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# ***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***

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Received and published: 12 December 2015

Reply to Referee #2. The reply of the authors is written after [AUTHOR'S RESPONSE], immediately after the comment of the referee.

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

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interpretation reasons.

[AUTHOR'S RESPONSE] First, we want to sincerely thank the reviewer for taking the time to review our manuscript. The comments and suggestions made are constructive and are all taken into careful consideration. We will incorporate them in our revised manuscript later, as explained below.

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”).

[AUTHOR'S RESPONSE] We thank the reviewer for pointing this out. This information is indeed important and we will add it in our revised manuscript. Briefly, all the water samples were taken approximately 30-50 cm below the surface. The samples were collected from piers reaching out about 8-15 m into the river channel with a grab sampler consisting of a 12-foot aluminum pole with a polyethylene bottle attached at the end of the pole. The samples were acidified to  $\text{pH} < 2$  at the time of collection in the field. On each trip, samples were collected in duplicate at one of the sites; however, subsequent analyses indicated no significant difference (less than 5%) in all constituents. As a result, duplicates data were removed from the data analysis. All the water samples were stored in a cooler with wet ice during transportation, and refrigerated until analysis. The above information will be added to our revised manuscript.

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

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tests were performed they should be a major portion of the manuscript to verify that the methods produced accurate measurements.

[AUTHOR'S RESPONSE] The point is well taken. We analyzed the water samples for element concentrations in two ways: 1) unfiltered samples with acid digestion, which yields 'total recoverable (EPA 200.7)' element concentrations (as described in the manuscript); 2) filtered samples without acid digestion, which yields dissolved element concentrations. The results show that for Ba, the dissolved (method 2) to total (method 1) ratio ranged from 0.70 to 1.01, with an average of 0.85. The average dissolved (method 2) to total (method 1) ratios for Sr and Ca are 0.95 and 1.02. In our revised manuscript, we will add the above information as well as replace the term 'dissolved' with 'total recoverable,' wherever it may cause confusion.

In particular, I wonder where the samples were taken for these tests (freshwater, marine, intermediate salinities, both?).

[AUTHOR'S RESPONSE] As described in the methods section, the samples were at six locations along an 88-km long reach of the Calcasieu River. Two locations show average salinity levels of <0.5, and average pH levels of <6.3. Therefore, one could consider these two locations from the upper river basin freshwater. For the lower 4 sites, the average salinities ranged from 3.05 to 19.91, so these sites can be considered as oligohaline water (Table 2).

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

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for the truly dissolved fraction.

[AUTHOR'S RESPONSE] We agree that Ba is usually elevated in fresh waters and then exhibits an oligohaline maximum, and shows generally conservative mixing afterwards for the remainder of the salinity range (e.g. Shaw et al., 1998; Walther and Nims, 2015). However, the mixing curves of Ba can be extremely different from the expected pattern. For example, Coey et al. (1997) showed that Ba concentrations in the Humber estuary increased almost linearly from salinity of 0 to 16. For the Calcasieu River, the Saltwater Barrier opens/closes depending on the freshwater flow above the barrier, and this may have changed/interrupted the mixing/desorption dynamics of Ba in this system. In the revised manuscript, we will interpret and explain our observations in the context of the existing literature on Ba dynamics in systems worldwide, taking the Saltwater Barrier into consideration.

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).

[AUTHOR'S RESPONSE] We have identified several studies on Ba spatial distribution in mixing zones around the world, including, among others: Wang et al., 2009; Nozaki et al., 2001; Stecher III and Kogut, 1999; Li and Chan, 1979. We appreciate the suggestion and will include the literature and thoroughly discuss this in our revised manuscript.

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,

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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?

[AUTHOR'S RESPONSE] We agree with the reviewer that submarine groundwater discharge (SGD) could be a significant contributor to the system and may serve as an additional source of Sr and Ca (e.g. Beck et al., 2013; Walther and Nims, 2015). However, we could not find any publications documenting evidence of significant groundwater contribution in this river. As the reviewer suggested, we remade graphs showing the mixing curves separately for each season for the Sr and Ca concentrations, and the Sr/Ca ratio (see attached/below). Overall, the data supports the interpretation of the linear relationship of Sr and Ca with salinity. The outliers may have made a noisy impression on the Sr/Ca pattern.

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.

[AUTHOR'S RESPONSE] We respectfully disagree that we have made such a conclusion as the reviewer stated above. While our data shows a clear trend of Sr and Ca with the salinity levels and proximity to the Gulf in this study, we cautiously stated that for low-gradient estuarine rivers with low freshwater discharge, such as the Calcasieu River, water chemistry upstream could experience substantial Sr and Ca enrichment.

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.

[AUTHOR'S RESPONSE] We mentioned a concern over Ba injection in the introduction, which may have been confusing. South Louisiana has a heavy concentration of oil

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and petrochemical industries (about 1/3 of all U.S. refineries). There are widespread concerns among government agencies and the general public regarding trace metal contamination in water and sediment in this region. However, we agree that the Ba concentrations found in our study do not reach the toxicity level; therefore, we mentioned in the discussion section that there is no evidence suggesting any effect on the Ba level from the surrounding petrochemical industry (Page 18439, line 1-3). We will further clarify this issue in the revised manuscript.

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.

[AUTHOR'S RESPONSE] Two of our six sampling sites (Sites 1 and 2) are located above the Saltwater Barrier (Fig. 1). The river water below the barrier, a reach that is over 60 km long, is affected by tidal water to different degrees. Saltwater intrusion in the Calcasieu River in southwest Louisiana has been a serious concern for the past decades. This was the reason for the construction of the Calcasieu River Saltwater Barrier in 1968 (e.g. LDWF 2012, USACE). In fact, saltwater intrusion is a widespread concern for many coastal rivers in south Louisiana, as the region faces rapid land subsidence, erosion, and sea level rise. Hence, the design of this study and the selection of the study sites reflected these concerns. Nonetheless, we will consider removing the phrase "implication for sea level rise effects on trace metal distribution" from the title in our revised manuscript.

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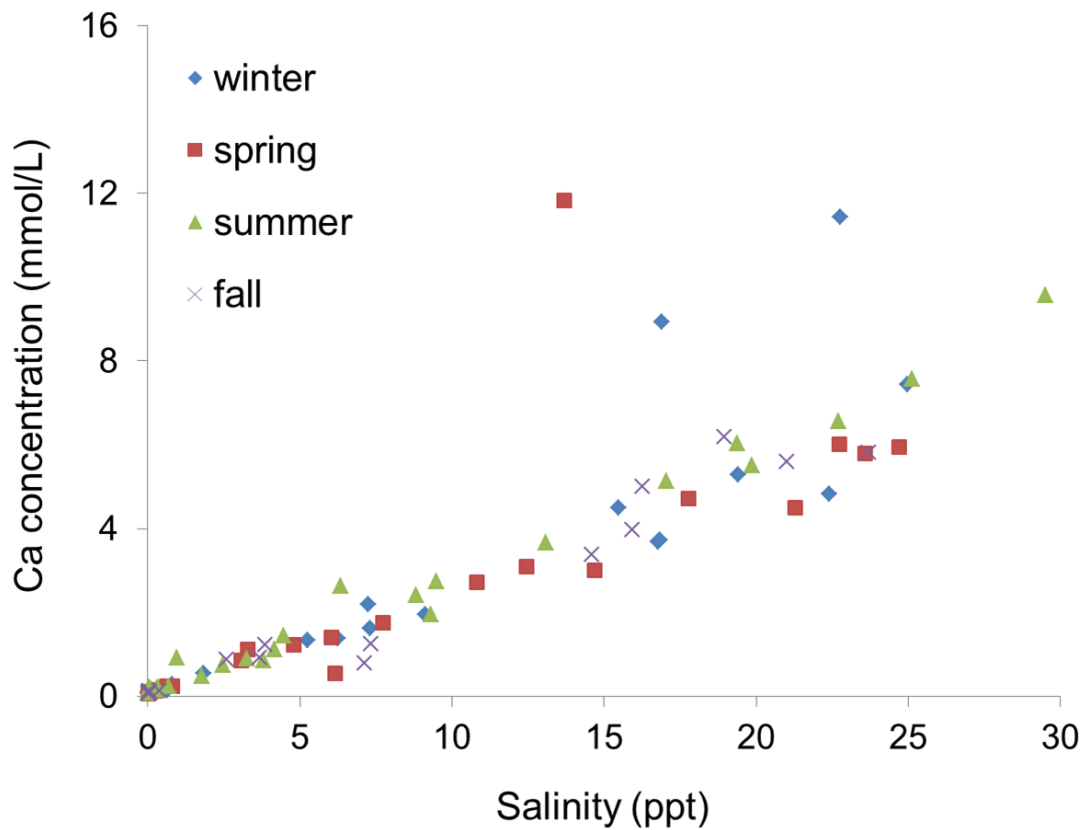


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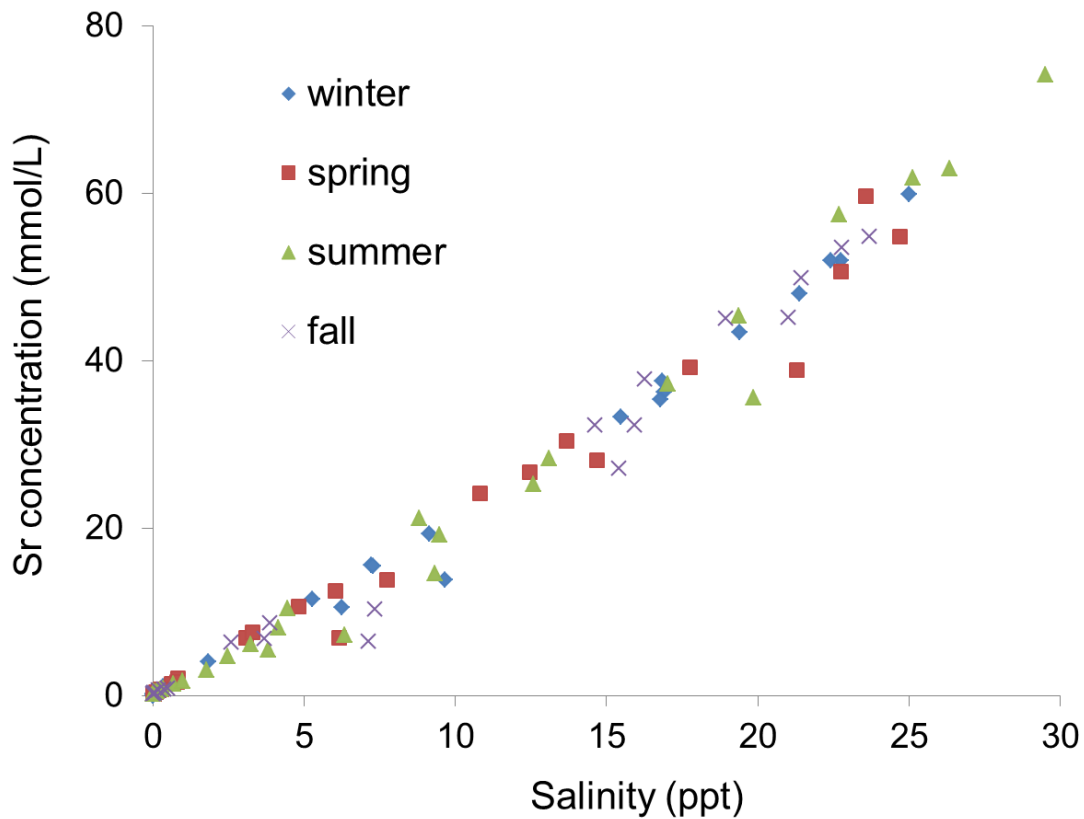


Fig. 2.

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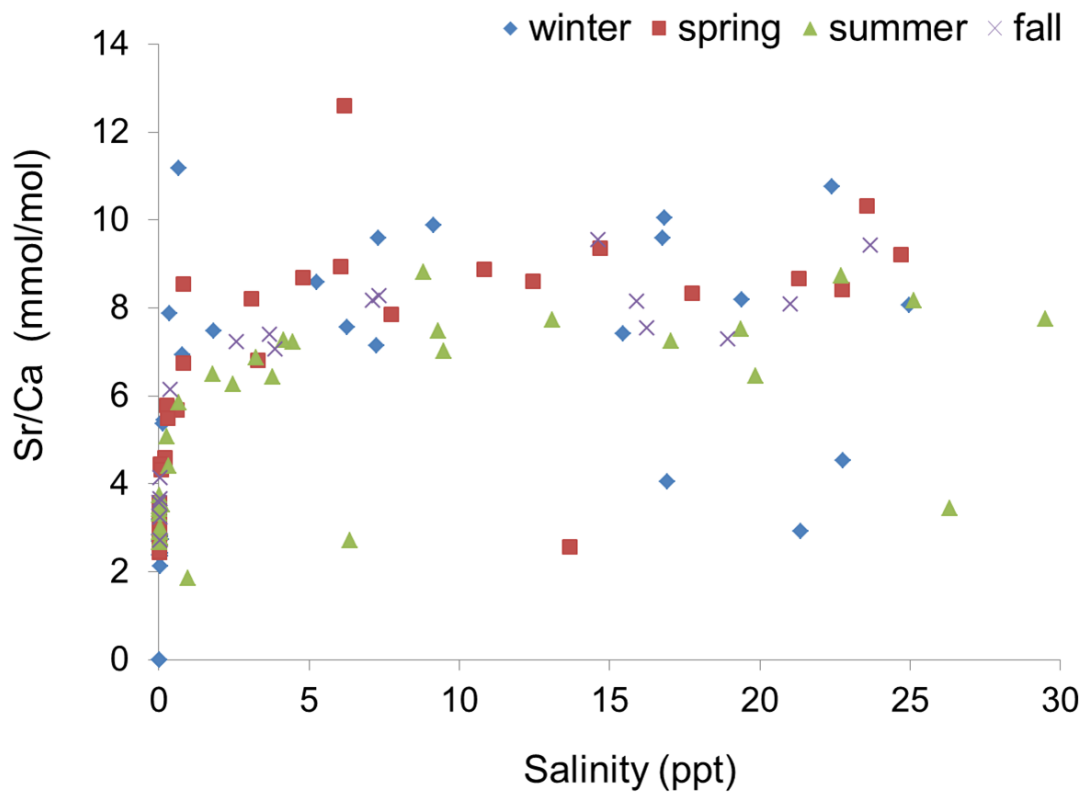


Fig. 3.

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