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Biogeosciences Discussions

Interactive comment on "Microbial reduction of iron and porewater biogeochemistry in acidic peatlands" *by* K. Küsel et al.

K. Küsel et al.

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The authors are very thankful for the two very encouraging reviews on our paper in Biogeosciences Discussions. We want to thank especially referee 2 for his/her thorough review.

You will find an itemized response list to the referee's reports below. In general, we followed the suggestions of the referees.

Anonymous Referee #1

This study reports on the porewater biogeochemistry of acidic fen soils in central Europe and the predominant role of iron reduction among anaerobic degradation processes after shifts from oxic to anoxic conditions. In addition, soils were screened for known iron reducing microorganisms by PCR. The study is well conducted and the

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conclusions are all supported.

Minor comments p. 2171 lines 19-26 The detection limits should not be given only for acetate but also for all other measured short chain aliphatic acids as well as for NH4+, NO3-/NO2-, sulfate and sulphide.

AC: Detection limits were added.

Anonymous Referee #2

General comments The present study provides field based experimental evidence for the relevance of iron and other alternative electron acceptors in acidic methanogenic peatlands with respect to carbon mineralization and methane formation. In contrast to lake sediments, detailed investigations of redox-processes in anoxic or temporal anoxic soils seem rather rare and therefore, this study is a valuable contribution to the understanding of soil biochemistry. It is based on well established biogeochemical concepts and includes a concentrated overview over relevant articles in the scientific literature. The addressed research gap is distinctly and persuasively framed. However, the study objectives should be linked to the research gaps more adequately, since the stated objectives seem rather the means then the objectives (see specific comments).

The experiments, which largely demand the complexity of anoxic conditions, seem accurately conducted and are in general adequately described or referenced. The results and discussion sections may be improved by some revisions in order to better guide the reader and to improve the comprehensibility of the valuable results. It takes the reader’s efforts to figure out the links between the introduction and the objectives formulated therein, on one hand, and the findings and conclusions, on the other hand. I missed the conclusive highlights and would appreciate the relevant findings to be pointed out more distinctly. The objectives given in the introduction should be addressed and remaining and new relevant gaps should be identified? A separate chapter on conclusions might help (see also specific comments).

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AC: The objectives were changed (see below) and we added a conclusion section.

Specific comments

Abstract p. 2166 l. 21: The reduced compounds are no longer alternative electron acceptors. I suppose the meaning is "...storage and enhanced re-oxidation of their reduced compounds."

AC: Changed as suggested.

Introduction

p. 2167, l. 5,6: If formiate is meant by H2-CO2 "formiate" should be written in analogy to acetate. The formula denotes formic acid (common formula HCOOH).

AC: Formate was not meant. Thus, the formula was not changed.

p. 2168 l. 15-20: With regard to the hypothesis outlined on p. 2176 l. 15-20 and to the statements on l. 10-14, the objective might rather be formulated as e.g. "providing experimental evidence on field based data for diverted flow of reductants from methane formation to other electron accepting processes upon drying and oxidation of upper soil layers" and "better understanding of the flow of carbon in acidic habitats and of their inherent Fe(III) reducing communities". The objectives given in l. 15-20 are rather means to achieve these objectives (see also general comments).

AC: Objectives were changed according to these suggestions (Page 4, L. 18-22). However, we did not include "upon drying and oxidation of upper soil layers"; to avoid the impression that the water table was manipulated in the field.

Materials and methods

p. 2170 Chap. 2.4: Enrichment of what? It is not clear what this medium is used for.

AC: We included the term "Enrichment of Fe(III) reducers" (Page 6, l. 28).

p. 2172 Chap. 2.6 - 2.9 I do not comment these sections due to unavailable experience

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on my side.

AC: No comment necessary.

Results

p. 2174 l.3-4: Units in Table 2 are not consistent with units in text. Keep either nmol or umol. In addition, it is not clear "...higher in March 2002". Higher than the 1177 nmol/g d in September 2001? Please specify.

AC: Units in the text were changed to nmol. Text was specified.

p. 2175 l. 8 and Table 2: Figures imply measurement uncertainty below 1 uM for Fe(II). Please indicate error bounds and reduce figures to significant digits.

AC: We had problems to understand this comment. We think referee 2 refers to Figs. 3 and 4 mentioned in p. 2175 l. 6. However, in none of the presented figures measurements of Fe(II) below 1 μM were shown. The second x-axis in Fig. 4 shows Fe(II) concentrations in mM and not in μM like the first x-axis. Fe(II) concentrations were shown in a range of 10 μM to 7 mM. Thus, we think that this comment is based on a misunderstanding. In addition, we cannot include error bounds in both figures, because each profile represents measurements from one dialysis chamber. We used 3 chambers for 3 sites and measured every 2 months to get profiles for 12 parameters over a 3-year period. We have no replicates at each time point.

p. 2175 l. 12-15: "Oxygenation occurred ..." seems to be a conclusion and "Drying of the upper 5- to 10cm ..." a site specific description. I suggest incorporating these statements in the discussion section and in the site description section, respectively.

AC: We weakened the first sentence and incorporated the second statement in the site description.

p. 2175 l. 15: The concentration of 50uM nitrate in September 03 do not appear in Fig. 3.

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AC: That is correct. Thanks for the correction. We deleted this sentence.

p. 2175 l. 18: Is 5uM sulfide the detection limit of the analysis? The solubility product KL of FeS is 1.59 10-19 (CRC Handbook of Chemistry and Physics, 67th edition). Thus, it is hard to detect sulfide at 30uMFe(II) in the pore water and would explain not detectable sulphide with a detection limit of 5uM.

AC: Thank you for this comment. The detection limit of sulfide was 5 μM. We corrected this sentence.

p.2175 l. 25: I can not read the concentration indicated here from Fig. 3 in December 2003. The figures might either be misleading or erroneous.

AC: In Fig.3 the time and depth integrated concentrations over the 3-year period were shown. The upper concentrations were combined in a range for better visualization of low concentrations. We added this explanation in the figure legend. The exact concentration profiles of December 2003 are additionally shown in Fig. 4b. For a better understanding, we highlighted Fig. 4b.

p.2176 l. 3-9: The findings here are not further discussed in the discussion section. The rate of Fe(II) formation might be evaluated by Michaelis-Menten kinetics, which may explain the rate as a function of readily degradable DOC. It seems as if Fe(III) reduction were DOC-limited in both, velocity and endpoint.

AC: Unfortunately, we de did not measure DOC concentration in the incubation experiments. However, we measured the concentrations of short chain fatty acids, alcohols, and sugars which are a dominant fraction of the DOC pool in the incubation experiments. Fe(III) reduction was not limited by this pool of DOC, because high concentrations were still available when the Fe(III) reduction stopped (see Fig. S2). Thus, we did not include Michaelis-Menten kinetics in the Discussion section.

p. 2176 l. 6: Fig 2 displays concentrations not rates as presented in the text. It is difficult to comprehend the difference in the rate from Fig 2. I would rather display the

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rates in a separate figure.

AC: That is correct. Rates are not shown as a regression line in Fig. 2, but the Fe(II) concentrations used for calculating the rates by linear regression. Thus, we modified the text. In addition, we added some statements about the calculations of the rates in the material and method section (Page 6, l. 24-26). As suggested I displayed the rates in a separate figure. However, the new figure is not really helpful and is, strictly speaking, a doubling of data. Thus, I would suggest to leave the old Fig. 2.

p.2176 l.8: What is the ratio of Fe(II)/Fed here as compared to the 70.

AC: Unfortunately, we determined the Fed contents only in soils samples collected in September 2001. Thus, we can not calculate the exact ratio.

Discussion

4.2 In situ relevance of Fe(III)-reducing activities I would appreciate some further discussion and conclusions which can be drawn with respect to the relevance of Fe(III) reduction found here. Questions arise such as: What is the merit of these results? Is it a new fact? Are such high contribution of Fe(III) reduction to the carbon mineralization in fens observed by other authors or are they specific at this site? Are the methane emissions still substantially reduced in comparison with non-Fe(III)-reduction sites despite the concomitant methane formation?

AC: We included some additional statements and compared the contribution of Fe(III) reduction to carbon mineralization with other habitats. We added a sentence about methane emission. However, we did not measure emission rates in the field and can not speculate about the amount of CH4 emission reduction.

4.3 Turnover of acetate Would "Accumulation of acetate" as title be more accurate? It seems to be the main focus of this section. The accumulation of acetate is well documented and explained. Further discussions or conclusions might address questions such as: Do temporal acetate accumulation characterize the fen as an environmental

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system with specific qualities? May this phenomenon be used to characterize other soil systems which are temporally anoxic?

AC: We changed "turnover of acetate" to "accumulation of acetate" as suggested (Page 15, l.22). We added this comment that temporal acetate accumulation might be a specific quality.

4.4 Fe(III)-reducing microbial communities of acidic habitats Is the conclusion from this section that the knowledge about communities which promote the Fe(III)-reduction in soils and fens is still not satisfactory and the results from phylogenetic analyses in this investigation provides an incomplete picture? If so, I suggest starting this section by the statement given on p. 2128 l. 7-9 "Due to our limited knowledge ..." and then discuss the findings e.g: 1) "Phylotypes related to cultured Acidiphilium or Acidispheras were detected ... . However, most Fe(III)- reducing prokaryotes cultured to date are either neutrophilic or acidopholic ...". 2) "Surprisingly, no PCR products of Anaeromyxobacter or Shewanella related species were obtained ..., although microorganisms from this genera ...." To terminate the section, the gaps might be highlighted and recommendations for further experiments might be given if not amended in a conclusions section.

AC: We modified this part of the text as suggested (Page 16, l. 23 to Page 17, l. 19).

4.5 Anaerobic activities under changing environmental conditions I suggest using this section as the conclusions section. For better guidance of the reader the last conclusive phrase (p.2182 line 4-6) of this section "Our field based experimental results corroborate the hypothesis that enhanced extreme weather conditions will not only ..." might be used for starting the section. The arguments given could then be used to support this initial statement.

AC: We used this section as a conclusion section, as suggested (Page 17, l. 21).

p. 2181 l.12: This first conclusion seems highly tentative. I doubt that increasing atmospheric depositions of nitrate and sulphate substantially contribute to enhanced

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activities of nitrate and sulphate reducers unless it is evidenced by quantitative estimations or referenced with a specific scientific article. E.g. atmospheric emissions of SO2 have decreased during the last decades and the sulphur supply in agricultural soils is going to be marginal.

AC: We deleted this sentence.

Fig. 3: The readability of the x-axis is inconvenient. Please enlarge the relevant marks. It would further be helpful if the relevant events such as snow melt, drought and heavy rainfalls were flagged.

AC: We flagged the relevant events such as snow melt, drought and heavy rainfalls.

Technical corrections

p. 2174 l. 3. "upper lowland fen" is misleading in the terminology of "upland fen" and "lowland fen". Suggestion: "topsoil of lowland fen".

AC: Corrected.

p. 2178 l. 8: A missing "and" between "... layer" and "receives ..."

AC: Corrected.

p. 2179 l. 24-25: Comprehensibility: The "not only"-clause implies a "but"-clause, which explains what else.

AC: Corrected.

Thanks for all the comments. We hope that the corrected version will be easier to understand and will highlight our conlusions.

Interactive comment on Biogeosciences Discuss., 5, 2165, 2008.