

Review of 'Heterogenous CO₂ and CH₄ content of glacial meltwater of the Greenland Ice Sheet and implications for subglacial carbon processes'

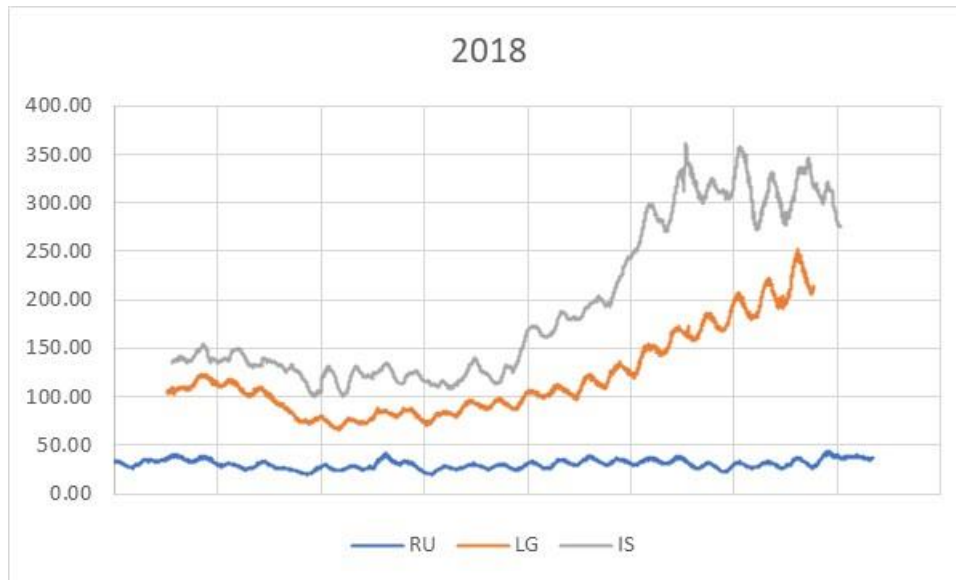
The authors measured CO₂ and CH₄ concentrations and C stable isotopic signatures in meltwater samples from three marginal catchments of the Greenland ice sheet (GrIS) to evaluate sources and sinks of these important greenhouse gases under the fast melting ice sheet. The study is timely, well-structured and -written, and uses adequate methods (with exceptions described below). However, interpretation of some of the results (especially the CH₄ part) relies on incorrect assumptions and/or is unsupported by data, and is therefore too speculative at best. The issues listed below need to be carefully addressed before the study can be published.

First, the authors misunderstand and/or misrepresent the regional hydrology of the Kangerlussuaq area. The large outlet Isunnguata Sermia drains into the Isortoq River/Isortup Kuua (N of the Watson River catchment); its catchment is indeed quite large and extends deep into the ice sheet (probably to the ice divide). However, the water samples collected in this study did not originate from this large catchment and using the name Isunnguata Sermia is erroneous. Rather, the authors' IS site falls into the Point660 subcatchment sensu Lindbäck et al 2015 (as the authors admit at line 88), with an area of ca 30-60 km². This is part of the Russell Glacier catchment system (sometimes treated as part of the Leverett Glacier catchment, eg in Lindbäck et al. 2015), which is complicated, but likely does not reach far into the ice sheet. Calculating the Russell catchment area (for the RU site) as the difference between two individual and independent estimates of the Leverett catchment is incorrect (for example, some authors estimated the Leverett catchment at >1000 km²); the catchment feeding the Russell river is likely much smaller than 300 km² (see eg van de Wal and Russell 1994). Figure 2b attributes the name Watson River to the river system originating at Point 660 and joining the larger river discharging from Leverett Glacier, which is problematic. Whereas the river terminology in the area is indeed somewhat confused, Watson River usually refers to the last short section of the river formed by the confluence of Akuliarusiarsuup Kuua and Qinnguata Kuussua which then enters Kangerlussuaq where the hydrology data used in the study (from van As et al 2018) were taken.

Moreover, it is difficult to compare the study sites with previous works as the authors neither give details of their positions nor show any pictures. I assume the IS site is identical to the site used in Christiansen & Jørgensen (2018). The CH₄ supersaturation referred to at lines 107-108 was measured in the air, with respect to atmospheric concentration, not in the water. The stream itself is very small (discharge at the portal was ca 1 m³/s at peak melt in July 2018) and partly/mostly of supraglacial origin (a supraglacial/marginal stream can be found flowing into the ice margin several hundred meters above the portal). In terms of the RU site, it is not clear whether the authors sampled the main stem of the Russell Glacier river or one of the short subglacial tributaries flowing into it from the Russell Glacier margin (as depicted eg in Dieser et al 2014). The Russell Glacier river in this area has already flowed through a number of lakes and the CH₄ signal would be difficult to interpret as purely subglacial. The order of magnitude difference in CH₄ concentrations reported here and in Dieser et al (2014) is not discussed in the text but suggests that indeed samples were collected from the main stem of the river. A better description of the sampling sites is essential for an adequate assessment of the authors' interpretation.

While the inaccuracies in the description of the regional hydrology are easy to fix, they led the authors to a more problematic aspect of the study: correlating the CH₄ and CO₂ concentrations and isotopic signals from the IS and RU sites with discharge data from the Watson River. While both the Russell Glacier and Watson rivers show clear diurnal variations in discharge, large scale dynamics (including subglacial outbursts) observed in the large rivers is missing in the smaller Russell Glacier river, possibly due to the buffering effect of the lakes along the course of the river, as illustrated in

the figure below comparing unpublished discharge data in m³/s from LG (Leverett Glacier river), RU (Russell Glacier river), and IS (Isunnguata Sermia river/Isortup Kuua) in the summer 2018. The Watson River discharge dynamics may be further complicated by the unaccounted for Qinguata Kuussua, which provides more than half of its water. This is in contrary to the authors' assumptions (line 217).



To my knowledge, this dataset has been made available to the authors, and it might be beneficial for the authors to use it for their correlations. Maybe it was not used because there were just 2 and 3 samples collected at RU and IS, respectively, in 2018 (as shown in Figures 3, 4, 6, 7, 9)?

The low number of samples and the fact they come from two different years, 2017 and 2018, is another weakness of the study. Figures 3, 4, 6, 7, 9 appear as though they show time series (suggested by the lines connecting the dots), which is not the case. I suggest the authors redraw the figure so it's clear the data come from two independent seasons. This should also be acknowledged in the text, and the possible differences in hydrology and the potential impact on the export of gases discussed more in detail. For example, Hawkings et al (2015) showed large interannual variations in total discharge and solute and particulate fluxes from the Leverett catchment between 2009-2012. Also, no statistical analysis of the results was done and it's unclear whether the differences in water chemistry were significant between the streams – was this due to the low number of samples? This should also be acknowledged and/or explained.

Analysis of stable isotopic signatures of C in CH₄ and CO₂ is a powerful tool for determining the origin of the respective gases; however, caution must be exercised when interpreting the results for glacial meltwater samples. Glacial meltwater is a very dynamic mixture consisting of several components with different origins: the water mostly comes from the surface and so has been in direct contact with the atmosphere (and its CO₂); the sediment is predominantly of subglacial origin. Dissolved CH₄ also likely originates from the subglacial environment, while CO₂ has multiple sources -- as the authors show and discuss throughout the ms. The isotopic separation factor ϵ_c (ie $\delta^{13}C_{CO_2} - \delta^{13}C_{CH_4}$), used in this study to assess the sources and sinks of CH₄, is suitable for closed systems (as defined in Whiticar 1999), but caution must be exercised when using it for glacial meltwater and the limitations should be acknowledged and discussed in the text. The authors also calculate the fraction of oxidised methane (f_{ox}) using a number of assumptions, some of which might not be substantiated. For example, Michaud et al (2017) modelled the kinetic isotopic fractionation factor α_{ox} beneath the West Antarctic Ice Sheet, an environment likely to be more representative of the bed of the GrIS, at

1.004. The authors use a value of 1.049, which may lead to an underestimation of microbial oxidation of CH₄ in the GrIS subglacial system. More importantly, outgassing, as a major process affecting meltwater gas concentrations, should not be ignored. In the turbulent flow of glacial rivers, most CH₄ will likely outgas very quickly: for example, in the Leverett Glacier river, virtually all CH₄ is gone after ca 2 km (Lamarche-Gagnon et al 2019). Moreover, outgassing affects not only the concentrations, but also the isotopic composition of gases due to fractionation (see eg Banks et al 2017), driving the remaining dissolved gas to more positive (heavier) values. This may result in an overestimation of CH₄ oxidation. While outgassing was probably less significant at IS (as the authors sampled only 10 m from the subglacial outlet), it may have affected gas concentrations at RU (100 m) and definitely would have at KS (>1 km and a proglacial lake; see below). Much more attention should be paid to the possible effects of this process in the discussion. Moreover, it should be pointed out that outgassing is likely enhanced in glacial systems by considering the large pressure differentials between the subglacial environment where the CH₄ is produced and the atmosphere, and the rapid depressurisation that results from pressurised subglacial waters exiting the ice. Such depressurisation effect is likely to also influence the isotopic signature of the sampled gases in runoff (Banks et al 2017). While accounting for outgassing/depressurisation and their effects on isotopic fractionation might be difficult, if not impossible, the authors should at least discuss the limitations and biases of not doing so, and whether or not the assumptions from their oxidation model would still hold true.

The KS site is additionally problematic as there is a large proglacial lake right by the portal, with an estimated water residence time in the order of 24 hours at peak discharge (Hatton et al 2019). This may significantly change the concentrations and isotopic signatures of the dissolved gases exported further downstream via outgassing (and possibly also microbial processes in the lake bottom sediment), and may be the reason why the CH₄ concentrations at KS are near atmospheric equilibrium. This should also be mentioned when discussing the results from KS.

In the discussion, the authors interpret the observed orders of magnitude variability in dissolved gas concentrations in the meltwater samples as differences in the sources and sinks of the gases (lines 290-291). However, some of the explanations of CH₄ variability are unnecessarily speculative and unsupported by data, and some rest on incorrect assumptions. First, the variability in subglacial OM substrates is invoked (312). This is certainly a factor affecting subglacial C cycling and export rates, but no supporting OC data are presented. Permafrost reservoirs, suggested based on the study by Ruskeeniemi et al (2018), are unlikely to be of importance (and were not alluded to in Lamarche-Gagnon et al 2019, as suggested at line 314), as they extend only a few km into the ice sheet bed. Moreover, Ruskeeniemi et al (2018) only focused on the thermal state of the sediments/soils, rather than the nature of OC. I agree the Holocene ice margin fluctuations were probably important in providing fresh OC substrate that could have been metabolised into CH₄ that is currently being exported. Older (Eemian) OC sources are however also present and exported in the meltwater (Kohler et al 2017) and may have been used as methanogenesis substrates. Reservoirs of old CH₄ are not considered in the study. Second, a direct effect of oxygen supply to the ice sheet bed by surface meltwater on methane production/oxidation is proposed, based on the negative correlation of CH₄ concentrations at RU and Watson River discharge (319-327). As explained above, linking gas concentrations and isotopic signatures at IS and RU to discharge data from the Watson River is misleading. In addition, the authors only consider live methanogenesis and ignore potential old CH₄ storage/leakage (see above). Dilution by meltwater is only acknowledged at lines 328-329 as an alternative explanation, although it plays a significant role. The local subglacial sources of CH₄ are probably limited to microbial activity (Lamarche-Gagnon et al 2019), which takes place in anoxic sediments buried under the ice. Whether it's recent activity or reservoirs of ancient CH₄, its export is dependent on meltwater tapping and flushing pockets of produced gas. As a result, CH₄

concentrations in the meltwater are necessarily discharge-dependent. This is indeed complicated by outburst events; however, these are limited to large outlets (lakes form at much higher altitudes further into the ice sheet than those to which this subcatchment extends), and explaining the lack of discharge-CH₄ concentration relationship at IS by outbursts (330-332) is therefore not justified. Last, CH₄ oxidation, discussed at lines 350-361, is certainly an important process controlling the amount of CH₄ that will be exported from under the ice to the atmosphere. However, in addition to the uncertainty in determining the degree of CH₄ oxidation, the authors' interpretation of the data again relies on correlating the CH₄ concentrations at IS and RU with Watson River discharge and on treating the 2017 and 2018 data as a time series, both of which are flawed (see above).

In summary, I recommend the authors revisit their local hydrology description and interpretation, rename their sampling sites accordingly, avoid correlating their small stream data with the Watson River discharge record, and properly acknowledge the limitations and uncertainties of the used geochemical calculations for interpretation of the subglacial gas sinks and sources, especially for CH₄.

Specific comments

53 please specify if Graly et al 2017a or b

58-60 relevant work should be cited here, eg the recent review by Wadham et al (2019)

66 Musilova et al (2017) did not study subglacial microbial activity; this reference is irrelevant here

107-110 methanogens have also been identified in Russell Glacier basal ice (Stibal et al 2012) and Leverett Glacier river suspended sediment (Lamarche-Gagnon 2019); CH₄ supersaturation in meltwater was also measured by Dierer et al (2014) but not by Christiansen & Jørgensen (2019)

306 Lamarche-Gagnon et al (2019) measured higher CH₄ concentrations than 600 nM (up to 4000 nM during early season)

405 how do the results compare to the recent paper by Andrews et al (2018) focused on dissolved C dynamics in Russell Glacier meltwater, including the sources of subglacial CO₂?

446 please explain 'chemostatic behavior'

695 Figure 1 is a weird combination of 2D and 3D which makes it difficult to interpret. Also, could the authors provide references for CO₂ and CH₄ evasion through crevasses?

700 Figure 2 needs redrawing to correct the river network names and to better indicate the sampling sites; please also use the newer transcription 'Kiattut', to be consistent with the text.

740 the regression line in Figure 8b doesn't look right – were some points omitted?

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