

Interactive comment on “Peat decomposition records in three pristine ombrotrophic bogs in southern Patagonia” by T. Broder et al.

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Authors' final response to the reviewers' interactive comments on “Peat decomposition records in three pristine ombrotrophic bogs in southern Patagonia” by T. Broder et al.

We thank the two anonymous reviewers for their constructive and clarifying reviews that helped to significantly improve our manuscript. Indeed the focus of our first manuscript version may have included too many statements about palaeoclimatic interpretation of our data, although we did not date our cores and thus such statements were poorly constrained. Therefore we carefully examined the manuscript, strengthened the presentation of the decomposition records and chemical data, eliminated paleoclimatic interpretation of the records, and rather focused on factors affecting decomposition in general. This was indeed our original intention of the study. We think that the presented

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impacts on decomposition records could be of potential relevance for the interpretation of decomposition records in a paleoclimatic sense, although in our case paleoclimatic interpretation of our particular records was beyond the scope of this work.

Anonymous Referee #1

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"This manuscript presents data on peat decomposition in three pristine ombrotrophic bogs in Patagonia. It is generally interesting and new material from the region that has not been so far very disturbed by human. Therefore, palaeoclimatic and autogenic explanation of the development of peatlands might be a good point but it is not explored in the text. The manuscript looks like a very technical study with sort of geochemical methods applied to estimate peat decomposition, with an uncertain approach to reconstruct climate on the basis of the analysed cores. This is important contribution that should be published, however some statements connected with palaeoclimatic reconstruction should be better balanced. The option is to make radiocarbon dating on the cores to make inferences more reliable or concentrate only on the mechanistic aspect of peat decomposition."

As outlined above, we removed all attempts to reconstruct climate development and paleoclimatic interpretation, but rather focus on the mechanistic aspects of peat decomposition as suggested.

specific comments

"I find palaeoclimatic approach as very controversial here because of lack of dating. Therefore I find some interpretations too speculative. We also do not have plant macrofossils description therefore it is not sure if decomposition is connected with different plant potential of decomposition or environmental change. I think that aspect might be a very important topic of the study."

The reviewer is right that paleoclimatic interpretation would require ¹⁴C dating of the

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profile and also records for vegetation (e.g. pollen or macrofossils) would be desirable. As this was beyond the scope of our study we now focus on the presentation of the decomposition records and factors affecting decomposition at the sites in a more general sense. The influence of vegetation on decomposition is now stated more clearly, especially when discussing the most recent parts of the investigated profiles for which we can assume a comparable vegetation as present to date.

"There are some trivial statements connected with potential causes of the decomposition (Page 10555 line 17-18), that show uncertainty of authors on the data presented."

We removed this part because the paleoclimatic interpretation was beyond the focus of the study. As known from available studies, decomposition mainly proceeds in the unsaturated peat (i.e. the acrotelm) while there is little further decomposition in the permanently saturated catotelm. To interpret changes in decomposition as changes of the thickness of the acrotelm (e.g. due to temporary dryness) or as differences in litter or nutrient input is still valid from our point of view. The text should be more concise now and we omitted unnecessary statements.

"Also, statements about climate are very speculative (Page 10555 lines 23-24). This section was shortened accordingly."

We removed climatic interpretations and focused on changes in decomposition that are commonly interpreted as changes from dry to wet conditions."

"Did the authors consider also autogenic development of the peatland? I mean processes within the dynamics of the plant communities connected with the different vegetation patterns."

There is to date little information available about the investigated sites. Present studies about the development of these peatlands have so far only investigated in near-surface layers of the peat (Kleinebecker et al., 2007, 2008) or have had a different focus, such as trace element distribution (e.g. Biester et al., 2003).

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"It is also not clear how sea sprays influence decomposition – is this through the different vegetation that is adapted to this input?"

We recognized that this point was not presented clearly enough. Basically, we see two potential impacts of sea spray on decomposition. The more obvious impact is a fertilizing effect of the sea salts, favoring different, probably more easily decomposable vegetation (Kleinebecker et al., 2008). We now focus on this idea. The second point could be a provision of electron acceptors for anaerobic respiration through input of sulfate. Sulfate has been shown to affect anaerobic carbon mineralization pathways in sulfate deposition studies (Gauci et al., 2008; Gauci and Chapman, 2006) and an effect may be postulated with sulfate deposition by sea spray input as well. As this second effect appears uncertain with regard to our data we do not discuss it in detail anymore and reworded parts of the introduction, discussion and conclusions accordingly.

"It is rather obvious that in cannot be corrected here, but I would like to stress that such data (decomposition, geochemistry) should be always supported by the other proxies like pollen and plant macros to draw reliable palaeo conclusions. The title of the manuscript suggests that only decomposition is going to be explored but authors are trying to draw palaeoenvironmental conclusions without time axis. Consequently, all attempts of palaeoenvironmental inferences are based on the depth axis."

The reviewer is right that for palaeoclimatic interpretations pollen and plant macrofossils would be needed. This was, however, not the intended focus of this study. The reviewer is right that the manuscript contained too much palaeoclimatic interpretation of the data, which was also in conflict to the title. Therefore, we removed or shortened such parts substantially. Certainly, there is still some time line in the interpretation of the data when we compare the three records in terms of different phases of decomposition. Nevertheless, we removed interpretations of the data which cannot be adequately supported, e.g. due to lack of dating, or that were too speculative. When discussing (palaeo)climatic interpretation of the recorded indices, we now focus on comparing the decomposition record in the upper profile of the sites. The indices would indicate con-

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trasting changes in climate for the PBr2 and Sky sites, which is difficult to argue for based on the relatively small distance between the sites. Therefore, we emphasize that the interpretation of the indices needs caution and they rather reflect site specific, local conditions.

"The stable isotopes results discussed in section "Decomposition and isotopic signatures of solid peat" might be biased as they were measured on the bulk peat where modern roots of vascular plant were also milled and measured. There are examples from the modern literature that it is better to use separated e.g. Sphagnum stems of known species to use this data to a potential quantitative reconstruction. This problem should be discussed in this and further parts of the manuscript."

The reviewer is correct that in many studies isotopes were analyzed on isolated Sphagnum material from the bulk peat, which is of course advantageous. Nevertheless, we think that our data are not substantially biased as suggested. Our sites were predominantly covered with sphagnum and the peat was in general not very decomposed. We did identify modern roots of vascular plants and removed them before milling. Nevertheless, we will certainly pay more attention to this suggestion in future studies.

"Please, explain what you mean "genesis of the bog" (Page 10557 lines 19-20)."

This was indeed unclear. We meant the hydrological and geomorphological setting, i.e. that the PBR site is located in a bowl shaped depression in this case. However, as the statement about recycling of isotopically light carbon cannot be backed up by our data set and remains a hypothesis, we shortened this part and removed this statement.

"The part Conclusions consists of several statements that are not based on the available data. Is there a sense to state that peat decomposition in Boreal peatlands was higher than in Patagonian peatlands? We would need a really detailed spatial data to make such a general conclusion! Furthermore, lack of a time scale does not give an opportunity to write that a process took place over time."

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We removed these parts of the conclusions and now focus on the available data in terms of interpreting the decomposition and factors affecting decomposition in general (e.g. bog wetness and ash deposition) only.

Anonymous Referee #2

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"This paper is an interesting contribution to an apparently rich body of literature on chemical and physical properties in Patagonian and/or ombrotrophic bogs. Using so many complementary tools to study the chemistry and degree of decomposition of the peat is a neat approach that does not seem well explored in the literature and is of great global importance as peat stores a great deal of carbon with is sensitive to decomposition. Although I do think that all of this great information should be published, I don't really think that this paper is quite ready for the reasons numbered below. It is my suggestion that this paper just describe the degree of decomposition rather than trying to attribute decomposition to paleoclimatic events or other physical and chemical properties (such as ash content, sea spray input, non-quantitative observations of soil moisture), unless a more rigorous approach is taken (see point 4 below). It feels too far reaching right now."

We agree, as also pointed out by reviewer 1, that the manuscript in our first version included too much interpretation in terms of paleoclimatology. According to both reviewers' suggestion, we now focus on the decomposition itself, compare the records of the indices and discuss possible factors affecting the records. We agree that a paleoclimatic study would require a more comprehensive approach, including pollen or macrofossil records, and ^{14}C dating. This was certainly beyond the scope of this study.

"My other major sticking point is that humification is never defined and when I read humification, I have to assume that someone means an increase in aromaticity. But, some evidence in your manuscript indicates that this is not what you mean. For example, your relationships between decreasing C/N and increasing humification index (see

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point 1)."

See below, response to point 1

"There are also a few methodological things I am worried up that I would like explained before this moves through (see points 3, 5, and 6). It's also just a very data rich study which is great, but it's hard to read because the message is getting lost (see point 2 for specifics)."

We admit that the study contains much data that has probably not been presented in sufficient clarity. Thereby our main points may have got lost. We carefully revised the manuscript, shortened and removed side aspects and strengthened the discussion and conclusion. We hope that we could successfully address the raised points (see below)

"Given that the methodological questions that I have in points 3,5, and 6 can be cleared up and assuming that either a more rigorous approach is taken to explain the controls on decomposition or the authors choose to simply put forth observations about soil chemistry, then this paper should be able to move into publication."

We hope that we could successfully clarify the raised issues (see below). We also shortened and simplified some observations that were either beyond the scope of this paper (a detailed paleoclimatic interpretation of the records) or that could not be sufficiently clarified by available data (e.g. the effects of sea spray)

"1. I think that the way that you have presented your FTIR data is really quite accessible. Using these ratios of various functional groups to polysaccharides has given you a neat way to interpret the data. On page 10549 around line 25 you list all of the functional groups that you are looking at, but none of these are cited. I am not as familiar with peat literature, but I am sure those citations are out there. There has been extensive work done on the application of FTIR to soils, and the confirmation of each of these regions in soils, so these should be cited."

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We rewrote the text to clarify, according to which references the interpretation of FTIR peaks was done (Niemeyer et al., 1992; Senesi et al., 1989).

"Also, when you introduce your ratios, it might be nice to include a table re-describing what each of those ratios is; for example, 1630/1090 is aromatic C=C or C=O of amides/polysaccharides."

We accept this suggestion and included a table to provide a quick overview of peak ratios.

"From a quick literature search, I see that there is a rich history of using the term "humification index" to describe the fraction of non-humic material to total humic and fulvic acids extracted using NaOH (Gigliotti et al. 1999) or to quantify molecular complexity and condensation (Kalbitz et al. 2003). My concern with use of the term humification in this manuscript is that there has been a shift from the traditional view that the oldest compounds in the soil are highly aromatic as a result of the condensation of quinones (Kononova 1961) to the concept that the oldest compounds in soils are chemically labile molecules (carbohydrates, long chain fatty acids, amino acids) that they are protected from degradation by the mineral matrix (see literature by Plante, AF; Paul, EA; Miltner; von Lustov; Kogel-Knabner). I guess I would just like to see a definition of humification in your text to better understand how you are interpreting humification and decomposition."

The reviewer is right that the term 'humification' has been used with different definitions. Therefore we clarified this ambiguity, stating that humification in the sense of our study is a qualitative change of organic matter due to alteration during decomposition. This would be in line with the interpretation of Kalbitz et al. (2003). We see that there is currently a new view being established that many 'old' compounds in soils are actually quite 'labile' compounds. Nevertheless, most studies in this field come from mineral soils, where such compounds may be protected by the mineral matrix. We are not aware of a study demonstrating such predominance of labile compounds in organic

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soils devoid or low in mineral components. We therefore kept to the interpretation of e.g. Holmgren and Norden (1988), Norden et al (1986), and also Chefetz et al. (1997), who investigated either peat soils or monitored molecular changes of humic acids during controlled decomposition experiment.

"2. I feel that the "take-home message" of the paper is a bit jumbled and mostly it is because you have a vast amount of data to discuss. Mostly, I have gotten confused about whether the discussions of ash and isotopes are included as paleoclimatic indicators of decomposition or whether you are trying to attribute some chemical characteristic to decomposition."

As outlined above, we revised the manuscript to improve clarity and now focus more on interpreting decomposition patterns and comparing potential decomposition indices. We now also better explain in which layers ash deposits apparently affected decomposition (i.e. input of nutrients, electron acceptor supply). The interpretation of $\delta^{13}\text{C}$ has also been strengthened. We also examined whether $\delta^{13}\text{C}$ may serve as a decomposition index itself (which was not the case in our study). Some discussion of paleoclimatic factors (e.g. dry/wet or warm/cold) compared to the respective signals in the decomposition indices C/N and humification index cannot be avoided, though because we investigated peat decomposition as preserved in records.

"At first, it seems that you measured the C and N isotopes to assess a degree of decomposition. To introduce this concept, more discussion about how microbial processes fractionate C and N would aid in the interpretation. But then when you discuss the results, it seems that there was no clear trend with decomposition and the isotopes. So, then you use them as indicators of age. It's just not clear what angle you are taking. Perhaps if they aren't important indicators of decomposition, you could just say that and then discuss them as indicators of age. Your message here is just not clear."

We now state clearly that in our case stable isotopic composition was not related to decomposition. We removed interpretation in terms of paleoclimatic phases, as this is

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not the focus of the study.

"The same tends to be true for the ash- sometimes you use it to date the profile and sometimes you are discussing the impact of the ash itself on decomposition. These should be separated. Perhaps all of the paleoclimate information should go together."

As both reviewers stated, the paleoclimatic interpretation was not well constrained due to a lack of ^{14}C dating and macrofossil and pollen data. We thus removed most paleoclimatic interpretations. We now discuss paleoclimate only in terms of bog wetness and dryness and the known impact of dry and wet periods on decomposition. We also tried to clarify in which way ash deposition may affect decomposition, i.e. in terms of fertilization and electron acceptor supply for respiration.

"3. On page 10555, lines 5-8, you seem to be trying to attribute the low HI to sea spray input. But, there is also a vegetation difference between your sites. How can you know that it's not just the vegetation that has affected the 1630/1090 input (and residual in the peat)? I see that the site you are referring to is Sphagnum dominated and that Sphagnum has the highest C/N of any of your plant samples. Perhaps vegetation is more of a control on HI/ decomposability than sea spray input. But, you haven't tested for this."

The reviewer is right that vegetation is a major control on decomposition through litter input. Therefore, we now focus more on this factor. As vegetation was shown to be affected by sea spray input (Kleinebecker et al., 2008) we still try to better explain why sea spray input also affects decomposition. We also mention that input of electron acceptors (sulfate) may have had an effect on anaerobic respiration as well without elaborating this hypothesis very much. An effect of sulfate deposition on anaerobic carbon mineralization pathways has been documented in methane studies, thus this effect may also apply to sulfate from sea spray input.

"4. Continuing with my concern of your attempts to attribute decomposition to environmental factors (sea spray input, precipitation, vegetation; see 10560 lines 24+ and

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10556 lines 7-8), it doesn't seem that these assumptions are validated very rigorously. Perhaps you could use some statistical tool (i.e. multiple linear regression) to determine what factors of the many that you measure control decomposition at each site. If this is beyond the scope of your intentions with this paper, then you should omit sweeping statements about controls on decomposition and just describe the chemical characteristics with depth. This is still novel and interesting."

We agree that assigning changes in peat decomposition degree to environmental factors remains a concept that cannot be rigorously validated in a study that examines information from peat cores. We also tested statistical tools (multiple linear regression) to get more information from the data, but we found that this approach does not add much information about possible causes. We decided not to include a statistical model, as this would require much space with limited new insight and the datasets for the individual sites are probably too small. On the lumped dataset (probably a limited approach), to predict the FTIR based decomposition index, most important variables were depth > N content > C content > Titanium (can be seen as a measure for dust and ash deposition) > Bromide (most probably sea spray) > Calcium (from ash deposits or bedrock?) > (C/N) > DOC (explained together 84.7 %). To predict C/N ratios it was Rb (ash deposition) > FTIR ratio (molecular changes) > Bromide (sea spray) > Iron (ash layers?) > d13C > d15N > manganese > Ni > Copper > Chromium (explained together 73.6 %). d13C could be only poorly explained (42.6 %). These are mostly the factors that we discuss and give possible causal explanations for. Therefore, we decided to rather discuss possible controls and according to the reviewers suggestions we strengthened and shortened the provided information where appropriate. We preferred to leave out statistical modeling as both reviewers stated that the article already contains a lot of data and information.

"5. How long was the extracted and filtered pore water stored before analysis? At what temperature was it stored?"

We added that the samples were stored at about 5° C for no longer than 12-14 days.

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According to our experience with comparable samples, this should not have affected DOC concentrations and stable isotopic composition.

"6. You admit that the mineral interference makes interpretation of you FTIR spectra near the ash impossible. But, how do you know that you did not have a large interference from ash in the non-ash layers. For example, you did not observe an ash layer in Sky I. How do you know it just not all mixed together? Did you ash your samples to see if it was all organic material?"

For calculation of the FTIR peak ratios, the spectra were examined for any interference with minerals. We consulted the appropriate literature for absorption bands of minerals in the IR range and characterized the samples also using X-ray diffraction. Usually, in case of presence of minerals, distinct and sharp peaks appear using these techniques, compared to rather broad features caused by organic material. Furthermore, we analyzed the peat using XRF analysis of element contents. As shown in Fig. 2, especially the XRF analysis turned out to be a sensitive tool for identification of ash layers, even in case they could not be identified visually and did not produce any signal in the FTIR or XRD. In total, 3 PBr2 samples, 3 Skyl samples, and 6 Skyll samples were therefore potentially regarded to be influenced by ashes, although they would mostly still fit the profile. Thus we think that the interpretation of our results is reliable.

7. Comments on tables and figures:

"a. In table 3, is there a standard error that should be reported for these vegetation samples?"

We now report a standard error of repeated measurements. As vegetation samples were from one site only, we included data from other references (Kleinebecker et al., 2009) to give an estimate for possible ranges.

"b. In table 4, you might consider including an average peat accumulation that can be referred to with text on page 10559."

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This has now been included as suggested.

"c. Figure 3- you never stated anywhere that you weren't investigating between 2000 and 4000 cm⁻¹."

We added to the methods section that for an evaluation of the organic matter properties we focused on the range from 300-2000 cm⁻¹. Most information contained in this spectral range. Characteristic absorption bands in the range from 2000-4000 cm⁻¹ are rather few and showing the whole spectrum would have caused difficulties in legibility of the relevant wavelength range.

"d. Figure 4, the $\delta^{13}\text{C}$ trends between the DOM and solid are different between the Sky samples and the PBr2. Do you know why? Also, the Skyll peat is enriched in ^{15}N at the surface while the other two samples are not. Do you know why? You don't discuss this in the paper."

Indeed, the $\delta^{13}\text{C}$ trends between DOM and solid peat are different between Sky samples (absolute depletion in ^{13}C) and PBr2 (trend towards enrichment of ^{13}C). So far, we have no explanation for this finding. To get some more insight additional methods for DOM characterization would have been necessary but unfortunately we could not do this. A similar point is the ^{15}N enrichment at the surface of Skyll, for which we also do not have an explanation. We know that such ^{15}N signatures are quite uncommon for sphagnum peat. A trend towards less negative values was reported for increasing wetness of the (micro)site (Loisel et al., 2010) and such high $\delta^{15}\text{N}$ was so far only reported for Sphagnum of elevated nitrogen content or herbs (Asada et al., 2005). Nitrogen enrichment can definitively be ruled out for the sites under study. Therefore we currently have no explanation for this observation. Without reasonable explanations at hand we did not discuss these findings in more detail.

Klaus-Holger Knorr - on behalf of all coauthors

References

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Asada, T., Warner, B., and Aravena, R.: Effects of the early stage of decomposition on change in carbon and nitrogen isotopes in sphagnum litter, *Journal of Plant Interactions*, 1, 229-237, 2005.

Biester, H., Martinez-Cortizas, A., Birkenstock, S., and Kilian, R.: Effect of peat decomposition and mass loss on historic mercury records in peat bogs from patagonia, *Environ. Sci. Technol.*, 37, 32-39, 10.1021/es025657u, 2003.

Chefetz, B., Adani, F., Genevini, P., Tambone, F., Hadar, Y., and Chen, Y.: Humic-acid transformation during composting of municipal solid waste, *J. Environ. Qual.*, 27, 794-800, 10.2134/jeq1998.00472425002700040011x, 1997.

Gauci, V., and Chapman, S. J.: Simultaneous inhibition of CH₄ efflux and stimulation of sulphate reduction in peat subject to simulated acid rain, *Soil Biol. Biochem.*, 38, 3506-3510, 2006.

Gauci, V., Blake, S., Stevenson, D. S., and Highwood, E. J.: Halving of the northern wetland CH₄ source by a large icelandic volcanic eruption, *J. Geophys. Res-Biogeol.*, 113, 2008.

Gigliotti, G., D. Businelli, and P. L. Giusquiani. 1999. Composition changes of soil humus after massive application of urban waste compost: a comparison between FT-IR spectroscopy and humification parameters. *Nutrient Cycling in Agroecosystems* 55:23- 28.

Holmgren, A., and Norden, B.: Characterization of peat samples by diffuse reflectance FT-IR spectroscopy, *Appl. Spectrosc.*, 42, 255-262, 1988.

Kalbitz, K., Schmerwitz, J., Schwesig, D., and Matzner, E.: Biodegradation of soil-derived dissolved organic matter as related to its properties, *Geoderma*, 113, 273-291, 2003.

Kononova, M. M. 1961. Soil organic matter, its nature, its role in soil formation and in soil fertility. Pergamon Press, Oxford.

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Kleinebecker, T., Holzel, N., and Vogel, A.: Gradients of continentality and moisture in south patagonian ombrotrophic peatland vegetation, *Folia Geobot.*, 42, 363-382, 2007.

Kleinebecker, T., Holzel, N., and Vogel, A.: South patagonian ombrotrophic bog vegetation reflects biogeochemical gradients at the landscape level, *J. Veg. Sci.*, 19, 151-160, 10.3170/2008-8-18370, 2008.

Kleinebecker, T., Schmidt, S. R., Fritz, C., Smolders, A. J. P., and Holzel, N.: Prediction of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in plant tissues with near-infrared reflectance spectroscopy, *New Phytol.*, 184, 732-739, 10.1111/j.1469-8137.2009.02995.x, 2009.

Loisel, J., Garneau, M., and Hélie, J. F.: Sphagnum $\delta^{13}\text{C}$ values as indicators of palaeohydrological changes in a peat bog, *Holocene*, 20, 285-291, 2010.

Niemeyer, J., Chen, Y., and Bollag, J. M.: Characterization of humic acids, composts, and peat by diffuse reflectance fourier-transform infrared-spectroscopy, *Soil Sci. Soc. Am. J.*, 56, 135-140, 1992.

Norden, B., Fyfe, C. A., and McKinnon, M. S.: ^{13}C CP/MAS NMR study of peat in the solid state, *International Peat Journal*, 1, 153-164, 1986.

Senesi, N., Miano, T. M., Provenzano, M. R., and Brunetti, G.: Spectroscopic and compositional comparative characterization of IHSS reference and standard fulvic and humic acids of various origin, *Sci. Total Environ.*, 81-2, 143-156, 1989.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/8/C6072/2012/bgd-8-C6072-2012-supplement.pdf>

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