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## ***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 #1**

Received and published: 22 September 2015

Title: Testing the D/H ratio of alkenones and palmitic acid as salinity proxies in the Amazon Plume. Authors: C. Häggi, C. M. Chiessi and E. Schefuß.

General comments:

I have read this manuscript with great pleasure. The authors have taken SPM samples from the Amazon plume along a salinity gradient and analyzed the hydrogen isotopic composition of the water, haptophyte derived alkenones and the more generally produced C16 fatty acid in order to test the hydrogen isotopic composition of organic molecules as potential paleosalinity proxy. They observed a good correlation between salinity and water  $\delta D$ , as expected and also between the C16 FA and salinity. The relationship between the hydrogen isotopic composition of the alkenones and that of water and/or salinity is less obvious, especially at low alkenone concentrations. The

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same holds for the alkenone based UK'37 paleotemperature proxy and measured temperature, this correlations is also not very good at low alkenone concentrations. The authors discuss this very thoroughly and I think the discussion is valid, although I would perhaps put the emphasis slightly different. I think this is an interesting contribution to the ongoing development, testing, application and evaluation of biomarker hydrogen isotopic composition as potential paleosalinity proxy and therefore I think it should be published in Biogeosciences.

As mentioned above, I think I would put the emphasis a little different. The authors very delicately suggest the option of overprint of the signal by advection of allochthonous alkenones especially at low alkenone concentrations. I think this is most likely the main reason for the lack of temperature and  $\delta D$  correlations between measured and alkenone derived values when the low concentration samples are included. Alkenones are less susceptible to degradation resulting in a relatively large fraction old or “fossil” alkenones in every individual SPM sample and this fraction is probably larger at low concentrations. The turnover rate of fatty acids is higher than that of alkenones and a large fraction of the C16 FAs will have been produced in the water mass they were obtained from, resulting in a better correlation between the C16 FA  $\delta D$  and water mass properties. SPM samples represent a snapshot in time and space which makes it really easy to miss an algal bloom or the production season of specific biomarker lipids such as alkenones. In that sense it would have been nice to compare the presented results with cell counts or molecular technique based community composition estimates. There are for instance alkenone producing haptophytes that thrive in low salinity environments, but their production season might be different from the more open ocean species (assuming that the authors did catch the open ocean alkenone production season). The “fossil” alkenones that affect the UK and  $\delta D$  correlations at low concentrations might be derived from other water masses, but also from different time intervals, possibly re-suspended from the (shelf) sediment and transported by the Amazon outflow. This is exactly why the authors suggest to analyze both C16 FAs (or another more general lipid) and alkenones and I think that is a good suggestion.

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However, the C16 FA has its own potential biases. It has become clear that the hydrogen isotopic composition of lipids from photoautotrophic organisms are correlated with salinity and/or reflect the  $\delta D$  of the water and photoautotrophic organisms fractionate to a similar extent. However, heterotrophic organisms fractionate very differently and might show no or a different relationship with salinity. The C16 FA can be derived from many different organisms and different contributions from organisms with different metabolisms could potentially affect the hydrogen isotopic composition of FAs. Fortunately, it seems that in many of these open ocean water column ecosystems photoautotrophic microorganisms are the dominant contributors to the C16 FA pool. The high turnover rate of the fatty acids also make them less interesting for paleo reconstructions on longer time scales.

I think the authors should emphasize the difference in turnover rates between FAs and alkenones a bit more and the perhaps put less emphasis on less alkenone production at low salinities.

Specific comments:

Page 2; line 14 to 19: I don't think it is necessarily true that alkenone production is low at low salinity, light limitation is something different. With sampling SPM during a cruise it is relatively easy to miss the main "production" season. Haptophyte community composition analysis might help answer these questions in the future.

Page 4; line 1 to 3: This is not what Kasper et al. 2015 have suggested. They suggested that there is no clear glacial interglacial  $\delta D$  alkenone shift because during the glacial the core location was closer to the coast due to low sea level, resulting in more freshwater influence (low salinity and  $\delta D$  water) and more negative  $\delta D$  alkenone values than "normally" found during glacials. On top of that there might be a small species effect. Species variability did not make salinity reconstructions impossible, they suggest that salinity might not have changed that much.

Page 6; line 8: methylated?

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Page 10; line 19: Schouten et al., 2006 does not discuss coastal haptophytes. This reference belongs to the first half of this sentence.

Page 12; line 17 to 19: I agree that at low alkenone concentrations the fraction “fossil” might be large and affecting  $\alpha$ , for instance, but could it be possible the authors missed the haptophyte bloom and/or main alkenone production season?

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