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# Constraints on the application of long chain diol proxies in the Iberian Atlantic margin

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ABSTRACT

Long chain diols are lipids that have gained interest over the last years due to their high potential to serve as biomarkers and diol indices have been proposed to reconstruct upwelling conditions and sea surface temperature (SST). However, little is known about the sources of the diols and the mechanisms impacting their distribution. Here we studied the factors controlling diol distributions in the Iberian Atlantic margin, which is characterized by a dynamic continental shelf under the influence of upwelling of nutrient-rich cold deep waters, and fluvial input. We analyzed suspended particulate matter (SPM) of the Tagus river, marine SPM and marine surface sediments along five transects off the Iberian margin, as well as riverbank sediments and soil from the catchment area of the Tagus river. Relatively high fractional abundances of the $C_{32}$ 1,15-diol (normalized with respect to the 1,13- and 1,15-diols) were observed in surface sediments in front of major river mouths and this abundance correlated strongly with the BIT index, a tracer for continental input of organic carbon. Together with an even higher fractional abundance of the $C_{32}$ 1,15-diol in the Tagus river SPM, and the absence of long chain diols in the watershed riverbank sediments and soils, we suggest that this long chain diol is produced in-situ in the river. Further support for this hypothesis comes from the small but distinct stable carbon isotopic difference of 1.3‰ with the marine $C_{28}$ 1,13-diol. The 1,14-diols are relatively abundant in surface sediments directly along the northern part of the coast, close to the upwelling zone, suggesting that diol indices based on 1,14-diols would work well as upwelling tracers in this region. Strikingly, we observed a significant difference in stable carbon isotopic composition between the mono-unsaturated $C_{30:1}$ 1,14- and the saturated $C_{28}$ 1,14-diol ($3.8 \pm 0.7$‰), suggesting different sources, in accordance with their different distributions. In addition, the Long chain Diol Index (LDI), a proxy for sea surface temperature, was applied to the surface sediments. The results correlated well with satellite SSTs offshore, but revealed a significant discrepancy with satellite-derived SSTs in front of the Tagus and Sado rivers. This suggests that river outflow might compromise the applicability of this proxy.



## 1. Introduction

One of the most important climate parameters that earth scientists try to reconstruct is sea surface temperature (SST). During the last decades, several organic proxies have been developed that have become important tools for climate reconstruction. Two organic proxies are commonly used for the reconstruction of past SSTs: the $U_{37}^{K'}$ index (Brassell et al., 1986; Prahl and Wakeham, 1987) based on the degree of unsaturation of long chain alkenones produced by haptophyte algae, and the $TEX_{86}$ index (Schouten et al., 2002; Kim et al., 2010), based on the distribution of isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs), mainly produced by Thaumarchaeota. Many studies have used alkenones, as these compounds are often abundant in marine sediments, occur worldwide, and are relatively easy to analyze. Since their producers, haptophyte algae, are light-dependent and live near the sea surface, the $U_{37}^{K'}$ index shows a good correlation with SST (Müller et al., 1998; Herbert, 2003). However, there are compromising factors such as interspecies variation (Conte et al., 1998), seasonality, habitat depth and oxic degradation (e.g., Hoefs et al., 1998). In contrast to haptophyte algae, Thaumarchaeota are not phototrophic

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but nitrifiers that depend on ammonium (Könneke et al., 2005; Wuchter et al., 2006), often sourced from the decay of phytoplanktonic organic matter. This means that the $TEX_{86}$ proxy often reflects subsurface water column temperatures rather than SST (Dos Santos et al., 2010; Kim et al., 2012; Schouten et al., 2013; Chen et al., 2014). In addition, it suffers from similar pitfalls as the $U^{K'}_{37}$ proxy, i.e., uncertainties in seasonality and degradation (e.g., Schouten et al., 2004, 2013; Kim et al., 2009b; Basse et al., 2014). Moreover, riverine continental organic matter input can bias the $TEX_{86}$ signal, although this can be assessed by means of the Branched versus Isoprenoid Tetraether index (BIT), a tracer for fluvial input of soil-derived and riverine organic carbon (e.g., Hopmans et al., 2004; Zell et al., 2013, 2014; De Jonge et al., 2014).

Long chain diols form a group of lipids increasingly investigated over the last decades because of their potential to serve as biomarkers. They were first identified in Black Sea sediments (de Leeuw et al., 1981). This discovery was followed by many studies that reported long chain diols in marine (e.g., Versteegh et al., 1997, 2000; Hinrichs et al., 1999; Sinninghe Damsté et al., 2003; Rampen et al., 2007, 2008, 2009) and lacustrine environments (e.g., Xu et al., 2007; Romero-Viana et al., 2012; Rampen et al., 2014b). From culture studies, it has become clear that marine and freshwater eustigmatophyte algae produce 1,13- and 1,15-diols, with chain lengths generally varying between $C_{28}$ and $C_{32}$. However, their role as source organism of these diols in the marine environment is still uncertain, since the distribution found in marine sediments differs from that found in cultures (Volkman et al., 1992; Versteegh et al., 1997; Rampen et al., 2014b). Apart from 1,13- and 1,15-diols, 1,14-long chain diols are also commonly found in marine sediments. These diols are usually assigned to *Proboscia* diatoms as Sinninghe Damsté et al. (2003) and Rampen et al. (2007) showed that this diatom genus produces saturated and mono-unsaturated $C_{28}$ and $C_{30}$ 1,14-diols. The saturated $C_{28}$, $C_{30}$ and $C_{32}$ 1,14-diols have also been reported in the marine Dictyochophyte *Apedinella radians* (Rampen et al., 2011). However, the importance of this organism as source for 1,14-diols in the ocean is still unknown.

Recently, a new proxy for past sea surface temperature has been proposed based on the distribution of long chain diols in marine sediments: the Long chain Diol Index (LDI; Rampen et al., 2012). Additionally, the Diol Index (Rampen et al., 2008; Willmott et al., 2010), a proxy for upwelling/high nutrient conditions, has been proposed. The LDI index is based on the fractional abundances of the $C_{28}$ 1,13-diol, $C_{30}$ 1,13-diol and $C_{30}$ 1,15-diol. Analysis of their distribution in a large set of marine surface sediments derived from all over the world shows that the abundance of these diols correlates strongly with annual mean SST: the $C_{30}$ 1,15-diol has the strongest positive correlation ($R^2 = 0.95$), whereas the $C_{28}$ and $C_{30}$ 1,13-diols reveal slightly lesser negative correlations ($R^2 = 0.88$ and $R^2 = 0.80$, respectively). The $C_{32}$ 1,15-diol does not correlate with SST ($R^2 = 0.01$). Based on this, the index is defined as the relative abundance of the $C_{30}$ 1,15-diol versus the $C_{28}$ and $C_{30}$ 1,13-diols:

$$\text{Long chain Diol Index (LDI)} = \frac{F_{C_{30}\,1,15\text{-diol}}}{F_{C_{28}\,1,13\text{-diol}} + F_{C_{30}\,1,13\text{-diol}} + F_{C_{30}\,1,15\text{-diol}}} \quad (1)$$

SST is calculated from the LDI index based on the following relation (Rampen et al., 2012):

$$\text{LDI} = 0.033 \times \text{SST} + 0.095 \quad (R^2 = 0.969; n = 162;\ \text{SE} \pm 2\,^\circ\text{C}) \quad (2)$$

*Proboscia* diatoms are often associated with high productivity and upwelling conditions (Hernández-Becerril, 1995; Lange et al., 1998; Koning et al., 2001). Their role as the most important 1,14-diol producers under upwelling conditions was confirmed by a sediment trap study in the Arabian Sea (Rampen et al., 2007), and based on this an index for upwelling intensity during the South Western Indian Monsoon was proposed (Rampen et al., 2008):

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

A second upwelling index was proposed by Willmott et al. (2010), for the Western Bransfield Basin (Antarctica) since the $C_{28}$ and $C_{30}$ 1,13-diols were more abundant than the $C_{30}$ 1,15-diol:

$$\text{Diol Index 2} = \frac{[C_{28} + C_{30}\ 1,14\ \text{diols}]}{([C_{28} + C_{30}\ 1,14\ \text{diols}] + [C_{28} + C_{30}\ 1,13\ \text{diols}])} \quad (4)$$

Preliminary application in sediment cores of the LDI and the two Diol Indices have shown their promise as proxies (Naafs et al., 2012; Rampen et al., 2012, 2014a; Seki et al., 2012; Lopes dos Santos et al., 2013; Smith et al., 2013; Rodrigo-Gamiz et al., 2014; Nieto-Moreno et al., 2015; Plancq et al., 2015). However, there are still uncertainties in the application of these biomarkers and it is crucial that additional studies are done to improve the reliability of these proxies. For example, studies have related increased abundances of *Proboscia* to stratified conditions rather than upwelling (e.g., Fernández and Bode, 1994). Indeed, Contreras et al. (2010) observed increased concentrations of the $C_{28}$ 1,14-diol in the Peruvian upwelling system during times of stratification (interglacials) and low concentrations during times of upwelling.

Here we tested the long chain diol proxies in surface sediments from the Atlantic Iberian margin. Previous organic geochemical work in this region has shown the presence of long chain diols in surface sediments (Schmidt et al., 2010). This region experiences upwelling during summer and downwelling during winter due to the northerly and southerly trade winds and the Azores high pressure system driving the surface circulation. Additionally, the margin receives freshwater input from different rivers, of which the two largest are the Tagus and Douro. We analyzed long chain diols in surface sediments of five transects along the Iberian margin (Fig. 1D). Transect I and IV are located in front of the Douro and Tagus rivers, respectively, allowing the ability to assess the potential influence of fluvial input on the long chain diol proxies. Transects II and V start in the estuaries of the smaller Mondego and Sado rivers, respectively, and transect III is not under the influence of riverine input. The results shed light on the applicability of long chain diol proxies in a coastal environment under the influence of a seasonal upwelling system, and with terrestrial input via riverine transport.

## 2. Materials and methods

### 2.1. Site description

The Atlantic Iberian margin is characterized by a steep slope dissected by different submarine canyons, of which the most important are the Nazaré, Cascais and Setúbal-Lisbon canyons (e.g., Vanney and Mougenot, 1981). The shelf is relatively narrow, ranging between 20 and 50 km in width. The shelf break is located at a water depth of around 140 m (Mougenot, 1988). The surface ocean circulation off the Western Iberian Peninsula is driven by the Portugal Current (PC) System. The PC is a slow equatorward current (e.g., Martins et al., 2002). Between May and September (summer upwelling), the Portugal Coastal Current (PCC), along the coast dominates. This current flows southward induced by northerly Portugal trade winds and the Azores anticyclone moving toward the Iberian Peninsula (e.g., Fiúza et al., 1982; Martins et al., 2002). As a result, the cold, nutrient-rich subsurface water rises to