

Methane Concentration in Fiji Air: A Study of its Emission Trends and Source Strengths

Francis Mani, Kanayathu Koshy and Matakite Maata

Chemistry Department,
The University of the South Pacific, Suva, FIJI.
E-mail: mani_f@usp.ac.fj

ABSTRACT

In this study we have developed an in house capacity at the Chemistry Department, the University of the South Pacific, to analyze methane in ambient air to a precision of 1.5% using a custom converted Gas Chromatograph with FID detector. The technical support to develop this capacity was provided by our overseas partner, National Institute of Water and Atmospheric Research (NIWA). The air samples were collected from known sources of methane such as the digester at the sewage treatment plant, rubbish dump, wetlands, sugar cane burning in the western side of Viti Levu, geothermal emission in Vanua Levu, rice farms and cattle farms from September 2001 to June 2002 and were analyzed. Through inter-laboratory measurements involving NIWA a mean drift of 0.8% was obtained. The methane concentration in the ambient air has a seasonal cycle with a minimum during late January and a maximum during the July to August period. The digester at the sewage plant recorded the maximum concentration of approximately 70 ppmv followed by Lami rubbish dump with values ranging from 4.37 – 13.35 ppmv. The data from cattle farms, wetlands, rice farms and hot springs recorded emissions in the range of 2.00 – 5.11 ppmv, 1.85 – 4.25 ppmv, 1.77 – 2.62 ppmv and 2.06 – 1.90 ppmv respectively.

Keywords: Methane, Gas Chromatography, FID detector, source strength, Fiji

1 INTRODUCTION

Methane is an important atmospheric trace gas constituent that plays a critical role in the photochemistry of the atmosphere. The atmospheric methane concentration before the pre-industrial era remained largely unchanged at about 700 ppbv (Lasseby *et al.* 1994; Brook *et al.* 1996) but increased rapidly to 1745 ppbv in 1998 (IPCC, 2001). The methane concentration increased by a factor of almost 2.5 (Chappellaz *et al.* 1990) and this is a clear indication of how anthropogenic activities have influenced the atmospheric composition of methane.

The atmospheric abundance of methane is currently increasing at an annual rate of about 1% yr⁻¹. This drastic and rapid change in atmospheric methane concentration has attracted tremendous scientific interest because methane is one of the key greenhouse gases due to the fact that it is about 20 to 30 times more efficient than carbon dioxide in trapping outgoing terrestrial infrared radiation (Koshy *et al.* 1997). It has been reported that methane contributed about 12% of greenhouse warming during 1980's (Crutzen, 1991)

Apart from inducing climate warming directly, methane undergoes chemical reactions in the troposphere and stratosphere, which consequently lead to indirect chemical effects on climate warming. In the troposphere there is a strong interaction between CH₄ and OH[•] that leads to the production of ozone and in the stratosphere the reaction involving OH[•] produces stratospheric water vapour. Both tropospheric ozone and stratospheric water vapour are

greenhouse gases thereby bringing about additional global warming. The final oxidation product of methane is carbon dioxide, which is also a greenhouse gas.

Methane not only affects the earth's radiative balance but also affects the chemical balance of the atmosphere. Approximately 90% of the atmospheric methane is removed by the hydroxyl radical (OH[•]), the best-known atmospheric oxidant that is responsible for cleansing the atmosphere from major pollutants. Continuing increases in methane concentration will lead to a decrease in the OH[•] levels, which in turn will lead to an increase in the lifetime of CH₄ and other greenhouse gases like hydrochlorofluorocarbons (HCFCs), whose degradation is also initiated by the hydroxyl radical.

To understand the drastic increase in methane concentration there is an urgent need to monitor the sources and sinks of methane. The global methane source inventory is not very well defined despite the recent progress in identifying the sources of atmospheric methane and quantifying its fluxes. Measurement of carbon isotope ratios constrained source data to some extent because different potential sources have different isotope ratios. If a methane sample is enriched in ¹⁴C or has relatively low ¹³C content then it is almost certain to be of a recent biogenic source. If a methane sample contains no ¹⁴C it is of fossil origin possibly derived from coal or natural gas (Lowe *et al.* 1991).

Methane of biogenic origin is produced when organic matter is decomposed under anaerobic oxidation by methanogens, as experienced in water logged wetlands, rice fields, landfills, sewage treatment plants and in the gastrointestinal tracts of ruminants. There are both natural and anthropogenic sources of methane. The natural sources constitute of emissions from wetlands, termites, oceans and CH₄ hydrate whereas the anthropogenic sources are agriculture and fuel production related. These include rice farming, ruminant animals, landfills, biomass burning, coal production, gas production (venting, flaring, distribution leaks) and domestic sewage treatment.

The source strengths are still uncertain due to the numerous factors affecting emission from a source that results in the difficulty in assessing the global emission rates of the biospheric sources. Consequently this leads to divergent results, however the average global source is estimated to be approximately 600Tg/yr and 60% of which are attributed to anthropogenic inputs (IPCC, 2001). The combined natural and anthropogenic methane emission was estimated to be 180 Tg/yr during the 15th century, 200Tg/yr in early 18th century and approximately 450 Tg/yr in early 1990's (Khalil and Rasmussen, 1994). Almost 50% of the increase has occurred over the last 40 years (Khalil and Rasmussen, 1994).

The principal sink for methane is photochemical scavenging by hydroxyl radical. The sink strength can be determined with high accuracy based on the OH[•] concentration as deduced from the methyl chloroform budget. The total sink is estimated to be 576 Tg/yr of which 506 Tg/yr is due to tropospheric OH[•] destruction, 30 Tg/yr due to aerated soil that consumes pore-borne methane and the remaining 40 Tg/yr due to minor loss in the stratosphere (IPCC, 2001).

The methane project is part of an ongoing collaborative effort between USP and NIWA and started in 1994. In the early stages all analyses were carried out at the laboratories of NIWA in Wellington, New Zealand. In 2001, USP developed the capacity to measure atmospheric methane concentration accurately to ppbv sensitivity. Using this facility, we have been measuring the concentration of methane from a variety of sources such as rice farms, hot springs, biomass burning, sewage treatment plant, rubbish dumps, wetlands and oceans were monitored and the values obtained are presented and discussed.

2 METHOD AND MATERIALS

2.1 Methane Monitoring Sites

The following sites were monitored (refer to fig. 1)

Lauca Bay (S1): This site is situated at Lower Campus of USP, Suva, and the sampling station is situated 5m above sea level. Air samples were collected when the wind speed is approx. 10 knots to ensure that the wind is not from inland or from any point sources. Air samples were collected on a weekly to biweekly schedule at this site.

Wetlands (S2): Two wetlands were monitored, one was an isolated wetland on the USP campus (Wetland A) and was

about 1 km away from the campus surrounded by dense housing infrastructure (Wetland B). Air samples were collected weekly at this site. Two representative samples were collected at each site.

Rice Farms (S3): Rice farms in Tokotoko, Navua were monitored. Two rice-farming seasons were monitored, 3 farms each season. Two representative samples were collected from each farm and were collected on a biweekly basis.

Cattle Farms: A cattle farm at Koronivia Research Station (S5) and another farm at Viti-Corp, Deuba (S4) was monitored. Biweekly to monthly samples were collected.

Rubbish Dump (S6): Representative samples were collected from the Lami Rubbish dump on a weekly basis.

Digester (S7): A digester at the Kinoya Sewage Treatment Plant was monitored. The air blowing over the digester was collected weekly.

Biomass Burning: Air samples from Nadi (S8), Lautoka (S9) and Ba (10) were collected. A 10 day sample was collected during the pre-intense burning period (early July), a 13 day sample was collected during the intense burning period (mid-November) and a 10 day sample was collected during the post-burning period (late January). A composite sample was collected daily over the sampling period, that is a sample was collected over a 6hour interval in the same sampling can.

Hot springs: Hot springs in Savusavu (S12), Tabia and Wainiqele in Labasa (S11) were monitored. Sampling was done twice within 4 months. Representative samples were collected from each site.

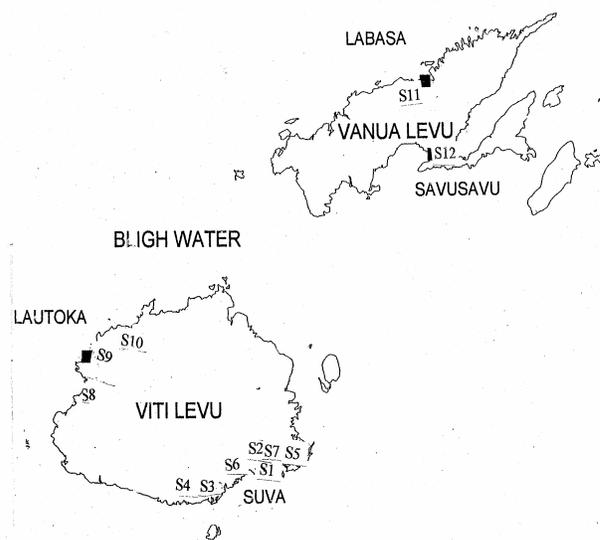


Figure 1 A map of Fiji Islands illustrating the study sites.

2.2 Sampling

At the sampling site, the air is drawn through polyethylene sampling tube from the windward side and compressed into a 2L light gauge stainless steel tank till 30

psi by a Thomas oil free piston compressor. The pressurized air in the tank is then vented out and this procedure is repeated twice before a final sample is collected. An air sample is collected from 0.5m to 1m above the source.

2.3 Analysis

The CH₄ mixing ratios were determined by a Perkin Elmer 8500 Gas Chromatograph with a FID detector as described by Steele *et al.* (1987) and Lowe *et al.* (1991). A 10-port valve was installed onto the GC with a back flush reversal mechanism to prevent high boiling residues reaching the main analytical column. A standard is usually analyzed first and then after every interval of 15 minutes (approximately after 2 samples). A sample is analyzed 3 times and then the ratio of the average area of the sample to the average area of the standard is found to calibrate the methane concentration in the sample.

A 5 ml sample loop and a 1.74 ppmv standard was used to calibrate the sample with methane concentration less than 12 ppmv. For a concentrated sample 1-ml sample loop and a 70-ppm std was used. The precision (%RSD for n = 17) of the system was 1.5%. A Certified Reference Material prepared by National Institute of Technology (NIST) was analyzed, the certified value was 3.90 ± 0.04 ppmv whereas the experimental value obtained was 4.02 ± 0.15 ppmv. Once a month a sample is sent to NIWA in New Zealand for inter-laboratory checking. Through this inter-laboratory measurement a mean drift of 0.8% from our measured values was obtained.

3 RESULTS AND DISCUSSION

In this paper, ambient concentrations near the sources were used to gather information about the source strengths and the emission trends. Khalil and Rasmussen (1998) used ambient concentrations as proxy for methane flux measurements from rice fields and was concluded that there was a close agreement ($\pm 10\%$) between the actual flux measurements and the proxy estimates of the seasonal patterns of emissions in the composite of all years of data. Fig 2 shows the maxima and minima values for the sources monitored for the period Jul 2001 to Jun 2002.

It is obvious from the above figure that methane emission from the digester at the sewage treatment plant is extremely high as compared to any other sources monitored. The maximum value observed is higher than those observed for the background air at Laucala bay by a factor of 40. The methane concentration at the digester range from 31.41–70.09 ppmv. The variability observed could be attributed to many factors such as temperature, amount of organic matter loading and also the efficiency of the digester.

Lami rubbish dump also contributes substantially to atmospheric loading of methane. The values observed range from 4.37 to 13.35 ppmv. The emissions from the landfills are affected from the site-specific factors such as waste composition, moisture, landfill size and temperature (Bingemer & Crutzen, 1987). High values were observed during February to March period when both high rainfall and

temperature was experienced and this could lead to optimal conditions for maximum methane production.

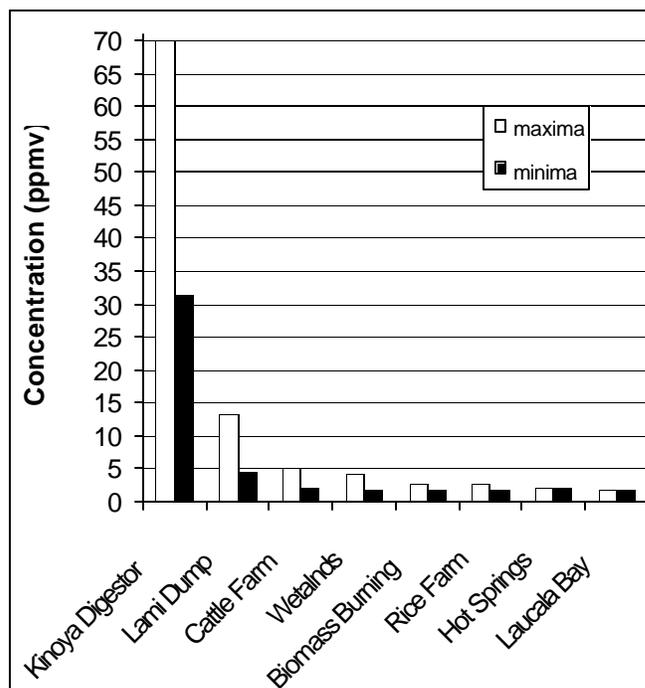


Figure 2 Maxima and Minima Values obtained for the sources monitored for the period Jul 2001 to Jun 2002.

The emission from the wetland was the dominant source in pre-industrial era and is the largest natural source accounting for almost 20% of the current global annual emission (Cicerone and Oremland, 1988; Fung *et al.* 1991). Methane emissions from natural wetlands show large variability resulting from the complex suite of environmental factors

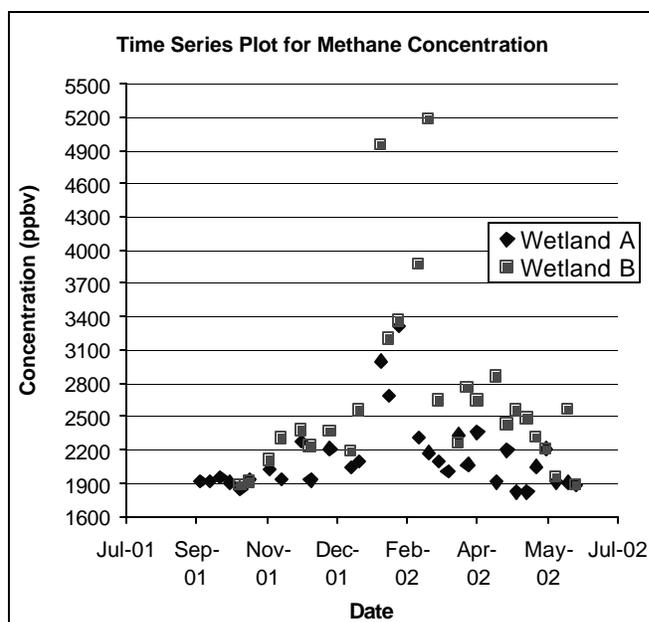


Figure 3 The time series plot for methane concentration for the wetland A and wetland B.

that affect the production of methane such as net primary productivity, temperature, water table and hydrology, transport of organics and sediments, vegetation type and morphology, chemical characteristics of organic minerals (lignin, N content, DOC quantity, chlorophyll), salinity, soil

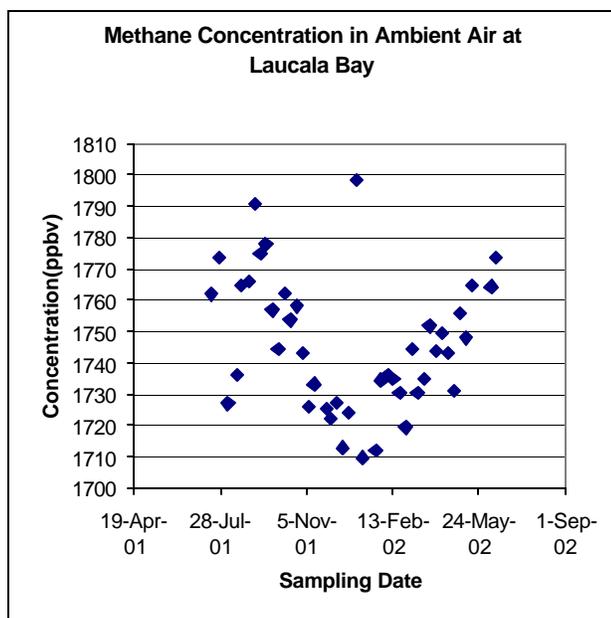


Figure 4 Time series plot for Methane concentration in ambient air at Laucala Bay for July 2001 to June 2002.

nutrient status and topography/geomorphology (Matthews, 2000).

The average maximum value observed for the two wetland sites was 4.25 ppmv and a minimum value of 1.85 ppmv was obtained. An extremely strong seasonal emission pattern was obtained from the wetlands monitored and similar pattern was exhibited by both wetlands (See figure 3). The emission was at its peak during the wet season when the temperature and rainfall were very high, both of which are critical factors controlling methane emissions. An emission trend such as this is typical of tropical wetlands because seasonal precipitation is the major controller of tropical methane emissions, affecting both the area inundated and the length of inundation periods (Matthews, 2000). The wetland emissions are moderately sensitive to the magnitude of temperature variations. A 3 - 5°C temperature rise with water status remaining constant is likely to increase emissions 2 fold (Aselmann & Crutzen, 1986). Methane flux in the great Dismal Swamp also showed greater dependence on temperature. Emissions increased as soil temperature increased (Harris *et al.* 1982).

The proxy data of methane concentration from the rice fields range from 1.77 to 2.62 ppmv. From this study the correlation between seasonal emission from the rice paddies and the growth stages was inconclusive due to the environmental factors that affect emissions and these variables were not controlled. One such critical factor was the water level, which was not controlled and as a result emission could not be correlated to a particular growth stage.

The lower limit of the range was obtained when the field was almost dried up.

The emissions from the Hot Springs remained consistent as highlighted from the 2 sets of data. The values ranged from 1.90 to 2.06 ppmv. The proxy data of methane concentration from the cattle farms range from 2.00 to 5.11 ppmv.

Sugar-cane burning also contributes positively to atmospheric methane loading. The values ranged from 1.69 to 2.71 ppmv, the upper limit was observed during intense sugar cane burning that is towards the end of the harvesting season. Values close to 2.70 ppmv were obtained when samples were collected from the vicinity of sugar-cane fields during the actual burning period. The lower limit of the range was observed after the burning period had come to an end.

The Laucala Bay site has been monitored since 1994 as a part of on-going study of CH₄ budgets in the Southern Hemisphere. This study revealed that air sampled at Suva is representative of the lower troposphere at about 17°S and is usually devoid of any continental influence as indicated by air trajectories (Koshy *et al.* 1997).

The seasonal trend of methane concentration in ambient air is shown in Fig. 4. The methane concentration is lower in summer and higher in late winter and this is in keeping with the trend obtained since 1994 (Koshy *et al.* 1997). Dlugokencky *et al.* (1994) also stated that in the Southern Hemisphere methane shows a relatively simple seasonal

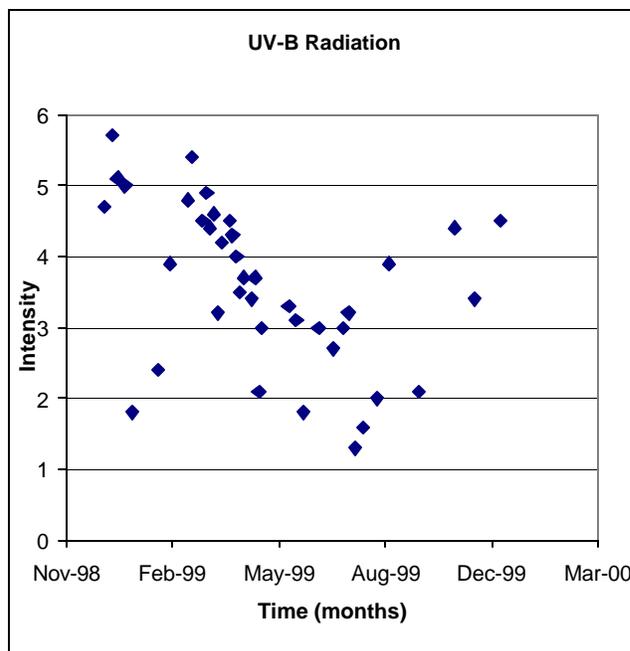


Figure 5 Intensity of UV-B radiation measured at a ground level at Laucala Bay for the period November 1998 to January 2000.

cycle with a minimum during the late summer, which is due to the chemical destruction by OH[•].

To explain the trend observed for the ambient concentration it is important to understand the factors that

affect the OH-production or concentration. Variables affecting hydroxyl production are tropospheric and stratospheric ozone, tropospheric water vapor concentration and UV-B penetration to the lower troposphere. During the summer period there is a lot of water evaporation, which consequently leads to higher concentrations of water vapor in the troposphere.

The UV-B measurements were carried out at Laucala Bay for the 1998 to 2000 period. It can be seen in Fig. 5 that intensity of UV-B radiation was highest during summer and was lowest during the July-August period. Therefore, higher concentrations of water vapor and greater UV-B influx in summer lead to greater production of OH[•] which subsequently lead to decreases in methane concentration in ambient air. In winter it is vice-versa and as a result a maximum is observed.

Relatively high values observed during cooler months could be accounted for by low dispersion in the winter season due to a stable atmosphere. Also, short day lengths, low solar intensity, and low ambient temperature would reduce photochemical destruction of CH₄ (Padhy and Vashney, 2000).

4 CONCLUSION

An important outcome of this research was developing the capacity to analyze methane locally at USP. This consequently led to the identification of methane source strengths and emission trends. However, more investigations covering wider temporal and spatial scales will be required to confirm the findings of this work.

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