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Biogeosciences Discussions

Interactive comment on "Concentrations and ratios of Sr, Ba and Ca along an estuarine river to the Gulf of Mexico – implication for sea level rise effects on trace metal distribution" *by* S. He and Y. J. Xu

Anonymous Referee #2

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The manuscript presents data on temporal and spatial measurements of Sr, Ba and Ca concentrations across a coastal plain river in Louisiana, and frame the results in the context of potential effects of saltwater intrusion due to sea level rise.

I share many of the concerns raised by the previous reviewer, both for methodological and interpretation reasons.

Methods: As pointed out before, there was a lack of information about sampling methods, materials used, and processing procedures. In addition to materials, how were the

samples extracted from estuarine locations? Surface or bottom water? Were samples acidified on site, and how were they stored between collection and analysis (beyond "a cooler with wet ice"). I am particularly concerned based on the manuscript and the author's response to the other reviewer that there does not seem to be any filtration involved, raising the potentiality that the samples acidified before analysis yielded greater elemental concentrations than truly in the dissolved fraction. In the response to the previous reviewer, the authors say that they performed tests of filtered vs. unfiltered samples and did not find any difference between the two. This is a critically important point, and if these tests were performed they should be a major portion of the manuscript to verify that the methods produced accurate measurements. In particular, I wonder where the samples were taken for these tests (freshwater, marine, intermediate salinities, both?). This concern about methods is of principle relevance to the Ba concentration data, which show some odd patterns. Typically, Ba is elevated in fresh waters and then exhibits an oligohaline maximum where ions desorb from particles at the initial salt wedge, and show generally conservative mixing afterwards for the remainder of the salinity range. But the results shown are quite different, with high and variable Ba across the entire salinity gradient. Either this is a particularly unusual mixing dynamic for Ba in this particular system (which is never really addressed or explained) or these methodological issues resulted in different dynamics than observed in most systems for the truly dissolved fraction. I agree with the other reviewer that more context of the existing literature on Ba mixing/desorption dynamics in systems worldwide is necessary to interpret and explain the observations (assuming the methodological concerns are laid to rest).

There are also some odd patterns in the Sr and Ca data which appear to fall off of a conservative mixing line in several places. Why do the authors think this is? This leads to some quite noisy patterns of Sr/Ca ratios, with particularly wide ranges of values at the freshwater endmember. This is not addressed or explained, and is concerning. I wonder if the authors should graph the mixing curves separately for each season to see if the variation is reduced for a given time of year. As it stands, I would not feel

confident using either of these elements as animal movement tracers in the system, given the large apparent degree of variation across the estuary and at each endmember. One additional possibility that may be at issue here is the potential contribution of groundwater, which may introduce a third endmember and cause deviations from a two-endmember mixing dynamic. Is there evidence of groundwater contribution in this river?

Finally, the authors present their paper in the context of sea level rise and saltwater intrusion, concluding that their results show evidence that significant differences in elemental cycling. The authors also raise the issue of elemental toxicity at high concentrations, and the potential problem of Ba-injection with drilling fluids. This really seems like a red herring, as there is no evidence that their elemental concentrations come close to toxic levels. Further, the data don't really show any particularly unique aspect of saltwater intrusion on elemental dynamics, other than simply moving the mixing gradient further upstream. Also of note is that the study system has a salt barrier, so it's unclear whether saltwater intrusion is truly a concern or not. I would strongly recommend removing the seawater intrusion/sea level rise text, as it doesn't seem to add much to the paper and the data aren't particularly convincing about projected effects of sea level rise on a global scale, as the authors currently posit.

Interactive comment on Biogeosciences Discuss., 12, 18425, 2015.