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Comment

***Interactive comment on “Fluxes and <sup>13</sup>C isotopic composition of dissolved carbon and pathways of methanogenesis in a fen soil exposed to experimental drought” by K.-H. Knorr et al.***

**K.-H. Knorr et al.**

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We thank Juul Limpens for the helpful remarks to improve our manuscript. Below, a detailed response to every comment is provided.

"The abstract and introduction are clear and well written, the rest of the paper, particularly the materials and methods section could be improved... Still, adapting the text style/ wording to a less knowledgeable reader, might broaden the accessibility of the paper to a wider public, as the special issue aims to do." This issue was raised by both reviewers. Thus, we went carefully through the manuscript and tried to improve readability and clarity to make it accessible for a broader audience.

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General remarks: "Methods: after reading the methods section I was left with quite a number of questions regarding the experimental set-up and the measurements. A schematic drawing of one columns with inserted TDR probes, silicon tubes, irrigation device (?), piezometers, 2 (?) gas collars and rhizons at different depths would be most welcome. In addition I suggest arranging the text into 2 subheadings: 1) experimental set-up (explaining the requested figure)& incubation conditions and treatments and 2) measurements, with a bit more information on the sampling procedures involved (see questions below)." As both reviewers asked for a schematic sketch of the columns, we decided to prepare an additional figure. Explaining the experimental set-up in much more detail may be difficult, minding the length of the methods section.

"What was the vegetation prior to the defoliation treatment? Was it similar to the other columns?" We added that the vegetation of DW-D prior to defoliation was quite similar to DW-V.

"Just curious. What was the cover of the Sphagnum? Was there any within your methane measurement-collars? Generally, presence of Sphagnum increases likelihood of methane oxidation before efflux." Sphagnum was only present in the collar of the W-V treatment, which was the one with the highest methane emission. Probably, the emission was enhanced by the Carex species present, as a calculation of diffusive efflux from concentration profiles yielded much lower emission rates and the concentrations at 5 cm depth were also quite low, when compared to the treatments with no Sphagnum present (see also Knorr et al., 2008).

"Can you describe the peat a bit more? From your carbon content data it looks as if there was quite some ash content/ mineral influence." We added some more general properties of the peat. Due to space limitations we could not include much more information. So, for more details the reader is sought to consult the cited references, as the manuscript is already very long.

"How was the irrigation water supplied: from above or from below, with a dripping

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device, or something else?" The water was spread homogeneously over the surface using a dripping device. A short sub clause was added to the manuscript.

"Did you check the concentrations of the elements applied with the irrigation water? ...Can the electron acceptors (NO<sub>3</sub>, SO<sub>4</sub>) applied with the irrigation water have influenced methanogenesis?" This point was also raised by the other reviewer. Therefore we added the information, how much the electron acceptors in the rain water contributed to electron acceptor flow in the peat. This was generally much less than 1 %. The effect should thus be small.

"Was the irrigation done by checking the water table depth in the piezometers? Or by weighing?" Weighing would indeed have been a desirable way to measure water content of the mesosoms. However, as also in other studies mostly a water table measured in a piezometer is given, we decided to base our irrigation on the measured water table level to allow for comparison.

"Please move the information on the relevance of the drying and rewetting treatment from page 1336, paragraph 4.2 to your methods. This avoids leaving the reader wondering about this for a couple of pages." We moved this paragraph into the methods section and indeed it seems to be better here.

"Please give the frequency and depth of all measurements. How often was soil moisture sampled through the rhizons? Was sampling still possible during the dry period in the DW treatments? What was measured in the soil solution? And how? What was the pH of the soil solution? Also 4.8? Did it change as a result of drought? What I always like is when the reason for the main measurements is explained; this is a question of personal taste I guess." Due to shortening the discussion we could include some more information on sampling and pH values. However, also in this case we had to restrict the information on the parameters needed for the discussion. For all further parameters the reader is kindly asked to consult two other manuscripts about this experimental set-up. One manuscript is already published (Knorr et al., 2008), the other one is still

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in preparation, but will be submitted soon.

"About the silicon tubes. I assume they were installed permanently? I was wondering about the following. You indicate that the gases in the silicon tubes were in equilibrium with the soil/gas solution surrounding the tubes. The gas diffuses from the surroundings into the tube. Is there any chance of a kind of fractionation to occur with lighter isotopes diffusing faster? I can imagine that heavier DIC is likely to be in the form of HCO<sub>3</sub><sup>-</sup> whereas lighter C shifts to the CO<sub>2</sub> form and diffuses. Did you check this maybe with measurements on the water itself? Associated with the above: As you did not measure CO<sub>2</sub> directly in its dissolved phase, but rather indirectly, I would not put DIC so prominently in the title. I suggest focussing your title on the main research aim: the mechanisms and pathways of CH<sub>4</sub> mobilisation/ turnover/ cycle after a drying and rewetting cycle. Most other things seemed to me tools to answer this question." We realized during this review that the silicon tubing sampling technique is indeed not well known to the peatland scientists. This technique was first described by Holter (1990) for analysis of air in dung pats. Later, this technique was also applied in a wide range of soils (Jacinthe and Dick, 1996, Kammann et al., 2001) and for groundwater sampling (e.g. McLeish et al., 2007). Therefore, we think that it is appropriate to call our CO<sub>2</sub> measurements 'DIC'. The fractionation of isotopes through diffusion inside of the tube may be a matter of concern. This has not been systematically investigated so far to our knowledge. Based the following points we think that this fractionation is negligible in our case: i) At a range of pH commonly observed in peat (3.5-6) DIC is mostly present as dissolved CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub>. Therefore the error through an enrichment of <sup>13</sup>C in HCO<sub>3</sub><sup>-</sup> should be small. ii) The equilibration times reported for silicon tube samplers are typically in a range of 5 to 50 hours for the gases measured in such samplers. Thus, an equilibration time of 1 week should lead to a relatively low fractionation. iii) The fractionation of <sup>13</sup>C during methanogenesis is exceptionally high and large differences occurred. When monitoring very small differences in d<sup>13</sup>C values, this technique may require further evaluation.

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"How exactly (and when: before/ after experiment) were the C, N contents and the porosity determined? Where they taken as a small core in each column and then separated into layers? And/or were the taken around each TDR? How did you manage to get 100 cm<sup>3</sup> samples without disturbing the water-soaked soil? Did you freeze the columns/ cores before cutting?" C and N contents were determined on small freeze-dried sub-samples at the begin and the end of the experiment. Porosity was determined using 100 cm<sup>3</sup> stainless steel corers. They were intruded in the intact peat, in triplicate and close to the TDR probes. To minimize compaction we used a scalpel to cut the peat while inserting the corer. The water content was then determined on the freshly extruded peat. To measure total porosity, the peat was saturated, applying extra water until saturation.

"Can you give an indication of the accuracy of the TDR probes? (in my experience, very wet and very dry are a bit difficult)" Obtaining accurate results from TDR sensors is indeed not easy and requires calibration. To this end we used different peats from different layers of the field site and made several calibration curves. The slope of the response was always comparable but the absolute water content had to be readjusted using water content and porosity data obtained from the extruded cores. This may indeed cause some error of the result. However, more exact ways to measure water content over time have not been established yet to our knowledge.

"How was this pulse-measurement done exactly? Were the columns measured simultaneously? Or after each other? Was the gas mixture applied before or after the chamber was placed on the vegetation? The text now suggests before. If this is correct, how did you prevent loss to the atmosphere?" This was indeed misleading. Actually, the chamber was placed on top of the mesocosm, tightened securely and thereafter the label was released by dissolving the Sodium bicarbonate. The cores were treated one after another.

"Being a bit unfamiliar with the procedure, I was wondering about the calculation of the anaerobic CO<sub>2</sub> flux page 1327 (lines 7 & onward). Could you perhaps elaborate a bit

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more on why you would want to calculate it, why you call it an anaerobic flux? Is this calculated over the whole experimental period, with the fractionation ratios taken from each experimental phase and layer? How does the mass balance cope with changes in pools? Such as acetate or uptake by vegetation? Or can we assume that this is negligible over the whole period? As it is now I find it rather speculative, both as a calculation and as a major result worth mentioning in the abstract." The calculations base on a study of Lansdown et al. (1992). We have to admit that there are certain assumptions within this approach and more information is needed. Therefore, we included some more background information. We think that the approach is really well thought and should be applied more often. It is known that the majority of respiration takes place in the aerobic part of the peat, as aerobic respiration rates exceed anaerobic rates. Respiration rates in the anaerobic part of the peat are much more difficult to determine. Most often, rates were obtained from laboratory incubations and thus represent potential rates rather than what may be relevant in situ. Other methods to determine in-situ respiration rates mostly rely on mass balances of CO<sub>2</sub> and diffusive fluxes along measured profiles. For very low rates, such approaches come to their limit. The method of Lansdown et al. (1992) uses a few assumptions to determine the anaerobic CO<sub>2</sub> production indirectly: i) there is no isotope discrimination during the breakdown of organic matter and ii) methane can only be oxidized in the aerobic part of the peat. Thus, using an isotope budget approach, the amount of anaerobically produced CO<sub>2</sub> may be determined from the CH<sub>4</sub> inventory, isotopic signature and efflux, CO<sub>2</sub> isotopic signature and inventory and soil organic carbon isotopic signature. The only unknown factor in eqs. 4-6 is thus the flux of CO<sub>2</sub>. We do think that such calculations could significantly improve our understanding of CO<sub>2</sub> and CH<sub>4</sub> fluxes in methanogenic environments. For a lake system Gu et al. (2004) for example found an extreme <sup>13</sup>C enrichment in the sediment over time, which the authors attributed to a selective removal of isotopically light CH<sub>4</sub>. This is the phenomenon which we also claim to happen in peatlands, as depicted in figure 7.

"Results I was wondering whether you could consider omitting one or two figures, as

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the paper is rather figure heavy at the moment. Perhaps figures 1 and 3 could be discussed in the text? In addition, could you reduce the overlap in information between the results and the discussion?" We wanted to include most of the measured data as figures to illustrate the dynamics over depth and time and to present the comprehensive data set as a whole. As the other reviewer stated that she/he would keep all figures if allowed, we decided to leave all figures in the manuscript. Up to now we would favour to combine Figs. 2 and 5 but put in a schematic sketch of the set-up in addition. The discussion part was to a major extent completely reworked, so we hope that we could successfully eliminate the unnecessary overlap.

"I would suggest using the following order when discussing results. 1) Major differences between columns. 2) Then, chronologically, the changes within each treatment as it goes through the 4 phases. Where applicable from deep layers to surface (or other way around). At present the order of descriptions varies between measurements: I find that a similar order of description facilitates quick reading of a text." We reworked the results section and hope that we successfully addressed this issue. The discussion now starts with the general observations independent of drying and rewetting and then discusses the impact of drying and rewetting on methane dynamics and pathways.

"I suggest adding the following information in the figures/figure legends. Flux direction to atmosphere/soil (Fig 1), Measurement frequency (Figs 2, 3 and 5; alternative option, convert to line graph, with one graph per depth to facilitate comparing treatments), Phase (almost all figures), In figs 4, 6 and 8 I would also indicate the phases in the figure instead of (only) the measurement dates. Why did you specifically select those days? Perhaps you can elaborate this in the methods? Why do the days between the figures not match: Figure 4 has different days than figs 6 and 8." We included the mentioned points into the graphs/figure captions. We also changed the dates into the phases, as this is probably easier to understand. Different dates arose from the fact that hydrogen and acetate concentrations as needed for fig. 6 and 8 were not available for the dates of fig. 4.

"Figure 1: out of curiosity: were those independent measurements from 2 different collars? Can tell something about the variability? Figure 4: Out of curiosity: the high methane concentrations measured at -5 cm in DW-V above the water table: is this the only point where you measured methane production in the unsaturated zone? This is also the layer where your C content is quite high (table 2). Is the porosity there also smaller?" Fluxes in Fig. 1 represent two replicate measurements in one single collar per treatment. This was also asked by reviewer #3. Due to the restricted surface area of the mesocosms we could not insert multiple collars (see now also Fig. 1). The -5 cm depth interval of DW-V was indeed the only point where we found CH<sub>4</sub> production above the water table when the water table level was at -10 cm below surface. In the other treatments, CH<sub>4</sub> production was high around the water table. According to our results, the porosity did not differ from that of the other treatments or from the layers below. However, the high C content and the highly decomposed nature of the peat could have lead to a different relation between soil water tension and soil moisture content, meaning that the degree of saturation may have been high here while in other layers air could already enter the soil at lower water tensions. There is only few data available for aeration depth of soil water potential and soil moisture relationships, however (Silins and Rothwell, 1999, Paul et al., 2006, Niedermeier and Robinson, 2007).

"Could you perhaps arrange figures 2 and 5 a bit closer to each other so that you can compare more easily? Why is the resolution of figure 5 smaller than that of 2" We will ask the editorial office if it will be accepted to combine Figure 2 and 5. The resolution is indeed different which comes from the fact that we could not measure isotopic composition of methane when the concentration was below 300 ppm in the sampler. Therefore, white spots are shown if there is no data available. For reasons of the interpolation method to work properly we had to reduce the interpolation grid resolution, what makes the figure look less smooth than fig. 2. We regret that it was not possible to improve this figure.

"I suggest indicating the fractionation factor range of the different methanogenesis

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pathways in figure 7." The factor range of the different pathways is now included.

"Discussion At present the discussion is very much chopped up into different paragraphs with in-depth discussion regarding very specific topics: some information is used more than once. To my mind this obscures the overall synthesis and main findings. Perhaps you could focus it more along the research aims (the effects of drying and rewetting on C fluxes and their isotopic fractionation as well as the mechanisms and pathways involved in belowground CH<sub>4</sub> production and oxidation) as stated in your introduction." This point was also raised by both reviewers. Thus, the discussion was reworked and we hope that we could eliminate this problem. We hope that the specific points are better linked to the research aim now. The language was also improved by letting two native speakers cross-read the manuscript.

"I suggest checking the text carefully regarding overlap with the results." While rearranging the discussion we hopefully eliminated these overlaps.

"Perhaps you could discuss/mention the role of pH as a reason for observation differences with bog-studies." We wonder whether pH may indeed play a role in the differences, as it is also 3.5-4.5 in this acidic fen under study here. We think that most differences arise from the better decomposability of the peat, the high electron acceptor content and the dense nature in terms poor aeration.

"How would/could the ability of shifting to Fe-reduction by methanogens affect your fractionation results (since you mentioned it in your introduction, but did not really come back to in your discussion?" We do not have any information about that, unfortunately. This information was provided in a sense to support the quick re-initiation of methanogenic conditions.

"Could you add a cross reference to the paper by Schrier et al (this special issue, also in Biogeosciences discussions), when discussing methane production/fluxes measured in the field?" After reworking and editing the discussion section, we regret to admit that this reference did not fit in, as we shorted the points about surface fluxes. The

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manuscript now focuses more on below-ground processes and dynamics.

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