Anonymous Referee review of cp-2023-7

Deglacial export of pre-aged terrigenous carbon to the Bay of Biscay

This manuscript by Queiroz Alves et al. presents a marine record of organic biomarkers, stable isotopes, radionuclides, and elemental ratios from the Bay of Biscay to reconstruct the carbon cycling history of this site which is hypothesized to be primarily driven by post-glacial fluxes of relict, terrestrial organic matter from western and central Europe since 24 ka. The authors also use a Bayesian mixing model framework to quantitatively estimate the contributions of three organic carbon endmembers: marine biomass, terrestrial material formed < 50 kyr, and ^{14}C-depleted (-1000‰) petrogenic material. Their results suggest that previously reconstructed flood events in the prehistoric Channel River were responsible for an increased flux of terrestrial organic matter (OM) into the Bay of Biscay, with the most significant episode occurring between 17.5 and 16.5 ka. The authors also use this evidence to suggest that some of the mobilized terrestrial organic matter was also released as CO_2, contributing to the rise in atmospheric concentrations observed during the period of major Channel River floods.

The methods used to produce the original data in this manuscript appear to be sound and the general structure of the text is well organized. However, there are a number of issues with the interpretations of the proxy records and modeling results generated that have significant implications for the main takeaways of this study. That being said, the findings within this manuscript have the potential to provide the scientific community with valuable paleoclimate insights as to how rapid permafrost thaw affects local and global carbon cycling dynamics and climate feedbacks. I provide comments about each issue below, which I think can be addressed with major revisions to the text.

General Comments

Proxy Interpretations: This study utilizes a number of biogeochemical proxies, including *n*-alkanes, *n*-alkanoic acids, GDGTs, hopanes, and elemental ratios to explore the carbon cycling history of this marine sediment core. However, it is often unclear to the reader how each proxy is being interpreted. In the methods section of the main text, the authors should include statements about how changes in each proxy value are interpreted in this study in addition to the references supporting them (i.e. "greater BIT index values are interpreted as an increased contribution of terrestrial organic matter (Hopmans et al., 2004)"). In Figure 2, it looks like most of the original data is already plotted such that positive changes in values are interpreted as an increase in the terrestrial organic matter signal. Perhaps the authors can annotate this in Figure 2 to help the reader understand the major trends plotted in this information-rich graphic.

CPI: As elaborated on in the specific comments below, the authors' interpretations of the Carbon Preference Index for sedimentary *n*-alkanes (CPI_{Alk}) simultaneously as a proxy for vegetation change and thermally/biologically degraded terrestrial material are confusing and not well supported by the referenced literature. I do not recommend interpreting CPI_{Alk} with a range from 4 to 6 as a signal of changing vegetation in this record. All vegetation, both terrestrial and aquatic, that is modern/contemporaneous or unaffected by organic matter degradation has a CPI_{Alk} value > 1 and the high variability of values within plant taxonomic groups and habitats do not make this proxy a reliable indicator of vegetation source changes (Bush & McInerney, 2013). The authors' secondary interpretation, that CPI_{Alk} being > 1 throughout the record suggests heavily degraded, petrogenic OM is not a significant component of this carbon cycling system, is much sounder. However, the overlapping plots of CPI_{Alk} and f*ßß* in Figure 2 can be misleading because CPI_{Alk} shows minimal change in labile vs. recalcitrant carbon sources over time while f*ßß* suggests a change in the amount of terrestrial organic matter export around 17 ka. To address this, the CPI_{Alk} plot could be separated from f*ßß* in Figure 2 or moved to the supplemental materials as a separate plot since the interpretations of the two records are substantially different.

Mixing Model Implementation: The authors should provide more details about how the MixSIAR model was used in this study and how the results support the key findings of this manuscript. The methods section only briefly mentions that a dual-isotope mixing model was used in this study without any mention of the endmembers involved until the end of the results section, with the rest of the information being in the supplemental text. The supplement is missing key descriptions of the MixSIAR settings used in the model runs, including prior structure and trophic discrimination factors, as stated in the specific comments below. Such settings can greatly impact the output of the model run (Stock et al., 2018) and their absence renders these mixing experiments non-replicable. In the main text, the mixing model results shown in Figure 3 are only referenced twice, once in the results section and once in the discussion, before the concluding statements. These model results should be more integrated into the discussion with how they compare to other proxy results generated in this study.

Petrogenic OM: The description of the petrogenic carbon endmember is not clear throughout the manuscript and appears to change between multiple sections. In the introduction, the authors spend an entire paragraph explaining how petrogenic OM sourced from carbon-rich sedimentary rocks may be an important source of ^{14}C-depleted OM that may mask sedimentary archives of changing permafrost export. Then in the discussion section 4.1, the authors use their results to explain how there is likely no rock-derived OM signal in the core, and that the ^{14}C-depleted endmember is actually lignite (brown coal); although the source of this lignite in western and central Europe is not explained. Shortly after, the authors explain that peat deposits, previously explained in this text to be the terrestrial OM endmember containing more ^{14}C than the petrogenic source, have also been preserved in western and central Europe since the last interglacial. In that case, why do the authors choose to interpret that the more mobile, ^{14}C-depleted endmember as lignite instead of peat that formed way before the LGM? In Figure 3, the modeled petrogenic OM/lignite contribution is as high as ~60% but it is unclear how lignite could be preferentially mobilized over peat or permafrost from the same region. The authors need to be more consistent throughout the text with defining endmembers as permafrost, or peat, or lignite because it becomes very unclear by the conclusions which endmembers are being interpreted.

Abstract

Line 5: Clarify that the location of the Bay of Biscay is off the coast of modern-day France in this abstract?

Line 6: I suggest rephrasing the start of the sentence to use more active voice, something like "we present a suite of biomarker and isotopic analyses…".

Line 6: I recommend listing the biomarkers used in this study or at least a couple of examples.

Line 8: Change "this result" to "our results".

Introduction

Lines 28-36: In this paragraph, the authors should clarify that there are notable bedrock formations in the western and central Europe that might function as a source of petrogenic OM.

Line 34-36: Can the authors include/reference an example study where distinguishing OM sources between petrogenic and permafrost was critical to the interpretation?

Line 37-51: I think that the section on the LGM history of the European landscape would make more sense, organizationally, as the 2nd paragraph in this introduction because similar concepts are discussed in the 1st paragraph. Perhaps switch the 2nd and 3rd paragraphs but keep lines 51-54 as the end of the introduction?

Line 51: Change "Here, organic biomarkers…" sentence to use active voice.

Materials and Methods

Lines 56-77: All equations for the various biomarker indices mentioned in this section should reference the supplemental text (i.e. CPI_{alk}; Eq. S1). Also, the authors should make a statement about each biomarker measurement being an original contribution of this study before describing the indices calculated using those biomarkers.

Line 58: The "e.g.," appears to be in the wrong location in this sentence. Is it supposed to begin the list of references in parentheses starting with "Dypvik and Harris, 2001"?

Line 64: Add ", respectively" at the end of the phrase "continental vegetation systems", since P_{aq} is not used to reconstruct OM degradation in this study.

Line 65-67: Based on the equation for P_{aq} listed in Eq. S2, wouldn't this ratio directly describe the predominance of mid-chain *n*-alkanes? I suggest adding a statement about the proxy is interpreted; that lower P_{aq} values reflect a greater contribution of terrestrial vascular plants.

Line 68: The statement about CPI_{alk} being an indicator of OM degradation was already made in line 64.

Line 69-70: The authors should clarify that the BIT index is calculated from GDGT abundances while f*ßß* is calculated from hopane abundances. There should also be statements about how higher/lower index values are interpreted for each one.

Line 71: Specify that MixSIAR is the Bayesian mixing model used in this study, according to the supplemental text, and reference Stock et al. (2018).

Lines 77: This statement about methodology details being in the supplement should be moved to the start of this methods sections/paragraph.

Results

Lines 79-99: The authors should include a statement about their *n*-alkanoic acid ^{14}C age results in this section.

Line 79: It would be helpful to have a statement about the length of geologic time recorded in this sediment core, based on the age-depth model results.

Lines 81-83: The information about Figure 2 in this sentence is already in the Figure 2 caption where it is more appropriate.

Lines 93-94: The BIT index record shown in Figure 2f should be referenced in this sentence.

Line 95-97: The reference to Supplementary Figure 2 is confusing in this sentence because that figure does not show any results of the MixSIAR model runs, only how the tracer values of the endmembers compare to the sediment mixture, which were determined before the model was run. The authors should remove the reference to that supplemental figure and only reference Figure 3 as they have also done in the following sentence.

Discussion

Line 102: The authors should restate/re-summarize the findings of Ménot et al. (2006) for ease of comparison with the results of this study. Also clarify which original results directly support the findings of the referenced study.

Lines 112-114: Please explain how terrestrial wetlands are a source of aquatic plants producing shorter *n*-alkane chain-lengths as opposed to other vegetation sources that may be contributing longer-chain waxes later in the downcore record. Wetlands also contain vascular, terrestrial plants which are often attributed as the primary source of longer-chain waxes (Freimuth et al., 2019).

Lines 114-116: I disagree with this statement that a CPI value between 4 and 5, compared to ~6 later in the record (Figure 2), confirms an increased flux of aquatic plants. CPI is typically not recommended for reconstructing vegetation changes with the interpretation used in this study. In Bush and McInerney (2013) and He et al. (2020), both referenced in the methods section, the CPI of aquatic/submerged vegetation is greater, on average, than that of some terrestrial plant types, albeit with very high variability. In that case, the P_{aq} and CPI records would be explaining opposite trends in vegetation source. Please clarify which references support CPI being interpreted as a proxy for vegetation change.

Lines 116-118: How does an arid steppe and tundra landscape correlate to a greater presence of wetlands with submerged aquatic vegetation? And is the implication that the development of woody biomes replaced wetlands with a more forested landscape in western and central Europe?

Lines 118-121: The wording of this sentence is confusing, please rewrite it.

Lines 118-123: Please clarify which period is being referred to as having more “mature OM fluvially transported”. Also, how can lower CPI values be interpreted as being both from aquatic plants and petrogenic sources during the same time period? I recommend using CPI to only infer the degree of organic matter degradation and not vegetation change since the former is much more robust.

Lines 121-127: This section starts by claiming that CPI are recording a signal of more mature OM but the proxy but then explain why CPI cannot be used for that purpose in this record. Also, Bush and McInerney (2013) only demonstrate that CPI between gymnosperms and angiosperms are statistically different, but that does not support the vegetation interpretation here. In general, plant CPI values within a given taxonomic growth form are too variable to interpret between groups.

Line 127-132: These sentences describing the difference between petrogenic and coal-derived OM should be a separate paragraph.

Line 133: This introduction to the compound-specific ^{14}C results is difficult to understand. Perhaps the authors can include an additional statement saying that the interpretation of an "ancient origin" for terrigenous biomarkers is derived from their ^{14}C ages being older than the modeled age vs. depth relationship for this core? See also comment on Figure 2f for clarifying the relationship between the core chronology and compound-specific ages.

Lines 134-136: Does the "recent" part of the record only refer to the Holocene as described in Line 136? Also, can clarifying point be made that at some point in this record, the Channel River ceases to transport terrestrial OM from the European mainland and, therefore, the ^{14}C reservoir and transportation mechanisms must be different during and after the presence of the Channel River?

Line 139: Change to "…petrogenic contributions are commonly thought to be absent [of] *n*-alkanoic acids"? As in, petrogenic OM typically do not contain *n*-alkanoic acids.

Line 142: List the ranges of $\delta^{13}C$ values for the core and organic-rich rocks referenced to demonstrate how much the two datasets differ.

Lines 144-146: I am not sure how the mixing model results support the argument that there is not a significant contribution of a true petrogenic OM endmember when it is not part of the model framework to begin with. Also, it is unclear where peak OM deposition is shown in Figure 3. Each endmember contribution in Figure 3 is plotted as a percentage of the total OM so the actual flux change in mass or volume unit per time is not obvious here.

Lines 151-152: This paragraph leading up to the concluding statement here needs more references to the specific time periods when terrestrial OM increased, both from the Figure 3 mixing model results and the referenced literature.

Lines 156-160: These sentences seem to suggest that while wetlands store carbon in the landscape, they might be responsible for releasing more relict carbon from Europe upon their establishment at the end of the LGM. This seems contradictory and requires further explanation of the cited literature. The compound-specific ^{14}C data in this paper only has one data point prior to the end of the LGM so it seems difficult to support these statements with the original findings presented here.

Lines 160-162: Is the term "peatlands" being used in this context, and throughout the manuscript in general, as a synonym for wetlands? If so, I recommend sticking with one term for the entire text and if not, the distinction between the two terms should be made clear early on.

Lines 165-167: If last interglacial peat deposits are widespread throughout the region that is exporting terrestrial, relict carbon via the Channel River, could they also be a source of ^{14}C-depleted in the studied core? The authors should explore whether this is may or may not be the case.

Lines 180-196: The paragraph presents a lot of background on the evidence for the increased export of permafrost OM following the LGM but only the P_{aq} record produced in this study is mentioned as corroborating with the other literature. How do the referenced paleoclimate records compare to the mixing model results from this paper?

Lines 200-204: What line of evidence is used (i.e. sedimentation rate, geochemical proxies) to support this statement about increased Channel River discharge at the core location in this study? Also, the references to "the core location", Antoine et al. (2003) and Bourillet et al. (2003), are somewhat confusing because the methods of this manuscript describe the core in question (GeoB 23303-2) to be original data. If the references are talking about a different core collected close by, then the authors should make that clear; perhaps even including it in Figure 1.

Lines 208-214: This information about subglacial meltwater should be in the introduction to provide the reader with more context early on about why the export of terrestrial OM to this core site may have changed over time.

Lines 214-217: This sentence about connecting peaks in the Ti/Ca and Fe/Ca ratios is very important to one of the key claims of this paper that core GeoB 23303-2 likely records Channel River flooding events which potentially export more pre-aged OM. In that case, I recommend that Supplementary Figure 3 be moved to the main text to readily illustrate this point.

Lines 225-227: Which results, specifically, support the hypothesis described?

Lines 229-231: How do changes in compound-specific ^{14}C ages in this study correlate to changes in the total amount of exported relict OM when three endmembers are involved? As stated in a previous comment, the MixSIAR results presented in Figure 3 show the proportional contribution of each endmember, not the total amount of OM which would require the total OM content of this core to be analyzed and presented, too. Without this information, it could be argued that the amount of exported OM did not increase at 17.5 ka, only the ^{14}C age of the *n*-alkanoic acids being mobilized. Plant-derived compounds, including *n*-alkanoic acids and *n*-alkanes, can be preserved in permafrost that formed prior to the LGM (Vonk et al., 2017) and even during multiple, previous interglacials (Jongejans et al., 2022). Therefore, this core site could be integrating a highly variable pool of compound-specific ^{14}C, even if the amount exported is not significantly changing over time.

Lines 239-240: The authors previously attribute their ^{14}C-depleted endmember to lignite, not degraded Eemian peatlands, which makes this statement confusing. Or was this supposed to say "Eurasian peatlands"?

Conclusions

Lines 260-261: Are European peatlands actually being interpreted as the ^{14}C-deplated, petrogenic endmember throughout this study instead of lignite? In Figure 3, the OC_petro endmember exceeds 60%, not the OC_terr endmember, which is describing the ^{14}C and $\delta^{13}C$ signature of peatlands in the supplemental text while OC_petro is based on ^{14}C-deplated lignite. This is also the first quantitative mention of the mixing model results, which should be addressed much more in the discussion section before making a concluding statement using them.

Figures

Figure 1: In the labels for the yellow and red dots, I suggest adding text to note which one refers to this study. Or maybe adjust the symbology to make it clearer which core is being presented as original data.

Figure 2f: For the compound-specific ^{14}C results plotted here, it is difficult to determine how their ages compare to the corresponding modeled age of the sediment from which they were extracted since the y-axis is in uncalibrated ^{14}C kyrs while the x-axis ages are adjusted to the ^{14}C Marine20 calibration curve. Perhaps these results could, instead, be presented as age offsets from the core chronology (i.e. Gaglioti et al., 2014).

Figure 2 Caption: Figure 2e is listed twice. The second mention should be corrected to "f:".

Figure 3: It would be helpful to have similar x-axis annotations for the geologic/climatic time periods as shown in Figure 2, especially since the x axes time scales are different between Figures 2 and 3. The bands showing major Channel River flooding events should be included in this figure, too.

Supplemental Text

Line S28-29: Reference the figures, both in the main text and supplement, where these data are reported.

Line S65: Clarify that both branched and isoprenoid GDGTs were analyzed and reported in this study to calculate BIT index values.

Line S82: Unclear what "ELEMENTAR" is referring to in the parentheses.

Line S91: How much core depth was integrated to have 100 g of sediment? Did the authors consider the depth/time being integrated for each sample when determining $OCter_{-bio}$ model input statistics?

Line S147: Do "temporal variations" refer to the standard deviation of $\Delta^{14}C$ measurements in the model inputs? If so, please clarify that.

Line S159-161: This paragraph is missing a number of important details on how MixSIAR was implemented for this study. Other sedimentary applications of MixSIAR (i.e. Menges et al., 2020; Douglas et al., 2022) include information of whether trophic discrimination factors were applied, which prior structure was used, what Markov Chain Monte Carlo settings were used to reach model convergence, etc. As it stands, the MixSIAR runs for this study are not replicable based on the information provided in the text. I also recommend including a table in the supplement that displays the summary statistics (mean and standard deviation) for each endmember from at least one model run since these details for endmember $\Delta^{14}C$ inputs are not specified elsewhere.

Figure S1: While the interpretation and units of the y-axis are described in the caption, the y-axis on the figure should be changed to something like “Depth (cm)” for ease of reading.

Figures S3-S5 Captions: It would be helpful to clarify in each caption that data from core GeoB23303-2 was produced in this study. Initially, it is unclear whether the other studies referenced in the captions refer to one or all of the core IDs mentioned.

References cited in this review

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