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Interactive comment on "A quest for the biological sources of the ubiquitous long chain alkyl diols in the marine realm" *by* Sergio Balzano et al.

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Balzano et al. report an attempt to identify the sources of long-chain alkyl diols in samples of marine particulate matter in the tropical North Atlantic. The major component that they observe, in common with most marine samples, is the C30 1,15-diol. However, this is not the main chain-length in microalgae known to produce alkyl diols. For example, in marine eustigmatophytes the major diol is the C32 1,15-diol and this is accompanied by other long-chain components such as n-alkenols and unsaturated alkyl diols. The use of 18S rDNA to identify possible sources of organic matter has been successful in other studies and thus the rationale for combining genetic and biomarker data is soundly based. The fact that a clear source could not be identified is salutary and raises useful questions as to how best to combine these techniques in future stud-

ies. The paper is well written and the datasets are extensive and nicely discussed. I support publication with some changes and corrections as set out below.

The Introduction provides all the background information, but the structure could be improved. The first few sentences are fine, but at line 52 the text jumps to various proxies that have been developed. I think that it would be better to move the information on possible sources (line 68) here so that the reader has a clear idea of the type of distributions found and the differences between species. This should include mention of which chain-lengths are abundant and what other biomarkers might be present. This might be incorporated into Supplementary Table S1. This Table also contains a number of unpublished results, but without detail. Some of these are surprising (e.g., Heterosigma) and it is a bit disconcerting to see them referred to as known diol producers when the information has not been published. Note that Rampen et al. (2012) were not the first authors to remark that the distributions in eustigmatophytes do not match those in marine samples (see Volkman et al., 1992).

The next paragraph can then introduce the proxies and add more discussion about their limitations. Like many biomarker proxies, these are empirically based from geographically limited datasets and in some cases do not have a strong mechanistic underpinning as to why they appear to correlate with oceanographic features such as temperature and upwelling. While a source of 1,14-diols is known from the diatom genus Proboscia which provides an explanation for why these isomers might be abundant where Proboscia is abundant, our lack of knowledge of the main source of the C30 1,15-diol weakens their use as a proxy. If the source can be identified then this will allow studies to underpin their use as proxy which is another justification for the type of work reported here.

In the methodology it is important to explain why base and acid hydrolysis was used rather than a simple solvent extraction. If the alkyl diols were present in polar lipids, as seems likely in Nannochloropsis, then this procedure converts them to free lipids. This is relevant to later discussion of the possible effects of non-living organic matter

(detritus) on the distributions. In aged samples, one might expect higher contents of free diols due to hydrolysis/degradation of polar lipids, but the method used here unfortunately does not differentiate between free and polar forms. It is well established that alkyl diols form the backbone of algaenans made by eustigmatophytes, but it is much less clear what other lipids they might occur in. Algaenans appear to be quite stable in seawater and are an unlikely source of free alkyl diols, but the possible role of other lipids is still uncertain.

The Discussion examines provides a good account of the reasons why the DNA results do not seem to match the measured abundances of the alkyl diols. I am a little concerned at the use of "LCD" as a shorthand for a variety of unrelated long-chain diol structures. I would restrict it to the C28–C32 group. It is quite likely that a number of distinct biosynthetic pathways have evolved over time in different organisms to produce compounds that are really only superficially similar in structure. To lump all these distributions together is not really appropriate.

The authors make a brief mention of other compounds found in Proboscia (line 402) and use this as evidence that this genus is an unlikely source of 1,14-diols in these particular samples. This is a useful observation. I would expand the discussion here to include other biomarkers known to be present in other producers of alkyl diols such as eustigmatophytes. Assignments of possible sources are usually much more robust when multiple biomarkers are used.

The Conclusion provides a nice summary of the problems of comparing DNA and biomarkers when their relative stabilities are so different. I agree that the choice of sample is very important. All samples of marine particulate matter are mixtures of living and dead material so it is important in DNA-biomarker studies to sample waters where living biomass is high (e.g. near-surface blooms). Also, if compounds exist as polar forms in living organisms then it is desirable to examine those compounds separately from hydrolysed forms in the same way that phospholipids can give information about living bacteria in a way that total fatty acids do not.

Minor points: I would use the common term eustigmatophyte rather than the more cumbersome eustigmatophycean, in the same way that we use diatom rather than bacillariophycean. Line 104: change to "these analyses". Line 121: no italics for "al." Line 139: It is not clear what the statement "cyanobacteria were not taken into account" means here. Were they present (even abundant), but not counted? The authors are undoubtedly aware that cyanobacteria were once proposed as a source of alkyl diols. Line 161: no spaces around the ":". Line 177: bis not Bis Line 180: 25 m not 2 5m. Line 183: SIM is usually an abbreviation for selected ion monitoring. If only these ions were run, rather than full scan, then there is a distinct possibility that other components would not be recognized. This need clarification. Line 184: the m and z in m/z should be in italics. Line 196: it is usual to use an n-dash (–) for number ranges. Line 198 and elsewhere: use a symbol prime (') not '. Line 207: dimethyl not Dimethyl Line 230: python-based Line 235: space after ")". Lines 236, 269, 521: no space before %. Line 282 and elsewhere: use correct $^\circ$ symbol. Line 282: if you use the expression "between" then you cannot state a range; either state "ranged from x to y" or "in the range x–y". Line 285: salinity now has a unit (mg/kg) and psu is no longer used. Lines 294, 297: use symbol $\times$ not x. Line 315: use station when referring to multiple stations, but Station when referring to a single numbered station. Line 393: correlated "with" rather than "to". Line 477: Cite Volkman et al., 1992 here rather than 1999. Line 531: Indent paragraph Line 542: space after comma Line 564: detritus not debris Line 677, 733, 756, 791, 800: Damsté. Line 871: subscripts for 30 and 32.

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