of the new methane data processing scheme, which we have applied to the data period 2003-2004, is presented in section 3. Carbon dioxide (1984-2002) and methane (1984-2004) nighttime daily mean mixing ratio time series are analyzed (in section 4) using the usual decomposition in three terms: interannual trend, annual cycle, and residual, but using a method different from the previous literature. Finally, in section 5 we summarize near future plans for implementing and developing new techniques for data processing and analysis, and for implementing new greenhouse gas measurement programmes: N_2O and SF_6.

5.8.2 Methane and Carbon Dioxide Continuous Measurement Programmes

The general ambient air inlet, which provides ambient air for all instruments that analyze it, is a 8cm inner diameter (ID) stainless steel pipe and has a high flow rate. This inlet is situated on top of the building tower; the height above the ground has changed through the years: 13 m (1984-2000), 8 m (2000- May 2005) and 30 m (June 2005).

Methane mixing ratio is measured using a DANI 3800 gas chromatograph with an FID. The column is MoleSieve 13X 60/80 Mesh 1.20m x 1/4" O.D., 4 mm ID. The oven temperature is 55^{o}C, whereas the FID temperature is 110^{o}C. The carrier gas is synthetic air. Ambient air is cooled to -45 ^{o}C to partially remove water vapour content before flowing towards the sample loop (10 ml). There is an 8-port valve with two positions: load and inject. A few seconds before switching the 8-port valve from load to inject position, the flow through the sample loop is stopped to balance internal loop and ambient pressures (diffusion of ambient air into the sample loop is prevented by a 2 m outlet). Sample loop temperature is not regulated. A software integrator provides the area and height of the CH_4 peak in the chromatogram. Four samples are automatically measured every hour: at 00 and 30 minutes the sample is ambient air, at 15 and 45 minutes the sample is working gas. The working gas tank is calibrated every two weeks against the methane Izana primary standard (prepared by NOAA/ESRL). In December 2004, WCC-Empa carried out a system and performance audit for surface ozone, carbon monoxide and methane at Izana (Zellweger et al.,2005). For methane, the report concludes: “The results of the inter-comparisons between the five WCC-Empa travelling standards and the GC system of Izaña showed good agreement over the concentrations range of 1790 to 1880 ppb. The audit results at Izaña are good when compared to methane audits conducted by WCC-Empa at other GAW sites. The station instrument also showed reasonable repeatability. Due to the good results no technical recommendations are made by WCC-Empa.”

Carbon dioxide mixing ratio is measured with a SIEMENS Ultramat 3 NDIR analyzer. A cryocool trap is used to reduce the dew point of ambient air and standard gases to -65 ^{o}C. Three levels of standard gases are used (primary, secondary and working gases). Between calibrations, ambient air is analyzed continuously; mean value and standard deviation are recorded every 10 minutes. Daily 20GMT-08GMT carbon dioxide mean mixing ratio (in the WMO scale) for the period

1984-2002 is shown in Figure 1. Details about the measurement system and processing can be found in Ripodas et al. (2000), and Navascues and Rus, (1991).

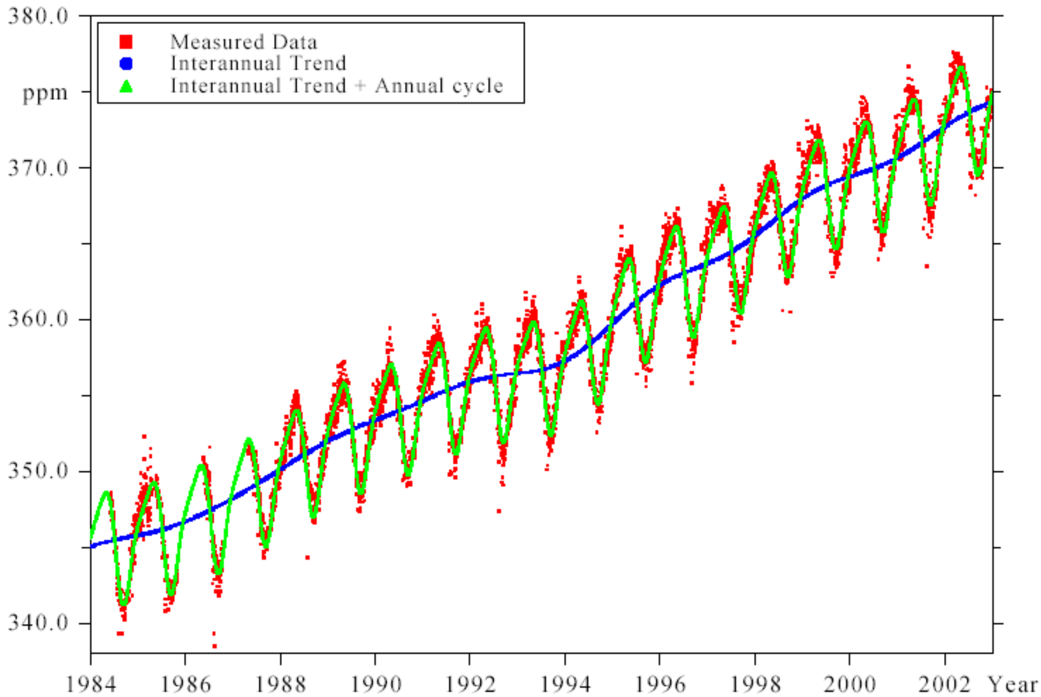

Figure 1: Carbon Dioxide daily nighttime mean mixing ratio at Izana Observatory (INM).

5.8.3 Processing Methane Raw Data To Mixing Ratios

In April 2005, we started to rebuid and improve, in Fortran 90, numerical code for processing methane raw data to mixing ratios. A preliminary version of the methane new data processing scheme, which we have applied to the data period 2003-2004, is presented here.

The response of the FID is assumed to be linear in methane mixing ratio (as it is usually stated in the literature). However, the response changes slowly with time due to variations in ambient conditions (pressure and temperature) and long term drift of the instrument. Peak area is used for data processing. We define the *response slope* (*RS*) of the instrument as the ratio: *(peak area/mixing ratio). RS* does not depend on mixing ratio, but does depend on time.

The data processing concerning the calibration of the working tank has not been changed yet. This tank is calibrated against the Izana methane primary standard every two weeks. The calibration sequence is as follows: every 5 minutes a gas is measured; the standard gas is measured first and then the working gas; this cycle is repeated 7 times, and the process is finished measuring the standard gas. So, for each calibration, there are 7 values for the mixing ratio of the working gas (the *RS* is obtained for the times in which the standard gas is measured, and it is assumed that *RS* changes linearly in time between adjacent standard gas measurements); mean value and standard deviation for the mixing ratio of the working tank are obtained. Typically, a working tank lasts 3.5 moths and is calibrated 8 times during its whole life. A unique value for the mixing ratio (the mean of the 8 calibrations) is used for the whole life of the working tank (usually no significant trend is observed in the mixing ratio of the working tank).

To detect and discard data obtained when the measurement instrument is not properly operating, we have implemented the following statistical procedure, which has been applied to the data period 2003-2004.

First, we consider the peak area time series (one value every 30 minutes) for the working gas. Dividing each value of these series by the corresponding working gas mixing ratio, we obtain the *RS* time series (*RS[t]*). For discarding outliers in the *RS* time series, the following steps are applied:

a) The time series $r(t) = RS(t) - \{RS(t)\}_{30.01d}$ is computed ($\{\ \}_{30.01d}$ indicates a 30.01 days running mean). Values *RS(t)* which have an associated $|r(t)|$ larger than $3.5\sqrt{\langle r^2(t) \rangle}$ are discarded ($\langle\ \rangle$ indicates series mean). $RS_a(t)$ denotes the *RS(t)* time series without those discarded values.

b) The time series $r(t) = RS_a(t) - \{RS_a(t)\}_{3.01d}$ is computed. Values $RS_a(t)$ which have an associated $|r(t)|$ larger than $3.5\sqrt{\langle r^2(t) \rangle}$ are discarded. $RS_b(t)$ denotes the $RS_a(t)$ time series without those discarded values.

c) The time series $r(t) = RS_b(t) - \{RS_b(t)\}_{0.26d}$ is computed. Values $RS_b(t)$ which have an associated $|r(t)|$ larger than $3\sqrt{\langle r^2(t) \rangle}$ are discarded. $RS_c(t)$ denotes the $RS_b(t)$ time series without those discarded values.

The 0.26-day running mean does not remove the *RS(t)* daily cycle, whereas the 30.01 and 3.01 days running means do. Because of this reason, we use a 3σ threshold for step c), and a 3.5σ threshold for steps a) and b). As an example, for the data period 2003-2004, 1.97% of the values in *RS(t)* have been discarded applying those three steps.

Second, we consider the peak area time series (one value every 30 minutes) for the ambient air: *A(t).* The time series $A_1(t)$ is built with the values *A(t)* for which values of $RS_c(t)$ from 15 minutes earlier and 15 minutes later are available. For the data period 2003-2004, 3.28% of the values in *A(t)* have been discarded applying this criterion. The time series *MR(t),* with the values of ambient methane mixing ratio, is computed using $MR(t) = A_1(t)/RS_d(t)$, where $RS_d(t)$ is the response slope in the times in which ambient air is measured. $RS_d(t)$ is obtained from $RS_c(t)$ by linear interpolation.

Third, for discarding outliers in the *MR(t)* time series, the steps a), b) and c) are applied to *MR(t)* . For the data period 2003-2004, 2.55% of the values in *MR(t)* have been discarded applying those three steps. Daily 20GMT-08GMT methane mean mixing ratio (in the CMDL83 scale) for the period 1984-2004 is shown in Figure 2.

5.8.4 Interannual Trend and Annual Cycle

Carbon dioxide (January 1th, 1984-December 31th, 2002) and methane (January 1th, 1984-December 31th, 2004) nighttime daily mean mixing ratio time series are analyzed using the usual decomposition in three terms: interannual trend, annual cycle, and residual, but using a method different from the previous literature. We carry out a least squares fit of the daily data to the function

$$f(t) = a_1 + a_2 t + \sum_{i=1}^{p} \left[b_i \cos(\omega_i t) + c_i \sin(\omega_i t)\right] + \sum_{j=1}^{4} \left[d_j \cos(k_j t) + e_j \sin(k_j t)\right]$$

where: t is the time in days (t=1 for January 1th, 1984); a_1, a_2, b_i and c_i are the parameters of the interannual trend to be determined; $p = 7$ for the methane analysis and $p = 6$ for the carbon dioxide analysis; d_j and e_j are the parameters of the annual cycle (which is assumed constant) to be determined; $\omega_i = 2\pi i/N$ where N equals the number of days in the considered period

($N = 7671$ for the methane analysis, $N = 6940$ for the carbon dioxide analysis); $k_j = 2\pi j / T$ with $T = 365.25$ days. The interannual trend in *f(t)* has two contributions: a linear term in *t,* and the discrete Fourier modes corresponding to the lowest *p* Fourier frequencies for an *N* points domain (the linear trend is introduced to allow the periodic function, with period *N* days, described by the Fourier modes to be continuous). We define the cut off frequency (linear) as $f_c = p/N$ ($f_c = 0.333$ year^{-1} for the methane analysis and $f_c = 0.316$ year^{-1} for the carbon dioxide analysis). The cut off frequency is the largest frequency in the considered interannual trend. The annual cycle term in *f(t)* is composed by the discrete Fourier modes of one year period and its first three harmonics.

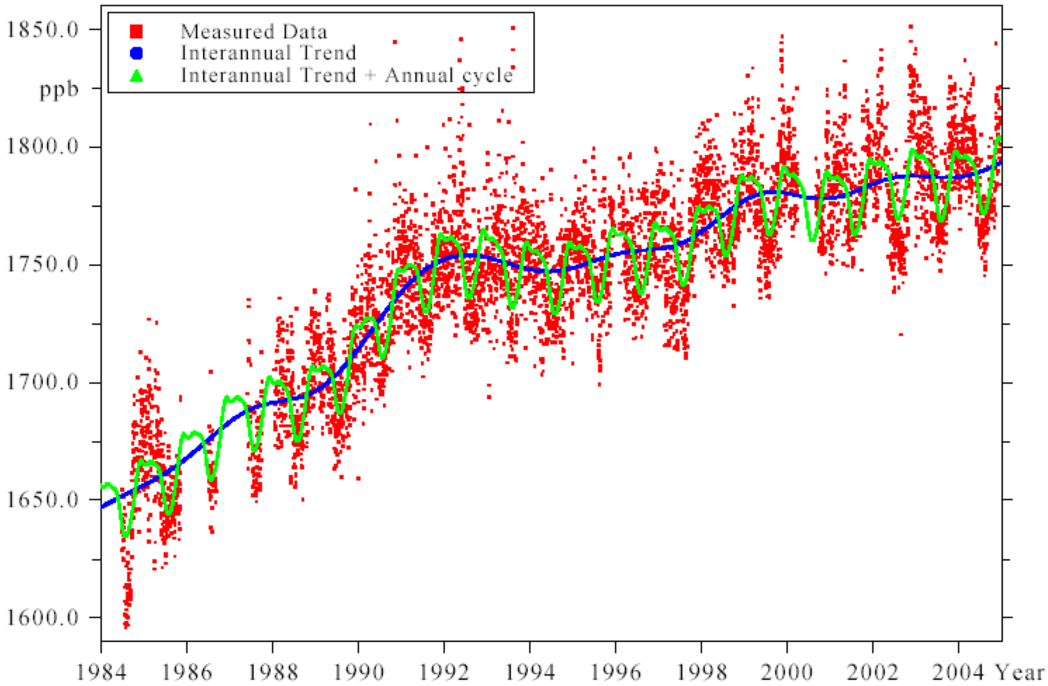

Figure 2: Methane daily nighttime mean mixing ratio at Izana Observatory (INM).

Other authors have obtained the Fourier transform directly (e.g. Thoning et al., 1989) or after applying a second order polynomial and annual cycle fit (e.g. Dlugokencky et al., 1994), and have applied two low-pass filters: one to obtain the interannual trend, and the other one to obtain a smoothed representation of the data. However, Fourier transform requires that the data be equally spaced in time and without gaps. So, data gaps must be filled by interpolation (e.g. Thoning et al., 1989, use linear interpolation). Interpolation introduces information that was not present in the original data. Our method to obtain interannual trend and constant annual cycle does not require interpolation.

Figures 1 and 2 show the interannual trend and the interannual trend+annual cycle for carbon dioxide and methane, respectively. Figure 3 shows the annual cycle for methane and carbon dioxide. For carbon dioxide, the standard deviation of the residuals is 0.84 ppm, the interannual mean growth rate for the period 1984-2002 is 1.54 ppm/year; the peak-to-peak annual cycle amplitude is 7.7 ppm; the annual cycle has its maximum at the beginning of May and its minimum at middle September. For methane, the standard deviation of the residuals is 17.4 ppb, the interannual mean growth rates for the periods: 1984-1991 is 13.1 ppb/year, 1992-1997 is 1.9 ppb/year, 1998 is 13.4 ppb/year, 1999-2004 is 2.7 ppb/year; the peak-to-peak annual cycle amplitude is 29.5 ppb; the annual cycle has its maximum at the beginning of December (with a plateau in winter) and its minimum at the beginning of August.

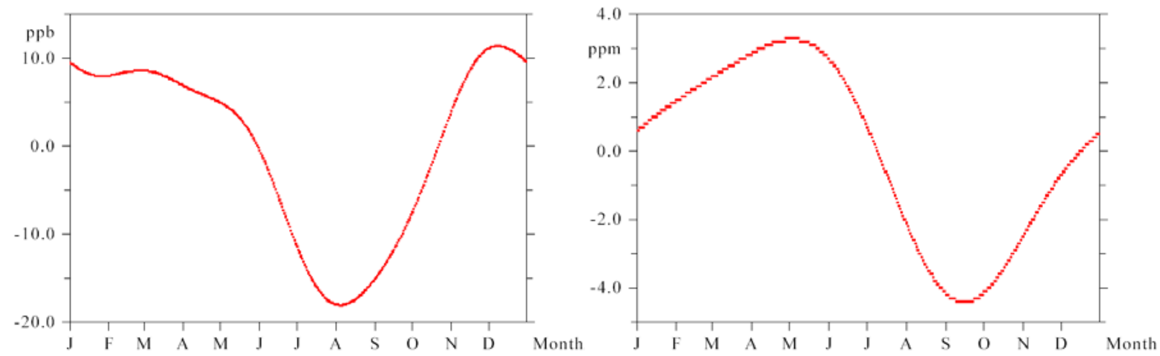

Figure 3: **Mean annual cycle for methane and carbon dioxide at Izana Observatory (INM).**

5.8.5 Near Future Plans

A Varian 3800 GC has been installed with two detectors: a FID to measure CH_4, and an ECD to measure N_2O and SF_6. In a few months, after optimizing the configuration of this instrument, routine atmospheric measurements will be started. A LI-COR 6252 NDIR analyzer will be installed to measure CO_2. So, CH_4 and CO_2 measurements will be duplicated. We are going to continue implementing and developing new techniques for CH_4, CO_2, N_2O and SF_6 data processing and analysis.

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