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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 also revealed uncertainties 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 like sea surface temperature (SST), salinity and nutrient concentrations. Previous cultivation efforts 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 in the diol saturation index (DSI) and diol chain length index (DCI), respectively. However, values of these indices in surface sediments show no relationship with annual mean SST of the overlying water. It remains unknown what determines the DSI, although our data suggests that it may be affected by diagenesis, while the relationship between temperature and DCI may be different for different *Proboscia* species. In addition, contributions of 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 previously been applied 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.

Keywords: Long chain alkyl diols; *Proboscia*; Upwelling index; Sea surface Temperature index

1. Introduction

Over the last decades, an increasing number of lipids from marine environments has been identified and linked to their natural sources, and some of them 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 have been identified widespread 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., 1999; 1992). In the environment, a recent study on lipids and 18s rRNA genes in a freshwater lake has shown that long chain alkyl diols are produced by eustigmatophytes in the surface waters 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 uncertainties concerning their sources, recent work has indicated a strong correlation between sea surface temperatures (SST) and the 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 of 0.984 and p-value of <0.001) between the LDI and SST was observed.

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 produce 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 being a likely source for long chain 1,14-alkyl diols, particularly in upwelling areas (Rampen et al., 2008), whereas the importance of *Apedinella* as a source for sedimentary long chain 1,14-alkyl diols remains uncertain (Rampen et al., 2011). These sources may be distinguished based on the occurrence of certain diols: C_{32} 1,14-diols may be useful as an indicator for *Apedinella* input, as they are produced by *Apedinella radians* and were absent from the 8 cultures of *Proboscia* spp. analyzed to date. Mono-unsaturated long chain 1,14-alkyl diols, on the other hand, may 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:

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

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

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 of 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 was 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; Koning et al., 2001; Lange et al., 1998; 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., 2008; 2007), whereas such a relationship was not observed for long chain 1,15- and 1,13-diols. Following this, Diol Index 1 was introduced:

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

Diol Index 1 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 analyses 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:

Diol Index 2 = [saturated C_{28} + C_{30} 1,14-diol] / ([saturated C_{28} + C_{30} 1,14-diol] + [saturated C_{28} + C_{30} 1,13-diol]) (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 where 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 (n = 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 waters, such as temperature, salinity, nutrient concentrations, stratification and mixed layer depths.

2. Methodology

We analyzed 209 marine surface sediments, globally distributed, although mostly 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 methanol (MeOH) (9:1; v:v) at 100°C and 7-8 × 10^6 Pa. For a selected set of samples, the ASE extracts were subsequently 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 trimethyl silyl (TMS) 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).

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), 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 sediments (generally 0 – 1 cm) were obtained at locations with water depths ranging from ca. 20 to ca. 6000 m and a large range in annual mean SST (-1.8 – 28.8°C), annual mean salinity (6.8 – 37.0), nutrient concentrations, chlorophyll content (0 – 280 µg/L) and mixed layer depth (0.1 – 65 m) (see Supplementary Table 2). 187 sediments of this 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 only detected in 146 sediments (70%). One sediment contained quantifiable amounts of long chain 1,13- and 1,15-alkyl diols without detectable amounts of long chain 1,14-alkyl diols. The observed 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 *Apedinella radians* (Rampen et al., 2011), was not detected.

Long chain 1,14-alkyl diols dominate in the Arctic and Antarctic surface sediments and the Arabian Sea (Fig. 2), while their fractional abundances show strong variation in the other oceanic areas. For most regions, fractional abundances of 1,15-alkyl diols are inversely related to 1,14-alkyl diol abundances, while 1,13-alkyl diol abundances are generally low with little variation – only in estuarine sediments from Hudson Bay and the Gulf of St. Lawrence do 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 previously 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 show a weak negative correlation with SST (R-value = -0.441, p-value < 0.001; Table 2; Fig. 3a), contrasting with the positive temperature correlation observed for cultured *Proboscia* diatoms by 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 correlations 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 in this study (Table 2; Supplementary Table 3) suggest that they do not significantly impact the DSI. In *Proboscia* cultures, concentrations of unsaturated long chain alkyl diols were always similar or higher than saturated long chain alkyl diols; 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 contain relatively high amounts of unsaturated 1,14-alkyl diols, higher than would be expected based on culture results (Fig. 3a). Another factor affecting the DSI could be that we mostly analyzed 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 comprise different distributions (cf. Hoefs et al., 2002; Shimokawara et al., 2010; Volkman et al., 1992). 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 versus annual SST. Filled symbols indicate the data for saponified (red circles) and non-saponified (blue triangles) surface sediments of the selected dataset. For most sediments tested, the DSI shows markedly lower values after saponification (Fig. 4a), indicating that the fraction of mono-unsaturated long chain alkyl diols released by saponification is higher compared to this fraction in free lipids. Nevertheless, neither the DSI-values of saponified nor free long chain alkyl diols show a strong correlation with temperature (Fig. 4a), suggesting the DSI is also affected by factors other than temperature.

We also observe no statistically significant correlation between SST and the chain length of the 1,14-alkyl diols (Fig. 3b), while weak to moderate correlations are observed between DCI and silicate, nitrate and, most strongly, phosphate concentrations (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 show high DCI values around 0.8-0.9, whereas Antarctic sediments show values around 0.1 without a temperature trend. Secondly, as shown before, DCI values from eastern South Atlantic sediments are 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 show substantially lower DCI values. Thirdly, only for surface sediments from the Central and Western South Atlantic Ocean do 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 SSTs remained weak (Supplementary Table 3). In addition, seasonal growth cannot explain why, for example, highest DCI-values were observed for Arctic sediments (Fig. 3b). As implied by the moderate correlation between DCI and nutrient concentrations (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 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 mainly based on cultures of *P. 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 observed between DCI and silicate, nitrate and phosphate concentrations. Alternatively, the indices may be affected by input of diols from species other than *Proboscia*. Analyses 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 *Apedinella radians* indicating that these lipids may indeed also be produced by algae other than diatoms. Moreover, the DCI value of the *A. radians* culture does not match with 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 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, Diol Index 1 and 2 (Eq. 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 the applicability of these two long chain alkyl diol indices as upwelling or stratification proxies on a global scale, we determined their values in our marine surface sediment set. This sediment set contains 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 (Capone and Hutchins, 2013; Orsi et al., 1995; Smith et al., 2001).

For Diol Index 1, highest values (>0.9) were observed in 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 index values (Fig. 5a), suggesting that Diol Index 1 is not an unambiguous indicator for upwelling conditions. The values of Diol Index 2 showed a geographical distribution distinctly different from Diol Index 1 (Fig. 5). Highest Diol Index 2 values are 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) show Diol Index 2 values, which are slightly lower than southern high latitudes. Based on its reasonable correspondence of high values with upwelling conditions, Diol Index 2 seems to be a better general indicator for upwelling conditions than Diol Index 1. We also examined a combination of both indices,

Combined Diol Index = [C_{28} + C_{30} 1,14-diol] / ([C_{28} + C_{30} 1,14-diol] + [C_{28} + C_{30} 1,13-diol] + [C_{30} 1,15-diol]) (5)

but the results of the Combined Diol Index strongly resembled those of Diol Index 1, indicating no additional value (data not shown). We also investigated the effect of bound long chain alkyl diols on these indices, but the Diol Index values before and after saponification of the extracts have similar values (Figs. 4c and d).

Quantitative correlation of the long chain alkyl diol indices with upwelling strength are hampered by the relatively small 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 (Kadko and Johns, 2011; Rhein et al., 2010). Furthermore, most upwelling studies areas are on a regional scale, whereas data on upwelling on a global scale is limited to indications of presence or absence of upwelling in specific areas (e.g. Capone et al., 2013). In order to provide some quantitative comparison with upwelling strength, and to investigate whether certain environmental factors affect the two Diol Indices, we correlated the indices with temperature, salinity and chlorophyll, phosphate, nitrate and silicate concentrations 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 the 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 shows an increase relative to 1,14-diol abundances with increasing temperature, similar to the LDI, whereas the C_{30} 1,15-diol also increase relative to C_{28} 1,13- and C_{30} 1,13-diols with increasing temperature (Rampen et al., 2012). However, the LDI correlates much stronger with SST (R-value = 0.984) and similar LDI-temperature correlations are observed in different regions indicating that this index is primarily affected by temperature. In contrast, for Diol Index 1, upwelling areas at low latitudes like the Arabian Sea and West Africa show distinctly higher Diol Index 1 values, whereas estuarine areas like the Hudson Bay and the Gulf of St. Lawrence show lower values for both Diol Index 1 and 2 compared to the global trends. This suggests that these diol indices are also affected by other factors than temperature (Fig. 6). In addition to temperature, nitrate, phosphate and silicate concentrations also showed significant correlations with the 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 with the Diol Indices (cf. Conteras 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 depths of the surface mixed layers. A significant correlation is 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 $T_o – T_{200}$. 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 depths and smallest temperature differences, but also this revealed no relationships (see 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 these correlations are not observed in this core top study, but regional differences in source organisms may play an important role. Analyses 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 distributions 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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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 & *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 waters	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 intensities, 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 & North Sea	Mild conditions + stratification	Nehring (1998) and Gómez and Souissi (2007)
P. inermis & *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.

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).

Figure legends:

Fig. 1. Sample location and presence of quantifiable amounts (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.

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 from cultured algae (data from Rampen et al., 2009; 2011).

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.

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

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).

Fig. 1.

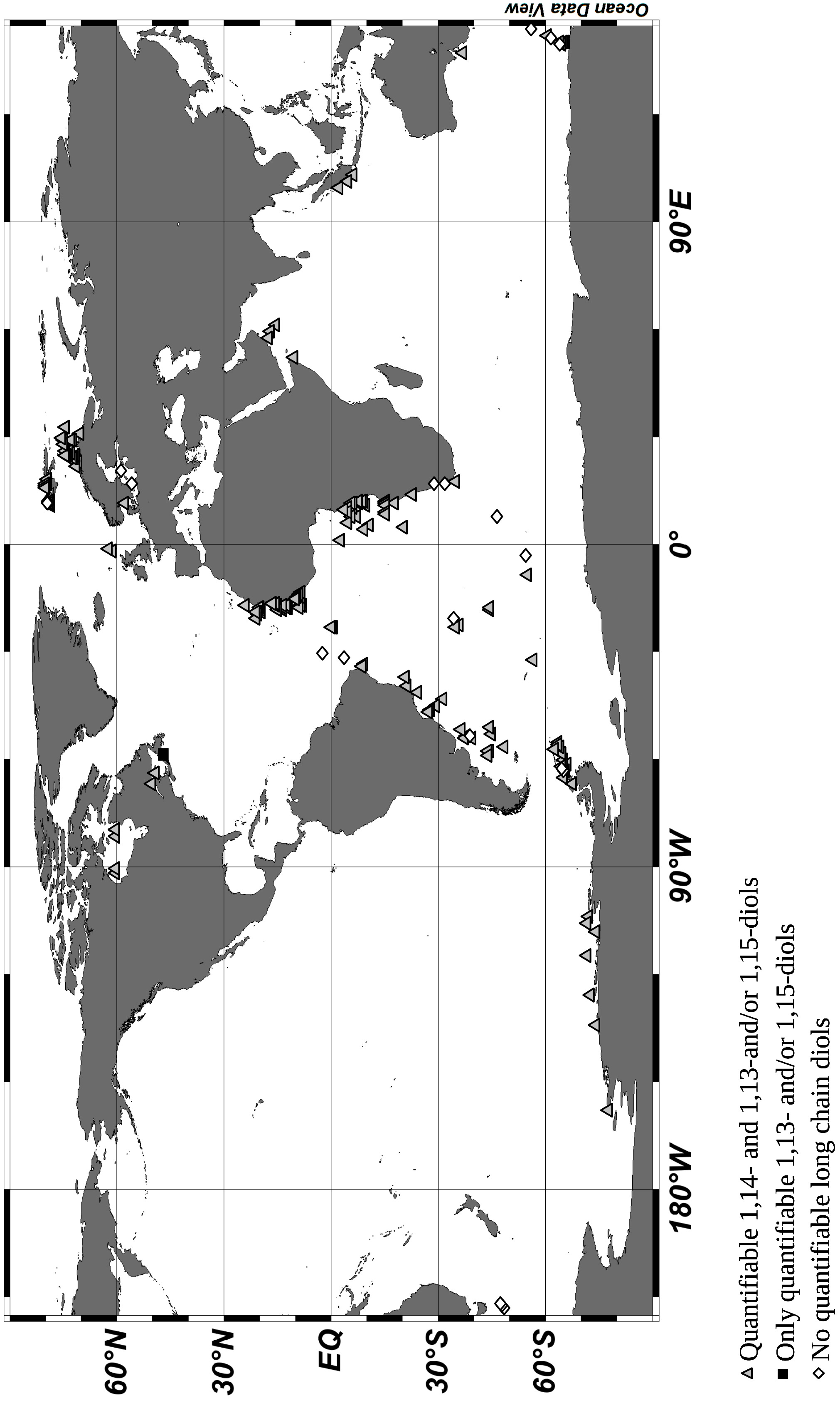

60°N
30°N
EQ
30°S
60°S
180°W
90°W
0°
90°E
Ocean Data View
▲ Quantifiable 1,14- and 1,13-and/or 1,15-diols
■ Only quantifiable 1,13- and/or 1,15-diols
◇ No quantifiable long chain diols

Fig. 2.

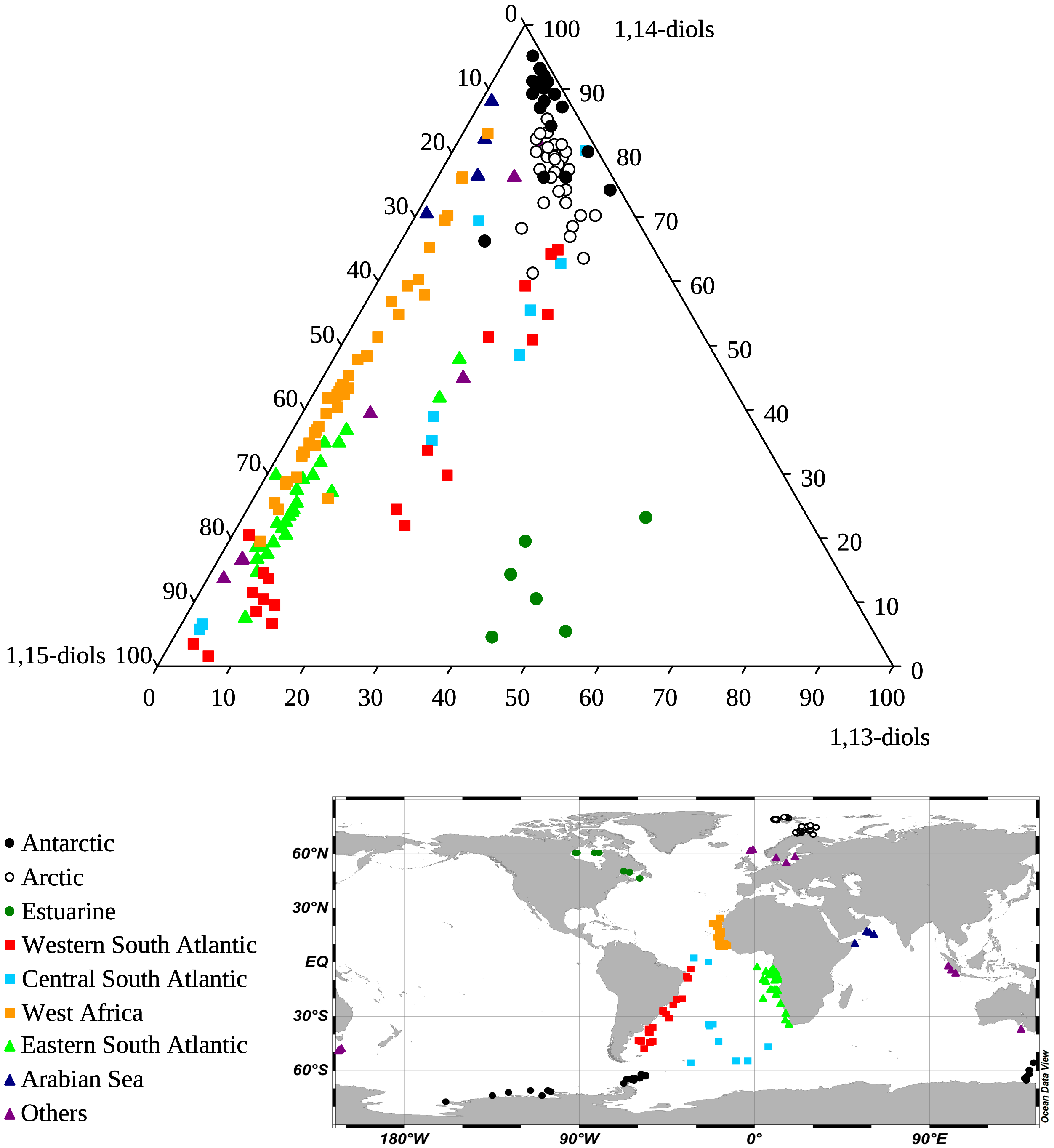

1,14-diols
1,15-diols
1,13-diols
0
10
20
30
40
50
60
70
80
90
100
Antarctic
Arctic
Estuarine
Western South Atlantic
Central South Atlantic
West Africa
Eastern South Atlantic
Arabian Sea
Others
60°N
30°N
EQ
30°S
60°S
180°W
90°W
0°
90°E
Ocean Data View

Fig. 3.

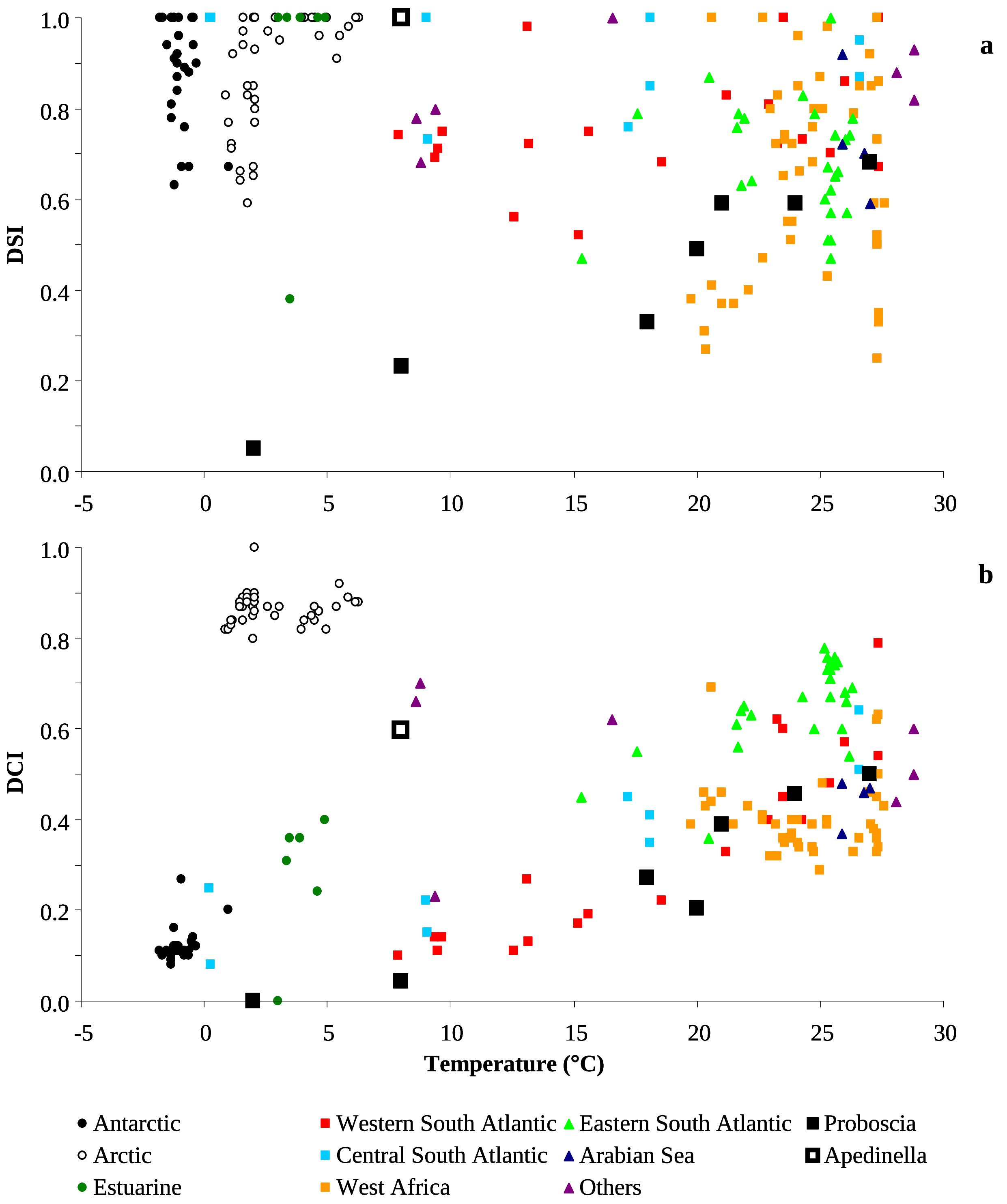
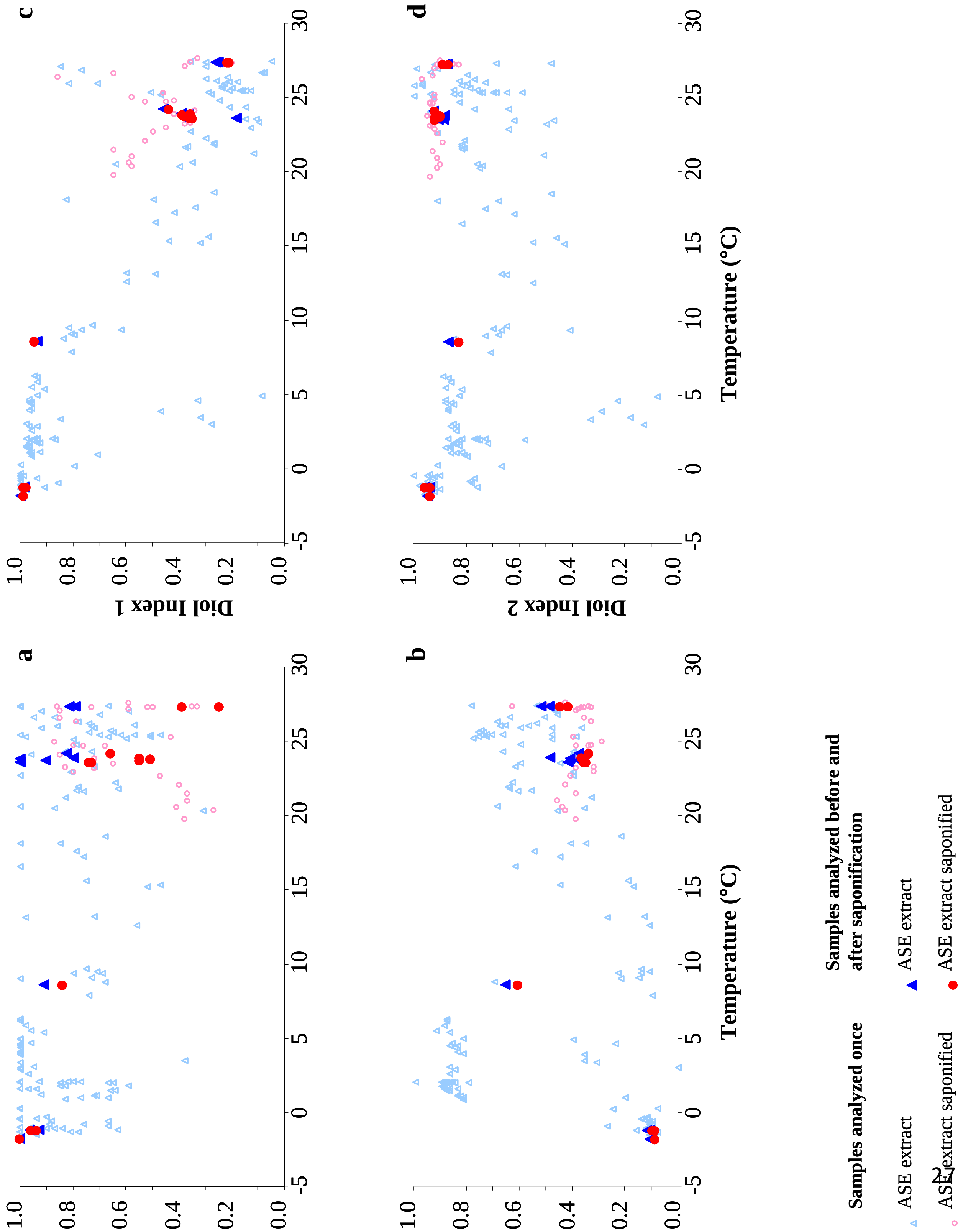

a
b
DSI
DCI
1.0
0.8
0.6
0.4
0.2
0.0
-5
0
5
10
15
20
25
30
Temperature (°C)
● Antarctic
○ Arctic
● Estuarine
■ Western South Atlantic
■ Central South Atlantic
■ West Africa
▲ Eastern South Atlantic
▲ Arabian Sea
▲ Others
■ Proboscia
□ Apedinella

Fig. 4.



a
b
c
d
DSI
DCI
Diol Index 1
Diol Index 2
Temperature (°C)
Temperature (°C)
0.0
0.2
0.4
0.6
0.8
1.0
-5
0
5
10
15
20
25
30
Samples analyzed once
ASE extract
ASE extract saponified
Samples analyzed before and after saponification
ASE extract
ASE extract saponified

Fig. 5.

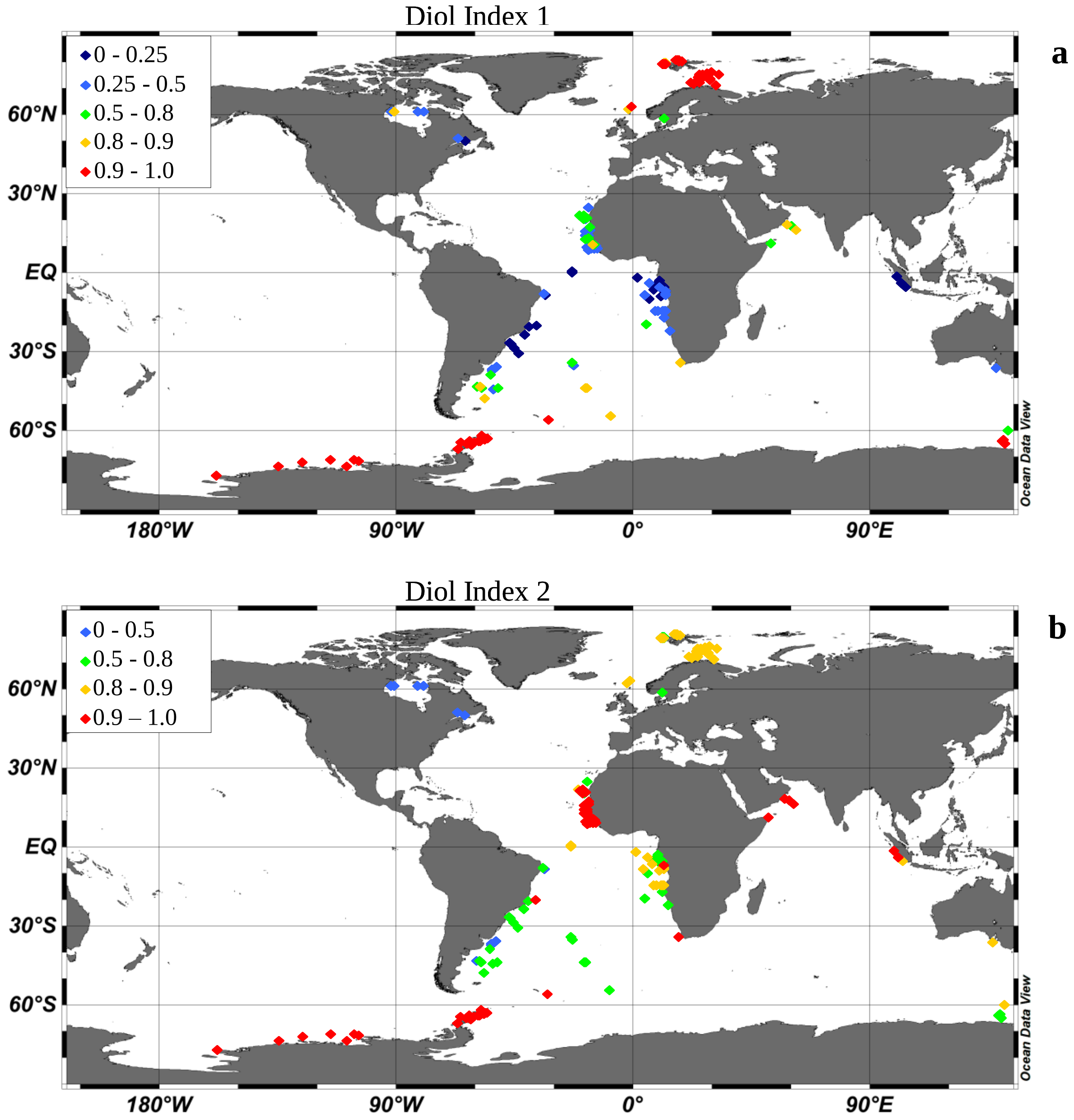
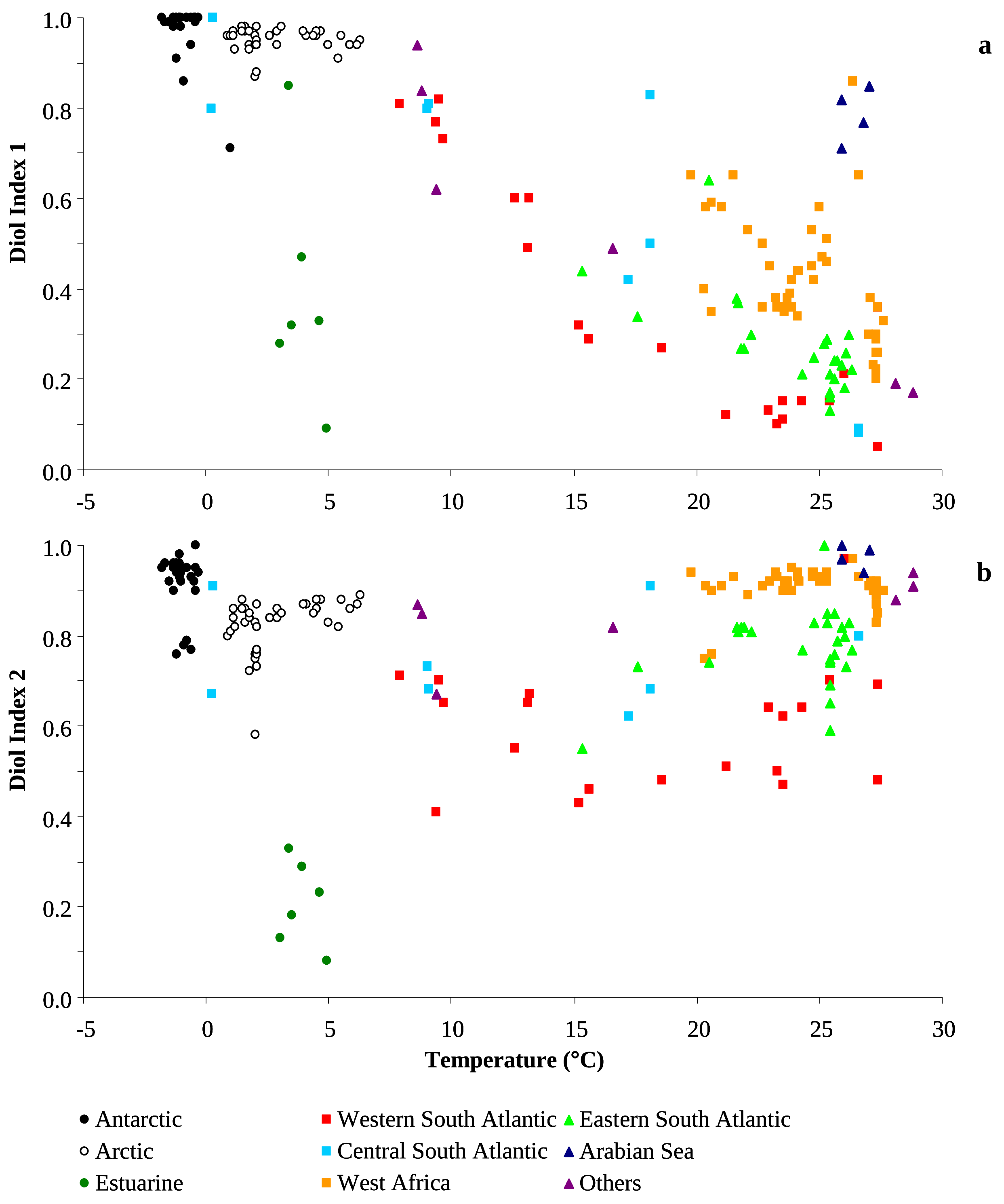

Diol Index 1
a
◆ 0 - 0.25
◆ 0.25 - 0.5
◆ 0.5 - 0.8
◆ 0.8 - 0.9
◆ 0.9 - 1.0
60°N
30°N
EQ
30°S
60°S
180°W
90°W
0°
90°E
Ocean Data View
Diol Index 2
b
◆ 0 - 0.5
◆ 0.5 - 0.8
◆ 0.8 - 0.9
◆ 0.9 – 1.0
60°N
30°N
EQ
30°S
60°S
180°W
90°W
0°
90°E
Ocean Data View

Fig. 6

570


a
b
Diol Index 1
Diol Index 2
1.0
0.8
0.6
0.4
0.2
0.0
-5
0
5
10
15
20
25
30
Temperature (°C)
● Antarctic
○ Arctic
● Estuarine
■ Western South Atlantic
■ Central South Atlantic
■ West Africa
▲ Eastern South Atlantic
▲ Arabian Sea
▲ Others