Spatial distribution of methane over Lake Baikal surface

V.A. Kapitanov, I.S. Tyryshkin, N.P. Krivolutskii, and Yu.N. Ponomarev

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

Received May 27, 2004

Anomalies in the atmospheric methane distribution over Lake Baikal have been studied with a diode gas analyzer having the threshold sensitivity of 0.04 ppm. Local areas, in which the methane concentration two to three times exceeded the background value equal to 2.00 ± 0.16 ppm, were detected.

Introduction

Methane is the most important representative of organic substances in the atmosphere,[1] and its concentration significantly exceeds the concentration of other organic compounds. In recent years, the amount of methane in the atmosphere has been increasing at a rate about 1% a year, and this increase favors the intensification of the greenhouse effect, because methane efficiently absorbs the Earth's thermal radiation in the IR spectral region. The contribution of methane to the greenhouse effect is about 30% of that from carbon dioxide. On the global scale, the natural sources of methane are wetlands, termites, forest fires, Global Ocean, and fresh water bodies, as well as gas-hydrates.

The discovery of methane gas-hydrates in the Earth's interior made by Vasil'ev with co-authors[2] in 1969 determined the increased interest in gas-hydrates and was followed by a series of investigations, which found huge fuel reserve in the form of gas-hydrates in the bottom of the Global Ocean. According to the estimates available, the reserves of the hydrocarbon fuel (mostly, methane) in the gas-hydrate form markedly exceed the combined fuel reserves in all other forms on the Earth. However, gas-hydrates attract the rapt attention not only because they can be used as fuel and chemical raw materials, but in connection with possible methane emissions into the atmosphere both in future field developments and at relatively small changes in thermodynamic (climatic) conditions, leading to the disturbance of the phase stability of gas-hydrates, which may result in ecological and climatic problems.

Gas hydrate crystals in Lake Baikal have been found quite recently.[3,4] Lake Baikal is a convenient object for investigation of such formations, as well as vent structures, through which gases are emitted. This is caused by the presence of a thick, reliable ice cover, which allows conducting long-term measurements with high spatial resolution, and by the long history of limnological studies of Lake Baikal. As was shown in Ref. 5, despite that direct or indirect data on gas emissions into water and the atmosphere have been obtained as long as two hundred years ago, the concentration of methane in water and the atmosphere has not been measured as yet.

The aim of this work was to find anomalies in the methane distribution in the atmosphere over Lake Baikal surface using a high-sensitivity laser methane detector.

Laser methanometer and measurement technique

To detect methane, we used the modernized version of the detector developed at the Institute of General Physics RAS based on a multifrequency near-IR diode laser and a multipass cell.[6] The detector used is shown schematically in Fig. 1.

The detector employs a GaInPAs diode laser as a source of radiation. The operating temperature of the laser is 0 ... +50°Ñ. Changing the current and the temperature, it is possible to tune the laser frequency in the range from 6000 to 6080 cm^{-1} (1.645–1.666 μm), which includes rather strong absorption lines of methane. The diode laser emits several (5 to 10) longitudinal modes, and the power of radiation in one of them is about 70% of the total laser power (3 mW); the width of an individual mode is 10^{-3} cm^{-1}. The laser frequency is tuned by changing the temperature of the diode laser. For this purpose, the laser is mounted on a Peltier element. The diode laser temperature is measured by a thermal sensor (thermistor), placed near the laser. The long-term temperature stability of the diode laser is 10^{-2} deg.

The diode laser operates in a repetitively pulsed mode with the period of 4.5 ms and the pulse duration of 4 ms. Current pulses supplying the laser have a trapezoid shape. This allows us to scan the laser frequency in the range of 1 cm^{-1} during a single pulse and to record the transmission spectrum of an individual line of a gas under analysis. The diode laser emits in two opposing directions. The principal laser beam comes into the multipass analytical optical cell with a photodetector installed at the exit. Atmospheric air is continuously blown through the cell.

0235-6880/04/08 553-03 $02.00

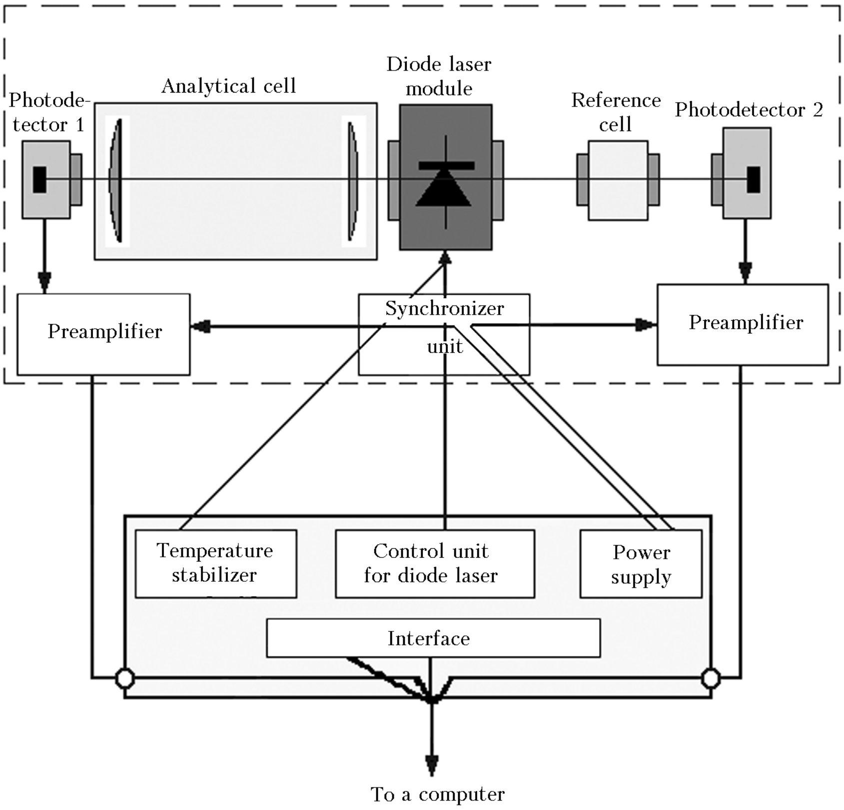

Fig. 1. Schematic diagram of methane detector.

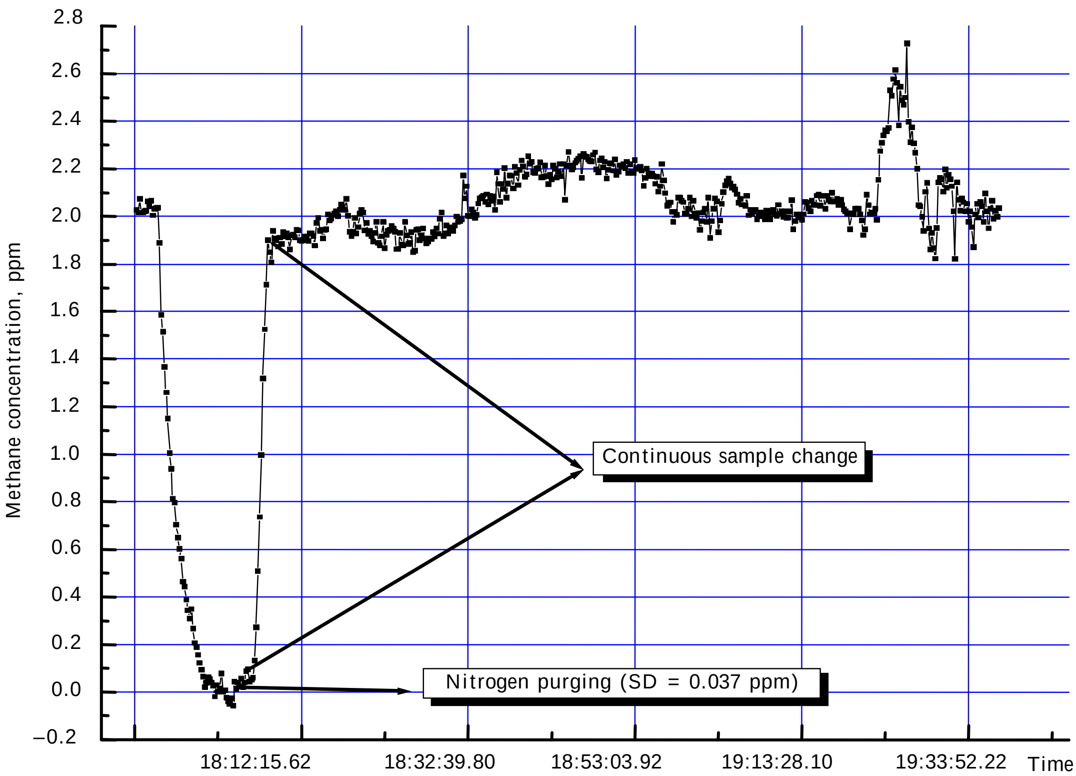

Fig. 2. The record of methane concentration measurements.

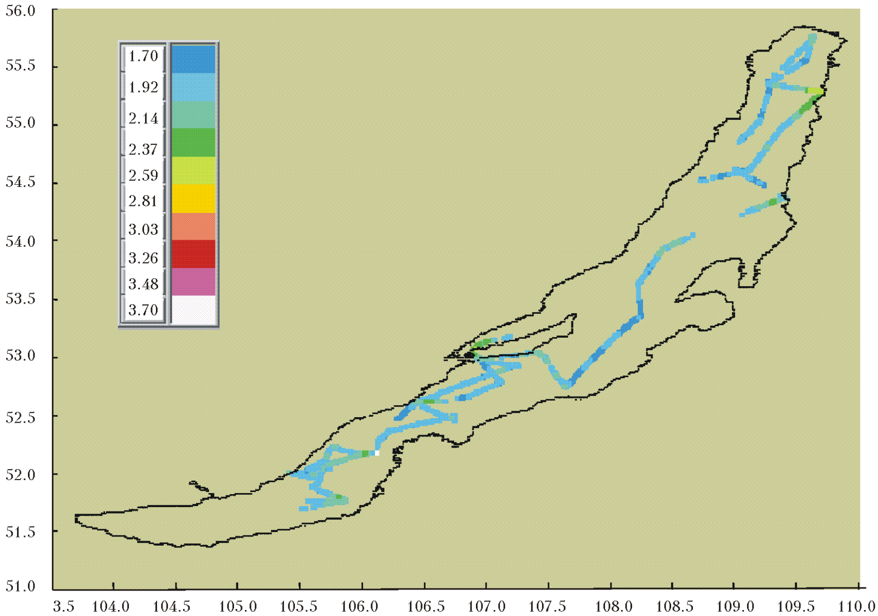

Fig. 3. General pattern of the methane spatial distribution over Lake Baikal.

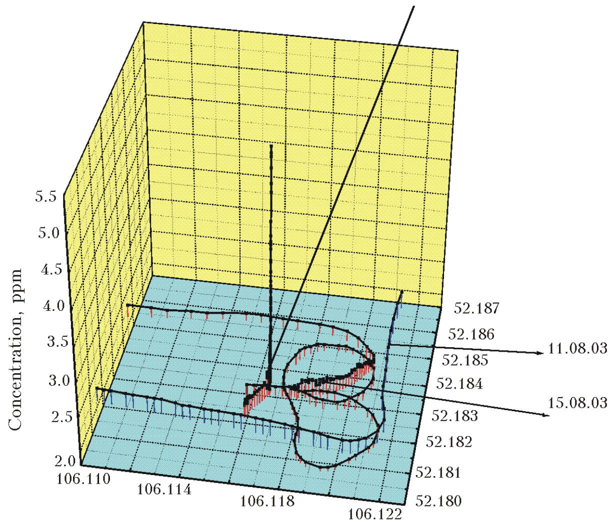

Fig. 4. Spatial distribution of the methane concentration in the range of maximal anomaly caused by the methane emission from the lake bottom in August 11 and 15.

The laser radiation emitted in the opposing direction passes through the reference cell filled with methane at a certain preset concentration and comes to another photodetector. The method of determination of the methane concentration is based on the calculation of the correlation function of the signals (absorption spectra of the methane–nitrogen mixture and the atmospheric air) in both channels. For this reason, the detector has a high selectivity with respect to other gases.

The multipass analytical cell was made as a Chernin matrix system[7] with the base length of 0.75 m, the optical path length of 157.5 m, and the reflection coefficient of the mirrors equal to 0.998. The cell capacity was 14 liter. The atmospheric air was continuously blown through the cell with a membrane pump at a rate of 0.2 l/s.

The main technical characteristics of the modernized methane detector were determined directly at the measurement site. The sampling period was 12 s, corresponding to the spatial resolution of about 50 m at the mean vessel speed of 16 km/h. The detector was calibrated against the nitrogen–methane mixture with the methane concentration of 2 ppm. The zero signal level was determined by purging the analytical cell with pure nitrogen. Figure 2 shows a typical record of the methane concentration measured as a function of time, from which we can determine the detection limit (standard deviation) – 0.037 ppm and the time constant of the detector on the whole (with the allowance for the pump productivity and the cell volume) – 99 s (spatial resolution of 450 m). The long-term stability caused by the zero drift was high enough – about ± 0.5 ppm for 5 h. To take it into account, determination and correction of zero were performed every 4 h.

Results and discussion

The measurements of the methane content in the atmosphere over Lake Baikal were conducted by the method of continuous air sampling from the height of 10 m above the water level from aboard *Vereshchagin* Research Vessel in the period of August 10 through 16 of 2003. The coordinates of the measurement points were determined by the shipborne GPS system. Figure 3 shows the generalized results of measurements of the spatial methane distribution over Lake Baikal (along the cruise route).

The mean value of the methane concentration over Lake Baikal was (2.00 ± 0.16) ppm, which agrees with the data obtained earlier (June of 2003) by the chromatographic method. Local anomalies of the methane content, 2 to 3 times exceeding the standard deviation, were observed in some lake regions. Figures 4 and 5 depict the spatial resolution and the time scan of the methane content in the area of the highest anomaly caused by the methane emission from the lake bottom. The measurements were conducted in the same Baikal region on August 11 and 15 (Fig. 5 for August 15).

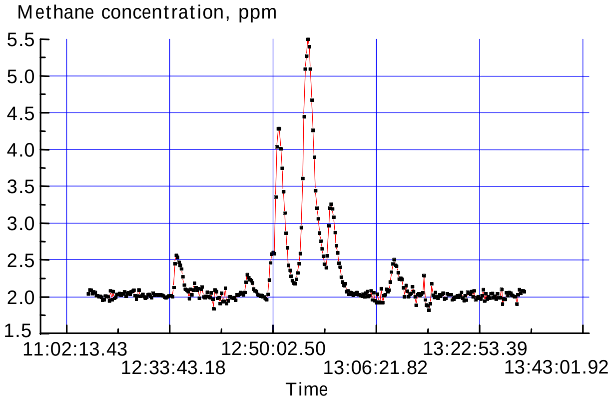

Fig. 5. Time scan of the methane content in the area of the highest anomaly caused by methane emission from the lake bottom on August 15.

It can clearly be seen that the anomalies of the methane content in the atmosphere due to methane emissions from the water surface of Lake Baikal have a pronounced local character with the area less than 100 m^2.

Acknowledgments

We would like to thank Nikolay Granin for initiation of this work and help in measurements.

This work was supported, in part, by the INTAS (grant No. 01-2309) and the Program of Basic Research of the Division of Physical Sciences RAS (Project No. 2.10.1 "High-Resolution Spectroscopy").

References

1. N.M. Bazhin, Khimiya v Interesakh Ustoichivogo Razvitiya **1**, 381–396 (1993).
2. V.G. Vasil'ev, Yu.F. Makogon, F.A. Trebin, A.A. Trofimuk, and N.V. Cherskii, *Discoveries in USSR in* 1968–1969 (TsNIIPI, Moscow, 1970).
3. M.I. Kuz'min, G.V. Kalmychkov, V.F. Geletii, V.A. Gnilusha, A.V. Goreglyad, B.N. Khakhaev, L.A. Pevzner, T. Kavai, N. Ioshida, A.D. Duchkov, V.A. Ponomarchuk, A.E. Kontorovich, N.M. Bazhin, G.A. Makhov, Yu.A. Dyadin, F.A. Kuznetsov, E.G. Larionov, A.Yu. Manakov, B.S. Smolyakov, M.M. Mandel'baum, and N.K. Zheleznyakov, Dokl. Ros. Akad. Nauk **362**, No. 4, 541–543 (1998).
4. J. Klerkx, R. Hus, M. De Batist, O. Khlystov, P. van Rensbergen, and J. Poort, in: *Abstracts of Reports at VI Intern. Conference on Gas in Marine Sediments*, St. Petersburg (2000), p. 56.
5. N.G. Granin and L.Z. Granina, Geol. i Geofiz. **43**, No. 7, 629–637 (2002).
6. *Methane Detector*. Technical specification (Institute of General Physics RAS, 1999), 21 pp.
7. S.M. Chernin, Infrared Phys. & Technol. **37**, 87–93 (1996).