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Biogeosciences Discussions

Interactive comment on "Spatial and temporal variations of dissolved organic carbon and inorganic carbon concentrations and delta;¹³C in a peatland-stream continuum: implications of peatland invasion by vascular plants" *by* S. Gogo et al.

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Overview

This is some very interesting data in this study, but the paper consists of several smaller projects cojoined to provide an overview, and in most cases of insufficient sampling frequency to support the breadth and depth of most conclusions (substantiated further below) other than those that are not novel, such as C budgets of peatlands must include

lateral export. As such the study is an excellent first pass at constraining a preliminary understanding of the site but offers limited interpretative capacity and some of the interpretations are questionable.

I support this summary as follows:

1. Flux estimates: Very little detail is given about the flux calculations and the paper that references the method is in preparation – to cite in prep material that fundamentally underpins a submitted paper is unfair on the reviewer as the calculations are not transparent. As such it is impossible to assess the validity of statements such as "The results suggest that a significant amount of DOC was either mineralized or precipitated through a flocculation reaction in the drain" (p3525, l18), and similarly, the comparative estimates with other sites become redundant as we have no overview of how these fluxes were reached to support such comparison.

2. CO2 critical zone: From the conclusions: "DIC export may be promoted by the occurrence of a CO2 critical zone just at the surface of the soil that prevents the CO2 from being degassed within the peatland". I agree there likely will be a microclimatic gradients in CO2 efflux but this will be controlled by the thickness of the boundary layer and thus wind speed and surface energy fluxes (which will vary in space and time). To cite this as a significant mechanism based on one measurement is inappropriate. It would be really interesting to follow up on this but would require high resolution atmospheric CO2 measurements accompanied by energy flux estimates and surface DIC concentration and isotopic composition and pH and temp measurements. The information presented here is too far from this depth of detail to be substantive and too take this further and then discuss impacts on isotopic fraction (section 4.4) is premature.

3. Fig. 6 is very interesting and this is a concept the DIC community, and the authors here need to further explore. The relationship with the rivers could represent mixing between groundwater and soil water derived sources indeed, the highest 13C is undersaturated and so could represent atmospheric drawdown, thus invoking degassing

induced 13C-fractionation is not necessary. The authors do not describe in their site description the geology so it is not know if there is a carbonate source in the region – this needs clarified.

It is more complicated for the peatland sites and unpicking the controls is complicated by lack of clarity from the authors of what the peatland waters represent: just the peatland or include the drains? This is important as at pH 4 (peatland sites) the DIC should be as free CO2 and so how significant is the inter-species isotopic fractionation during degassing? At the higher drain pH bicarbonate will still be a small component of the pool.

I think this data set needs explored further and it would be useful to see the graph plotted as a function of site, sampling time (as proxy for temperatute) and free CO2 pool as a proportion of the overall DIC pool (this may be more revealing that EpCO2 which is a ratio). This relationship is the most significant part of the paper and it is covered lightly.

Fig 7 is not so novel as it merely documents a negative linear relationship between pH and EpCO2 as would be predicted by equation 1.

Example comments about the quality of the conclusions:

1. There is no contextualization of the degree of variation around a sampling points, when it is known the physiochemical characteristics can vary considerably over very short timescales. See for example continuous pH and reconstructed peatland stream [DIC} and 13C-DIC profiles in Waldron et al., 2007, EST. The authors are basing their interpretation of an annual response on 4 snapshots of C dynamics and these will likely vary considerably around the measured composition.

2. I find the authors interpretation of DOC systematics in open and closed sites confusing: section 3.1, paragraph 2 is not consistent with the data in Fig 3b and so we cannot be sure of the stats in Table 2. P3522: The authors state that “The isotopic analysis

showed that the DOC of the water collected in open plots tended to be enriched in 13C compared to the water collected in the closed plots and that there was no difference in 13C-DIC”. Have they mislabeled Fig. 3b as it appears the other way around to me: 13C-DOC is undifferentiable and there is a large difference in 13C-DIC.

3. Section 4.3. There are so many questions here it is difficult to accept a definitive statements offered by the authors e.g. How do we know it is just microbial respiration and not release of CO2 production from acetoclastic methanogenesis? How much of the increase in DIC is controlled by changes in water table height than production (lower water table, same pool size = concentration; any mass balance possible to test this?).

Other comments: Are the interpretations and conclusions adequately supported by the evidence presented? That is, are the assumptions valid, is the methodology sound, is the evidence adequate, and do the conclusions logically follow?

In addition to my comments in the overview it is important to return to the comment about the intensity of the sampling being insufficient to substantiate some of the conclusions the authors reach e.g. section 3.1 “In peatland water, both DIC and DOC concentrations were higher during summer than during the other seasons”. An accurate statement here is the both DIC and DOC concentrations were higher in the set of measurements made in summer than when sampled three other times during different seasons. The authors cannot extend one sampling campaign to be representative of a whole season and from this infer seasonal differences.

Similarly for the next sentence it should be stated that “On each of the 4 sampling campaigns DOC concentrations in peatland were always higher than in rivers” which is quite different to stating “DOC concentrations in peatland were always higher than in rivers”. This concentration difference may well hold at all times, but the data does not exist to support it and so the statement has to be more conservative.

Line 10, section 4.1, La Guette peatland waters contained more DOC than the regional

rivers should be rephrased as La Guette peatland waters contained more DOC than the other drainage systems forming part of this study.

There is insufficient study of the 'CO2 critical zone' for it to form a key conclusion'. Statistical analysis are required to differentiate the upstream/downstream sites to assess if there is an chemical (pH, conducitivity) signal from the peatland.

Further to undertake some analysis is somewhat futile given the pH can vary over a wide range within a site and therefore comparing points in time is challenging without hydrological control (see for example continuous pH profiles in Waldron et al., 2007, EST) As such this paper probably needs some more references to contextualize hydrological controls on C concentrations and hydrological / biogeochemical cycle controlled magnitude of short timescale temporal change.

Comments on presentation/ technical comments: Generally the paper is clearly written, with only a few examples of unclear statements e.g. p 3519, lines 10: An intense sampling effort was made in the most intensive discharge area of the peatland: sites 7, 8, 9 and 10. Do the authors mean considerable effort was expended in sampling the full extent of drainage or that these 4 sites were sampled intensively (= frequently)? Further, what is an intensive discharge site?

Techniques need a little more expansion e.g. why were the DOC samples acidified prior? To drop pH and remove DIC prior to [DOC] analysis (necessary for the samples from sites 10-16) or to lower pH and reduce bacterial activity? How long were sample stored for before measurement? How was DIC removed before [DOC] analysis?

Some typos e.g. p3520 line 14: d instead of delta; capital W when it should be w on 'where' on p3512 line 19; concentration inappropriately italicized in header 2.6? Some less good terminology e.g. richer on p3522 line 19 – the authors mean 'have higher concentrations'.

Please define 'supersaturation' – I see it used so commonly and it is a subjective term.

I do not think this term is quantitative – it is open to interpretation and so should be replaced with the more technically correct terminology of oversaturated. Unless there is a quantitative definition of supersatures, it cannot be deciphered at what concentration level a system moves from oversaturated to supersaturated and so I think it should be avoided.

The abstract does not reflect well the content e.g. the rhizosphere was mentioned in the abstract and not again in the text.The title implies that there is going to be significant discussion and evidence for the encroachment of vascular plants and this is a minor component of the paper (discussion comprises three paragraphs, page 3526) rather than the focus.

Fig. 1 needs a scale bar. I am questionning if there is a mistake in Fig. 3.

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