Short-lived climate forcers in the Russian Arctic atmosphere according to ship-borne measurements in 2015-2019

N Pankratova\textsuperscript{1}, I Belikov\textsuperscript{1}, V Belousov\textsuperscript{1}, V Kopeikin\textsuperscript{1}, A Skorokhod\textsuperscript{1}, Yu Shtabkin\textsuperscript{1}, G Malafeev\textsuperscript{2}, V Muravya\textsuperscript{2}, M Flint\textsuperscript{2}

1. A.M. Obukhov Institute of Atmospheric Physics RAS, Moscow, 119017, Russia.
2. P. P. Shirshov Institute of Oceanology RAS, Moscow, 117997, Russia.

\textit{e-mail: pankratova@ifaran.ru}

\textbf{Abstract.} We observed the surface concentration and isotopic composition ($\delta^{13}\text{C}_\text{CH}_4$) of methane ($\text{CH}_4$), ozone ($\text{O}_3$), nitrogen oxide (NO/NO\textsubscript{2}) and carbon monoxide (CO), as well as black carbon (BC) content in the Russian Arctic seas aboard the research vessel. The effect of emissions from the vessel chimney on the data obtained is analyzed. We investigate the local areas of CH\textsubscript{4} emissions from seabed where the concentration of CH\textsubscript{4} can increase to 3.5 ppm. Notwithstanding that fact, mainly large-scale processes of air mass transfer determine the average concentration of methane in surface air in the Arctic seas. In addition, we analyze the distribution of BC along the route of the vessel. It was found that excess concentrations of BC over background values are observed occasionally during advection of air masses from the mainland, from areas of associated gas burning and forest fires.

\textbf{1. Introduction}

Methane ($\text{CH}_4$) is the second most important greenhouse gas after carbon dioxide, while its radiation forcing is up to 32 times higher than that of CO\textsubscript{2} [1]. Since pre-industrial times, the concentration of methane has increased by more than 150\% [2]. At the same time, over almost the entire 20th century, the methane content in the atmosphere increased, only in the period from 1998-2005, there was some stagnation, the reasons for which are still not clear. After a short break, the methane concentration began to increase again [2]. For example, the average global concentration of CH\textsubscript{4} in 2018 was 1858 ppb, and the growth rate in 2018 was 11.5 ppb (Ed Dlugokencky, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends_ch4/). An increase in atmospheric methane concentration by 7.5 ppb per year is equivalent to an increase in its emissions by $\sim$ 23-24 Tg CH\textsubscript{4} per year [3].

In addition, atmospheric pollution from anthropogenic emissions, including black carbon (BC), is increasing in the Arctic region. BC is the product of incomplete combustion of various types of fuel (especially coal and diesel fuel), biomass (forest, grass, agricultural waste) or biofuel. Potentially BC makes a significant contribution to climate change. It is considered as one of the potential sources of climate change in the Arctic [4]. According to model estimates, black carbon leads to a decrease in the albedo of the Arctic snow-ice cover, according to a number of estimates [for example, 5] this can cause an increase in heat supply due to solar radiation in the amount of about 0.3 W m\textsuperscript{-2}, which will inevitably lead to even higher temperatures in the Arctic.
A significant deficit of observational data on the concentrations of greenhouse gases and other small gas impurities in the Arctic region is noted. The available monitoring stations are not enough to restore the full field of key impurity concentrations. Satellite observations in the Arctic latitudes have a significant error and require special correction. Largely, it is possible to compensate for the lack of observations using measurements from the research vessels. Ship observational data is also relevant for the validation of numerical models and satellite measurements.

2. Measurements and methods

For measurements, we used an automated complex based on the analyzer G2132-i manufactured by Picarro Inc. (USA). This complex is intended for measuring methane concentration in the range from 1.8 to 12 ppm with precision <0.005 ppm, and the value of $\delta^{13}$C$_{CH_4}$ - with precision <1 ‰. A detailed description of the calibrations and installation of instruments on scientific vessels is presented in [6, 7].

![Figure 1](image_url)

**Figure 1.** a) Route of the R/V "Akademik Mstislav Keldysh" from August 25 to October 10, 2015; b) route of the R/V "Akademik M. A. Lavrentyev" from September 24 to November 2, 2016; c) Route of the R/V "Akademik Mstislav Keldysh" from August 16 to September 19, 2018; d) route of the R/V "Akademik Mstislav Keldysh" from July 2 to August 5 2019.

To analyze the effect of influence by the vessel chimney exhaust on the data obtained, the concentrations of CO$_2$ are commonly used [8]. In our studies, this approach was used for 2015, 2016 and 2019 expeditions data. During the 2018 expedition we provided synchronous measurements of CO (by Thermo TE48S analyzer), NO (by Thermo TE42C-TL analyzer) and O$_3$ (by Dasibi 1008-AH...
analyzer) surface concentrations. Our data analysis showed that it is more reliable to use CO and NO concentrations as a criterion for assessing the flow of polluted air from the vessel’s smokestack. When contaminated air enters to the analyzer’s air intake, we observe strong increase of CO, NO and NO$_2$, concentrations as well as sharp decrease of O$_3$ concentration, due to chemical reaction of ozone destruction. At the same time, the CO$_2$ concentration may not increase, and vice versa, with an increase in CO$_2$, contents of CO, NO, and NO$_2$ may stay low. To filter the contaminated data, the NO threshold of 0.2 ppb [9] was used. As a result of processing, 21% of the data was filtered out.

In this study we analyze the results of four cruise campaigns of measurements in the surface concentration and isotopic composition ($\delta^{13}$C$_{\text{CH}_4}$) of methane, CO$_2$ and H$_2$O: from August 25 to October 10, 2015 (the R/V "Akademik Mstislav Keldysh", P. P. Shirshov Institute of Oceanology RAS) – AMK-63; from September 24 to November 2, 2016 (the R/V "Akademik M. A. Lavrentyev", V.I. Ilyichev Pacific Oceanological Institute FEB RAS) – LVR-78; from August 16 to September 19, 2018 (the R/V "Akademik Mstislav Keldysh", P. P. Shirshov RAS Institute of Oceanology RAS) – AMK-72; from July 2 to August 5, 2019 (the R/V "Akademik Mstislav Keldysh", P. P. Shirshov Institute of Oceanology RAS) – AMK-76.

The expedition routes passed through the seas of the Russian Arctic. In 2015, from the port of Arkhangelsk through the White, Barents, Kara and Laptev Seas, including via the areas described in [10] (Fig. 2a). The 2016 expedition route ran from the Tiksi port through the Laptev and East Siberian Seas, and then through the Chukchi, Bering and Sea of Japan to the port of Vladivostok (Fig. 2b). In 2018 and 2019, the expeditions partially repeated the route of 2015, the ship left the port of Arkhangelsk and passed through the White, Barents and Kara Seas (Fig. 2 c and 2d).

All routes cover the entire territory of the Russian Arctic, but they took place at different times and under different meteorological conditions. During of expeditions of 2015, 2018 and 2019 coastal areas were free of snow. In 2016, measurements were taken in a later autumn period, when the advection of cold air occurred on the coast of the Arctic seas, and a stable snow cover began to form.

3. Discussion

Because the measurements were carried out at different times, the values of the concentration of methane and its isotope cannot be compared, however, the data set obtained in the expeditions allows us to determine some regularities of the spatial and temporal variability of methane concentration in the lower atmosphere. Figure 3 shows the series of observations of surface concentration and $\delta^{13}$C of methane, with an averaging of 1 minute. The statistical characteristics of the time series are presented in table 1.

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.

Increased values of methane concentration were observed in the Kara Sea, from September 2 to 5, 2015, and in the Laptev Sea, from September 12 to 14, 2015, when there was an active removal of air masses from the mainland, so, in all probability, the observed the increase in methane concentration was associated with emissions from the tundra regions of Western and Eastern Siberia. The prevalence of the microbiological source of methane is also confirmed by the results obtained using the Keeling method [11]. The value of $\delta^{13}$C$_{\text{CH}_4}$ was about -73‰.

During the 2016 expedition, the spatial distribution of methane content is more uniform (the standard deviation is about 0.02 ppm), while the concentration of CH$_4$ stably exceeds the global average value typical for the autumn period. At the same time, in the Laptev and East Siberian seas, localized areas with an increased concentration of methane in surface air were identified. Of greatest interest are the polygons described in [14]. One of these polygons was located approximately at 75° N and 160° E. The R/V passed this polygon from October 11 to October 13, 2016. Figure 3 shows the peak concentration of methane. In a more detailed analysis, the time series of methane is characterized
by a large number of peaks up to 2.0 ... 2.2 ppm or more. From the side of the vessel, the exit of methane bubbles from water was visually observed.

Table 1. Statistical characteristics of the measured values CH\textsubscript{4} and $\delta^{13}$C\textsubscript{CH4}

| Year      | Area                        | Arkhangelsk – Laptev Sea - Arkhangelsk | Laptev Sea | East Siberian Sea |
|-----------|-----------------------------|----------------------------------------|------------|------------------|
|           | $\delta^{13}$C\textsubscript{CH4} | $\text{CH}_4$ ppm | $\delta^{13}$C\textsubscript{CH4} | $\text{CH}_4$ ppm | $\delta^{13}$C\textsubscript{CH4} | $\text{CH}_4$ ppm |
| 2015      | Min                         | -50.7                   | 1.857      | -49.74           | 1.887 |
|           | Max                         | -45.3                   | 2.064      | -45.29           | 2.050 |
|           | Mean                        | -47.6                   | 1.918      | -47.55           | 1.928 |
|           | STD                         | 0.8                     | 0.039      | 0.81             | 0.033 |
| 2016      | Min                         | -57.12                  | 1.938      | -54.86           | 1.935 |
|           | Max                         | -44.10                  | 2.133      | -44.96           | 3.537 |
|           | Mean                        | -49.59                  | 1.962      | -50.12           | 1.958 |
|           | STD                         | 1.46                    | 0.015      | 1.2              | 0.024 |
| 2018      | Min                         | -59.9                   | 1.909      | -56.6            | 1.926 |
|           | Max                         | -44.1                   | 3.541      | -44.3            | 2.126 |
|           | Mean                        | -50.1                   | 1.964      | -50.2            | 1.953 |
|           | STD                         | 1.84                    | 0.076      | 2.08             | 0.024 |
| 2019      | Min                         | -56.6                   | 1.902      |                  |      |
|           | Max                         | -43.4                   | 2.294      |                  |      |
|           | Mean                        | -50.6                   | 1.942      |                  |      |
|           | STD                         | -50.6                   | 1.931      |                  |      |

According to the vessel sonar, methane bubbles came directly from the bottom, the depth in the observation area reached 45-50 meters. It should be noted that the values of the maxima of the observed peaks are largely stochastic in nature and strongly depend on the response time of the instrument used and the observation conditions. The duration of the peaks in time does not exceed tens of seconds. Thus, the peaks generated by release of methane bubbles to the surface almost did not imply its average concentration in the surface air in the investigated area.
At the same time, the high mosaicity of the areas of seeps and difficult observation conditions (strong wind, waves, inability to take air directly from the surface of the water) significantly complicate the studies and, apparently, can underestimate the real atmospheric response from seabed methane emissions.

In 2018, increased methane concentrations were noted when passing east in the Kara Sea in the region of the Gulf of Ob. The reduced salinity of surface water corresponds to the same region, which may indicate the influence of river runoff from the Ob and Yenisei. When crossing the same region in a westerly direction, no higher values of methane concentration were noted, while salinity in the Ob-Yenisei region became close to the typical values for the Kara Sea.

Localized areas with an increased methane concentration (up to 2083 ppb) in the surface layer, which, most likely, are caused by gas emission from the shelf zone of the Laptev Sea, were also identified. During the expedition, two regions were examined in detail, where the places where methane bubbles from bottom sediments were found earlier were discovered [6].

In 2018, using a marine echo sounder, methane torches were again recorded. At the polygon "C15", located in the area with coordinates 76.78° N, 125.85° E (Fig. 3), local peaks of methane concentration with a maximum of 2083.2 ppb were revealed. The average methane concentration was only 1930 ppb, lower than the average along the entire route. At the "Oden" polygon (Fig. 3), on the contrary, there was an increase in methane concentration relative to the average - 1971 ppb, with individual peaks not exceeding 2037 ppb.

In addition to the described polygons, methane seeps were revealed in other areas, for example, on
the slope of the continental shelf, but due to the considerable depth there methane has time to dissolve in water, and the bubbles do not reach the surface of the ocean.

In 2019, the cruise route passes the White, Barents and Kara Seas. The table shows the data for the entire expedition. Of interest is the increased methane concentration that was observed when passing from north to south of the Kara Sea in the region of the Gulf of Ob. In this case, there was a gradual increase in methane content with a maximum of 2005 ppb. It should also be noted that an increase in methane concentration was accompanied by a decrease in the salinity of surface water (and vice versa), which may indicate the influence of the river flow of the Ob and Yenisei.

The maximum values (2092 ppb) of methane in the Kara Sea were recorded west of the Yamal Peninsula on July 20. Throughout the time when peak values were noted, the removal of air masses from the mainland was observed. Reduced methane concentrations were generated by advection of air masses from the North Atlantic, with a northwest wind.

![Figure 4. Surface BC content along the route of AMK-72 (the size of the circle is proportional to the value of BC concentration).](image)

The results of BC study have somewhat common behavior. As a sample, the results of observations of black carbon during AMK-72 are shown in Figure 4. As can be seen from the figure, the nature of the variations in the concentration of black carbon is partially similar to the previously analyzed variations in the concentration of methane.

In the Barents Sea on August 19 and September 17, 18, the average soot concentration is 54 ng/m³ and 14 ng/m³, respectively. Trajectory analysis showed that the increased soot content in the surface air is due to the arrival of air masses from the northwestern regions of the land of Western Europe, and low values were obtained in air masses coming from the European part of Russia from high altitudes (approximately 1300 m. a. s. l.). In addition, the results of measurements of the radiosondes showed that the state of the atmosphere along the movement of the air masses contributed to the dispersion of air pollutants, because there were no temperature inversions.

In the Kara Sea on August 21, in the case of air mass coming from the north of European part of Russia and the Scandinavian Peninsula, we recorded a soot concentration of 46 ng/m³, but if the air
mass trajectories passed over the water surface from the sector from NW to NW, the average concentration of soot was 11 ng/m$^3$.

The lowest concentrations for the expedition were obtained for the Laptev Sea: when air masses moved over the Taimyr Peninsula, on August 24 and 25, an average concentration of 6 ng/m$^3$ was obtained, and in the case of air masses passing on August 31 and September 5 above the northern water surface - 2 ng/m$^3$.

An analysis of the observations showed that the concentration of BC in the atmospheric surface layer in the Arctic is mainly at the background level and is about 58 ng/m$^3$, with a variation range from 18 to 110 ng/m$^3$. The lowest concentrations are observed in the eastern regions for the north wind. An increase in the concentration of BC is observed occasionally upon receipt of air masses from the mainland, mainly from areas of associated gas combustion and forest fires.

4. Conclusions

The observations and their subsequent analysis allows to conclude that the spatial distribution of the methane in the air above the seas is a result of large-scale transport of air masses.

The range of $\delta^{13}$C values indicates the multiplicity of methane sources in the Arctic. Enhanced in methane concentration is observed in some areas of the Kara and Barents Seas due to advection of air masses from the mainland, mainly from the gas fields of Yamal and Western Siberia, as well as wetland ecosystems. The minimum methane concentration is observed during advection of air masses from the regions of the North Atlantic. These conclusions are also confirmed by observational data at the Zeppelin station (Svalbard), where the minimum methane content is noted relative to other Arctic stations. [EBAS: Data from Zeppelin Station available at http://ebas.nilu.no].

An increased content of black carbon in the air above the water surface was also observed in the Kara and Barents Seas, mostly under conditions of transport of air masses from the mainland. The minimum values of black carbon content are observed with north winds.

The measurement results for the first time confirmed the existing assumptions about the possibility of the formation of high peak methane concentrations in atmospheric air due to bubble emission. However, the obtained data do not yet allow even rough estimates of the integral emissions of bottom methane.

The performed work allowed for the first time to obtain similar information on the identification of sources of atmospheric methane in the Arctic, which will help to more accurately assess the ongoing climate change.

Conflict of Interest
The authors declare no conflict of interest.

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