



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



Sebastiaan W. Rampen<sup>a,\*</sup>, Verónica Willmott<sup>a,1</sup>, Jung-Hyun Kim<sup>a</sup>, Marta Rodrigo-Gámiz<sup>a</sup>, Eleonora Uliana<sup>b</sup>, Gesine Mollenhauer<sup>b,c</sup>, Enno Schefuß<sup>b</sup>, Jaap S. Sinninghe Damsté<sup>a</sup>, Stefan Schouten<sup>a</sup>

<sup>a</sup> NIOZ Royal Netherlands Institute for Sea Research, Department of Marine Organic Biogeochemistry, P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands

<sup>b</sup> MARUM Center for Marine Environmental Sciences, University of Bremen, Leobener Strasse, D-28359 Bremen, Germany

<sup>c</sup> Alfred-Wegener-Institute for Polar and Marine Research, Am Handelshafen 12, D-27570 Bremerhaven, Germany

### ARTICLE INFO

#### Article history:

Received 31 March 2014

Received in revised form 7 July 2014

Accepted 17 July 2014

Available online 30 July 2014

#### Keywords:

Long chain alkyl diols

*Proboscia*

Upwelling index

Sea surface temperature index

### 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<sub>30</sub> 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  $[(C_{28} + C_{30} \text{ 1,14-diols}) / ((C_{28} + C_{30} \text{ 1,13-diols}) + (C_{28} + C_{30} \text{ 1,14-diols}))]$  as a general indicator for high nutrient or upwelling conditions.

© 2014 Elsevier Ltd. All rights reserved.

### 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<sub>28</sub>–C<sub>32</sub> 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<sub>28</sub> 1,13-, C<sub>30</sub> 1,13- and C<sub>30</sub> 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<sub>30</sub> 1,15-diol abundance relative to those of C<sub>28</sub> 1,13-, C<sub>30</sub> 1,13- and C<sub>30</sub> 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.

\* Corresponding author.

E-mail address: [sebastiaan.rampen@nioz.nl](mailto:sebastiaan.rampen@nioz.nl) (S.W. Rampen).

<sup>1</sup> Present address: Alfred-Wegener-Institute for Polar and Marine Research, Am Handelshafen 12, D-27570 Bremerhaven, Germany.

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<sub>28</sub> and C<sub>30</sub> 1,14-diols and, in addition, saturated C<sub>28</sub>, C<sub>30</sub> and C<sub>32</sub> 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<sub>32</sub> 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:

$$\text{DCI} = \frac{[\text{saturated C}_{30} \text{ 1, 14-diol}]}{[\text{saturated C}_{28} + \text{C}_{30} \text{ 1, 14-diol}]} \quad (1)$$

$$\text{DSI} = \frac{[\text{saturated C}_{28} + \text{C}_{30} \text{ 1, 14-diol}]}{[\text{saturated} + \text{unsaturated C}_{28} + \text{C}_{30} \text{ 1, 14-diol}]} \quad (2)$$

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:

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

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<sub>28</sub> and C<sub>30</sub> 1,14-diols in a sediment core from the Western Bransfield Basin ([Willmott](#)

[et al., 2010](#)). However, unlike the Arabian Sea, C<sub>30</sub> 1,15-diol concentrations are low, whereas C<sub>28</sub> and C<sub>30</sub> 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:

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

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<sub>28</sub> 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<sup>6</sup> 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. \(2009\)](#).

Download English Version:

<https://daneshyari.com/en/article/5162238>

Download Persian Version:

<https://daneshyari.com/article/5162238>

[Daneshyari.com](https://daneshyari.com)