Response to Anonymous Referee #1

(Referee's comments in italics.)

Our response 1.0:

We would like to thank the referee for the very valuable comments and suggestions.

This modelling study seeks to test whether the oceanic distribution of dissolved ^{230}Th could serve as an indicator of reduced biogenic $CaCO_3$ formation as the ocean acidifies due to anthropogenic CO_2 emissions. It proposes that ^{230}Th concentrations, particularly in the deep ocean, may be a more sensitive indicator of such change than direct observations of changing alkalinity in the surface ocean. In some ways, the modelling work described is a rather incremental advance relative to earlier work assessing the ^{230}Th response to change in the $CaCO_3$:POC ratio presented in Heinze et al. 2006. The present manuscript, however, focuses specifically on testing how this ratio might be influenced by future ocean acidification, and whether this could be detected by ^{230}Th measurements.

The ability to detect systematic change in the production of biogenic $CaCO_3$ in response to ocean acidification would be a useful tool, making this modelling endeavour potentially useful. The idea that ^{230}Th may allow such detection is not intuitive, but interesting and worthy of consideration. So the general direction of this contribution is welcome. I am, however, unsure from the present manuscript that the utility of ^{230}Th to assess $CaCO_3$ flux has been demonstrated.

Our response 1.1:

This study here goes beyond the work of Heinze et al. (2006), where only the effect of an instantaneous switch in $CaCO_3$ rain ratio for one single grid point time series has been shown and only a few lines of text were devoted to ocean acidification (Figure 8 and pages 10-11 of Heinze et al. (2006)). In our study here, we investigate the global ocean ^{230}Th reaction for a series of realistic CO_2 emission scenarios, we employ an improved model with respect to simulation of the $CaCO_3$:POC rain ratio pattern, have recalibrated the scavenging rate constants, and add an analysis of the time of emergence of a clearly identifiable signal in ^{230}Th. Further, we test the ^{230}Th reaction for different sensitivities of $CaCO_3$ to ocean acidification (based on the option as used in the study by (Ilyina et al., 2009). In addition, there seems some urgency to establish methods for detecting large-scale ocean acidification impacts as the respective integrated effect on ecosystems is not well known (see Gattuso et al. (2015), citation: "*Most studies have investigated the effects of ocean acidification on isolated organisms; far less is known about the effects on communities and ecosystems.*"). Therefore, our study here is fully justified. We address possible improvements of the assessment of $CaCO_3$ fluxes through ^{230}Th below.

1. Threshold for detection: The authors assume that detection of change in ^{230}Th depends only on the analytical uncertainty of measurement. Measurements of ^{230}Th in seawater shows significant spatial and temporal variation, however, which far exceed measurement uncertainty. Some of this variation reflects known processes, such as productivity or large-scale circulation, which cause consistent spatial patterns. But other variation is akin to 'noise', caused by seasonality of particle flux, eddying circulation, variability in boundary scavenging etc. To assess the possibility to detect change in the profile of ^{230}Th due to variation in the composition of settling particles requires consideration of the natural variability of the ^{230}Th field. One way to consider this might be to statistically compare closely spaced samples in the ever-growing observational ^{230}Th dataset to assess small-scale natural variability. My guess is that a more realistic detection threshold is likely to be 2 to 3 times higher than the value assumed in this study. That would not prevent detection in the deep ocean (e.g. in Fig 9) but

would delay the date of detectability in that setting, and would prevent detection at shallower depths. Intuitively that seems realistic given that intermediate depths typically show quite large (and presently poorly explained) temporal changes in ^{230}Th concentrations.

Our response 1.2:

We agree with the referee that the detection levels shown in Figures 8, 9, and 10 would be the earliest possible (assuming that the preindustrial levels would be known as well). This has also been written in the text (page 10, line 22). If other factors than changes in $CaCO_3$ would occur this could change. However, Figures 8-10 show large-scale averages for entire oceans within the model world. It should be legitimate to show this earliest possible detection threshold for the average of a large region. Figures 8-10 do not make a judgement on how good an observing system should be to fully exploit the potential of ^{230}Th to diagnose large-scale changes in $CaCO_3$ flux. Figures 8-10, however, demonstrate the potential of ^{230}Th to detect such changes. For large-scale averages, the noise should cancel out. We plan to add a few sensitivity experiments to clarify the issue raised by the referee. Because we use an annual average constant velocity field, adding "natural variability" is not possible in our model set up in a dynamical sense (see also our response 1.3). This would require work on the dynamical physical model delivering the velocity field including synoptic forcing, new spin-ups of the circulation model as well as the biogeochemical model, and possibly new parameter tuning. We will explore simpler methods in order to address the point. We are currently thinking about two options. We could use a Monte-Carlo-sub-sampling method taking into account different length-scales away from the respect central model grid point and see how robust the signal for detection would remain. Another method would be to randomly perturb the nutrient uptake velocity (V_{max}) and the half saturation constant (K_s) in the Michaelis-Menten formulation for biogenic organic particle production. We also will try to find estimates on the area of influence for Eulerian time series stations (and how it may change with depth).

2. Sensitivity to other changes: To be a useful monitor for $CaCO_3$ flux change, future ^{230}Th concentrations must be more responsive to that process than to other possible changes. There is very little consideration in the manuscript of other likely controls on the ^{230}Th distribution. These might include future changes in circulation driven by changing wind fields or freshwater inputs; changing productivity of organic carbon due to circulation changes; changing remineralisation of organic carbon due to altered O_2 levels; changing fluxes of silicate dust due to changing winds and continental aridity; or changing ballasting related to ecosystem change. I do not have an instinct about whether any such changes are likely to generate substantial changes in the ^{230}Th field, but this seems a fundamental issue for a modelling study such as this one to address. Can the authors do more to assess whether $CaCO_3$ fluxes are really the dominant control on ^{230}Th change? Or only one of several global changes that will alter the field?

Our response 1.3:

Our paper focuses on ^{230}Th as a tool for detecting $CaCO_3$ production changes. We have discussed the limitation of our approach on page 16, lines 10-22, including the use of a constant velocity field. We will extend this discussion in order to spell out the various uncertainty sources more clearly to the reader. For this we also will explore the possibility of further useful sensitivity experiments (as the one on randomly varying V_{max} and K_s, see our response 1.2). We will choose a limited number of parameters that we will perturb and assess the effect on the marine ^{230}Th distribution as compared to the effect of varying $CaCO_3$ fluxes, such as variations in the dust flux (i.e., the admixture of inert clay material from continental sources), natural variability in the rain ratios POC:$CaCO_3$:BSi or changes in the particle specific scavenging. Potentially, we also could think of changing the velocity

field though this would be done through a kinematic and not dynamically consistent approach. Thus, the approach may be of limited explanatory power. In such an approach, we would combine the presently used field with a pseudo-glacial field of reduced overturning and by scaling such a combination with the meridional overturning variability time scale as found in simulations with a fully-fledged earth system model.

3. Accuracy of the model: The ^{230}Th model used is well established and has been thoroughly documented in the literature before, but there are some presentational issues in the present manuscript that limit the reader's ability to assess its prediction of future ^{230}Th change:

i. Since Heinze 2006, there are significantly more ^{230}Th observations, including long ocean sections (see http://www.egeotraces.org/?group=Dissolved%20Natural%20Radionuclides,variable=Th%20230%20dissolved). It is now possible to directly compare modelled sections (e.g. Fig 3) with observations, and this should be done in this manuscript. Doing so reveals some quite important discrepancies, particularly in the deep ocean, which is being touted here as a sensitive indicator for changing $CaCO_3$ fluxes. These discrepancies include deviations related to scavenging at the seafloor and in MOR plumes. If these processes are not considered, the deep-ocean sensitivity of ^{230}Th to downward particle flux may well be overestimated.

Our response 1.4:

We intend to add a meridional Atlantic cross section of dissolved ^{230}Th for both model and observations and discuss the discrepancies and their potential implications for diagnosing $CaCO_3$ flux changes through ^{230}Th.

ii. Perhaps I have misunderstood, but Figures 8-10 indicate that even the control run shows a significant change in deep ^{230}Th, despite the lack of $CaCO_3$ change in this run. This is puzzling, and seems to suggest a problem with the long-term handling of ^{230}Th in the model?

Our response 1.5:

We explain this already in the submitted manuscript on page 11, lines 1-4: "For constant $CaCO_3$ production, the intermediate and deep water ^{230}Th activities start to rise around year 2100 as well (see black curves in Figures 8-10). This effect is due to the increasing dissolution of $CaCO_3$ particles in the water column in parallel with downward mixing of waters that carry anthropogenic loads of dissolved organic carbon and hence subsurface and deep acidification." We will expand this paragraph in order to explain this more clearly. The effect becomes important only in areas, where anthropogenic carbon is mixed down quickly and induces a significant shoaling of the $CaCO_3$ saturation level and $CaCO_3$ lysocline as wall the Carbonate Compensation Depth through deep-water acidification. Most of the deep Pacific is not really influenced much by this within the 21st century.

iii. Less significant, but it would also be good to see how the model predicts change as a profile or section, rather than as a time series at a single depth. As you go to greater depth in the ocean, the residence time of ^{230}Th increases, so change might be slower, but the flux of organic carbon decreases so the influence of a $CaCO_3$ change will be more important. Seeing how such depth-related effects compete in the model would be interesting, and help to assess how realistic it is in representing the natural cycle.

Our response 1.6:

We plan to add either the same section as mentioned in response 1.4 or representative profiles for subsequent time slices based on data from the additional sensitivity experiments. We will then discuss these diagrams for depth-related effects.

Overall, these three concerns leave me unconvinced that this study is ready for publication. The idea of using ^{230}Th to assess $CaCO_3$ fluxes is interesting, however, so I'd encourage the authors to seek to address these issues. A revised version of the work could then be a useful contribution.

Our response 1.7:

We will address this issue in the revised version, please, see our responses 1.3-1.6.

Other comments:

P4-6: The description of the model set up could be reduced, given that this is a previously described model, and that some aspects (e.g. C isotopes) are not relevant to this study.

Our response 1.8:

In reviews of previous publications, where we omitted a detailed model description, the respective referees asked us to include a more detailed description so that readers would not have to read another (or more) articles in parallel. We, therefore, would like to keep the model description but will remove those elements, which are not relevant for this manuscript.

P7: It's good to see the GEOTRACES data used, but the source of this data is strangely attributed. Neither de Baar nor Boyle were involved in collection of ^{230}Th data. Please cite the relevant papers directly for this data (e.g. Hayes et al., Deng et al) in addition to the Mawji et al. paper.

Our response 1.9:

We will add respective references to the paper – many thanks for pointing this out.

Are any spatial changes expected because of changing rain-ratio? High latitude waters will decrease saturation faster than mid-latitude, so changes may be more acute there. I wonder if looking at the relative change in ^{230}Th between regions may be a more sensitive indicator of the specific response to changing carbonate saturation than the general deep-ocean response?

Our response 1.10:

This is an interesting metric for analysis – many thanks. We will look for such changes between selected regions and discuss this in the revised manuscript. See also our response 2.3 to Referee #2 concerning the comparison between different regions.

REFERENCES:

Gattuso, J. P., Magnan, A., Bille, R., Cheung, W. W. L., Howes, E. L., Joos, F., Allemand, D., Bopp, L., Cooley, S. R., Eakin, C. M., Hoegh-Guldberg, O., Kelly, R. P., Portner, H. O., Rogers, A. D., Baxter, J. M., Laffoley, D., Osborn, D., Rankovic, A., Rochette, J., Sumaila, U. R., Treyer, S., and Turley, C.: Contrasting futures for ocean and society from different anthropogenic CO2 emissions scenarios, Science, 349, ARTN aac4722, 10.1126/science.aac4722, 2015.

Heinze, C., Gehlen, M., and Land, C.: On the potential of Th-230, Pa-231, and Be-10 for marine rain ratio determinations: A modeling study, Global Biogeochemical Cycles, 20, Artn Gb2018, 10.1029/2005gb002595, 2006.

Ilyina, T., Zeebe, R. E., Maier-Reimer, E., and Heinze, C.: Early detection of ocean acidification effects on marine calcification, Global Biogeochemical Cycles, 23, Artn Gb1008, 10.1029/2008gb003278, 2009.