Natalia Pankratova[1*], Andrey Skorokhod[1], Igor Belikov[1], Nikolai Elansky[1], Vadim Rakitin[1], Yury Shtabkin[1], Elena Berezina[1]
[1]A.M. Obukhov Institute of Atmospheric Physics of Russian Academy of Sciences, Moscow, Russia
*** Corresponding author:** pankratova@ifaran.ru

EVIDENCE OF ATMOSPHERIC RESPONSE TO METHANE EMISSIONS FROM THE EAST SIBERIAN ARCTIC SHELF

ABSTRACT. Average atmospheric methane concentration (CH_4) in the Arctic is generally higher than in other regions of the globe. Due to the lack of observations in the Arctic there is a deficiency of robust information about sources of the methane emissions. Measured concentrations of methane and its isotopic composition in ambient air can be used to discriminate sources of CH_4. Here we present the results of measurements of the atmospheric methane concentration and its isotope composition ($\delta^{13}C_{CH4}$) in the East Siberian Arctic Seas during the cruise in the autumn 2016. Local sections where the concentration of methane in the near-water layer of the atmosphere reaches 3.6 ppm are identified. The measurements indicated possibility of formation of high methane peaks in atmospheric surface air above the East Siberian Arctic Shelf (ESAS) where methane release from the bottom sediments has been assumed.

KEY WORDS: atmospheric methane, methane emissions, Arctic, sub-sea permafrost, warming, shipborne measurements, atmospheric surface layer, East Siberian Arctic Shelf

CITATION: Natalia Pankratova, Andrey Skorokhod, Igor Belikov, Nikolai Elansky, Vadim Rakitin, Yury Shtabkin, Elena Berezina (2018) Evidence Of Atmospheric Response To Methane Emissions From The East Siberian Arctic Shelf. Geography, Environment, Sustainability, Vol.11, No 1, p. 85-92
DOI-10.24057/2071-9388-2018-11-1-85-92

INTRODUCTION

Methane (CH_4) is a second greenhouse gas after carbon dioxide which atmospheric concentration has increased by 150% since pre-industrial times (IPCC, 2013). However, the CH_4 global warming potential is approximately 28 times higher than that of CO_2 over a 100-year frame (Myhre et al. 2013). It accounts for 20% of the global radiative forcing of well-mixed greenhouse gases (Quay et al. 1999; Dlugokencky et al. 2014).

As is thought, methane contributes greatly to warming in the Arctic region, which is characterized by abundant methane sources such as, for example, wetlands of the northern Eurasia, shelf areas of the Arctic seas (Shakhova et al. 2014), gas combustion (Stohl et al. 2005), and anthropogenic emissions. It is assumed that the influence of methane sources on the climate of the region should progressively increase with temperature growth in the Arctic (Shakhova et al. 2015).

Sub-sea permafrost and hydrates in the shelf regions of the seas of the Eastern Arctic are significant methane pool and potentially can be large source of atmospheric methane emissions (Berchet et al. 2015). A significant number of localized seeps of methane in offshore regions of the East Arctic seas have been found (Shakhova et al. 2015; Thornton et al. 2016), but the quantity and quality of the available experimental data is currently insufficient to obtain stable estimates of CH_4 emissions into the air above-sea layer, which are still very contradictory (Berchet et al. 2015; Shakhova et. al. 2014). The evidence of methane release from the ESAS bottom layers have been previously reported (Thornton et al. 2016; Shakhova et al. 2010), while the ability of benthic methane to penetrate into the atmosphere had not yet been proven. Satellite measurements of the surface methane concentration cover the whole Earth but do not have sufficient accuracy. Very little data are available for the isotope $\delta^{13}C_{CH4}$ in methane, which provides information on sources of methane in the atmosphere (Warwick et al. 2016; Fisher et al. 2011). Thus, it is very important to expand the experimental studies of methane concentrations in the Arctic to check whether methane released from the seawater into the atmosphere. Present work is continuing the Arctic methane study started during previous observation campaign of 2015 described in (Skorokhod et al. 2016).

MATERIALS AND METHODS

Atmospheric CH_4 mixing ratio and changes in the ^{13}C:^{12}C ratio in CH_4 (reported a changes relative to a reference ratio and denoted as $\delta^{13}C_{CH4}$) were measured from aboard the research vessel (R/V) Akademik M.A. Lavrentiev from 23 September to 3 November 2016 in the Laptev, East Siberian and Chukchi Seas and as well as the North Pacific and the Sea of Japan (see Fig. 1). The measurements were performed using a Cavity-Ring-Down Spectrometer (CRDS) from Picarro™ (model G2132-i). Together with methane concentrations of other trace gases (CO_2, NO, NO_2, O_3) were measured.

CRDS (G2132i) allows to measure the methane concentration in the range from 1800 to 12000 ppb with an error of less than 5 ppb, and the value of $\delta^{13}C_{CH4}$ with an error of less than 1 ‰. The cameral experiments showed that the intrinsic noise of the device did not exceed the indicated error values.

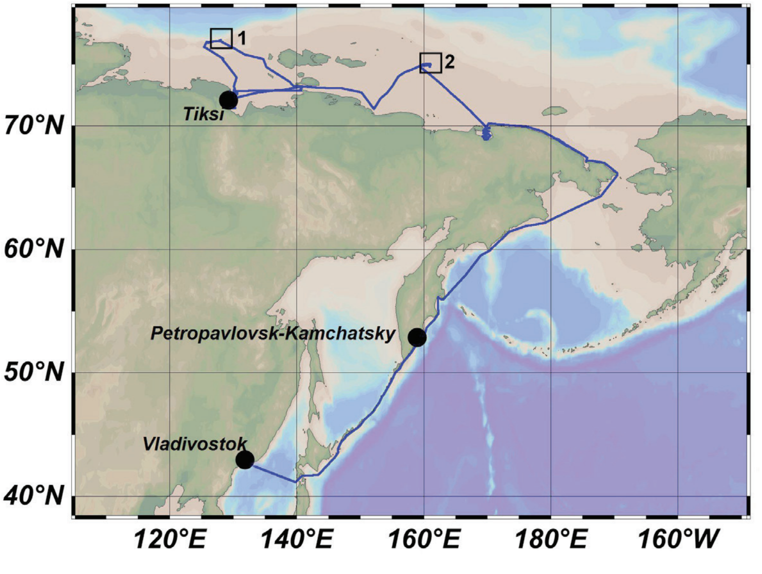


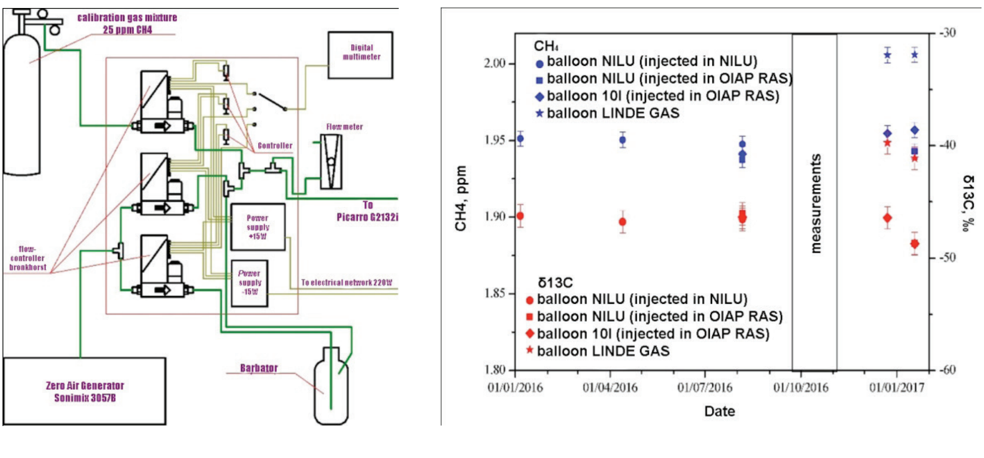
Fig. 1. The route of R/V Akademik M.A. Lavrentiev, Tiksi - Vladivistok, 24.09-03.11.2016. The areas with the high methane concentration are in the frames. 1 - corresponds to the Laptev sea polygon with CH4 maximum (2.133 ppm); 2 - CH_4 maximum in the East Siberian sea (3.537 ppm)

Calibrations of the CRDS (G2132i) 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 values of methane and $\delta^{13}C_{CH4}$ concentrations. The relative error of this measurement did not exceed 0.03% for methane and 0.1% for $\delta^{13}C_{CH4}$. The secondary standard was calibrated by primary standard known as NOAA04 (Dlugokencky et al. 2005) for CH_4, while calibration for $\delta^{13}C_{CH4}$ was made by method described in (Fisher et al. 2006).

Calibrations of the G2132i were carried out with a period of 1-2 months, immediately before and after the ship campaign. The scheme of the experimental setup and the calibration results are shown in Fig. 2. All obtained values differ within error of the CRDS, indicated in its technical specification (5 ppb). A special study of the short-period drift of the instrument readings showed that the root-mean-square deviation of the instrument readings did not exceed 0.05% within a time period of 10-20 minutes. All the observational data were recalculated in accordance with the obtained calibration coefficients, and a series of data were averaged over the intervals of 1 min and 10 min.

During the ship campaign, the air was sampled from the inlet at the front of the deck at height of 11 meters above sea level. The length of the pipeline was 30 m, and the inner diameter was 10 mm with air flow rate of 3 litres min^{-1}. Such arrangement of the air intake allows minimizing the perturbations of the airflow by the vessel during air sampling (Edson et al. 1998). The diesel fuel used by ship engine does not contain methane, though it contains hydrocarbons, such as, for example, cetane and alpha-methylnaphthalene-an aromatic hydrocarbon. If smoke from ship chimney occurs into the G2132-i air intake, hydrocarbons may distort the methane concentration value. Thus, to exclude the influence of the ship itself, data on the CO_2 concentration were analyzed. CH_4 data, which were corresponding to a high concentration of CO_2, were excluded from analyses.

The measurements were carried out in the autumn period, when advection of cold air occurred on the coast of the Arctic seas, and a snow cover began to form. During the cruise the temperature was lower than 0ºC coastal zone was under the snow cover. Under these conditions, the mainland natural sources of methane were not active.



(a) (b)

Fig. 2. a - Schematic diagram of the experimental setup for calibration of the CRDS (G2132i) with different humidity of the analyzed air, b - Calibration results for the CRDS (G2132i) before and after the campaign

It was confirmed by the wind direction analysis. The frequency of wind direction were calculated for four sectors (316-45, 46-135, 136-225, 226-315 degrees) for the Laptev, the East-Siberian and the Chukchi seas and the mean CH_4 concentration for each sector was obtained. There is no significant dependence of the methane concentration on the direction of the wind in the seas of the Eastern Arctic - difference between the mean methane concentrations calculated for the each sector is less than 1 %.

RESULTS AND DISCUSSION

Table 1 gives the statistical characteristics of the results of observations for the Laptev and East Siberian seas, calculated with averaging of 1 minute. As follows from these data, in general, the methane content in the near-surface air of the seas of the Eastern Arctic and in the northern Pacific regions is very uniform in October (the standard deviation of the series is about 0.02 ppm) and stably exceeds the average global value characteristic for this period.

At the same time, in the Laptev and the East-Siberian seas, localized areas with a high concentrations of methane in the above-sea air have been identified (Fig. 3). Of greatest interest are the so-called methane-emission polygons described in (Shakhova et al. 2014). One of these polygons was located approximately at the coordinates of 75° N and 160° E (Fig. 4). The vessel was there from October 11 to October 13, 2016. Figure 3 shows the graph of the dependence of the methane concentrations on time according to the measurements by the G2132i instrument with averaging of 10 seconds. As can be seen from the graph, the concentration of methane above the water surface is characterized by a large number of peaks by the value of 2.0-2.2 ppm and more. From the board of the vessel raising of methane bubbles from the water was visually detected. According to sonar data from the vessel, methane bubbles came directly from the bottom, as the depth in the observation area reached 45-50 meters.

Information on $\delta^{13}C_{CH4}$ is important for identifying sources of atmospheric methane in the Arctic (Quay et al. 1999; Fisher et al. 2011). The average value of $\delta^{13}C_{CH4}$ for well-mixed atmospheric air is about -47.1 ‰, but it strongly depends on the season and latitude (Rigby et al. 2012). Our results show the average $\delta^{13}C_{CH4}$ value -49.86 ‰ for Laptev and East Siberian seas.

Arctic wetlands are characterized by values of $\delta^{13}C_{CH4}$ within -69 ÷ -60 ‰ (Fisher et al. 2011), methane emissions from fossil fuel vary from -50 ‰ to 26 ‰. Biomass burning gives $\delta^{13}C_{CH4}$ in the range of -18 ÷ -30 ‰ (Rigby et al. 2012). The $\delta^{13}C$ composition of methane for methane hydrate emission has a magnitude -50 ± 3‰ (Dlugokencky et al. 2011). The average $\delta^{13}C_{CH4}$ over the seep polygon was -51.16 ‰ that corresponds to this magnitude. Herewith the standard Keeling plot analysis (Fisher et al. 2011; Pataki et al. 2003) shows the inconclusive result, that prevents clear determination of CH_4 source.

The presence of methane concentration peaks generated by the release of methane bubbles to the surface causes a slight increase in CH_4 average concentration in the surface air above the seeps.

Table 1. Statistical characteristics of 1-min data sets of the methane concentrations and $\delta^{13}C_{CH4}$ measured over the Laptev and the East-Siberian Seas in autumn of 2016

Parameter	Laptev Sea		East-Siberian Sea	
	$\delta^{13}C_{CH4}$ ‰	CH_4 ppm	$\delta^{13}C_{CH4}$ ‰	CH_4 ppm
Minimum	-57.12	1.938	-54.86	1.935
Maximum	-44.10	2.133	-46.96	3.537
Mean	-49.59	1.962	-50.12	1.958
Standard deviation	1.46	0.015	1.2	0.024

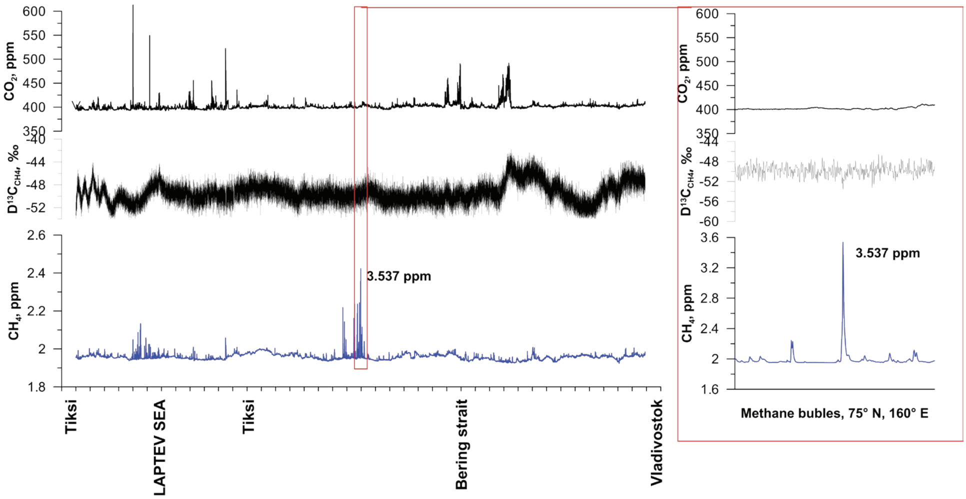


Fig. 3. Observed CH4 and CO2 concentration and δ13CCH4 during the ship campaign of R/V 'Akademik M.A. Lavrentiev' (24 Sept– 02 Nov 2016). Scaling up CH4 peak for methane emission polygon (of 75° N and 160° E) is shown in the frame on the right

Thus, the average daily methane concentration level on the seep polygon (October 12) is by few percent higher than the average daily methane concentration outside of this polygon (October 10 and 14). It is comparable with regional variations in the average daily concentration (for example, on October 9, when the vessel was near of Kolyma delta). However, the AIRS data Level 2 show the area with the excess total CH_4 content which can be connected with releasing of the methane from the sea water to the surface air (see Fig. 4). One can notice relatively slight decrease of $\delta^{13}C_{CH4}$ opposite the highest methane peaks (see Fig. 3). This can be explained by similar isotopic signatures of ambient air and air from hydrates (Fisher et al. 2011) that makes application of isotopic analyses methods (like Keeling plot) for seeping regions not clear (Skorokhod et al. 2016).

CONCLUSIONS

Our measurements of CH4 in the atmosphere across ESAS during September and October 2016 in general show stable CH_4 and $\delta^{13}C_{CH4}$ concentrations in the surface air. However, the possibility of CH_4 high peak (up to 3.54 ppm according to our measurements)

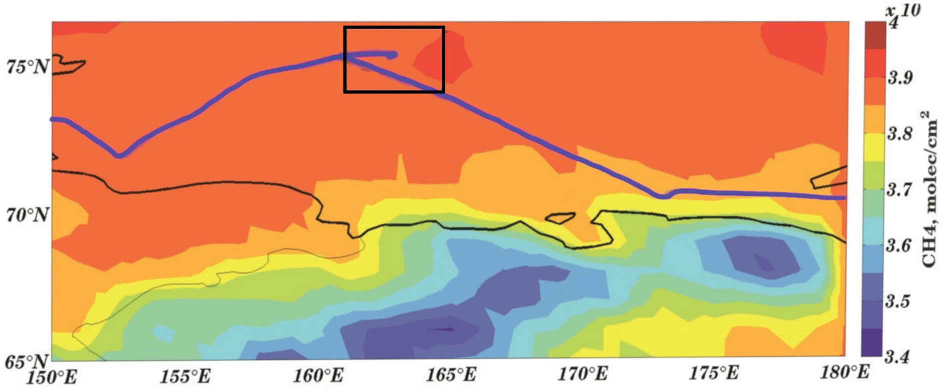


Fig. 4. Average CH4 Total column over the East Siberian Sea for October 2016 and the route of R/V 'Akademik M.A. Lavrentiev' with marked polygon of seep measurements (black square). AIRS level 3 v6 ascending data with the spatial resolution 1°x1° were used. Data available on https://airs.jpl.nasa.gov/

formation in the atmospheric air above the ESAS in the areas of methane seeps was indicated. These enhancements cannot be associated with air pollution (including influence ship emissions) and terrestrial methane sources, which were likely to be inactive during the ship campaign. Therefore, the performed measurements were likely to be the first direct evidence of atmospheric response of benthic methane escape into the atmosphere in the Arctic.

On base of these data, it is difficult to assess real amount of methane released from the Arctic seas into the atmosphere. Meteorological conditions were not favorable to methane accumulation within the boundary layer. On the contrary, strong winds and unstable stratification led to fast dissipation of released methane. One can assume nevertheless that those methane emissions are significant enough to make quite stable footprint on maps built from satellite data. Thus, satellite data of AIRS (Atmospheric Infrared Sounder) steadily show an increased total methane content in the vertical column of the atmosphere in the area corresponding to the seep area. For instance, in October, 2016 CH_4 total column exceeded 3.90x10*19 mol/cm2 inside the polygon comparing to 3.85x10*19 mol/cm2 out of it (see Fig. 4).

The local peaks of atmospheric methane in this region is a strong indication in favor of the hypothesis that the ESAS shelf is a potential significant source of atmospheric methane. But further studies are needed to clarify the quantitative characteristics of this source nowadays and in the future.

ACKNOWLEDGEMENTS

We are grateful to the crew of the V/R «Academik M.A. Lavrentiev» and to the staff of the Il'ichev Pacific Oceanological Institute RAS, and personally to Prof. Igor Semiletov for organizing the expedition and comprehensive support for the measurement. The work was supported by the Russian Science Foundation (grant № 14-47-00049).

REFERENCES

Berchet A., Bousquet P., Pison I., Locatelli R., Chevallier F., Paris J.-D., Dlugokencky E. J., Laurila T., Hatakka J., Viisanen Y., Worthy D. E. J., Nisbet E., Fishe, R., France J., Lowry D., Ivakhov V., and Hermansen O. (2016). Atmospheric constraints on the methane emissions from the East Siberian Shelf, Atmos. Chem. Phys., 16, 4147-4157, doi:10.5194/acp-16-4147-2016.

Dlugokencky E.J., R.C. Myers P.M. Lang, K.A. Masarie, A.M. Crotwell, K.W. Thoning, B.D. Hall, J.W. Elkins, and L.P. Steele (2005), Conversion of NOAA CMDL atmospheric dry air methane mole fractions to a gravimetrically-prepared standard scale, J. Geophys. Res., 110, D18306, doi : 10.1029/2005JD006035.

Dlugokencky E. J., Nisbet E. G., Fisher R. E., and Lowry D. (2011), Global atmospheric methane: Budget, changes, and dangers, Philos. Trans. R. Soc. London, Ser. A., 369, pp. 2058–2072.

Edson J. B., Hinton A. A., Prada K. E., Hare J. E., and Fairall C. W. (1998). Direct covariance flux estimates from mobile platforms at sea, J. Atmos. Oceanic Technol., 15, 547–562, doi:10.1175/1520-0426

Fisher R., Lowry D., Wilkin O., Sriskantharajah S., Nisbet E.G. (2006). High-precision, automated stable isotope analysis of atmospheric methane and carbon dioxide using continuous-flow isotope-ratio mass spectrometry, Rapid Communications in Mass Spectrometry V. 20, pp. 200-208.

Fisher R. E., Sriskantharajah S., Lowry D., Lanoisellé M., Fowler C. M. R., James R. H., Hermansen O., Lund Myhre C., Stohl A., Greinert J., Nisbet-Jones P. B. R., Mienert J., and Nisbet E. G. (2011).

Arctic methane sources: Isotopic evidence for atmospheric inputs, Geophys. Res. Lett., 38, L21803, doi:10.1029/2011GL049319.

Myhre G., Shindell D., Bréon F.-M., Collins W., Fuglestvedt J., Huang J., Koch D., Lamarque J.-F., Lee D., Mendoza B., Nakajima T., Robock A., Stephens G., Takemura T., and Zhang H.(2013). Anthropogenic and natural radiative forcing, in: Climate Change 2013: the Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. M., Cambridge University Press, Cambridge, UK, New York, NY, USA, pp. 659–740.

Pataki D. E., Ehleringer J. R., Flanagan L. B., Yakir D., Bowling D. R., Still C. J., Buchmann N., Kaplan J. O., and Berry J. A. (2003). The application and interpretation of Keeling plots in terrestrial carbon cycle research, Global Biogeochem. Cycles, 17, 1022, doi:10.1029/2001GB001850, 1.

Quay P., Stutsman J., Wilbur D., Snover A., Dlugokencky E. J., and Brown T. (1999). The isotopic composition of atmospheric CH4. Glob. Biogeochem. Cy., 13, pp. 445-461.

Rigby M., Manning A. J., and Prinn R. G.(2012). The value of high-frequency, high-precision methane isotopologue measurements for source and sink estimation, J. Geophys. Res: Atmos., 117(D12), doi:10.1029/2011JD017384.

Shakhova N., Semiletov I., Sergienko V., Lobkovsky L., Yusupov V., Salyuk A., Salomatin A., Chernykh D., Kosmach D., Panteleev G., Nicolsky D., Samarkin V., Joye S., Charkin A., Dudarev O., Meluzov A., Gustafsson O. (2015). The East Siberian Arctic Shelf: towards further assessment of permafrost-related methane fluxes and role of sea ice. Phil. Trans. R. Soc. A 373: 20140451. http://dx.doi.org/10.1098/rsta.2014.0451.

Shakhova N., Semiletov I., Leifer I., Sergienko V., Salyuk A., Kosmach D., Chernykh D., Stubbs C., Nicolsky D., Tumskoy V., Gustafsson O. (2014). Ebullition and storm-induced methane release from the East Siberian Arctic Shelf. Nature Geoscience, Vol. 7, pp. 64–70.

Shakhova N., Semiletov I., Leifer I., Salyuk A., Rekant P., and Kosmach D. (2010). Geochemical and geophysical evidence of methane release over the East Siberian Arctic Shelf, J. Geophys. Res., 115, C08007, doi:10.1029/2009JC005602.

Skorokhod A.I., Pankratova N.V., Belikov I.B., Thompson R. L., Novigatsky A. N., Golitsyn G. S. (2016). Observations of atmospheric methane and its stable isotope ratio (δ13C) over the Russian Arctic seas from ship cruises in the summer and autumn of 2015, Dokl. Earth Sc. 470: 1081. doi:10.1134/S1028334X16100160.

Thornton B. F., Geibel M. C., Crill P. M., Humborg C., and Mörth C.-M. (2016). Methane fluxes from the sea to the atmosphere across the Siberian shelf seas, Geophys. Res. Lett., 43, DOI: 10.1002/2016GL068977.

Warwick N. J., Cain M. L., Fisher R., France J. L., Lowry D., Michel S. E., Nisbet E. G., Vaughn B. H., White J. W. C., and Pyle J. A. (2016). Using δ13C-CH4 and δD-CH4 to constrain Arctic methane emissions. Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-408.

Received on November 1st, 2017 Accepted on March 1st, 2018

Natalia V. Pankratova currently works as Scientific Researcher in the Laboratory of Atmospheric Gaseous Species at the A.M. Obukhov Institute of Atmospheric Physics RAS. The focus area of her interest is atmospheric chemistry, atmospheric compositions, and methane cycle. In 2002 she graduated from Department of Meteorology and climatology of Geographical Faculty of Lomonosov Moscow State University. She received her PhD in 2014. In 2015 and 2016 took part in two ship cruises providing shipborne measurements of greenhouse and reactive gases in the lower atmosphere over the Arctic, Northern Atlantic and Northern Pacific.