Interactive comment on "A global scavenging and circulation ocean model of thorium-230 and protactinium-231 with realistic particle dynamics (NEMO–ProThorP 0.1)" *by* Marco van Hulten et al.

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The authors of this paper claim that they report on an improved formulation of a global scavenging and circulation ocean model of Th and Pa nuclides, using realistic particle dynamics. With "realistic", the authors mean that they now consider 2 particle size classes rather than one, and they use the sum of Fe, Mn, Al and Ti to calculate the concentration of suspended particulate matter from terrestrial (mineral matter) sources. Also, single Kd values are used to parameterize particle sorption. Finally, the paper reads more like a progress report than a paper, and needs improvement in style and clarity.
In addition, I have some serious reservations on this paper. First, I question their use of 'realistic' in the title, and recommend its deletion. While Hayes et al., 2015b (cited in the paper), found strong evidence for a particle concentration effect on Kd values in the Geotraces data sets from the North Atlantic Ocean, that is ignored in the model. The particle concentration has been documented numerous times (not just by Honeyman and Santschi, 1989, cited in Hayes et al., 2015b) for radioisotopes of Th and other elements, and is ascribed to the existence of sorbing and complexing colloidal organic matter in the filter-passing fraction. This then causes linear correlations of the log of the particle-water partition coefficient (K or Kd) vs. the log of the suspended particle concentration, as well as linear correlation of the log of the sorption rate constant vs. the log of the suspended particle concentration. It would gather that this should be pretty straightforward to incorporate that in the model. This would be important, especially if they intend to model boundary scavenging and nepheloid layer scavenging, where particle concentrations would be expected to be higher, and associated Kd values lower.

Another omission is the fact that the rich experimental data sets, documenting the facts that pure CaCO3 and SiO2 surfaces are poor sorbents for radioisotope and metal ions, compared to the associated natural organic matter compounds with these phases. Chuang et al. (2014, 2015) and Lin et al. (2017) clearly showed that the sorption of Th and Pa radionuclides onto diatoms and coccolithophores is due to sorption on associated organic matter molecules, and not the mineral phase. It must also be noted that most of the experiments with supposedly pure particle phases in the literature did not pre-clean their supposedly "pure" CaCO3 and SiO2 surfaces, which can be critical for the outcome of the experiments. For example, the cited experimental results from Geibert and Usbeck (2004) did not preclean their particle phases. Many of these papers mentioned above also review the literature on this subject, whereas the references cited in van Hulten et al. manuscript do not. Van Hulten et al. then simply use a limited field data set, and pick one single value from each radionuclide and each phase in Table 2 (see more comments below). Their model has plenty of adjustable parameters

that can be tuned one way or the other to fit the mostly open ocean observations, which only means that their chosen Kd value might be realistic in the sense that it would be within the range of observed values (which, incidentally, can be quite a bit larger than cited in the manuscript).

Table 2. The chosen Kd values for POC, Silica, CaCO3, and lithogenics, all big and small, are unrealistic and highly questionable, as they disagree with actual measurements (see references below). Also, the nomenclature and units used in this table are non-conventional. At least, it should be mentioned what the unit of Kd (Mg/g) in Table 2 is, i.e., 10ˆ6 g water/g particles. It is not obvious as M can be used for 10ˆ3 and for 10ˆ6.

In Table 3, they review the very limited data sets that they used for their model. By doing that, they omit data sets from many other researchers and oceans. For example, the Th and Pa nuclide data from the Gulf of Mexico (Roberts et al., 2009), or the 230Th and 234Th data sets from the North Atlantic by Guo et al. (1995), which also exhibit the common particle concentration effect, could have been used as well.

Table 4 is totally confusing and to some extent, mislabeled, and needs a better caption stating what the numbers in each column signify, and their units.

It should therefore be more clearly stated in the manuscript what they are doing with a very limited data set from which they chose their adjustable parameters. Thus, using more realistic values of K, for example, the simulations might be different.

Another limitation is that only towards the end of the paper is it stated that the large/small particle designation is using a 50 μm boundary. It should then also be considered that not everywhere in the ocean do the large particles sink fast, and the small ones slow. For example, Xu et al. (2011) and Hung et al. (2010, 2012) demonstrated through thorium radioisotopic evidence and microscopic analysis of sediment trap particles collected in oligotrophic waters in the Gulf of Mexico and the Pacific Ocean that the fast sinking particle assemblage is mostly composed of smaller than 50μm diatom

particles. Thus, without considering this detailed data set, the modeling of van Hulten et al. is, to say the least, unrealistic.

In conclusion, I do not recommend this paper for publication without substantial revisions.

References cited above:

Chuang, C.-Y., Santschi, P.H., Jiang, Y., Ho, Y.-F., Quigg, A., Guo, L.D.,, Ayranov, M., Schumann, D. 2014. Important role of diatoms in the scavenging of particle reactive radionuclides, Thorium, Protactinium, Lead, Polonium and Beryllium, in the ocean: a case study with Phaeodactylum tricornutum. Limnol. Oceanogr., 59(4), 1256–1266.

Chuang, C.-Y., Santschi, P.H., Wen, L.S., Xu, C., Zhang, S., Ho, Y.-F., Schwehr, K.A., Jiang, Y., Ho, Y.F., Schwehr, K.A., Quigg, A., Hung, C.-C., Guo, L.D.,, Ayranov, M., Schumann, D. 2015. Binding of Th, Pa, Pb, Po and Be radionuclides to marine colloidal macromolecular organic matter. Marine Chemistry, 173, 320–329.

Guo, L., Santschi, P.H., Baskaran, M., and Zindler, A. 1995. Distribution of dissolved and particulate 230Th and 232Th in seawater from the Gulf of Mexico and off Cape Hatteras, as measured by SIMS, Earth Planet. Sci. Lett., 133, 117-128.

Hung, C.-C., Xu, C., Santschi, P.H., Zhang, S., Schwehr, K.A., Quigg, Guo, L., Gong, G.-C., A., Pinckney, J., Long, R., and Wei, C.-L. 2010. Comparative evaluation of sediment-trap and 234Th-derived POC fluxes from the upper oligotrophic waters of the Gulf of Mexico and the subtropical northwestern Pacific Ocean. Mar. Chem, 121, 132–144.

Hung, C.-C., Gong, G.-C., Santschi, P.H. 2012. 234Th in different size classes of sediment trap collected particles from the Northwestern Pacific Ocean. Geochim. Cosmochim. Acta, 91, 60–74.

Lin, P., Xu, C., Zhang, S., Sun, L., Schwehr, K.A., Bretherton, L., Quigg, A., Peter H. Santschi, P.H. 2017. Partitioning of natural radionuclide analogues for particle cycling

in the ocean (234Th, 233Pa, 210Pb, 210Po and 7Be) with biopolymers associated with coccolithophores: a case study with Emiliania huxleyi. Journal of Geophysical Research: Biogeosciences, 122, 2033–2045.

Roberts, K.A., Santschi, P.H., Hung, C.-C., Xu, C., Conte, M.H. 2009. Thorium vs. Protactinium fractionation in the ocean, as determined from particle-water partitioning experiments with sediment trap material from the Gulf of Mexico and Sargasso Sea. Earth Planet Sci. Lett., 286(1-2), 131-138.

Xu, C., Santschi, P. H., Hung, C.-C., Zhang, S. , Schwehr, K,A., Roberts, K.A., Guo, L.D., Gong, G.-C., Quigg, A., Long, R., Pinckney, J., Duan, S.W., Amon, R., Wei, C.-L. 2011. Controls of Th-234 removal from the oligotrophic ocean by polyuronic acids and modification by microbial activity. Marine Chemistry, 123, 111–126.