Response to Referee 3

The authors of "A Late Quaternary climate record based on long chain diol proxies from the Chilean margin" analyzed a suite of organic biomarkers in a marine sediment core from the coast of Chile to a) assess glacial-interglacial dynamics in marine productivity (ie. upwelling) and associated climate change, and b) to establish the efficacy of long-chain diols in paleoenvironmental reconstruction, particularly with regards to the recently proposed Nutrient Diol Index (NDI) as a metric for marine productivity. They compared diol-based indices to independent records of SST (alkenones and GDGTs) and productivity (algal lipid fluxes, total organic carbon fluxes, etc.) and show that NDI is distinctly different than other upwelling proxies and so is not widely interpretable as an upwelling indicator, suggesting instead that the principal C28 1,14-diol producer, Proboscia alata, occurs more commonly in non-upwelling settings. Furthermore, the Diol Index appears to reflect all Proboscia productivity, but still does not capture the upwelling signature expressed in other paleoproductivity proxies. The dataset seems robust and these topics are of broad interest to the paleoceanography and organic geochemistry communities. In general, I think the paper could be published after addressing issues regarding the clarity of the paleoclimate implications and the writing structure.

We thank the referee for the positive assessment and for the comments, which we discuss below and will use to improve our manuscript.

Please include the full name for each abbreviation the first time abbreviations are mentioned. Likewise, provide the diol-specific equations in the introduction because it would help the reader follow the introduction section easier without flipping through the paper to find the equations.

We will include the full names. However, we do not think that including the diol equations in the introduction will improve the clarity of the text, and we already describe specifically on which LCDs the equations are based.

The goal stated in the first sentence of the abstract stands in contrast with the goal of the title.

We agree with the referee, and we will change the title as follows: "Testing the applicability of long chain diol proxies in the Chilean margin for the Late Quaternary"

Page 12-13: The relationship between temperature and productivity should be discussed more explicitly. I think this section relating the broader climate system and the productivity regime needs clarification. A plot showing the temperature and the nutrient/upwelling indicators together is warranted, given that the paper is drawing links between these two variables. Can either 'northward migration of the SWW' or 'southward migration of the subtropical high' or global cooling induce more upwelling and is there a way to distinguish between these factors in the paleoceanographic record?

We are not sure on how to more explicitly discuss the relation between productivity and temperature. We start the discussion by illustrating the general idea on how the latitudinal movement of the ACC and SWW linked to the transition of the Last Glacial Maximum to the Holocene might affect productivity. In short, different studies suggest that during the LGM productivity was likely stimulated by greater nutrient input deriving from the ACC (being in the north) and enhanced river runoff due to the northern position of the SWW. Accordingly, productivity would be lower during the Holocene due to the southern position of the ACC and SWW. However, during the Holocene, the winds associated with the subtropical high pressure system might induce upwelling. Moreover, there are also studies that propose that the northern position of the SWW during the LGM might in fact prevent upwelling and thus inhibit productivity despite the greater input of nutrients. Hence, we discuss coastal productivity in light of the main current and wind regimes linked to glacial-interglacial variability. However, most studies have focused on the last ~30 kyrs, and therefore little is still known about upwelling

and productivity during for instance the Last Interglacial. Nevertheless, we discuss our biomarker records in light of the knowledge that we have of the LGM and Holocene, by for instance proposing that the potential maximum in upwelling intensity around 100 ka, might be related to the subtropical high pressure system which could have stimulated upwelling along the coast, similar as for the Holocene, as proposed by Romero et al. (2006).

Page 14: Many ideas are put forward about P. alata ecology, but I am left with an uncertain idea of what NDI (aka P. alata productivity) variations signify in a specific climatic or ecological sense. Is there a suggestion of why P. alata varies so dramatically during some periods, but not during MIS 1/2/3/4? I think the discussion on the modern observations of P. alata blooms and distributions are helpful, but should be related more explicitly to the paleoceanographic record if possible. Is the author's suggestion that reduced NDI around 100 ka is an indication that upwelling occurred continuously, rather than on a seasonal basis, thereby eliminating the "early- or post-upwelling nutrient conditions"?

Both the NDI and the Diol Index reflect the relative abundance of *Proboscia* diatoms as the 1,14-diols are specific for this group of diatoms. Since along the Chilean margin *Proboscia alata* has been observed, we propose that for our location the NDI reflects *P. alata* productivity. However, in other regions the C_{28} 1,14-diol might be produced by other *Proboscia* species and the NDI might thus not reflect *P. alata* productivity. In this light we will also partly adjust our hypothesis that the NDI potentially reflects *P. alata* productivity; it is merely more species-specific as compared to the Diol Index since it excludes the C_{30} 1,14-diol from the numerator.
As for the question why the NDI/*Proboscia* activity is relatively constant during MIS 1/2/3/4 but shows large variation during MIS 5: this is one of the main issues we have addressed in the manuscript. We propose, based on the maximum in MAR_{TOC} during MIS 5 concurrent with e.g. the highest abundances of preserved *Chaetoceros* valves, that around 100 ka the upwelling intensity was likely to be strong and primary productivity was stimulated. What we know from the modern-day *Proboscia* ecology, is that this diatom genus proliferates when nutrients increase, i.e. during upwelling. However, it is particularly able of dominating the diatom pool during early upwelling conditions when silicate concentrations are still low, and the nutrients are still in the deeper waters. When actual upwelling occurs, and the nutrients are transported to the surface and silicate concentrations increase, *Proboscia* is likely outcompeted by for instance *Chaetoceros* which is more heavily silicified. Accordingly, we think this might explain the relatively low Diol Index and NDI around 100 ka, as the relative abundance of *Proboscia* was likely to be low. However, before and after this event, i.e. around ca. 120 and 90 ka, upwelling was likely less intense, and conditions were more favorable for *Proboscia*.
As for the referee's last question: the reduced NDI around 100 ka does not indicate that upwelling occurred continuously throughout the year and thus does not eliminate the seasonal basis of upwelling. However, the NDI and Diol Index reflect integrations of multiple years and thus an averaged signal of *Proboscia* productivity over these years. We believe that the minimum in the NDI around 100 ka, suggesting that phosphate and nitrate concentrations were around 0 µmol/L, is not realistic, because the "mean annual nutrient concentrations" were not likely to be ~0 during this upwelling interval. Even though nutrients can be used up at the end of an upwelling season, mean annual nutrient concentrations are likely to be relatively high.

There is an increase in TOC-MAR and importantly, 1,13- and 1,15-diols in MIS 4. Please comment on if this is an indication of specific upwelling or nutrient conditions that might promote the eustigmatophyte but not other algal groups.

Yes, this is true, and we will discuss this in the revised manuscript. Moreover, similar comments were put forward by referees 1 and 2. We believe that the increase in MAR_{TOC} during MIS 4 is likely linked to the evident increase in sedimentation rate during this period (Fig. 3a). During MIS 5, the maximum in MAR_{TOC} corresponds to elevated TOC levels and a constant

sedimentation rate, suggesting an increase in primary productivity. However, during MIS 4, the TOC levels are almost twice as low, but the sedimentation rate is clearly higher, suggesting that the increased MAR_{TOC} is a result of enhanced particle settling.

P. 15 Starting line 31: Regional differences in the timing of deglacial warming might be expected, but this does not address the different timing among proxies at Site 1234. Please elaborate on the significance of the LDI versus UK37 difference during ∼10 kyr around the LGM.

Yes, we completely agree with referee 3, and in our new version of the manuscript we will try to elaborate on this. However, we are not certain on how to explain this ±10 kyr time lag between the deglacial warming as recorded by the LDI and the $U^{K'}_{37}$ and TEX^{H}_{86}. The LDI-temperatures are also considerably lower as compared to the other proxy temperatures. Although, the producers of the 1,13- and 1,15-diols are unknown, they are likely to be phototrophs living in the upper part of the photic zone (e.g., Rampen et al., 2012; Balzano et al., 2018), and therefore we would expect similar temperature estimates for the LDI and $U^{K'}_{37}$. Potentially, due to regional climatic change associated with the southward migration of the ACC and SWW upon the deglacial warming, the main season of production of the 1,13- and 1,15-diols shifted, resulting in lower reconstructed SSTs. The difference in timing of the deglacial warming stays elusive.

Some points need grammatical correction:

P1. L. 11: Change "proxies" to "indices" because the Diol Index is stated to be an indicator rather than a proxy in Line 12.

We will adjust this.

P1. L.12: ". . .the NDI as a quantitative proxy. . ."

We will rephrase as follows: "… ***the NDI index as proxy for…*****".**

P1. L. 15: Either specify the number of glacial/interglacial periods or just remove this clause.

We will adjust this.

P2. L. 16:: Provide the equation for DI, or rephrase, because it is not simply the ratio, but rather the percentage.

We agree that this formulation is unclear, and we will rephrase this.

P2. L 24: Remove "sea", or change to "marine"?

We will change this in "marine".

P2. L 24-25: If possible, specify if the change in saturation is related to changing species or interspecies diol adjustments.

In section 4.2 (page 14, around line 1-5) we will add some information on the (un)saturation of the 1,14-diols. In sediments, mono-unsaturated 1,14-diols are generally lower in abundance as compared to the saturated 1,14-diols. However, culture data show that ***Proboscia*** **diatoms often produce more unsaturated diols, and that the degree of unsaturation is strongly affected by temperature (Rampen et al., 2009; OG). This temperature relationship was however not observed in marine surface sediments (Rampen et al., 2014) and the low abundance of unsaturated 1,14-diols might be the result of preferential degradation. However, the regional differences in 1,14-diol distributions are likely also the result of different species producing different 1,14-diols.**

P2. L. 27: Remove “Preliminary”

We will remove this.

P2. L28: “paleo-upwelling” could be used instead of past upwelling. Remove “as”. Also, change “proxies” to “indicators” unless the reconstruction of upwelling rates is a quantitative transfer function.

We will correct this.

P3. L. 10: The Holocene is part of the Quaternary – no need to mention separately. orzet

We will remove “and Holocene”.

P3. L. 10: “large climate cycle” is kind of arbitrary

We will remove “large”.

P3. L. 10: remove “bulk organic matter”

We will remove this.

P3. L. 29: Can you include more specifics about the connection – namely, specify if stronger ACC and Westerlies result in warmer or cooler climate.

The relationship between the ACC and Westerlies with productivity and upwelling is described in section 4.1, but we agree that we should elaborate more on the link between the ACC/Westerlies and temperature, which we will do in the new manuscript, something along the lines of:

Lamy et al. (2002) showed that millennial- to multicentennial scale variations in past temperature and productivity lags variations in rainfall, and thus the latitudinal migration of the Westerlies. However, the authors found a strong relationship between past seawater temperature variability and Antarctic climate change, and thus the latitudinal position of the ACC. When the ACC migrates northward, potentially associated with an expansion of Antarctic sea ice, cold, subantarctic waters are advected into the southern hemisphere midlatitudes, including the Chilean margin (e.g., Lamy et al., 2004; Kaiser et al., 2005).

P. 3 L. 30-33. Does not follow from previous part of paragraph. I think it needs a segue from climate to upwelling/sedimentation dynamics, because this statement isn’t about climate like the rest of paragraph. Also, please describe the subtropical high pressure system clearly because it is referred to later as a possible explanation.

We agree that this structure is not optimal, and we will reorganize. Additionally, we will describe the subtropical high pressure system as well, as this is indeed required for the discussion.

P. 4 L. 2: There might be some variation in this, but I think a better spelling is Biobío

We will correct this.

P. 4, L. 3: remove “both” and “large” to read “. . .which drain basins of 24,000 km2. . .”

We will adjust this.

P. 4 L. 13: Remove “providing the potential for high-resolution records” because it’s not necessary and I don’t think the author’s did that kind of sampling.

We will remove this.

P. 5 L. 5: If these benthic foraminifera data are already published, I don't think this paragraph is necessary, is it? Are any adjustments made to the McManus and Heusser paper? For brevity, this could be folded into the age model paragraph because it provides the basis for the correlations of the cores. This change is not critical for publishing the paper.

The correction of 0.64‰ is new information and therefore relevant. We agree that this might be better suited in the age model section.

P. 6 L 9: Specify that the GDGT naming scheme in the following descriptions relates to the structures in Castañeda and Schouten, or some other appropriate reference

We will clarify this.

P. 6 L. 28: Remove "in this case" and clarify that the BAYSPAR refers to the Tierney and Tingley citation.

We believe that "in this case" is relevant here, since the core-tops on which the calibration is based, is different for every paleo-reconstruction; it depends on the assumed prior mean temperature and search tolerance. We used a prior mean of 13 °C and a search tolerance of 0.2 TEX_{86} units, resulting in the 62 high latitudinal grid boxes on which in this case the calibration is based. We will refer to Tierney and Tingley (2014, 2015).

P. 6 L. 31-32. Awkward phrasing because of passive voice.

We will rephrase this sentence.

P. 7. "Conductive"?

We thank the referee for remarking this typo: it should be "conducive".

P. 7, L. 7: "isomers can indicate these types of environments in the past. . ." should be rephrased because it is confusing as written.

We will rephrase this sentence.

P. 7 L. 8: Include a reference suggesting 0.3 is acceptable threshold for Methane Index.

We refer here to Zhang et al. (2011): "*Combined GDGT distribution and isotopic evidence suggest that 0.3 to 0.5 of the MI might be a reasonable threshold for distinguishing gas hydrate impacted and/or methane-rich environments from normal marine realm.*"

P. 7 L 34: What was the injector configuration?
On-column injection, we will clarify this.

P. 8 L. 8: Helium does not need to be capitalized.
We will correct this.

P. 8 L. 23: The first part of this sentence should be rephrased because it is confusing as written.
We will rephrase this part.

P. 8 L. 27: "..potentially riverine derived. . ." should be rephrased for grammar.
We will change as follows: "*which is potentially derived from rivers*".

P. 8 L. 30: Given that you are testing the effectiveness of the NDI index, insert: "..The NDI index, a proposed proxy for PO43-. . ."
We will adjust this.

P. 10 L 34: Insert a comma after “In all sediments”
We will correct this.

P. 10: It seems strange that crenarchaeol is the first biomarker presented when it has only been mentioned as a standard in the first part of the paper, and is never discussed or interpreted in any details. Could remove statement about crenarchaeol, else it should be discussed. Similarly, figures 4f and 4g and 4h come before 4a, 4b, etc. in the text. I recommend rearranging this so that diol results come first and things don’t seem out of order, or just refer to them as figure 4.

We will clarify that crenarchaeol is a specific biomarker for Thaumarchaeota and thus is indicative for Thaumarcheotal productivity. We agree that the order in Figure 4 is in contrast with the results, and we will rearrange the panels in this figure.

P 10 L 4: The reported accumulation rate for crenarchaeol does not match what is shown in figure 4f.

We thank the referee for noticing this, we will correct this.

P. 10 L. 16: Figure “4i”, not figure 4j. Also, the data are labeled pg g-1, but the text states μg g-1. Likewise ng versus mg for the 1,14-diol accumulation rates.
We thank the referee for pointing out these inaccuracies, and we will correct these.

P. 11 L 26-27: State on which proxies these estimates are based.
We agree that this was unclear, and we will clarify this.

P. 11, L 28: The spline curves show a decrease of 4-6◦C not 6-7◦C. Smallest change is for iGDGTs.

We will correct this.

P. 12 L 27: “. . .since neither opal concentration nor opal or TOC-MAR increased simultaneously with TOC concentration” might help clarify this sentence.

We will change accordingly.

P. 13, L 16: Intervals of enhanced upwelling are not explicitly labeled in Figs 3b and 3c.

We agree that this is unclear and we will change as follows: “*… with enhanced upwelling (i.e., around 100 ka; dashed line in Fig. 3)*”.

P. 13, L 27. Rephrase “As for the diol index and the. . .” because this phrase has another common meaning than as it is used.

We will rephrase this sentence.

P. 14 L 10: "during/under" could just be "in"

We will correct this.

Figure 4: How can there be sometimes more chaetoceros counts than total diatom counts?

This is because the counts are not quantitative, but descriptive: F=few; C=common; A=abundant; VA=very abundant. However, we now realize that we did not clarify this is in the caption, which we will correct in the new version.

Figure 5: What are the orange versus blue lines in the Site 1234 Benthic oxygen isotopes? It is not mentioned in the figure caption.

We thank the referee for noticing this, and we will clarify this in the caption. The color scheme is similar to Fig. 2, where the two colors reflect the two separate age models. The blue data reflect the benthic $\delta^{18}O$ dated by correlation to Atlantic core MD95204, whereas the orange data represent the $\delta^{18}O$ data correlated to the Vostok ice core chronology.