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Comment

Comment on "Understanding the Permafrost–Hydrate System and Associated Methane Releases in the East Siberian Arctic Shelf"

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Abstract: The recent paper in *Geosciences*, "Understanding the Permafrost–Hydrate System and Associated Methane Releases in the East Siberian Arctic Shelf" by Shakhova, Semiletov, and Chuvilin, (henceforth "S2019"), contains a number of false statements about our 2016 paper, "Methane fluxes from the sea to the atmosphere across the Siberian shelf seas", (henceforth "T2016"). S2019 use three paragraphs of section 5 of their paper to claim methodological errors and issues in T2016. Notably they claim that in T2016, we systematically removed data outliers including data with high methane concentrations; this claim is false. While we appreciate that flawed methodologies can be a problem in any area of science, in this case, the claims made in S2019 are simply false. In this comment, we detail the incorrect claims made in S2019 regarding T2016, and then discuss some additional problematic aspects of S2019.

Keywords: methane; East Siberian Arctic Shelf; laptev sea; East Siberian Sea; methane hydrates

1. Responses to Claims about *Thornton* et al. GRL, 2016

The recent 2019 paper in *Geosciences*, "Understanding the Permafrost–Hydrate System and Associated Methane Releases in the East Siberian Arctic Shelf", by Shakhova, Semiletov, and Chuvilin [1], (henceforth "S2019"), contains a number of false statements about our 2016 paper published in *Geophysical Research Letters* "Methane fluxes from the sea to the atmosphere across the Siberian shelf seas" [2], (henceforth "T2016"). Here, we address these statements in the order they appear in S2019.

In Section 5, S2019 present a paragraph describing problems with removing outliers from a dataset, including the *mea culpa* that they themselves made this mistake with seawater methane (CH_4) concentrations in the past. They then state that we (in T2016) "removed outliers from the analysis". This is false, we did not remove outliers of CH_4 concentration in surface seawater from the analysis in T2016.

S2019 continue: "Based on applied methodology, and despite clearly observed ebullition, they [T2016] suggested that diffusive fluxes alone can explain observed atmospheric mixing ratios that are slightly elevated in some areas". This is a true representation of the results we stated in T2016. Diffusive CH_4 flux from the sea to the atmosphere was, across the studied areas of the Laptev and East Siberian seas, greater than the bubble flux. The bubble fluxes, driven by bubble streams from the seafloor easily visible on sonar, were confined to small spatial areas. Large bubble fluxes in small areas near seeps were observed to be insignificant compared to smaller diffusive fluxes observed across the vast Siberian Arctic shelf during the SWERUS research expedition in 2014. Strangely, S2019 seem

to understand this, as they write two sentences later that the "majority of the surface water samples [in the T2016 dataset] were above saturation level"—implying that positive diffusive sea–air flux is widespread across the Siberian Arctic shelf seas, exactly as we wrote in T2016.

However, next S2019 state that "all measured concentrations of atmospheric CH_4 were above the latitude specific monthly mean of 1.85 ppm". It is absolutely true that the T2016 atmospheric measurements of CH_4 were above 1.85 ppm. But a "latitude specific monthly mean" is not a constant; as long as CH_4 is increasing globally [3], any latitudinal average will also increase with each passing year. S2019 are implying that 1.85 ppm was a reasonable background CH4 concentration in 2014; it was not—see, e.g., figures in [3]. In T2016 we used 1.875 ppm as the background CH_4 level, based on pan-Arctic ground monitoring stations at Tiksi, Russian Federation; Alert, Canada; and Barrow, Alaska.

S2019 continue: "(1) Methods used to measure both atmospheric mixing ratios and concentrations of dissolved CH_4 were not calibrated; that is, they did not estimate the time required for sample equilibration before determining the measurement frequency. Because time of equilibration was longer than the time between measurements, they measured unequilibrated samples, and measured levels were lower than they would have been if samples had been allowed to equilibrate."

The basic claim S2019 is making, that in T2016 we did not calibrate the measuring equipment and measurement techniques, is false. As described in T2016, both the atmospheric and waterside spectrometers were frequently calibrated before, during, and after the SWERUS expedition. The spectrometers were calibrated against NOAA Earth Systems Research Laboratory standards, and cross-calibrated with secondary "target" gas standards. The methods are fully described in T2016.

S2019's suggestion that our measurements did not take into account equilibration time is also false. (Presumably they are referring to our CH_4 in seawater measurements, as the statement makes no sense for the atmospheric measurements presented in T2016). Again, S2019 are simply incorrect about our methods; we used a showerhead equilibrator, a well-known and widely used technique e.g., [4–6] to produce high seawater sample surface areas, minimizing equilibration times [7]. We were well aware of the need to take equilibration times into account, and thus we validated our methods and equilibration times beforehand. It is true that the spectrometer we utilized is capable of measuring CH_4 at 1 Hz, but this does not imply that the system's equilibration time was <1 s. Finally, our equilibrator-measured CH_4 concentrations agreed with CH_4 concentrations in CTD-obtained seawater samples taken at the same depth as the ship's seawater intake during the cruise. We refer the reader to T2016 and [7,8] for more information.

S2019 then write: "(2) While collecting the raw data, 1 SD from the mean was set as a data filter; as a result, all outliers, which are values of major interest when studying ebullition, were removed and only 68% of the observed values were used for analysis. This corrupted the data range and the applied statistics, because the atmospheric mixing ratios of CH_4 in fact varied by up to 4.2 ppm, but the authors only reported variation by up to 2.5 ppm."

We did not remove data that was greater than 1 standard deviation from the mean; we did not apply any data filters based on standard deviations of any sort. The only filters we applied, as described in T2016, were wind direction and wind speed, and CO_2 greater than 450 ppm. These are extremely conservative filters, but we believe it incorrect to include in our analysis air which had flowed over the exhaust stack of a 24,500 horsepower diesel-powered icebreaker with more than 70 persons onboard, a few seconds before sampling.

Nevertheless, in 2015, at the request of Dr. Semiletov, we ran the analysis presented in T2016 with no filters whatsoever; the results—and our conclusions—did not change. This is because the high atmospheric CH_4 values were profoundly rare in the T2016 dataset—even when we included obviously contaminated air that had flowed over the icebreaker's superstructure and exhaust. We explained this in detail to Dr. Semiletov in 2015, when he was still a coauthor on T2016.

We are mystified by S2019's claim (presumably developed from looking at our raw data, which had been provided to Dr. Semiletov as a co-investigator and one of the cruise's principal investigators) that the atmospheric mixing ratios during the SWERUS cruise presented in T2016 "in fact varied by up

to 4.2 ppm". Perhaps S2019 were misled by our every-two-hours calibration cycles in the raw data files, which sequentially injected two target gases, one of which contained $CH_4 > 4$ ppm. Further, S2019 claim that "the authors only reported variation by up to 2.5 ppm." This is equally puzzling, as the highest value reported in T2016 is 2.1724 ppm—in the supplementary material—and this value was measured 4 m above the sea surface, over an active seafloor gas seep. Again, we assume that S2019 are referring to a handful of high CH_4 values in the raw data stream, which were removed due to potential ship contamination (wind direction, speed, or high CO_2), or were part of the aforementioned calibrations. We emphasize again that even if we had left these ship-contaminated data in the analysis, they were rare enough to have no significant effect on the values reported in T2016. For completeness, we note that we also operated a high-frequency system for CH_4 and CO_2 eddy covariance flux measurements during the cruise reported in T2016 [8]. However, these data are not part of or discussed in T2016, but this high-frequency dataset does contain spikes of higher CH_4 concentrations, when viewed at 10 Hz resolution. This 10 Hz CH_4 dataset has not yet been published except for mention in a meeting abstract [9]. Averaging these 10 Hz CH_4 data and processing them with the same filters as the 1 Hz data presented in T2016 would result in similar conclusions: Brief, transient spikes of CH_4 concentration from localized gas seep sources do not represent the dominant sea-to-atmosphere flux in the studied ESAS region.

S2019 then state: "(3) They interpolated a very limited data set (collected on just one expedition) obtained under very specific conditions—mostly ice-covered water, collected in the outer-shelf area (deep water), along a single ship's track (which exists in two-dimensional space)—to the entire shelf area (which is a three-dimensional space)."

It is true that T2016 used only a single cruise's data. We are well aware that Drs. Shakhova and Semiletov have been involved in far more expeditions on the Siberian Shelf seas than we have. We hope that they publish more of the CH_4 data collected during the "40 annual expeditions" mentioned in S2019; few of these data are, to our knowledge, published in the literature. S2019 also seem to be implying here that we would have measured more CH_4 had the ship been operating in open waters, as they state that the dataset in T2016 was "mostly [in] ice-covered water". This is not true; as can be seen in Figure 1C of T2016, during the cruise the entire studied area of the Laptev Sea and parts of the East Siberian Sea were ice free (including areas containing numerous gas seeps in the Laptev Sea). Dr. Semiletov was onboard *Oden* during the cruise and should be aware of this. Additionally, we measured higher surface seawater CH_4 concentrations in ice-covered areas of the East Siberian Sea—again, this is described in detail in T2016.

It is true that the cruise described in T2016 spent considerable time on the outer, and mid-shelf areas; however, the cruise track average water depths were shallower than that of 43% of the Laptev Sea and 50% of the East Siberian Sea's areas, based on their hypsographic curves [7,10]. We fully agree that bubbles of CH_4 released at the seafloor in shallower waters are more likely to reach the atmosphere, indeed, T2016 are careful to point out that higher sea-to-air CH_4 fluxes are possible in shallower waters nearer to shore, as reported in [11]. Basically, the T2016 study effectively surveyed the vast areas of the ESAS not close to shore. Again, intense bubbling in a small area may locally raise atmospheric CH_4 levels, but if the vast expanse of the ESAS is dominated by small diffusive fluxes of CH_4 and only highly localized bubble fluxes, the overall CH_4 flux and overall impact on atmospheric CH_4 would be relatively small.

Finally, S2019 state: "After all these questions were raised, the co-author from our team was asked to leave the authors' team." Once again, this is not true. In September 2015, and Dr. Semiletov requested to be removed from the coauthor list of T2016. At no time did we "ask" or require Dr. Semiletov to leave T2016. Given that Drs. Semiletov and Shakhova had access to the T2016 dataset long before T2016 was published and the data were posted online at the Bolin Centre Database (https://bolin.su.se/data), we are disappointed that they have chosen to publish false claims about our work.

Much remains to be learned about CH_4 emissions from the oceans to the atmosphere, especially in the Arctic Ocean and its marginal shelf seas. We emphasize that the sea–air CH_4 fluxes which we reported in T2016 are quite large compared to reported fluxes from other seas, though smaller than those reported by Shakhova and Semiletov and coworkers [11]. Further, the T2016 results are in agreement with an atmospheric inversion modelling study for CH_4 emissions from the ESAS [12]. We intend to continue our research on marine CH_4 emissions to the atmosphere, and hope that others will as well.

2. Additional Concerns

Below are some additional concerns we have with S2019, not directly related to their discussion of T2016.

In the introduction, S2019 state: "This vast yet shallow region has recently been shown to be a significant modern source of atmospheric CH4, contributing annually no less than terrestrial Arctic ecosystems [19,20]". Neither reference being cited here reports an annual emission flux of CH_4 greater than that from terrestrial arctic ecosystems—which are dominated by wetlands. Arctic wetland emissions are estimated between 23–31 Tg of CH_4 per year [13–16], exceeding the sea emission estimates provided in S2019's references 19 and 20. Additionally, terrestrial Arctic ecosystem emissions include other freshwater systems, such that the total terrestrial CH_4 emission easily exceeds the fluxes predicted in S2019's references 19 and 20.

S2019 also state in the introduction that "Releases could potentially increase by 3–5 orders of magnitude, considering the sheer amount of CH_4 preserved within the shallow ESAS seabed deposits and the documented thawing rates of subsea permafrost reported recently [22]." Reference 22 of S2019 does not support the assertion that ESAS CH_4 releases could increase by 3–5 orders of magnitude, and the claim itself is unsupported and untenable. If we consider the largest "best estimate" of annual ESAS CH_4 emission to the atmosphere published from Drs. Shakhova and Semiletov's work [11], 17 Tg $year^{-1}$, 3 orders of magnitude more is 17,000 Tg of CH_4 per year, and five orders of magnitude is 1,700,000 Tg of CH_4 per year, an absurd annual flux value, not only compared to the current annual emissions of CH_4 from all sources (~555 Tg CH_4 $year^{-1}$, [17]), but the larger also vastly exceeds estimates of the entire global CH_4 hydrate inventory (estimated at 1800 gigatonnes carbon, or ~239,400 Tg CH_4) [18]. We also wonder if S2019 are conflating seawater-to-air fluxes with seafloor-to-seawater fluxes in this section. The text in S2019 is also unclear as to whether this postulated massive increase in flux applies to the entire ESAS, or some subsection, which is critical when determining how large future CH_4 emissions might be. It may be helpful if S2019 reported their actual predicted flux, instead of a multiplication factor.

Section 3.1:

"In one observed well 5×10^7 m^3 (2.1 Tg) of CH_4 was released over 11 months [57]."

Assuming this is at STP (unspecified by S2019 but sensible for releases to the atmosphere), 5×10^7 cubic meters of methane is not 2.1 Tg of CH_4, it is 0.033 Tg of CH_4, (~63 times less). We wonder if this error was due to confusion with the density of liquefied CH_4 (a <−162 °C cryogenic fluid not found naturally on Earth), but in that case, 5×10^7 m^3 would equal 21 Tg, not 2.1 Tg.

Section 4.1:

S2019 write, regarding their earlier work in [19]: "The total annual venting flux of ~8 Tg C–CH_4 from the ESAS to the atmosphere was calculated, which did not include ebullition from the seep fields, because understanding the role and contribution of bubble-borne CH_4 at that time was insufficient due to lack of observations."

This statement appears to be a misrepresentation of the results of [19], which clearly counts both diffusive and ebullitive (bubble) fluxes in the ~8 Tg C–CH_4 year total (see Table 1 of [19]). In [19], a different type of ebullition: "nongradual catastrophic event ebullition" is mentioned, but not

quantified. However, to our knowledge, all ebullitive CH_4 fluxes originate from seafloor gas seeps or seafloor seepage, so at best it is very confusing when S2019 write that the total flux reported in [19] does not include ebullition from seep fields.

Section 4.2:

"It was important to incorporate fluxes from the outer ESAS shelf with water depth > 50 m, where permafrost has presumably degraded the most, because seawater started to submerge this area > 12 thousand years ago at the beginning of the Holocene. Thus, it was logical to assume that CH_4 flux from this area would represent the maximum possible CH_4 flux in the ESAS and indicate the potential for flux increase if ESAS permafrost thawing progresses."

This does not necessarily follow logically—the deeper areas of the shelf, being inundated longer, could potentially be depleted of any CH_4 stored in or trapped by the subsea permafrost after such long inundation periods. Moreover, similarly to other sections of S2019, this section seems to conflate seawater-to-atmosphere flux with seafloor-to-seawater fluxes, the latter always being smaller, due to bubbles dissolving into the water column before rising to the sea surface (a factor which is much more important in the deeper waters of the outer continental shelf).

In conclusion, we are disappointed that the S2019 paper has been published with many false statements about our T2016 paper. Even a cursory glance at T2016 would cause one to question the claims being made in S2019 and could have provoked more inquiries prior to publication. It seems to us that a more careful evaluation of S2019 could have corrected many of these issues.

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References

1. Shakhova, N.; Semiletov, I.; Chuvilin, E. Understanding the permafrost–hydrate system and associated methane releases in the east Siberian Arctic Shelf. *Geosciences* **2019**, *9*, 251. [CrossRef]
2. Thornton, B.F.; Geibel, M.C.; Crill, P.M.; Humborg, C.; Mörth, C.-M. Methane fluxes from the sea to the atmosphere across the Siberian Shelf seas. *Geophys. Res. Lett.* **2016**, *43*, 5869–5877. [CrossRef]
3. Nisbet, E.G.; Manning, M.R.; Dlugokencky, E.J.; Fisher, R.E.; Lowry, D.; Michel, S.E.; Myhre, C.L.; Platt, S.M.; Allen, G.; Bousquet, P.; et al. Very strong atmospheric methane growth in the 4 years 2014–2017: Implications for the Paris agreement. *Glob. Biogeochem. Cycle* **2019**, *33*, 318–342. [CrossRef]
4. Broecker, W.S.; Takahashi, T. Calcium carbonate precipitation on the Bahama banks. *J. Geophys. Res.* **1966**, *71*, 1575–1602. [CrossRef]
5. Johnson, J.E. Evaluation of a seawater equilibrator for shipboard analysis of dissolved oceanic trace gases. *Anal. Chim. Acta* **1999**, *395*, 119–132. [CrossRef]
6. Rhee, T.S.; Kettle, A.J.; Andreae, M.O. Methane and nitrous oxide emissions from the ocean: A reassessment using basin-wide observations in the Atlantic. *J. Geophys. Res. Atmos.* **2009**, *114*. [CrossRef]
7. Humborg, C.; Geibel, M.C.; Anderson, L.G.; Björk, G.; Mörth, C.-M.; Sundbom, M.; Thornton, B.F.; Deutsch, B.; Gustafsson, E.; Gustafsson, B.; et al. Sea-air exchange patterns along the central and outer East Siberian Arctic Shelf as inferred from continuous CO_2, stable isotope, and bulk chemistry measurements. *Glob. Biogeochem. Cycle* **2017**, *31*, 1173–1191. [CrossRef]
8. Prytherch, J.; Brooks, I.M.; Crill, P.M.; Thornton, B.F.; Salisbury, D.J.; Tjernström, M.; Anderson, L.G.; Geibel, M.C.; Humborg, C. Direct determination of the air-sea CO2 gas transfer velocity in Arctic sea ice regions. *Geophys. Res. Lett.* **2017**, *44*, 3770–3778. [CrossRef]
9. Geibel, M.; Thornton, B.; Prytherch, J.; Brooks, I.; Salisbury, D.; Tjernstrom, M.; Semiletov, I.; Mörth, C.; Humborg, C.; Crill, P. Characterization of Sea-Air Methane Fluxes Around a Seafloor Gas Seep in the Central Laptev Sea. In Proceedings of the AGU Fall Meeting Abstracts, San Francisco, CA, USA, 14–18 December 2015.

10. Jakobsson, M. Hypsometry and volume of the Arctic ocean and its constituent seas. *Geochem. Geophys. Geosyst.* **2002**, *3*, 1–18. [CrossRef]
11. Shakhova, N.; Semiletov, I.; Leifer, I.; Sergienko, V.; Salyuk, A.; Kosmach, D.; Chernykh, D.; Stubbs, C.; Nicolsky, D.; Tumskoy, V.; et al. Ebullition and storm-induced methane release from the East Siberian Arctic Shelf. *Nat. Geosci.* **2014**, *7*, 64–70. [CrossRef]
12. Berchet, A.; Bousquet, P.; Pison, I.; Locatelli, R.; Chevallier, F.; Paris, J.D.; Dlugokencky, E.J.; Laurila, T.; Hatakka, J.; Viisanen, Y.; et al. Atmospheric constraints on the methane emissions from the East Siberian Shelf. *Atmos. Chem. Phys.* **2016**, *16*, 4147–4157. [CrossRef]
13. Thornton, B.F.; Wik, M.; Crill, P.M. Double-counting challenges the accuracy of high-latitude methane inventories. *Geophys. Res. Lett.* **2016**, *43*, 12569–12577. [CrossRef]
14. Zhuang, Q.; Zhu, X.; He, Y.; Prigent, C.; Melillo, J.M.; David McGuire, A.; Prinn, R.G.; Kicklighter, D.W. Influence of changes in wetland inundation extent on net fluxes of carbon dioxide and methane in northern high latitudes from 1993 to 2004. *Environ. Res. Lett.* **2015**, *10*, 095009. [CrossRef]
15. Bruhwiler, L.; Dlugokencky, E.; Masarie, K.; Ishizawa, M.; Andrews, A.; Miller, J.; Sweeney, C.; Tans, P.; Worthy, D. CarbonTracker-CH_4: An assimilation system for estimating emissions of atmospheric methane. *Atmos. Chem. Phys.* **2014**, *14*, 8269–8293. [CrossRef]
16. Bousquet, P.; Ringeval, B.; Pison, I.; Dlugokencky, E.J.; Brunke, E.G.; Carouge, C.; Chevallier, F.; Fortems-Cheiney, A.; Frankenberg, C.; Hauglustaine, D.A.; et al. Source attribution of the changes in atmospheric methane for 2006–2008. *Atmos. Chem. Phys.* **2011**, *11*, 3689–3700. [CrossRef]
17. Saunois, M.; Bousquet, P.; Poulter, B.; Peregon, A.; Ciais, P.; Canadell, J.G.; Dlugokencky, E.J.; Etiope, G.; Bastviken, D.; Houweling, S.; et al. The global methane budget 2000–2012. *Earth Syst. Sci. Data* **2016**, *8*, 697–751. [CrossRef]
18. Ruppel, C.D.; Kessler, J.D. The interaction of climate change and methane hydrates. *Rev. Geophys.* **2017**, *55*, 126–168. [CrossRef]
19. Shakhova, N.; Semiletov, I.; Salyuk, A.; Yusupov, V.; Kosmach, D.; Gustafsson, O. Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf. *Science* **2010**, *327*, 1246–1250. [CrossRef] [PubMed]