16.1   ATMOSPHERIC METHANE AT SUVA, FIJI: THE IMPACT OF TROPICAL METEOROLOGY

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1. Introduction

Atmospheric methane mixing ratios have more than doubled over the last 200 years due to an excess of sources over sinks; Etheridge et al (1998). This increase is viewed with concern because methane plays a significant role in both tropospheric and stratospheric chemistry and is an important contributor to the earth's enhanced greenhouse effect. Methane is released into the atmosphere by many kinds of anaerobic sources eg wetlands and rice paddies, leakage and venting of natural gas and biomass burning, especially in the tropics Spivakovsky et al (2000). The major sink for atmospheric methane is oxidation by hydroxyl, OH radicals and the current global loss rate of methane by this process, which depends strongly on OH mixing ratios and the reaction rate constant, is* estimated at 400-600 Tg yr^{-1}.

Seasonal cycles observed in the mixing ratio of atmospheric methane vary greatly between the hemispheres. In the northern hemisphere (NH) the cycles are irregular, have relatively large amplitudes and are highly dependent on their sampling location Dlugokencky et al (1994) In the extra tropical southern hemisphere (ETSH) however, the cycles are much more sinusoidal, relatively independent of their sampling location and are believed to be predominantly controlled by seasonal variations in OH. During the destruction of methane by OH, a kinetic isotope effect (KIE) results in the preferential removal of $^{12}CH_4$ and the methane remaining in the atmosphere becomes more enriched in $^{13}CH_4$. This process should lead to smooth seasonal cycles in $\delta^{13}C$ in atmospheric methane [$\delta^{13}C(CH_4)$] in the ETSH with seasonal amplitudes of about 0.1‰ assuming a KIE for methane removal by OH of 5.4‰. Lowe et al (l999) The seasonal cycles in $\delta^{13}C(CH_4)$ observed at Baring Head and Scott Base however, are highly irregular with amplitudes that are typically a factor of 2 to 3 higher than those predicted by a KIE of 5.4 ‰. These cycles may be driven by irregular southwards transport of methane from seasonal biomass burning (typically from August to October) from southern tropical regions.

In 1994, in collaboration with the University of South Pacific at Suva, Fiji, NIWA set up an air-sampling project to determine background levels of atmospheric methane mixing ratios and $\delta^{13}C(CH_4)$ in the vicinity of Suva in the tropical South Pacific. Major aims of the work include resolution and interpretation of seasonal cycles in methane mixing ratios and $\delta^{13}C(CH_4)$ in the southern tropics and comparison with similar cycles observed further south in the ETSH. Biomass burning is a major source of atmospheric methane and other trace gases in southern tropical regions with a strong signal in $\delta^{13}C(CH_4)$ compared to background levels in the

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atmosphere and we expect evidence of this in the $\delta^{13}C(CH_4)$ in air samples collected at Suva. In addition we examine the effects of meteorological convergence zones and El Nino Southern Oscillation (ENSO) events on the record, particularly in 1998 and 1999.

2. Experimental

To avoid contamination of the air samples by local sources of methane, the sampling site is located on the south east coast near Suva, Fiji where winds are predominantly on shore. Air samples are collected approximately twice monthly at the site using 1 litre (L) electro polished canisters and 22 L light gauge stainless steel tanks. After sampling the sample containers are returned by airfreight to the NIWA laboratory in Wellington, New Zealand for analysis. The methane mixing ratio measurements were made using a gas chromatograph fitted with a flame ionisation detector. The precision of the measurement (1 sigma) is typically better than 2 ppb or about 0.1%. The data are reported with respect to primary standard reference materials (SRMs) prepared by the US National Institute of Standards and Technology (NIST) and laboratory working standards calibrated against these. To determine $^{13}C/^{12}C$ ratios in the methane contained in air samples collected in Fiji, we use an isotope ratio mass spectrometer (IRMS). However the methane must first be quantitatively extracted from the air samples and converted to carbon dioxide on a vacuum conversion line. This is done using procedures reported by Lowe et al (1999) where 20 L air samples are processed to produce about 30-35 μl of CO_2 quantitatively derived from the methane in the original air sample. $\delta^{13}C$ measurements are made with a Finnigan MAT 252 IRMS running in dual inlet mode.

3. Results and Discussion

From the start of the record at Suva in 1994 to mid 1998 the methane mixing ratio data show regular seasonal cycles superimposed on an increasing trend. During this period the growth rate of methane at Baring Head averaged less than 5ppb/year but in mid 1998 it increased to 15 ppb/year. This continued into 1999 but reduced to almost zero in 2000. Current growth rates, 2001 and early 2002, are about 5ppb/year. Similar growth rate changes occurred at Suva. The seasonal cycles have the same phase as those observed at Baring Head but the seasonal minima are typically about 5ppb higher and the amplitude of the seasonal cycle at Suva is therefore smaller. In 1999 there was no pronounced seasonal minimum in the record. We attribute the higher minima to a variety of causes, notably enhanced interhemispheric transport during the austral summer. Because the methane mixing ratio in the NH is about 10% higher than the SH the summer minima of the mixing ratio are reduced at sites in the equatorial southern hemisphere. In addition, although OH levels are relatively high in tropical regions, seasonal changes in its mixing ratio are much smaller

than those in mid and high latitudes thus leading to reduced amplitudes in methane mixing ratio cycles expected for regions like Fiji.

As reported by Gregory et al (1999) however, the inter-hemispheric transport of trace gases like methyl chloroform is remarkably sensitive to ENSO events. The coincidence of seasonal (eg the late Austral summer as above) and cold phase ENSO conditions in March and April of 1999 was optimum for the transport of aged polluted air from the NH into the SH below 4km. At this time the SPCZ was located south of the Suva sampling site, the ITCZ was split into two branches and the Fiji methane mixing ratio data show no summer minimum probably due to large intrusions of methane with a higher mixing ratio from the NH. In addition there are a few samples collected in late 1998 and during 1999 that show methane mixing ratios up to 10% higher than at any time during the rest of the record. Two of these samples show $\delta^{13}C(CH_4)$ values depleted by about 0.2 to 0.3‰ compared to the rest of the record. These data are consistent with NH air, which is more depleted in $\delta^{13}C$ and has a higher mixing ratio due to its proximity to the major northern continental sources of methane. Lowe et al 1999 also show that atmospheric methane becomes more enriched in $\delta^{13}C$ during an average 1 year transit from the northern to the southern hemisphere with an average inter hemispheric gradient of 0.25‰, consistent with the KIE described earlier. If the transit time from the NH to the SH is shorter than 1 year the methane retains a more depleted ^{13}C signature because there has been less time for reaction with OH.

The Suva and Baring Head $\delta^{13}C(CH_4)$ data show highly irregular seasonal cycles with minima in the winter and maxima in the summer. Although the amplitude of the Suva cycle is similar to that observed at Baring Head and Scott Base, the record shows higher $\delta^{13}C(CH_4)$ values than Baring Head, especially in the latter half of the year. From July to November 1995 for example, $\delta^{13}C(CH_4)$ values at Suva were an average of 0.1‰ higher than the Baring Head record. In particular from 1997 to mid 1998 several of the Fiji data points lie more than 0.2‰ above the equivalent Baring Head data. This coincided with unprecedented biomass burning in Indonesia, especially Kalimantan, and was exacerbated by the strong warm phase ENSO event at that time.

4. References

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