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Measurement of Methane Concentration in a Rice Paddy Field with a Tunable Diode Laser Absorption Spectrometry

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SYNOPSIS

A prototype device based on the tunable diode laser absorption spectrometry was constructed and the atmospheric methane concentration near the terrain in a rice paddy field was measured. An open optical path of 50 m length was employed along with a PbSnTe diode laser. Diurnal change of methane density with 30 seconds temporal resolution was recorded associated with meteorological parameters. A feasibility was proven for a practical application for in situ study of atmospheric methane.

1. INTRODUCTION

Atmospheric methane attracted special interest because of its greenhouse effect equivalent to one third of that given by carbon dioxide. Its concentration has increased since the outbreak of the industrial revolution in 18th century and the rate of change has become more rapid in the last decade. This is considered, at least partly, a consequent of human activity[1)].

Methane is produced by methanogenic bacteria during the final step of mineralization of organic matter under strictly anaerobic condition. Suitable habitats is provided by flooded soils such as swamps and rice paddy fields[2,3)]. Holzaphel-Pschorn and Seiler have measured the methane flux in an Italian rice paddy field using a chamber method and found the largest flux in June, some weeks after the replantation [4)].

The dominant rice production is expected, however, in southeast Asia sustaining more than 20 billion Asians, and the in situ measurement of total methane flux measurements in this area is required to forecast the long-term trend of the global temperature rise[5)]. A method to monitor methane concentration is indispensable to control the generation of methane while maintaining the rice production.

A tunable diode laser absorption spectrometry (TDLAS) has been improved in the last decade[6,7)], and is now ready for field applications having overcome various difficulties such as etalon fringes and the cryogenic cooling.

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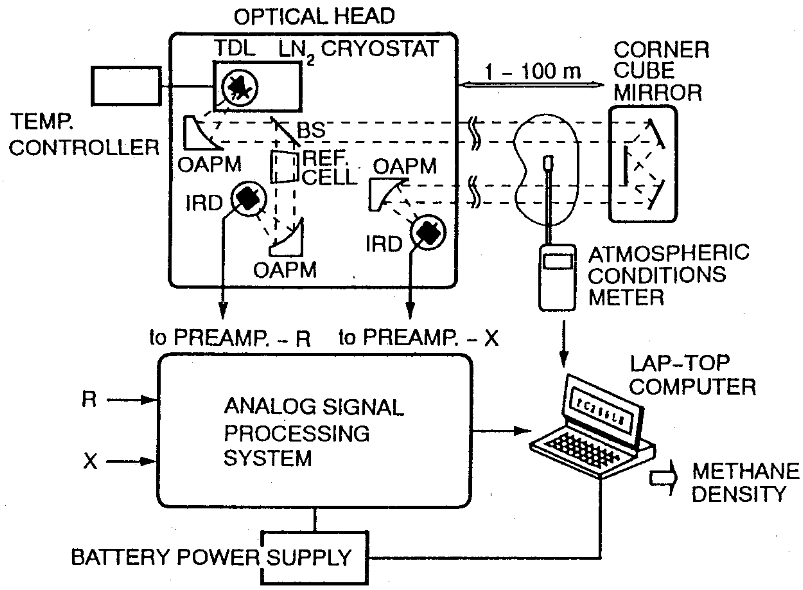

Fig. 1 Block diagram of a portable TDLAS for field measurements of atmospheric methane, making use of the adjoint spectrum processing technique.

The authors have developed a various TDLAS systems exploiting newest electronic techniques[8,9,10]. This paper reports the results of their first series of field measurements of methane in Japan. Their device is featured by its high temporal resolution as short as 30 seconds and its length of open optical path as long as 50 m just above the rice paddy field. Densities are obtained in real time and *in situ.*

2. MEASUREMENT SYSTEM

A schematic diagram of the apparatus is shown in Fig.1. The absorption spectrum over an optical path of from 100m to 300m round trip length is measured with a collimated beam emitted from a PbSnTe tunable diode laser (TDL). The transmitted beam is reflected back with a retro- reflector and received by a HgCdTe infrared detector (MCT-IRD). A part of the laser beam is split to measure a spectrum of standard gas in a cell for the reference spectrum. Another MCT-IRD is prepared for this purpose. The TDL is temperature controlled in the region of 80-100 K cooled by liquid nitrogen and temperature controlled with an accuracy of 10 mK even in the field use. The laser frequency is roughly controlled by the cold-head temperature to choose a methane line in the ν_4 band around 1300 cm^{-1}(λ = 7.6μm) and also its tuning range spans about 1 cm^{-1} which is enough to cover a few methane lines under atmospheric pressure. The laser current is controlled to scan the frequency over 4 seconds and is blanked out for 8 μs to measure the received power, P_R, at every 1/60 second which is designed to give a digital data item. The laser current is also modulated with a frequency of f = 7.68 kHz to implement the second harmonic detection scheme in cooperation with an electronic subsystem based on the phase-sensitive detection. Both the atmospheric spectrum and that of the reference gas are measured simultaneously, which guarantee that the laser frequency is absolutely common between the two spectrum: a small drift in the reference laser frequency within the order of the methane line width is admissible.

Two laser beams, one transmitted forward and the other reflected back, are separated 240 mm from center to center. This is achieved with a corner-cube mirror system of three flat rectangular mirrors of 60 mm× 80 mm large and with a clear circular aperture of 60 mm in diameter. The three mirrors are mounted on a aluminum-arroy housing that avoid the distortion from the thermal expansion and angles between the mirrors can be finely adjusted with micrometer-head screws. The beam separation is secured to avoid interference fringe should stand at the receiver input even if the slightest error in the orthogonalities between three mirrors should exist.

The atmospheric spectrum and the reference gas spectrum are scanned at the same time with the same frequency-scanned laser and are once stored in a computer. Each spectrum comprises 256 data items of 12 bits. Two spectra are compared each other with a weighting distribution, S^*, named as adjoint spectra by the authors, resulting to the concentration C_x of atmospheric methane., *viz.*

$$C_X = \frac{L_R C_R}{L_X} \frac{\langle S^*, S_X \rangle}{\langle S^*, S_R \rangle} \quad , \tag{1}$$

where subscripts X and R stand for the atmospheric optical path and the reference path, respectively. The letter L stands for the optical pathlength, C, the concentration of methane, and S an absorption spectrum measured by the second harmonic method. The quantity S is expressed as

$$S = \Delta^2 \ln\left(\frac{P_R}{P_T}\right) \quad , \tag{2}$$

where P_R and P_T are the power of the transmitted beam and the received, respectively. The symbol Δ^2 stands for an operator that gives second harmonic component of the absorptance $\ln(P_R/P_T)$ in reference to the laser frequency modulation signal.

By means of this data processing procedure, spectral interferences which arise from adjacent water vapor lines, non-linearity between the laser power and the drive current, etc. can be removed from the measured spectrum giving the true methane concentration.

3. MEASUREMENT IN THE RICE PADDY FIELD OF OKAYAMA UNIVERSITY

Experimental measurements have been tried four times since June to September of 1992. Their objective is to test stability, tractability and reliability of our device. There are three rice paddy fields of 60m×120m each in the experimental farm of Okayama University located at the northern end of Okayama City's urban area. The rice paddy field is cultivated by the faculty of agriculture for a research purpose of larger rice production.

The soil is granite originated, light clayey Fine-textured Gray Lowland Soils (grayish brown type). The pH (H_2O) at the adjacent paddy field was measured as 6.0. In order to increase the rice production, whole rice straw of the previous crop has been plowed back every year. Chemical fertilizer was applied at the rate of 116 kg N/ha, 68 kg P_2O_5/ha and 124 kg K_2O/ha, and rice (*Oryza sativa*, var. Japonica, Akebono) seedlings were transplanted on May 20th †.

†by Prof. Miyake of Faculty of Agriculture, Okayama Univ.

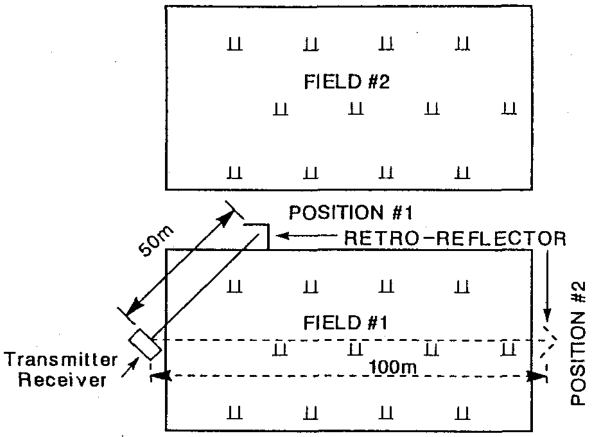

Fig. 2 Plane view of the experimental rice paddy field and the arrangement of the measuring devices.

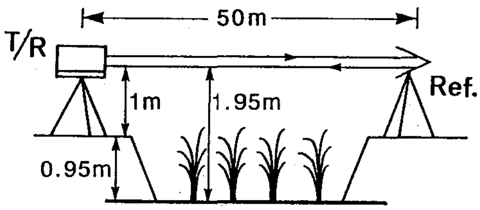

Fig. 3 A schematic elevational arrangement of the optical beam spanned above the rice paddy field.

After some preparatory experiments to test and modify our device, a continuous monitoring for 24 hours was carried out since noon of July 2nd, 1991. Our devices were placed on side roads of the rice paddy field-#1 and the optical path was set as Fig.2 and Fig.3. The path-length was adjusted to 50 m in order that the signal to noise ration in the IRD output signal should be maximum. The emitted power was about 100 μW and the received power was only 10 nW. This was far less than that expected from a calculation based on the measured beam-waist size at the transmitter exit and the clear aperture of the retro-reflector. We consider this is because the laser beam is heavily distorted from the ideally monomodal Gaussian as we had ever measured actually. A pair of spectra measured in this experiment is shown in Fig.4, where three spectra, S_X: the spectra of atmosphere and S_R: a reference gas spectrum. Spectrum of water vapor which may overlie on the S_X is also associated.

Results are shown in Fig.5. It was overcast when the experiment began but later it rained intermittently till the next morning. Methane concentration was continuously measured for about 45 minutes and a calibration procedures were followed before and after the measurement for about one minutes each. This was repeated 22 times.

Whole data including the spectra of atmosphere and the reference cell were recorded on a digital magnetic tape along with atmospheric temperature, humidity, wind velocity, and water and soil temperatures. The uppermost trace, (a), is the recorded methane concentration. In the trace (b), the calibrating data are eliminated from the first and only atmospheric methane densities are given with an expanded vertical scale. The fluctuation found in this trace is mainly due to the actual

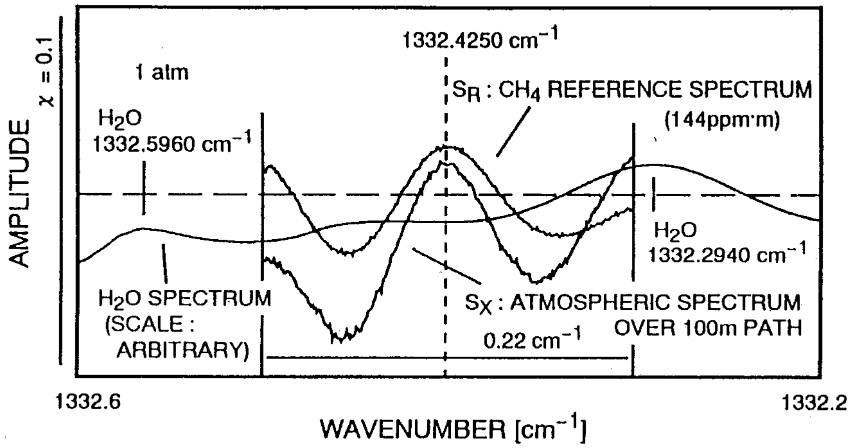

Fig. 4 Spectra measured in the rice paddy field: S_X, atmospheric and S_R: reference methane. The spectrum of water vapor would overlie on the S_X.

concentration change in the atmosphere and is not due to an instability of our device, which can be convinced by inspecting spectra recorded on the magnetic tape. Among the interval of 21:00-0:30, the optics were dewed because of the temperature drop and the received infrared beam power decreased below the level of our system sensitivity: the signal-to- noise-ratio deteriorated gradually and finally the signal disappeared. By putting an incandescent electric lamp which had eventually been prepared for lighting was put into the housing of the optics to warm it up, the dew disappeared and the measurement were resumed.

Data of methane concentrations are smoothed and shown as the solid linesas given in the same figure. For the interval when the system was in calibrating procedure absent data are supplemented by the interpolation. A reference data taken at the Minamigata monitoring station operated by the government of Okayama Prefecture are shown by the broken line ‡. The station is set up for monitoring the roadside atmospheric environment and is located in urban area about 1 km distant from our position. The methane concentration is measured with a gas- chromatograph(GC) with a flame ionization sensor. Soil temperature at 50 mm below the surface, water temperature and atmospheric temperature are shown in (c). The absolute humidity, (d), and wind velocity,(g), are also given.

Inspecting these results, diurnal variation of methane concentration is fairly steady. It should be noted that it was overcast whole the day and no rapid change in soil temperature was found. Only in between 12:00-18:00 the value is slightly high, whereas the background data are rather constant.

We had a little more violent rainy season this year than ever. Repeated rain-storms attacked us as furious as electric poles were once broken down by a gust of 50 m/s. Our apparatuses fortunately kept alive after these storms though actual measurements were interrupted for a while. This was an eventual endurance test against bad weather, and our devices showed unexpectedly good performance

‡by Dr. T. Mori of the Okayama Prefectural Institute for Environmental Science and Public Health.

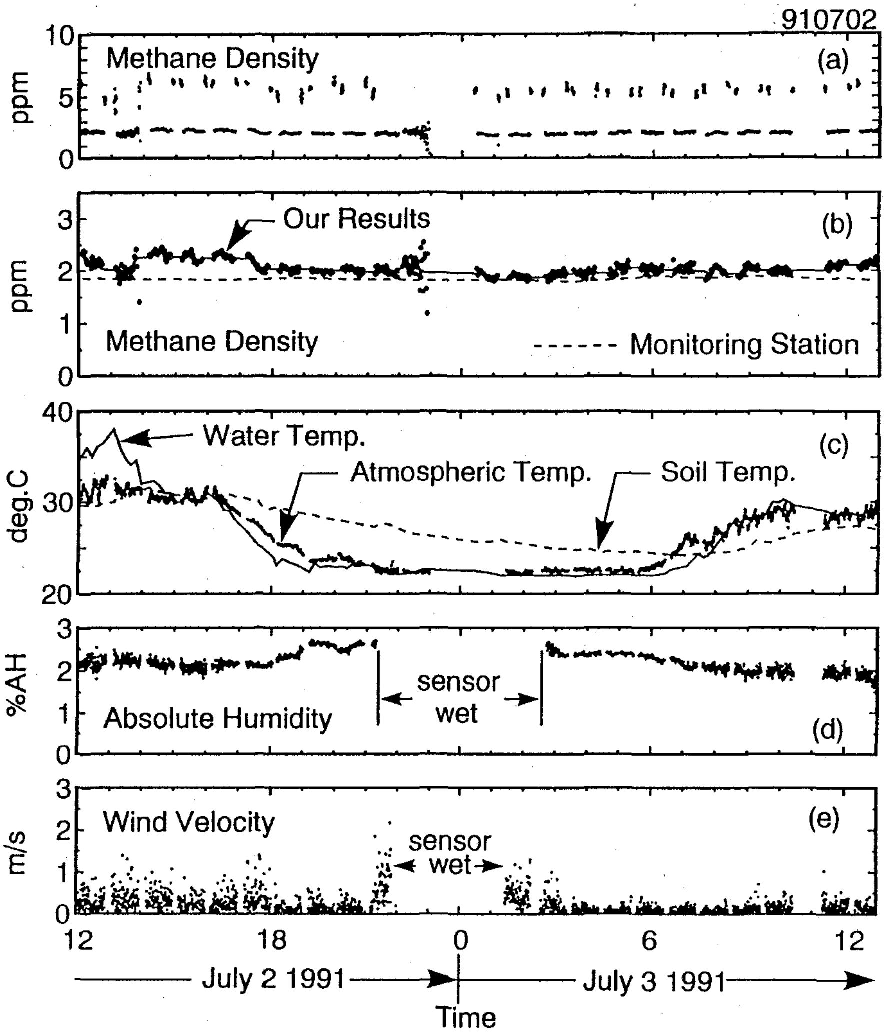

Fig. 5 Records of a 24 hours field measurement on 2, July, amid the rainy season.

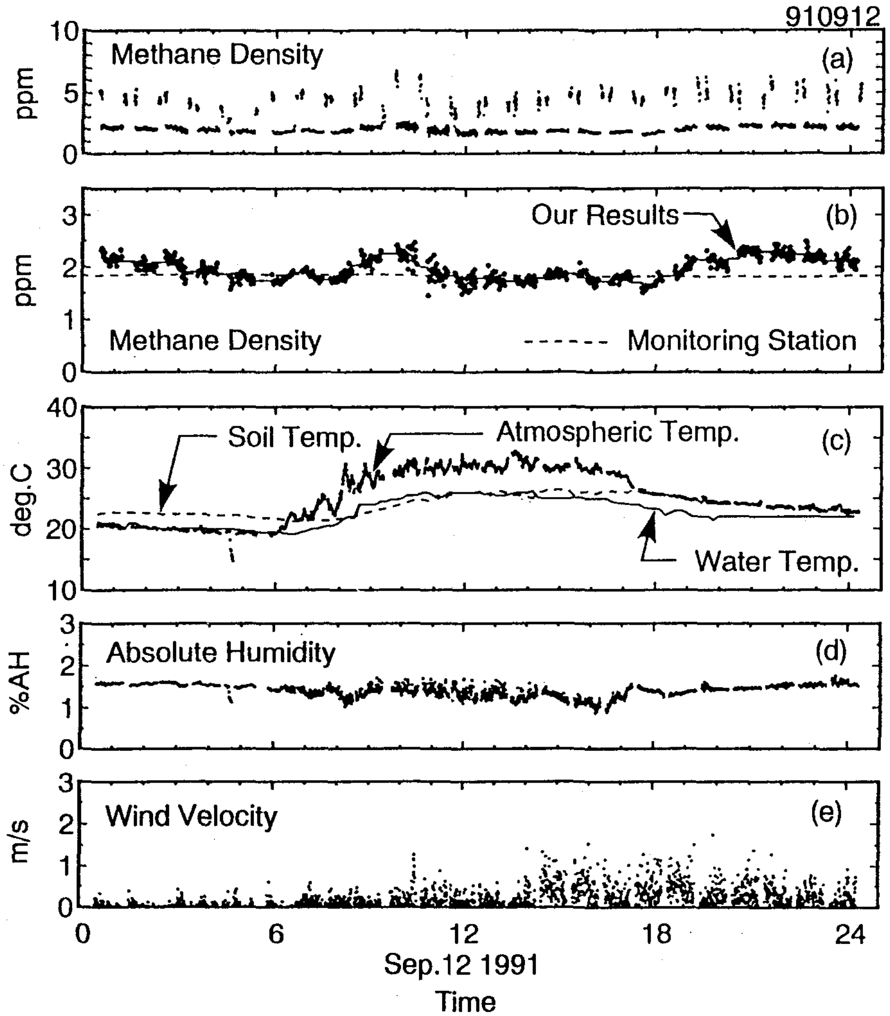

Fig. 6 Record of a field measurement from the noon of 12th Septmber to the next noon. It was fine whole the day and the sunshine was brilliant. The methane density changes significantly according to the soil temperature.

still unveiling some weak points.

Another 24-hours measurement was done since midnight of Sep. 12, 1991. It had been fine for one week and rice-paddy had grown 60cm high at the top of the canopy, just before its heading stage. Results are shown in Fig.6. Since it was fine whole the day, atmospheric temperature rose up in the morning, and the water temperature and the soil temperature were heated up by the strong sunshine through the clear sky as often found in Japanese autumn. Different from the results of Fig.5, methane concentration changes according to these temperature variation. Peaks are found in the morning and also in the evening, which conincides with results by Holtzaphel-Pschorn and Seiler[4]. Through the inspection of data recorded on the magnetic tape, the fluctuation in the morning is suspected partly induced by the agitating water vapor lines adjacent to the methane line involved in this measurement.

4. CONCLUSIONS

Results of the first series of our measurements for atmospheric methane concentration in the rice paddy field of Okayama University are reported. These are in an early stage for examination of the methane effluence flux from rice paddy fields. A vertical concentration distribution would be desirable to know the flux and the beams will be scanned vertically at the next stage in the near future. Our device weigh about 50 kg, which is too heavy for a person to manage: reduction of weight is desirable. Electronic system configuration is still complicated and simplification for better tractability would be desirable. These improvements are under way.

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