Preliminary data on the methane emission from lake seeps of the Western Siberia permafrost zone

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Abstract. Lakes are one of the most important sources of the greenhouse gas methane. Usually, only diffusive emission is counted towards in estimates of the Arctic lakes contribution to the atmospheric methane budget. At the same time, for some regions, giving the importance for the ebullition of various genesis significantly increases previous assessments of ecosystem-based lake methane emission. This paper presents the results of a study of two gas seeps on the Central Yamal lake. The methane concentration in seep gas varies from 94.2 to 100%. Mean annual methane emission from each seep is estimated as 46.1 and 67.1 kgCH₄ per year respectively. According to the analysis of the methane isotopic composition, it is of biogenic origin. Studied gas seeps are obviously direct channels of methane emission from permafrost to the atmosphere.

1. Introduction

Climate changes are the topical problem for modern fundamental science so far, in particular in the fields of climatology, ecology, and mathematical modeling. One of the most potent greenhouse gases affecting climate change is methane. Natural sources contribute 35–50% to the global atmospheric methane emission, and among them, lakes are the third-biggest source emitting from 10 to 50 TgCH₄ year⁻¹ [1–3]. Lakes occupy 5% (17 thousand km²) of the Western Siberia tundra zone [4]. Those located in the northern territories of Western Siberia are still underinvestigated as a source of methane; currently, there are just a few studies on estimates of CH₄ emission from these lakes [4–6], and only the diffusion component has been studied. At the same time, data from [7] obtained for several regions of Alaska, shows that if we include the value of CH₄ emission from the lake gas seeps to the previous ecosystem-based lake methane emission estimates, the latter can be increased by 80–350%. Seeps in the lakes of the Western Siberia permafrost zone have not been studied yet as a source of methane. The above-enumerated facts let us suppose that the existing assessment of CH₄ emission from the lakes of Western Siberia northern territories can be significantly underestimated. The study relevance of this region is emphasized in [7]: the territory of Western Siberia, rich in natural gas, is covered with permafrost, which, according to [8], will significantly degrade by 2100. This can lead to a more rapid release of stored CH₄ into the atmosphere with possible influence on feedbacks between the carbon cycle and climate warming.
The purpose of our research was to study lake gas seeps in Western Siberia as a source of greenhouse gas methane. Two main objectives were set:

- assessment of the methane emission into the atmosphere from lake seeps;
- identification of the seep methane origin.

2. Study area
The research area is located in the Central part of the Yamal Peninsula (Western Siberia, Russia) in a typical tundra zone. The climate of this territory is moderate continental with the mean annual temperature of the surface air from $-8$ to $-6^\circ$C. The mean January and June air temperatures are $-24^\circ$C and 6–8°C respectively. The average duration of the annual period with positive mean daily temperatures is 110–120 days. The annual precipitation is 300–400 mm year$^{-1}$ [9,10].

More than 350 water bodies with an area greater than 1000 m$^2$ are located within the study area near the “Vaskiny Dachi” research station, resulting in approximately 12% limnicity [11]. The area is underlain by permafrost with a thickness varying between 150 and 500 m depending on the geomorphology [12]. Gas shows from boreholes and gas-emission craters have been documented in the Central Yamal [13,14]. These processes are linked to significant gas storages in the form of free gas or self-preserved gas hydrates at depths 50–120 m [15].

3. Object and methods
Studied gas seeps were found within the lake LK-008 (70.2754°N, 68.8112°E) at distance around two meters between them. This lake is located in the vicinity of the “Vaskiny Dachi” research station and was previously studied in the framework of the permafrost monitoring program of the Earth Cryosphere Institute TymSC SB RAS [16]. Lake basin intersects the third lacustrine-alluvial plain. The area, mean and maximum depths of this lake are 41.9 ha, 5.5 and 20.7 m respectively. The lake has a relatively flat bottom surface with the exception of two deep depressions close to the southern shore (Figure 1,2). The area of these depression does not exceed 11–12% of the total lake area [17].

Field sampling and measurements were carried out on August 19, 2019. Gas samples from seeps were collected using a bubble trap of the original design (Figure 3). The ebullition intensity was determined in tenfold replicate with the exposure time of 40–60 seconds. Gas samples were taken by a
plastic syringe and immediately placed into the capped 15 ml glass vials filled completely with saturated sodium chloride solution. The volume of released gas was determined with a 50 ml “Black Diamond” plastic syringe.

Figure 3. Seepage gas sampling.

Methane concentrations in the seepage gas samples with tenfold air dilution were determined by gas chromatograph Crystal 5000.2 (ZAO Chromatec, Russia) with a flame ionization detector (FID) in three and five replicates. The sampler volume of chromatograph is 0.250 ml. The length and the diameter of the chromatographic column are 3 m and 2 mm respectively. Hayesep-N 800/100 was used as a column packing. The carrier gas was the nitrogen of 99.999% purity with the delivery rate of 30 ml min\(^{-1}\). Temperature regimes of the analysis both for column and FID were constant with 60ºC and 150ºC; hydrogen and air are supplied to the FID by a flow of 20 ml min\(^{-1}\) and 400 ml min\(^{-1}\) respectively. Standard with 10.15±0.04% of methane (OAO Monitoring, Saint Petersburg) was used for calibration.

Analysis of the \(\delta^{13}C\) and \(\delta^D\) isotope content in methane was conducted by isotope mass spectrometer Delta V Plus with GC Isolink modules and elemental analyzer Flash HT plus (Thermo Fisher Scientific, USA) in three replications. Samples were injected with a gas-tight syringe in a volume of 25–50 µl. The sample was oxidized to carbon dioxide and water in a redox reactor, water was reduced to hydrogen in a pyrolytic reactor, the substances were separated in a gas chromatograph, and the mass spectra of individual substances were recorded in a mass spectrometer. Roof-mean-square deviations over a series of consecutive measurements of \(\delta^{13}C\) and \(\delta^D\) content were \(<0.18‰\) and \(<2.15‰\) respectively. IVA33802174 Urea Isotopic Working standard and VSMOW2 standard were used.

Statistical characteristics of the seep gas fluxes are calculated according to [18,19]. Mean concentrations of methane in the sampled gas were calculated with consideration for the dilution, calibration and chromatograph errors (hereinafter errors are calculated according to [20]). and the following values were obtained: 103.4±7.2% of CH\(_4\) for seep №1 and 102.0±7.8% of CH\(_4\) for seep №2. These error values are accounted for the impact of random and systematic uncertainties. Since due to the physics the substance concentration in the sample can be no more than 100%, to further evaluation we took the interval of methane concentration with the left boundary of 96.2% for seep №1 and 94.2% for seep №2 and 100% as a maximum for both seeps. Annual CH\(_4\) emission from seep to
the atmosphere was calculated separately for each seep as a multiplication of the CH$_4$ concentration, mean gas flux (intensity of seep ebullition) and the emission time. This preliminary assessment is based on the assumption that the gas emission was equable during the year. Since it was not possible to give point estimation of the CH$_4$ concentration in the sample, we calculated emissions for three cases: for the minimum and maximum concentrations, and estimated the mean value as well.

4. Results and discussion
Statistics on gas seepages are shown in Table 1. Methane concentrations and isotopic composition are given in Table 2. Annual methane emissions from studied seeps are shown in Table 3.

| Seep № | Number of samples | Seep gas flux, ml min$^{-1}$ |
|--------|------------------|-----------------------------|
|        |                  | I quartile | Median | III quartile | Mean with 95% CI |
| 1      | 10               | 160        | 175    | 203          | 182±19           |
| 2      | 10               | 122        | 127    | 137          | 127±7            |

| Seep № | Concentration, % | δ$^{13}$C vs VPDB, ‰ | δD vs VSMOW, ‰ |
|---------|------------------|----------------------|-----------------|
| Min     | Max              | Mean | STD | Mean | STD |
| 1       | 96.2             | 100   | −75.73 | 0.25 | −226.68 | 3.46 |
| 2       | 94.2             | 100   | −76.97 | 0.11 | −222.31 | 0.83 |

| Seep № | Annual emission values with 95% CI, kgCH$_4$ yr$^{-1}$ |
|---------|--------------------------------------------------------|
|         | Min | Mean | Max |
| 1       | 65.8±2.6 | 67.1±3.8 | 68.5±7.1 |
| 2       | 44.8±2.5 | 46.1±1.9 | 47.5±2.7 |

Table 1. Statistical characteristics of gas emission from seeps at lake LK-008.

Table 2. Methane content in gas seeps and its isotopic composition.

Table 3. Estimation of annual methane emissions.

Isotopic composition corresponds to the biogenic origin of methane (according to the classification given in [21]). The initial methane source can be in the form of a meta-stable methane-hydrate or free gas which is widely described for Central Yamal [15]. Presumably, gas migrates through sub-lake talik and further through the water column into the atmosphere.

Walter Anthony et al. [7] do not show precise concentration values of methane in gas seepages and describe it as the concentration reaches 99.5% by volume. Skorobogatov et al. [13] measured methane concentrations of 87–99% for gas samples from methane-hydrates without explicit air contamination. These results correspond to our calculations with a concentration range of 94.2–100%. Considerably fewer concentrations (69.6% on average) are measured in gas samples taken within 0–5 m of seawater column in the Laptev Sea [22].

The total amount of subcap gas seeps found in Alaska, supposedly similar to those we have studied, is more than 150000 with an annual emission of 0.25±0.03 TgCH$_4$ [7]. Average methane emission from one gas seep can, therefore, be assessed as ~1.7×10$^3$ kgCH$_4$ yr$^{-1}$ which is ~25 and ~37 times higher than estimated in this study. In [22], averaged data on methane emission from the sea bottom to the water column are estimated for three seepage classes: small, medium and large flare. Calculated mean annual methane emissions for these three groups are 0.9×10$^3$, 721×10$^3$ and 2703×10$^3$ kgCH$_4$ yr$^{-1}$ respectively. However, according to [22], it is not possible to calculate methane emission from the sea surface to the atmosphere.

5. Conclusion
Studied gas seeps are obviously direct channels of methane emission from permafrost to the atmosphere. The gas is of biogenic origin. The intensity of methane emission from gas seep №1 is
estimated as 65.8–68.5 kg yr\(^{-1}\) given the methane concentration 96.2–100%; from seep №2: 44.8–47.5 kg yr\(^{-1}\) given the methane concentration 94.2–100%.

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