Reviewers' comments are italicised, our response is not. Our direct actions are highlighted in red text. Line numbers refer to the marked-up version of the manuscript

Reviewer 1.

The Ms "Pingos as hot spots of methane emissions" is a very interesting ms about the groundwater flow related to the special features of pingos. The Ms is very well written, the results are presented and discusses in concise manner. Almost perfect.... Only one major drawback I realized at the end of the study: The emissions or flux of methane from a water body (river, sea, lake) is related to the difference between the measured concentrations (Cw) and the equilibrium concentration (Cequ) of methane in this water; and the gas-water transfer velocity (k). J = (Cw - Cequil) x k Thus, the calculation and assumptions drawn are wrong, and this part has to be corrected! Also, the way the flux / emission is finally calculated should be explained in the M&M section.

We appreciate the positive comments and acknowledge that the perceived drawback related to our flux calculations needs to be addressed in the paper. Since no comments other than the flux calculation issue require consideration, we deal only with this point below.

Our manuscript acknowledged that it "crudely" estimates the methane release from pingo waters to the atmosphere. It did so by assuming that all waters achieve equilibrium with the atmosphere due to turbulence and freezing effects. This is further simplified by the fact that the equilibrium concentration is negligible compared to the initial concentration and so can be ignored. The equation given by the reviewer is most relevant for cases where equilibrium is not achieved – for example with standing water bodies like lakes, or the sea, with a continuous influx and significant residence time caused by storage. However, envisage a turbulent spring flowing without such storage in a pond, and freezing while it does so. These conditions render the above calculations rather unsuitable, and they fail because the coefficient *k* is impossible to define. A further issue is that the proposed method does not account for the ebullition of gas, and so might underestimate the gas flux. The reviewer's comment is valid for one or two of our sites during the summer though, and we completely accept this criticism. In fact we have already employed the recommended approach in a different paper about one of these sites (Hodson et al, 2019). Given these uncertainties, we took the Editor's advice and presented a more qualitative argument about the likely importance of the fluxes to the atmosphere. Further details are below – but note the extensive changes to Section 4.3.

Reviewer 2.

We thank the reviewer for also complementing the paper for being and well-written.

The development of an open system pingo should be explained in more detail. It was unclear to me, how liquid water may find it's way through the permafrost. What is the temperature of the permafrost? Are these open system pingos particularly

developing above marine sediments? What is the difference to a 'normal' pingo? It's particular difficult to understand since the cited reference (L57) is not given in the list of references.

The citation, which describes the formation process for lagoon Pingo has been corrected (line 58). Since only a brief description about formation is given in the introduction (lines 58 – 61), more comments on the Adventdalen pingos are included in Section 2.1 (lines 73 – 81), where there are three further citations. Unfortunately, we do not know the temperature of the permafrost in this area.

Furthermore, more background information should be given on the geology of the study sites, including the geology of the surrounding mountains that may affect the composition of the spring water. Is there a connection between the springs and fresh meltwater (as suggested in lines 275ff)? Is there a talik below the river and might this be connected to the springs?

We acknowledge the need for more background information regarding the genesis of the pingos, the geology and the type of methane that might be present. This information is now included in the field site section, in lines 95 onwards. We also improved the representation of the geology in Figures 1 included a new Figure 2b – all described from lines 95 to 108. Two new citations have been included too. From lines 110 to 117, we have used new citations and added additional text (some of which was originally described in "Section 2.4: Other data resources") to better integrate existing knowledge into the description of the field site. The discussion also uses this information to explore the links between the shale unit and the geochemistry, due to the unusual observations at River Bed Pingo (distal site) in 2017 (line 297 onwards).

Furthermore, more background information on the potential source of the methane in the spring water should be given. The authors differentiate biogenic and geogenic sources. However, it should be made more clear which ge-ogenic sources might be present, gas hydrates or natural gas from deep deposits? Is there information on these sources in the region, and what is the carbon stable isotope signature of these sources?

We have included more information in the above section between lines 110 – 117. Since hydrates could be composed of any gas origin (ie bio or geo-genic) and since it is not known if any are indeed present in the valley, we decided not to discuss hydrates in the introduction.

Concerning the biogenic source, it should be explained why high methane concentrations in marine waters are expected. Generally, no methane is produced as long as sulfate is present. In contrast, methane, e.g. from gas hydrates is oxidized with sulfate as electron acceptor.

The reviewer raises a good point here on account of the potential for sulphate reduction to out-compete methanogenesis. We made the point because Cl correlates with methane concentrations. We now think other processes could cause this and so we have removed this point.

The discussion concerning the methane sources is rather speculative due to a lack of data. The carbon stable isotope signature is only a weak indicator for differentiating geogenic and biogenic methane sources. If only the carbon stable isotope signatures of methane are available and no delta D or concentrations of further hydrocarbons, as in this manuscript, no differentiation between geogenic and biogenic sources is possible. E.g., gas hydrates may have carbon stable isotope signatures between about -40 and-70‰ a range covering the whole values given in this manuscript.

The reviewer implies that our discussion about methane provenance is weak because it is entirely based upon 13C-CH4. The reviewer then implies that we cannot discriminate between geogenic methane, biogenic methane and hydrates. But hydrates are not a source of methane – they are a transient store of either geogenic or biogenic methane (or a mixture of the two). We therefore seek only to assess whether there is any evidence for geogenic methane in the water, largely because previous work has demonstrated a clear dominance of biogenic methane just beneath the permafrost at our field site. As a result, we respectfully suggest that there is no need for the dD-CH4 isotopes because:

i) 13C-CH4 alone can rule out geogenic when the values are low, and we have many low values that fall outside this "geogenic range".

ii) An earlier study of methane in pore spaces conducted at our site uses CH4 concentrations, δ^{13}C-CH4, δ^{13}C-DIC and the presence of other hydrocarbons to establish the relative abundance of biogenic versus geogenic methane from the surface down to ca. 900m (Huq et al, 2017). This work clearly shows that the geogenic methane fails to migrate effectively into the aquifer beneath the permafrost. This work does not require delta-D because the presence of other hydrocarbons is used as a reliable indicator of geogenic CH4 instead (Huq et al, 2017). This information is included in Figure 4.

iii) The above study shows that there is a methane source in an aquifer immediately below the permafrost that is largely biogenic.

iv) The biogenic methane inferred from Huq's study was also found by a mining company, who reported a salty groundwater body just beneath the permafrost with a 13C-CH4 range (-48.9 ‰ to -52.9‰) that is almost identical to that found at our nearby pingos sites (ie River Pingo and Innerhytte Pingo: -49.7 ‰ to -57.8‰ as in Table 2). Their reported salt content was 1500 mg/L, which is also almost identical to that found at these two pingos (1380 –1540 mg/L: Table 1).

v) At the other two pingo sites, the 13C-CH4 values either lie within the same range as the above, or are even lower (more 13-C depleted) and therefore too low to be geogenic.

We therefore conclude that there is almost no evidence for a significant geogenic methane contribution to our springs. We have edited lines 250 - 261 and Figure 4 to make incorporation of these other data clearer and more compelling. We also included reference to our new publication about the deeper geogenic gas (Ohm et al, 2019).

But the weakest part of the discussion is the part on the pingos as methane emission hotspots. The authors derive spring water fluxes from an unpublished study on Adventdalen's groundwater system, add unpublished data on methane concentrations in a 'neighboring lake', which contributes about 1/3 to the total flux estimate and assume that 100% of the methane in the water will be emitted to the atmosphere. Estimating methane fluxes from water concentrations comes along with high uncertainties. It might be possible for pond, lake or sea water. However, in soils, bacteria will likely oxidize a large fraction of the methane as soon as oxygen is available. Hence, methane fluxes will likely be much lower. To derive meaningful data on methane fluxes from soil surfaces, emission measurements should be conducted.

We tend to agree that the emission estimates are the weakest part of the paper, but feel that their potential significance should still be addressed. We have therefore followed both the reviewer's and the editor's suggestion to achieve this with a more qualitative approach, which is now described between lines 344 – 348.

However, since we respectfully disagree with some of the criticisms directed towards our emission estimates, we first wish to offer the following explanation (that could have been clearer in our initial manuscript):

Methane consumption in soils "will likely oxidize a large fraction of the methane as soon as oxygen is available".

We point out that soils are frozen for much of the year, yet the springs we study are constantly discharging, usually over a smooth ice surface. Furthermore, we seldom find the springs infiltrating into soils before much of their methane has been lost. In summer, the springs erode turbulent channels through impermeable marine clays or cascade down the flank of the pingo – which is also conducive to rapid degassing to the atmosphere but not really to methanotrophy. However, at pingos where lakes form upon their summit, then methanotrophy is indeed more likely. These points have been incorporated into the new Section 4.3 along with some new empirical evidence and a new figure (Figure 5) (see lines 371 - 404) that demonstrates rapid methane loss.

To derive meaningful data on methane fluxes from soil surfaces, emission measurements should be conducted.

We do not wish to derive such data because we are describing emission from springs, not soils. Our springs by-pass the soil environment. We hope that the new text described above helps clarify this

The authors derive spring water fluxes from an unpublished study on Adventdalen's groundwater system...

This study is Hornum et al, currently under revision and available to the reader as a discussion paper. It provides a lot of necessary background data, but we have greatly reduced the dependence upon this paper (at the Editor's request) and have made the whole section simpler and easier to follow. All speculation about springs not sampled in our study has been removed. One additional site, "Lagoon Lake" has been included though, because it is clearly part of the Lagoon Pingo system, and we present sufficient measurements from this site to justify its inclusion (lines 360 – 362). Table 3 has been changed and the source of the information used for the fluxes made clear in the caption.

Furthermore, there seems to be a mistake in the calculation of the land fluxes from Adventdalen valley using the Pirk et al. (2017) paper and the active layer fluxes seems twice as high (see specific comments) as given in this manuscript. In this case the relative contribution of the sub-permafrost fluids is reduced by 50%.

We regret that the reviewer has made a mistake – which is easy to do on account of the wording in the Pirk paper. This issue is dealt with under specific comments below.

Furthermore, the winter fluxes are not considered in these estimates, which might be as high as the summer fluxes (see Zona et al., 2016).

The Pirk et al (2017) study does in fact include the freeze-up processes that were emphasised by Zona et al's (2016) study. After this period, the (late) winter emissions in Adventdalen have not been studied much, although Pirk et al (2016) did some pre-melt chamber work one April/May and found great suppression of the methane flux by icing layers. Where such layers were less prolific (in Zackenberg, Greenland – not Svalbard), the winter fluxes were one to two orders of magnitude lower that those before the end of freeze up. Therefore, no amendments to the manuscript were deemed necessary concerning this point.

Concluding, I suggest changing the title of the manuscripts, since it indeed does not measure methane emissions. Furthermore, I would downplay the calculations of methane emissions and more clearly consider their uncertainties. The authors mention that it is only a 'crude' estimate, which is correct. In this case, this crude estimate should not be in the focus of the manuscript by mentioning it in the title and elaborating it over more than half of the discussion. The authors may dicuss the emissions in a more qualitative way and also include information about the abundance of such springs, if available.
We have changed the title to better reflect the role of the pingos and have also changed the signposting at the end of the introduction section to emphasise that the paper is largely about the exploitation of pingos by the gas-rich fluids (line 62 to 70). We have also changed the emphasis of Section 4.2 to remove emission estimates.

Finally, the reference list needs attention.

Done

Specific comments:
L31: This quote does not fit here very well, better cite particular studies that are 'quantifying the release of methane from the active layer during summer thaw' and not a general review on the permafrost carbon feedback.

A new citation has been added that incorporates active layer emissions and methane cycling into a global review. I changed the sentence to make the lack of explicit active layer studies acceptable.

L57: This reference is not given in the list of references

The citation has been corrected (see line 58)

L138 ff: How were gas pressures measured in the vials and which CH4 solubility was assumed?

Details of the number of standards, the linear calibration range used and the detection limit are now included lines 171 - 174. The analytical process does not measure pressure as no pressurisation occurs during headspace formation. Appropriate amendments have been made to the text to make this clear (line 169). We use the Bunsen Solubility Coefficient (a proxy for gas solubility) to account for temperature effects upon the solubility value.

L214: Excess CO2 seems to correlate with methane concentration not it's variation.

Changed (line 239)

L225f: What means 'overlaps closely'?

Changed (on line 250)

L239ff: The last part of this paragraph belongs to the discussion.

Done. See deletion from line 269

L258ff: The 'distal' samples not only seem to be different but they very obviously are.

Sorry, there might be some British understatement in here. We have completely changed how we introduce these "distal samples" because it is now obvious to us that they aren't linked to the pingo like we thought they might have been. See lines 134 and then again in the results (lines 213 - 215) and discussion (lines 280 -286).

L265ff: I find this paragraph confusing and the conclusions not convincing. It is indeed counterintuitive to expect that the influence of marine waters are higher the farther one comes from the sea. Furthermore, this conclusion is only supported if a part of the dataset (distal samples) is omitted from the analysis, but there is no justification given to do so.

We felt we simply cannot ignore the strong influence of sea water upon the methane concentrations that is made obvious by our results. The likely causes of the counter-intuitive Cl- gradient are explained in our companion paper (Hornum et al, TC Discussions) and have been addressed in lines 295 - 301. We have also worked hard to justify the omission of the River Bed

Pingo Distal samples throughout the paper (see above), after realising that we had done a poor job of explaining it in the first manuscript. However, it is perfectly reasonable to do this in our opinion.

Furthermore, it is unclear why the system is more diluted downstream by fresh groundwater from snow and ice melt.
The system is increasingly diluted by fresh groundwaters because the valley is flanked by plateau highlands (line 301 and Figure 2a). See also response to next point.

I understand, also from Fig. 4 that the sampled water originates from below the permafrost. In this case, the up-valley sites should be more influenced by melt water.

Not really. The permafrost thicknesses are greater inland, so waters could be emerging from greater depths. This means the likelihood of denser, more saline springs increases inland. The issue is discussed at length in Hornum et al and so we feel uncomfortable extending our discussion to cover all of this hypothesis. However, we hope that the substantial amendments from line 295 cover the matter sufficiently without heavy reliance upon Hornum et al (In Review) at the request of the Editor.

L286ff: The explanation of the variability in CH4 stable isotopes is unclear. Why should CH4 oxidation preferentially take place while the fluids are trapped below an ice lid and not during it's transport to the surface or after surface thaw?

We argue that rapid switching in the source signature of the methane arriving at the pingo is unlikely because the system has a constant flow and long residence time. Rapid switching to 13C-enriched methane therefore seems most likely to be caused by the variable outburst cycle from beneath the ice blisters that form on the pingos. Methane gradually oxidises beneath the lid, then outbursts and refills once more, allowing "fresh" methane to mix with any residual "old" methane. Since the outbursts occur i) from different elevations on the pingo (thus emptying the ice blister to different degrees), and ii) after different storage times beneath it, the variability in 13C results from different mixing ratios between "fresh" and "old" methane at the time of sampling. It is unlikely that oxidation occurs during transport to the surface because the process is rapid compared to the storage time beneath the ice lid. Far less oxidation effects are therefore apparent in summer, when no such storage exists. See lines 311 – 323. Some oxidation prior to the ascent to the surface is also described in the discussion ending on line 340.

To oxidize methane, an electron acceptor is needed, the respective microorganisms and liquid water but not stagnant water. And what might be the electron acceptor for methane oxidation? The fluids seem mostly oxygen free and low in sulfate.

We appreciate the comments here. We will describe methanotrophy in a forthcoming paper, which has found that it occurs in the marine muds (at Lagoon Pingo and Forstehytte Pingo) but not the shale rock debris mantle on Innerhytte and River Pingos. We think it is beyond the scope of the present paper to describe this molecular work here, not least because we have found a novel organism at Lagoon Pingo. It will also support our assertions about why 13C-CH4 signatures at Lagoon+Forstehytte Pingos differ to Innerhytte+River Bed Pingos.

L310: What means 'favorable thermodynamic conditions' in this context? Favorable for which process?

The comment has been removed.

L317ff: I understood from L286ff that the springs are frozen in winter. Please clarify.

Partial freezing of the springs in winter forms an ice lid. This gradually expands upwards, then fractures and releases the spring water. It then flows over ice, releases methane and refreezes to form an icing. We regret not describing these processes further and have included appropriate text to describe what happens on lines 122 - 127

L 331FF. Please give the reference for 'this paper'. Furthermore, clarify to which paper the newly introduced data from the 'neighboring lake' belong.

Done (re proper reference of Hornum et al, TC Discussion paper). The additional data were the authors' own observations from just prior to submission and methane levels and dates of sampling are included in the text (line 360).

L345: Pirk et al., 2017?

Yes, corrected

L347f: This calculation neglects aerobic methane oxidation, which might oxidize up to 100% of the methane before it is released into the atmosphere. Hence, the flux assumption from the springs is the upper limit of methane fluxes from the springs.

We agree it is an upper estimate, but would like to point out that 100% removal is impossible in the system under study. We have changed the emphasis of the discussion to avoid direct discussion of emission (see earlier comments and lines 344 - 348)

L363: Pirk et al. (2017 not 2018) report 'typically...a...seasonal budget of around 2gC m-2' (not 1 g C m-2) for the summer thaw season (1st June to 30th September) in Adventdalen. According to my calculation the annual flux from 4.7 km2 would then be about 12,600 kg methane yr-1 (not 6,040 kg methane yr-1).

Citation corrected. The quote from the Pirk et al paper unfortunately refers to the median of two sites: Adventdalen and Zackenberg (in Greenland). The emissions from Zackenberg are greater than those from Adventdalen. Quick scrutiny of Figure 5 in Pirk et al (2017) clearly shows that all of the median values at Adventdalen lie below 2. It is therefore hard to justify using 2 gC m-2 y-1 as a spatially representative value (not least because it includes data from elsewhere). For this reason, I digitised Figure 5 in Pirk et al and determined the minimum and maximum median values from their three year study. These values were used to produce the range of likely emissions from wetlands for comparison with our emission estimates from springs. This range is presented in Table3.

Furthermore, the winter fluxes are not considered in these estimates, which might be as high as the summer fluxes (see Zona et al., 2016).

We have responded to this above.

L375f: The meaning of this sentence ('The sensitivity...') is unclear.

Appropriate amendments to this sentence and the next.

L376ff: I cannot follow this calculation. Where does the number 50 L sec-1 come from? What is the Adventdalen terrestrial methane flux? In addition, why compare the total annual runoff of Adventdalen with the groundwater flux of 50 L- sec-1? The authors are aware that the methane concentration in surface melt water is several orders of magnitude lower than what they found in the springs with sub-permafrost fluids. This comparison is without meaning.

We intended a straight-forward discussion of the sensitivity of potential methane emissions to a change in the water budget here. Every river has a baseflow largely driven by groundwater. Here we have just 1.6 L/s of sub-permafrost groundwater contributing to baseflow. Literature argues that the amount is likely to increase (citation of Victor Bense's work, who has been consulted directly). We therefore demonstrate that for an increase to 50 L/s then the flux of methane available for emission from the entire valley could increase by five times. Although 50 L/s seems high relative to the situation at the moment, it would still only represent 0.001% of total annual runoff. Most watersheds have a far higher degree of groundwater flow contributing to total runoff, but this is continuous permafrost terrain. Appropriate amendments have been made to the paragraph (lines 412 – 419) to help explain the purpose of this paragraph. Note that the criticism deserves less attention now that we have decided to not attempt a direct emission estimate.

Table 2: Please also differentiate the "distal" samples from the River Bed Pingo

Done

Fig. 2 is difficult to read. Please give references for the published pore water data and please use units that make a comparison with the data in the tables possible (e.g. mgL-1 not µL mL-1)

We appreciate that the diagram (Figure 4) needs time to understand properly and have tried once more to make it less cluttered with some edits. However, the units cannot be changed because the graph brings in pore gas analyses for comparison to our aqueous concentrations.

Open system pingos as conduits for highly concentrated methane seepage in Svalbard

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Abstract. Methane release from beneath lowland permafrost represents an important uncertainty in the Arctic greenhouse gas budget. Our current knowledge is arguably best-developed in settings where permafrost is being inundated by rising sea level, which means much of the methane is oxidised in the water column before it reaches the atmosphere. Here we provide a different process perspective that is appropriate for Arctic fjord valleys, where local deglaciation causes isostatic uplift to out-pace rising sea level. We show how the uplift induces permafrost aggradation in former marine sediments, whose pressurisation results in methane escape directly to the atmosphere via ground water springs. In Adventdalen, Central Spitsbergen, we show how the springs are historic features, responsible for the formation of open system pingos, and capable of discharging brackish waters enriched with high concentrations of mostly biogenic methane (average 18 mg L^{-1}). Thermodynamic calculations show that the methane concentrations sometimes marginally exceed the solubility limit for methane in water at 0 °C (41 mg L^{-1}). With a combined discharge of just 1.6 L s^{-1}, four pingo springs transport a flux (1050 kg CH_4 a^{-1}) equivalent to between 10 and 17% of the methane emissions measured in local wetlands. This confirms that sub-permafrost methane migration deserves more attention for improved forecasting of Arctic greenhouse gas emissions.

1 Introduction

Methane evasion to the atmosphere from thawing Arctic permafrost represents a significant risk to future greenhouse gas management, and so great emphasis has been placed upon quantifying the global importance of methane release from the active layer (see Dean et al, 2018). However, the potential for methane evasion from deeper sub-permafrost sources also exists (Anthony et al, 2012; Betlem et al, 2019; Kohnert et al, 2017), but since the means by which the gas by-passes the permafrost are unclear, their possible timing, magnitude and impact are very uncertain. Recent research has provided significant insights

into the role of landscape change and methane release from low relief Arctic shelf environments typical of the Canadian, Siberian and North Alaskan coastlines (Kohnert et al, 2017; Frederick et al, 2016; Dmitrenko et al, 2016). Here, sea level inundation has enhanced methane escape by inducing permafrost thaw (Frederick et al, 2016). However, this mechanism is not relevant to many fjord coastlines in the Arctic because isostatic uplift has out-paced sea level rise (Dutton et al, 2015). Here, the uplift of sediments deposited in the fjord since the Last Glacial Maximum (LGM) has caused their exposure to the atmosphere, resulting in a period of freezing and permafrost aggradation (e.g. Cable et al, 2018; Gilbert et al, 2017, Gilbert et al, 2018). Fjord coastlines which have undergone significant isostatic uplift are typical of Svalbard, Novaya Zemlya, northern Greenland and the Canadian Arctic archipelago. It is therefore significant that these areas are poorly represented in our current understanding of pan-Arctic methane emissions from the land surface.

Fjords are notable for some of Earth's most rapid rates of sedimentation and organic carbon burial during glacial retreat, producing thick sediment sequences potentially conducive to biogenic methane production (Smith et al, 2015; Syvitski et al, 1986; Włodarska-Kowalczuk et al, In Press). In addition, the rocks underlying many Arctic fjords support either proven or highly probable natural gas resources (Gautier et al, 2009). Therefore methane from geogenic sources such as coal beds and shale is also likely to be present. At the LGM, widespread methane hydrate stability zones were present under the ice sheets, providing a transient reservoir for both the biogenic and geogenic methane. The warmer period that caused the onset of ice sheet retreat after the LGM caused the gas hydrates to become thermodynamically unstable, and the methane began to escape rapidly through the recently uncovered sea floor (Crémière et al, 2016; Smith et al, 2001; Weitemeyer and Buffet, 2006). Evidence for such rapid fluid escape include pockmarks (Crémière et al, 2016; Portnov et al, 2016) (Figure 1a), whose occurrence in Svalbard is particularly well-documented because some of them remain active today (Liira et al, 2019; Sahling et al, 2014). Sea floor methane emissions are subject to very significant removal processes due to dissolution and oxidation within the overlying water column (Mau et al, 2017). Further, Pohlman et al (2017) have shown that sea floor gas emissions in coastal waters off Svalbard may also be offset by far greater rates of atmospheric CO_2 sequestration into the overlying surface waters, because the rising bubbles help nutrient-rich bottom waters rise up to fuel the photosynthesising plankton community. However, Hodson et al (2019) showed that pockmarks exposed by isostatic uplift have the potential to form methane seepage pathways on land. Since any groundwater carrying the gas through the permafrost will be subject to freezing temperatures, these features are likely to become discernible as small, ice-cored hill forms known as open system pingos (Figure 1b). Therefore, pingos and other terrestrial seepages must be considered as migration pathways through what is otherwise regarded as an effective seal or "cryospheric cap" formed by the permafrost (Anthony et al, 2012). Such routes potentially represent the most harmful greenhouse gas emission pathway for methane trapped beneath permafrost, because gas can escape directly to the atmosphere without removal by oxidation within the overlying water column of the fjord.

This paper therefore investigates how methane-rich fluids readily escape from beneath permafrost by exploiting the open system pingos that have formed following isostatic uplift and permafrost aggradation in Svalbard's fjord landscape. We show

that the pingos form natural "hotpots" for the ventilation of sub-permafrost methane directly to the atmosphere, with the potential to account for a meaningful proportion of the total annual methane emissions in Adventdalen, a representative, well-researched fjord valley system in Central Spitsbergen, Svalbard.

2 Methods

2.1 The field site

Adventdalen's open system pingos are located in a lowland valley that has been rapidly in-filled by a pro-grading delta system throughout the Holocene. This was driven by ice sheet retreat commencing ca. 11 000 years ago (Gilbert et al, 2018) and is represented by the landscape model in Figure 1. As with many open system pingos in Central Spitsbergen, their formation was intricately linked to changes in groundwater dynamics that occur after such deltaic sediments emerge from below sea level and start to freeze. This permafrost aggradation increases hydraulic pressure and thus forces residual groundwaters toward the land surface. Since the hydraulic conductivity of the fine-grained, uplifted marine sediments is very low (Toft-Hornum et al, In Review), the fluids are likely to exploit any former pockmarks that are uplifted with them (e.g. Hodson et al, 2019). Further freezing near the surface then results in expansion and the formation of a small hill with an ice core, or "pingo" up to 40 m higher than the surrounding topography (Liestøl, 1996; Yoshikawa et al, 1995; Yoshikawa, 1993). Figure 2a shows that two pingos (Lagoon Pingo and Førstehytte Pingo) are situated in the lower part of the valley, whilst two others (Innerhytte Pingo and River Bed Pingo) are up-valley, and just beyond the former marine limit at ca. 70 m asl. Lagoon Pingo, nearest to the coast, is thought to be less than 200 years old, and has had springs documented from as early as 1926 (Liestøl, 1996; Yoshikawa and Nakamura, 1996). At Førstehytte Pingo, a spring has also been known to exist since the 1920's, but the pingo is thought to be much older. Radio-carbon dates for molluscs in the marine sediments uplifted by the Førstehytte Pingo give a maximum age limit of 7000 ± 70 years (Yoshikawa, 1993; Yoshikawa and Nakamura, 1996). Innerhytte Pingo and River Bed Pingo are of unknown age, and since they lack a cover of marine sediments containing mollusc shells, no radiocarbon dates are available.

Like many fjord valleys, the rate of sedimentation was extremely high during ice sheet retreat, and so a "wedge" of up to 60 m of valley in-filling has occurred within the former marine limit (Cable et al, 2018; Gilbert et al, 2018). However, the permafrost in the valley floor of Adventdalen is up to 120 m thick, so much of the fine sediments have frozen since their exposure by isostatic uplift during the Holocene, with the exception of the sediments closest to the contemporary shoreline and pockets of saline "cryopegs" further up-valley (Keating et al, 2019). There are no taliks beneath the river, because river discharge volumes drop rapidly in late August and allow freezing to commence early in the winter. Although the typically fine-grained, frozen marine sediment infill in the valley has a low hydraulic conductivity, the underlying glacial tills, and in particular the upper (unfrozen) geological strata beneath that, both seem to support important sub-permafrost fluid migration pathways (Huq et al, 2017; Hornum et al, In Review: Figure 2b). Unique insights into the sub-permafrost geology were provided by the legacy of geological exploration in the region, currently managed by the Store Norske Spitsbergen Kulkompani

(SNSK). This provided unpublished borehole records and geochemical data that allowed us to better understand the presence of methane and groundwater beneath the permafrost. Furthermore, geochemical and geophysical analysis of deep rock cores have also been undertaken in the valley as part of the UNIS CO_2 Project (Braathen et al, 2012; Olaussen et al, 2019). Key sites for these earlier investigations are shown in Figure 2a. Of particular importance are the permeable, fractured sandstones of the Lower Cretaceous Helvetiafjellet Formation immediately beneath the permafrost westwards of Innerhytte Pingo, and a ca. 400 m-thick Lower Cretaceous to Middle Jurassic mudstone-dominated succession beneath that (the Rurikfjellet and Agardfjellet Formations). The mudstone succession also outcrops eastwards from Innerhytte Pingo, as well as to the north at the base of the mountains (see cross section, Figure 2b). Fractured, uplifted mudstone clasts therefore form the mantle lying over the Innerhytte and River Bed Pingos, whilst younger marine muds form the mantle over Førstehytte and Lagoon Pingos.

Earlier work has shown that the fractured sandstones host an important, biogenic methane-rich aquifer, whilst the mudstones form an effective flow boundary that seems to suppress the upward migration of its own geogenic methane resource (Huq et al, 2017). The gas-rich upper sandstone aquifer therefore contains few hydrocarbons other than methane, whilst in the lower mudstone successions, ethane and propane have been detected at levels indicative of a geogenic gas source (Huq et al, 2017; Ohm et al, 2019). Fluid migration through the outcropping mudstones to Innerhytte and River Bed Pingos is therefore likely to exploit faults (shown conceptually in Figure 2b, but very poorly understood), whilst fluid migration towards Førstehytte and Lagoon Pingos is likely to exploit the fractured sandstones of the Helvetiafjellet Formation and glacial tills immediately beneath the permafrost (Figure 2b).

Four of six open system pingos in Adventdalen discharge groundwaters all year (Figure 2). In the summer, the springs are discernible as a discrete conduit discharging either into the base of a small pond (e.g. Lagoon Pingo), directly out of the pingo and down its flank (Førstehytte Pinge, Innerhytte Pingo) or straight out of the base of the pingo and into the Adventelva river bed, which may or may not be flooded due to its braided nature (River Bed Pingo). During summer, surface meltwater flooding in the valley hinders access to the pingos, since the river must be crossed to gain access. At other times of the year, after freezing has commenced (usually late September until mid-May), spring water accumulates beneath a large ice blister. The pressure caused by continuous flow expands the ice blister, forcing its summit upwards by as much as 4 m by the end of winter. The expansion is periodically checked by turbulent outbursts of water that typically freeze within 100 m of the pingo. All four springs were sampled before the melt season after drilling up to 2 m through their winter ice cover, releasing pressurised flow.

2.2 Fieldwork

Field work involved consecutive spring-time sampling campaigns (March - April) at the four pingos from 2015 until 2017. In addition, opportunistic sampling at the pingos was conducted in summer 2017, where low river levels made access to the field

sites possible. We focussed our sampling on the larger, discrete springs that were closest to the pingo summit, but in 2017 the spring that was sampled at River Bed Pingo was in a different location to previous years (away from the foot of the pingo). This site is hereafter referred to as "River Bed Pingo Distal" and is discriminated for reasons that become apparent when our results are considered.

Pingo springs were sampled after drilling up to three metres through their winter ice cover using a 7 cm diameter Kovacs drill and Stihl two-stroke engine. Although the icing surfaces were sometimes visibly cracked, with an outflow of water, drilling was still employed to reduce the likelihood of oxygenation before sampling and contamination from local snow. At the sampling site, pH, temperature, dissolved oxygen and Oxidation-Reduction Potential (ORP) were recorded using Hach Lange HQ 40D meters and dedicated electrodes/sensors. These were calibrated prior to use with the exception of the dissolved O_2 measurement, which was conducted using the luminescence method and thus used a factory calibrated sensor tip. To prevent freezing problems and electrode malfunction, water samples were pumped through a bespoke, air-tight flow cell with an internal heating element maintaining the sample flow at ca. 7 ºC.

2.3 Analytical work

Samples for dissolved iron and manganese analysis were syringe-filtered immediately in the field through 0.45 µm filters into pre-cleaned 15 mL Eppendorf Tubes, before acidification to pH ~ 1.7 using reagent grade HNO_3^-(AnalaR 65% Normapur, VWR, IL, USA). The analysis of dissolved Fe and Mn was then completed using Inductively Coupled Plasma Mass Spectrometry or ICP-MS (PerkinElmer Elan DRC II, MA, USA). Precision errors of the analyses were < 5% according to repeat analyses of mid-range standards, with a detection limit of 1.0 µg L^{-1}. No contaminants were detected above this limit in the analyses of blank deionised water samples. Samples for major ion analysis (here Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}) were also filtered in the same manner (but not acidified) and stored in 50 mL Corning centrifuge tubes after being triple rinsed with filtrate. The analysis was conducted on Dionex DX90 Ion Chromatographs with a detection limit of 0.02 mg L^{-1} for the lowest, undiluted analysis. Precision errors for these ions were all <5% for mid-range standards.

Charge balance calculations were used to provide the indicative values of HCO_3^- and CO_3^{2-}, given (as DIC or dissolved inorganic carbon) in Table 1. Excess CO_2 levels were estimated from calculations of the partial pressure of CO_2 using the online WEB-PHREEQ Geochemical Speciation Software (https://www.ndsu.edu/webphreeq/).

Samples for the determination of dissolved methane and carbon dioxide concentrations as well as δ^{13}C-CH_4 and δ^{13}C-DIC of the waters were taken directly from the spring following immersion, complete filling and sealing of a 22 mL Wheaton bottle with a crimp-top lid with septum. The samples were stored inverted under water at 4°C until analysis. The analysis of the CH_4 was performed by gas-chromatography on a Shimadzu GC-2014 instrument equipped with a methaniser and flame ionisation detector, using a 30 m GS-Q, 0.53 mm internal diameter column with N_2 as a carrier gas at a flow rate of 8 mL/minute, and

injection, oven and detector temperature of 60, 40 and 240 °C, respectively. The sample size was 100 µL and the sample run time was 3 minutes at 40 °C. Concentrations of dissolved CH_4 were obtained according to a mass balance calculation for the samples (McAuliffe, 1971), in which a known volume of N_2 was injected into sample vials to create a headspace whilst allowing sample displacement through an outlet needle to prevent pressurisation (Tyler et al, 1997). After shaking and equilibration (2 h) the CH_4 partitioned into the headspace was analysed by GC-FID and the corresponding mass in the gas and aqueous phase was determined by Henry's law, to obtain a final concentration in the water sample. Six c~~C~~alibration gas standards were prepared on the day of analysis by serial dilution of certificated 60% CH_4: 40% CO_2 mixed gas using O_2-free N_2 as the balance gas. The calibration was linear across the range 0 – 140000 ppm v and the detection limit equivalent to ~ 0.017 mg L^{-1}. Repeat analyses of mid-range standards indicated a precision error < 1.3%.

Analysis of dissolved methane isotopic composition and concentration was performed using the gas headspace equilibration technique (Magen et al, 2014) (5mls sampled water were injected into a Viton-stoppered, He-flushed 120 mL glass serum vial). 10mls of the headspace was then flushed through a 2 mL sample loop, and injected onto a 25 m MolSieve column within an Agilent 7890B GC attached to an Isoprime100 Isotope Ratio Mass Spectrometer (IRMS) (Tyler et al, 1997). Analytical precision errors for samples > 3 ng-C were better than 0.3‰ for isotopic values, and < 3.5% for concentration, based on methane standard injections. $\delta^{13}C_{DIC}$ was measured by a Continuous Flow Isotopic Ratio Mass Spectrometer (Thermo-Finnegan Delta V with gasbench interface) and an error of 0.1‰. All $\delta^{13}C_{DIC}$ and $\delta^{13}C_{CH4}$ values are reported vs. the Vienna Pee Dee Belemnite standard.

Samples for water isotope analysis were collected as unfiltered 20 mL aliquots in a screw-top HDPE bottle. The bottles were subsampled into 1.5 mL vials with septa closures and loaded into the auto-sampler tray of a CDRS instrument (Picarro V 1102-i model). Each sample was injected and measured 6 times using 2.5 µL of water for each injection. Together with the samples, two secondary international standards (USGS 64444 and USGS 67400) and one internal laboratory standard (NTW – Norwich tap water) were measured, each injected 10 times in order to minimise memory effects. Final isotopic compositions were calculated using the calibration line based on the secondary international standards and reported in ‰ units with respect to V-SMOW on the V-SMOW – SLAP scale. The precision error of the measurements was 0.1‰ for $\delta^{18}O$ and 0.3‰ for δD.

~~**2.4 Other data resources**~~

~~Unique insights into the sub-permafrost environment in Adventdalen were available to our study on account of the legacy of geological exploration in the region, currently managed by the Store Norske Spitsbergen Kullkompani. This includes many unpublished borehole logs and other insights into gas accumulation beneath the permafrost in Adventdalen, which were used for the benefit of the present paper. Furthermore, deep coring, borehole investigation and geophysical surveys have also been~~

~~undertaken in the same region as part of the UNIS CO_2 Project (Braathen et al, 2012; Huq et al, 2017), whose published data resources are used below to augment both our own data from the pingo springs, and unpublished data from the mining reports.~~

3 Results

3.1 Sub-permafrost groundwater chemistry inferred from pingo springs

Table 1 shows the geochemistry of all the water samples collected prior to the onset of snow melt from the open system pingos in Adventdalen. These waters were typically brackish (Cl^- concentrations 390 – 1600 mg L^{-1}), largely lacking in dissolved oxygen (0.00 – 2 mg L^{-1}) and NO_3^- (≤0.15 mg L^{-1}) and with a pH from circum-neutral to alkaline (pH 6.8 – 8.2). Figure 3A shows oxidation-reduction potential (ORP) measurements, indicating that strongly reducing conditions (negative ORP) existed nearest the coast (typically < -180 mV at Førstehytte and Lagoon Pingos) whilst higher, more variable values were encountered up-valley (-189 to + 130 mV) at Innerhytte and River Bed Pingos.

With the exception of the River Bed Pingo Distal samples from 2017, the generally observed water type was Na-HCO_3 with a saturation index (SI) for calcite indicating near-equilibrium ($SI_{calcite}$ = 0.1 ± 0.4) according to WEB-PHREEQ. The dominance of Na^+ over the other cations (Ca^{2+}, Mg^{2+} and K^+: Table 1) and the increasing Na^+ to Cl^- ratios towards the coast (Figure 3A) show how cation exchange (freshening) and rock-weathering effects were increasingly influential down the valley. Concentrations of SO_4^{2-} in most samples were far lower than expected when compared to late summer baseflow concentrations in local rivers (e.g. Hodson et al, 2016; Rutter et al, 2011; Yde et al, 2008). However, the River Bed Pingo Distal samples revealed a distinctly different spring water chemistry, with a Mg-Ca-SO_4 water type, far higher SO_4^{2-} concentrations and a saturation index for gypsum that reached equilibrium (SI_{gypsum} = 0.0 ± 0.1) according to WEB-PHREEQ. Otherwise, the River Bed Pingo samples from 2015 and 2016 showed sub-saturation with respect to gypsum (SI_{gypsum} = -2.9 ± 0.5). The markedly different Mg-Ca-SO_4 water type therefore suggested a different groundwater source whose composition was governed by gypsum-driven de-dolomitization, a process wherein very reactive gypsum catalyses the replacement of dolomite by calcite (Bischoff et al, 1994). ~~However, these samples were collected a greater distance from the pingo than those in 2015 and 2016. Further field observations in 2018 and 2019 (data not shown) clearly suggest there is another groundwater source here and further east.~~ This is further supported by the different $\delta^{18}O$-H_2O and δD-H_2O stable isotope characteristics of the River Bed Pingo Distal waters, which Figure 3B suggests were more similar to those encountered at Lagoon Pingo.

With the exception of the River Bed Pingo Distal waters, Figure 3B indicates a general westward depletion (decrease) in both water isotopes towards the coast, where water samples also lie closest to the Local Meteoric Water Line (LMWL) (Rozanski et al, 1993). Although Figure 4B shows that none of the waters depart significantly from the LMWL, a linear regression model

produces a lower slope (6.09) than that which is associated with the LMWL (i.e. 6.97), suggesting minor isotopic fractionation associated with partial re-freezing (Lacelle, 2011).

3.2 Methane geochemistry in the pingo springs

Table 2 shows that concentrations of methane in pingo spring waters in both the pre-melt season and the summer periods lay in the range 0.6 – 42.6 mg L^{-1}, which is up to five orders of magnitude greater than calculated atmospheric thermodynamic equilibrium values, and places the most concentrated values marginally above the solubility limit for fresh water at 0 ^{o}C (i.e. 41 mg L^{-1}). The data include samples collected opportunistically from the springs during the summer melt season. The dissolved carbon dioxide concentrations were also in excess of atmospheric equilibrium, by as much as 700 mg L^{-1} at Innerhytte Pingo. Temporal variability in the dissolved gas concentrations was significant at all sites, but greatest at River Bed Pingo Distal, where there were generally much lower methane and excess CO_2 concentrations. The methane concentration (at all sites) was positively correlated ($p < 0.05$) with excess CO_2 ($r = 0.86$: Figure 3C), the stable isotopes of water ($\delta^{18}O$-H_2O, $r = 0.86$ and δD-H_2O, $r = 0.91$: Figure 4D) and Na^+ ($r = 0.74$).

Table 2 shows that the $\delta^{13}C$ of methane and dissolved inorganic carbon ($\delta^{13}C$-CH_4 and $\delta^{13}C$-DIC respectively) were variable, especially at Lagoon Pingo and Førstehytte Pingo. The $\delta^{13}C$-CH_4 lay between -70.7‰ and -48.2‰ VPDB, which is indicative of biogenic methane at the ^{13}C-depleted (more negative) end of the scale, and either partially oxidised biogenic or geogenic methane at the ^{13}C-enriched (more positive) upper end (Schoell, 1980). Table 2 also includes samples collected opportunistically from the springs during the summer. These show that the methane concentration in summer is within the range reported during late winter. The $\delta^{13}C$-CH_4 and $\delta^{13}C$-DIC values of the summer samples are also similar to the late winter, although the $\delta^{13}C$-CH_4 is marginally lower (^{13}C-depleted) at Lagoon Pingo and the summer $\delta^{13}C$-DIC values at Førstehytte Pingo and Innerhytte Pingo are slightly higher (^{13}C-enriched) than typical values in late winter.

Figure 4 shows that all measured $\delta^{13}C$-CH_4 values in the pingo springs compare well with the results of the pore gas extractions (range – 53‰ VPDB to – 69‰ VPDB) from the upper core sections at the CO_2 Well Park (Well Site B in Figure 2: data from Huq et al, 2017). Here, the methane in the permafrost and underlying host rocks of the sub-permafrost aquifer has been attributed to a biogenic source because the $\delta^{13}C$-CH_4 values are moderately ^{13}C-depleted (i.e. more negative) and the concentrations of other hydrocarbons (propane and ethane) are low relative to methane (see Figure 4). Nearby, methane with $\delta^{13}C$-CH_4 between -48.9 and -52.9‰ VPDB, and no other detectable hydrocarbons, was also found immediately beneath the permafrost at Well Sites C and D in association with a Cl-rich (1500 mg L^{-1}) groundwater (Store Norske Spitsbergen Kullkompani, Unpublished Report SN1983-004). In this case, both the $\delta^{13}C$-CH_4 and the Cl^- concentrations compare favourably to the values at Innerhytte and River Bed Pingos. By contrast, the $\delta^{13}C$-CH_4 values from the pingos did not compare well with the ^{13}C-enriched $\delta^{13}C$-CH_4 values (range -50 ‰ to – 32 ‰ VPDB) recorded from the deeper shale unit (ie > 300 m:

see Figure 4) at Well Site B by Huq et al (2017). These values were assumed to indicate the deeper geogenic methane source because ethane and propane were also detected at significant concentrations relative to the methane (see also Ohm et al, 2019).

Figure 4 also shows that the δ^{13}C-DIC values (range -8.5‰ to +26‰ VPDB) observed in the pingo springs do not compare well with the values from the lower shale-rich units of the rock cores either (range -26‰ to +21‰ vPDB: Huq et al, 2017). This difference cannot be attributed to differences in the DIC speciation among our water samples (containing $CO_{2(aq)}$, H_2CO_3, HCO_3^- and CO_3^{2-}) and the published rock pore gas samples ($CO_{2(g)}$ only). The low δ^{13}C-DIC that is missing from the pingo water samples derives from organic matter respiration and is known to be present in local riverine runoff (δ^{13}C-DIC range -15‰ to -4‰ VPDB: Hindshaw et al, 2016). Therefore, the higher δ^{13}C-DIC signatures of the pingo springs are most similar to those seen in the upper aquifer zone of the cores~~, and for δ^{13}C-DIC in excess of +10‰ VPDB, may be attributed to the carbon isotope fractionation during the reduction of CO_2 to CH_4 during hydrogenotrophic methanogensis (Huq et al, 2017; Schoell, 1980)~~.

4 Discussion

4.1 Groundwater geochemical environment and methane concentrations

The geochemistry of the pingo springs is significantly different to surface waters in the Adventdalen watershed (see Hodson et al, 2016; Rutter et al, 2011; Yde et al, 2008). Their high Cl^- concentrations and distinct Na-HCO_3 freshening signature indicate ~~flushing~~ incorporation of brackish-marine ~~pore~~ water from either the uplifted, Holocene marine sediments, the fjord, or a mixture of the two. Importantly, the removal of nitrate and sulphate and the presence of biogenic methane indicate that microbially-mediated processes operate (denitrification, sulfate reduction and methanogenesis, respectively). These decrease the redox potential of the groundwaters towards the low ORP conditions found at the coast (Figure 3a). The strikingly different water chemistry dominated by Mg-Ca-SO_4 in the River Bed Pingo Distal samples during 2017 seems to indicate an additional ground water type that is strongly influenced by the gypsum- and dolomite-bearing rocks that outcrop east of Adventdalen, or lie at considerable depth (beneath the Agardfjellet Formation) within the study area in Figure 2. Due to the low hydraulic conductivity of the shale units of the Rurikfjellet and Agardfjellet Formations, their influence upon springs at the River Bed Pingo Distal site is presumably made possible by groundwater migration along the faults in the vicinity of pingo (Figure 2a). Otherwise, sub-permafrost groundwater migration in the study area seems dominated by the exploitation of the sub-permafrost aquifer hosted by the Helvetiafjellet Formation in the lower valley (see Hornum et al, In Review).

The strongest predictors of the methane content in the pingo springs are δ^{18}O-H_2O and δD-H_2O (Figure 3d). Since the δ^{18}O-H_2O and δD-H_2O show only a minor departure from the LMWL (Figure 3b), this indicates a strong water source control upon the gas concentration emerging from the pingos. Methane concentrations generally increase up-valley where δ^{18}O-H_2O and δD-H_2O become more ^{18}O-enriched. Since sea water is δ^{18}O- and δD-enriched relative to freshwater, the simplest, although

initially counter-intuitive explanation for this change, is an inland increase in the mixing ratio of marine ~~pore~~ water~~s~~ within the sub-permafrost groundwater. A statistically significant ($p < 0.05$) relationship between Cl^- and methane ($r = 0.74$) also becomes apparent when the River Bed Pingo Distal samples are excluded. The dependence of the methane concentration upon Cl^-, $\delta^{18}O\text{-}H_2O$ and $\delta D\text{-}H_2O$ is therefore consistent with deeper, denser sub-permafrost brines providing the water source to the pingo springs further inland. Hornum et al (In Review) show how this most likely reflects a general increase in the thickness of the permafrost with distance from the coast (shown crudely in Figure 1b). The presence of the Mg-Ca-SO_4 groundwater in the River Bed Pingo Distal samples is also consistent with this interpretation, because the gypsum-hosting Permian strata lie beneath the Agardfjellet Formation. Further down-valley, where permafrost is thinner, a greater mixing ratio of fresher, low density groundwater discharges from the pingo springs. Its more depleted (lower) $\delta^{18}O\text{-}H_2O$ and $\delta D\text{-}H_2O$ signature is consistent with dilution by snow and ice melt from the mountains that flank the main valley axis near the coast (Yde et al, 2008).

4.2 Methane sources and removal

Comparison of the pingo $\delta^{13}C\text{-}CH_4$ to the rock core gas samples in Figure 4 shows that mixtures of biogenic methane (lower $\delta^{13}C\text{-}CH_4$ signatures) and geogenic methane (higher $\delta^{13}C\text{-}CH_4$ signatures) might be present beneath the permafrost. However, evidence for a significant geogenic methane contribution to the pingo springs is equivocal and seems unlikely given the low rates of fluid migration that may be expected in the deeper shale-rich Rurikfjellet and Agardfjellet Formations. Therefore, the partial oxidation of biogenic methane most likely explains the occasionally higher $\delta^{13}C\text{-}CH_4$ signatures in the pingo springs, due to the preferential oxidation of the ^{12}C isotopes (leaving the residual pool ^{13}C enriched: Schoell, 1980). The most variable $\delta^{13}C\text{-}CH_4$ values were encountered at Førstehytte and Lagoon Pingos (mean ± 1 standard deviation: -58.8 ± 7.11‰ VPDB and -62.2 ± 8.81‰ VPDB, respectively) and include the only low $\delta^{13}C\text{-}CH_4$ values which can be attributed to biogenic methane with reasonable certainty (Table 2). Significant variations in these $\delta^{13}C\text{-}CH_4$ values sometimes occurred relatively rapidly, for example from -55.3 to -67.4 ‰ VPDB in just nine days at Førstehytte Pingo (April 2016), or from -62.0 to -48.3 to -55.6 ‰ VPDB over 34 days at Lagoon Pingo (March to April 2017). Rather than invoking an unlikely, rapid switching between geogenic ($\delta^{13}C\text{-}CH_4$-enriched) and a biogenic ($\delta^{13}C\text{-}CH_4$-depleted) methane sources, it is far more plausible that this variability was caused by changing degrees of oxidation of biogenic methane during storage beneath the surface ice blisters at the pingos. We therefore contend that as storage beneath an ice lid proceeds, the $\delta^{13}C\text{-}CH_4$ at these sites will become increasingly $\delta^{13}C\text{-}CH_4$-enriched until hydraulic or thermal fracturing allows the trapped fluids to escape. Methanotrophic microbial communities in the marine muds represent a plausible mechanism for the enrichment (Hodson et al, 2019). After an outburst event, refreezing then seals the system and the void fills once more with $\delta^{13}C\text{-}CH_4$-depleted, biogenic methane. As a consequence, the time elapsed since the last fracture event, as well as the volume fraction of the fluids that managed to escape before refreezing, are both likely to cause the notable variations in the $\delta^{13}C\text{-}CH_4$ of our samples. For this reason, Table 2 shows that samples collected opportunistically at these sites during late summer (when no ice lid existed) consistently showed the depleted $\delta^{13}C\text{-}CH_4$ values (i.e. between -60 and -70‰ VPDB) expected of a biogenic source.

The high methane concentrations at Innerhytte Pingo, sometimes observed near the solubility limit (ca. 41 mg L^{-1}), were characterised by limited variability in $\delta^{13}C\text{-}CH_4$ (mean (-54.4 ± 2.82‰ VPDB). The $\delta^{13}C\text{-}CH_4$ values at nearby River Bed Pingo (-54.5 ± 1.76‰ VPDB) were almost identical, and again showed far less variability than at Førstehytte and Lagoon Pingos. If the high concentrations and invariable $\delta^{13}C\text{-}CH_4$ are indicative of minimal removal or carbon isotope fractionation beneath an ice lid, then these results reveal a different (more ^{13}C-enriched) $\delta^{13}C\text{-}CH_4$ source signature than at Lagoon Pingo and Førstehytte Pingo. A mixture of geogenic and biogenic gas therefore seems more plausible here, not least because the $\delta^{13}C\text{-}CH_4$ signatures lie close to the geogenic methane $\delta^{13}C\text{-}CH_4$ signature inferred from the lower shale units by Huq et al (2017) (i.e. $\delta^{13}C\text{-}CH_4$ ca. -45‰ VPDB and above: Figure 4). However, the $\delta^{13}C\text{-}CH_4$ signatures are in fact closest to the gas discovered in the Helvetiafjellet aquifer just below the permafrost at Wells C and D (i.e. $\delta^{13}C\text{-}CH_4$ between -48.9 and -52.9‰ VPDB), which is known to be almost entirely biogenic because there are low or undetectable levels of other hydrocarbons (ethane and propane) according to both SNSK reports and Huq et al (2017). Furthermore, the high $\delta^{13}C$-DIC (> 10‰) at both Innerhytte and River Bed Pingos, also observed in the sub-permafrost aquifer by Huq et al (2017), are strongly indicative of CO_2 reduction by the hydrogenotrophic pathway of biogenic methanogenesis (Schoell, 1980). Therefore, the partial oxidation of biogenic methane also provides the simplest explanation for the presence of this gas at high concentrations in pingo outflows further up-valley.

4.3 Pingos and springs as methane emission hotspots

In spite of there being evidence for sub-surface oxidation and/or methanotrophy in our winter samples, our data clearly show that others reach, or even marginally exceed, the methane solubility limit (i.e. 41 mg L^{-1} in freshwater at 0 ^{O}C) prior to their discharge from the pingo. The potential contribution of the pingos to the annual land-to-atmosphere methane flux therefore deserves appraisal. We address this by first showing that the flux of methane transported to the land surface is significant compared to known wetland methane emissions in our study area. Then we describe how removal processes immediately after the spring waters discharge from the pingos are far less effective than is known to be the case with submarine emissions in the Svalbard region (Mau et al, 2017).

The flux of methane transported to the land surface was estimated from the product of the pingo outflow rates (water discharge) and their average methane concentration. The water discharge was assumed constant at each site, on account of the likelihood of prolonged residence time beneath the permafrost, our own visual inspection of the flows throughout the study, and the fact that discharge is largely driven by the gradual process of permafrost aggradation in response to isostatic uplift (Hornum et al, 2019; Yoshikawa and Harada, 1995). Our flow observations include monitoring that was undertaken at Lagoon Pingo, which demonstrated little seasonal variation in groundwater flow (Hodson et al, 2019). Published values of the pingo spring discharges are scarce, but range from 0.01 to 3 L s^{-1} (Hodson et al, 2019; Hornum et al, In Review; Liestøl, 1996; Yoshikawa, 1993). The flows used for each site are described in Table 3 and amount to a combined discharge of ca. 1.6 L s^{-1}. In addition

to the four pingo springs, a large spring discharge (measured at 0.52 L s^{-1} in October 2018) at a site 100 m west of Lagoon Pingo has been included after it was discovered to contain high methane concentrations. The average methane concentration of this site "Lagoon Pool" was 22.2 ± 1.9 mg L^{-1} (n = 4) according to samples taken through an ice cover in February, March and October, 2018. At these times, the electrical conductivity was very similar to the outflow at Lagoon Pingo and it was inferred to be the same water source.

Table 3 shows that the total methane flux from the pingo springs is ca. 1051 kg CH_4 y^{-1}. For comparison, rates of methane emission from chambers installed over the course of three years in an ice wedge polygon site in Adventdalen lie in the range 0 – 5 gC m^{-2} yr^{-1} according to Pirk et al (2017), with a median of ca. 1 gC m^{-2} yr^{-1}. Assuming that all other wetlands in the valley floor contributed equally (from an area of 4.7 km^2), the total active layer emissions were probably between 6040 and 10400 kg CH_4 yr^{-1}. Our estimates of pingo spring methane fluxes are therefore equivalent to up to 17% of the active layer emissions.

The magnitude of annual methane emission from the springs to the atmosphere very much depends upon the hydrological and meteorological conditions at each pingo site, as well as their variation during the year. During winter, all the sites were characterised by a large ice blister, from which periodic outbursts of methane-rich water occurred. During these outbursts, methane emission is most efficient on account of the flow turbulence and likely rejection of methane from the icing formed by the runoff as it gradually freezes (usually within 100 m of the outburst source). Measurement of the methane evasion from the outburst was impossible under winter conditions, although it was possible to capture the rapid, downstream loss of dissolved methane using samples taken opportunistically during an outburst event on 22nd April 2015. Figure 5 shows how the downstream methane concentration decreased with distance from the pingo icing summit in a manner described by a regression model of the form:

$$\left(CH_{4\,(aq)}\right)_x = 16.9X^{-0.384} \quad \text{Eq. 1)}$$

Where $(CH_{4(aq)})_x$ is the dissolved methane concentration at distance X (m) from the pingo icing summit. The coefficient of determination was 0.90 (n = 6) using only the 2015 data. Other samples from the base of the pingo in 2014 are used to show how methane concentrations at greater distances away from the pingo are far lower and thus consistent with further methane loss (see Table 2). The rapid loss of methane was not well accounted for by an exponential model, which yielded a coefficient of determination of 0.70 (not shown). Although this outcome is highly sensitive to the single data point at 3 m from the icing summit, it most likely implies that turbulence was non-linear along the flow path and greatly enhanced the rate of methane evasion as the spring descended the steep, initial part of the pingo flank. Freezing effects were not discernible in the 2015 transect until after the spring flowed onto the flat valley floor (ie beyond 50 m in Figure 5), where the flow velocities decreased markedly. With this being the case, the data show that 94 % of the methane was most likely lost to the atmosphere within 44 m of the inferred spring source. During winter, turbulence-driven gas exchange therefore seems most effective near the pingo summit, whilst freezing effects dominate once springs have flowed onto the valley floor (but add little to the overall flux).

During summer, significant changes at the surface of the pingos means that two key emission scenarios require consideration: i) a low emission scenario, caused by springs discharging straight into a receiving water body, such as a pool (Lagoon Pingo and Lagoon Pool) or the river (River Bed Pingo), and ii) a higher emission scenario caused by turbulent discharge down the flank of the pingo (Førstehytte Pingo and Innerhytte Pingo) and therefore similar to the winter emission scenario but with less freezing effects. Hodson et al (2019) examined the first scenario at Lagoon Pingo and showed that the pond which forms above the groundwater spring during summer reduces the annual emission flux to 42 kg CH_4 y^{-1}, which is 0.65 times the spring discharge flux according to Table 3. This reduction was caused by inundation of the site by meltwater (including that derived from ablation of the ice lid) and rainfall. We presume a similar reduction occurs every summer at River Bed Pingo Site, where a large river engulfs the entire spring. However, the pond that forms above Lagoon Pingo does not form every year due to the susceptibility of the drainage pathway at this site to the disturbance caused by its ice lid collapse. Therefore, by 2020, the system had reverted to a single spring discharging from a point source, rather like the situation at Innerhytte Pingo. Interannual variations in atmospheric methane emissions from pingos are therefore very likely.

The discovery of methane-rich sub-permafrost groundwaters discharging from Svalbard's open system pingos means that other perennial springs also deserve attention, because they may be carrying the same fluids. Modelling studies also imply that an increase in the discharge of groundwater systems into surface hydrological networks can be expected as climate change proceeds (Bense et al, 2012). Since these perennial springs result in the formation of winter icings similar to those encountered on the summit or flanks of the pingos, their detection is greatly facilitated. As a consequence, it is well known in Svalbard that they constitute groundwater flows greatly in excess of those observed flowing from pingos (Bukowska-Jania and Szafraniec, 2005). The sensitivity of the total atmospheric methane flux caused by the ventilation of sub-permafrost groundwater discharge is therefore potentially very important. For example, a total discharge of sub-permafrost groundwaters of just 50 L s^{-1} with a methane concentration of 17.9 mg L^{-1} (i.e. average of all values in Table 2) would mean more than five times more methane is available for emission from the land surface to the atmosphere (if active layer emissions remain constant). Such a groundwater discharge would still only represent 0.001% of the total annual runoff in Adventdalen during the study (A. Nowak and A. Hodson, Unpublished Data). Evidence for similar coastal groundwater springs with high methane concentrations that contribute meaningfully to emission fluxes exist elsewhere in the Arctic, including the MacKenzie Delta, Alaska, where they are thought to contribute approximately 17% of the emission from the delta (Kohnert et al, 2017). All forms of sub-permafrost groundwater discharge in Arctic coastal lowlands therefore deserve closer attention in order to better understand changes in the release of sub-permafrost methane to the atmosphere.

5 Conclusion

The development of open system pingos in Svalbard's coastal lowlands is linked to permafrost aggradation following isostatic uplift. This mechanism results in the expulsion of methane-rich sub-permafrost fluids over the course of centuries at individual sites, and establishes pingos as potential hotspots for greenhouse gas emissions. In Central Spitsbergen, the concentrations of methane in the springs that discharge from open system pingos are high (flow weighted average 17.9 mg L^{-1}, and can even marginally exceed the solubility limit of ca. 41 mg L^{-1}). The methane appears to be largely biogenic in origin and subject to moderate levels of oxidation. However a geogenic methane origin cannot be ruled out because it is present at greater depths beneath the permafrost. The methane is brought to the surface of Adventdalen after groundwaters have exploited faults through mudstones of low hydraulic conductivity to the east, and sandstones of high hydraulic conductivity to the west. The study of open system pingos therefore offers rare insight~~s~~ into sub-permafrost methane and groundwater dynamics. Since this is one of the least understood potential emission sources, open system pingos deserve greater research attention, so that sub-permafrost emission sources can be integrated with those from the active layer for better emission forecasts. In our study, ca. 1051 kg CH_4 yr^{-1} was transported to the land surface at~~released from just~~ four pingos with a trivial combined groundwater discharge of ca. 1.6 L s^{-1}. The high gas concentrations in the pingo springs that is responsible for this potentially significant emission shows that all types of sub-permafrost groundwater spring, however small, deserve appraisal as methane emission sources.

6 Data Availability

Detailed water quality parameters, including methane concentrations and isotopic composition, for groundwater springs discharging from open system pingos in Adventdalen, Svalbard (2015-2017) are available at https://doi.org/10.5285/3D82FD3F-884B-47B6-B11C-6C96D66B950D.

Author Contributions

AJH, AN, PB and MTH collected the samples and analysed the data, with significant input from SJ, KR and AVT. The laboratory samples were analysed by SFT, AJH, KR and AVT. AJH wrote the manuscript, with equal editorial input from the remaining authors.

Competing financial interests

The authors declare no competing financial interests.

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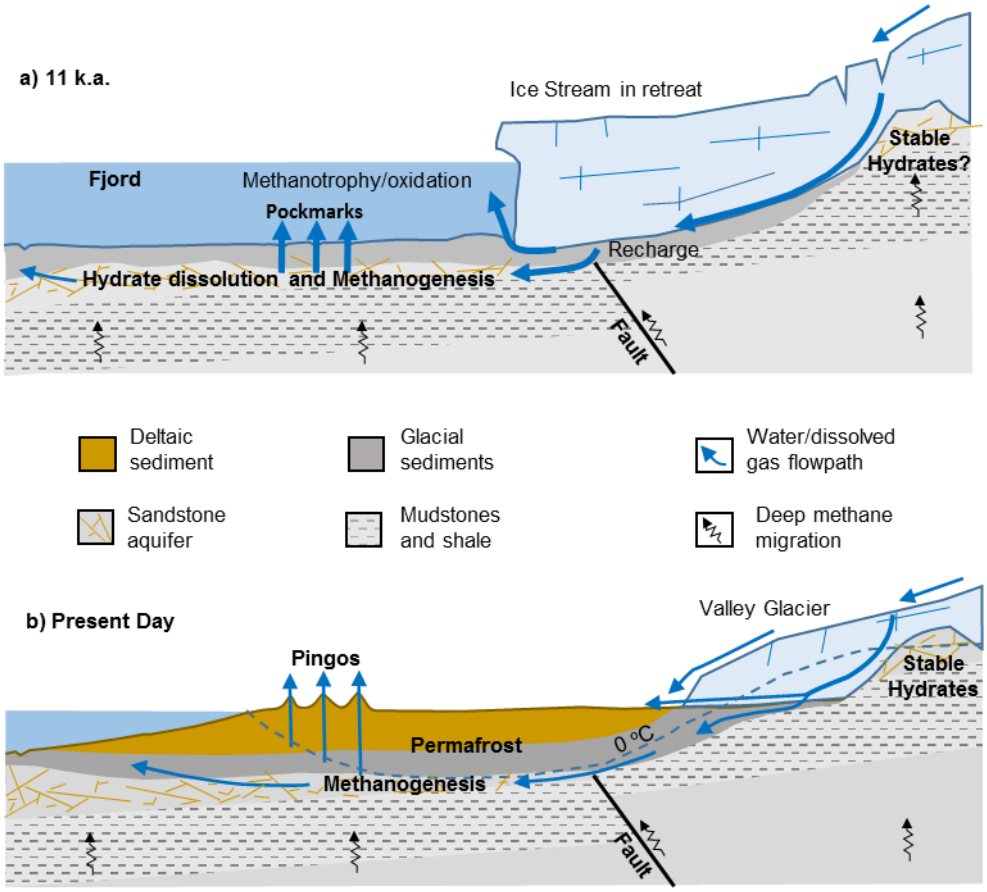

573

574 **Figure 1.** Landscape change and likely methane migration pathways in Adventdalen (thickness of geological units and
575 sediments not to scale): a) during deglaciation after the Last Glacial Maximum ca. 11 000 years ago, b) today, following delta
576 progradation, isostatic uplift and permafrost aggradation. The conceptual model of landscape change was based upon Gilbert
577 et al (2018).

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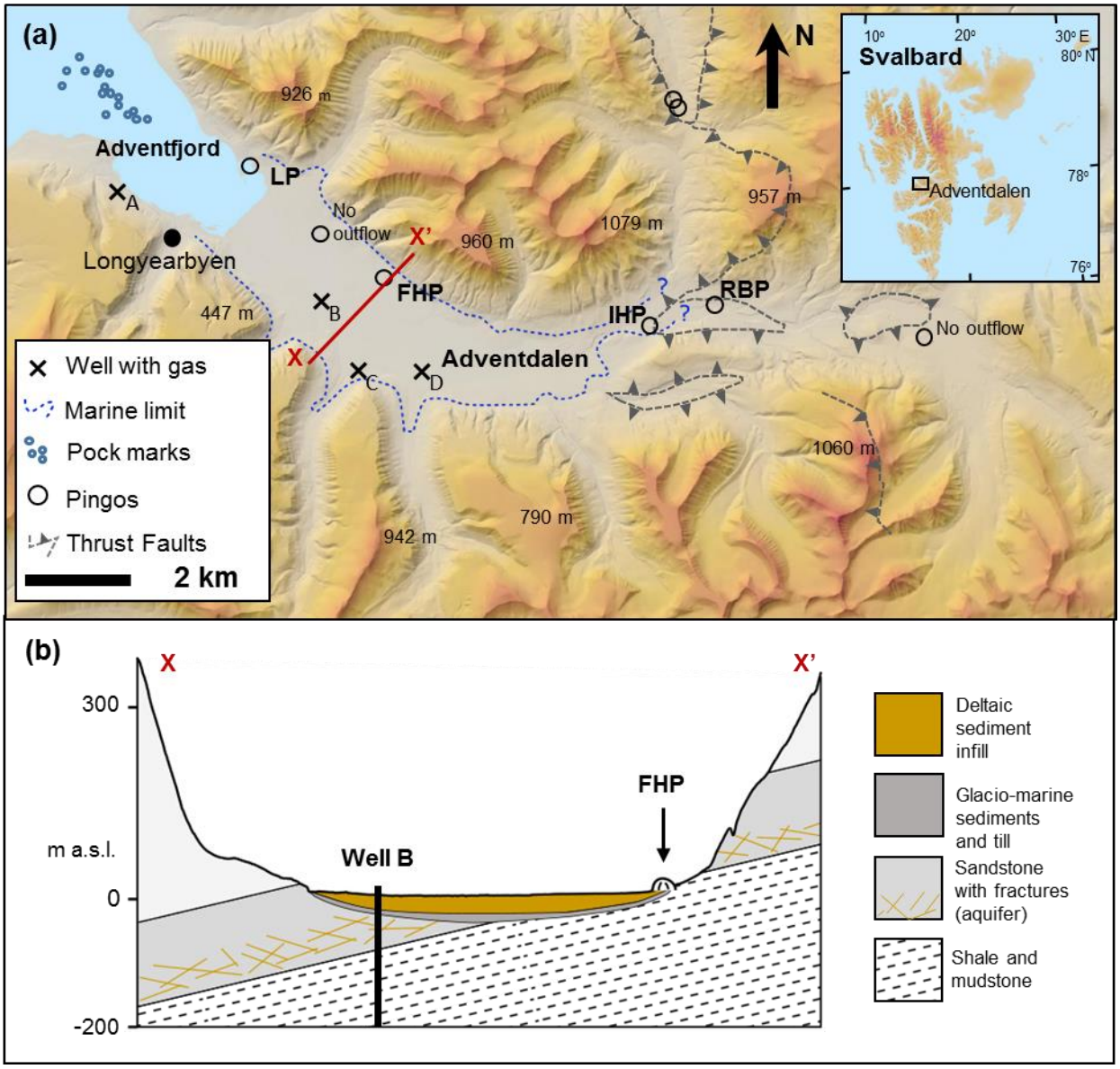

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586 **Figure 2.** Adventdalen topography, pingos and geology. Active springs exist at Lagoon Pingo, Førstehytte Pingo, Innerhytte
587 Pingo and River Bed Pingo (LP, FHP, IHP and RBP respectively). Well Sites A and B are part of the UNIS CO_2 Well Park
588 (Braathen et al, 2012), whilst Well Sites C and D are part of the Store Norske Spitsbergen Kulkompani (SNSK) operations.
589 Map developed online at www.svalbardkartet.npolar.no.

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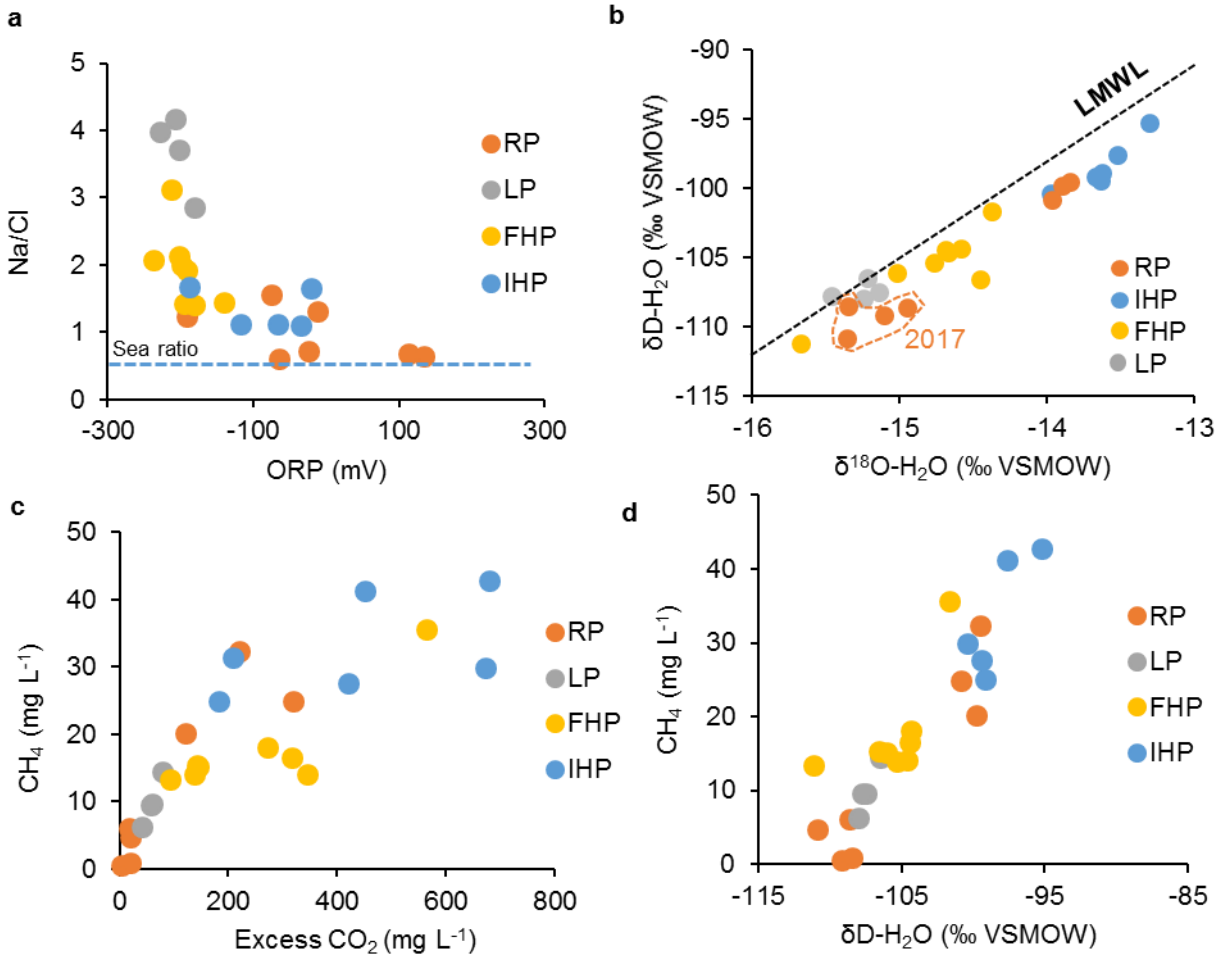
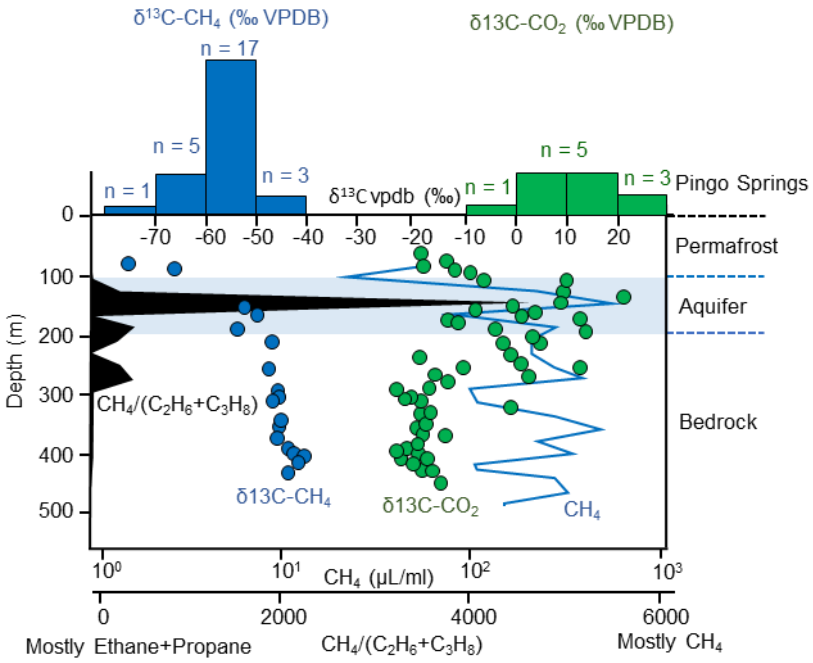


Figure 3. Key geochemical and dissolved gas characteristics in spring waters draining River Bed Pingo (RP), Innerhytte Pingo (IHP), Førstehytte Pingo (FHP) and Lagoon Pingo (LP). "LMWL" denotes the Local Mean Water Line. The legend in Figure 3a applies also to Figures 3b – 3d.



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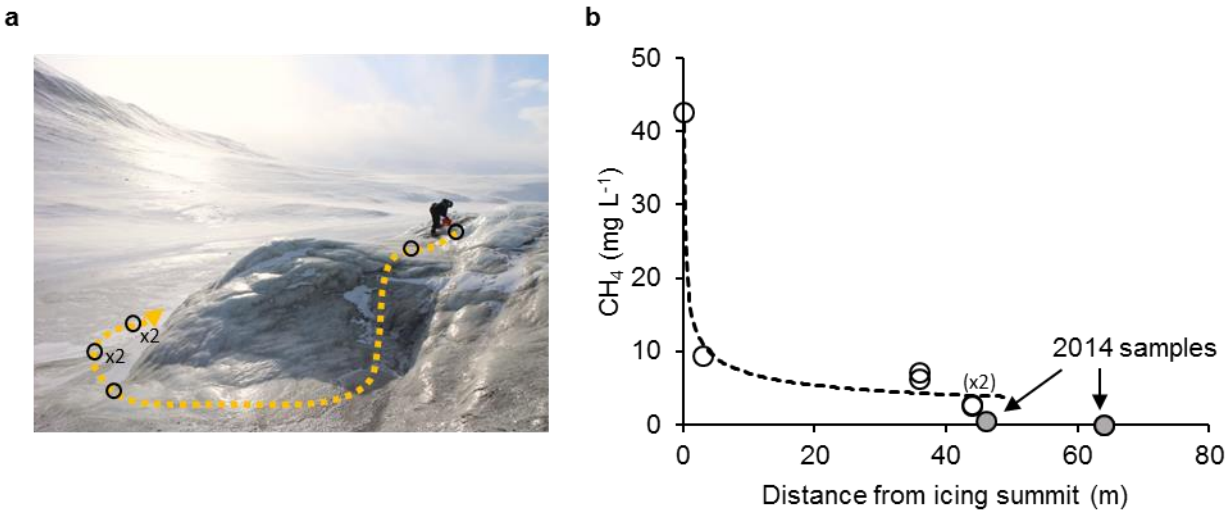
599

600 **Figure 4.** Histograms showing stable isotope composition of methane and CO_2 in pingo spring waters (from Table 2) for
601 comparison with published pore gases from different depths at the CO_2 Well Park (Well Site B in Figure 2). The ratio of
602 methane to the sum of ethane and propane (all in µL mL^{-1}) is shown to indicate where biogenic methane is most likely (i.e.
603 high values). Also shown are the approximate lower boundary of the permafrost and the aquifer beneath it.

604



605

606 **Figure 5.** Rapid decrease in dissolved methane concentration with distance from the source of a sub-permafrost groundwater
607 outburst at Innerhytte Pingo summit April 2015.

Date	pH	ORP (mV)	O_2	$\delta^{18}O_{H2O}$ ‰ vsmow	δD_{H2O} ‰ vsmow	Cl	NO_3	SO_4	DIC	Na	K	Mg	Ca
River Bed Pingo (distal)													
21/4/17	7.18	134	1.1	-15.4	-111	1560	b.d	2880	229	1020	7.89	518	459
5/4/17	7.32	-64.1	0.0	-14.9	-109	1520	b.d	1950	281	916	6.89	353	381
17/3/17	8.15	-25.1	0.0	-15.1	-109	775	b.d	3670	305	563	6.30	537	534
19/3/17	7.22	113	2.2	-15.3	-109	780	b.d	3510	236	539	5.96	495	480
River Bed Pingo													
16/4/16	7.21	-192	0.31	-14.3	-102	1540	0.04	40.1	2700	1910	4.99	13.8	31.6
12/4/16	7.06	-12.1	0.17	-14.0	-101	1510	0.08	43.2	2770	1980	4.95	13.0	30.7
12/4/15	7.61	-74.9	0.68	-13.9	-99.8	1450	b.d	24.3	3710	2270	6.92	20.1	32.6
Innerhytte Pingo													
19/4/17	7.16	-35.4	0.77	-13.7	-99.2	1530	b.d	b.d	2000	1690	4.14	12.7	19.3
15/4/17	7.11	-119	0.0	-13.6	-98.9	1490	b.d	b.d	2023	1680	4.13	11.7	18.4
17/3/17	6.81	-67.4	0.30	-13.6	-99.4	1520	b.d	1.40	2043	1700	4.48	12.3	18.9
21/4/16	6.89	-189	0.43	-14.5	-103	1380	0.03	38.6	3930	2310	3.70	20.6	40.0
12/4/16	7.07	-20.7	0.23	-13.5	-97.6	1410	0.02	14.5	3990	2330	3.54	20.2	39.6
22/4/15	6.88	-20.7	0.22	-13.3	-95.2	1490	b.d	17.4	3870	2360	5.30	17.7	28.1
Førstehytte Pingo													
19/4/17	7.35	-195	1.1	-14.4	-107	1100	b.d	11.3	2430	1580	5.89	13.4	20.4
15/4/17	7.34	-180	0.0	-15.0	-106	1130	b.d	12.1	2390	1580	7.41	15.2	20.1
16/3/17	7.35	-140	0.34	-14.8	-105	1070	b.d	15.6	2360	1540	5.43	13.7	21.1
21/4/16	7.31	-238	0.49	-15.7	-110	1058	0.03	48.5	4180	2190	5.54	21.6	40.7

12/4/16	7.20	-199	0.30	-14.7	-105	1100	0.15	63.7	4130	2210	5.76	21.5	42.0
9/4/16	7.21	-192	0.31	-14.7	-105	1100	0.10	59.3	3870	2110	5.69	21.6	40.9
10/5/15	7.81	-202	0.90	-15.7	-111	1100	b.d	35.0	4540	2340	10.6	23.8	30.8
23/4/14	7.25	-212	0.60	-14.4	-102	1100	b.d	53.9	7560	3430	12.0	25.8	39.6
Lagoon Pingo													
19/4/17	7.9	-229	2.44	-15.1	-108	392	b.d	121	3540	1560	25.4	28.1	12.9
15/4/17	8.05	-202	0.00	-15.2	-108	418	b.d	128	3480	1550	26.3	29.3	13.3
16/3/17	7.71	-181	1.71	-15.5	-108	396	b.d	115	2340	1130	19.7	21.0	9.20
10/4/16	7.94	-207	0.48	-15.2	-106	541	0.05	248	5250	2260	39.2	63.2	38.2

608

609 **Table 1.** Geochemical characteristics of Adventdalen pingo springs during pre-melt season sampling. All units are in mg L^{-1}

610 unless otherwise stated. NO_3 is reported as mg-N L^{-1} and "b.d" means "below detection" (ca. 0.02 mg L^{-1}).

611

Date	CH_4 (mg L^{-1})	eCO_2 (mg L^{-1})	$\delta^{13}C$-CH_4 (‰ VPDB)	$\delta^{13}C$-DIC (‰ VPDB)
River Bed Pingo (distal)				
21/4/17	4.78	19.6	-54.4	12.6
5/4/17	6.23	17.3	-55.0	12.5
17/3/17	0.61	2.36	b.d.	10.1
19/3/17	0.97	18.9	b.d.	10.1
River Bed Pingo				
16/4/16	32.4	221	-55.6	n.d.
12/4/16	24.9	320	-51.5	n.d.
12/4/15	20.2	121	-55.9	n.d.
Innerhytte Pingo				
23/9/17	25.0	183	-53.8	27.1
19/4/17	31.4	208	-55.9	26.7
15/4/17	27.6	420	-56.1	12.6
17/3/17	30.0	672	-55.7	26.3
21/4/16	41.3	451	-57.8	n.d.
12/4/16	42.6	678	-51.8	n.d.
22/4/15	25.0	183	-49.7	n.d.
Førstehytte Pingo				
3/10/17	11.9	641	-64.2	2.5
13/9/17	16.5	770	-64.7	2.7
19/4/17	15.3	143	-48.2	1.7
15/4/17	15.1	145	-52.3	2.4
16/3/17	14.0	139	-54.0	2.4
21/4/16	18.1	271	-67.4	n.d.
12/4/16	14.1	346	-55.3	n.d.
9/4/16	16.6	317	-56.1	n.d.
10/5/15	13.4	93.0	-67.1	n.d.
Lagoon Pingo				
28/9/17	7.26	210	-70.7	-8.4
24/8/17	9.50	58.7	-69.8	n.d.
19/4/17	6.30	40.7	-55.6	n.d.
15/4/17	9.63	60.1	-48.3	n.d.
16/3/17	13.7	79.6	-62.0	n.d.
10/4/16	9.50	58.7	-66.8	n.d.

Table 2. $\delta^{13}C$ composition and concentration of methane and dissolved inorganic carbon (DIC) in pingo springs. "eCO_2" is the excess of CO_2 relative to equilibrium with the atmosphere. Samples collected opportunistically during the summer are underlined, "n.d." means "not determined, whilst "b.d." means results were below the detection limit.

Source	Spring discharge ($L\ s^{-1}$)	Average CH_4 concentration ($Mg\ L^{-1}$)	Annual CH_4 Flux ($kgCH_4\ y^{-1}$)
River Bed Pingo	0.11*	25.8	89.6
Innerhytte Pingo	0.29**	31.8	291
Forstehytte Pingo	0.46**	15.0	218
Lagoon Pingo	0.26**	9.3	76.4
Lagoon Lake	0.52**	22.9	376
Total	1.64	20.2	1051
Active layer emissions			6040 - 10400

Table 3. Sub-permafrost groundwater discharge and CH_4 flux estimates. ~~The atmospheric flux is the sum of all separate flux except that discharging into the sea ("Fjord"), which is uncertain and assumed to be oxidised.~~ Active layer emissions are median annual fluxes from individual chambers, reported by Pirk et al (2017). (Source: *Hornum et al (In Review); **authors' own measurements).