We are very grateful to the Referee, prof. Nigel Roulet for his positive evaluation of our paper, for the interesting questions and constructive critics. Below we try to answer every comment.

General comments

Good interesting paper. The authors cannot explain their observed methane fluxes by using 'conventional' relationships with environmental and biotic variables that have been related to methane fluxes in other published research – including work by the authors at other arctic wetlands. They, therefore, develop an inferential argument that attempts to explain their observations. This argument is only partially successful, largely because they lack the necessary to deductively test their ideas. This is the frustrating aspect of the manuscript but it is not an unreasonable outcome the apparent complexity of the problem. The physical dynamics related to the refreezing of the soils in the autumn, and thawing of the soils in the spring, adds a significant new factor to the seasonal methane dynamics that has not received much attention in the past. This is surprising given the importance of northern wetlands as methane sources. They use their data set well to reject what I would refer to as the easy accepted explanations of what controls the methane flux. The rejection of these explanations is very solid. The authors' conjectural alternative explanations are inductive. They also suffer from the problem of equifinality - i.e. multiple hypotheses are equally plausible and their observations does not provide a basis for confirming or rejecting alternative ideas.

This is a very precise characteristic of the paper and its background. In this manuscript we carry out three main messages (following this and the other Referees comments, the abstract will be changed in the revised manuscript to emphasize them more clearly):

- 1. We have documented the interannual variability in growing season CH₄ fluxes, that can not be explained by "traditional" environmental factors (although the seasonal variability within each specific year is quite "normal" and can be related to these environmental variables).
- 2. We have documented late season CH_4 and CO_2 fluxes and argue for the reasons behind their dynamics.
- 3. We hypothesize that CH_4 emission during late season can affect the flux during the next growing season, and show how this hypothesis can explain our interannual variability.

Message 1. could deserve a publication on its own, however such a manuscript would only then report on negative findings. Message 2. could also deserve a publication on its own, however, we try to avoid seeing the "autumn burst" only as a phenomena *per se*, but rather try to find its place in the annual and multiannual functioning of ecosystems where it happens. Message 3. is admittedly very speculative so far, but it seem reasonable to us, it and it fit our observations. Adding this message to the manuscript we turn it from negative to be pointing at challenges for the future.

The paper is generally well written but the discussion is too long. The rejection of the usual environmental variables vs methane could be much reduced.

We will try to further compact this part in the revised manuscript, although as this is one of the main messages we find it should be properly explained. We think that the negative results are as important for the science as the positive are, and studies where some correlations are proved not working should be published along with other, positive findings.

There are a lot of nice observations in this paper but I think the paper would benefit from more structure. I would suggest the authors pose a clear set of research questions and/or hypotheses in the introduction. This would set up the various tests they go through to see if the explanations stick - i.e. their process if falsifcation and rejection. This would be a clear sequence of deductive tests and it shows where convention wisdom fails. This then set up the logic of the more inductive speculation that occurs in the second half of the discussion.

The abstract and introduction will be revised in the revised manuscript in order to meet these suggestions.

The authors pose several alternative explanations (hypotheses) but do not have the ability to test them directly. Right now the argument is one based on Occam's razor. The paper would benefit from the authors describing some experiments or observational analyses that could be used to test their conjectures. Right now the paper does not really end – it kind of runs out of steam and leaves a reader hanging.

We thank the Referee for this recommendation and will add the description of suggested experiments and observational analyses to the revised manuscript.

Specific comments/questions/suggestions

15855-13&14: Bit redundant - if we have a good understanding why would you do this research?

This sentence will be corrected in the revised manuscript.

15856-1: Do you have any hypotheses or expectations that led this research?

The simultaneous monitoring of CH_4 and CO_2 fluxes was expected to help us monitoring ecosystem functioning (via NEE) during a growing season, and throw light upon mechanisms of high CH_4 fluxes during the freezing season. If CH_4 burst would be caused by a decrease of methanotrophic activity, we would be able to detect corresponding (in C units) decrease in CO_2 emission. If the CH_4 burst is caused by a physical squeezing, we should see similar effect for any gas, entrapped in subsurface, including CO_2 – and that we have documented is the case.

15856-28: What are dunlin fens? I have not heard this term before.

This is the translation of the Danish name (*Rylekærene*) for this individual fen complex. Following the examples of *Mer Bleue* and *Stordalen*, which names were to our knowledge never translated in scientific papers, we will remove the translation from the revised manuscript.

15859-8: Were standard additions used to calibrate the effective volume of the chamber? Did the effective chamber volume change over the growing season? Was there any evidence of the ventilation of the soils due to wind shear stress or pressure changes – i.e. did the effective chamber volume change with wind shear? Were these potential effects tested for?

Unfortunately effective volumes of the chambers were not monitored due to technical reasons (mainly problems with transport of calibration mixtures with high CH_4 concentrations to Zackenberg). This is one of the first priorities in our plans for the nearest future. So far we just monitor the physical volume of the chambers (weekly measurements of vertical distances between chamber lid and surface – moss, dense vegetation or water – averaged from 10x10 cm grid). A few times we tried to estimate the effective volumes manually using low concentration calibration standards, and the effective volumes seemed to agree with the physical volumes we monitor, however, the low precision of these estimations did not allow us to use them anyhow. An indirect evidence, that the effect of ventilation of the soils due to wind shear stress or pressure changes is not very pronounced in our ecosystem, may be the smooth CH_4 flux dynamics during long time intervals (weeks) of growing season. Windy days and calm days give us similar fluxes, as long as the chamber closure is well enough.

15866-23: Not sure I understand this? Do you mean the surface of the wetland relative to an arbitrary datum varied more than 10 cm? Further, was the movement of the surface related to changes in water table or frost table? This could be important to the methane flux if the water carries DOC. If the surface changes are not associated to water storage or active layer depths as implied in this paragraph what causes the change and how do you know it is not important in methane flux? There is something confusing about this paragraph.

We will try to clarify this paragraph in the revised manuscript.

What we see is 1) seasonal changes in the surface level relative to the georeferenced point; 2) lowering of the surface level from year to year. The reasons for 1 are probably changes in water table and frost table, the reason for 2 is probably gradual thawing of permafrost (interannual change of the frost table). These processes may be important for methane fluxes, and we plan to study them more intensively in the future.

Studies of the hydrological regime and DOC transport are also in our close plans (some work is planned already in 2013 season).

15866-24 to 27: Do you the permafrost thaw or do you mean changes in active layer depth? Do you know that the permafrost thickness is actually changing?

Here we meant permafrost thaw (how much from the upper permafrost is a part of the active layer every year). We are not able to monitor the actual permafrost thickness (which is estimated to be about 400 m), what we did was installing a reference point inside permafrost (about 1 m deep) and monitoring frozen table relative to this reference point. The lowest frozen table each season was taken as the permafrost table (per definition). The change of this permafrost table was 17 cm during 2007-2010; active layer increased by 7 cm, so 10 cm was "lost" due to the surface subsidence. This paragraph will be rewritten to explain this more clearly.

15868-20: Does this not suggest a multivariate problem? It is not surprising that you find strong correlations between temperature and fluxes across within a single year but not across years. This only means that the initial conditions and/or other abiotic and biotic variables are involved. This is what I would expect.

We totally agree. That is why later we hypothesize, that the important initial condition for each growing season is the amount of methane, stored in the subsurface pool to the beginning of this season. This amount, in turn, depends on the amount build up during the previous year, and, hence,

the balance between production, lateral transport, oxidation and emission during the previous season, as well as the autumn discharge (which in our hypothesis has the main importance) and possible winter/spring losses.

In your analysis is does not look like you attempted to examine covariance among the physical variables – e.g. ALD and WTD, or do some multivariate analysis across a number of variables. Have you thought of using regression trees to try and tease out associations?

We thank the Referee for this suggestion. Following it, we have applied a regression tree analysis on our data, both for individual years and for the whole dataset. The predictor variables used (daily resolution) were active layer depth (ALD), day after snow melt (DASM), NEE, soil temperatures and water table level (WTL). The regression tree analysis showed a similar picture as simple correlation analysis (Table 1 of the discussion paper) and the multiple regression analysis (our reply to Referee 1), in the sense that the regression trees differed from year to year. A regression tree based on the whole dataset is shown in Figure 2.1.



Figure 2.1. Regression tree based on whole data set. A minimum of 20 observations was set for each tree leaf.

Using the regression tree in Figure 2.1 to model CH_4 flux (regtree1 in Figure 2.2) yields similar results as did the multiple regression analysis, in the sense that fluxes during 2007 are underestimated while fluxes during 2008 and 2009 are (partly) overestimated. These results certainly highlight that one or more important predictor is missing. Interestingly, if we add a year variable to the regression tree analysis, the first split divides the dataset into 2007 and 2008-2010, respectively (regression tree not shown). Modelling based on such tree improves the fit with observed fluxes (regtree2 in Figure 2.2).



Figure 2.2. Observed (blue circles) and modelled CH₄ fluxes using regression tree analysis without (red circles) and with (green circles) additional "year" variable.

Thus, the regression tree analysis fully supports Message 1 of our manuscript: the seasonal dynamics of CH_4 flux can be quite well explained by the common environmental factors, but the interannual variability can not. The results do indicate that one or more vital predictor is missing. Such predictor may then well be the subsurface methane concentration.

We will include a short description of this exercise in the revised version of the manuscript.

15869-3: Surprised that you do not reference to the multiyear fluxes reported for another more northern wetland such as Stordalen? All your comparisons are with boreal peatlands that do not contain permafrost.

Albeit CH₄ flux studies at Stordalen have a long history, unfortunately not so much was published for the moment. Following the Referee suggestion, we will add comparison of our results with 4 years chamber THC flux study by Bäckstrand et al. (JGR, 2008) and 2 years eddy covariance CH₄ flux study by Jackowicz-Korczynski et al. (JGR, 2010). The problem comparing our Zackenberg CH₄ fluxes with Stordalen ones is that, despite this palsa mire is partly underlain by permafrost, CH₄ emissions were (and can be only) measured at wet locations, having no permafrost underlain, while dry palsa locations have permafrost, but do not have methane emission and storage. So the Zackenberg situation, where methane is produced and stored above the permafrost, can not be found at Stordalen.

15870-5: Did you test for relationships between the saturated zone thickness? When dealing with permafrost the active layer thickness needs to be considered along with the water table to estimate the zone of saturation – i.e. potential anaerobic conditions. Similarly a change in AL depth can change the thickness of the oxic zone without changing the thickness of the zone of production, or the thickness of the saturates zone.

We tried different combinations of water table, thaw depth and surface level – saturated zone thickness (from the frost table to the water table), aerobic zone thickness (from the water table to the surface), aerobic/anaerobic ratio (quotient of the two above), thawed organic soil depth (as the organic soil thickness is about 20 cm only, this variable is the same as the frost table depth until 20 cm, then stays at 20 cm), aerobic/anaerobic zones of the unfrozen soil (these max 20 cm divided by WTL), unfrozen inorganic layer (below 20 cm), layer of permafrost, involved in the turnover (zero until the seasonal melt reaches the last year ALD, and reaching the difference between current year ALD and last year ALD at maximum). None of these approaches seem to be a "magic key" to explain CH₄ flux dynamics.

We will add a note on this to the revised manuscript.

15872-27: The lack of biomass information seems to be a rather large omission given the inference you are making here. Presumably you attempt to address this issue another way later on in the paper when at NEE vs CH_4 ?

We totally agree and we try to establish some indirect procedure for biomass quantification (shoot count for key species, etc.). In the current paper we operate by NEE as a functional attribute of biomass.

15873-2 to 4: Yes but what is relevant here is the actual exchange - NEE. You are interested in determining the productivity and the exchanges concurrent with the CH_4 fluxes.

We absolutely agree. NEE was and is measured since 2006, and is presented/discussed in the current manuscript.

Recently (after 2010, not included in the current manuscript) we established a routine of regular dark chamber measurements, when the same chambers are manually covered by non-transparent material as soon as they close.

15873- 12 to 25: Fig 7 is not really necessary. It shows that the fluxes from the two measurements approaches have similar seasonal and daily variations but it also show the magnitude is systematically less for the EC measurements than the chambers. The EC flux seems less regardless of the direction of the flux but there does seem to be an asymmetry the differences? It is very likely that the biomass in the chambers is higher than the average for the footprint of the EC tower. We tend to locate chambers over healthy, good stands of vegetation.

Following this and the first Referee's suggestion, we agree to move Figure 7 with the supporting text to a supplement.

As the Referee has noted above, having no direct biomass estimations, we rely on NEE instead to prove that nothing goes too artificial in our chambers. That is why direct comparison with bigger scale "undisturbed" NEE was implemented. We are pleased if this is not necessary.

15876- 5 to 8: If you integrate the area under the curve for the freeze back period (Table 2) does this equal a mass of methane that could be stored? What would the concentration need to be in the saturated zone? Using the data in the tables and graphs of ALD and WTD you would one to two orders magnitude difference in storage, while total growing season fluxes differ by a factor of 2 or 3?

We are not sure we understand the question. The integration of all post - season CH₄ fluxes is given in Table 1 as CH₄ total (3.76 g C m⁻² for 2007, etc.) This amount is not exactly equal to the amount of CH₄, squeezed out from storage, because 1) it includes also the "tail" of gradually decreasing ongoing emission; 2) the measurements were never continued to the very end of emissions, so the last unknown part is not included. However, this is out approximation of the storage loss during autumn bursts. This amount, as discussed later in the manuscript, is shown by blue arrows at figure 11 (vertical size of the arrows is numerically equal to he numbers in Table 1). To let our discharge hypothesis work, the full amounts of stored during the growing season CH₄ should be as large as red bars on the Figure 11. The relative sizes of the red bars between the years reflect the relative difference in peak season fluxes – and they differ by a factor of 2 or 3; the arrows (discharge) are different by one to two orders magnitude (arrow for 2008 is not shown as it should be 22 times less than 2010).

The figure shows an idea, how very different discharge can cause different (but not so much) storage and growing season fluxes.

Very roughly, the longest blue arrow should be about 4-5 g C m⁻², so the highest red bar – about 5-6 g C m⁻² and the lowest – about 1-2 g C m⁻². The magnitude seems realistic – for example, Strack and Waddington (2008, JGR 113, G02010) report the total peat profile bubble CH₄ stock of 0.3 - 1.0 mol m⁻² (3.6 - 12 g C m⁻²) for a boreal Canadian fen.

Let us assume, that our maximum 2007 storage (5-6 g C m⁻²) was distributed within 20 cm anaerobic layer (200 liters of soil). According to Wilhelm et al. (Chemical Reviews, 77, 1977), CH₄ solubility in water at 0°C is 4.6E-5 mol/mol, which is 6.13 g per 200 liters. Our 5-6 g can almost fit into the solution! Of course volume of H₂O in 200 liters of soil is less then 200 liters, but remembering that most of the CH₄ should be stored in the entrapped gases, we see no doubts that this storage is realistic.

I see you do the comparison two pages down – it might be a good idea to signal to the reader that you do this as it seems logical to raise the question here.

We tried to separate the basic part of the discussion, where we operate with known processes and relations, from the novel part, where we explain things by our hypotheses.

15876- 9 & 10: It appears you have one burst (2007), a couple puffs of 4 to 8 times smaller (2009 & 2010), and nothing in 2008. Based on this record nothing to puffs seems normal and the burst is the exceptional event - i.e. right now you can say the burst is a one in four event? Maybe it is much less?

We can not say for sure that is was nothing in 2008, and we can not say for sure that the puffs in 2009 and 2010 were so small – we have not seen the whole picture, having to stop measurements before the last flight out of Zackenberg. For the moment we tend to think that a huge burst like we saw in 2007 is a coincidence of high storage and "right" conditions during freezing. However, if no proper conditions occur for few years, the storage grows, and the probability of high burst increases. There might be some varying periodicity, like geysers have.

However we can not know anything for sure until we have many more years of monitoring.

15877-5: This is strong evidence for the physical release of the methane. I am convinced.

We appreciate this.

The most interesting question is why there was so much methane stored to release in 2007 versus the other 3 years?

Unfortunately we can not say anything for sure. The peak season emission in 2007 was higher than in 2006, which should speak (according to our hypothesis) for no substantial autumn burst in 2006, and, probably, a couple of years before. This is just a speculation.

What is difference among 2007 and the other years' freeze back? I note that 2007 has intermediate depths of both AL and WTD compared to the other three years? Large enough saturated zone to allow the storage on methane but an unsaturated surface layer in the soil that provides a pathway to allow gas to be pushed out. Two of the year the soil is saturated right to the surface. This would alter the rate of freezing and alter the zero curtain effect. It also restricts pathways for mechanical gas transport. One year is quite dry.

The large methane storage accumulated towards the autumn of 2007 is one reason for a strong burst, and freezing conditions during this autumn may be the other. We also think that a combination of saturated and unsaturated zones, which let CH_4 be stored, but let it escape during freezing may have been pivotal.

It is unfortunate there are no measurements of methane storage in the soils.

We are totally agree. In the future we will try to conduct such measurements.

15877-8: See comment above - in 2008 and 2009 the soil was effectively saturated but in 2010 the WTD was \sim -25. How does this fit the argument?

Probably the physical conditions in 2010 were quite suitable for the autumn burst. Then why were the CH_4 fluxes we have seen so much lower than in 2007? There may be at least two possibilities:

- 1) The autumn burst of CO_2 was as high in 2010 as it was in 2007 that should indicate that the squeezing worked good enough. But the storage of CH_4 was still much lower in 2010, so the autumn CH_4 burst was lower.
- 2) The freezing time came much later in 2010 comparing with 2007 this can be seen both in soil temperatures (Figure 1 A,B,C) and in CO₂ burst (Figure 5 A). Thus we should expect the CH₄ burst to be later than in 2007 also; there is a chance that what we seen as a small puff was just a beginning of something bigger.

15877-12: Does methane dissolved in water change under pressure – what does this do for the solubility?

Using a Matlab program by William Waite

(<u>http://www.mathworks.com/matlabcentral/fileexchange/36963</u>; uses the formulae by Tischenko et al., 2005, and Duan et al., 1992, 2006) we calculated methane solubility in non-saline water at 0°C (Figure 2.3)



Figure 2.3. Methane solubility in water at 0°C.

Not sure what happens between 7 and 8 bars, but otherwise very roughly we can say that the solubility is proportional to the pressure (increases twice when the pressure increases twice).

What kinds of pressures would build up at that freezing front? When the phase change occurs with the soil water is methane exsolved? How much? Some back-of-the-envelope calculations here might put more meat into this argument.

For such calculations we would need pressures, but those we can not estimate. Freezing water can cause enormous pressures, if it is trapped in space, that strongly resist expanding – it can bend steel and crack stones. Practically measured (Vidovskii, Hydrotechnical Construction, 1972) pressure in a steel vessel at -10°C reached almost 100 MPa (1000 bar), and can be higher at lower temperatures. It is not a question what pressure can freezing water force, it is a question which pressure the freezing peat matrix can resist before it deforms. In 2008 we tried to monitor these pressures at our site at Zackenberg using pressure sensors at 0.1-0.4 m depth (Tagesson et al., Global Change Biology, 2012) and registered pressure buildup up to 4 bar over ambient. However, this pressure was probably affected by the sensors themselves, as they alter the peat structure.

Figure 11: Put units on the y-axis.

We apologize for the possible misinterpretation of Figure 11. In this figure we try to draw the hypothetical storage of CH_4 in the subsurface pool, however, we do not have any measures of this storage. As we tried to explain in the text (this part will be rewritten to be more clear in the revised manuscript), we make an assumption, that the peak growing season emission reflects the storage in the peat matrix; so we use peak emissions as a proxy for storage. Red bars in Figure 11 are numerically equal to peak CH_4 emission values (shown in Table 1 and Figure 4); however, in Figure 11 they represent storage.

The Y scale is on this figure is relative, as we have no measurements of this storage, so we can not put any units on it.

In the revised manuscript we will change the style of Figure 11 - it should look more like a sketch (as Figure 12, which seems admissible without Y axis units).

15878-12: I suggest the word "hypothesis" is more appropriate for the conjectural nature of this statement rather than "theory". They are not interchangeable words.

The suggested wording change will be made in the revised manuscript.

15878-22 to 24: Point raised earlier. Need connect the logic here to the points raised at 15876-5 to 8.

This part will be rewritten in the revised manuscript.

15880-5: Any ideas on how would you test this - examine the temporal variability in 13-C and D in the stored and flux of methane as well as 13-DOC?

We plan to do examination of 13-C fluxes and subsurface concentrations during field season 2013. Preliminary tests done in 2012 show that gas emitted during autumn burst (October) is generally more depleted in C13 comparing with July.

We are also looking for options of doing deuterium analysis.