

Interactive comment on “Testing the D/H ratio of alkenones and palmitic acid as salinity proxies in the Amazon Plume” by C. Häggi et al.

Anonymous Referee #2

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This paper presents evidence from suspended water column particles in Amazon plume. The data show that palmitic acid dD values track water mass salinity changes (as a result of mixing between sea water and freshwater resulting in salinity and hydrogen isotopic gradients), but alkenones, which are commonly considered more specific algal biomarkers (haptophytes), do not. As many studies have proposed using alkenone dD to reconstruct paleosalinity changes, this study is the first to go down to the basics, using modern water column samples to test the viability of the approach. I think it is an important and timely piece of work, and should be published in Biogeosciences Discussions.

I have a few comments for the paper for authors to consider during revision.

1. The observation that palmitic acid, a compound produced by all organisms on Earth,

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display nearly constant hydrogen isotopic fractionation across large environmental and salinity gradient should be discussed further. There are all kinds of different algae and bacteria living in these water masses with different water chemistry. This observation would mean palmitic acid hydrogen isotopic fractionation relative to environmental water is highly conserved in various organisms. A couple of previous papers also support this conclusion. For example, Li et al (2009, GCA, 73, 4803) shows that palmitic acid hydrogen isotopic values are constant in the sediment core when δD values of other compounds show large variations: the most probable explanation for the constant palmitic acid δD values is that various organisms living in the water column display the same hydrogen isotopic fractionation relative to the sea water. Although Li et al., argue, based branched fatty acid δD values, heterotrophic bacteria have different hydrogen isotopic fractionation values, the fact that the resulting sedimentary combined PA δD values show constant values (hence faithfully recording sea water isotopic ratios) indicate either the contribution of heterotrophic bacteria is small (even in the sediments), or the suggested difference between phototrophs and heterotrophic bacteria is not manifested in the real natural system. The sediment data are particularly important for supplementing the evidence presented in this paper, because sediment will have, undoubtedly, large heterotrophic bacteria input. One possibility is to consider if the newly produced PA from a heterotrophic bacteria during biodegradation may actually have the same hydrogen isotopic values as the PA in the decomposing organic matter. It is not impossible to consider a scenario that, because PA exists in all organisms, the enzymes leading to produce this compound may share such a great deal of similarity, and hence the hydrogen isotopic fractionation relative to source water is all constant across different organisms. For heterotrophs some of the hydrogen on PA would come from food rather than water, but perhaps that proportion is relatively small when all heterotrophs are considered.

2. To say that when alkenone concentrations are higher than 10 ng/L, its hydrogen isotopic ratios are correlated to water δD and salinity is an overstatement. P values are too high, and if residual is plotted, it is too large across the salinity gradient. If

alkenone advection is the culprit, surely PA will also be affected. If the argument is the PA gets degraded faster hence the influence on hydrogen isotopic ratios is smaller than alkenones (which is more recalcitrant), one has to explain why regenerated PA from decomposers would not have been messed up for its H isotopic signal. I think overall alkenones simply do not track water hydrogen isotopic ratios or salinity trends. The main reason is probably the species effect and do not think the C37/C38 ratio is a reliable indicator of species (the ratio changes at different grow rate and salinity, and in particular different strains of the same species). E Hux has much greater hydrogen isotopic fractionation than the coastal species I Galbana, and any water isotopic signal (about 40 per mil in modern Amazon plume) is simply overwhelmed by the species effect. Clearly, the percentage of galbana and E hux does not change linearly across the salinity gradient, otherwise one could still expect to see some kind of linear relationship between alkenone dD and salinity. This corroborate with the results from Chesapeake Bay where species effect basically cancels the salinity effect.

3. I do not think paired measurement of dD values of PA and alkenones will improve paleosalinity reconstruction based on the results from this study: the chances are that more confusion will be generated when two disagrees. However, I would suggest in future get the core top sediments across this salinity gradient, and measure the hydrogen isotopic ratios of PA and alkenones. Sediment would integrate all input sources, include heterotrophic bacteria, and can serve as a better test or calibration of paleosalinity reconstruction using PA dD values.

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