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Measurements and data processing of atmospheric CO₂, CH₄, H₂O and $\delta^{13}\text{C}_{\text{CH}_4}$ mixing ratio during the ship campaign in the East Arctic and the Far East seas in autumn 2016

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Abstract. Here we present the results of measurements of the atmospheric methane concentration and its isotope composition ($\delta^{13}\text{C}_{\text{CH}_4}$) in the East Arctic and Far East Seas during the cruise in the autumn 2016 by two different types of analyzers. Open path LI-7700 and LI-7500 analyzers measuring correspondingly methane (CH₄), and carbon dioxide (CO₂) and water vapor (H₂O) have high time resolution (10Hz) that allow to fix instantaneous values of gas concentration. We obtained high CH₄ concentration (more than 8 ppm) at the location of methane bubbles yields from sea water to atmospheric air. However, due to contamination and icing of the mirrors of these analyzers, significant part of data was rejected for analysis. The data sets of contact gas analyzer G2132-i shows good reliability but the peaks of CH₄ concentration obtained by G2132-i are lower (up to 3.7 ppm) and longer due to instrument's slower responding time. For 10-min averaging, data sets of both CH₄ analyzers gives good agreement, the differences between two types measurements of methane values are less than analyzers' accuracy.

1. Introduction

Subsea permafrost and hydrates in the Eastern Arctic seas shelf are significant methane pool and potentially can be large source of atmospheric methane emissions [1]. By now a lot of localized seeps of methane in East Arctic seas have been found [2, 3], but the quality of the obtained experimental data is currently insufficient to reliable estimate CH₄ emissions into the atmospheric air, which are still very poorly quantified [1, 4, 5]. Satellite measurements of the concentration covering the entire globe, but do not have sufficient accuracy [6]. Arctic CH₄ source can be identified by isotopic signature [7-10], but measurements of $\delta^{13}\text{C}_{\text{CH}_4}$ are even rarer. Thus, it is very important to expand the experimental studies and analyze new full-scale data on methane concentrations in the Arctic.

Atmospheric carbon dioxide, water vapor, and methane mixing ratios and changes in the $^{13}\text{C}:^{12}\text{C}$ ratio in CH₄ (reported a changes relative to a reference ratio and denoted as $\delta^{13}\text{C}_{\text{CH}_4}$) were measured during ship campaign from 23 September to 3 November 2016 in the Laptev, East Siberian and Chukchi Seas and as well as in the North Pacific and in the Sea of Japan. In this study we pay attention to the methodological aspects of received results.



2. Measurements and methods

The measurements were made from aboard the research vessel (R/V) "Akademik M.A. Lavrentiev" (78th cruise). The R/V route started from the Tiksi port and gone through the East Arctic seas: the Laptev and East Siberian seas, than through the Chukchi, Bering and Japan seas to the Vladivostok port. Route map is shown at Figure 1.

An automated measuring complex was used for direct observations of surface air composition. It included the following instruments:

- 1) Cavity-Ring-Down Spectrometer (CRDS) produced by Picarro Inc., USA (model G2132-i) to measure concentrations of methane, carbon dioxide, water vapor and isotopic signature;
- 2) methane concentration analyzer with an open optical path, model LI-7700, produced by Li-Cor Inc., USA;
- 3) carbon dioxide and water vapor concentrations analyzer with an open optical path, model LI-7500, produced by Li-Cor Inc., USA.

Target parameters of measuring system, including time resolution are presented in Table 1. According to this table, the concentrations of methane and carbon dioxide as well as content of water vapor were measured synchronously by two analyzers. As it will be shown below, this significantly improved the quality and reliability of the data sets.

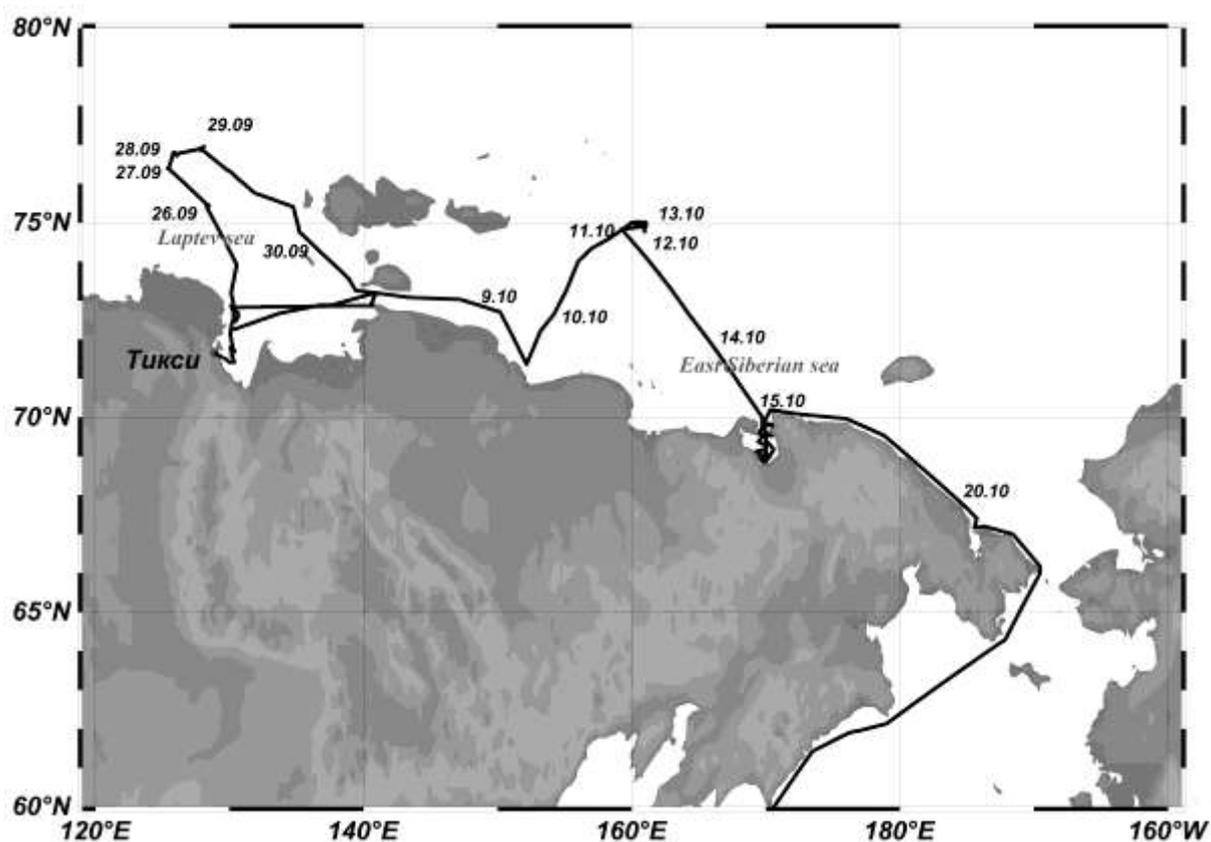


Figure 1. Route of 78th cruise of R/V "Akademik M.A. Lavrentiev" with dates (dd.mm) of the R/V locations along the ship's trajectory.

The core of the G2132-i is Picarro's unique Cavity Ring Down Spectroscopy (CRDS) technique, a time-based measurement that uses a laser to quantify spectral features of gas phase molecules in a

small optical cavity, which has an effective laser path length of up to 20 kilometers. Characteristics of G2132-i are shown in Table 2.

Table 1. Used analyzers and measured parameters.

#	Analyzers	Time resolution, sec	$\delta^{13}\text{C}_{\text{CH}_4}$	CH_4	CO_2	H_2O	Atmospheric pressure	Air temperature
1	G2132-i	>30	•	•	•	•		
2	LI-7700	0.1		•			•	•
3	LI-7500	0.1			•	•	•	•

Table 2. G2132-i characteristics for HP (High Precision) mode

#	Performance Specifications	$\delta^{13}\text{C}_{\text{CH}_4}$	CH_4	CO_2	H_2O
1	Dynamic Range	-	1.8-12 ppm	200-2000 ppm	0-2.4 % guaranteed range
2	Precision	<0.8 ‰	5 ppb + 0.05% of reading	1 ppm + 0.25% of reading	100 ppm
3	Max Power Requirements, W	< 260 W start-up (total)			
4	Dimensions, mm	Analyzer 431.8 x 177.8 x 445.7 External pump 90 x 102 x 280			
5	Weigh, kg	25.4			

We made an integrated constructional unit for the G2132-i analyzer to simplify its installation on board the R/V. It included the instrument itself, uninterrupted power supply (model PowerCom Smart King Pro SKP-1000), the GPS (model Global Sat BU-353G GPS/GLONASS), additional N86 KNE compressor and rotameter, the Transcend TS500GSJ25M2 external hard disc, the 19" keyboard with touch pad, and 15" TFT video monitor.

The main features of this unit were maximum simplification of installation and maximum operating automation. Using of the additional compressor within the unit is necessary due to long air inlet tubing, so the G2132-i instrument belongs to the class of contact gas analyzers, and it is necessary to supply the analyzer by air and pump it through its internal cavity.

Besides contact analyzer, we used the LI-7700 and LI-7500 open path analyzers, which measure the concentration of gas impurities in the open air at the place of installation. The LI-7700 uses a single-mode tunable near-infrared laser source, measuring the absorption of infrared laser radiation at the wavelength of absorption band of CH_4 between the mirrors of the instrument. LI-7700 also uses so-called Wavelength Modulation Spectroscopy (WMS). This feature provided high performance and reliability of the instrument. Main technical parameters of the LI-7700 are shown in Table 3.

Open path $\text{CO}_2/\text{H}_2\text{O}$ Analyzer LI-7500 also uses the principle of measuring the absorption of infrared radiation at wavelengths corresponding to the absorption bands of carbon dioxide and water vapor. This instrument has small size and weight. The main operational parameters of the analyzer are shown in Table 4.

All analyzers have comparable characteristics of precision, in particular, of methane concentration, that is typically $5\div 10$ ppb. So, at an average level of methane concentration over the water surface of about 2 ppm, the relative error is approximately $0.25\div 0.5\%$.

Table 3. Characteristics of open path LI-7700 analyzer.

#	Performance Specifications	CH ₄
1	Dynamic Range	0-40 ppm for 25°C, 0-25 ppm for -25°C
2	Precision	5 ppb
3	Linearity	1 % of reading
4	Power Consumption, W	16
5	Dimensions, mm	143.3 x 143.3 x 828.0
6	Weight, kg	5.2

Accuracy at constant temperature: typically <1%, maximum < 2%

Table 4. Characteristics of open path LI-7500 analyzer

#	Performance Specifications	CO ₂	H ₂ O
1	Calibration Range	0-3000 ppm	0-6 %
2	Precision	1 % of reading	2 % of reading
3	Max Power Consumption, W:	30	
4	Dimensions, mm	65.0 x 65.0 x 300.0	
5	Weight, kg	0.75	

The G2132-i was installed in the vessel laboratory with air intake at the ship mast at 11 m above the water level. The analyzed air came into G2132-i through the Teflon tubing of 30 m long and 10 mm inside diameter, with an air flow of about 3 l/min. Open path analyzers LI-7700 and LI-7500 were installed on the vessel mast, together with the acoustic anemometer that was also a part of the measurement complex. The general views of the complex is shown in Figure 2.



(a)



(b)

Figure 2. G2132-i in the R/V laboratory (a); open path LI-7500 and LI-7700 analyzers, acoustic anemometer at the mast (b).

Calibrations of the G2132-i were carried out according to the secondary standard, which was a 1-liter compressed air cylinder provided by the Norwegian Institute for Air Research (NILU) with known CH₄ and CO₂ and $\delta^{13}\text{C}_{\text{CH}_4}$ values. The relative error of that measurements did not exceed 0.03% for methane and 0.1% for $\delta^{13}\text{C}_{\text{CH}_4}$. During measurements in NILU, a standard known as NOAA04 [11] for CH₄ was used. Calibration for $\delta^{13}\text{C}$ was made by the method described in [12]. Further, we use a 10-liter cylinder with calibration gas of Russian State standard reference sample 10700-2015 produced by "Linde Gas Rus" and 1-liter cylinder filled with compressed air with a certain concentration of methane. According to the Russian technical specifications 2114-009-05015259-2015 for calibration gas, the relative errors of concentration are significantly higher than the precision of the analyzer. For the calibration gas provided by "Linde Gas Rus" (cylinder No. 516934, passport No. 290), the concentrations errors are presented in Table 5.

This Table shows that the errors in the methane concentration in the calibration gas is about 4%, so this mixture cannot be directly used to calibrate the G2132-i with a significantly better accuracy. Because of the G2132-i was previously calibrated for the secondary NILU standard, we measure the concentration of CH₄ in the cylinder with calibration by analyzer. As a result we obtained a low value of the standard deviation (0.0006 ppm) for period of measurements 10 minutes and 10 seconds averaging. So, we obtained the methane concentration in the cylinder with calibration gas $C_0=2.0471$ ppm that was used for further calibrations.

Table 5. Technical characteristics of calibration gas provided by "Linde Gas Rus"

#	Gas Impurity	Units	Mixing ratio	Absolute error
1	CH ₄	ppm	2.09	0.08
2	CO	ppm	1.98	0.10
3	CO ₂	ppm	409	14
4	C ₃ H ₈	ppm	1.13	0.06

To estimate the long-term stability of analyzers readings we made several calibrations of the G2132-i during 2015-2017 years. The results are shown in Figure 3. Variations of obtained values are less then precision of analyzer (± 5 ppb). In Figure 3, this is additionally illustrated by horizontal dash-lines, which correspond to the average values for all calibrations for each standard.

Similarly we calibrate the G2132-i for CO₂ and $\delta^{13}\text{C}_{\text{CH}_4}$ (see Fig. 3), using the same standards. The obtained results confirm the conclusion that the long-period (several months or more) drift of the calibration coefficients of the G2132-i does not exceed the accuracy value declared by Picarro Inc. As a result of the calibration, we confirmed the conclusion that the used contact gas analyzer is characterized by a sufficiently small short-period drift of the readings.

To calibrate the LI-7700 we use the same calibration gas of "Linde Gas Rus". The calibration was carried out using the chamber (shroud), supplied with the LI-7700 by its manufacturer, into which the optical trace of the analyzer is placed. The chamber was filled in with a calibration mixture at a flow rate of about 1 liter/min until a stable reading of the instrument was reached, after which the calibration was continued for another 10 minutes. The calibration results are shown in Table 6.

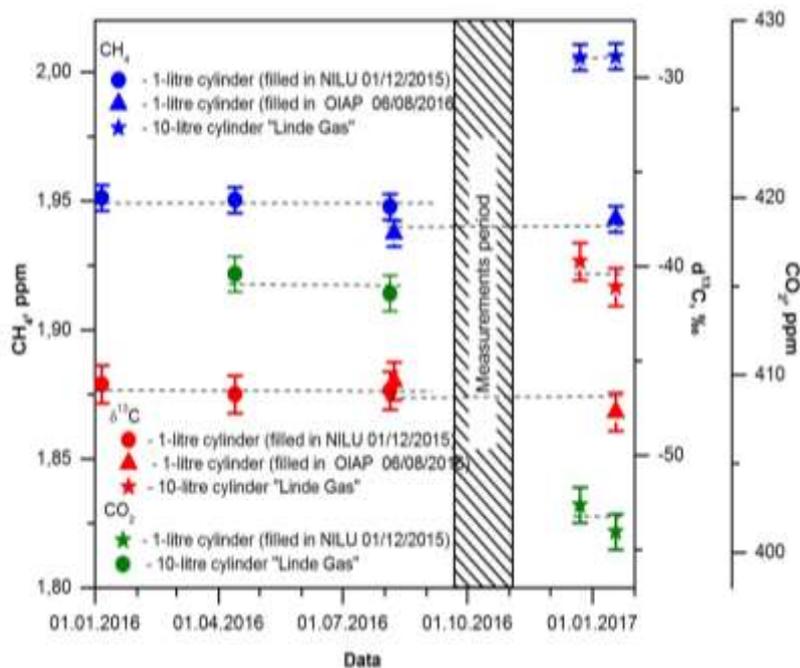


Figure 3. Calibrations of G2132-i

Table 6. Results of LI-7700 calibration

#	Averaging, sec	CH ₄ , ppm	σ_{CH_4} , ppm	Calibration coefficient $C_0 = 2.0471$ ppm
1	10	2.0998	0.0007	0.9749
2	1	2.0998	0.0009	0.9749
3	0.1	2.0998	0.0017	0.9749

Due to the previous measurements of calibration gas by the G2132-i (that was calibrated by the secondary NILU standard (see above) the calibration coefficient for the LI-7700 was found to be equal 0.9749.

All measured concentration values of gas components obtained during the ship campaign were corrected according to calibration coefficient. Further, we calculated data sets with 1 second, 10 seconds, 1 minute and 10 minutes averaging. Time series of CH₄ mixing ratio and $\delta^{13}\text{C}_{\text{CH}_4}$ (10 min averaging) and the geographical objects of the ship course are shown in Figures 4.

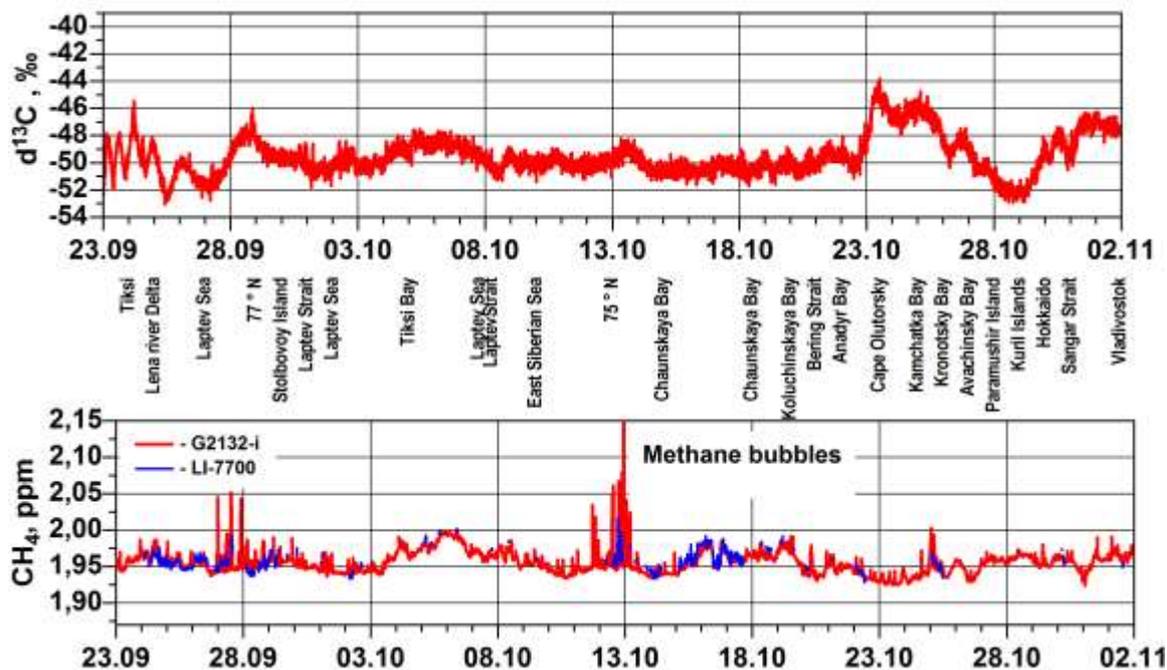


Figure 4. G2132-i time series of $\delta^{13}\text{C}_{\text{CH}_4}$ (upper plot) and G2132-i and LI-7700 time series of CH_4 (bottom plot) in ambient air during the ship campaign of 2016.

As will be shown further, the obtained calibration coefficient for LI-7700 analyzer makes very similar data of open path analyzer and data of G2132-i. The resulting variance is less than the accuracy of analyzer. That fact proves the correctness of the LI-7700 calibration.

3. Discussion

Analysis of LI-7700 data sets shows the strong sensitivity to the pollution and icing of mirrors forming on its open optical path. The analyzer software automatically calculates the RSSI (received signal strength indicator) parameter. When RSSI is less than 10% the analyzer readings are considered as unreliable.

Practically, during decreasing of RSSI to 35...40% and less, the difference between LI-7700 and G2132-i readings increases more than several percents. When the RSSI is more than 50% there are a complete coincidence of all analyzers. However, due to contamination and icing of the LI-7700's mirrors, only less than 20% of obtained data during the ship campaign are reliable. These remains of LI-7700 data are shown at Figure 4. The instrument's build-in mirrors icing protection facilities (washing and heating) were not used during the cruise.

Due to the same reason, the LI-7500 data on CO_2 and H_2O concentrations were rejected for analysis, and not shown in this study. Figure 2 clearly shows the icing of the exterior surfaces of the analyzers during the cruise.

Figure 5 shows time series of CO_2 and water vapor values obtained by G2132-i during the route. The main feature of almost constant background CO_2 value during all the route with some peaks, caused possibly by local air contamination. The more detailed analysis of CO_2 and water vapor behavior will be made in following publications.

It is actual to compare available data sets in methane seeps locations (75°N , 160°E). The vessel was located in that place from 11 to 13 October 2016. According to the LI-7700 readings, the methane concentration above the water surface is characterized by a large number of CH_4 peaks with value from 2-3 ppm to more than 8 ppm. The duration of this peaks is tens of seconds. Raising of methane bubbles from the water was visually detected from the board of the vessel. According to sonar data

from the vessel, methane bubbles came directly from the sea bottom, as the depth in the observation area reached 45-50 meters. In the same time the peaks of CH_4 concentration obtained by G2132-i were lower (up to 3.7 ppm) and longer in time due to slower responding time of the G2132-i instrument. It should be noted that the observed peaks of CH_4 concentration have stochastic character and strongly depend on the response time of the analyzers and observation conditions.

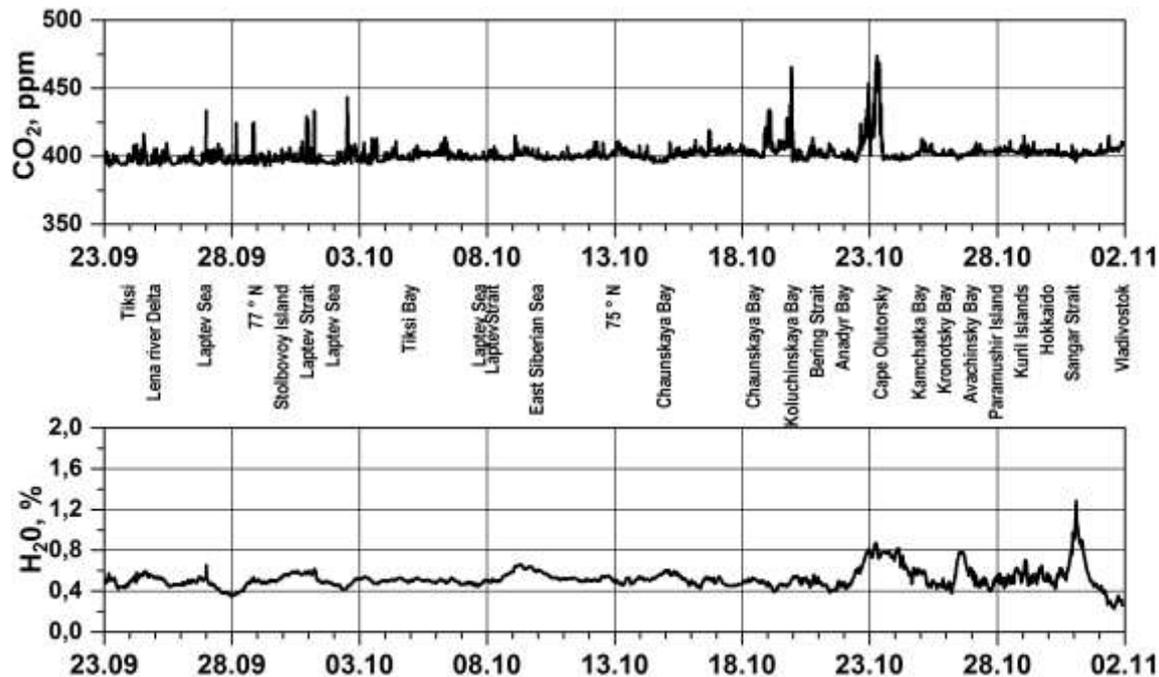


Figure 5. G2132-i time series of CO_2 (upper plot) and water vapor (bottom plot).

It is necessary to pay special attention to the fact that we obtain practically complete coincidence of the peaks of methane concentration using two essentially different types of gas analyzers: contact and open path. This means that the dithering of the signal is almost excluded in spite of pumping atmospheric air through the gas path, at least on the time intervals of about 10 seconds.

In our case, the time delay between the concentration peaks recorded by two analyzers is a result of the passage of air through the tubing from the air inlet to the G2132-i (it takes about 46 seconds) and the possible difference in the system clock of the instruments and their recording computers. This delay was calculated from the location of the peaks on the time axis (approximately 190 seconds), further the data sets were recalculated to bring them to a single time scale.

The G2132-i instrument with a response time of almost 1 minute, actually integrates each peak, underestimating its amplitude and increasing the duration. This phenomenon is clearly illustrated in Figure 6 (a), which presents the case of the release of a methane bubble from the water near the vessel.

Nevertheless, the G2132-i data can be used to determine the average methane concentration above the water surface. This is illustrated in Figure 6 (b), which presents the same fragment of observation data as in Figure 6 (a), but with averaging of 10 minutes. It is clearly visible that the data for all analyzers practically coincide, within their accuracy. The coincidence of the data also proves the correctness of the calibrations performed.

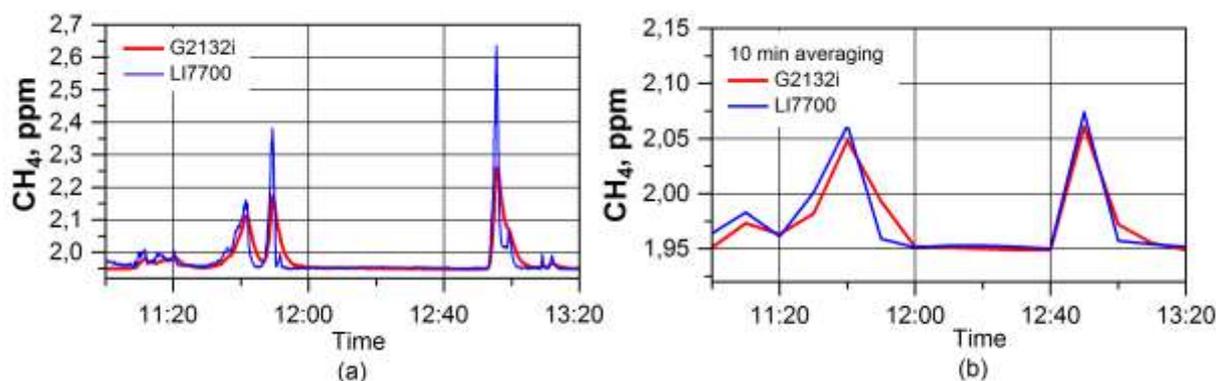


Figure 6. Examples of comparison of G2132-i and LI-7700.

4. Conclusions

The study allow us to make conclusions about the levels of methane concentrations in the surface air East Arctic seas. On the one hand, despite the very high peak of CH_4 concentrations near with the bubbles yield, enhancements of average methane concentration above the water surface in the seeps location is not significant. Average daily CH_4 concentration for 12th October exceeds average level of CH_4 beyond the seeps location (October, 10 and 14) only by a few percents. It is comparable with the regional variations of CH_4 content (for example, on October, 9 near the Kolyma Bay of the East Siberian Sea).

On the other hand, the a significant amount of methane yields from the sea bed in the Arctic seas observed during several expeditions [2, 4, 13, 14] is a reason to assume that that may have played a significant role in the enhanced atmospheric CH_4 level in the Arctic region where mean CH_4 concentration exceeds mean global level on 0.1 ppm.

The values of $\delta^{13}\text{C}_{\text{CH}_4}$ range from -57 ‰ to -44 ‰, that indicates the multiplicity of methane sources in the Arctic. The maximum of $\delta^{13}\text{C}_{\text{CH}_4}$ is from -46 ‰ to -44 ‰ presumably corresponding to thermogenic methane. It occurs during the passing of the Kuril - Kamchatka Trench (see Fig.4 a).

The main results of the study are as follows.

1. Both methane analyzers G2132-i and LI-7700 used in the ship campaign are effective instruments for recording variations in the concentration of methane. Analyzers have extremely low short-period drift and high long-period stability of the calibration coefficients within the limits of their own accuracy. Used analyzers, both contact and with an open optical path, provide a reliable record of both short-term peaks of methane concentration generated by the methane release to the surface from the bottom hydrates and the mean CH_4 values of the surface air concentration. We obtained a good agreement between the data sets of two types analyzers.

2. It is necessary to use specific protection for open path analyzers during the observation from the ship to minimize data losses, especially for Arctic condition when the icing of mirror is frequent.

3. The measurements indicate possibility of formation of high methane peaks in atmospheric surface air over the East Siberian Arctic Shelf above the locations of methane release from the seabed.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgements

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