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Dissolved methane in Lake Baikal: a modified technique for determining concentrations and vertical distribution in the water column

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ABSTRACT. We have developed a modified method of headspace analysis of water samples with the control of temperature and total pressure in the gaseous phase of a closed heterogeneous system followed by a gas chromatographic measurement of methane concentration with the methane content in the lake water of < 500 nl CH_4/L. Here, we describe the background concentrations and vertical distribution of dissolved methane in the water column of Lake Baikal, which were obtained for several years.

Keywords: methane dissolved in water, vertical distribution, Lake Baikal, modified method of static headspace analysis

1. Introduction

The formation of the gas composition in surface natural waters occurs during the interaction of water bodies with the atmosphere, biochemical processes in the water column and bottom sediments as well as during metamorphization of rocks and degassing of mantle substances (Alekin, 1970). Under global warming and change in the concentrations of greenhouse gases in the atmosphere, the study of the composition and distribution of carbon dioxide and methane in the World Ocean and inland waters is of an undoubted scientific and practical interest.

East Siberian Branch of the Imperial Russian Geographical Society initiated the investigations of gases at Lake Baikal (Lomonosov and Chekanovsky, 1869; 1897). In the 1930s, significant attention was paid to oil and gas seepages at Lake Baikal (Ryabukhin, 1933; Vereshchagin, 1933). V.P. Isaev (2001) studied methane seepages in the Selenga shallow area. N.G. Granin and L.Z. Granina (2002) made a review of the available materials on the investigations of gas seepages in Baikal.

To determine the dissolved methane content in seawater and pore waters of sediments, oceanographers practise static headspace analysis (Bolshakov and Egorov, 1987; Vereshchagina et al., 2013) and vacuum extraction of gas (Obzhirov, 1993) followed by measurement of methane in gaseous phase with gas chromatography-flame ionization detector (GC-FID). These techniques, which differ in the method for extracting the volatile component from the condensed phase, were used at Lake Baikal during the collaboration of Limnological Institute (LIN SB RAS) with oceanographers (Egorov et al., 2005; Granin et al., 2005; Schmid et al., 2007; Granin et al., 2013).

The first data on methane concentrations in the water and bottom sediments of Southern Baikal, estuarine areas of rivers and river-lake mixing zones were obtained in 1988 and 1994 (Fedorov et al., 1997)

The discoveries of methane hydrates (Golmshtok et al., 1997; Duchkov, 2003), mud volcanoes on the Baikal floor (Van Rensbergen et al., 2002) and hydrates in the surface sediments (Klerkx et al., 2003) initiated a systematic research of methane seepages from bottom sediments and methane distribution in the water column of the lake. In 2003, A.V. Egorov and coauthors (2005) studied methane in the samples from several stations of Southern Baikal.

In 2002-2004, researchers from the LIN SB RAS Laboratory of Hydrology and Hydrophysics together with researchers from Pacific Oceanological Institute Far Eastern Branch Russian Academy of Science (POI) investigated the methane content in the waters of all three basins of the lake. Background concentration of methane dissolved in water was determined by vacuum extraction of gas (Obzhirov, 1993) followed by the GC-FID measurement (Granin et al., 2005; Schmid

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et al., 2007; Granin et al., 2013). In 2013-2019, the investigations were continued.

The vacuum extraction of methane used in gas geochemistry studies to extract trace amount of dissolved gases from natural water and pore waters of bottom sediments, with all its advantages, requires special equipment and the extraction completeness control, which, according to (Bolshakov and Egorov, 1987), additionally complicates the operational processing of a large number of samples in expeditionary conditions. This led to the necessary use of a more efficient static headspace technique for gasometric studies (Bolshakov and Egorov, 1987; A technical guide …, 2000; Kolb and Ettre, 2006; Boeva et al., 2012).

The standardized technique of (Boeva et al., 2012) yields good results at a concentration of methane dissolved in water of ≥ 500 nL CH_4 /L.

Our methodological work has revealed that at the background concentrations of 10-250 nL CH_4/L typical of the open Baikal waters, the conventional headspace analysis with helium (Vereshchagina et al., 2013) and air (Bolshakov and Egorov, 1987) yields underestimated results. Moreover, the calculated methane concentration decreases with an increase in the initial sample volume at a constant volume of the gas bubble. The stepwise calculation has indicated that the transition process from the initial state of a closed heterogeneous system (neutral individual dry gas – an aqueous solution with a mixture of atmospheric gases) to the dynamic equilibrium state is accompanied by the change in the total pressure in the gaseous phase. This inevitably affects the partial pressure of methane in both phases with the established equilibrium. Ignoring this fact leads to significant errors.

This study aims to develop modified static headspace analysis for detecting nanoconcentrations of dissolved methane with subsequent identification of the features in its content and vertical distribution in the water column of Lake Baikal.

2. Methods, equipment and calculations

The method is briefly described in (Mizandrontsev et al., 2020). Here, we describe the procedure of the proposed modification of headspace analysis, its theoretical justification, sample preparation, preparation of calibration gas mixtures and aqueous solutions with methane as well as methodological experiments.

The water from the lake was sampled using Niskin bathometers, and its temperature was simultaneously measured using a CTD probe (temperature can be also measured in a separate portion of water from the bathometer). A water sample was transferred through a hose attached to the bathometer with a twofold pouring to the 120 mL bottle. The bottle was closed with a rubber stopper (for penicillin bottles) with a syringe needle in the centre; then the needle was removed. The bottle was turned upside down to check for the absence of a gas bubble.

The stopper was fixed with the 20 mm aluminium cap having a round hole for syringes. This procedure is mandatory because in a closed system, the pressure changes during establishing the equilibrium state. The cap was crimped by collets (crimper hand sealing machine). Then, a needle of the empty syringe was inserted through the stopper for 5 mL (with a piston at zero value). Another needle was introduced, which was connected with a plastic bag filled with pure nitrogen (99.99% N_2 without CH_4) at atmospheric pressure. Using the syringe, 3 ml of water were slowly taken (to avoid the release of dissolved gases). They were synchronously replaced by 3 mL of pure nitrogen from the bag; then, the needles were removed from the stopper. Experiments with the 3 to 24 mL gas bubbles indicated that considering the measured pressure in the closed system, the results of the analysis are independent of the bubble volume and its radius.

K.M. Kucher, a researcher from the LIN SB RAS Laboratory of Hydrology and Hydrophysics, has developed a device that measures pressure in the gaseous phase of a closed system. The bottled samples prepared in this way were shaken on a shaker for one hour (four hours in methodological experiments with air without methane as the gaseous phase) until equilibrium in the heterogeneous system was established. Then, the final total pressure in the gaseous phase was measured. Using a syringe, 500 μg of the gaseous mixture were taken from the gaseous phase. In this mixture, molar (volume) fraction of methane was determined on an EKHO-PID GC-FID. The final temperature of the water in the bottle was measured immediately after sampling the gaseous phase for analysis.

In gas chromatographic measurements, the retention time of methane is 7.8-12 s. The isotherm is a fragment of a parabola with a slight deviation from linearity; the value of the signal/noise ratio varies from 6.5 at 11 nL CH_4/L to 200 at 465 nl CH_4/L; the relative error in determining methane concentration is ± 5%.

The chromatograph was calibrated according to the standards of LLC PGS-Service (Zarechny): Zero air (air + 4 ppm CH_4) and Nitrogen (N_2 + 8.6 ppm CH_4), as well as according to the standard Analysed Gases Scotty II mix 212 (100 ppm CH_4 in nitrogen) from Alltech Associates Inc. An additional test was carried out by determining the methane concentration at the equilibrium of distilled water with the atmosphere having constant atmospheric pressure and temperature, as well as by a saturated NaCl aqueous solution.

Methane concentration in water reduced to normal conditions, C_0 [nL CH_4/L H_2O], was calculated according to the formula based on the law of conservation of the methane mass in a closed system, Mendeleev-Clapeyron equation of state of a gas mixture, Bunsen solubility coefficients for methane, Henry's and Dalton's laws:

$$C_0 = \left(\frac{P_{en}}{101.325} - p_{en}\right) N_{en} \times 1000 \left(\alpha + \frac{273.15}{273.15 + t_{en}} \times \frac{V_g}{V_s - V_g}\right) - \\ -N_{in} \times 1000 \left(\frac{P_{in}}{101.325} - p_{in}\right) \times \frac{273.15}{273.15 + t_{in}} \times \frac{V_g}{V_s - V_g}, \quad (1)$$

where P is the measured total pressure in the system, [kPa]; p – the vapour pressure in the atmosphere units; α – the value of Bunsen absorption coefficient [L CH_4 /L H_2O] for methane at a temperature T [ºK]; t – the temperature,[ºC]; V_s – the initial volume of the water in a bottle before the formation of the gas bubble, [L]; V_g – the volume of the gaseous phase, [L]; 273.15 is the normal temperature T_0, [ºK]; and 101.325 is the normal pressure P_0, [kPa]. Subscripts *in* and *en* correspond to initial and final state of the system; N_{en} is the volume (molar) fraction of methane measured on a chromatograph at the established phase equilibrium, [ppm_v]; N_{in} is the molar fraction of methane at the initial time, [ppm_v]. $N_{in} = 0$ when high purity nitrogen (helium, methane free air) is used to form the gas bubble in the bottle with the studied water. Because water expansion is small a narrow temperature range, the V_w and V_g are assumed to be constants.

The partial pressure of methane was calculated according to the following equation:

$$p_{gT} = N_{CH_4}\left(P_{mes} - \frac{h}{100}\cdot p_{wp}\right), \tag{2}$$

where N_{CH_4} is the molar (volume) fraction of methane in the gaseous phase determined using gas chromatography; P_{mes} – the total pressure in the gaseous phase measured by the device minus the vapour pressure p_{wp}; and h – the humidity of the gaseous phase equal to 100% at the equilibrium.

The regression equations for the temperature dependence of the Bunsen coefficient for methane (Handbook of chemistry, 1964) and vapour pressure in the closed system, respectively, are as follows:

$$\alpha = 0.237329X^4 - 0.457531X^3 + 0.373582X^2 - \\ - 0.170859X + 0.055612 \tag{3}$$

$$p_{wp} = 0.597544X^4 + 0.140527X^3 + 0.157524X^2 + \\ + 0.043273X + 0.005999 \tag{4}$$

where $X = (T - T_0)/100$.

According to Wiessenburg and Guinasso, 1979, α values in the range of 273.15 ÷ 303.15 ºK:

$$\alpha = 0.548059X^4 - 0.681712X^3 + 0.427184X^2 - \\ - 0.176244X + 0.057378 \tag{3a}$$

differ from those of (3) by $+3.2\%$.

In case of using pure nitrogen or methane free air to form the initial gaseous phase in a closed system, the initial value of the partial pressure of methane is zero, and in the application of standards, it is calculated considering the gaseous mixture ratings in the cylinder.

Preparation of gaseous standard solutions. An empty 34 ml calibrated bottle was closed with a rubber stopper, and a syringe needle was inserted there. Through another needle, the bottle was filled with pure nitrogen (methane free) from the cylinder. Then, both needles were removed. A standard of 8.37 ppm CH_4, which is necessary to form the gaseous mixture with a given methane concentration, was inserted into the bottle with a syringe.

Several bottles were prepared containing gaseous solutions with methane concentrations ranging from 0.2 to 4.0 ppm:

amount of standard (mL)	31.1	18.9	14.5	19.7	7.4	4.6	2.2	1.7	1.3	0.8
resulting concentration (ppm)	4.0	3.0	2.5	2.0	1.5	1.0	0.5	0.4	0.3	0.2

Preparation of aqueous solutions with given methane concentrations. An aqueous solution with a methane concentration of 188.94 nL/L calculated according to (1) was prepared from the gaseous standard of 25 ppm. To do this, 1 mL standard was added with a syringe to the closed 120 mL bottle with distilled water, and 3 mL were replaced by high purity nitrogen. The initial temperature and total pressure in the closed system were measured. The bottle was shaken on a shaker for one hour to establish the equilibrium state in the gas-aqueous solution system. Before determining methane concentration in the gaseous phase, the pressure in the bottle was measured through chromatography, and then, the temperature in the bottle was measured.

The data on parallel measurements in 15 bottles enabled to calculate methane concentrations in the prepared aqueous solution. At a theoretical value of 188.94 nL/L, the measured concentration was 188.94 nL/L.

Similarly, two aqueous solutions with the calculated concentrations of 529.91 and 530.49 nL/L were prepared from the gaseous standard with a methane concentration of 70.81 ppm. In one of them, the average value from 15 measurements was 529.77 nL/L with a span of 3.65 nL/L, and in the other – 529.12 nL/L and 6.37 nL/L, respectively.

Choosing gas to form a gas bubble in a closed system. We carried out experiments to determine methane in water with the formation of a gas bubble from the air, methane free air, pure helium, and pure nitrogen. The static headspace measurements followed by gas chromatography of low methane concentrations in fresh water indicated that the use of pure nitrogen (99.99% N_2 without CH_4) or pure methane free air as a neutral gaseous phase yields stable results. At the same time, using nitrogen is more preferable, because the cost of the with pure nitrogen is much lower than the pure methane free air.

Pure helium as a neutral gas is inconvenient to form the initial gaseous phase due to its high volatility, which leads to the instability of the total pressure in the closed system. Atmospheric air as well as gaseous phase lead to significant error in measurements of methane concentrations at the equilibrium with atmosphere (at the Baikal level of ~100 nL CH_4 /L).

The device for measuring pressure in the gaseous phase of a closed heterogeneous gas-aqueous solution system of the gas mixture consists of an electronic absolute pressure sensor, a microcontroller, an indicator, and accumulator. All components of the device are arranged in a sealed housing that protects the electronics from moisture. Transparent walls of the housing allow reading pressure values on the indicator. Measurement unit is millibar (mbar). The precision of the pressure sensor is ±2 mbar in the temperature range from 0 to 50°C. (In subsequent calculations, mbar are converted to atm).

The device is equipped with the Luer cone for the installation of standard medical needles that allow piercing the bottle's cap without loss of tightness. Internal volume of the pressure sensor and a needle is filled with liquid to minimize the error caused by the gas expansion into the measurement cavity. The integral battery allows the device to operate for two days; a standard mini USB connector is provided for charging.

The use of the device revealed the need for periodic replacement of needle due to clogging with pieces of rubber during piercing the caps. The clogging is easy to track when the pressure does not return to the atmospheric one between measurements.

Methodological experiments revealed that with control of the temperature and total pressure the change in the ratio of the volumes V_g and $V_w = V_s - V_g$ in the formula (1) does not affect the value of the determined methane concentration. The optimal V_w / V_g values are 10-40. The further decrease in the water volume to the volume of a gas bubble reduces the equilibrium volume concentration of methane in the gaseous phase to a level limited by ratings for chromatography.

Experimental assessment of the incomplete extraction of dissolved methane by vacuum method. According to the extraction theory, the transition of a component from one phase of a heterogeneous system to another is never complete. Therefore, during vacuum extraction, standard experimentally established conditions should be met, which guarantee a sufficiently complete extraction of the investigated gas. Our modification of headspace outgassing does not require this. From the moment the dynamic equilibrium is established, the total pressure in the gaseous phase of a closed system becomes constant under invariable temperature.

A comparison of the results obtained using this modification of headspace analysis and single vacuum extraction has shown that the headspace analysis/vacuum extraction ratio is 1.39 ± 0.045 at a confidence level of 0.95, with a relative error of the average value of ± 3.2%. With two- and threefold extraction, the conversion factor approaches one. Previously (2002-2004), the correction for the incomplete extraction was assumed as 1.375 (Granin et al., 2005; Schmid et al., 2007).

Correlation of the results obtained by static headspace analysis with and without pressure control. According to the methodological experiments with the gaseous phase of pure nitrogen, headspace outgassing without the temperature and pressure control in the closed system yields unstable results in determining the concentration of dissolved methane C^0. The $C^0(P)/C^0$ ratio, where $C^0(P)$ is the concentration subject to pressure, varies from 1.1 to 1.6 (Fig. 1). Therefore, the average value of the conversion factor of C^0 into $C^0(P)$ is 1.35 with a maximum error of ± 20%, and the standard error of the average value should not exceed 10%.

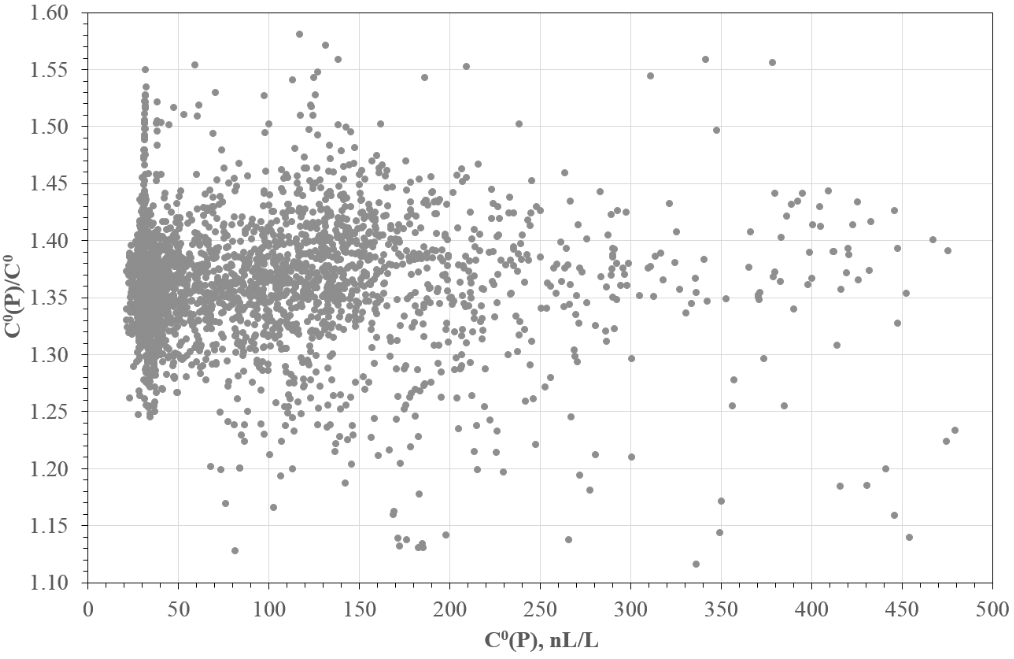

Fig. 1. Dependence of the ratio of the methane concentration determined with pressure $C^0(P)$ and without pressure control on the value C^0.

Experimental data on air being the gaseous phase indicated that in this case, the $C^0(P)/C^0$ value varied from 0.5 to 3. In case of other gases used to form the gaseous phase, the conversion requires special experimental work to determine the $C^0(P)/C^0$ ratio.

Justification. Modified headspace analysis to determine low concentrations of methane dissolved in natural water (from tens to first hundreds of nL CH_4/L) is based on the law of the conservation of its mass in a closed system consisting of the gaseous phase and an aqueous solution with a gas mixture as well as on gas laws.

For example, there is a bottle of the V_s volume filled with an aqueous solution with a mixture of atmospheric gases. Dry individual gas free of the determined *i*-th gas replaces some part of this volume equal to V_g. Then, the formed heterogeneous system closes.

In the initially non-equilibrium closed system, the transition process begins to establish the thermodynamic equilibrium for all present gases, including water vapour. The gaseous phase takes the temperature of the aqueous phase. The amount of evaporating water comprises a small fraction of its volume. At a high heat capacity and low thermal expansion of water over a limited temperature range, the change in its volume V_w, as well as the volume V_g in the gaseous phase, can be neglected.

Mendeleev-Clapeyron equation describes the state of a mixture of ideal gases:

$$PV = NRT\,, \tag{5}$$

where P is the total pressure of the mixture; V is the volume of the mixture; $N = \sum_{i=1}^{k} n_i^{(g)}$ is the total number of gas moles in the gaseous phase; $n_i^{(g)}$ – the number of moles of the *i*-th gas in the mixture; R – the universal gas constant; and T – the absolute temperature. According to Dalton's law, the pressure of the gas mixture is equal to the sum of their partial pressures, $P = \sum_{i=1}^{k} p_i$. Thus, for the *i*-th gas, the equation of state is as follows:

$$p_i V = n_i^{(g)} RT\,, \tag{6}$$

In a closed system consisting of the aqueous solution with a mixture of gases and the gaseous phase, the total number of moles for the *i*-th gas is constant, $n_i = n_i^{(g)} + n_i^{(w)} = const$, but the current values, $n_i^{(g)}$ and $n_i^{(w)}$, change during the transition process. The calculations indicate that during the transition process, the total pressure P in the gaseous phase of the closed heterogeneous system increases sequentially due to the gas exchange between the phases and evaporation of water. The establishment of the constant value of the total pressure in the gaseous phase terminates transition process. At the same time, the value of the partial pressure for each gas present in the system equalizes in both phases.

We solve the equation of state (6) relative to n_i and generate the expressions for the number of moles of the *i*-th gas in the aqueous solution and the gaseous phase. At the initial time, the total number of moles of the studied component in the heterogeneous system is $n_i = n_{ii}^{(g)} + n_{ii}^{(w)}$, where $n_{in}^{(g)} = \frac{p_{in\,T_{in}}^{(g)} \cdot V_g}{R \cdot T_{in}}$; $n_i^{(w)}$ is the initial number of moles in the aqueous phase, whose volume is equal to the volume of the system V_s minus the volume of the introduced gas bubble V_g; and $p_{inT_{in}}^{(g)}$ is the initial partial pressure of the *i*-th gas in the gaseous phase at the initial temperature T_{in}.

With the established equilibrium, the number of moles of a given gas in the gaseous phase and the aqueous solution is respectively as follows:

$$n_i^{(g)} = \frac{p_{iT_{en}}^{(g)} \cdot V_g}{R \cdot T_{en}} \text{ and } n_i^{(w)} = \frac{p_{iT_{en}}^{(g)} \cdot \alpha_{iT_{en}} \cdot V_w}{R \cdot T_0},$$

whereaccordingto(2) $p_{iT_{en}}^{(g)} = N_{CH_4}\left(P_{mes} - h/100 \cdot p_{wp}\right)$ is its equilibrium partial pressure at the absolute temperature of measurement T_{en}; V_g – the volume of the gaseous phase, V_w – the volume of the aqueous phase; $\alpha_{iT_{en}}$ – the Bunsen coefficient for the *i*-th gas; and $T_0 = 273.15$ °K – the normal temperature.

From the law of conservation of mass for the *i*-th gas, $n_i^{(g)} + n_{ii}^{(w)} = n_{ie}^{(g)} + n_{ie}^{(w)}$, it follows that:

$$n_{in}^{(w)} = \frac{p_{iT_{en}}^{(g)} \cdot V_g}{R \cdot T_{en}} + \frac{p_{iT_{en}}^{(g)} \cdot \alpha_{iT_{en}} \cdot V_w}{R \cdot T_0} - \frac{p_{inT_{in}}^{(g)} \cdot V_g}{R \cdot T_{in}}\,, \tag{7}$$

At a zero initial concentration of the *i*-th gas in the gaseous phase (initially, this gas is absent in the gas bubble), the last summand in the equation vanishes. Otherwise (for example, during the calibration of chromatograph according to the standards), the value of this summand should be considered.

After reducing $n_i^{(w)}$ in moles to the dimension of the C_0 concentration in nmoles of CH_4 per one litre of water, we have $C_0 = n_i^{(w)} \frac{V_0}{V_w} 10^9$. The latter expression, considering (7) and the equation of state under normal conditions for one mole of gas, $V_0 p_0 = RT_0$, we reduce to the following expression:

$$C_0 = \frac{10^9 V_g}{V_w}\left[\left(\frac{p_{gT}}{p_0}\right) \cdot \alpha \frac{V_w}{V_g} + \left(\frac{p_{gT}}{p_0}\right) \cdot \frac{T_0}{T_{en}} - \left(\frac{p_{in\,gT}}{p_0}\right)\frac{T_0}{T_{in}}\right],$$

which considering (2), becomes (1) after the identical transformations.

3. Materials

In 2002-2004, during six cruises and winter expeditions on the ice, researchers from the LIN SB RAS Laboratory of Hydrology and Hydrophysics together with researchers from POI investigated 1280 water samples from all three Baikal basins for the background methane concentration (Granin et al., 2005; Schmid, et al., 2007; Granin et al., 2013). The bulk of the data was obtained from the water column of Southern Baikal. The background concentration of methane dissolved in water was determined by single vacuum extraction (Obzhirov, 1993) with the correction for the complete extraction of 1.375. Materials of the investigations were partially published in (Granin et al., 2005; Schmid et al., 2007; Granin et al., 2013).

In 2013-2019, the investigations were continued. Figure 2 shows the shceme of the stations where vertical water sampling was carried out. The methane concentration was determined by static headspace analysis with direct measurement of the total pressure in the closed gas-water system. The comparison of the methods has indicated that the ratio of the results of the headspace analysis/vacuum extraction having a confidence level of 0.95 is 1.39 ± 0.045 with a relative error of the average value of ± 3.2%. At the twofold extraction, the conversion factor of headspace analysis/ twofold extraction is from 0.99 to 1.11 with the average value of ~1.

4. Results and discussion

Procedure of static headspace analysis (Vitenberg and Ioffe, 1982; Vitenberg, 2003; Kolb and Ettre, 2006) used in oceanographic studies (Bolshakov and Egorov, 1987; Egorov, 2000; Vereshchagina et al., 2013) consists in single extraction of the investigated gas from the condensed phase into the gaseous phase followed by gas chromatographic determination of its concentration. In a closed system, which initially consists of an aqueous solution with atmospheric gases and neutral gaseous phase, phase equilibrium is established. Unlike the outgassing in a vacuum, this method does not require the mandatory assessment of the completeness in the extraction of the volatile component from the condensed phase into the gaseous phase.

The initial concentration of the investigated gas in the aqueous solution is calculated according to the basic formula for direct headspace analysis (Vitenberg and Ioffe, 1982):

$$C_w^0 = C_g\left(K + V_g/V_W\right), \tag{8}$$

where C_w^0 is the initial concentration of the determined gas in the condensed phase; C_g – its concentration in the gaseous phase; $K = C_w/C_g$ – the distribution coefficient of concentrations in phases; V_g and V_w – the volumes of the gaseous and aqueous phases, respectively. The formula (8) is valid at К = const, constant correlation of the volumes, compliance with isothermal conditions, and an invariable total pressure *P* in the system.

A theoretical analysis of the case when the total pressure *P* increases in the closed gas-liquid system under an isothermal regime with a decrease in the volume fraction of the gaseous phase was carried out in (Vitenberg and Marinichev, 1985). The change in *P* causes the associated changes in the equilibrium mass-volume concentration of the investigated volatile substance in the gaseous phase and the distribution coefficient *K*. Our direct measurements of the total pressure in the closed system have indicated that the change in the ratio of the volumes of the condensed and gaseous phases is accompanied by the change in the pressure at the established equilibrium (Fig. 3).

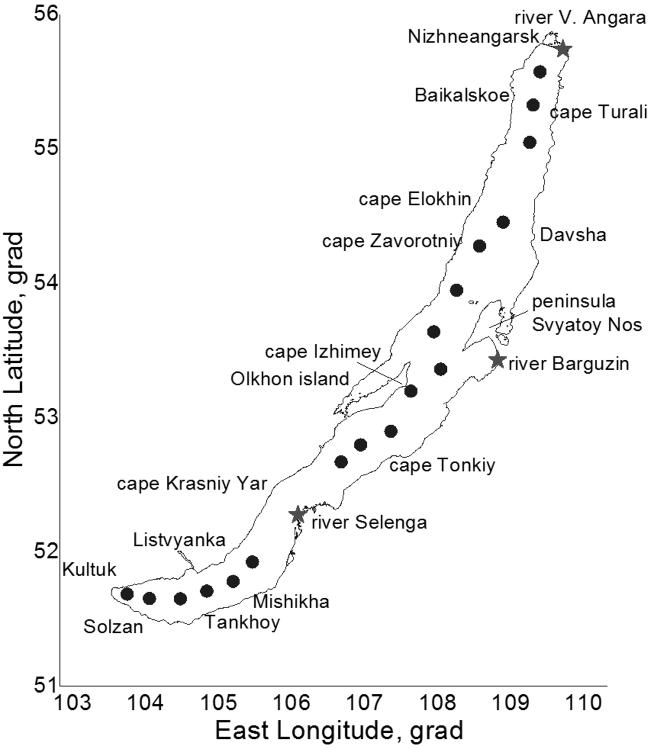

Fig. 2. The scheme of the water sampling stations for studying the background concentration and vertical distribution of methane in the water column of the lake (asterisks indicate large tributaries).

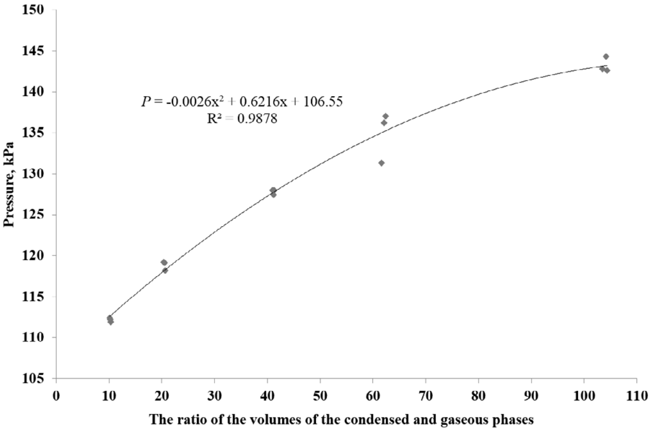

Fig.3. Dependence of the total pressure in the closed system of the gas and the aqueous solution with a gas mixture at the established phase equilibrium on the ratio of the volumes of the condensed and gaseous phases (according to Mizandrontsev et al., 2020).

Thus, the static headspace analysis with the gas chromatographic determination of low methane concentrations in natural water requires knowledge of the initial and final values the total pressure in a closed system as well as the initial and final temperature of the sample. These conditions are not provided in the methodologies by (Bolshakov and Egorov, 1987; Egorov, 2000; Vereshchagina et al., 2013), which leads to the errors in estimating the desired concentration of methane dissolved in water. Our methodological work revealed that measuring the concentration of methane dissolved in water through headspace analysis without control of the initial and final values of the pressure and temperature in the closed system yields significantly underestimated and unstable results in the range from 10 to 300 nL CH_4/L. Moreover, the law of conservation of mass is not met: at a constant volume of the gaseous phase, an increase in the volume of the water sample is accompanied by a decrease in the CH_4 concentration determined in this sample (Fig. 4).

The results obtained by headspace analysis using pure nitrogen or methane-free air to form the initial gas bubble with measurement of the initial and final temperature but without the control of the change in the total pressure in the gaseous phase of the closed system underestimated significantly the actual background concentration of dissolved oxygen in the water column of Lake Baikal (Fig. 4). The same measurements using gas bubble as the initial gaseous phase in the closed system without control of the total pressure showed a deviation towards a decrease in methane concentration by 30-70% at its content of 30-50 nl per one litre of water and by 20-40% at 100-150 nL CH_4/L).

Considering pressure and temperature during the establishment of the equilibrium in the closed system allow obtaining methane concentrations independent of the sample volume and the ratio of the gaseous and aqueous phases in the system. To demonstrate this, we analysed four series of water samples with different initial methane concentrations (Fig. 5).

Vertical methane distribution in open Baikal outside the zones of influence of tributaries, gase seeps and mud volcanoes shows the maximum value in the surface water (Fig. 6b, Fig. 6f) or the maximum concentrations in the subsurface layer of the water column with a subsequent decrease in the concentrations to the bottom in the main deep zone of the lake (Fig. 6a, Fig. 6b, Fig. 6c, Fig. 6e).

This distribution is similar to the type I methane distribution in oceans, which is observed at a low methane concentration (approximately 10^{-5} mL/L or less) that decreases from the near-surface layer to the bottom. Such distribution is the most widespread in the vast internal area of the ocean and is often found at its margins and in separate water areas of inland seas (Lamontagne et al., 1971; 1973; Geodekyan et al., 1979; Obzhirov et al., 2002).

In the main deep part of the water column of open Baikal, the concentration of dissolved methane are below equilibrium values with the atmosphere (~ 100 nL/L), which is due to the activity of aerobic methanotrophs (Hanson and Hanson, 1996; Galchenko, 2001). The *in situ* rate of methane oxidation in the lake was estimated in (Schmid et al., 2007; Granin et al., 2013).

In the near-bottom area, there is often a relatively slight increase in methane concentration under the influence of its flux from the bottom sediments (Fig. 6c, Fig. 6f). In some cases, this increase can be significant (Fig. 6d).

In the active layer of the lake (0-300 m), especially in its upper part, the concentrations of dissolved methane can significantly exceed their equilibrium value with the atmosphere. This is due to the methane paradox, i.e. methane generation in oxygen-saturated waters (Lamontagne et al., 1973; Oremland, 1979; Lilley et al., 1982; Schmidt and Conrad, 1993; Lein and Ivanov, 2005; Tang et al., 2014). In deep water of Lake Baikal, the formation of the near-surface methane maximum can be also associated with the decomposition of methane hydrates floating from the bottom (Granin et al., 2012). The causes and manifestations of methane paradox in Baikal will be discussed in the future article.

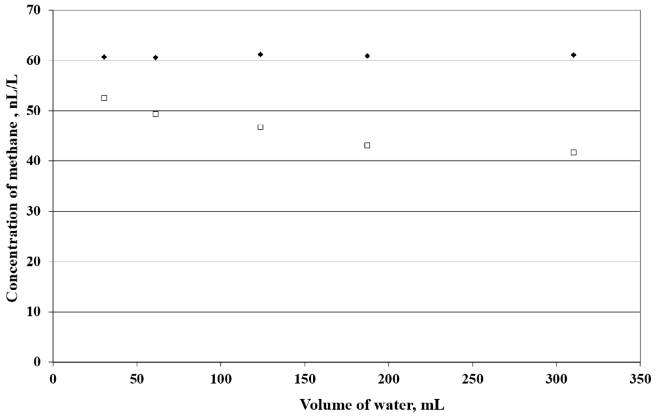

Fig. 4. Measured concentrations of dissolved methane with the control of the initial and final values of temperature and pressure in the closed system (black diamonds) and without pressure (squares). The volume of the gaseous phase (pure nitrogen) is 3 mL; the volume of water is variable (according to Mizandrontsev et al., 2020).

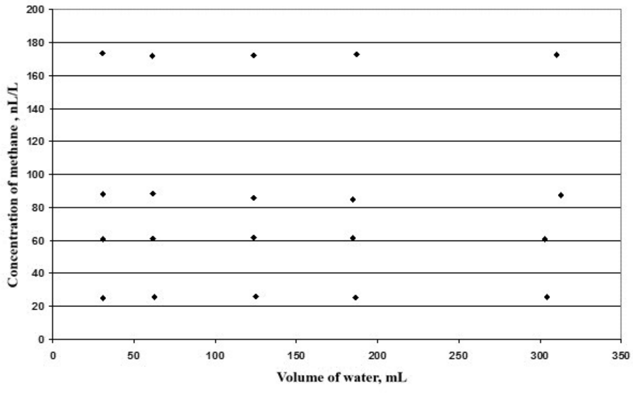

Fig.5. Measured methane concentrations in different volumes of water considering the initial and final values of pressure and temperature in the closed system (initial gaseous phase is 3 ml of pure nitrogen).

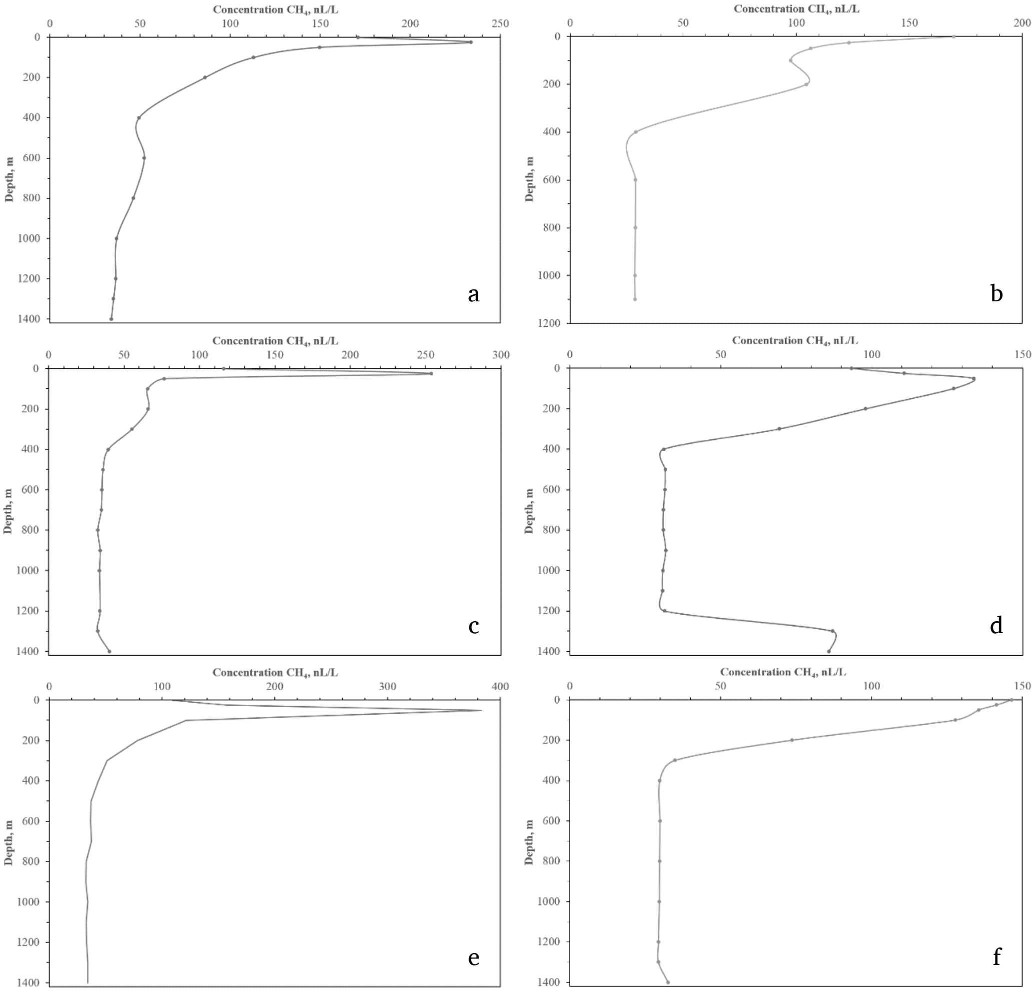

Fig.6. Examples of the vertical distribution of dissolved methane in the water column of different stations in Lake Baikal.

Increase in the concentrations of dissolved methane in the water column of the lake was observed in 2017-2019 in comparison with 2003 owing to its intensified discharge from the bottom sediments (Fig. 7). Methane concentration increased both in the deep zone of open Baikal (2-3 times higher on average) and its active layer (1.2-1.7 times higher).

The possible modern increase in methane concentration was discussed in (Granin et al., 2010; 2013). This phenomenon is likely due to the transition process initiated by the change in the water level of Lake Baikal after the launch of the Irkutsk Hydroelectric Power Station. As the water level rose, the boundary of the thermodynamic stability zone of methane hydrates in the stratum of the lake's bottom sediments shifted downwards. This led to the lowering the gas hydrates stability boundary. Due to this formation of gas hydrates have taken place at the lower boundary and the intensity of gas seepages decreased. At the end of the transition process, which lasted for a few tens of years pressure at the lower boundary of gas hydrate occurrence began to increase. It was accompanied by an increase in the intensity of gas seepages from the sediments and methane concentration in the water column.

Dissolved oxygen is transported into the water column of Lake Baikal through the weakened sediment areas associated with numerous faults during the discharge of the products from the decomposition of gas hydrates (Levi et al., 1999). In this case, the upward flow of water and methane forms a secondary accumulation of methane in the near-surface zone of bottom sediments (Granin et al., 2012).

The activation of the gas bubbles also contributes to an increase in methane concentration. The transition process should terminate when a new equilibrium is established in the gas-water-gas hydrates system at the modern water level of Lake Baikal. Perhaps, the same transition process and its consequences can be observed in the Caspian Sea as a result of an increase in its water level.

5. Conclusion

We have developed the modified headspace analysis with the pressure and temperature control in the closed system of water and aqueous solution with atmospheric gases, which enables to obtain stable methane concentrations in natural water, with methane content ranging from 10 to 500 nL/L. The results of the analysis are independent of the ratio of the volumes of aqueous and gaseous phases. This modification of headspace analysis can be used to determine low concentrations of volatile components in an aqueous solution (trace gases and pollution components).

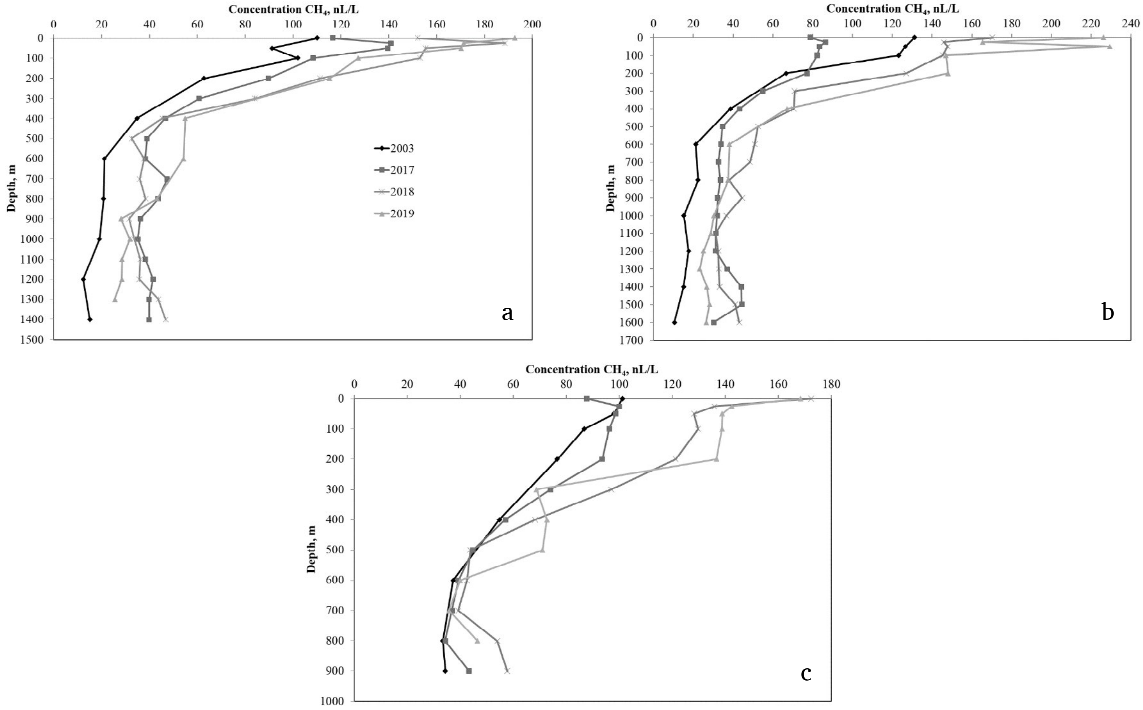

Fig.7. Increase of methane concentrations in the water column of open Baikal 2003-2019 (average for a – south, b – central, c- north, years on Fig. 7a).

Vertical distribution of dissolved methane in the water column of the lake is similar to that in oceans: methane concentration decreases from the top of the active layer to the lake floor. At depths from the surface layer to 150-200 m, there are the maximum methane concentrations. Sometimes, the maximum degenerates into its greatest value in the surface water.

Over the past decade, there was an increase in methane concentrations in the water column of open Baikal. This phenomenon is a consequence of the final stage of the transition process that was initiated by the rise in the water level of Baikal during the construction of the Irkutsk Hydroelectric Power Station.

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