

HYDROGEN ISOTOPIC VALUES OF LONG-CHAIN DIOL ISOMERS IN SEDIMENTS ACROSS A SALINITY GRADIENT

J. Lattaud, Z. Erdem, G. M. Weiss, M. T. J. van der Meer, E. C. Hopmans, D. Rush, J. S. Sinninghe Damsté, S. Schouten

NIOZ, Royal Netherlands Institute for Sea Research, Department of Marine Microbiology and Biogeochemistry (MMB), and Utrecht University, PO Box 59, 1790 AB Den Burg, The Netherlands

Long-chain diols (LCDs) are widely used to reconstruct past environmental changes. They occur widespread in marine environments but also in lakes and rivers. In marine settings, LCDs can be used to reconstruct past sea surface temperatures via the Long-chain Diol Index (LDI¹). However, this proxy is potentially biased in coastal environments under riverine influence due to the contribution of riverine LCDs, which alter the signature of the marine LCDs^{2,3}. The fractional abundance of the C₃₂ 1,15-diol can be used to infer the input of riverine LCDs³ but it is uncertain how the different LCDs are affected by this riverine input.

Here we used the hydrogen isotope composition (δD) of LCDs to determine their source (marine or freshwater) as hydrogen isotopes are known to be different between river and marine waters. Furthermore, it would be interesting to determine if the δD of LCDs is related to salinity as other biomarkers do, e.g. alkenones^{4,5}, palmitic acid⁶ or brassicasterol⁶.

To investigate these questions, we used surface sediments across a salinity gradient (28 to 36 psu) in the Gulf of Mexico from the Atchafalaya River mouth until 2000 m depth (Fig. 1).

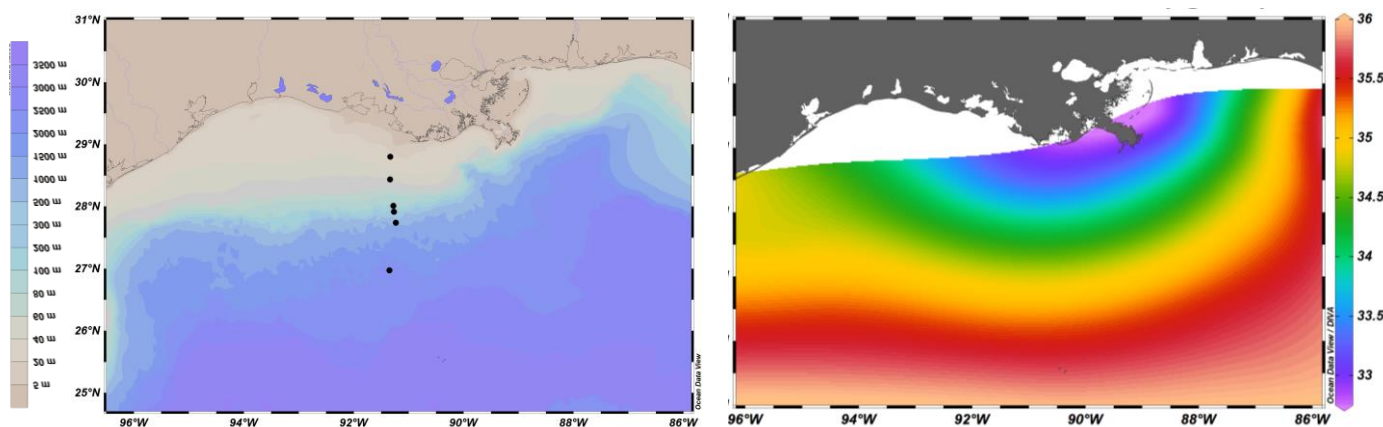


Figure 1 Location of the surface sediments and annual sea surface salinity.

The LCD distribution is dominated by the C₃₀ 1,15-diol, with fractional abundance between 0.4 to 0.7 and increases with increasing distance from the river mouth. On the contrary, the fractional abundance of the C₃₂ 1,15-diol decreases with increasing distance from the river mouth (0.2 to 0.05), aligning with previously published results^{2,3}. To measure the hydrogen isotope ratios of the different isomers we used semi-preparative liquid chromatography (LC) and gas-chromatography isotope ratio mass spectrometry (GC-irMS). This LC method, which has previously been developed for carbon isotopes measurements on LCDs², was adapted for

δD measurements. To avoid isotope fractionation as a results of the LC step, we aimed to retrieve at least 90% of the LCD isomer in a single fraction.

The δD ratios of the C_{32} 1,15-diol were similar in all surface sediments ($-199 \pm 2\text{‰}$, $n=4$) and do not reflect changes in salinity suggesting as previously hypothesized that the C_{32} 1,15-diol is riverine produced. However, δD ratios of the C_{30} 1,15-diol and integrated $C_{37:2}$ and $C_{37:3}$ alkenones were more enriched with increasing salinity (-164‰ to -154‰ , $n=6$ and -185‰ to -178‰ , $n=5$, respectively). The difference in δD ratios for the two LCDs indicates different source organisms. These enriched values, in combination with a salinity effect suggest that this diol is primarily marine sourced as marine lipids, including alkenones, have shown to increase in δD ratios with increasing salinity in culture studies^{4,6,7,8}. This raises the potential of the C_{30} 1,15-diol to be used as a salinity proxy (cf. alkenones⁹). Indeed, preliminary results on cultures of *Nannochloropsis* spp. showed that the δD ratios of the C_{32} 1,15-diol (main diol in cultures of *Nannochloropsis*¹⁰) also show a positive correlation with salinity.

In contrast, δD ratios of cholesterol show an opposite relationship with salinity, with depleted δD ratios corresponding with higher salinities, fitting with previously published results from a Japanese transect⁵. This indicates that cholesterol is originating from terrestrial plants close to the river mouth and from phytoplankton in the open-ocean environment and thus indicates a shift of producing organisms and not a relationship to salinity.

Alkenones and the C_{30} 1,15-diol show similar trend: δD ratios increase with increasing salinity leading to the conclusion that δD ratios of the C_{30} 1,15-diol can be used to trace salinity in a similar manner the δD ratio of alkenones do. Whereas the δD ratios of the C_{32} 1,15-diol show no influence of salinity, and can therefore be used to track freshwater input or reflect the δD of the riverine water.

References

- ¹Rampen et al. (2012) *Geochim. Cosmochim. Acta*, 84, 204–216.
- ²De Bar et al. (2016) *Org. Geochem.*, 184-195.
- ³Lattaud et al. (2017) *Geochim. Cosmochim. Ac.*, 202, 146-158.
- ⁴Schouten et al. (2006) *Biogeosciences*, 3, 113–119.
- ⁵Chikaraichi et al. (2005) *Limnol. Oceanogr.*, 50(6), 2005, 1763–1770.
- ⁶Sachs et al. (2016) *Geochim. Cosmochim. Ac.*, 189, 96-109.
- ⁷M'Boule et al. (2014) *Geochim. Cosmochim. Ac.*, 130, 126–135.
- ⁸Weiss et al. (2017) *Biogeosciences*, 14(24), 5693-5704.
- ⁹Weiss et al. (accepted) *Geochim. Cosmochim. Ac.*
- ¹⁰Rampen et al. (2014) *Geochim. Cosmochim. Ac.*, 144, 59–71.