September 22, 2014

Response to Reviewer Comments and Short Comments

We are grateful for our reviewers' comments on our manuscript. Based on their comments and suggestions, we have revised our manuscript in an effort to improve it and address their concerns. Below is our response to each of their comments (reproduced in bold).

V. Stepanenko

p.10864, l.19 Reference to (IPCC, 2013) is not relevant to an estimate of 35% contribution of lakes in global natural surface methane emissions. Fig.6.2 at p. 474 of (IPCC, 2013) gives us an upper estimate of 25% for freshwaters, i.e. for lakes, rivers and reservoirs.

This comment was very helpful, as it highlights an ambiguity in our original manuscript with respect to how we obtained our estimate of 35%. We have revised the manuscript to include the original figures that were used in this calculation and to hopefully make the calculation more transparent. We have also changed our estimate from 35% to 30% to reflect the significant degree of uncertainty in this figure, as discussed below.

This reviewer notes that our estimate is greater than that given by IPCC (2013) (30% vs. 25%). Presumably, this is because the magnitude of freshwater CH_4 emissions given by IPCC (2013) (40 Tg CH_4 yr^{-1}; see Fig. 6.2 and Table 6.8) is less than that given by Bastviken et al. (2011) (72 Tg CH_4 yr^{-1}). We chose to use the figure from Bastviken et al. (2011) because it (a) is specific to lakes, not all fresh bodies of water, and (b) was published more recently than the studies that informed the estimate given by IPCC (2013). As identified by IPCC (2013), there is a significant degree of uncertainty associated with this figure; estimates of freshwater CH_4 emissions in the report range from 8 to 73 Tg CH_4 yr^{-1}. Because of this uncertainty, we chose to round the value we report in our manuscript to 30%.

p.10866, l.8-10 This goal is very broad and formally involved numerous processes in a lake, that are not covered (and can hardly be) by the paper.

We agree with this comment and have revised this goal in the manuscript to something narrower: "to gain insight into how some physical and biogeochemical processes within a thermokarst lake interact to determine seasonal and annual CH_4 emissions via diffusion, ebullition, and IBS."

p.10864-10866 The authors give a traditional view on the origin of methane in lakes (via organics decomposition in anoxic environment), but there is evidence for other important sources of methane in lacustrine systems (see, e.g. Tang et al., 2014, http://www.aslo.org/lo/toc/vol_59/issue_1/0275.html)

It is very interesting that methanogenesis can occur in oxic conditions, as Tang et al. (2014) have noted. We have included this in Sec. 1 of our revised manuscript as a potential source of methane in lakes in general.

Tang et al. (2014) cite as evidence of oxic methanogenesis high methane concentrations at the upper boundary of the thermocline. We did not observe such a consistent pattern in methane concentration-depth profiles in Goldstream Lake during the open-water period (Fig. 9). During the ice cover period, throughout most of which dissolved oxygen concentrations are low, we observed relatively uniform CH_4 concentration-depth profiles. We therefore believe that this is not a significant mode of methanogenesis in Goldstream Lake during the period of field data collection.

p.10868, l.2-7 Not clear, how the interpolation of water level using atmospheric precipitation was done during the ice-period.

To improve clarity, we have revised Sec. 2.2.2 to include a definition of the "water level" in Goldstream Lake as applied in our study. The water level is essentially a metric of the total amount of water, in liquid or frozen form, within or on the surface of Goldstream Lake. We converted all precipitation to the liquid water equivalent to interpolate the water level during the ice-cover period.

p.10870, l.18-20, It is not clear, why 30-day averaging was needed to perform three times. Single 30-day averaging smooths time series considerably. Moreover, was it checked that three-times smoothing didn't change significantly the annual (seasonal) accumulated fluxes?

We have included additional details in the manuscript to explain why we smoothed averages of daily fluxes three times. We found that smoothing one or two times did not adequately remove irregularities in the annual ebullition cycle that were artifacts of low sample sizes during some time periods. We wanted our smoothed flux data to represent the average annual cycle instead of the irregular daily ebullition dynamics of individual seeps. In our original manuscript, we discussed in more detail the impact on our results of applying smoothed ebullition fluxes instead of more realistic individual-seep ebullition dynamics in Sec. 3.2. We also confirmed that three-times smoothing did not change the seasonal or annual fluxes.

p.10873, l.16-17, It is appropriate to mention the method for footprint estimation.

We have included a reference to a study that explicitly gives the footprint radius for a 50 cm measurement height (Gash, 1986). The footprint radius given in this study was obtained from an analytical solution (with approximations) to the diffusion equation and is likely more accurate than the rule-of-thumb radius (100 times the measurement height) we originally reported. Consequently, we changed the footprint radius reported in our manuscript from 50 m to 60 m.

With this change, the majority of the footprint is still comprised of the lake surface (see Sec. 2.2.9).

Section 2.2.10. Since the bottom diffusive flux of methane is usually very variable across the lake bottom, with much higher values on shallow sediments, more details should be given on how the diffusive flux was measured in Vault Lake: the number of replicates, the location of measurements, etc. Moreover, as the temperature in shallow sediments undergo profound annual cycle, the annual cycle of diffusive methane flux there is also significant. So, assuming constant rate of methane release from sediments for all the study period may cause considerable errors.

We have revised our manuscript to provide more details on how we calculated the diffusive flux from the sediments of Vault Lake. Additionally, we have revised our model and manuscript to include the temperature dependence of the diffusive flux of CH_4 from sediments. Details of the methods for this were added to Sect. 2.2.10. Based on the reviewer's suggestion, in our revised manuscript, we do not assume that this rate is constant throughout the study period; rather the rate of diffusive flux from sediments varies seasonally according to temperature (Fig. B2).

p.10875, l.16 Equation (3) does not come from (2) if z_w = z_s = 0.

We agree with this comment and have revised our manuscript accordingly. Equation (3) is an analytical solution to the differential equation describing black ice growth in our model. Equation (2) represents a discretized form of this differential equation (i.e., the derivative dz_b/dt is essentially replaced by $\Delta z_b/\Delta t$), so while Eq. (3) does not strictly follow from Eq. (2), they are related. We have revised our manuscript to convey this relationship more clearly.

p.10876, l.14-15 "...the amount of released..." → probably, should be "...the amount of methane released..."

Yes, it should. We are grateful to our reviewer for noting this typographical error.

p.10877, l.22 Avoid referring to gas bubbles below the ice as to "air bubbles", as their composition is very different from that of air.

We agree with the reviewer's comment that methane bubbles trapped within the ice have gas compositions that differ markedly from that of air, but in this case we are referring to actual air bubbles (not gas bubbles sourced from the lake's sediments) that we introduced beneath the ice ourselves. We have revised our manuscript to clarify this.

p.10880, l.2 (Lofton et al., 2013) reference is missing in bibliography.

We have added this reference to our bibliography and thank the reviewer for noting its absence.

p.10880, l.6-9 Including vertical methane and O_2 concentration gradients would have had significant effect on the water-column-top methane concentration and hence on its emission to the atmosphere via diffusion and during "ice flooding" events.

We are grateful to this reviewer for identifying this possible source of uncertainty in our results. Measured surface O_2 and CH_4 concentrations often differed from measured water column averages, suggesting that the average concentrations calculated in the model do not necessarily represent surface concentrations. To evaluate the impact of this difference on our estimate of emissions during "flooding" events, we combined the volume of water involved in each event calculated by our model (V_{flood}, see Sect. 2.3.4) with our measurements of surface CH_4 concentrations. We averaged surface CH_4 concentrations measured in two locations within the lake (lake center and thermokarst zone, see Sect. 2.2.5) and linearly interpolated between measurements on different dates when measurements were unavailable on the exact date of a "flooding" event. The total amount of CH_4 emitted from "flooding" events during the study period, calculated by this method, was 5% less than that calculated by the model (with its assumption of uniform concentration-depth profiles). Given this small discrepancy, we believe that using the calculated uniform CH_4 concentration to estimate emissions during "flooding" events is justified. We have added this result to Sect. 2.3.5 of our manuscript.

During the spring ice-melt period, we modeled the lake's water column as two layers, each with uniform CH_4 and O_2 concentrations. Concentration gradients within the top layer would impact the calculation of the rates of CH_4 and O_2 exchange with the atmosphere in a process-based model of diffusion. However, we estimate that the other sources of uncertainty in such a model (e.g. ice candling and the associated difficulty in calculating the extent of ice permeability to water, water advection through the ice layer, difficulty in calculating an effective boundary layer thickness, δ_{eff}, for a highly irregular lake surface, etc.) would have far greater impacts on the rate of gas exchange. We therefore chose to employ an empirical model of gas exchange during the spring ice-melt period, in which parameters were adjusted to fit the modeled amounts of dissolved CH_4 and O_2 to measurements. To a first approximation, the rate of exchange is proportional to the difference of the average and equilibrium gas concentrations in the top layer. Given the empirical nature of the gas exchange model, its agreement with our measurements, and the complexity of modeling vertical and horizontal concentration gradients in light of the sources of uncertainty noted above, we feel that using the average top-layer concentration instead of a surface concentration is justified.

p.10881, l.6-9 Did this CH_4 concentration behaviour occur before ice-melt? Explicitly mentioning it in this part of text would clarify for the reader that this top-water-column methane accumulated before ice-melt.

This is an interesting question, but, unfortunately, we do not have enough temporal resolution in our field measurements to answer it precisely. CH_4 concentrations in the upper 1 m of the water column were relatively low on 2 May 2012, when some ice was still present on the lake surface.

They were elevated on the next measurement date, 8 May 2012, one day after ice-off, and they were low again on 14 May 2012. We have revised our manuscript to indicate that we do not know whether this behavior occurred before or after ice-off.

p.10881, l.12-16 To my opinion this is a weak point in the methodological part of the study and might affect results significantly. First, the diffusive methane flux to the atmosphere largely depends on the turbulent state of the lake mixed-layer and the near surface atmospheric layer. Thus, instead of using two constants in (1), D_{CH_4} and \delta_{eff}, in many studies wind-dependent exchange coefficient is used (Cole & Caraco, 1998) or more sophisticated parameterizations (MacIntyre et al., 2010)(Heiskanen et al., 2014). And second, using the same summer CH_4 concentration in 2011 and 1012 may also impose significant errors in emission rate to the atmosphere. The authors should provide estimates on how these approximations affect the results that are of the main focus in the paper.

Unfortunately, we did not measure wind speed at Goldstream Lake during the study period, so we are unable to apply a wind-dependent parameterization of the exchange coefficient in our model. Because Goldstream L. is surrounded by trees, we believe that the average wind speed at Goldstream Lake during the open-water periods is similar to that of the low-wind Mirror Lake, studied by Cole and Caraco (1998), so we revised our study to use the average value of the exchange coefficient they reported instead of the value of δ_{eff} by Kling et al. (1992). This revision did not appreciably change our results, as the exchange coefficient calculated from the δ_{eff} from Kling et al. differed by 2% from that from Cole and Caraco (1998).

We have included an additional section (A5) in our manuscript with a sensitivity analysis of how these approximations affect our results. As an extreme scenario, we assume that we grossly underestimated the magnitude of CH_4 Diffusion emissions during the open-water periods and that all dissolved CH_4 is released by diffusion during this time. In this case, the magnitude of open-water Diffusion emissions would double, and they would constitute 16% instead of 9% of yearly CH_4 emissions. We would like to emphasize that these approximations have no effect on our calculation of the magnitudes of IBS and Direct Ebullition emissions, which we consider to be the focus of this study.

p.10882, l.20-25 These two sentences cause two confusions. First, for C seep sites 85% vs. 72% CH_4 contribution to bubble composition in fresh and encapsulated bubbles, respectively, is called significant difference. However, the very similar difference for B-type bubbles in the next sentence is called "not significant" (83% vs. 72%). I can guess, that it is due to large standard deviation in the second case (83% +- 12%), but for the C seep bubbles standard deviation is not given. And second confusion is caused by the difference between methane concentration in two B-type encapsulated bubbles (72% and 14%), whereas no comment is given on such large difference.

This comment highlights an ambiguity in our original manuscript, and, for the sake of clarity, we have omitted some of these details from our revised manuscript. We used t-tests to compare the set of measured fresh bubble concentrations (mean 83%, standard deviation 12%, n = 3 for B-

type bubbles) to the set of measured encapsulated bubble concentrations (72% and 14% for B-type bubbles, with mean 43% and standard deviation 41%). Due to the small sample sizes, the mean concentration of fresh B-type bubbles was not significantly different from the mean concentration of encapsulated B-type bubbles. We were not, as the reviewer's comment suggests, comparing the mean concentration of fresh B-type bubbles to individual measured concentrations of encapsulated B-type bubbles. However, given that the difference was not significant, we felt that it was not important to report the concentrations of the two encapsulated B-type bubbles we sampled.

The significant degree of variability in the measured concentrations of encapsulated B-type bubbles is similar to that observed in other Arctic lakes (K. M. W. A., unpublished data). This can be attributed to variability in the volume of fresh bubbles from ebullition events and variability in the amount time required for bubbles to become encapsulated.

p.10885, l.10-11, I would remove "either by seep ebullition or diffusion", or rephrase appropriately, because it may be understood by a reader from this sentence, that for both methane transport modes the fraction of methane consumed by methanotrophs is the same.

We have revised this sentence to clarify this point. We are hesitant to remove it completely, as we want to emphasize that we are not only referring to the fate of ebullition-sourced CH_4. We have similarly revised the caption for Table 1.

<u>**M. Sasaki**</u>

1. Since diffusion rate in the air is much greater than that in water, the rate limiting process is diffusion of methane in water in air-water exchange. The diffusion rates of dissolved gases in water strongly depend on wind velocity. The effective thickness of diffusion layer in Eq.(1) in this manuscript might be change in wind velocity. Generally, since it is too difficult to measure the thickness of diffusion layer or to measure the concentration distributions of gases in the thin layer, the gas transfer coefficients k are empirically determined as proportional coefficients to the difference of bulk concentrations (chemical potentials) between air and water. Many values were proposed for CO2 exchange between air and ocean (Nightingale and Liss, 2003). I believe (Sasaki et al., 2010) that the air-lake transfer coefficient of CO2 proposed by Cole and Caraco (1998) is applicable to such small and shallow lakes in this manuscript, though the conversion of value for CO2 to that for CH4 is needed using Schmidt number. In this equation, the wave effect by wind (bubble formation with wave breaking) is evaluated weaker. I would like to ask authors to consider the wind effect on lake to air diffusive flux of methane in the future.

We appreciate the reviewer's sugggestions and believe we have addressed their recommendation in our response to one of V. Stepanenko's comments above (p.10881, l.12-16). We used the transfer coefficient from Cole and Caraco (1998) and converted it appropriately using the Schmidt number of CH_4.

2. There are no dissolved oxygen concentrations (DO) of water column during the ice-covered season in this manuscript. When an oligotrophic lake is capped by ice cover, DO is supersaturated because of biological activity (perhaps, photosynthesis of mosses and algae at the bottom of lake) (Yoshida, et al., 1975). If similar phenomenon commonly occurs in seasonal ice-covered shallow lakes, the supersaturated DO must accelerate the methanotrophy of dissolved methane during the ice-covered season analyzed by Eq.(6) in this manuscript.

Our measurements (Fig. 8) indicate that the concentration of dissolved O_2 is essentially zero during the majority of the ice-cover periods in this study. Snow covered the entire lake surface during this time, and our field observations indicate that essentially no sunlight penetrated the ice/snow layer, suggesting that photosynthesis did not occur during this time. Measured dissolved O_2 concentrations begin to increase at the beginning of the ice-melt period in the spring, which we attribute to diffusion from the atmosphere through a degrading snow/ice layer.

We have added a sentence to our revised manuscript stating that measured dissolved O_2 concentrations were similar to those calculated in the model (i.e., they were near-zero throughout most of the ice cover period).

<u>S. Zimov</u>

The only thing I would like to suggest to the authors - to add some photos. For big part of science community, thermokarst lakes are unfamiliar.

We thank this reviewer for this suggestion and have added a new figure (Fig. 1) with some photos that exemplify ice-trapped bubbles in thermokarst lakes.

We thank the reviewers for the time and thought they put into their comments, which have helped us improve our manuscript. We hope that our revised manuscript will be considered suitable for publication in *Biogeosciences*.