Response to reviewers

Submission bg-2019-15 to *Biogeosciences*

Editor

Dear Marijke et al.,

I have now received two reports on your contribution. Both find your manuscript suitable for publication in BG following (minor) revisions. Please follow their detailed comments closely in revising your ms.

Sincerely,

Markus

We thank the editor for the positive assessment of our manuscript. We have revised the manuscript and below we provide point-to-point answers to the comments of the reviewers: when applicable, we indicated where adjustments were made in the text (note: when we refer to line numbers in which we have made adjustments, we refer to the line numbering of the revised manuscript with "track changes"/All Markup). The reviewers' comments are in regular font; our replies are in bold font.

Sincerely, also on behalf of all co-authors,

Marijke de Bar

Response to referee #1

Review: This manuscript investigates long-chain diols (LCDs) in sediment trap time series from five tropical sites (tropical North Atlantic, Cariaco Basin, Mozambique Channel) to assess seasonal variations in fluxes of LCDs and associated proxies (Long chain Diol Index and Diol Index). These data are compared with other lipid proxies (alkenones and GDGTs) and previous published data (primary production, SST,..). Results show that surface sediment LDI temperatures in the Atlantic and Mozambique Channel compare well with the average LDI-derived temperatures from the overlying sediment traps, as well as with decadal annual mean SST. In the Mozambique Channel and the tropical Atlantic, the LDI temperatures reveal minimal seasonal change although there are clear seasonal SST contrasts, which is likely due to lateral advection of re-suspended sediment. In the Cariaco Basin, a strong seasonality in the LDI is observed, which is linked to the upwelling season and stratification of the water column. In addition, in the Atlantic, the Diol Index reflects a pre-upwelling signal, whereas in the Cariaco Basin, the Diol Index seems to be an indicator of upwelling intensity. This paper is a valuable contribution to the understanding of the seasonal production of LCDs in marine environments and how it is translated in the temperature proxy LDI and the Diol Index (upwelling proxy). A strength of the paper is that the LCD data has been compared with other available data for each site (primary production, SST, alkenones, GDGTs,…), which gives a broader picture and supports the interpretations based on LCDs. The writing style is clear and precise and the interpretations are generally supported by the data. This manuscript is thus suitable for Biogeosciences. However, the current manuscript could be improved before publication. Please find my comments below.

We thank the referee for the positive assessment and for the comments, which we will discuss below.

General comments:

Diol index and upwelling: The authors argue that, in the Cariaco Basin, the Diol Index is an excellent indicator of upwelling intensity (Lines 476-480). However, when looking at the 1999-2000 time series, high values of the diol index actually occur when the primary production decreases. What are the R2 values (and p values) that justify "a strong correlation with primary production rates"?

We agree with the reviewer that for the 1999-2000 time series there is a disagreement during January/February when the diol index increases and primary production rates decrease. We now mention this in the revised version of the manuscript. The 'strong correlation' between the diol index and primary production is based purely on the visual agreement between both time series. We were not able to perform a correlation analysis since the data are differently spaced in time. We have also emphasized this in the revised version manuscript (lines 493-496):
"In the Cariaco Basin, the Diol Index shows a strong correlation (visually as correlation analysis was not possible due to differently spaced data in time) with primary production rates, suggesting that Proboscia productivity was synchronous with total productivity (Fig. 8), although for the 1999-2000 time series there is a disagreement during January/February."

In addition, for the eastern Atlantic (M1 trap), the authors argue that the Diol Index reflects a preupwelling signal, consistent with the current knowledge on Proboscia ecology (Lines 509-526). I would like to see more discussion that explains why at one location the Diol index indicates preupwelling conditions, whereas it seems to be an indicator of upwelling intensity at another location.

We agree that this seems contradictory and requires more discussion, which we have implemented in the revised version of the manuscript. The Diol Index is an upwelling indicator based on the assumption that *Proboscia* diatoms generally thrive in upwelling regions. However, the index is in fact an indicator for *Proboscia* productivity, and whether it reflects upwelling/pre-upwelling/stratification/etc. conditions will depend on the region and the local ecological dynamics determining the role of *Proboscia* diatoms (e.g., Rampen et al., 2014; de Bar et al., 2018). Studies have shown that *Proboscia* diatoms are often more dominant during early/pre-upwelling because they need relatively little silica and they are able to migrate to deeper waters to obtain nutrients (Koning et al., 2001) and sediment trap data from Wakeham et al. (2002), Prahl et al. (2000), Sinninghe Damsté et al. (2003) and Rampen et al. (2007) show that *Proboscia* lipids (diols and/or hydroxyl methyl alkanoates) are highest during early upwelling. Therefore, we hypothesize that this Diol Index maximum during spring which we observe for station M1 in the Atlantic might be a pre/early-upwelling signal since the upwelling in the Guinea Dome often occurs between July and October (Siedler et al., 1992). Indeed, *Proboscia* diatoms do not reflect early-upwelling in every region. Reports of *Proboscia* spp. blooms vary from stratification to early-upwelling to postbloom, and from high nutrients to low nutrients (see Rampen et al., 2014; references in Table 1). Apparently, in the Cariaco Basin, *Proboscia* diatoms bloom relatively synchronous with general productivity, as evidenced from the agreement between the Diol Index and primary production time series, emphasizing the value of sediment trap studies like ours in revealing regional differences in proxy signals. We have added the following lines (546-549):

"Our results clearly show that the Diol Index reflects different things in different regions. This is due to the ecology of Proboscia spp. where blooms occur during stratification to early upwelling to postbloom, and from high nutrients to low nutrients (see Rampen et al., 2014; references in Table 1). Therefore, the type of conditions reflected by the Diol Index is specific for every region."

Keto-ols as oxidation products (Lines 578-586): An alternative explanation for the non-detection of 1,14-keto-ols would be that keto-ols are not oxidation products of LCDs, but rather produced by unknown organism(s) (Versteegh et al., 1997). Previous studies have indeed shown the absence of evidence of conversion of diols into their corresponding oxidized keto-ols (Jiang et al., 1994; Méjanelle al 2003; Shimokawara et al., 2010). I think the authors should acknowledge this.

We agree, and we have mentioned this hypothesis as well (lines 611-615):
"Alternatively, the keto-ols are not oxidation products but are produced by unknown organisms in the water column. In fact, Méjanelle et al. (2003) observed trace amounts of C_{30} 1,13- and C_{32} 1,15-keto-ols in cultures of the marine eustigmatophyte Nannochloropsis gaditana. Thus, an alternative explanation for the non-detection of 1,14-keto-ols is that in contrast to the 1,15-keto-ols, they were not produced in the water column."

Figures: I think the current order of the figures does not necessarily follow the logic of the results/discussion. For more clarity, I would suggest modifying the order as follows: Fig. 2 should be Fig. 8; Fig. 3 should be Fig. 2; Fig. 8 should be Fig. 8; Fig. 4 should be Fig. 3; Fig. 5 should be Fig. 8; Fig. 6 should be Fig. 4; Fig. 8 should be Fig. 5; Fig. 8 should be Fig. 6.

We have re-ordered as follows:
Fig. 2 → Fig. 2
Fig. 3 → Fig. 3
Fig. 4 → Fig. 9
Fig. 5 → Fig. 4
Fig. 6 → Fig. 5
Fig. 7 → Fig. 6
Fig. 8 → Fig. 7
Fig. 9 → Fig. 8

Specific comments:

Line 25: specify "with emphasis on the temperature proxy Long Chain Diol Index".

We have corrected this accordingly.

Line 27: specify "similar to the two other lipid-based temperature proxies TEX86 and UK'37".

We have corrected this accordingly.

Line 27: "In addition" instead of "However".

We have corrected this accordingly.

Line 29: Could be rephrased as: "In contrast, the LDI in the Cariaco Basin shows larger seasonal variation".

We have corrected this accordingly.

Line 48: Need references.

We have added the review of Tierney (2014) as reference.

Lines 48-50: Could be rephrased as: "However, research showed that despite their highest abundance being recorded in the upper 100 m of the water column, Thaumarchaeota can be present down to 5000 m depth (Karner et al., 2001; Herndl et al., 2005)".

We have corrected this accordingly.

Line 69: "for autumn to summer" should be "for autumn and summer".

We have corrected this accordingly.

Figure 1: indicate in the caption what NEC, NECC, SEC, MC, GD, NBC and GC stand for. Is it possible to add the position of the ITCZ during the boreal winter?

We have clarified the abbreviations in the figure caption and indicated the position of the ITCZ during boreal winter.

Line 200: What are CTD measurements?

We refer here to temperature measurements of seawater at 1m water depth sampled by CTD. We have clarified this.

Line 256-258: Could diols be found in the DCM:MeOH (1:1; v/v) fraction? Have you checked?

We thank the reviewer for noticing this, since the sentence is incorrect: not the MeOH fractions were analyzed for diols, but the DCM:MeOH (1:1, v/v) fractions. We have corrected this.

Line 369: Should be as: “C28 and C30 1,13- (0–3 %), the C30 1,15- (44–99 %), and the C32 1,15-diols (0–7%)”.

We have corrected this accordingly.

Lines 367-376: I think a table showing the presence/absence for each diols (and the % of total LCDs) at the different traps (M1, M2,...) and different sites (Atlantic, Mozambique Channel, Cariaco Basin) would be useful to clearly see which diols are detected for each location. The Figure 2 is used to discuss the preservation between traps and sediments rather than showing the diols detected.

We do not fully agree, since the number of figures is already extensive, as is the result section, and we consider this relatively detailed.

Line 392: Fig. 4 is cited before Fig. 8. I think the order of the figures should be changed (see previous comment).

We have changed the order of figures, see comment above.

Line 397: cite Figure 7.

We have corrected this.

Response to referee #2

General comments

In this study, de Bar et al. presented long-chain diol (LCD) data from five sites; three along a longitudinal transect in the tropical Atlantic, the Cariaco Basin and the Mozambique Channel. LCD derived indices, i.e. Long-chain Diol Index (LDI) and Diol Index, are used to reconstruct past SST and upwelling, respectively. These proxies are relatively new compared to those based on alkenones and GDGTs, thus have not been as well studied. This is where this study comes in. de Bar et al analyzed LCDs from sediment traps and underlying sediments. For the sites where alkenones and GDGT data do not yet exist, the authors also analyzed these biomarkers in addition to LCDs C1 to allow multi-proxy comparison for all the sites. The well-designed experiment thus allows the authors to investigate various aspects of the LCDs and their associated proxies, including the temporal evolution (seasons to years), settling processes, as well as comparison with other commonly applied biomarker proxies. The data presented by de Bar et al. generally show that LDI-derived temperatures agree within error with instrumental data in the Atlantic, albeit with different amplitude of change. At upwelling sites, the Diol Index seems to either record a pre-upwelling signal or show the same trend as in primary productivity.

The study fits the scope of Biogeosciences, and will also be of interest to readers from other community such as paleoclimate. The manuscript is generally well-written and accessible. I do, however, feel that some figures could be further improved for clarity. I find the "Results" section too long and some discussion unclear or not fully supported by the data, especially in section 4.3. Below are suggestions and comments that I hope will help the authors in further improving the manuscript. Once the concerns are addressed, I strongly recommend the publication of this manuscript.

We thank the referee for the positive assessment and for the comments, which we will discuss below.

Specific comments

#Line 34-36: Clunky sentence. Please rephrase.

We have rephrased as follows (lines 35-39):
"Lastly, we observed large seasonal variations in the Diol Index, as indicator of upwelling conditions, at three sites: in the Eastern Atlantic potentially linked to Guinea Dome upwelling, in the Cariaco Basin likely caused by seasonal upwelling, and in the Mozambique Channel where underlying mechanisms are indefinable but where Diol Index variations may be driven by upwelling from favorable winds and/or eddy migration."

#Line 43: "Conte 2006" should be "Conte et al 2006"

We have corrected this.

#Line 96-97: "ITCZ migrates southward during boreal winter" - would be useful to have this marked in Figure 1 too.

We have indicated the approximate position of the ITCZ during boreal winter in Figure 1.

#Line 100: Insert abbreviation (SEC) after South Equatorial Current.

We have inserted this abbreviation.

#Line 116: replace "/" with either a space or comma.

We have replaced it with a comma.

#Line 119: "as result" should be "as a result"

We have corrected this accordingly.

#Line 125: "latitudinal transect" is a transect across latitudes. What you have is a "longitudinal transect", i.e. with sites spanning longitudes at a fixed latitude (∼12◦N). C2

Thank you for this correction, we have corrected this throughout the manuscript.

#Line 183-184: Varved sediments have annual resolution. Since you mentioned "annually to decadally resolved climate records", do you mean "laminated sediments" instead?

Yes, we have corrected this accordingly.

#Line 224: "weight sub-aliquots" is confusing. Suggested rephrasing "sub-aliquots (by weight)".

We have corrected this accordingly.

#Line 237-238: Confusing sentence. Sounds like you analyzed both ketone and GDGT fractions by both GC and GC/MS - which is likely not the case. Please rephrase.

We have rephrased as follows (lines 244-247):
"The ketone fraction was also dissolved in ethyl acetate, and analyzed by GC and GC/MS. The GDGT fraction was dissolved in hexane:isopropanol (99:1, v/v), filtered through a 0.45 µm polytetrafluoroethylene (PTFE) filter and analyzed by HPLC-MS."

#Line 285-287: Technically this is a variant of the original BIT index proposed by Hopmans et al 2004. Please rephrase the paragraph to reflect this.
We have rephrased as follows (lines 293-296):
"The Branched Isoprenoid Tetraether (BIT) index is a proxy for the relative contribution of terrestrial derived organic carbon (Hopmans et al., 2004). We have calculated the modified version as reported by de Jonge et al. (2014; 2015) which is based on the original index as proposed by Hopmans et al. (2004), but includes the 6-methyl brGDGTs."

#Line 296: This is not the first time GC is mentioned in the manuscript. Spell out "gas chromatograph" at the first mention instead of here. Also, there is no need to define the abbreviation at each mention.

We have corrected this accordingly.

#Line 308-309: Tierney and Tingley (2018) is not the first to notice the warm-end limit of UK'37, i.e. an issue which has been in debate since the 90s. Please include the original references.

We have rephrased as follows (lines 316-321):
"We have also applied the recently proposed BAYSPLINE Bayesian calibration of Tierney and Tingley (2018). They and others have shown that the $U^{K'}_{37}$ estimates substantially attenuate above temperatures of 24 °C (e.g., Conte et al., 1998; Goñi et al., 2001; Sicre et al., 2002). The Bayesian calibration moves the upper limit of the $U^{K'}_{37}$ calibration from approximately 28 to 29.6 °C at unity. Since our traps are located in tropical regions with SSTs > 24 °C, we have applied this calibration as well."

#Line 313: "gas chromatograph (GC)" see comment to Line 296.

We have corrected this accordingly.

#Line 314: "mass spectrometer (MS)" see comment to Line 296.

We have corrected this accordingly.

#Section 2.5 Time-series analysis: Since the result of the time-series analysis is not a main part of the results and discussion, I would suggest to either (A) remove this rather long section or (b) move it to the supplement and add a supplementary figure depicting the result (which is briefly discussed in the text but not shown).

We agree, and we have moved these methods to the supplements.

#Section 3. Results: I had a hard time going through the 4-page long results section. Given the large data set spanning several sites and including several biomarkers and their associated proxies (for which I applaud the authors), this is perhaps inevitable. But I think that it will make the section more accessible for the reader if the authors could reduce the text by 10 to 20%, either by restructuring the text, tabulating some of the results and/or limiting the result description to only the main findings that are discussed in the following section.

We agree that the results section is a bit on the long side, and we have removed a few sentences.

#Line 362: "longitudinal" not "latitudinal".

We have corrected this.

#Line 368-369: Confusing. Rephrase please.

We have rephrased as follows (lines 378-380):
"The LCDs detected in the sediment trap samples and surface sediments from the tropical North Atlantic (Fig. 2) are the C_{28}, C_{30} and $C_{30:1}$ 1,14-, C_{28} and C_{30} 1,13-, the C_{30} 1,15-, and C_{32} 1,15-diols."

#Line 430-431: "during January and July" - replace with "between January and July". Also, it is not clear at all in Fig 5d that the TEX86H temperatures are lower during these months. Please rephrase.

We have rephrased accordingly, and we agree that for M4 this decrease in TEX_{86}^{H} temperatures is not clearly visible and we have removed this statement.

#Line 444: I'd argue that there's some structural similarity between the Diol Index and chlorophyll-a records.

We do not believe this (visual) agreement is strong enough to make a statement about this. Therefore, we would like to refrain from discussing this.

#Line 482: What are "15 and 18◦ "? Latitude?

We have added the latitude.

#Line 491-497: I strongly urge the authors to at least show the wavelet analysis in the supplementary info to support their claim. Please also mark the cool water events in Figure 8b to support the claim that ". . .the timing of the observed time periods of enhanced Diol Index variability are similar to those of the cool water events. . ."

We now show the wavelet analysis in the supplements. However, we cannot mark the cool water events in Fig 8b since we do not know the timings of these events for this specific time interval. We merely wanted to emphasize that Malauene et al. (2014) reported bimonthly frequency and a boreal winter timing for these cold events, which we also observe in our wavelet analysis. Below are the wavelet results which we have included in the supplements:

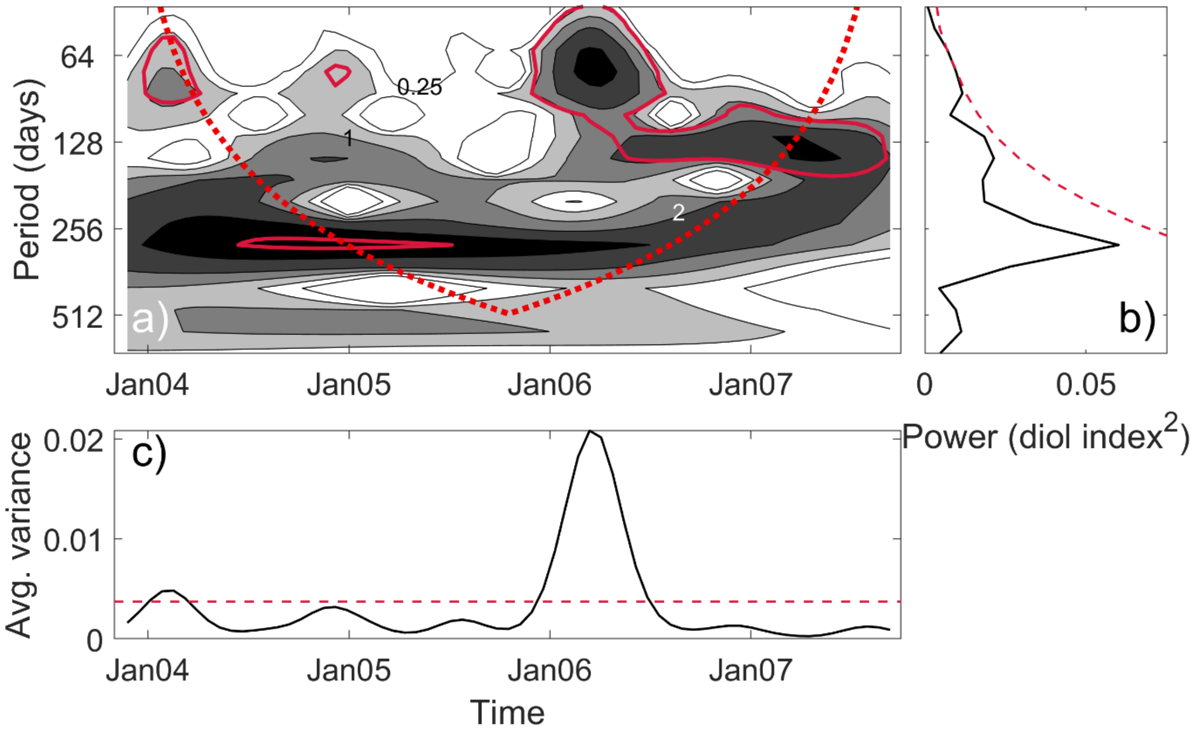

Fig. S1. a) The local wavelet power spectrum of the Diol Index in the sediment traps of the Mozambique Channel using the Morlet wavelet, normalized by the standard deviation. On the *x*-axis is time, and the *y*-axis shows the Fourier period in days. The shaded contours are at normalized variances of 0.25, 0.5, 1, 2, and 4. The bold red contour encloses regions of greater than 95% confidence for a red-noise process with a lag-1 coefficient of 0.72. Regions below the dotted red curve are where edge effects become important (Torrence and Compo, 1998). b) Global wavelet spectrum of Diol Index – the wavelet spectrum averaged in time over the whole time series. The red dashed line is the 95% confidence level. c) Wavelet power averaged over the range of scales from 42 to 90 days. The black line is the time series of the average variance within the 42-90-day range. The red dashed line is the 95% confidence level.

#Line 496-497: I am not following this. Assuming a sampling interval of 21 days - that would give us about 21 data points per year. With so few data points in the time series, it would be impossible to detect 4 cycles in the first half of 2006. Please clarify.

With a sampling interval of 21 days, the highest frequency we can detect is half the sampling rate, i.e. 1/42 cycles per day (or 8.7 cycles per year). As we describe on line 508-511, and now show in figure S1, the wavelet analysis showed significant variability at about bimonthly frequency (60-day period) during some parts of the time series, most notably the first half of 2006. We have rephrased the sentence on line 516-517 to: “*The strongest variability of the Diol Index at about bimonthly frequencies occurred in the first half of 2006.*”

#Line 498-499: It would be helpful to mark the timing of the passage of eddies in Fig 8b.

This is a good suggestion; however, it is not completely straightforward to do this in a thorough way. We first need to decide on a definition of a passing eddy – there are several possibilities, for example using the instrumental records of temperature, salinity, or current velocity at the

moorings (one useful criterion could be, for example, lateral velocity shear between the eastern and western side), or an independent record such as dynamic height derived from satellite altimetry. Because of this uncertainty we refrain from indicating this.

#Line 504: "Fig 5c"shows LDI not Diol Index.

We have corrected this.

#Line 508: "Fig 5e" shows LDI not Diol Index.

We have corrected this.

#Line 522: Change "due its closer vicinity" to "due to its closer vicinity"

We have corrected this accordingly.

#Line 523: "NW Africa" This is mentioned only once in the text. Spell out NW.

We have corrected this accordingly.

#Line 556: r (and p) values are more appropriate as a metric to describe the correlation between two variables than r2 (which is used to describe how well the data fit the linear regression model).

We now mention the *r* and *p* values here.

#Line 570-571: Explain briefly why one can expect LCD and levoglucosan to have similar response to degradation, e.g. in terms of their chemical behavior/structure.

We have included the following (lines 594-596):
"Both are functionalized polar lipids with alcohol groups and thus are chemically relatively similar when compared to e.g. fatty acids (carboxyl group) or n-alkanes (no functional groups)."

#Line 578: "for" or "in" the Atlantic?

We have corrected this sentence.

#Line 583-586: Include in the sentence the producers of 1,13- and 1,15-diols.

We have corrected this accordingly.

#Line 614: Replace "minimal differences" with "minimal variations/variability".

We have corrected this accordingly.

#Line 625-627: It is true for LDI and UK'37 that the difference between proxy temperatures and instrumental SST increase during the warmer months, but not for TEX86H. The difference between TEX86H and SST for the cooler months are almost as large as that during the warmer months, and these differences are within the calibration error. Please rephrase the sentence to reflect this.

We have added the following (lines 655-657):
"Interestingly, the $U^{K'}_{37}$- and TEX^{H}_{86}-derived temperature trends show the same phenomenon (Turich et al., 2013; Fig. 8), where the proxy temperatures are cooler than the measured temperatures during the warmer months. However, in contrast to the $U^{K'}_{37}$ and LDI, the TEX^{H}_{86} also overestimates SST overestimation during the cold months."

#Line 638-640: Taken into account proxy uncertainty, I do not think it is possible to discern if the LDI temperatures are closer to SST or 20m (some temperatures are even higher than SST!), as the isotherms of the upper 30m are so close to each other anyway during the upwelling season. In any case, a habitat depth of the upper 20m is consistent with previous studies as well (as mentioned in line 646 - 649). Please rephrase the sentence.

We agree, and we have now emphasized that the temperature differences are within calibration error (lines 669-673):
"During upwelling, LDI-temperatures agree better with SST, implying that the habitat of the LCD producers potentially was closer to the surface, coincident with the shoaling of the nutricline and thermocline (Fig. 10). However, these absolute differences in LDI-temperatures are generally within the calibration error (2 °C), and these seasonal variations in LDI-temperatures should thus be interpreted with caution."

#Line 676-690: This discussion is not supported by the < 2 ^{0}C of temperature difference between TEX86H and satellite-SST that is well within the calibration error of TEX86H. In fact, the difference is even smaller than that between the LDI temperature and satellite SST in the North Atlantic (Fig 5), which the authors did not discuss since the differences are mostly within the calibration error. The authors also need to justify why they compared the 0-150m (instead of from the same water depths as the calibration) temperatures with the temperature estimates calculated using the 0-200m calibration. Since the focus of the paper is on LCD proxies, and this subsurface TEX86 finding was not mentioned in the abstract nor the conclusions, I would suggest to remove this paragraph.

We agree with the referee that this discussion is outside the scope of this manuscript, and that indeed we are discussing temperature differences which are within calibration error. We therefore have removed this part of the discussion.

#Line 700-703: See comment on #Line 638-640.

We have rephrased as follows (lines 732-736):
"In the Cariaco Basin we observe a seasonal signal in the LDI linked to the upwelling season reflecting temperatures of the upper ca. 30 m of the water column."

#Fig. 2: It took me a while to understand this figure. I think stacked bar chart would make a better option here, so instead of 12 panels with 3 bars each, you'd have 12 stacked bars which give you the same amount of information.

We have tried this option, but to our opinion this did not improve clarity as it visually suggests that the preservation percentages are summed. We therefore chose to use our original figure.

#Line 1184: Change "concentration" to "concentrations".

We have corrected this accordingly.

#Line 1185: Change "than" to "then".

We have corrected this accordingly.

#Fig. 3: It is impossible to tell which lines/variables correspond to which y-axes without going through the caption. I would suggest to change the color of the right y-axis and its label (Total mass flux) to grey, i.e. the same color as the plot for the variable.

We agree, and we have adjusted the figure accordingly.

#Fig. 8: This figure is mentioned for the first time at line 5XX in the section "Discussion" - I suggest to renumber it according to the order of its appearance in the text.

We have re-ordered the figures, also on suggestion of referee#1.

#Fig. 6: Specify at least in the caption if the annual mean WOA SST is averaged over latitudes or at a fixed latitude. I would also remove the panel on the left and the annual mean T0-150m in panel d if line 676-690 are removed.

The annual mean WOA SSTs are specific for the coordinates of the surface sediments; we have now emphasized this in the caption.
Since we have removed the discussion part on the subsurface TEX_{86}, we have also removed the left panel (a) and the annual mean T_0-T_{150}m and TEX_{86}-subsurface temperatures in panel d.

Additional comment:

We have replaced Fig. 9 since we by accident previously plotted the summed 1,13-/1,15-diol concentrations instead of the summed flux-weighted 1,13-/1,15-diol concentrations.

Long chain diols in settling particles in tropical oceans: insights into sources, seasonality and proxies.

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ABSTRACT

In this study we have analyzed sediment trap time series from five tropical sites to assess seasonal variations in concentrations and fluxes of long-chain diols (LCDs) and associated proxies with emphasis on the Long chain Diol Index (LDI) temperature proxy. For the tropical Atlantic, we observe that generally less than 2 % of LCDs settling from the water column are preserved in the sediment. The Atlantic and Mozambique Channel traps reveal minimal seasonal variations in the LDI, similar to the two other lipid-based temperature proxies TEX$_{86}$ and U$^{K'}_{37}$. ~~However~~In addition, annual mean LDI-derived temperatures are in good agreement with the annual mean satellite-derived sea surface temperatures (SSTs). In contrast, ~~the Cariaco Basin~~ the LDI in the Cariaco Basin shows larger seasonal variation, as do the TEX$_{86}$ and U$^{K'}_{37}$. Here, the LDI underestimates SST during the warmest months, which is likely due to summer stratification and the habitat depth of the diol producers deepening to around 20 to 30 m. Surface sediment LDI temperatures in the Atlantic and Mozambique Channel compare well with the average LDI-derived temperatures from the overlying sediment traps, as well as with decadal annual mean SST. Lastly, we observed large seasonal variations in the Diol Index, as indicator of upwelling conditions, at three sites~~,~~: in the Eastern Atlantic potentially linked to Guinea Dome upwelling~~ (Eastern Atlantic)~~, in the Cariaco Basin likely caused by seasonal upwelling~~, (Cariaco Basin)~~ and in the Mozambique Channel where Diol Index variations may be driven by upwelling from favorable winds and/or eddy migration. ~~seasonal upwelling and/or eddy migration (Mozambique Channel).~~

1. Introduction

Several proxies exist for the reconstruction of past sea surface temperature (SST) based on lipids. The $U^{K'}_{37}$ is one of the most applied proxies and is based on the unsaturation of long-chain alkenones (LCAs), which are produced by phototrophic haptophyte algae, mainly the cosmopolitan *Emiliania huxleyi* (Volkman et al., 1980; Brassell et al., 1986; Prahl and Wakeham, 1987; Conte et al., 1994). This index exhibits a strong positive correlation with SST (Müller et al., 1998; Conte et al., 2006). Another widely used organic paleotemperature proxy is the TEX_{86}, as originally proposed by Schouten et al. (2002), based on the relative distribution of archaeal membrane lipids, i.e. glycerol dialkyl glycerol tetraethers (GDGTs), and in the marine realm are mainly thought to be derived from the phylum Thaumarchaeota. Schouten et al. (2002) showed that the TEX_{86} index measured in marine surface sediments is correlated with SST, and since then its application in paleoenvironmental studies has increased (see e.g. review by Tierney, 2014). However, research showed that despite their highest abundance being recorded ~~of Thaumarchaeota~~ in the upper 100 m of the water column, ~~they~~ Thaumarchaeota can be present down to 5000 m depth (Karner et al., 2001; Herndl et al., 2005). Accordingly, GDGTs may be found in high concentrations below 100 m depth (e.g., Sinninghe Damsté et al., 2002; Wuchter et al., 2005) and several studies have indicated that TEX_{86} might be more reflective of subsurface temperatures in some regions (e.g., Huguet et al., 2007; Lopes dos Santos et al., 2010; Kim et al., 2012; 2015; Schouten et al., 2013; Chen et al., 2014; Tierney et al., 2017; see Zhang and Liu, 2018 for review).

Most recently a SST proxy based on the distribution of long-chain diols (LCDs), called the Long-chain Diol Index, or LDI was proposed (Rampen et al., 2012). This index is a ratio of 1,13- and 1,15-diols (i.e., alcohol groups at position C-1 and C-13 or C-15), and the analysis of globally distributed surface sediments revealed that this index strongly correlates with SST. Since then, the index has been applied in several paleoenvironmental studies (e.g., Naafs et al., 2012; Lopes dos Santos et al., 2013; Jonas et al., 2017; Warnock et al., 2017). However, large gaps still remain in the understanding of this proxy. The largest uncertainty is that the main marine producer of LCDs is unknown. Although these diols have been observed in cultures of certain marine eustigmatophyte algae (e.g. Volkman et al., 1992; 1999; Méjanelle et al., 2003; Rampen et al., 2014b), the LCD distributions in cultures are different from those observed in marine sediments. Furthermore, Balzano et al. (2018) combined lipid analyses with 18S rRNA gene amplicon sequencing on suspended particulate matter (SPM) and did not find a significant direct correlation between LCD concentrations and sequences of known LCD-producers. Rampen et al. (2012) observed the strongest empirical relation between surface sediment derived LDI values and SSTs for autumn ~~to~~ and summer, suggesting that these are the main growth seasons of the source organisms. Moreover, the strongest correlation was also observed for the upper 20 m of the water column, suggesting that the LCDs are likely produced by phototrophic algae which thrive in the euphotic zone. Nevertheless, LDI-temperatures based on surface sediments reflect an integrated signal of many years, which complicates the interpretation of the LDI in terms of seasonal production and depth of export production.

One way of resolving seasonality in LCD flux and LDI is to analyze time series samples from sediment traps that continuously collect sinking particles in successive time intervals over periods of a year or more. Such studies have been carried out for the $U^{K'}_{37}$ as well as for the TEX_{86} and associated lipids (e.g., Müller and Fischer, 2001; Wuchter et al., 2006; Huguet et al., 2007; Fallet et al., 2011; Yamamoto et al., 2012; Rosell-Melé and Prahl, 2013; Türich et al., 2013). However, very few studies have been done for LCDs. Villanueva et al. (2014) carried out a sediment trap study in Lake Challa (East Africa) and Rampen et al. (2008) in the upwelling region off Somalia. The latter study showed that 1,14-diols, produced by *Proboscia* diatoms strongly increased early in the upwelling season in contrast to 1,13- and 1,15-diols and thus can be used to trace upwelling. However, ~~none~~ neither of these sediment trap studies have evaluated the LDI.

In this study, we assess seasonal patterns of the LDI for sediment trap series at five sites, i.e., in the Cariaco Basin, the Mozambique Channel and three sites in the tropical North Atlantic and compared the LDI values to satellite-derived SST, as well as results obtained for other temperature proxies, i.e. the TEX^{H}_{86} and $U^{K'}_{37}$. Moreover, for the Atlantic and Mozambique Channel, we compare the sediment trap proxy signals with those preserved in the underlying sediments, after settling and burial. Finally, we assess the applicability of the Diol Index, based on 1,14-diols produced by *Proboscia* diatoms (Sinninghe Damsté et al., 2003), as tracer of upwelling and/or productivity in these regions.

2. Materials and methods

2.1 Study sites and sample collection

2.1.1 Tropical North Atlantic

The ocean current and wind patterns of the tropical Atlantic are mostly determined by the seasonal latitudinal shift of the intertropical convergence zone (ITCZ; Figure 1). The ITCZ migrates southward during boreal winter, and northward during boreal summer. During summer, the south-east trade winds prevail, whereas during winter the north-east trade winds intensify. The north-east trade winds drive the North Equatorial Current (NEC) which flows westward. South of ~~this current~~ the NEC, ~~flows~~ the North Equatorial Countercurrent (NECC) flows towards the east (Stramma and Schott, 1999). The South Equatorial Current (SEC) flows westward and branches off in the north Brazil Current (NBC; Stramma and Schott, 1999). When the ITCZ is in the north, the NBC retroflects off the South American coast, and is carried eastward into the NECC, and thus into the western tropical Atlantic (e.g., Richardson and Reverdin, 1987). North of the NBC, the Guiana Current (GC) disperses the outflow from the Amazon River towards the Caribbean Sea. (Müller-Karger et al., 1988; 1995). However, during boreal summer the NBC may retroflect, carrying the Amazon River plume far into the western Atlantic (e.g., Lefèvre et al., 1998; Müller-Karger et al., 1998; Coles et al., 2013). In fact, every late summer/autumn, the Amazon River outflow covers around 2×10^6 km^2 of the western North Atlantic, and the river delivers approximately half of all freshwater input into the tropical Atlantic (see Araujo et al., 2017 and references therein).

The eastern tropical North Atlantic is characterized by upwelling caused by the interaction between the trade winds and the movement of the ITCZ. Cropper et al. (2014) measured upwelling intensity along the NW African coastline between 1981 and 2012, in terms of wind speed, SST and other meteorological data. They recognized three latitudinal zones: weak permanent annual upwelling north of 26° N, strong permanent upwelling between 21° and 26° N and seasonal upwelling between 12° and 19° N related to the seasonal migration of the trade winds. Southeast of Cape Verde, large-scale cyclonic circulation forms the Guinea Dome (GD; Fig. 1), which centers around 10° N~~/~~,22° W (Mazeika, 1967), i.e., close to mooring site M1. ~~It~~ The GD is a thermal upwelling dome, formed by near-surface flow fields associated with the westward NEC, the eastward NECC and the westward North Equatorial Undercurrent (NEUC) (Siedler et al., 1992). It forms a cyclonic circulation as a result of the eastward flowing NECC and the westward flowing NEC (Rossignol and Meyrueis, 1964; Mazeika, 1967). The GD develops from late spring to late fall due to the northward ITCZ position and the resulting Ekman upwelling, but shows significant interannual variability (Siedler et al., 1992; Yamagata and Iizuka, 1995; Doi et al., 2009) judging from general ocean circulation models. According to Siedler et al. (1992), upwelling is most intense between July and October when the ITCZ is in the GD region and the NECC is strongest.

At three sites, we analyzed five sediment trap series along a ~~latitudinal~~ longitudinal transect in the North Atlantic (~12° N) to determine seasonal variations in the LDI. This transect has been studied previously for Saharan dust deposition in terms of grain sizes (van der Does et al., 2016), as the tropical North Atlantic receives approximately one third of the wind-blown Saharan dust (e.g., Duce et al., 1991; Stuut et al., 2005), which might potentially act as fertilizer because of the high iron levels (e.g., Martin and Fitzwater, 1988; Korte et al., 2017; Guirreiro et al., 2017; Goudie and Middleton, 2001 and references therein). Furthermore, Korte et al. (2017) assessed mass fluxes and mineralogical composition, Guerreiro et al. (2017) measured coccolith fluxes for two of the time series, while Schreuder et al. (2018a; 2018b) measured long-chain *n*-alkanes, long-chain *n*-alkanols and fatty acids, and levoglucosan for the same sediment trap samples and surface sediments as analyzed in this study.

At site M1 (12.00° N, 23.00° W), the sediment trap, referred to as M1U, was moored at a water depth of 1150 m (Fig. 1). This mooring is located in the proximity of the Guinea Dome, and might therefore potentially be influenced by seasonal upwelling. At station M2 (13.81° N, 37.82° W), two sediment traps were recovered, i.e., an ‘upper’ (M2U) trap at a water depth of 1235 m, and a ‘lower’ (M2L) trap at a depth of 3490 m. Lastly, at mooring station M4 (12.06° N, 49.19° W), also an upper and lower trap series were recovered and analyzed (M4U and M4L), at 1130 and 3370 m depth, respectively. This mooring site may seasonally be affected by Amazon River discharge (van der Does et al., 2016; Korte et al., 2017; Guirreiro et al., 2017; Schreuder et al., 2018a). All sediment traps were equipped with 24 sampling cups, which sampled synchronously over 16-day intervals from October 2012 to November

2013, using $HgCl_2$ as a biocide and borax as a pH buffer to prevent in situ decomposition of the collected material.

2.1.2 Mozambique Channel

The Mozambique Channel is located between Madagascar and Mozambique and is part of the Agulhas Current system hugging the coast of South Africa (Lutjeharms, 2006). The Agulhas Current system is an important conveyor in the transport of warm and salty waters from the Indian to the Atlantic Ocean (Gordon, 1986; Weijer et al., 1999; Peeters et al., 2004). The northern part of the channel is also influenced by the East African monsoon winds (Biastoch and Krauss, 1999; Sætre and da Silva, 1982; Malauene et al., 2014). Between September and March, these winds blow from the northeast, parallel to the Mozambique coastline, favoring coastal upwelling. Additionally, the Mozambique Channel is largely influenced by fast-rotating, mesoscale eddies which migrate southward towards the Agulhas region. Using satellite altimetry, Schouten et al. (2003) observed on average 4 to 6 eddies, ca. 300 km in diameter, propagating yearly from the central Mozambique Channel (15° S) toward the Agulhas area (35° S) between 1995 and 2000. Seasonal upwelling occurs off Northern Mozambique (between ca. 15 and 18° S) (Nehring et al., 1987; Malauene et al., 2014), from August to March with a dominant period of about two months although periods of one to four weeks have also been observed (Malauene et al., 2014).

The sediment trap was moored at 16.8° S and 40.8° E, at a water depth of 2250 m (Fig. 1; Fallet et al., 2010, 2011) and of the same type as used for the North Atlantic transect. We analyzed the LCD proxies for two respective time intervals: the first interval covers ca. 3.5 years, from November 2003 to September 2007, with a sampling interval of 21 days. The second interval covers another year, between February 2008 and February 2009, with a sampling interval of 17 days. Previously, Fallet et al. (2011) published foraminiferal, $U^{K'}_{37}$ and TEX_{86} records for the first time interval, and the organic carbon content for the follow-up time series. For further details on the deployments and sample treatments, we refer to Fallet et al. (2011, 2012). The two surface sediments are located across the narrowest transect between Mozambique and Madagascar, and were analyzed for $U^{K'}_{37}$ and TEX_{86} by Fallet et al. (2012) and for LCDs by Lattaud et al. (2017b).

2.1.3 Cariaco Basin

The Cariaco Basin is one of the largest marine anoxic basins (Richards, 1975), located on the continental shelf of Venezuela. The basin is characterized by permanent stratification and strongly influenced by the migration of the intertropical convergence zone (ITCZ). During late autumn and winter, the ITCZ migrates to the south which results in decreased precipitation and trade wind intensification which in turn induces upwelling and surface water cooling. This seasonal upwelling is a major source of nutrients that leads to strong phytoplankton growth along the Venezuelan coast (e.g., Müller-Karger et al., 2001; Thunell et al., 2007). Between August and October, the ITCZ moves northward again, resulting in a rainy season and diminishing of the trade winds inhibiting upwelling. During this wet season the contribution of terrestrially derived nutrients is higher. Due to the prevalent anoxic conditions in the basin, there is no bioturbation which has resulted in the accumulation of ~~varved~~ laminated sediments which provide excellent annually to decadally resolved climate records (e.g., Peterson et al., 1991; Hughen et al., 1996; 1998). Moreover, in November 1995, a time series experiment started to facilitate research on the link between biogeochemistry and the downward flux of particulate material under anoxic and upwelling conditions (Thunell et al., 2000). This project (CARIACO; http://imars.marine.usf.edu/cariaco) involved hydrographic cruises (monthly), water column chemistry measurements and sediment trap sampling (every 14 days). One mooring containing four automated sediment traps (Honjo and Doherty, 1988) was deployed at 10.50° N and 64.67° W, at a bottom depth of around 1400 m. These traps were moored at 275 m depth, just above the oxic/anoxic interface (Trap A), 455 m (Trap B), 930 m (Trap C) and 1255 m (Trap D). All traps contain a 13-cup carousel which collected sinking particles over 2 weeks, and were serviced every half year. For further details on trap deployment and recovery, and sample collection, storage and processing we refer to Thunell et al. (2000) and Goñi et al. (2004). In addition to the sediment trap sampling, the primary productivity of the surface waters was measured every month using ^{14}C incubations (Müller-Karger et al., 2001; 2004). For this study, we investigated two periods, i.e., May 1999–May 2000 and July 2002–July 2003 for Traps A and B. These years include upwelling and non-upwelling periods, as well as a disastrous flooding event in December 1999 (Turich et al., 2013). Turich et al. (2013) identified the upwelling periods, linked to the migration of the ITCZ, as indicated by decreasing SST in the CTD (temperature at -1 m water depth) and satellite-based measurements (indicated by grey boxes in figures ~~9~~ 8 and 10), and shoaling of the average depths of primary production and increased primary production. Moreover, Turich et al. (2013) evaluated the $U^{K'}_{37}$ and TEX_{86} proxies for the same two time series for which we analyzed the LCD proxies.

2.2 Instrumental data

Satellite SST, precipitation and wind speed time series of the M1, M2 and M4 moorings in the Atlantic derive from Guerreiro et al. (2017 and in revision) who retrieved these data from the Ocean Biology Processing Group (OBPG, 2014) (Frouin et al., 2003), the Goddard Earth Sciences Data and Information Services Center (2016) (Huffman et al., 2007; Xie and Arkin, 1997) and NASA Aquarius project (2015a; 2015b) (Lee et al., 2012) (see supplement of Guerreiro et al., 2017 for detailed references). The SST and Chlorophyll *a* time series data for the Mozambique Channel were adapted from Fallet et al. (2011), who retrieved these data from the Giovanni database (for details see Fallet et al., 2011). Surface sediment proxy temperatures were compared to annual mean SST estimates derived from the World Ocean Atlas (2013) (decadal averages from 1955 to 2012; Locarnini et al., 2013). Sea surface temperature data for the Cariaco Basin were adopted from Turich et al. (2013) and combined with additional CTD temperatures from the CARIACO time series data base for the depths of 2, 5, 10, 15 and 20 m (http://www.imars.usf.edu/CAR/index.html.; CARIACO time series composite CTD profiles; lead principal investigator: Frank Müller-Karger).

2.3 Lipid extraction

2.3.1 Tropical North Atlantic

The 120 sediment trap samples were sieved through a 1 mm mesh wet-split into five aliquots (van der Does et al., 2016), of which one was washed with Milli-Q water, freeze-dried and homogenized for chemical analysis (Korte et al., 2017). For organic geochemistry, ~~weight~~ sub-aliquots (by weight) were extracted as described by Schreuder et al. (2018a). Shortly, ca. 100 mg dry weight of sediment trap residue, and between 1.5 and 10 g of dry weight of surface sediment were extracted by ultrasonication using a mixture of dichloromethane:methanol (DCM:MeOH) (2:1; v/v), and dried over a Na_2SO_4 column. For quantification of LCDs, LCAs and GDGTs, we added the following internal standards to the total lipid extracts (TLEs): 2.04 µg C_{22} 7,~~16~~ 16-diol (Rodrigo-Gamiz et al., 2015), 1.50 µg 10-nonadecanone ($C_{19:0}$ ketone) and 0.1 µg C_{46} GDGT (Huguet et al., 2006), respectively. Subsequently, the TLEs were separated into apolar (containing *n*-alkanes), ketone (containing LCAs) and polar (containing LCDs and GDGTs) fractions over an activated (2h at 150 °C) Al_2O_3 column by eluting with hexane/DCM (9:1; v/v), hexane/DCM (1:1; v/v) and DCM/MeOH (1:1; v/v), respectively. The apolar fractions were analyzed by Schreuder et al. (2018a) for *n*-alkanes. Polar fractions were split for GDGT (25 %) and LCD (75 %) analysis. The LCD fraction was silylated by the addition of BSTFA (*N*,*O*-bis(trimethylsilyl)trifluoroacetamide) and pyridine, and heating at 60 °C for 20 min, after which ethyl acetate was added prior to analysis. The ketone fraction was also dissolved in ethyl acetate, and analyzed by GC and GC/MS. ~~and t~~The GDGT fraction was dissolved in hexane:isopropanol (99:1, v/v), ~~and analyzed by GC and GC/MS. Next, the GDGT fractions were~~ filtered through a 0.45 µm polytetrafluoroethylene (PTFE) filter and analyzed by HPLC-MS.

2.3.2 Mozambique Channel

Aliquots of the sediment trap samples from the Mozambique Channel were previously extracted and analyzed by Fallet et al. (2011) and Fallet et al. (2012), respectively. The sediment trap material was extracted by ultrasonication using a mixture of DCM/MeOH (2:1; v/v), dried over Na_2SO_4, and separated into apolar, ketone and polar fractions via alumina pipette column chromatography, by eluting with hexane/DCM (9:1; v/v), hexane/DCM (1:1; v/v) and DCM/MeOH (1:1; v/v), respectively. These existing polar fractions of the sediment trap material were silylated (as described above), dissolved in ethyl acetate and re-analyzed for LCDs by GC-MS. Since no record was kept of the aliquoting of extracts and polar fractions, we report the results in relative abundance rather than concentrations and fluxes of diols.

2.3.3 Cariaco Basin

Sediment trap material was extracted as described by Turich et al. (2013). Briefly, 1/16 aliquots of the trap samples were extracted by means of Bligh-Dyer extraction with sonication using a phosphate buffer and a trichloroacetic acid (TCA) buffer, after which the extracts were separated by adding 5 % NaCl in solvent-extracted distilled deionized water, and the organic phase was collected and the aqueous phase was extracted two more times. The extracts were pooled and dried over Na_2SO_4 and separated by means of Al_2O_3 column chromatography, eluting with hexane:DCM (9:1; v/v), DCM:MeOH (1:1; v/v) and MeOH. For this study, ~~this latter~~the DCM:MeOH (1:1; v/v) fraction was silylated (as described above), dissolved in ethyl acetate, and analyzed for LCDs using GC-MS. Similar to the Mozambique Channel samples, no record was kept of the aliquoting of extracts and polar fractions, and thus we report the results in relative abundance.

2.4 Instrumental analysis

2.4.1 GDGTs

The GDGT fractions of the surface sediments and sediment traps SPM samples of the tropical North Atlantic were analyzed for GDGTs by means of Ultra High Performance Liquid Chromatography Mass Spectrometry (UHPLC-MS). We used an Agilent 1260 HPLC, which is equipped with an automatic injector, interfaced with a 6130 Agilent MSD, and HP Chemstation software according to Hopmans et al. (2016). Compound separation was achieved by 2 silica BEH HILIC columns in tandem (150 mm x 2.1 mm; 1~~,~~.7 µm; Waters Acquity) in normal phase, at 25 °C. GDGTs were eluted isocratically for 25 min with 18 % B, followed by a linear gradient to 35 % B in 25 minutes and finally a linear gradient to 100 % B in the last 30 min. A = hexane; B = hexane:isopropanol (9:1; v/v). The flow rate was constant at 0.2 mL min^{-1}, and the injection volume was 10 µL. The APCI-MS conditions are described by

Hopmans et al. (2016). Detection and quantification of GDGTs was achieved in single ion monitoring (SIM) mode of the protonated molecules ($[M+H]^+$) of the GDGTs. We used a mixture of crenarchaeol and the C_{46} GDGT (internal standard) to assess the relative response factor, which was used for quantification of the GDGTs in the samples (c.f. Huguet et al., 2006).

Sea surface temperatures were calculated by means of the TEX^H_{86} as defined by Kim et al. (2010), which is a logarithmic function of the original TEX_{86} index (Schouten et al., 2002):

$$\mathrm{TEX}_{86}^{H} = \log \frac{[GDGT{-}2] + [GDGT{-}3] + [Cren']}{[GDGT{-}1] + [GDGT{-}2] + [GDGT{-}3] + [Cren']} \tag*{[1]}$$

where the numbers indicate the number of cyclopentane moieties of the isoprenoid GDGTs, and *Cren´* reflects an isomer of crenarchaeol, i.e. containing a cyclopentane moiety with a *cis* stereochemistry (Sinninghe Damsté et al., 2018). The TEX^H_{86} values were translated to SSTs using the core-top calibration of Kim et al. (2010):

$$\mathrm{SST} = 68.4 \times \mathrm{TEX}_{86}^{H} + 38.6 \tag*{[2]}$$

The Branched Isoprenoid Tetraether (BIT) index is a proxy for the relative contribution of terrestrial derived organic carbon (~~de Jonge et al., 2014; 2015~~Hopmans et al., 2004). We have calculated the modified version as reported by de Jonge et al. (2014; 2015) which ~~This ratio~~ is based on the original index as proposed by Hopmans et al. (2004), but includes the 6-methyl brGDGTs:

$$\mathrm{BIT} = \frac{[brGDGT\ Ia] + [brGDGT\ IIa{+}IIa'] + [brGDGT\ IIIa{+}IIIa']}{[brGDGT\ Ia] + [brGDGT\ IIa{+}IIa'] + [brGDGT\ IIIa{+}IIIa'] + [Cren]} \tag*{[3]}$$

where the numbers reflect different branched GDGTs (see Hopmans et al., 2004) and *Cren* reflects crenarchaeol. The branched GDGTs were always around the detection limit in the Atlantic samples, implying a BIT index of around zero and thus minimal influence of soil organic carbon (Hopmans et al., 2004), and thus the BIT index is not discussed any further.

2.4.2 LCAs

The ketone fractions of the surface sediments and sediment traps samples of the tropical North Atlantic were analyzed for LCAs on an Agilent 6890N gas chromatograph (GC) with flame ionization detection (FID) after dissolving in ethyl acetate. The GC was equipped with a fused silica column with a length of 50 m, a diameter of 0.32 mm, and a coating of CP Sil-5 (film thickness = 0.12 µm). Helium was used as carrier gas, and the flow mode was a constant pressure of 100 kPa. The ketone fractions were injected on-column at a starting temperature of 70 °C, which increased by 20 °C min^{-1} to 200 °C followed by 3 °C min^{-1} until the final temperature of 320 °C was reached. This end temperature was held for 25 min.

The $U^{K'}_{37}$ index was calculated according to Prahl and Wakeham (1987):

$$U^{K'}_{37} = \frac{[C_{37:2}]}{[C_{37:2}] + [C_{37:3}]} \quad [4]$$

The $U^{K'}_{37}$ values were translated to SST after the calibration of Müller et al. (1998):

$$SST = \frac{U^{K'}_{37} - 0.044}{0.033} \quad [5]$$

We have also applied the recently proposed BAYSPLINE Bayesian calibration of Tierney and Tingley (2018). They and others have shown~~ showed~~ that the $U^{K'}_{37}$ estimates substantially attenuate above temperatures of 24 °C (e.g., Conte et al., 1998; Goñi et al., 2001; Sicre et al., 2002). The Bayesian calibration ~~, moving~~ moves the upper limit of the $U^{K'}_{37}$ calibration from approximately 28 to 29.6 °C at unity. Since our traps are located in tropical regions with SSTs > 24 °C, we have applied this calibration as well.

2.4.3 LCDs

The silylated polar fractions were injected on-column on an Agilent 7890B ~~gas chromatograph (GC)~~ GC coupled to an Agilent 5977A ~~mass spectrometer (~~MS~~)~~. The starting temperature was 70 °C, and increased to 130 °C by 20 °C min^{-1}, followed by a linear gradient of 4 °C min^{-1} to an end temperature of 320 °C, which was held for 25 min. 1µL was injected, and separation was achieved on a fused silica column (25 × 0.32 mm) coated with CP Sil-5 (film thickness 0.12 μm). Helium was used as carrier gas with a constant flow of 2 mL min^{-1}. The MS operated with an ionization energy of 70 eV. Identification of LCDs was done in full scan mode, scanning between *m*/*z* 50–850, based on characteristic fragmentation patterns (Volkman et al., 1992; Versteegh et al., 1997). Proxy calculations and LCD quantifications were performed by analysis in SIM mode of the characteristic fragments (*m*/*z* 299, 313, 327 and 341; Rampen et al., 2012; *m*/*z* 187 for internal diol standard). For quantification of LCDs in the sediment traps and seafloor sediments of the tropical Atlantic, the peak areas of the LCDs were corrected for the average relative contribution of the selected SIM fragments to the total ion counts, i.e., 16 % for the saturated LCDs, 9 % for unsaturated LCDs and 25 % for the C_{22} 7,16-diol internal standard.

Sea surface temperatures were calculated using the LDI ~~index~~, according to Rampen et al. (2012):

$$\text{LDI} = \frac{[C_{30}\ 1{,}15\text{−}diol]}{[C_{28}\ 1{,}13\text{−}diol] + [C_{30}\ 1{,}13\text{−}diol] + [C_{30}\ 1{,}15\text{−}diol]} \qquad [6]$$

These LDI values were converted into SSTs using the following equation (Rampen et al., 2012):

$$\text{SST} = \frac{\text{LDI} - 0.095}{0.033} \qquad [7]$$

Upwelling conditions were reconstructed using the Diol Index as proposed by Rampen et al. (2008):

$$\text{Diol Index} = \frac{[C_{28}\ 1{,}14\text{−}diol] + [C_{30}\ 1{,}14\text{−}diol]}{[C_{28}\ 1{,}14\text{−}diol] + [C_{30}\ 1{,}14\text{−}diol] + [C_{30}\ 1{,}15\text{−}diol]} \qquad [8]$$

In 2010, Willmott et al. introduced an alternative Diol Index, which is defined as the ratio of 1,14-diols over 1,13-diols. Since the index of Rampen et al. (2008) includes the C_{30} 1,15-diol, it can be affected by temperature variation, and therefore we would normally prefer to use the index of Willmott et al. (2010). However, we often did not detect the C_{28} 1,13-diol, or it co-eluted with cholest-5-en-7-one-3β-ol, compromising the calculation of the Diol Index of Willmott et al. (2010). Moreover, the temperature variations in all three sediment traps are minimal as recorded by the LDI. Accordingly, we chose to apply the Diol Index according to Rampen et al. (2008).

Potential fluvial input of organic carbon was determined by the fractional abundance of the C_{32} 1,15-diol (de Bar et al., 2016; Lattaud et al., 2017a):

$$FC_{32}\ 1{,}15\text{-diol} = \frac{[C_{32}\ 1{,}15-diol]}{[C_{28}\ 1{,}13-diol] + [C_{30}\ 1{,}13-diol] + [C_{30}\ 1{,}15-diol] + [C_{32}\ 1{,}15-diol]} \quad [9]$$

The fractional abundance of the C_{32} 1,15-diol was always lower than 0.23, suggesting low input of river derived organic carbon (Lattaud et al., 2017a).

~~2.5 Time-series analysis~~

~~We performed time-series spectral analysis on the Diol Index data from the Mozambique Channel to assess the influence of meso-scale eddies. Analyses were performed in MATLAB®. The two parts of the Diol Index time series, i.e. the 2003–2007 and the 2008–2009 periods, were analysed both separately and together. The data were linearly interpolated in time (to 21-day intervals for the 2003–2007 period, and 17-day intervals for the 2008–2009 period) to adjust for disjunct sampling intervals or short gaps, and detrended. A runs test for randomness (Gibbons & Chakraborty, 2003) showed that for the second, shorter time series (2008–2009) the null hypothesis – that the values in the series are in random order – could not be rejected at the 5 % significance level. The second series also lacked statistically significant autocorrelation according to the Ljung-Box test (Ljung & Box, 1978). Therefore, there was little point in analysing the shorter 2008–2009 time series for periodicity. We performed a wavelet analysis to detect transient features in the Mozambique Channel Diol Index 2003–2007 time series following the methods of Torrence and Compo (1998; http://paos.colorado.edu/research/wavelets/) and using the Morlet wavelet as mother wavelet.~~

3. Results

3.1 Tropical North Atlantic

We have analyzed sediment trap samples from a ~~latitudinal~~ longitudinal transect (~ 12°N) in the tropical North Atlantic (two upper traps at ca. 1200 m water depth, and three lower traps at ca. 3500 m; Fig. 1), covering November 2012–November 2013, as well as seven underlying surface sediments, for LCDs, LCAs and GDGTs. Below we present the results for these lipid biomarkers and associated proxies.

3.1.1 LCDs

The LCDs detected in the sediment trap samples and surface sediments from the tropical North Atlantic (Fig. 2) are the C_{28} ~~and~~, ~~(mono-unsaturated and saturated)~~ C_{30} and $C_{30:1}$ 1,14-~~ (between 1 and 49 % of all LCDs)~~, C_{28} and C_{30} 1,13-~~ (0–3 %)~~, ~~and~~ the C_{30} 1,15-~~ (44–99 %),~~ and C_{32} 1,15-diols~~s (0–7 %)~~. ~~In the M2 and M4 traps, the C_{30} 1,15-diol constitutes between 87 and 95 % of total LCDs.~~ We detected the C_{28} 1,14- diol and C_{29}-OH fatty acid in the traps from M1 and M4, in a few samples of the M2 traps and in all surface sediments. ~~Similarly, the C_{28} 1,14-diol was detected in all samples from M1 and M4, in only a few M2 samples and in all surface sediments.~~ For most samples from M2U and M2L, the C_{28} 1,14-diol was often part of a high background signal, making identification and quantification problematic. In these cases, 1,14-diol fluxes and Diol Index were solely based on the (saturated and mono-unsaturated) C_{30} 1,14-diol.~~ In contrast, the saturated C_{30} 1,14-diol was detected in all samples.~~

The average [1,13+1,15]-diol flux is 2.6 (± 1.0) μg m^{-2} d^{-1} at M1U, 1.4 (± 1.2) and 1. 2 (± 1.1) μg m^{-2} d^{-1} for M2U and M2L, respectively, and 7.0 (± 7.8) and 2.2 (± 3.3) μg m^{-2} d^{-1} for M4U and M4L, respectively (Fig. 3). The [1,13+1,15]-diol and 1,14-diol concentrations in the underlying sediments vary between 0.05 μg g^{-1} and 0.50 μg g^{-1}, and between 3 ng g^{-1} and 0.06 μg g^{-1}, respectively. ~~The [1,13+1,15]-LCD flux is more than three times higher in the upper trap of M4 than in the lower trap, whereas at M2, where the average LCD fluxes are much lower, the difference is not appreciable.~~ The 1,14-diol flux for M1U averages 0.5 (± 0.8) μg m^{-2} d^{-1} with a pronounced maximum of 3.5 μg m^{-2} d^{-1} in late April (Fig. ~~6a~~5a), irrespective of the total mass flux. The average 1,14-diol flux at M2 is much lower and similar for the upper and lower traps, being around 0.01–0.02 (± 0.01) μg m^{-2} d^{-1}. At M4, the average 1,14-diol fluxes are 0.3 (± 0.5) and 0.1 (± 0.2) μg m^{-2} d^{-1} for the upper and lower trap, respectively. There are two evident maxima in the [1,13+1,15]-diols and 1,14-diol fluxes in late April and during October/November, concomitant with maxima in the total mass flux (Fig. 3d and 3e). However, in the lower trap this flux maximum is distributed over two successive trap cups, corresponding to late April/early May (Fig. 3e and 3j).

The LDI ranged between 0.95 and 0.99 in all traps, corresponding to temperatures of 26.0 to 27.3 °C with no particular trends (Fig. ~~5~~4). For most M2 and M4 samples the C_{28} 1,13-diol was below quantification limit and, hence, LDI was always around unity, corresponding to 26.9 to 27.3 °C (Fig. ~~5~~4), whereas in others samples the C_{28} 1,13-diol co-eluted with cholest-5-en-7-one-3β-ol, prohibiting the calculation of the LDI and Diol Index (Fig. ~~5~~ 4 and ~~6~~5). The flux-weighted annual average LDI-derived SSTs are 26.6 °C for M1U, and 27.1 °C for M2U, M2L, M4U and M4L. The underlying sediment is very similar, with LDI values between of 0.95 and 0.98 corresponding to 26.0 and 26.9 °C (Fig. 6). The Diol Index varied from 0.03 to 0.30 in M1U, showing a pronounced maximum during spring (Fig. ~~6a~~5a). The Diol Index at M2 ranges between 0.01 and 0.05 without an evident pattern, while the Diol Index at M4 ranges from 0.01 to 0.10 and shows the same pattern in the lower and upper trap, with highest values during spring (ca. 0.1), followed by a gradual decrease during summer (Fig. ~~6d~~5d; ~~6e~~5e).

3.1.2 LCAs

We detected C_{37}, C_{38} and C_{39} long-chain alkenones in the sediment trap and surface sediments. The $C_{37:3}$ alkenone was generally around the limit of quantification for the M2L and M4L traps, and below the limit of quantification for 4 out of the 7 surface sediment samples, while the $C_{37:2}$ alkenone was always sufficiently abundant. The annual mean fluxes of the C_{37} LCAs are 4.3 (± 3.5) μg m^{-2} d^{-1} for M1U, 1.2 (± 0.9) μg m^{-2} d^{-1} and 0.4 (± 0.2) μg m^{-2} d^{-1} for M2U and M2L, respectively, and 2.8 (± 5.0) μg m^{-2} d^{-1} and 1.2 (± 2.0) μg m^{-2} d^{-1} for M4U and M4L, respectively. The concentrations of the C_{37} LCAs in the underlying surface sediments range between 0.02 and 0.41 μg g^{-1}. At M4, the two total mass flux peaks at the end of April and during October/November are also clearly pronounced in the C_{37} alkenone fluxes (Fig. 3d, 3e and ~~6g~~5g), as well as the increased signal in the cup reflecting the beginning of May, which follows the cup which recorded the peak in total mass flux at the end of April. The $U^{K'}_{37}$ varied from 0.87 to 0.93, corresponding to 25.1 to 27.0 °C (Fig. ~~7c~~6c) for 3 out of 7 surface sediments in which the $C_{37:3}$ was above quantification limit. The flux-weighted average SSTs are 26.1 °C for M1U, 25.7 and 26.4 °C for M2U and M2L, respectively, and 28.2 and 27.5 °C for M4U and M4L, respectively (Fig. ~~7~~6). SST variations per sediment trap are generally within a 2–3 °C range (Fig. ~~5~~4) with no apparent trends.

3.1.3 GDGTs

The main GDGTs detected were the isoprenoidal GDGT-0, -1, -2, -3, crenarchaeol and the isomer of crenarchaeol. Branched GDGTs were typically around or below quantification limit. ~~Additionally, we detected three hydroxyl GDGTs (OH-GDGTs), i.e. OH-GDGT-0, -1 and -2. These OH-GDGTs contributed ca. 0.1–0.2 % to the total GDGT pool (i.e., hydroxyl and isoprenoidal) in the sediment traps, but in the surface sediments their fractional abundance was higher, around 1 %.~~ The average iGDGT flux in M1U is 15.5 (± 4.6) µg m^{-2} d^{-1}, 2.4 (± 1.1) and 2.6 (± 0.3) µg m^{-2} d^{-1} in M2U and M2L, respectively, and 4.3 (± 1.5) and 2.9 (± 1.2) µg m^{-2} d^{-1} in M4U and M4L, respectively (Fig. 3f). The surface sediments exhibit iGDGT concentrations between 0.4 and 1.7 µg g^{-1}. Sediment TEX^{H}_{86} values vary between 0.62 and 0.69, corresponding to 24.3 to 27.4 °C. The TEX^{H}_{86} flux-weighted average SSTs are 25.2 °C for M1U, 27.3 and 26.6 °C for M2U and M2L, respectively, and 27.8 and 26.7 °C for M4U and M4L, respectively. SSTs vary typically within a range of 1 and 2 °C. At M2U~~ and M4U~~, the TEX^{H}_{86} temperatures decrease slightly (ca. 1–2 °C) ~~during~~ between January and July (Fig. ~~5b~~ 4b~~and 5d~~).

3.2 Mozambique Channel

For two time series (November 2003–September 2007 and February 2008–February 2009), we have analyzed LCDs collected in the sediment trap at 2250 m water depth as well as nearby underlying surface sediments (Fig. 1). The main LCDs observed in the sediment traps and surface sediments are the C_{28} 1,12-, 1,13- and 1,14-diols, the C_{30} 1,13-, 1,14- and 1,15-diols and the C_{32} 1,15-diol. We also observed the $C_{30:1}$ 1 1,14 diol in some trap samples, and the C_{29} 12-OH fatty acid in all trap and sediment samples. ~~The C_{30} 1,15 is generally highest in abundance, varying between 28 and 85 % of the total LCD assemblage. The C_{28} and C_{30} 1,14-diols contribute between 11 and 67 % of total LCDs.~~ In 24 samples, the C_{28} 1,13-diol co-eluted with cholest-5-en-7-one-3β-ol, and henceforth we did not calculate the LDI for these samples. The C_{28} 1,14-diol was not affected by this cholest-5-en-7-one-3β-ol due to its much higher abundance compared to the C_{28} 1,13-diol and the Diol Index was therefore still calculated. The

LDI varied between 0.94 and 0.99, i.e., close to unity, corresponding to 25.5 to 27.2 °C, without an evident trend (~~Fig. 8~~Fig. 7a). The Diol Index ranges between 0.11 and 0.69, showing substantial variation, although not with an evident trend (~~Fig. 8~~Fig. 7b). The average LDI-derived temperature of two underlying surface sediments is 26.0 °C.

3.3 Cariaco Basin

We analyzed LCDs for two time series (May 1999–May 2000 and July 2002–July 2003) from the upper (Trap A; 275 m) and the lower trap (Trap B; 455 m) in the Cariaco Basin. The main LCDs detected for both time series are the C_{28} 1,14-, C_{30} 1,14-, $C_{30:1}$ 1,14-, C_{28} 1,13-, C_{30} 1,15- and C_{32} 1,15-diols, as well as the C_{29} 12-OH fatty acid. ~~The C_{30} 1,15-diol contribution varies between 3 and 92 % of all LCDs, the C_{28} and C_{30} 1,14-diol contribution between 3 and 96 %, and the C_{28} and C_{30} 1,13-diols constitute between 0 and 8 %.~~ For some samples we did not compute the LDI, as the C_{28} 1,13-diol co-eluted with cholest-5-en-7-one-3β-ol. Similarly as for the Mozambique Channel, the C_{28} 1,14-diol was not affected by this co-elution due to its much higher abundance compared to the C_{28} 1,13-diol and the Diol Index was therefore still calculated. The calculated LDI values range between 24.3 and 25.3 °C and 22.0 and 27.2 °C for Trap A and B of the 1999-2000 time series, respectively, with the lowest temperature during winter, and the highest during summer. For the 2002-2003 time series, LDI temperatures for Trap A range between 23.3 and 26.2 °C, and for Trap B between 22.5 °C and 26.5 °C.

For the May 1999–May 2000 time series, the Diol Index varies between 0.05 and 0.97 for Trap A, and between 0.05 and 0.91 for Trap B (~~Fig. 9~~Fig. 8) with similar trends, i.e. the lowest values of around 0.1-0.2 just before the upwelling period during November, rapidly increasing towards values between ca. 0.8 and 1 during the upwelling season (January and February). For the time series of July 2002–July 2003, the Diol Index shows similar trends, i.e. Diol Index values around 0.8-0.9 during July, which rapidly decrease towards summer values of around 0.2-0.3. Similar to the 1999-2000 time series, the lowest index values (ca. 0.2) are observed just before the upwelling period (during September), after which they increase towards values of around 0.8-0.9 between December and March at the start of the upwelling season. At the end of the upwelling season the Diol Index increases, followed by another maximum of around 0.6 during May.

4. Discussion

4.1 LCD sources and seasonality

The 1,14 diols can potentially be derived from two sources, i.e. *Proboscia* diatoms (Sinninghe Damsté et al., 2003; Rampen et al., 2007) or the dictyochophyte *Apedinella radians* (Rampen et al., 2011). The non-detection of the C_{32} 1,14-diol, which is a biomarker for *Apedinella radians* (Rampen et al., 2011), and the detection of the $C_{30:1}$ 1,14 diol and C_{29} 12-OH fatty acid, which are characteristic of *Proboscia* diatoms (Sinninghe Damsté et al., 2003), suggests that *Proboscia* diatoms are most likely the source of 1,14-diols in the tropical North Atlantic, the Mozambique Channel and the Cariaco Basin.

In the Cariaco Basin, the Diol Index shows a strong correlation (visually as correlation analysis was not possible due to differently spaced data in time) with primary production rates, suggesting that *Proboscia* productivity was synchronous with total productivity (~~Fig. 9~~Fig. 8), although for the 1999-2000 time series there is a disagreement during January/February. Primary productivity in the Cariaco Basin is largely related to seasonal upwelling which occurs between November and May when the ITCZ is at its southern position. Hence, the Diol Index seems to be an excellent indicator of upwelling intensity in the Cariaco Basin.

The index also shows considerable variation over time in the Mozambique Channel (~~Fig. 8~~Fig. 7b). Previous studies have shown that upwelling occurs in the Mozambique Channel between ca. 15 and 18°S (Nehring et al., 1987; Malauene et al., 2014), i.e. at the location of our sediment trap. Upwelling is reflected by cool water events and slightly enhanced Chlorophyll *a* levels, and Malauene et al. (2014) observed cool water events at ca. two month intervals although periods of 8 to 30 days were also observed. The two main potential forcing mechanisms for upwelling in the Mozambique Channel are the East African monsoon winds and the meso-scale eddies migrating through the channel. Fallet et al. (2011) showed that subsurface temperature, current velocity and the depth of surface-mixed layer all revealed a dominant periodicity of four to six cycles per year, which is the same frequency as that of the southward migration of meso-scale eddies in the channel (Harlander et al., 2009; Ridderinkhof et al., 2010), implying that eddy passage strongly influences the water mass properties. Wavelet analysis of the Diol Index for the period 2003–2007 (~~not shown~~supplemental Fig. S1) revealed short periods, occurring around January of 2004, 2005, and 2006, of significant (above the 95 % confidence level) variability at about bimonthly frequencies (60-day period). Both the frequency (bimonthly) and the timing (boreal winter) of the observed time periods of enhanced Diol Index variability are similar to those of the cool water events as observed by Malauene et al. (2014), associated with upwelling (~~Fig. 8~~Fig. 7b). The strongest variability of the Diol Index at ~~frequencies of four cycles~~about bimonthly frequencies~~ per year and higher~~ occurred in the first half of 2006. During the same period, salinity time series showed the passage of several eddies that had a particularly strong effect on the upper layer hydrography (Ullgren et al., 2012). Malauene et al. (2014) showed that neither upwelling-favorable winds, nor passing eddies, can by themselves explain the observed upwelling along the northern Mozambique coast. The two processes may act together, and both strongly influence the upper water layer and the organisms living there, potentially including the LCD producers.

The least (seasonal) variation in the Diol Index is observed at M2 in the tropical North Atlantic (Fig. ~~6b~~ 5b and 5c), which is likely due to its central open ocean position, associated with relatively stable, oligotrophic conditions (Guerreiro et al., 2017). In contrast, M4 and M1 are closer to the south American and west African coast, respectively, and thus are potentially under the influence of Amazon river runoff and upwelling, respectively, and specific wind and ocean circulation regimes (see Sect. 2.1.1). However, at M4, the Diol Index is also low (max. 0.1), suggesting low *Proboscia* productivity (Fig. ~~6d~~ 5d and 5e). At M1, by contrast, we observe enhanced values for the Diol Index of up to ~0.3 during spring (Fig. ~~6a~~5a). Most likely, an upwelling signal at this location is associated with the seasonal upwelling of the Guinea Dome. This upwelling is generally most intense between July and October (Siedler et al., 1992), due to the northward movement of the ITCZ and the resulting intensified Ekman upwelling. Specifically, during this period, the trade winds are weaker, atmospheric pressure is lower, and the regional wind stress is favorable to upwelling of the North Equatorial Undercurrent (Voituriez, 1981). Indeed, a decrease in wind speed and increased precipitation during summer to autumn was observed (Fig. ~~6a~~5a) which confirms that during these seasons the ITCZ was indeed at a northern position, and that during 2013 the upwelling associated with the Guinea Dome was most favored between July and October. The timing of the Diol Index peak, i.e., between March and June is consistent with previous sediment trap studies elsewhere which have shown that *Proboscia* diatoms and 1,14-diols are typically found during pre-upwelling or early upwelling periods (Koning et al., 2001; Smith, 2001; Sinninghe Damsté et al., 2003; Rampen et al., 2007). The surface sediment at 22° W just east of M1 also reveals the highest Diol Index (0.53), likely due to its closer vicinity to the Guinea Dome center. Several studies have reported *P. alata* diatoms offshore North West Africa (Lange et al., 1998; Treppke et al., 1995; Crosta et al., 2012; Romero et al., 1999), pointing to *P. alata* as a plausible source organism. The sedimentary annual diol indices compare well with the sediment trap indices (Fig. ~~7e~~6e), which is consistent with the results of Rampen et al. (2008). Our results clearly show that the Diol Index reflects different things in different regions. This is due to the ecology of *Proboscia* spp. where blooms occur during stratification to early upwelling to postbloom, and from high nutrients to low nutrients (see Rampen et al., 2014; references in Table 1). Therefore, the type of conditions reflected by the Diol Index is specific for every region.

To assess variations in seasonal production of 1,13- and 1,15-diols in the tropical Atlantic, for which we have the most complete dataset, we calculated the flux-weighted 1,13- and 1,15-diol concentrations for the different traps, and summed these per season (Fig. ~~4~~9). Highest production is observed in autumn, followed by summer and spring, with the lowest production during winter (~60 % compared to autumn). This is in agreement with Rampen et al. (2012) who observed, for an extensive set of surface sediments, the strongest correlation between LDI and SST for autumn, suggesting that production of the source organisms of the LDI mainly occurs during autumn. At M4, there are two evident peaks in the 1,13- and 1,15-diol fluxes at the end of April and October 2013. These maxima correlate with peaks in other lipid biomarker fluxes (i.e., 1,14-diols, C_{37} alkenones and iGDGTs), total mass flux, calcium carbonate ($CaCO_3$), OM and the residual mass flux which includes the deposition flux of Saharan dust (Korte et al., 2017). According to Guerreiro et al. (2017), the maximum in total mass flux at the end of April 2013 is likely caused by enhanced export production due to nutrient enrichment as a result of wind-forced vertical mixing. The peak at the end of October 2013, is likely associated with discharge from the

Amazon River. Moreover, both peaks are concomitant with prominent dust flux maxima, suggesting that Saharan dust also acted as nutrient fertilizer (Korte et al., 2017; Guerreiro et al., 2017). Guirreirro et al. (2017) suggested that during the October-November event the Amazon River may not only have acted as nutrient supplier, but also as buoyant surface density retainer of dust-derived nutrients in the surface waters, resulting in the development of algal blooms within just a few days, potentially explaining the peak 1,13- and 1,15-diol fluxes, as well as the peak fluxes of the other lipid biomarkers. However, they might also partially result from enhanced particle settling, caused by e.g. dust ballasting or faecal pellets of zooplankton (see Guerreiro et al. 2017 and references therein). This agrees with the results of Schreuder et al. (2018a) who show that the *n*-alkane flux also peaks concomitant with the peaks in total mass flux and biomarkers, whereas *n*-alkanes are terrestrial derived (predominantly transported by dust) and increased deposition can therefore not result from increased primary productivity in the surface waters.

The C_{37} alkenone flux at M4U also reveals these two distinct maxima at the end of April and October during 2013 (Fig~~,~~. ~~6g~~5g). Interestingly, this flux, as well as the alkenone flux at M2U, is consistent with coccolith export fluxes of the species *Emiliania huxleyi* and *Gephyrocapsa oceanica* (Guerreiro et al., 2017). In fact, when we combine the coccolith fluxes of both species, we observe strong correlations with the C_{37} alkenone fluxes for both M2U and M4U (Fig. ~~6f~~ 5f and ~~6g~~5g, respectively; ~~R^2~~ r = 0.~~60~~ 77 and 0.~~84~~ 92 for M2U and M4U, respectively; *p*-values < 0.001). This implies that these two species are the main LCA producers in the tropical North Atlantic, which agrees with previous findings (e.g., Marlowe et al., 1984; Brassell, 2014; Conte et al., 1994; Volkman et al., 1995).

4.2 Preservation of LCDs

The sediment trap data from the North Atlantic can be used to assess the relative preservation of LCDs, as well as other proxy lipid biomarkers, by comparing the flux-weighted concentration in the traps with the concentrations in the surface sediments. For all four biomarker groups, i.e., C_{37} alkenones, iGDGTs, 1,14-diols and 1,13- and 1,15-diols, we observe that in general the flux-weighted concentrations are higher in the upper traps (ca. 1200 m) as compared to the lower traps (ca. 3500 m; Fig. 2) by a factor of between 1.2 and 4.4, implying degradation during settling down the water column. The concentrations in the surface sediments are 2 to 3 orders of magnitude lower in concentration (i.e., between 0.1–1.5 % of upper trap signal), implying that degradation of lipids is mainly taking place at the water-sediment surface rather than the water column. A similar observation was made for levoglucosan in these sediment traps (Schreuder et al., 2018b). Both are functionalized polar lipids with alcohol groups and thus are chemically relatively similar when compared to e.g. fatty acids (carboxyl group) or *n*-alkanes (no functional groups). ~~This~~ These ~~is~~ degradation rates are likely linked to the extent of the oxygen exposure time (Hartnett et al., 1998; Hedges et al., 1999) at the seafloor (Hartnett et al., 1998; Sinninghe Damsté et al., 2002), since during settling the lipids are exposed to oxygen for weeks, whereas for surface sediments this is typically decades to centuries. Our results compare well with several other sediment trap studies which showed that LCDs, LCAs and iGDGTs generally have a preservation factor of around 1 % (surface sediment vs. trap) (e.g., Prahl et al., 2000; Wakeham et al., 2002; Rampen et al., 2007; Yamamoto et al., 2012).

We have also identified the C$_{30}$ and C$_{32}$ 1,15-keto-ol ~~for~~ in the Atlantic as well as the Mozambique and Cariaco sediment traps and surface sediments. These lipids are structurally related to LCDs and occur ubiquitously in marine sediments (e.g., Versteegh et al., 1997; 2000; Bogus et al., 2012; Rampen et al., 2007; Sinninghe Damsté et al., 2003; Wakeham et al., 2002; Jiang et al., 1994), and were inferred to be oxidation products of LCDs (Ferreira et al., 2001; Bogus et al., 2012; Sinninghe Damsté et al., 2003). We have not detected 1,14-keto-ols, which supports the hypothesis of Ferreira et al. (2001) and Sinninghe Damsté et al. (2003) that the silica frustules of *Proboscia* diatoms sink relatively fast and thus are exposed to oxygen for a shorter period than the producers of 1,13- and 1,15-diols, and thus less affected by oxidation. Alternatively, the keto-ols are not oxidation products but are produced by unknown organisms in the water column. In fact, Méjanelle et al. (2003) observed trace amounts of C$_{30}$ 1,13- and C$_{32}$ 1,15-keto-ols in cultures of the marine eustigmatophyte *Nannochloropsis gaditana*. Thus, an alternative explanation for the non-detection of 1,14-keto-ols is that, in contrast to the 1,15-keto-ols, they were not produced in the water column.

For both the tropical Atlantic and the Cariaco Basin, we observe highly similar LDI values for the upper and the lower traps. In the Atlantic there is no statistical difference between upper and lower trap that are 2200 m apart (two-tailed $p > 0.8$), but we have too little data for the Cariaco Basin for statistical comparison (Fig. ~~7b~~6b, ~~9c~~ 8c and ~~9f~~8f). This suggests that degradation in the water column does not affect the LDI proxy. This is in agreement with the study of Reiche et al. (2018) who performed a short-term degradation experiment (< 1 year) and found that the LDI index was not affected by oxic exposure on short time scales. However, the oxygen exposure time on the seafloor is much longer, and Rodrigo-Gámiz et al. (2016) showed for sediments in the Arabian Sea, deposited under a range of bottom water oxygen conditions, that different LCDs had different degradation rates, which compromised the LDI ratio. For the three sites in the tropical North Atlantic, we have calculated the flux-weighted average proxy values for every sediment trap and compare these with the underlying surface sediments (Fig. ~~7b~~6b-~~7e~~6e). For all indices, i.e., Diol Index, LDI, $U^{K'}_{37}$ and TEX$_{86}$, we observe very good correspondence between the sediment trap and surface sediment values, implying minimal alteration of the proxies after settling and during burial. Similarly, for the Mozambique Channel, the mean Diol Index and LDI from the sediment trap (i.e., 0.41 and 0.97, respectively) are very similar to the surface sediment values (i.e., 0.42 and 0.95, respectively). In agreement with the consistent diol indices, we observe that all individual LCDs are also preserved relatively equally in the tropical Atlantic (1.2-4.3 % at station M1, 0.1-2.9 % at station M2 and 0.03-0.16 % at station M4). This contrasts with the findings of Rodrigo-Gámiz et al. (2016) who found that the 1,15-diols have the highest degradation rate, followed by the 1,14- and 1,13-diols. Only the C$_{32}$ 1,15-diol seems relatively better preserved than the other LCDs at all three North Atlantic mooring sites (Fig. 2), suggesting that the C$_{32}$ 1,15-diol is less impacted by degradation. The C$_{32}$ 1,15-diol likely partially derives from the same source as the other 1,13- and 1,15-diols, but is also produced in fresh water systems (e.g., Versteegh et al., 1997; 2000; Rampen et al., 2014b; de Bar et al., 2016; Lattaud et al., 2017a; 2017b). Hence, the different preservation characteristics might be the result of a different source for this LCD.

4.3 Relationship between LDI and SST

In the tropical Atlantic and Mozambique Channel, the LDI-derived SSTs show minimal ~~differences~~ variability (<2 °C), while in the Cariaco Basin we observe much larger changes that range from 22.0 °C to 27.2 °C (~~Fig. 9~~Fig. 8). Both time series in the Cariaco Basin show low temperatures between November and May associated with the seasonal upwelling and surface water cooling, and significantly higher temperatures during the rainy summer. However, during the warmest periods, the LDI temperatures are generally lower than measured at the surface by CTD, whereas during the colder phases, the LDI agrees well with the measurements. The LDI calibration reaches unity at 27.4 °C, and therefore it is not possible to resolve the highest temperatures which are between ca. 28 and 30 °C. However, the LDI-derived temperatures are sometimes well below 27.4 °C where the CTD data suggest SSTs > 28 °C. Consequently, the LDI-based temperatures agree with CTD-based SSTs within calibration error for most of the record, but during summer when SST is highest, are offset outside the calibration error (ΔT ~2.5-4.5 °C). Interestingly, the $U^{K'}_{37}$- and TEX^{H}_{86}-derived temperature trends show the same phenomenon (Turich et al., 2013; ~~Fig. 9~~Fig. 8), where the proxy temperatures are cooler than the measured temperatures during the warmer months. However, in contrast to the $U^{K'}_{37}$ and LDI, the TEX^{H}_{86} also overestimates SST- during the cold months. For $U^{K'}_{37}$, Turich et al. (2013) pointed out that a time lag between synthesis, export and deposition could potentially explain the difference between the proxy and CTD temperatures. However, previous analysis of plankton biomass, primary productivity, bio-optical properties and particulate organic carbon fluxes for the same time period (Müller-Karger et al., 2004), as well as the total mass and terrigenous fluxes assessed by Turich et al. (2013) showed best correlation at zero-time lag on the basis of their 14-day sample interval. We compared our LDI temperature estimates with monthly CTD measurements between 0 and 50 m depth, the temperature at depth of maximum primary productivity and the temperature at the chlorophyll maximum (Turich et al., 2013; http://www.imars.usf.edu/cariaco) (Fig. 10). During the upwelling season, temperatures are significantly lower due to the upward migration of isotherms, whereas during the non-upwelling period, temperatures are higher, particularly in the upper 20 m, and the water column is more stratified (Fig. 10). LDI underestimates SST during stratification, which suggests that the LCD producers may thrive at depths of ca. 20–30 m. During upwelling, LDI-temperatures agree better with SST, implying that the habitat of the LCD producers potentially was closer to the surface, coincident with the shoaling of the nutricline and thermocline (Fig. 10). However, these absolute differences in LDI-temperatures are generally within the calibration error (2 °C), and these seasonal variations in LDI-temperatures should thus be interpreted with caution. Turich et al. (2003) found that the $U^{K'}_{37}$-derived temperatures agreed reasonably well with the measured temperatures at the chlorophyll maximum, which is generally found below 20 m depth (average 30–34 m depth; ranging between 1 and 55 m) in the Cariaco Basin. The LDI temperatures are almost always higher than the temperatures at the chlorophyll maximum (Fig. 10), and higher than the temperatures at 30 m depth, implying that the LDI producers may reside in the upper 30 m of the water column, which is consistent with the results of Rampen et al. (2012), who showed that LDI-derived temperatures have the strongest correlation with temperatures of the upper 20 m of the water column. This also agrees with Balzano et al. (2018) who observed highest LCD abundances within the upper 20 m of the water column in the Tropical Atlantic.

In the Mozambique Channel, the LDI temperature variations are much smaller (< 2 °C; ~~Fig. 8~~Fig. 7a) than the seasonal SST variation ranging between ca. 24.5 and 30.5 °C. Accordingly, during the warmest months of the year, the difference between LDI-derived and satellite-derived SST is outside of the calibration error (i.e., > 2 °C). However, this is similar to the $U^{K'}_{37}$ and TEX^{H}_{86} which also did not reveal seasonal variations. This lack of seasonality was explained by lateral advection and re-suspension of fine sediment material by migrating meso-scale eddies and thus ending up in the deeply moored sediment trap (Fallet et al., 2011; 2012). Most likely, this also explains the lack of seasonal variation in our LDI record (~~Fig. 8~~Fig. 7a). Nevertheless, the average LDI temperature for the sediment trap of 26.4 °C agrees reasonably well with the annual mean satellite-derived SST of 27.6 °C for the sampled years. Additionally, there is a good agreement with the average LDI temperature of 26.0 °C for two underlying surface sediments, as well as with the decadal average SST of 26.7 °C for 1955-2012 (Locarnini et al., 2013) given by the World Ocean Atlas (2013). For the North Atlantic, we also observe rather constant LDI temperatures during the year (Fig. ~~5~~4) which contrasts with seasonal variations in satellite SSTs of ca. 3 to 5 °C. Nevertheless, differences are mostly within the calibration error, except at M1 and M2 where during winter and spring LDI-derived temperatures are between 0.5 and 2.8 °C higher than satellite SSTs. Similar to the LDI, also the TEX^{H}_{86} and $U^{K'}_{37}$-derived SSTs for the tropical Atlantic sediment traps do not reveal clear seasonal variation. As all three proxies show minimal seasonal variability, this might indicate that the lipids are potentially allochtonous and partially derive from distant regions, resulting in an integrated average temperature signal, similar to the Mozambique Channel. Nevertheless, the flux-weighted annual LDI temperatures of the tropical Atlantic sediment traps (26.6 for M1 and 27.1 °C for M2 and M4) agree well with the annual mean satellite-derived SSTs of 26.1, 26.0 and 27.5 °C for M1, M2 and M4, respectively. Moreover, the LDI-derived temperatures in the underlying sediments (26.5, 26.6 and 26.7 °C, respectively) do not only agree well with those found in a single year in the sediment traps but also with the decadal average SSTs for 1955 to 2012 (26.2, 27.1 and 26.3 °C, respectively; Locarnini et al., 2013; Fig. ~~7b~~6b).

~~Interestingly, TEX^{H}_{86} temperature estimates are relatively similar for traps M2 and M4 but at M1 they are lower than satellite SST in both the sediment trap and surface sediments (Fig. 7d). This underestimation of SST at M1 might suggest GDGT addition from colder subsurface waters. Indeed Balzano et al. (unpublished results) show that crenarchaeol is typically abundant between ca. 40 and 100 m water depth, agreeing with previous findings which have shown that the TEX_{86} can reflect subsurface temperatures rather than surface temperature in some regions (e.g., Huguet et al., 2007; Kim et al., 2012; 2015; Schouten et al., 2013; Chen et al., 2014; Wuchter et al., 2006). Consequently, for the surface sediments, we also calculated subsurface temperatures, using the calibration of Kim et al. (2012) (Fig. 7d), and compared these with the depth-integrated annual mean temperatures of the upper 150 m (Locarnini et al., 2013), caclulated following Kim et al. (2008), which indeed shows a better correspondence for the eastern Atlantic surface sediment, i.e., the sediments close to M1. This is likely caused by the steepening of the thermocline towards the east, as shown in Fig. 7a,d, in which we have indicated the approximate production depths of the temperature proxies. The thermocline at M1 is much steeper and shallower, which implies that GDGTs produced at ~ 100 m depth will record a lower temperature than at M2 and M4.~~

5. Conclusions

In this study we have evaluated LCD-based proxies, particularly the LDI, in sediment trap time series from five sites in the tropical North Atlantic, the Cariaco Basin and the Mozambique Channel. For the North Atlantic we found that in the water column ca. 25–85 % of the export of these lipid biomarkers is preserved during settling from 1200m to 3500m, and that generally less than 2 % was preserved in the surface sediments. Despite substantial degradation at the seafloor, likely linked to the prolonged oxygen exposure time, LCD-derived temperatures from the sediments are generally very similar to the annual mean LCD-derived temperatures in both the deep and shallow traps as well as to annual mean SST for the specific sampling year and on decadal time scales for the specific sites. In the Cariaco Basin we observe a ~~strong seasonality~~seasonal signal in the LDI~~ which is~~ linked to the upwelling season ~~at~~ reflecting temperatures ~~associated with a water depth of up to ca~~of the upper ca. 30 m ~~during summer stratification, and at SST during winter upwelling accompanied by shoaling of both the nutricline and isotherms~~of the water column. The LDI temperatures in the Mozambique Channel and the tropical Atlantic reveal minimal seasonal change although seasonal SST contrasts amount to 3-5°C. For the Mozambique Channel this is likely caused by lateral advection of re-suspended sediment by meso-scale eddy migration, a signal not substantially altered by diagenesis. Seasonal variations in the Diol Index are minimal in the central and western North Atlantic and 1,14-diol concentrations are rather low, implying little *Proboscia* diatom productivity. However, in the eastern Atlantic closest to the African continent, the Diol Index attains a clear spring maximum that is likely associated with upwelling in the Guinea Dome during summer to autumn, suggesting the Diol Index reflects a pre-upwelling signal, consistent with the current knowledge on *Proboscia* ecology. In the Cariaco Basin, controlled by seasonal upwelling, the Diol Index reveals the same clear seasonal trend observed in primary productivity, arguing that for this location the Diol Index is an excellent indicator of upwelling intensity.

Data availability. The data reported in this paper is archived in PANGAEA (www.pangaea.de.)

Author contributions. MWdB, JSSD, and SS designed the experiments and MWdB carried them out. JU carried out the time-series analysis. JBWS, GJAB, and RCT deployed sediment traps and collected sediment trap materials. MWdB prepared the paper with contributions from all coauthors.

Competing interests. The authors declare that they have no conflict of interest.

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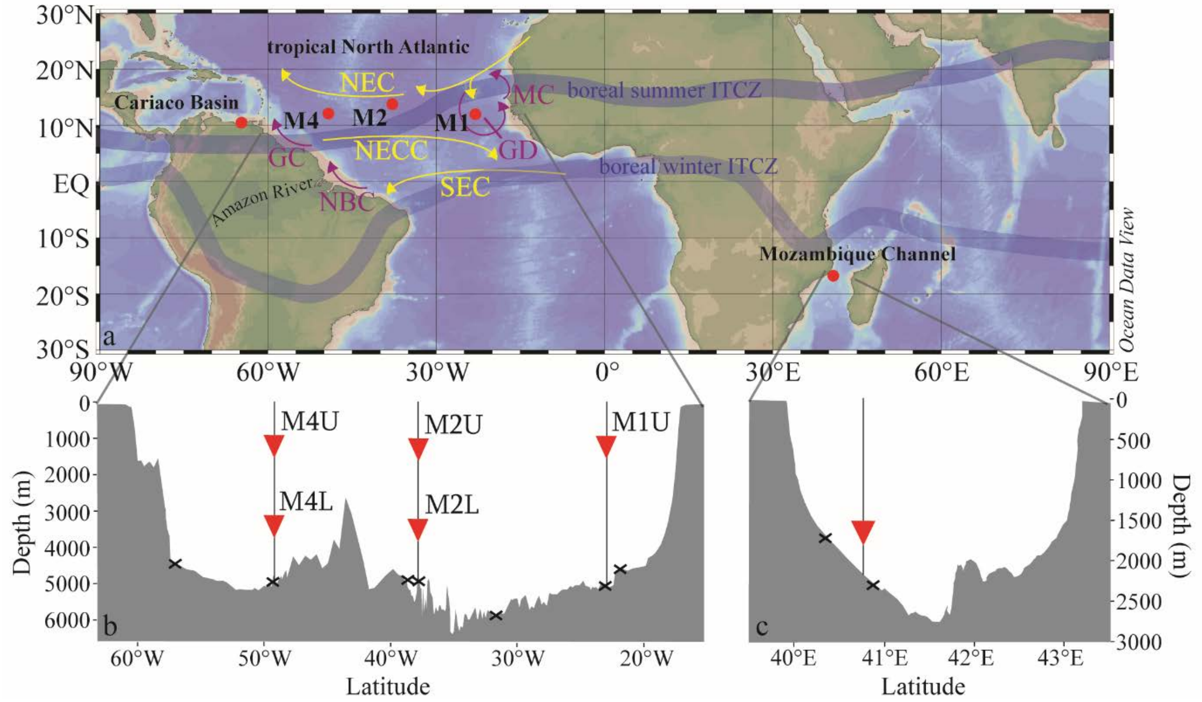


Fig. 1 **(a)** Location map showing the five sediment trap mooring sites in the Cariaco Basin, the tropical North Atlantic (M1, M2 and M4) and the Mozambique Channel. Two of the moorings in the tropical North Atlantic (M2 and M4) contain an upper (‘U’) and a lower (‘L’) trap, shown in the bathymetric section below **(b)** with traps depicted as red triangles and surface sediments shown as black crosses. A similar section profile is shown for the Mozambique Channel (c), where also the sediment trap and the surface sediments are indicated. All maps/sections are generated in Ocean Data View (Schlitzer, 2015). Indicated are the approximate seasonal positions of the ITCZ. NEC = North Equatorial Current; NECC = North Equatorial Countercurrent; SEC = South Equatorial Current; MC = Mauritania Current; GD = Guinea Dome; NBC = North Brazil Current; GC = Guiana Current.

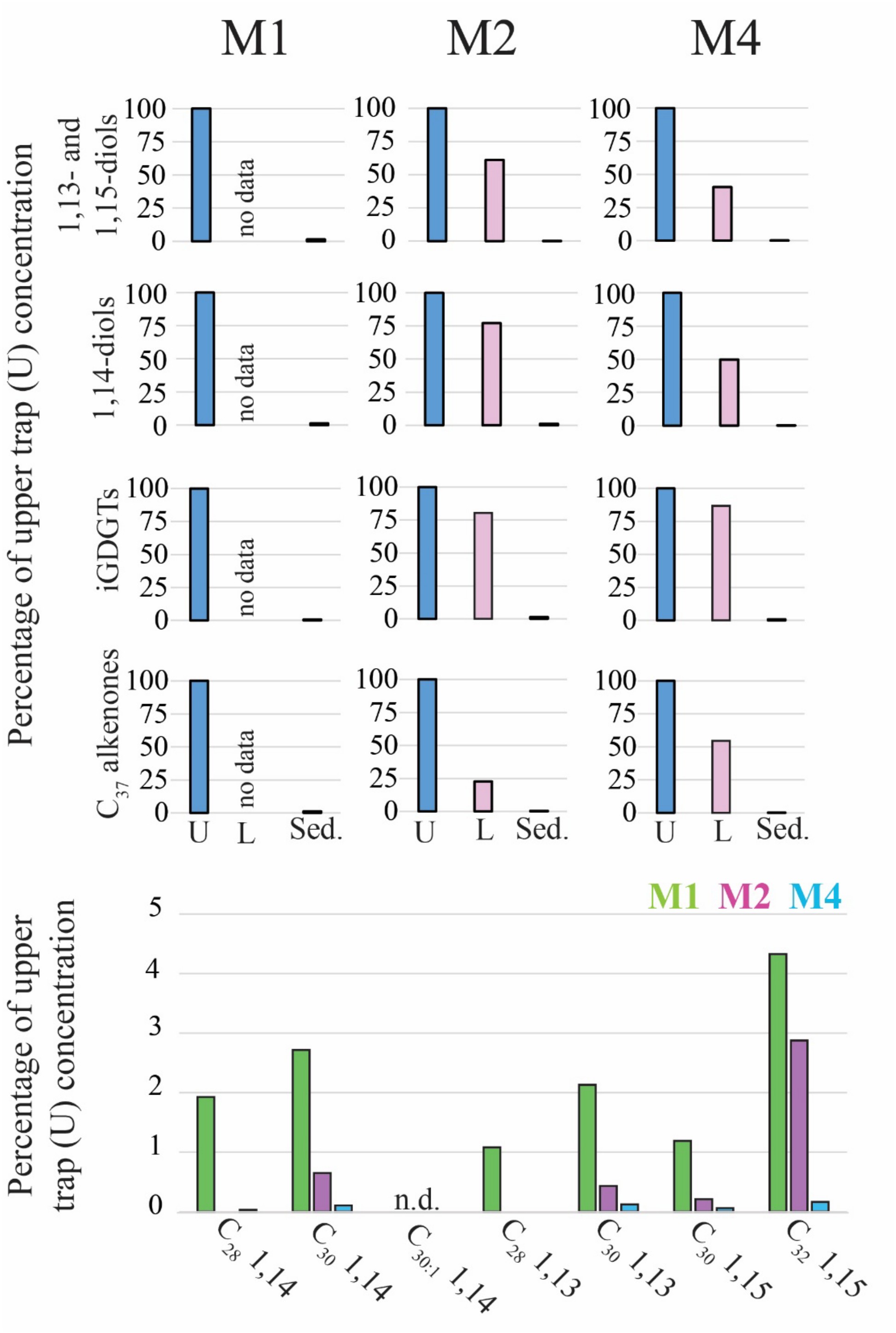


Fig. 2 Relative concentrations of biomarker lipids for the mooring sites M1, M2 and M4 in the tropical North Atlantic. Upper panel: percentages of lipid biomarkers in the lower traps (‘L’; 3500 m) and the surface sediments (‘Sed.’) relative to the annual flux-weighted concentrations in the upper traps (‘U’; 1200 m; set at 100%). The lower panel shows the preservation of the individual LCDs (sediments versus upper trap flux-weighted concentration) for the three sediment trap sites. For M1 and M2 the sedimentary LCD concentrations were based on the average of the two nearby underlying surface sediments (Fig. 1). When no bar is shown ~~than~~ then the LCD was not detected.

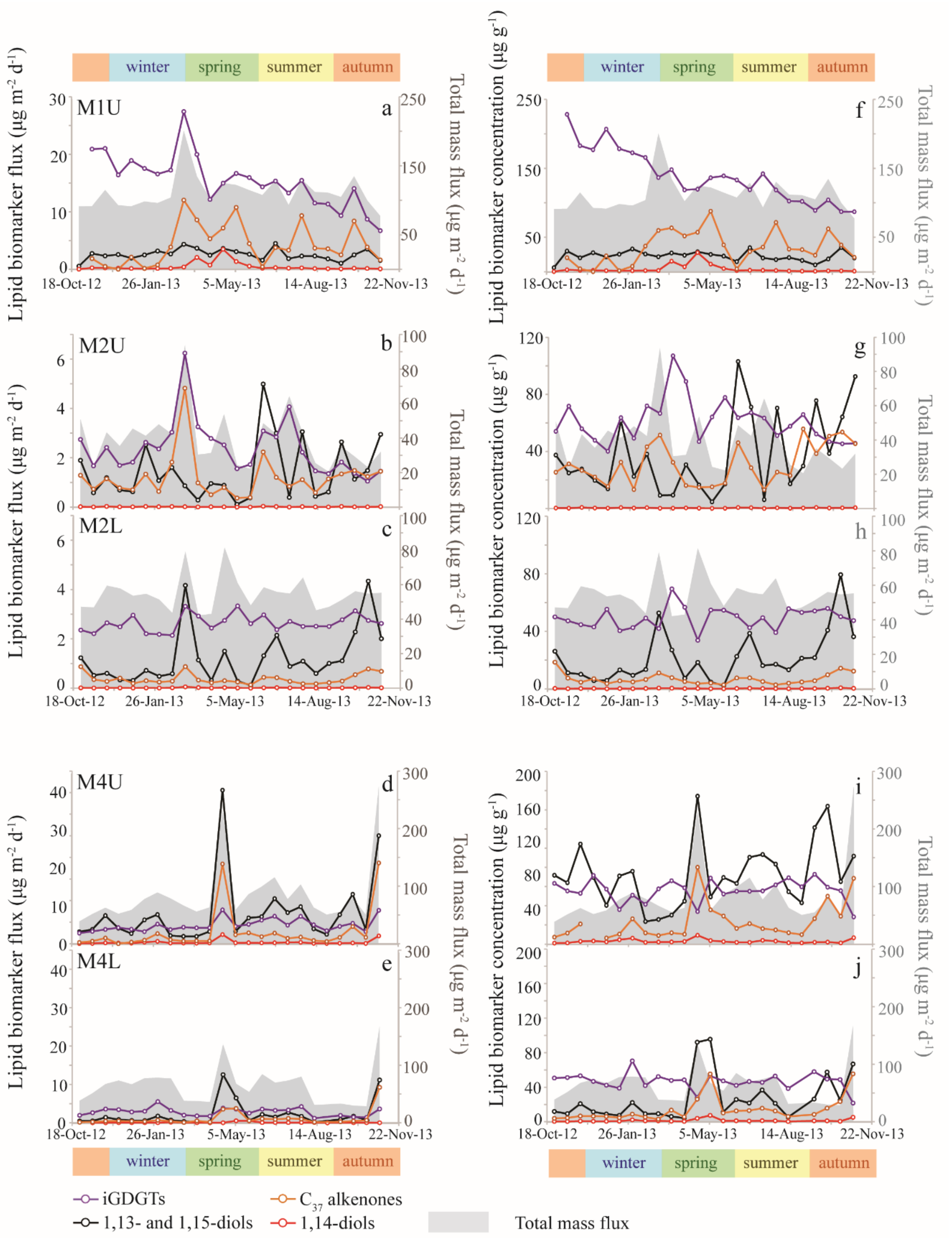


Fig. 3 Lipid biomarker fluxes for the tropical North Atlantic sediment traps, i.e., M1, upper and lower M2, and upper and lower M4 in panels **(a)** to **(e)**. Lipid biomarker fluxes (iGDGTs in purple; C_{37} alkenones in orange; 1,13- and 1,15-diols in black; 1,14-diols in red) are indicated on the left *y*-axis, and the total mass flux (grey stack; Korte et al., 2017) on the right *y*-axis. Lipid biomarker concentrations are plotted in panels **(f)** to **(j)**, with biomarker concentrations on the left *y*-axis, and the total mass flux on the right *y*-axis. Note that the *y*-axes are different per sediment trap site, but identical for upper (U) and lower (L) traps.

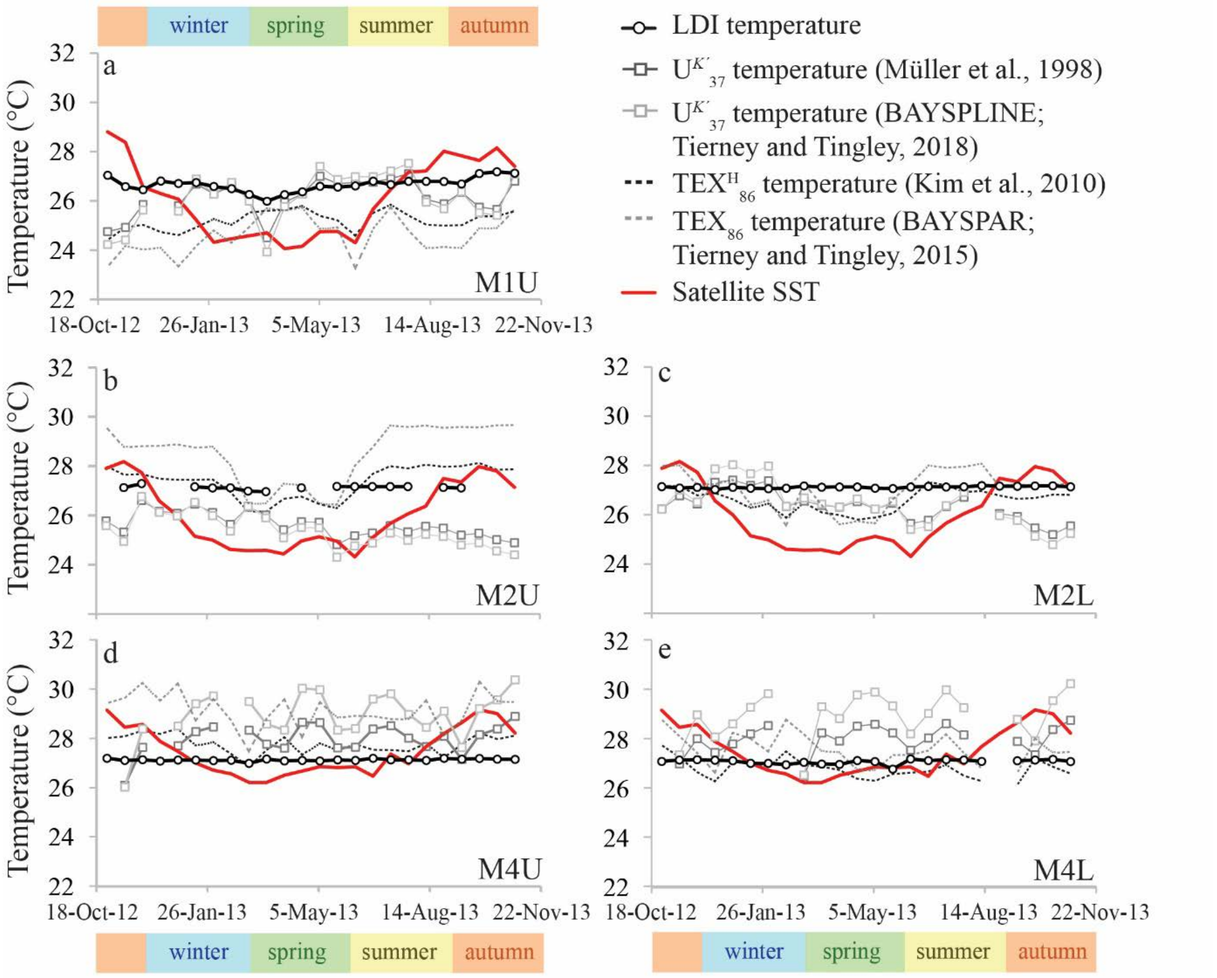


Fig. ~~5~~ 4 Temperature proxy records for the tropical North Atlantic. Panel **(a)** shows upper trap station M1, **(b)** upper trap station M2 and **(c)** lower trap M2, respectively, **(d)** upper trap station M4 and **(e)** lower trap station M4, respectively.

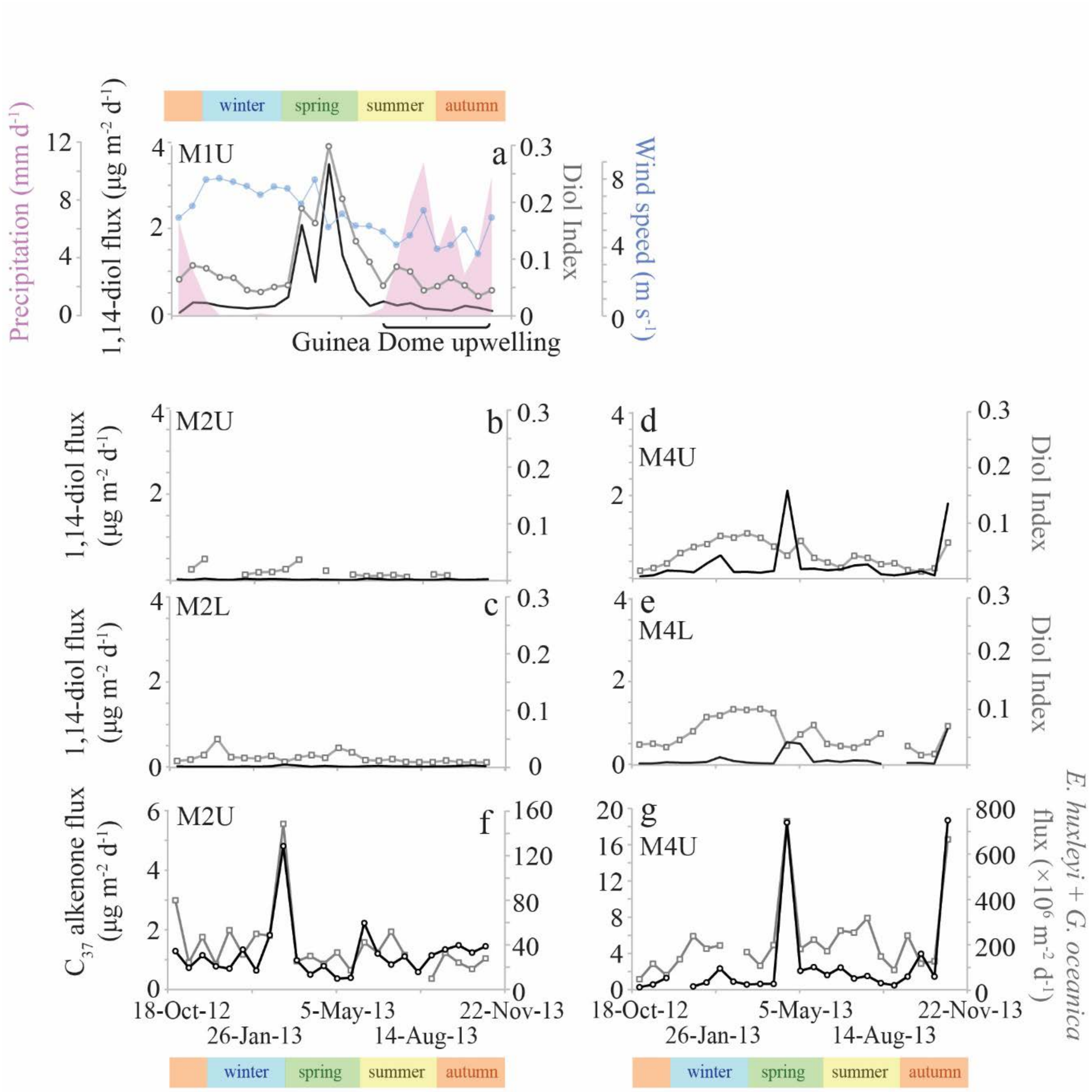


Fig. ~~6~~ 5 Phytoplankton productivity records for the tropical North Atlantic. Panels **(a)** – **(e)** show the 1,14-diol fluxes (left *y*-axis; black) and the Diol Index (right *y*-axis; grey) for sediment traps. The *y*-axes are the same for these panels. Wind speed and precipitation data were adapted from Guerreiro et al. (in revision); for references regarding remote sensing parameters, see Guerreiro et al. (2017). Panels **(f)** and **(g)** show the C_{37} alkenone fluxes (left *y*-axis; black) and combined fluxes of *E. huxleyi* and *G. oceanica* (from Guerreiro et al., 2017; right *y*-axis; grey) for the upper traps of M2 and M4.

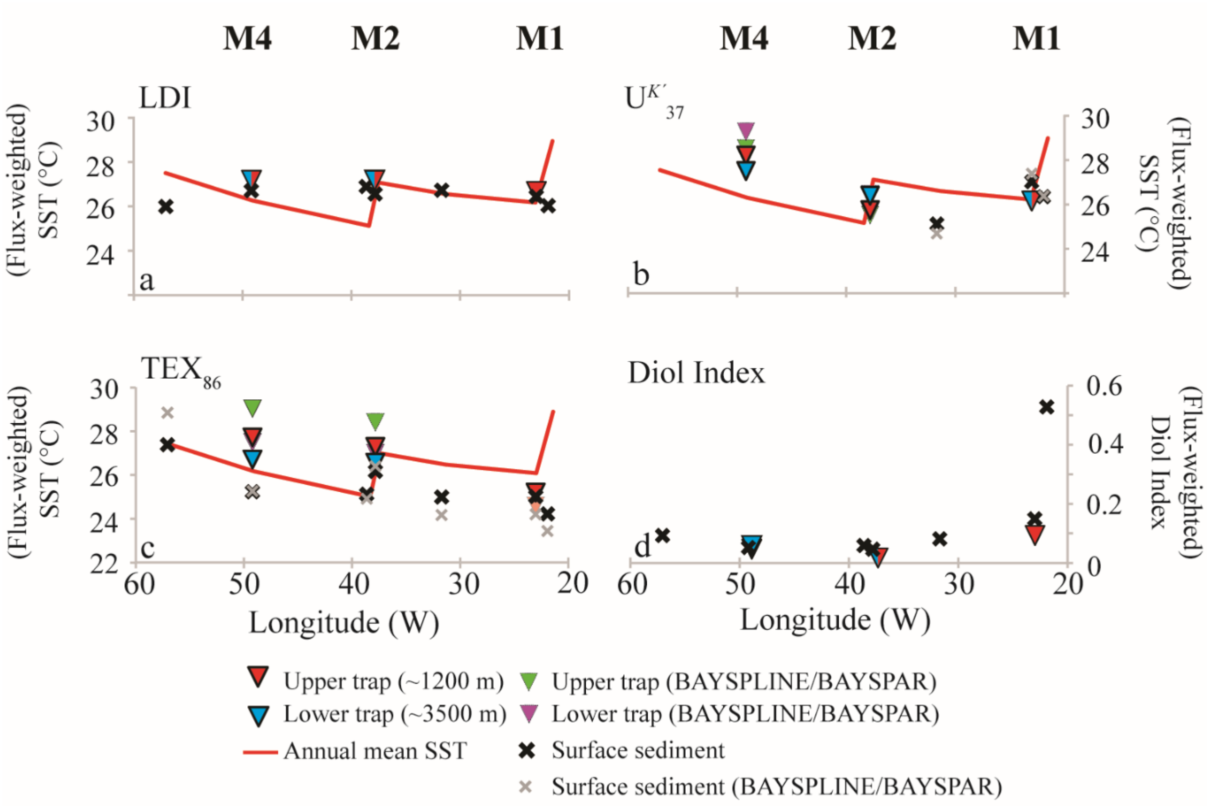
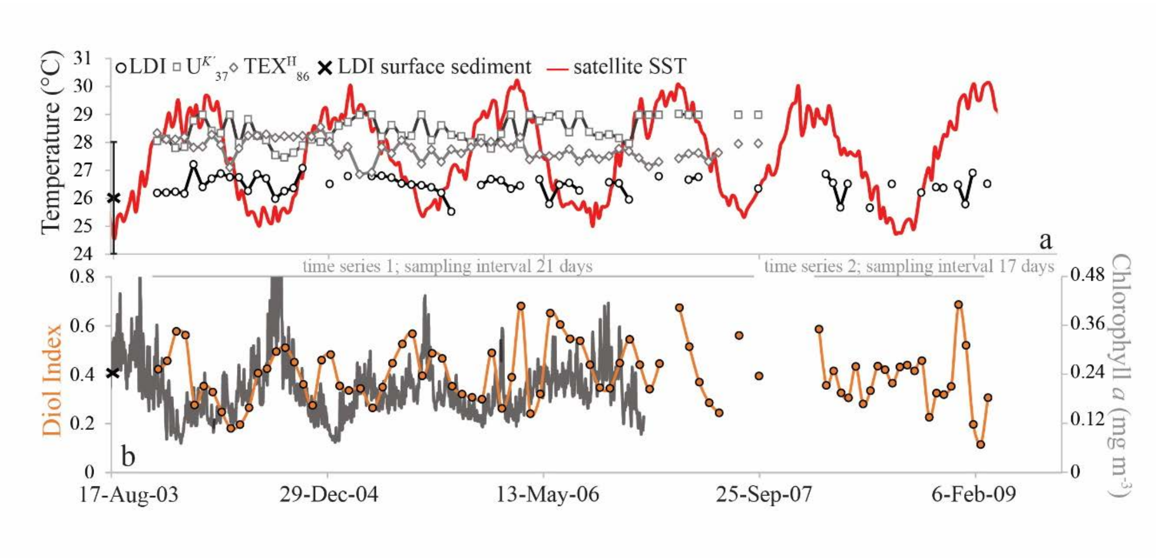
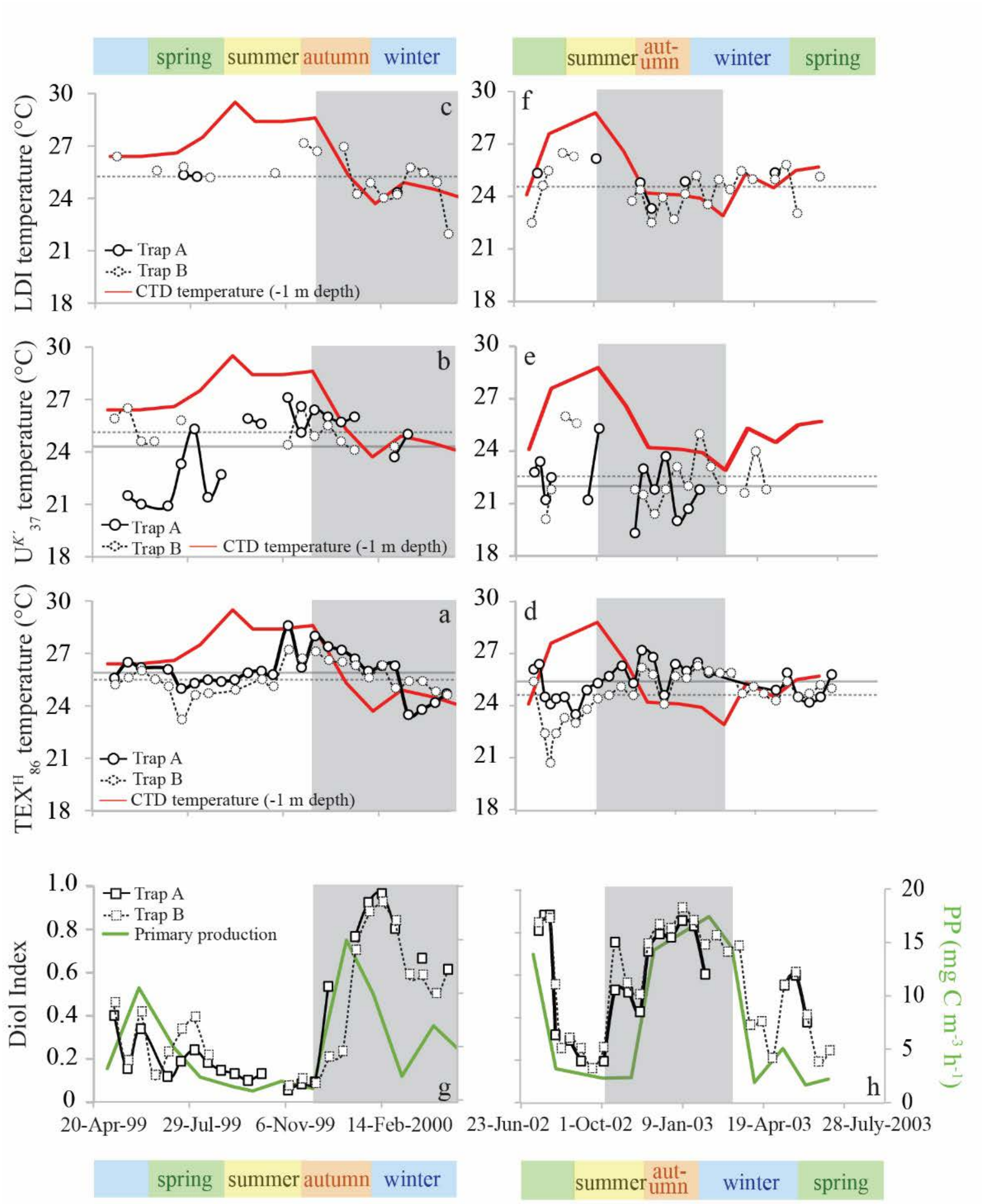


Fig. ~~7~~ 6 ~~**(a)** Annual mean temperature profiles at the sediment trap locations (World Ocean Atlas 2013) with approximate proxy-lipid production depths indicated, as deduced from Balzano et al. (unpublished results).~~ ~~**(b)**~~ Flux-weighted average (annual) proxy results for the sediment traps compared with the underlying sediments (crosses) and annual mean SST (red line; specific for coordinates of the surface sediments; World Ocean Atlas 2013 ¼ grid resolution~~World Ocean Atlas 2013~~). Panel **(~~b~~a)**, **(~~c~~b)** and **(~~d~~c)** show the LDI, $U^{K'}_{37}$ and TEX$_{86}$ temperature results, respectively. Triangles reflect sediment trap results (red = upper/~1200 m; blue = lower/~3500 m), and crosses represent surface sediments. In case of the $U^{K'}_{37}$ and TEX$_{86}$, the green and purple triangles and grey crosses reflect the temperatures calculated using the BAYSPLINE and BAYSPAR models (Tierney and Tingley, 2014; 2015; 2018), whereas the other temperatures were calculated by means of the Müller et al. (1998) and Kim et al. (2010; TEX$^{H}_{86}$) calibrations, respectively. Panel **(d)** shows the flux-weighted average Diol Index values for the sediment traps, and the Diol Index estimates for the surface sediments.



~~**Fig. 8**~~**Fig. 7** The LDI-derived temperatures, together with the TEX^{H}_{86} and $U^{K'}_{37}$-derived temperatures and satellite SST (Fallet et al., 2011) (**a**) and the Diol Index (**b**) for the Mozambique Channel sediment trap. The black cross in panel (**a**) reflects the average LDI temperature of two underlying surface sediments, with the LDI calibration error. The chlorophyll *a* data is from Fallet et al. (2011).



~~Fig. 9~~Fig. 8 Seasonal proxy derived temperature and upwelling/productivity records for the sediment traps in the Cariaco Basin. Panels **(a)**, **(b)** and **(c)** show the May 1999 – May 2000 time series TEX$^{H}_{86}$-, U$^{K'}_{37}$- and LDI-derived temperature reconstructions for Trap A (275 m depth; solid symbols) and Trap B (455 m depth; dashed symbols), respectively. Panels **(d)**, **(e)** and **(f)** show the proxy data for the July 2002 – July 2003 time series, with CTD-temperatures (1 m depth) in red. The U$^{K'}_{37}$, TEX$^{H}_{86}$ and CTD temperatures are adopted from Turich et al. (2013). The horizontal lines reflect the average proxy-derived temperatures (Trap A = solid; Trap B = dashed). Panel **(g)** and **(h)** show the 1,14-diol based Diol Index (Rampen et al., 2008) for the 1999-2000 and 2002-2003 time series, respectively, for Trap A (275 m depth; solid symbols) and Trap B (455 m depth; dashed symbols). Primary productivity in mg C m^{-3} h^{-1} is plotted in green (data adopted from Turich et al., 2013). The shaded area reflects the period of upwelling.

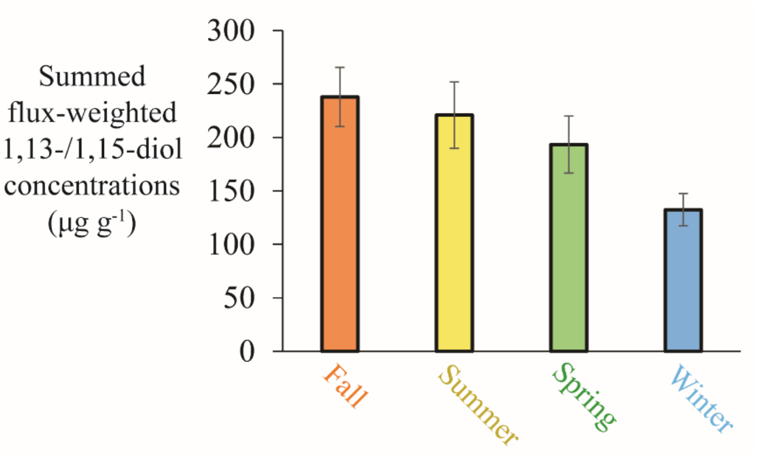


Fig. ~~4~~ 9 Seasonal summed flux-weighted average of 1,13-/1,15-diol concentrations in all sediment traps (station M1 upper trap, station M2 upper and lower trap and station M4 upper and lower trap) of the tropical North Atlantic.

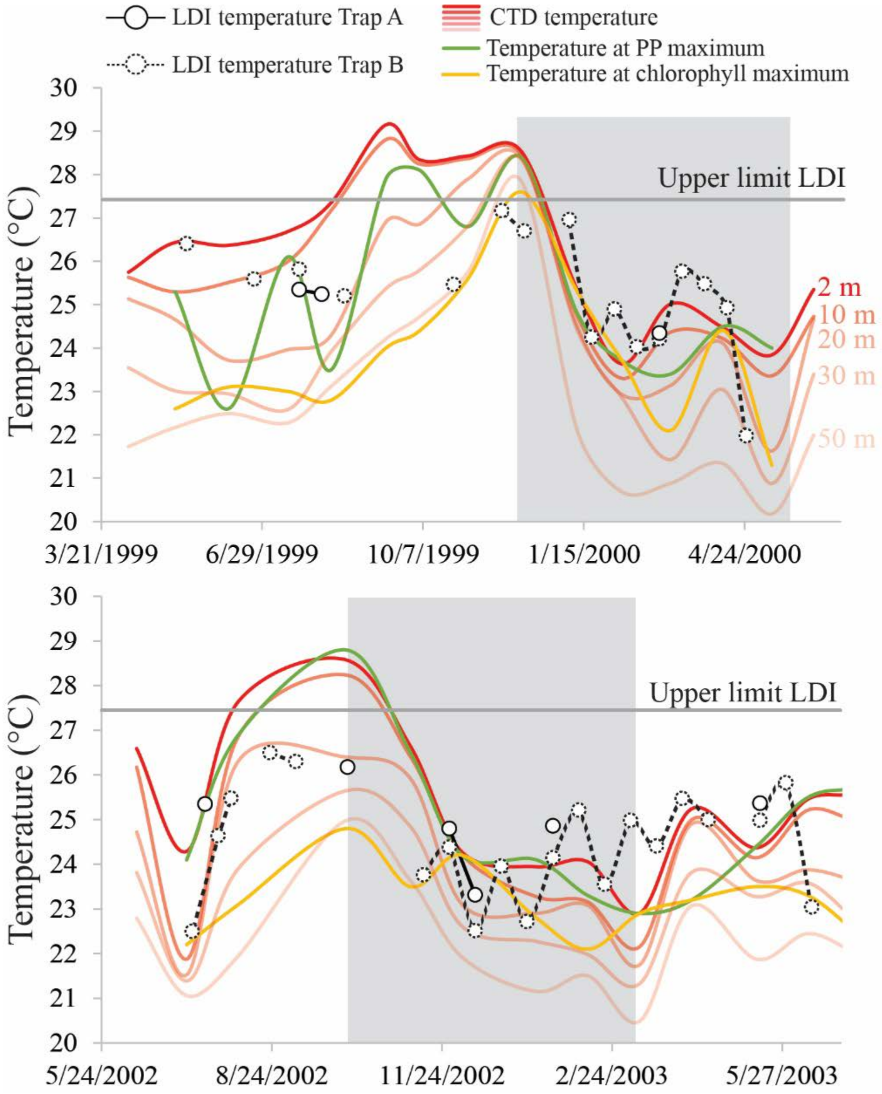


Fig. 10 LDI temperature records for the Cariaco Basin time series May 1991 – May 2000 and July 2002 – July 2003 for Trap A (275 m depth; solid symbols) and Trap B (455 m depth; dashed symbols), with CTD-derived temperatures at 2, 10, 20, 30 and 50 m depth (in red; http://www.imars.usf.edu/CAR/index.html; CARIACO time series composite CTD profiles), the temperature at the depth of maximum primary production (green) and the temperature at the depth of the chlorophyll maximum (yellow; data adapted from Turich et al., 2013). The shaded area represents the upwelling season.