Biogeosciences Discuss., 5, S1130–S1144, 2008
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Biogeosciences Discussions



# *Interactive comment on* "The significance of organic carbon and nutrient export frompeatland-dominated landscapes subject to disturbance" *by* S. Waldron et al.

**S. Waldron et al.**

Received and published: 18 July 2008

Response to all three referees for their comments on bgd-2008-0011. We thank the referees for their valuable reviews, all of which have contributed to improving a revised version of the manuscript. We are pleased to note that there were few comments related to main scientific observations and interpretation, rather more requests were made to address issues of structure and requests for additional information. Only comments or recommendations made by the reviewers that have not been accommodated in a revised manuscript are dicusssed below. Our answer to each comment is prefaced with A. Anything that has not been addressed below has been changed in the text as suggested. There are several comments common to more than one reviewer e.g. that parts of the discussion would also fit better in the introduction; that the writing can be

made clearer; that more info is needed on the disturbance dates. We have noted this advice, with information from the discussion now incorporated in the introduction or methods as appropriate.

Biogeosciences Discuss. J. Limpens (Referee) General Comments: When reading your introduction (and discussion) I wondered about the relative importance of autogenic degradation (uv-degradation) of DOC in respect to heterotrophic respiration. I assume that for the use of nutrient stochiometry, uv-degradation must play a less important role than heterotrophic respiration. Could you maybe expand on this? A. Referee two also asks for comment on the proportions of heterotrophic respiration to uv oxidation, thus the response to referee two is also addressed here. As we note in the introduction, uv-oxidation is another process responsible for processing of DOM. However, perhaps not clear in the original version is that uv-oxidation and heterotrophism are linked e.g. the oxidative process can render recalcitrant molecules more labile and release nutrients (e.g. He, 2006), thus making nutrients available to the biological community. As such there is interaction between uv-oxidation, bacterial metabolism, nutrients and carbon dioxide efflux. Our calculations of carbon dioxide efflux assume this linkage is active, that all carbon in excess of nutrients could be oxidised and this could either be by respiration or uv-oxidation. We have tried to make this clearer in the text. It is not possible to attribute relative importance to each process. In addition to the interaction described earlier, the relative importance will vary depending on quality of DOM, amount of sunlight (influential here are catchment differences in slope, aspect, over-hanging vegetation.

Could you elaborate a bit more on the statistical models you used? Did you use repeated measurements?, What factors were in the model, was your assumption of normality correct? A. The data did comprise multiple catchments sampled over the range of flow conditions, so repeated sampling of each of the nine catchments took place, with each sample considered to represent a point in time that due to external environmental controls may be different from the past. The statistical models were simple



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linear regressions with cross-catchment pooling to look for larger scale trends e.g. for the Whitelee analysis, data from four and five catchments were pooled for the north and south data sets respectively. These linear regressions are not being used in a predictive manner, but simply to demonstrate the best-fit line to the data set and that there are significant relationships. The assumption of normality was generally correct; there are occasional outlying points, but residual plots showed random scatter above and below zero with no evidence of pattern. Spearman-rank correlations for the related data sets in Fig. 5. range from 0.551 to 0.800 and are all significant demonstrating correlation between variables.

M&M:Perhaps you could explain why you measured the different P fractions? A. This response is given here rather than in the methods as i) the reviewers note the methods are long and ii) measurement of different P fractions is a standard approach to characterise the different chemical forms of P found naturally, that are of different bioavailability e.g. those that need hydrolysed require enzymatic release to be bioavailable. Soluble reactive orthophosphate (SRP) represents the soluble phosphate plus easily hydrolysed inorganic and organic phosphates. As the colorimetric method can not specifically measure true phosphate in solution water chemists call it SRP rather than soluble phosphate. Hydrolysable P represents in addition the inorganic phosphates. Total P represents that plus the organic P.

M&M:Line 23, p1147. Could you elaborate on the way this measurement would affect the concentrations measured? Did you perhaps test this on the Whitelee samples, as you implied in the results on page 1149, line 24? A. Referee 2 also asks about this, thus a combined response is given here. P is not a volatile species, nor likely the organic molecules it can be bound too, thus it is considered unlikely that freeze-drying of a liquid pre-concentrated by rotary evaporation (at 50 degrees C and 70mbar) would significantly impact the P content. Redissolution of the powder took place prior to analysis and the analysis proceeded as with liquid samples, thus from redissolution onwards, the sample treatment is identical, with SRP measured from the easily released



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component, and TP measured to represent all P in the sample, released using more aggressive chemistry. The implication on p1149 that there may have been a difference in [TP] in the powdered versus a liquid sample was not due to matrix differences, but that the particulates did not constitute part of the pool in the Brocky sample as they did with the Whitelee samples. The accuracy of analysis was assessed using internal standards and blanks were used as a measure of quality control.

M&M: I miss methods followed for the 13C or 14C analyses. A. Detail for the radiocarbon isotope analyses was missing, and has been included, however carbon stable isotope measurements was outlined. All referees have suggested that the paper could be more concise, and as such analyses are standard, these have not been expanded on further.

Results: At present you do not refer to the disturbance dates in the Whitelee catchment in your results, leaving the reader wondering about possible correlations. Perhaps you could include some information on this in the text (and the figures, with numbered arrows?). Alternatively you could add an additional result-paragraph relating to correlations between measurements and disturbances, it being one of the aims of the study. A. Unfortunately we do not yet have access to information regarding the exact pattern of disturbance e.g. which coup was felled on which dates and what peat excavation has taken place where for what turbine base or road / cable construction. The site is closed and we have asked the company authorising this work for such information several times, but they have not responded.

Discussion: One of the assumptions behind using TP in the stochiometry calculations is that microorganisms can use DOP if P becomes scarce. The reference you use however (Lovdal et al. 2007), is not really representative for peatland waters. I wouldn't be surprised that a (large) part of the DOP is inaccessible for the microbes; perhaps bound to DOC/organo-metallic complexes? Do you have any references referring to a study system more akin to peatlands? A. Whilst the Lovdal paper uses marine mesocoms, the research relies on the principle that when phosphate is unavailable, it can



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be released from DOP by bacterial extracellular enzymes (Chróst 1990, referenced in Lovdal et al, 2007). Thus whilst DOP in systems more akin to peatlands may be bound to DOM (or POM) of a different composition than the Lovdal study, theoretically bacterial enzyme activity may release P from any material. P is found in natural organic matter from various sources, but mainly in the humic fraction, indeed mobile humic substances may leach P from forest soils (He et al., 2006), an observation relevant to this study site where deforestation on peatland is on-going. However, it is likely that the chemical composition of the humic substances plays a critical role in determining the P availability (He et al., 2006). For example, in their study of International Humic Substance Society peat-derived reference humic acids, He et al. (2006) found that most of the P detected was orthophosphate but that 5% of that pool could be released by phosphatase hydrolysis (a hydrolysis which estimates the bioavailable organic P). In comparison, Bedrock et al. (1995) found that most of the P in their peat humic substances was organic. These contrasting findings indicate that without detailed knowledge of the nature of the DOM and subsequent experiments on P release specific to water samples from our study site, we can only say there is likely to be considerable inter-sample variability in enzymatic P release. Thus estimates of C:P from total P are minima as not all P may be available. The text has been amended appropriately and the He et al 2006 reference added. Bedrock, C.N.et al 1995. Effect of pH on precipitation of humic acid from peat and mineral soils on the distribution of phosphorus forms in humic and fulvic acid fractions. Commun. Soil Sci. Plant Anal. 26:1411-1425.

Specific comments Abstract: Lines 8-10. I suggest to change sentence into Whitelee development to host a windfarm. (delete the particulars). A.It is not clear to us what the referee means here.

Introduction: Presently your introduction is very short, whereas your discussion is rather long. I would suggest moving some parts of the discussion into your introduction. A. Referee 2 also advocated moving some of the discussion to the introduction. The only section that has not been moved from those advocated is P1150 (ref. 1) as



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a) some of this is results so we are unsure this reference is to the correct section, and b) if it refers to the second sentence in the paragraph beginning Fig. 6; this section is needed to justify how we calculated TP and therefore should be in the methods.

Materials and methods Maybe you could consider ordering the text using the following structure to facilitate quick reading. Under site description: 1) position, and climate (are there any data available for precipitation/ mean temperature for Whitelee?), then 2) geomorphology (including explanation of N, S draining slopes) and 3) land use/vegetation type (including area were most developments will take place/ are planned and where possible also relate this to the N, S draining catchments). All three points nested within site. So first all three points for one site, then for the other. After this, under a new subheading maybe: experimental set-up and sampling. Here you could indicate the nine sub-catchments for Whitelee and the differences in sampling schemes. A. We have sub-headed the site description into the two different sites but considered the ordering suggested by the referee would break up the text too much. Temperature and rainfall data are not available for Whitelee. We have stream temperature data, and rainfall per se is not important as we are not considering water level in the headwater peatlands;rather the hydrograph demonstrates the drainage integrated rainfall pattern and intensity. The sub-heading the referee suggest is effected by the use of the chosen paragraph structure.

I would also describe here the dates of the development plans in relation to your sampling period. Do you have dates/periods during which the trees were removed, also relating to the N, S draining catchment? A.Despite repeated requests for the development Scottish Power has not yet supplied that detail of information. This is unfortunate as it would help with the interpretation and we too would like to include it as suggested.

At present the site description is extensive. Perhaps you could shorten it a bit by removing information not directly relating to the study. You could just refer to the literature source for further details. A. Ref. 2 and 3 also asked if the site description could be shortened. We have tried to shorten the site descriptions as much as possible. How-



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ever, retaining some of the information asked to be removed has value as the site descriptions are held in Scottish Power Environmental Impact Statements, which are not easily sourced, thus detail here puts this info more easily into the public scientific domain. Further, given that many carbon rich stores are now under pressure for development from windfarms (as noted by referee three in a UK context, but this is not just limited to the UK e.g. The 1st International Windfarms and Peat Conference was held in May 2008 in Galicia, Spain in recognition of the pressure on their peatlands to development) it is important to know the scale of this disturbance and how it is managed. For example, at Whitelee peat is not taken off-site but stored; if this slumped during heavy rainfall this could significantly affect [POC]. That large parts of the catchments currently being studied are those that would be subject to further disturbance is worth also flagging - in terms of carbon export budgets the engaged reader will realise that these could be higher if the windfarm is extended, which in turn adjusts the balance for the capacity of the catchment to sequester carbon

Results I suggest to stress the conclusions/process more than the values you mentioned. Now you start each paragraph with a numerical statement followed by the conclusion that you draw from it. Personally I find a text more easy to read if the most important statement (and for me this is the conclusion) can be found early in the paragraph. A. The results section has been sub-headed as suggested by reviewer 1 to facilitate quick reading. The first sentence in each section gives the data ranges, which cannot be accurately determined from the accompanying figures, nor which catchment miminum and maximum concentrations are found in, and thus are needed. The data ranges does not equate exactly to the next section which notes important trends or data patterns. Thus this order has not been changed as the second section is not always, nor fully drawn from the description of the data range.

I suggest first discussing the DOC relationship with TP, then with SRP (change current order) A. We have not changed this order as it is more natural to compare the DOC with SRP - both are dissolved constituents, whereas TP includes POC. Thus the nat-



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ural comparison is with SRP, we note for interest that there is a relationship with TP, but this has less scientific basis that expecting a relationship between the dissolved components.

Discussion I suggest using subheadings to facilitate quick reading A. Subheadings were used in the original version submitted, linked to the aims outlined in the introduction, but these have been made more formal to facilitate reading.

Page 1156:line12-17. I suggest moving this information to the materials & methods section A. The first two sentences of this section link the findings back to important times of the development and thus are needed to make sense of the profiles. The remainder, and larger part of this section is discussion and should not be in materials and methods.

Conclusions Could you maybe shorten this part a bit, only mentioning the most important parts/ Take home messages? A. Ref. 2 also notes that the conclusions are extensive. We do think they are overly long given that there are three aims to this paper. In reworking the paper, the conclusions have changed such that some material has been placed elsewhere but additional material has been incorporated. The main points of the paper are summarised here, but we are trying to make the conclusions not simply a repeat of the abstract and instead be more though-provoking, specifically, how should we treat our carbon landscapes and what significant processes take place in the receiving waters.

Figures Could you perhaps indicate the type of disturbances/ disturbance dates into figs 3 & 4? A. As stated earlier insufficient detail has been supplied about this from the site developers.

Are figures 2 and 7 really necessary? Maybe mentioning/ describing these results in the text is enough? A. Referee 2 also asked if Figures 2 and 7 were necessary. In a paper journal, both may be the type of diagram suitable for archive in the electronic supporting info, but with this e-journal, the manuscript is the electronic archive. We



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consider therefore these figures should be retained for the following reasons. Figure 2 is important as is shows clearly that sampling straddles a range of flows, but this figure also provides information on catchment response to rainfall important to those interested in hydrologically mediated DOC export e.g. very responsive rising limb, a reasonably quick recovery on the falling limb. There is much information, not strictly the focus of this paper, that can be gleaned from consideration of the hydrograph, e.g. that the seasonal signal is somewhat independent of the size of the event. To describe this type of detail in the text precludes others with related interests consulting this publication for their research. Figure 7 presents the Whitelee data in the context of collated UK data, but in a form not presented in the Dawson and Smith paper. This figure shows more efficiently the inter-catchment and inter-site differences/ similarities than a written description could and allows the point to be made in the text succinctly that there is not a strong relationship between catchment size and OC loss for these catchments at this scale. However, budgets are rarely considered as a function of catchment size (we have seen no other publications to this effect) and thus we think this figure important as it prompts thought of what may happen with increasing catchment size with respect to for example the river continuum concept. We did not plot this figure to include the megacatchments in Dawson and Smith, as the detail of the study site was lost, but these catchment sizes show different responses as [DOC] is much lower. This diagram is also a useful way to prompt consideration of catchment management of carbon.

Anonymous Referee #2: I believe this manuscript could be suitable for publication in Biogeosciences, as it falls within the remit of original papers for the journal. The main aims of this work were to establish how aquatic C, N and P species will be affected by an upstream windfarm development. Allied to this, stoichometric ratios have been applied to determine potential maximum production of carbon dioxide from the DOC/POC within the stream itself. However, I have some comments with regard to focussing the manuscript to establish the main points of the work and at times found the language could be improved for conciseness, clarity and precision of the work. Overall, the indi-



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vidual sections could be better signposted to express each of their main points more clearly. A. We hope that concerns have been addressed. As before comments dealt with have not been detailed below and some responses have been incorporated into the response for reviewer 1.

The sampling protocol at Whitelee, in particular for POC, which is particularly important in disturbed catchments, must be taken as only a basic estimate of potential carbon losses from the catchments under investigation as one sample approximately every 3 weeks will underestimate this flux and is not bimonthly, particularly as hydrological events were not targeted. Therefore, the interpretation of the budget/flux data should be viewed with this in mind. It might be better to remove this section reliant on budgets and focus the paper on stoichiometry relationships and affects of disturbance on these parameters. A. The importance of the stoichiometrical overview is to consider the fate of excess carbon; ultimately it may be converted to atmospheric carbon dioxide. Calculating this potential efflux is not possible with estimates of total flux, thus this would have to be done anyway and for understanding it is better that the protocol for this and the estimates arising are documented, thus this section should be retained. With respect to under-estimation, it was made clear in the submitted paper that there are certain assumptions that have to be made in calculating fluxes of all determinants, not just POC, and that the sampling strategy in addition to other factors are likely to lead to an under-estimation of potential flux (original version, page 1157, lines 23). However, given the interest in freshwaters as a source of atmospheric carbon dioxide, these estimates are still important and should be included.

Abstract:The abstract could be more concise and for clarity state that this work is about a comparison between disturbed and non-disturbed peatlands and that at Whitelee, it is offsite receiving waters that the study is taken from pre and post disturbance. The 14C measurements described in the abstract are not actually part of this work but more a discussion point and should be removed from the abstract. A. 14C has been removed from the abstract and we have tried to be more concise.



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Introduction: A concise introduction could be rearranged in order that the literature leads to the aims more fluently. For clarity, the 3rd aim of the paper (budgets for carbon export) needs to be stated more clearly in the introduction to match the 3 aims described in the discussion section. A. We hope that by rearrangement of some discussion to the intro this has been done. The third aim has been made clearer.

P1141, Line 10: The general proportions of sources of carbon dioxide in headwater streams should be stated here. A. Agreed that in headwaters degassing will be an important component, but at times, depending on flow drainage from soils can be reduced and here heterotrophic activity may be as, if not more, important in producing carbon dioxide. Relative proportions will vary between sites and temporally, thus it would be inappropriate to generalise at present about general proportions.

Although in stream processing of DOC to carbon dioxide does occur in these environments, what are the proportions of heterotrophic respiration to uv oxidation? A. Answered in response to reviewer 1.

P1141, Line 24: From the site area details later on, Glen Dye does undergo major land management practices (heather strip burning for grouse, sheep grazing) but could be considered a less disturbed environment. A. The manuscript acknowledges that there is land management, but notes that in comparison to Whitelee, Glen Dye is little managed.

Methods: I found the methodology generally well written but overlong in places and feel that this section could be reduced without lowering the impact and understanding of how the work was carried out. With a more extensive use of references, particularly in the site description, this section could be reduced to concentrate on the more important parts relevant to the present study. A. Ditto previous comments that documents describing site are not easily accessible and this information best given here. Wihtout this info the scale of the disturbance is not clear.

P1144, Line 11: How long was the period of collection prior to disturbance? What



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are the disturbance dates? How far downstream were the sampling sites from the actual development? A. Again the answers to these questions are unknown without information from the developers (which has not yet been forthcoming).

P1144, Line 20: As stated earlier this sampling protocol is a major limitation on POC measurements. What was the sampling frequency at Glen Dye? A. Included in text.

P1144, Line 22: This section is results and the discussion of limitation of light penetration is important in terms of the limited UV oxidation that might be occurring. A.Discussion of uv-oxidation considered previously.

P1145, Line 30: Particulate load is described as low, what are this actual value? Moreover, in the Water of Charr catchment (upstream from the 41.7 km2 Water of Dye site), the particulate load is substantially higher than other parts of Glen Dye due to eroded areas in the upper part of its catchment. Due to deposition in the main channel, this higher POC might not be observed at the Water of Dye. This spatial variation is an important consideration at the Whitelee catchment, as much of the POC generated could have been deposited, resuspended or undergone decomposition to DOC and carbon dioxide in the stream prior to reaching the outflow measurement sites. A.The particulate load value has been added in. What happens upstream of a sampling point in a problem is any catchment study and short of very detailed spatial sampling, remains somewhat unknown. Our aim here was to assess inter- not intra-catchment differences. To some extent the sampling point integrates all processes upstream. Thus, whilst the POC influx upstream may have been reworked and contributed to the DOC pool, such reworking will also contribute to the SRP and dissolved N pools too. Although the form may have changed, these pools represent export from the catchment, whether as SRP or TP, DOC or POC and the observed relationships are still valid.

P1147, Line 18: Why mention the limit of detection for nitrite when the data is not presented in this paper? A. Nitrate is quantified by subtraction of nitrite concentration from total oxidised nitrogen, thus whilst nitrite data is not presented (as very low, approxi-



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mately, two orders of magnitude less than nitrate), nitrate concentrations are and the ability to quantify this depends on how well nitrite and TON can be measured.

Results: P1150, Line 12: what value of primary production is considered insignificant? Even in upland headwaters of Glen Dye, PP exists and can be determined. A. This is a fair point, and we have clarified the text to indicate that was a visual assessment, an approach not satisfactory for a study of primary production. However, quantifying primary production is not the mainstay of this paper, and our field experience with Glen Dye, where significant algal mat and filamentous algae can be visibly present for prolonged periods of time under low flow conditions, allows us to say that there was little visible evidence of in-stream production.

Discussion: P1153, Line 10: Temporal variation in the carbon dioxide efflux in these catchments is also influenced by the soil pore water carbon dioxide inputs. This should be stated as being the initial control on carbon dioxide in the stream waters. Temperature also controls carbon dioxide efflux both in terms of soil production of carbon dioxide and carbon dioxide water solubility and hence atmospheric equilibrium and efflux. P1157, Line 27: As much of the DOC is clearly allochthonous in origin, it is even more reason to discuss the influence of soil-derived carbon, (DOC and carbon dioxide) rather than just in-stream production of these carbon species. P1159, Lines 17: This should describe the maximum proportion of organic carbon that could be available for respiration and end up in the atmosphere or remain as organic carbon to the ocean. How does this take into account further continual inputs form soil waters? What is the carbon dioxide equilibria? is it with atmosphere or with the bicarbonate/ carbonate ions? either way requires pH and temperature. A. The above three comments are all related to the source, passage and release of carbon dioxide or DOC in the lotic system. Whilst this is an important process some of the detail the referee suggests is not required in this paper. Comment has been added to note that carbon dioxide is introduced in the headwater catchments. In acknowledging the source of DOC is allochthonous it is implicit that soil-derived carbon is important; here we focus on the



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capacity for that material to be reworked. Comment has been added to make clear that the carbon dioxide efflux potential is based on conversion of the DOC pool and that there is another separate carbon dioxide pool. We are aware that the potential for efflux is based in the carbon dioxide equilibria and this requires pH and temperature (see for example Waldron 2007 where we use this approach) but as we do not have that data for Whitelee it is not possible to convert potential efflux to true efflux, nor differentiate easily the mixed contributions to true carbon dioxide efflux (a problem also discussed in Waldron et al 2007). The calculation of an annual budget assuming integrated DOC concentrations between samples helps accommodate the continual inputs i.e. each sequential calculation accommodates a loss or gain in DOC, which in turn could be respired to carbon dioxide.

Tables and Figures: Table 1 is unnecessary and could be detailed in the text. A. There are still significantly fewer published measurement of 14C-DOC than other tracers of carbon source, thus increasing the published library is desired by the community and will be of use to others in understanding carbon flow. For these reasons we would prefer to retain this table.

Figure 1: The area of each catchment is detailed already in Table 2. However, WL17 is 15.1 km2 in Table 2 but 34.5 km2 in Figure 1. A.Table 2 provides the area of the catchment that does not contain the nested catchments 9A and 9D (this was noted in the legend) and has been presented like this to allow differentiation of the additional potential flux from the non-nested part of WL17.

Figure 5: The N and S draining catchment legends should also be stated in this figure so that each figure stands alone. A. This was not done due to difficulties with the drawing package. To show the legend it was not possible to remove the regression lines and the diagram become too busy. The important aspect is that it is clear what the reader is considering.

Anonymous Referee #3 Most of referee 3 comments have been dealt with in response



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to refs 1 and 2.

It is perhaps surprising to see little nitrate response to forest harvesting / disturbance as this has been commonly reported for UK felling studies on organo-mineral soils. The response is generally less extreme for gleyed soils and there have been few studies on peat soils. The explanation for a lack of nitrate increase is rather left hanging on p1156, lines 10 and 11. A. Yes, the lack of response from nitrate is intriguing, but we do not yet have another interpretation for this. It may be the peat soils / microbial communities in the headwater catchments retain any N that is released. However, this is speculative interpretation and that is why it is left hanging.

The discussion of the impact of the current disturbance on peatland carbon balance needs to be set in the context of the historical effects of the forest development on the long-term carbon balance at the site. The conversion of some of the peatland to forestry has already influenced the C balance at this site. Work by Milne, Cannell and Harrison specifically address this issue for afforested peatlands. A.In previous drafts of this paper Hargreaves, Milne and Cannell (2003) was considered to be cited, but it considers just C-gas exchange, not aquatic export, thus was not included as not considered to directly relevant. Harrison's papers have also not been cited as there is little there on the papers we considered on aquatic C export from afforested or deforested peatlands. Instead Dawson and Smith (2007) was chosen for the section on C balance as this provides data on aquatic C export from many different studies, including for example the Hargreaves, Milne and Cannell 2003 paper. Cummins and Farrell's 2003 publication on the impact of clearfelling and reforestation on P export has now been included.

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