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Evaluation of long chain 1,14-alkyl diols in marine sediments as indicators for upwelling and temperature

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ABSTRACT

Long chain alkyl diols form a group of lipids occurring widely in marine environments. Recent studies have suggested several palaeoclimatological applications for proxies based on their distributions, but have also revealed uncertainty about their applicability. Here we evaluate the use of long chain 1,14-alkyl diol indices for reconstruction of temperature and upwelling conditions by comparing index values, obtained from a comprehensive set of marine surface sediments, with environmental factors such as sea surface temperature (SST), salinity and nutrient concentration. Previous studies of cultures indicated a strong effect of temperature on the degree of saturation and the chain length distribution of long chain 1,14-alkyl diols in *Proboscia* spp., quantified as the diol saturation index (DSI) and diol chain length index (DCI), respectively. However, values of these indices for surface sediments showed no relationship with annual mean SST of the overlying water. It remains unknown as to what determines the DSI, although our data suggest that it may be affected by diagenesis, while the relationship between temperature and DCI may be different for different *Proboscia* species. In addition, contributions from algae other than *Proboscia* diatoms may affect both indices, although our data provide no direct evidence for additional long chain 1,14-alkyl diol sources. Two other indices using the abundance of 1,14-diols vs. 1,13-diols and C_{30} 1,15-diols have been applied previously as indicators for upwelling intensity at different locations. The geographical distribution of their values supports the use of 1,14 diols vs. 1,13 diols [$C_{28}+C_{30}$ 1,14-diols]/[($C_{28}+C_{30}$ 1,13-diols) + ($C_{28}+C_{30}$ 1,14-diols)] as a general indicator for high nutrient or upwelling conditions.

1. Introduction

Over the last few decades, an increasing number of lipids from marine environments have been identified and linked to their natural sources, and some are now being used as proxies for past climate conditions (e.g. Eglinton and Eglinton, 2008 and references therein). Long chain alkyl diols form one group with high biomarker potential. After their discovery in the Black Sea (De Leeuw et al., 1981), they were found in Quaternary sediments from low to high latitudes (Versteegh et al., 1997, 2000 and references therein). Cultured marine and freshwater eustigmatophyte algae produce series of long chain alkyl diols, consisting mainly of C_{28}–C_{32} 1,13- and 1,15-diols (Volkman et al., 1992, 1999). In the environment, a recent study of lipids and 18S rRNA genes in a freshwater lake has shown that long chain alkyl diols are produced by eustigmatophytes in the surface water of the lake (Villanueva et al., 2014). However, the role of eustigmatophytes as a source of marine long chain alkyl diols remains unclear. Reports of eustigmatophyte algae in marine environments are sparse and the long chain alkyl diol composition of marine eustigmatophytes does not match those of marine sediments (Volkman et al., 1992; Versteegh et al., 1997; Rampen et al., 2012). Despite uncertainty concerning their sources, recent work has indicated a correlation between sea surface temperature (SST) and fractional abundances of C_{28} 1,13-, C_{30} 1,13- and C_{30} 1,15-diols in marine sediments. Based on this, a new temperature proxy, i.e. the long chain diol index (LDI), which expresses the C_{30} 1,15-diol abundance relative to those of C_{28} 1,13-, C_{30} 1,13- and C_{30} 1,15-diols, was introduced (Rampen et al., 2012). A strong correlation (R value 0.984 and p value < 0.001) between the LDI and SST was observed.

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Besides 1,13- and 1,15-diols, long chain 1,14-alkyl diols are commonly reported in marine sediments. Sinninghe Damsté et al. (2003) and Rampen et al. (2007) showed that cultivated *Proboscia* diatoms produced both saturated and mono-unsaturated C_{28} and C_{30} 1,14-diols and, in addition, saturated C_{28}, C_{30} and C_{32} 1,14-diols were recently reported in the marine Dictyochophyte *Apedinella radians* (Rampen et al., 2011). Sediment trap studies confirmed *Proboscia* diatoms as being a likely source of long chain 1,14-alkyl diols, particularly in upwelling areas (Rampen et al., 2008), whereas the importance of *Apedinella* as a source of sedimentary long chain 1,14-alkyl diols remains uncertain (Rampen et al., 2011). These sources may be distinguished on the basis of the occurrence of certain diols: C_{32} 1,14-diols may be useful as an indicator for *Apedinella* input, as they are produced by *A. radians* but were absent from the 8 cultures of *Proboscia* spp. analyzed to date. Mono-unsaturated long chain 1,14-alkyl diols may, on the other hand, indicate *Proboscia* as a source, as these lipids have been identified in *Proboscia* cultures but not in *Apedinella*.

We previously reported that the chain length distribution and degree of saturation of long chain 1,14-alkyl diols in *Proboscia* cultures are related to growth temperature, indicating the potential of these diols to be used as a tool for reconstructing SST (Rampen et al., 2009). Changes in the chain length and degree of unsaturation of lipids are known adaptation mechanisms for bacteria, yeast, fungi and algae to changing environmental conditions (e.g. Russell and Fukunaga, 1990; Suutari and Laakso, 1994) and the following two indices, the diol chain length index (DCI) and the diol saturation index (DSI), were used to quantify the chain length distribution and degree of saturation of long chain diols:

$$\mathrm{DCI} = [\text{saturated } C_{30}\,1,14\text{-diol}]/[\text{saturated } C_{28} + C_{30}\,1,14\text{-diol}] \quad (1)$$

$$\mathrm{DSI} = [\text{saturated } C_{28} + C_{30}\,1,14\text{-diol}]/[\text{saturated} + \text{unsaturated } C_{28} + C_{30}\,1,14\text{-diol}] \quad (2)$$

However, application of these indices using surface sediments from the eastern South Atlantic Ocean showed only a moderate correlation of DCI with annual mean SST, while no correlation was observed between DSI and SST (*R* values 0.72 and 0.55 and *p* values < 0.001 and 0.535, respectively; Rampen et al., 2009). It was suggested that factors other than temperature could also play a role, indicating that more data were required to validate the use of long chain 1,14-alkyl diols as a proxy for temperature.

Proboscia diatoms are often abundant in nutrient-rich environments like upwelling areas (Hernández-Becerril, 1995; Lange et al., 1998; Koning et al., 2001; Smith, 2001) and their lipids may therefore be useful as tracers for these conditions. Indeed, sediment trap studies showed that, in the Arabian Sea, long chain 1,14-alkyl diols were found almost exclusively under upwelling conditions (Rampen et al., 2007, 2008), whereas such a relationship was not observed for long chain 1,15- and 1,13-diols. Following this, diol index 1 was introduced:

$$\text{Diol Index 1} = [\text{saturated } C_{28} + C_{30}\,1,14\text{-diol}]/([\text{saturated } C_{28} + C_{30}\,1,14\text{-diol}] + [\text{saturated } C_{30}\,1,15\text{-diol}]) \quad (3)$$

It has been used as a proxy for upwelling in the Arabian Sea (Rampen et al., 2008), the Benguela Upwelling System (Pancost et al., 2009), the Eastern Equatorial Pacific (Seki et al., 2012), offshore southeastern Australia (Lopes dos Santos et al., 2012) and the westernmost Mediterranean (Nieto-Moreno et al., 2013).

Proboscia diatoms are also abundant in Antarctic waters and lipid analysis confirmed the presence of C_{28} and C_{30} 1,14-diols in a sediment core from the Western Bransfield Basin (Willmott et al., 2010). However, unlike the Arabian Sea, C_{30} 1,15-diol concentrations are low, whereas C_{28} and C_{30} 1,13-diols are more abundant in this area, and consequently Willmott et al. (2010) introduced the diol index 2 to reconstruct upwelling of nutrient rich Upper Circumpolar Deep Water in the Western Bransfield Basin:

$$\text{Diol Index 2} = [\text{saturated } C_{28} + C_{30}\,1,14\text{-diol}]/([\text{saturated } C_{28} + C_{30}\,1,14\text{-diol}] + [\text{saturated } C_{28} + C_{30}\,1,13\text{-diol}]) \quad (4)$$

How widely applicable these long chain alkyl diol indices are as tracers for upwelling and nutrient rich conditions is unknown. In a study of Pliocene sediments from the Benguela Upwelling System, Pancost et al. (2009) observed both periods in which trends in 1,14-diol abundances and diol index 1 were consistent with those of other productivity markers, and periods when they differed. Contreras et al. (2010) related the increasing abundance of the C_{28} 1,14-diol in the Peruvian upwelling system during the last interglacial to enhanced stratification, the abundance being low during periods with presumed strengthened upwelling. In addition, several studies reported high *Proboscia* diatom abundance under stratified rather than upwelling conditions (e.g. Table 1). Hence, perhaps the diol indices should rather be used as indicators for *Proboscia* productivity, which can be linked to different environmental conditions depending on the region studied.

To constrain the applicability of long chain 1,14-alkyl diols as indicators for temperature, upwelling/nutrient availability and other climate conditions, we have analyzed the long chain alkyl diol distributions in a comprehensive set of marine surface sediments (209), previously studied for long chain 1,13- and 1,15-alkyl diols (Rampen et al., 2012), and compared various long chain 1,14-alkyl diol indices with environmental parameters of the overlaying surface water, such as temperature, salinity, nutrient concentration, stratification and mixed layer depth.

2. Methodology

The sediments were globally distributed, although mainly from the North and South Atlantic Oceans (Fig. 1 and Supplementary Material). Long chain alkyl diol fractions were obtained and analyzed as described by Rampen et al. (2012). Briefly, sediments were extracted using accelerated solvent extraction (ASE) using a DIONEX 200 instrument with a mixture of dichloromethane (DCM) and MeOH (9:1; v:v) at 100 °C and 7–8 × 10^6 Pa. For a selected set of samples, the extracts were saponified with 6% KOH, according to De Leeuw et al. (1983), to release extractable ester-bound long chain alkyl diols. Extracts and saponified extracts were separated into apolar and polar fractions using a pipette column filled with activated alumina and elution with hexane/DCM (9:1; v:v) and DCM/MeOH (1:1; v:v), respectively, or into apolar, keto and polar fractions using a pipette column filled with silica gel (silica 60) with hexane, hexane/DCM (1:4; v:v) and DCM/MeOH (1:1; v:v), respectively. The polar fraction was analyzed, after silylation of alcohols to the trimethylsilyl (TMS) ether derivatives, with gas chromatography–mass spectrometry (GC–MS). Fractional abundances of the long chain alkyl diols were calculated from relevant peak areas of mass chromatograms obtained using selected ion monitoring (SIM) of *m*/*z* 299, 313, 327, 341 and 355, which represent characteristic fragment ions of the relevant diols (Versteegh et al., 1997). Differences in the contribution of the selected ions to the total mass spectra (*m*/*z* 50–800) of saturated and unsaturated long chain alkyl diols were taken into account as described by Rampen et al. (2009).

Table 1
Reports of dominant *Proboscia* occurrence, including location, season and typical conditions.

Species	Season[a]				Location	Water column features	Reference
	Sp	Su	Au	Wi			
P. alata and *P. indica*	X				Arabian Sea	Pre-upwelling	Koning et al. (2001)
P. subarctica	X				Subarctic Pacific	High nutrients and low light	Takahashi et al. (1994)
P. alata	X	X			Southern Bay of Biscay (Northeast Atlantic Ocean)	Spring mixing and haline stratification	Fernández and Bode (1994)
P. alata[b]	X				Black Sea	Below euphotic zone	Eker-Develi and Kideys (2003)
P. alata[b]		X	X	X	Black Sea	Mixed water	Silkin et al. (2013)
P. alata[b]		X			Skagerrak (North Atlantic)		Lange et al. (1992)
P. alata[b]		X			Baltic Sea		Wasmund et al. (2008)
P. alata[b,c]		X			Coastal waters around Ireland	Stratification	O'Boyle and Silke (2010) and references herein
P. alata[b]		X			Lisbon Bay (North Atlantic)	Mature oceanic waters near upwelling	Moita et al. (2003)
P. alata		X			Cap Blanc (tropical Atlantic)		Lange et al. (1998)
P. alata[b]		X			Bering Sea	Stratification	Sukhanova et al. (2006)
P. alata		X		X	Suwannee estuary (Florida)		Quinlan and Phlips (2007)
P. alata[b]		X	X	X	Subarctic Pacific	High light intensity, high temperatures and stratification	Takahashi (1987) and Takahashi et al. (1994)
P. alata		X			Weddell Sea (Antarctica)	Postbloom	Estrada and Delgado (1990)
P. indica[c]		X			Southern Bay of Biscay (Northeast Atlantic Ocean)	Stratification	Fernández and Bode (1994)
P. indica			X		English Channel and North Sea	Mild conditions + stratification	Nehring (1998) and Gómez and Souissi (2007)
P. inermis and *P. truncata*		X			Western Antarctic Peninsula shelf		Pike et al. (2008)
P. inermis[b]		X			Ryder Bay (Antarctica)	Stratification + low nutrients	Annett et al. (2010)
P. inermis			X		Bellingshausen Sea (Antarctica)		Brichta and Nöthig (2003)

[a] Sp = spring, Su = summer, Au = autumn, Wi = winter.
[b] Strongly dominating total biomass.
[c] Dominating the diatom population.

The long chain alkyl diol data were compared with temperature and salinity data from the 0.25° grid 2001 World Ocean Database (WOA; Boyer et al., 2005), nitrate, phosphate and silicate concentrations from the 1° grid 2009 WOA (Levitus, 2010) and chlorophyll abundance from the 1° grid 2001 WOA (Levitus, 2002), and with mixed layer depth data (defined as the depth at which the temperature differs more than 0.5 °C from the ocean surface temperature), obtained from the 1° grid 1994 WOA (Monterey and Levitus, 1997).

3. Results and discussion

Surface sediment (generally 0–1 cm) was obtained at locations with water depth ranging from ca. 20 to ca. 6000 m and a large range in annual mean SST (−1.8 to 28.8 °C), annual mean salinity (6.8–37.0), nutrient concentration, chlorophyll content (0–280 μg/l) and mixed layer depth (0.1–65 m) (see Supplementary Table 2); 187 sediments of the set (89%) contained quantifiable (i.e. signal to noise ratio > 10) 1,13- and/or 1,15-alkyl diols, together with 1,14-alkyl diols, although unsaturated long chain 1,14-alkyl diols were detected in only 146 sediments (70%). One sample contained quantifiable amounts of long chain 1,13- and 1,15-alkyl diols without detectable amounts of long chain 1,14-alkyl diols. The chain lengths were C_{28} and C_{30} for 1,13- and 1,14-alkyl diols, and C_{30} and C_{32} for 1,15-alkyl diols. The C_{32} 1,14-alkyl diol, previously reported in *A. radians* (Rampen et al., 2011), was not detected.

Long chain 1,14-alkyl diols dominated in the Arctic and Antarctic surface sediments and the Arabian Sea (Fig. 2), while their fractional abundances showed strong variation in the other oceanic areas. For most regions, fractional abundances of 1,15-alkyl diols were inversely related to 1,14-alkyl diol abundances, while 1,13-alkyl diol abundances were generally low with little variation – only in estuarine sediments from Hudson Bay and the Gulf of St. Lawrence did 1,13-alkyl diols contribute > 25% of the total long chain alkyl diols.

3.1. Effect of environmental conditions on long chain 1,14-alkyl diol distributions

The degree of saturation (as expressed in the DSI) and the chain length distribution (as expressed in the DCI) of long chain 1,14-alkyl diols in *Proboscia* diatom cultures have been reported to show a strong relationship with growth temperature, although the relationships were less apparent in a limited set of surface sediments from the eastern South Atlantic (Rampen et al., 2009). In order to examine the influence of various environmental factors on the DSI and DCI, we correlated their values with annual mean temperature, salinity, chlorophyll, phosphate, nitrate and silicate concentrations from the overlaying water at 0 m water depth, and with stratification (Table 2; Supplementary Table 3).

The DSI values showed a weak negative correlation with SST (R value −0.441, p value < 0.001; Table 2; Fig. 3a), contrasting with the positive temperature correlation for cultured *Proboscia* diatoms of Rampen et al. (2009). We observed no regional pattern in the distribution of DSI values – strong differences in values were found for surface sediments taken within the same oceanic areas with similar annual mean SST (Fig. 3a). Moreover, analysis of data sets of different regions also did not reveal any strong correlation with annual or seasonal SST (Supplementary Table 3), confirming that temperature is not the only factor affecting DSI (Rampen et al., 2009). The lack of correlation between DSI and other environmental parameters included (Table 2; Supplementary Table 3) suggests that they do not significantly impact on the DSI. In *Proboscia* cultures, the concentration of unsaturated long chain alkyl diols was always similar to or higher than saturated long chain alkyl diols;

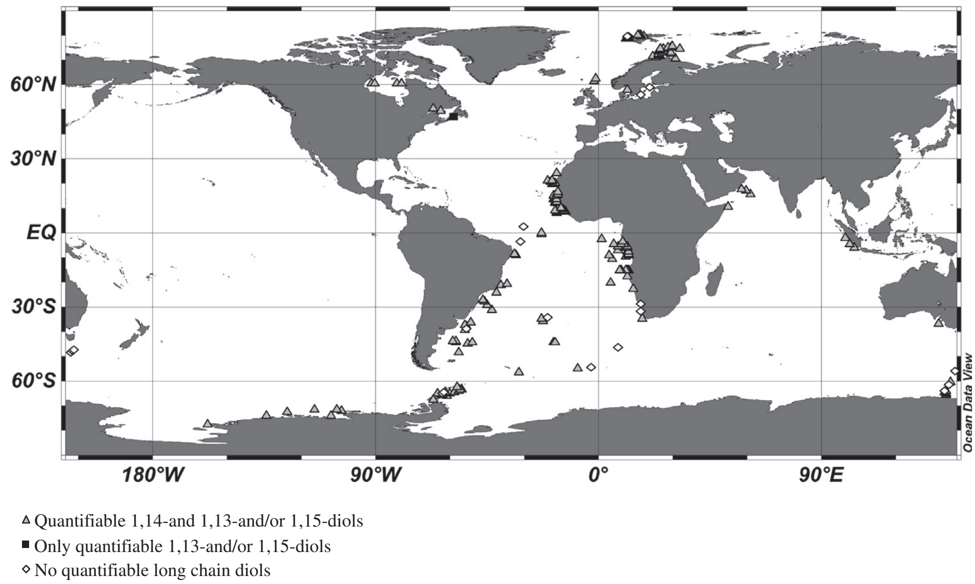

Fig. 1. Sample location and presence of quantifiable amount (signal to noise > 10) of different long chain alkyl diols.

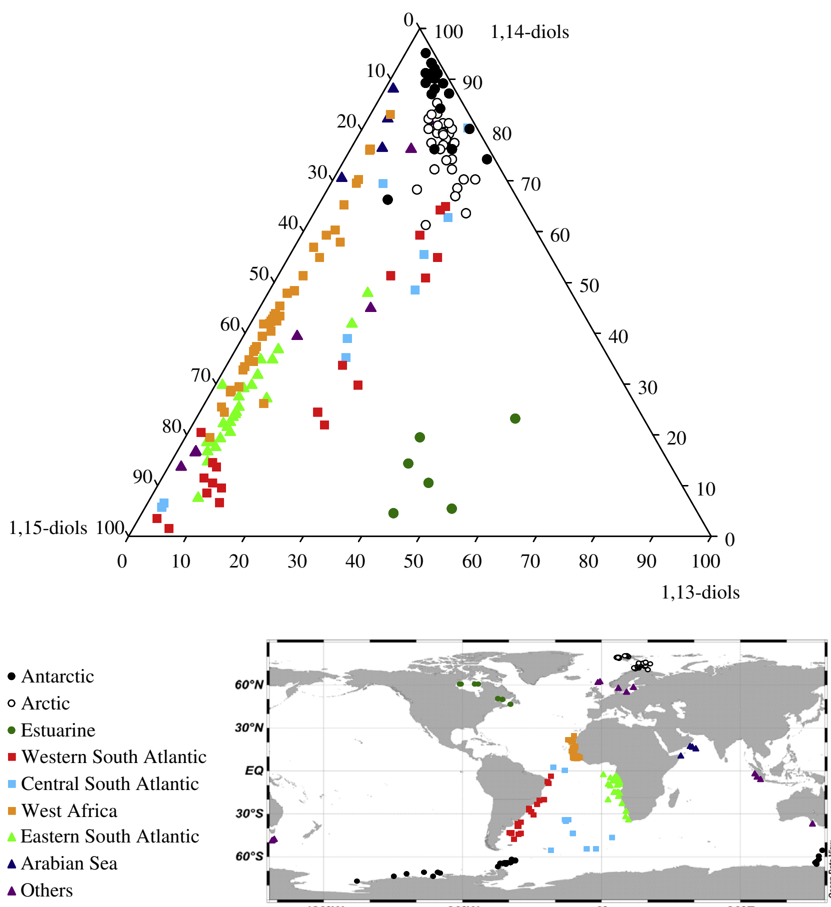

Fig. 2. Ternary diagram showing relative abundance of C_{28} and C_{30} 1,13-alkyl diols, C_{28} and C_{30} 1,14-alkyl diols and C_{30} and C_{32} 1,15-alkyl diols in surface sediments. Colours indicate different sampling areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the often low abundance and sometimes absence of unsaturated 1,14-alkyl diols in marine surface sediments may indicate that unsaturated long chain alkyl diols are more strongly affected by diagenesis than saturated long chain alkyl diols. On the other hand, some of the surface sediments from the West African coast and the eastern South Atlantic contained relatively high amounts of unsaturated 1,14-alkyl diols, higher than would be expected on the basis of culture results (Fig. 3a). Another factor affecting the DSI could be

Table 2
Correlation between CDI, DSI, diol index 1, diol index 2 and annual mean values for environmental conditions for whole sample set ($n = 185$. Correlation coefficients > 0.5 or < −0.5 are indicated in **bold**; R, correlation coefficient; P, p value). See supplementary data for correlations on a regional scale.

	SST[a]	Salinity[a]	Chlorophyll[b]	Nitrate[c]	Phosphate[c]	Silica[c]	MLD[d]	T_0–T_{200}[a]
DSI								
R	−0.441	−0.160	−0.028	0.237	0.263	0.258	0.220	−0.398
P	<0.001	0.030	0.702	0.001	<0.001	<0.001	0.003	<0.001
DCI								
R	0.049	0.132	−0.150	**−0.589**	**−0.660**	**−0.570**	0.133	0.045
P	0.510	0.073	0.042	<0.001	<0.001	<0.001	0.072	0.542
Diol index 1								
R	**−0.855**	−0.126	0.017	**0.579**	**0.549**	0.479	0.303	**−0.840**
P	<0.001	0.088	0.819	<0.001	<0.001	<0.001	<0.001	<0.001
Diol index 2								
R	0.068	0.447	−0.077	0.185	0.131	0.275	0.001	−0.001
P	0.359	<0.001	0.297	0.012	0.075	<0.001	0.988	0.993

[a] Boyer et al. (2005).
[b] Levitus (2002).
[c] Levitus (2010).
[d] Mixed layer depth (Monterey and Levitus, 1997).

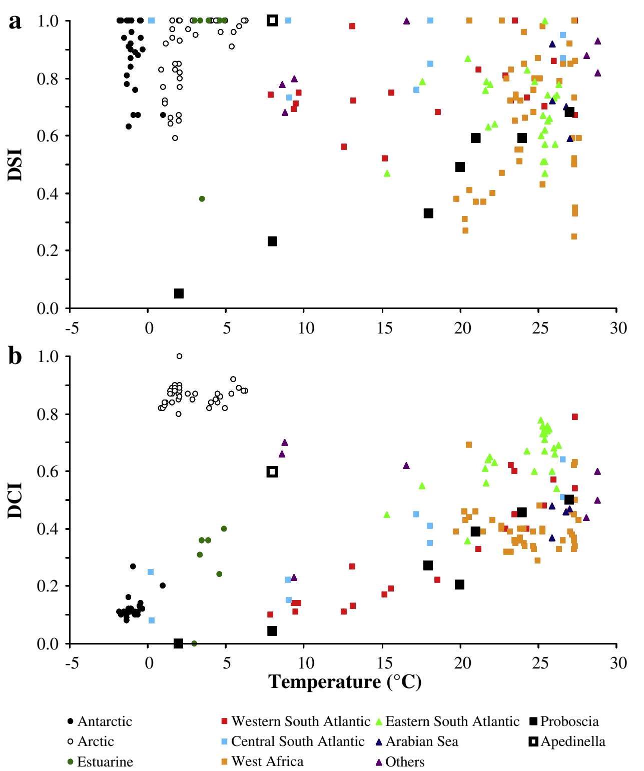

Fig. 3. Cross plot of (a) degree of saturation in long chain 1,14-alkyl diols (DSI) and (b) 1,14-alkyl diol chain length index (DCI) vs. annual mean SST. Colours indicate different areas (see Fig. 2 for map), while black squares DCI values are from cultured algae (data from Rampen et al., 2009, 2011). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

that we analyzed mainly freely occurring long chain alkyl diols (see Fig. 4, where open blue triangles indicate data for samples where extracts were not saponified, and open red circles indicate samples where extracts were saponified), whereas these lipids also occur in various bound forms, which may have different distributions (cf. Volkman et al., 1992; Hoefs et al., 2002; Shimokawara et al., 2010). To test this, we selected a subset of surface sediments for which diols were analyzed both without and with prior saponification of the extract. Fig. 4 shows the various long chain alkyl diol indices plotted vs. annual SST. Filled symbols indicate the data for saponified (red circles) and non-saponified (blue triangles) surface sediments of the selected dataset. For most of the sediments, the DSI showed markedly lower values after saponification (Fig. 4a), indicating that the fraction of mono-unsaturated long chain alkyl diols released by saponification was more abundant than this fraction in the free lipids. Nevertheless, neither the DSI values of saponified or free long chain alkyl diols showed a strong correlation with temperature (Fig. 4a), suggesting the DSI is also affected by factors other than temperature.

We observed no statistically significant correlation between SST and the chain length of the 1,14-alkyl diols (Fig. 3b), while weak to moderate correlations were observed between DCI and silicate, nitrate and, most strongly, phosphate concentration (Table 2). Saponification of the extracts resulted in slightly lower DCI values (Fig. 4b) and, apparently, the release of bound long chain 1,14-alkyl diols did not substantially improve the correlation between DCI and SST. The lack of correlation between the DCI and SST is in contrast with previous results for surface sediments from the eastern South Atlantic (Rampen et al., 2009) and a more detailed analysis shows that the DCI values from specific areas follow distinct patterns (Fig. 3b). Firstly, Arctic sediments from the Barents Sea and around Svalbard all showed high DCI values, around 0.8–0.9, whereas Antarctic sediments showed values around 0.1, without a temperature trend. Secondly, as shown before, DCI values from eastern South Atlantic sediments were higher than expected on the basis of culture experiments (Rampen et al., 2009), while surface sediments along the West African coast with a similar SST showed substantially lower DCI values. Thirdly, only for surface sediments from the central and western South Atlantic Ocean did DCI values correlate with SST, with the western South Atlantic data resembling the temperature correlation observed for *Proboscia* cultures. Previous studies have shown that *Proboscia* species proliferate in different seasons (e.g. Table 1) and therefore their long chain 1,14-alkyl diol distributions may reflect different seasonal temperatures, which may be an explanation for some of the scatter in the DCI–SST relationship. However, even correlations between regional DCI values and monthly SST values remained weak (Supplementary Table 3). In addition, seasonal growth cannot explain why, for example, the highest DCI values were observed for Arctic sediments (Fig. 3b). As implied by the moderate correlation between DCI and nutrient concentration (Table 2), the DCI may also be affected by environmental factors other than temperature or by the physiological state of the long chain 1,14-alkyl

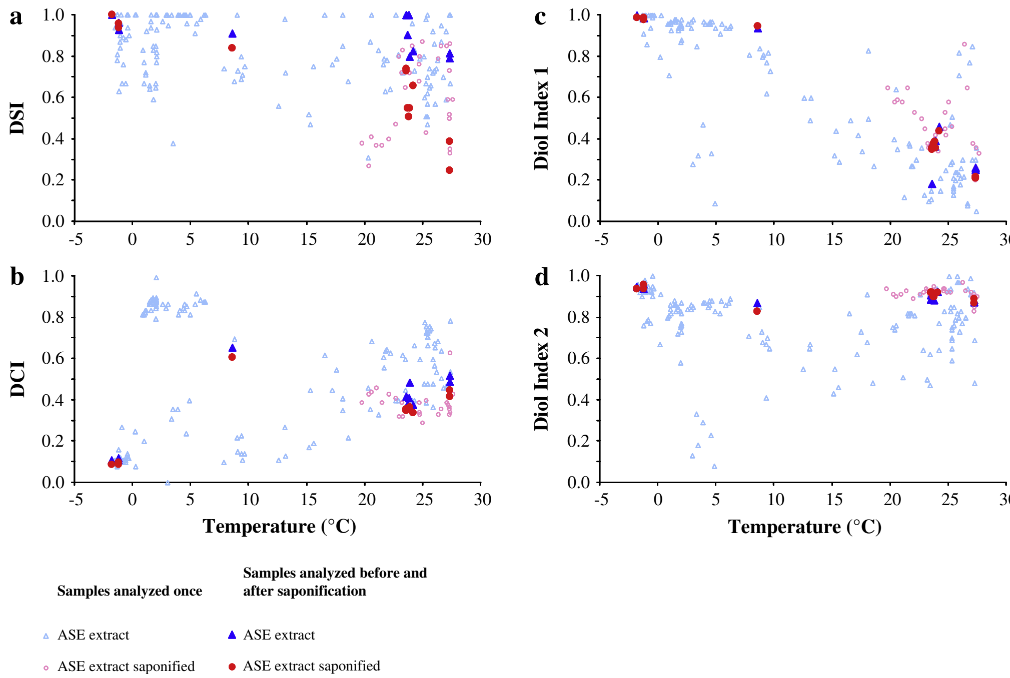

Fig. 4. Cross plots of long chain diol indices vs. annual mean SST. Open blue triangles indicate data from free lipids in ASE extracts while open pink circles indicate data from samples which were analyzed after saponification of the ASE extracts. Filled symbols indicate the data from a selected set of samples which were analyzed both before and after saponification; the filled blue triangles indicate free lipids in ASE extracts while the filled red circles indicate data obtained after saponification of the ASE extracts. (a) Degree of saturation in long chain 1,14-alkyl diols (DSI), (b) 1,14-alkyl diol chain length index (DCI), (c) diol index 1 and (d) diol index 2 values vs. annual mean SST. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

diol producers. The different DCI/SST patterns for the various locations could also be an indication that different species of *Proboscia* have their own specific relationship with temperature. The correlation between DCI and growth temperature is based mainly on cultures of *Proboscia indica* (Rampen et al., 2009). *Proboscia alata* is a cosmopolitan species (Table 1), but other *Proboscia* spp. are restricted to specific areas, which may be related to specific environmental factors like nutrient availability, salinity or temperature (e.g. Jordan et al., 1991; Takahashi et al., 1994). A regional occurrence, related to environmental factors, of *Proboscia* species with specific long chain diol distributions may also explain the weak correlation between DCI and silicate, nitrate and phosphate concentration. Alternatively, the indices may be affected by a input of diols from species other than *Proboscia*. Analysis of an extensive set of diatom cultures indicated that, except for *Proboscia* species, diatoms are an unlikely source for long chain alkyl diols (Rampen et al., 2007). However, recently, Rampen et al. (2011) did report long chain 1,14-alkyl diols in the heterokont marine Dictyochophyte *A. radians*, indicating that these lipids may indeed be produced by algae other than diatoms. Moreover, the DCI value of the *A. radians* culture does not match the results from *Proboscia* cultures (Fig. 3b). On the other hand, strong similarities between *Proboscia* frustule flux and long chain 1,14-alkyl diol flux in the Arabian Sea (Rampen et al., 2008) suggest that, at least in the Arabian Sea, *Proboscia* are the main source of long chain 1,14-alkyl diols. Furthermore, *A. radians* also contained the C_{32} 1,14-diol (Rampen et al., 2011), which was not detected in this study. Possibly in areas like the central and western South Atlantic the source of long chain 1,14-alkyl diols is predominantly a single *Proboscia* species and this may explain the apparent relationship between DCI and SST in these areas. Hence, the DCI may only be applicable as a temperature proxy if the biological source does not change over time and its temperature–proxy relationship is known.

3.2. Effect of environmental conditions on relative abundances of long chain 1,14-alkyl diols

Previously, we introduced two diol indices, 1 and 2 (Eqs. 3 and 4), to reconstruct past upwelling conditions in the Arabian Sea and the shelf waters of the Western Antarctic Peninsula, respectively (Rampen et al., 2008; Willmott et al., 2010). To test their applicability as upwelling or stratification proxies on a global scale, we determined their values in our marine surface sediment set. The set contained samples from major coastal upwelling regimes like the Canary Current system (off Northwest Africa), the Benguela Current system (off Southern Africa), the Somali Current system (off Somalia and Oman) and the Southern Ocean around Antarctica (Orsi et al., 1995; Smith, 2001; Capone and Hutchins, 2013).

For diol index 1, the highest values (> 0.9) were observed for both northern and southern high latitude areas (> 60°), while typical upwelling areas in the Arabian Sea, off the coast of West Africa, and in the eastern South Atlantic Ocean showed moderate to low values (Fig. 5a), suggesting that diol index 1 is not an unambiguous indicator for upwelling conditions. The values for diol index 2 showed a geographical distribution distinctly different from diol index 1 (Fig. 5). Highest diol index 2 values were observed near Antarctica, the Arabian Sea and West Africa, and moderate to high values in the eastern South Atlantic Ocean. Northern high latitude areas (> 60°N) showed diol index 2 values which were slightly lower than for southern high latitudes. Based on its reasonable correspondence of high values with upwelling conditions, diol index 2 seemed to be a better general indicator for upwelling conditions than diol index 1. We also examined a combination of both indices,

$$\text{Combined diol index} = [C_{28} + C_{30}\,1,14\text{-diol}]/([C_{28} + C_{30}\,1,14\text{-diol}] + [C_{28} + C_{30}\,1,13-\text{diol}] + [C_{30}\,1,15\text{-diol}] \quad (5)$$

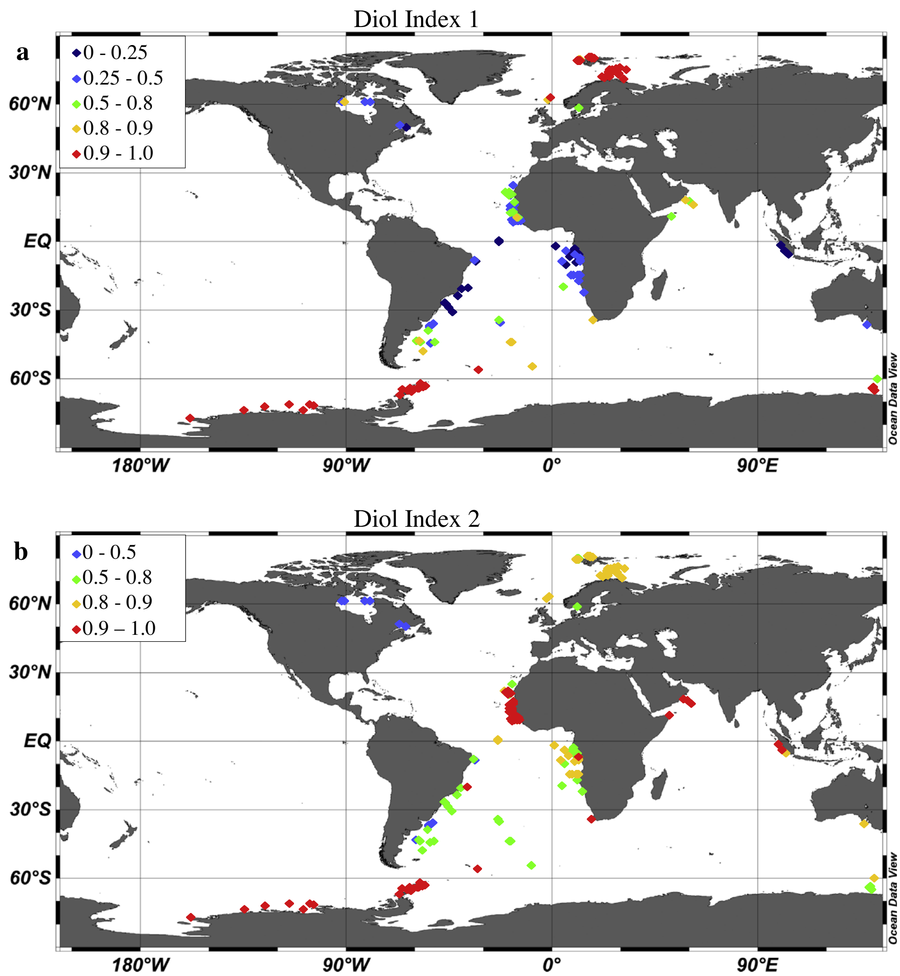

Fig. 5. World map with values of (a) diol index 1 and (b) diol index 2 at the sample locations.

but the results strongly resembled those from diol index 1, indicating no additional value (data not shown). We also investigated the effect of bound long chain alkyl diols on the indices, but the values before and after saponification of the extracts had similar values (Fig. 4c and d).

Quantitative correlation of the long chain alkyl diol indices with upwelling strength is hampered by the relatively few quantitative data on upwelling strength, which is why upwelling is often inferred by indirect methods like measurements of wind stress, tracer observations, salinity, nutrients and temperature (Rhein et al., 2010; Kadko and Johns, 2011). Furthermore, most upwelling studies areas are on a regional scale, whereas data on upwelling on a global scale are limited to indications of presence or absence of upwelling in specific areas (e.g. Capone and Hutchins, 2013). In order to provide some quantitative comparison with upwelling strength, and to investigate whether certain environmental factors affect the two diol indices, we compared them with temperature, salinity and chlorophyll, and phosphate, nitrate and silicate concentration of the overlaying water (Table 2). Diol index 2 showed no correlation with these environmental factors, while diol index 1 showed a significant inverse correlation with SST (R value -0.855; p value < 0.001, Fig. 6). The correlation between SST and diol index 1 is remarkable since the index is composed of lipids supposed to be produced by different organisms, so shifts in their relative abundance are unlikely to be related to physiological adaptation within single organisms. C_{30} 1,15-diol abundance showed an increase relative to 1,14-diol abundance with increasing temperature, similar to the LDI, whereas the C_{30} 1,15-diol also increased relative to C_{28} 1,13- and C_{30} 1,13-diols with increasing temperature (Rampen et al., 2012). However, the LDI correlated well with SST (R value 0.984) and similar LDI-temperature correlations were observed in different regions, indicating that this index is affected primarily by temperature. In contrast, for diol index 1, upwelling areas at low latitude like the Arabian Sea and West Africa showed distinctly higher diol index 1 values, whereas estuarine areas like Hudson Bay and the Gulf of St. Lawrence show lower values for both diol indices 1 and 2 compared with the global trends. This suggests that these indices are also affected by factors other than temperature (Fig. 6). In addition to temperature, nitrate, phosphate and silicate concentration also showed significant correlation with diol index 1, but these are likely due to the underlying correlation of these nutrients with SST (Rampen et al., 2012).

To investigate whether the degree of stratification is related to the diol indices (cf. Contreras et al., 2010), we compared the indices with the temperature differential between sea surface and subsurface at 200 m depth (T_0–T_{200}, suggested as a measure for stratification by Dave and Lozier, 2013) and mean annual depth of the surface mixed layer. A significant correlation was only observed between diol index 1 and T_0–T_{200}, but again this may also be due to the strong correlation between SST and T_0–T_{200}. To examine the possibility of seasonal production of long chain 1,14-diols during months with maximum stratification, diol indices were also compared with stratification and mixed layer depth values for months with the shallowest mixing depth and smallest

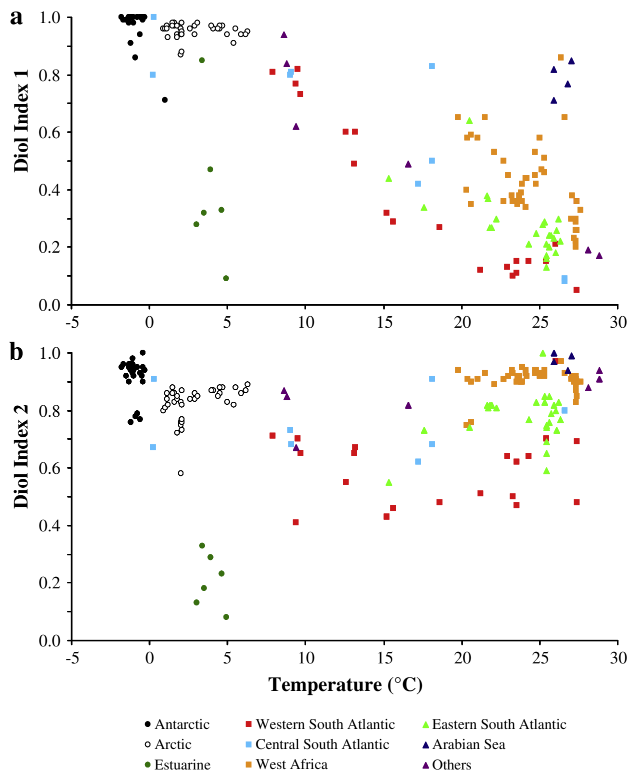

Fig. 6. Cross plot of (a) diol index 1 and (b) diol index 2 vs. annual mean SST. Colours indicate different areas (see Fig. 2 for map). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

temperature differences, but this also revealed no relationships (Supplementary Table 3).

These results indicate that diol index 1 is unsuitable as a globally applicable upwelling indicator, although it does seem to work in certain regions (e.g. Rampen et al., 2008), while diol index 2 seems applicable as a global indicator for upwelling, although this will likely also depend on the local ecological niche of *Proboscia* diatoms.

4. Conclusions

Although it was previously reported that the chain length distribution and degree of saturation of long chain 1,14-alkyl diols in *Proboscia* cultures are related to growth temperature (Rampen et al., 2009), our comprehensive study of marine core tops does not show a strong correlation between SST and chain length distribution or degree of saturation of long chain 1,14-alkyl diols in marine surface sediments, indicating that these compounds are not widely applicable as a temperature proxy. It remains uncertain why the correlations were not observed in this core top study, but regional differences in source organisms may play an important role. Analysis of long chain alkyl diol indices proposed as indicators for upwelling/high nutrient factors indicate that diol index 1 is affected by temperature. The geographical distribution of diol index 2 values suggest that this index may be more widely applicable as an indicator for upwelling conditions, although this will depend on the local ecological niche of *Proboscia* diatoms and their relationship with upwelling conditions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orggeochem.2014.07.012.

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