Biogeosciences Discuss., 12, C8119–C8124, 2015
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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: 1 December 2015

Reply to Referee #1. The reply of the authors is written after [AUTHOR'S RESPONSE], immediately after the comment of the referee.

The authors present an overview of Ca, Sr, and Ba concentrations in the Calcasieu River estuary in southwest Louisiana. I see several fundamental problems with the manuscript, some of which are addressable while others may not be.

[AUTHOR'S RESPONSE] First of all, we would like to sincerely thank the reviewer

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for taking the time to review our manuscript. We appreciate the reviewer's helpful comments and suggestions, all of which have been addressed and will be incorporated in our revised manuscript later, as explained below.

In particular, there is a fair amount of literature on estuarine Ba geochemistry (see Joung & Shiller, GCA 141: 303 doi: 10.1016/j.gca.2014.06.021, and references therein), as well as Sr (e.g., Xu & Marantonio, doi:10.1016/j.marchem.2007.01.004), that the authors seem unaware of. Most of these previous papers also provide higher quality data than that of the authors.

[AUTHOR'S RESPONSE] We thank the reviewer for the information. We were indeed aware of the two publications and found the findings very interesting. However, these studies were conducted near the Mississippi River/Atchafalaya River outlets in waters that are strongly affected by the freshwater flow of these two large rivers, while the Calcasieu River in our study is a small river and is very much affected by saltwater intrusion. The sampling locations of the two studies mentioned are also far offshore in open waters (south of Lat $\sim$29°30' N) when compared with the sampling locations of our study (north of Lat $\sim$29°50' N). Also, the scopes of these three studies are not entirely the same. We felt that the findings of Joung & Shiller and Xu & Marantonio had little connection with our results and we consequently did not cite them. Because of the differences, it is arguable which data are of higher quality than the others. Nonetheless, we appreciate the reviewer's comments and will cite the two publications in our revised manuscript later.

Some specific comments: 1. The methods section contains little information regarding detection limits or accuracy. I am astounded by their reported 0.05% reproducibility: it's difficult in this sort of work to get 1% reproducibility.

[AUTHOR'S RESPONSE] Thanks for pointing out the mistake, as it should be 0.05 or 5%. The method detection limits in our study for TSS, Sr, Ca, and Ba are 4 mg/L, 0.0088 μmol/L, 0.50 μmol/L, and 0.14 μmol/L, respectively. We will correct the error

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and add information on detection limits in our revised manuscript.

And, Fig. 6 would seem to imply that for Ba they could only determine concentrations to +/- 100 nM which is about 25% of their typical Ba concentration. This makes the Ba data fairly worthless, especially when compared to the many other estuarine Ba papers which have uncertainties for this element in the low nM range.

[AUTHOR'S RESPONSE] Thanks for spotting the mistake. That figure (relationship between Ba concentration and salinity) was made using data that had been rounded to the nearest hundredth. This resulted in the discontinuities which appeared in the figure due to the small range of the Ba concentration. We made a new figure using the true data (see attached/below). We will replace the existing figure with the one we made using un-rounded data (see attached/below) in our revised manuscript.

2. Although these elements are not especially contamination-prone, some information on clean techniques used would be relevant (e.g., types of samples bottle and how they were pre-cleaned).

[AUTHOR'S RESPONSE] Thanks for the suggestion. In our study, High Density Polyethylene (HDPE) bottles were used to collect water samples, and all the bottles were thoroughly acid-cleaned before use. All efforts were made to avoid any possible contamination in the field, during transportation, and in lab. This information will be added in the Methods section in our revised manuscript.

3. There can be significant desorbable Ba on suspended particles. Even at 30 mg/L SPM concentrations, acidification of unfiltered samples could have significantly increased the 'dissolved' Ba concentrations reported by the authors.

[AUTHOR'S RESPONSE] We agree that the level of SPM is not negligible with regard to the analysis of the trace element. Therefore, when we started our project, we first analyzed Ba, Sr and Ca in both filtered and unfiltered water samples (data not shown in the existing manuscript).We found that the unfiltered samples had a slightly, but

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insignificantly, higher Ba concentration, but showed no differences in the Sr and Ca concentrations. Hence, we mentioned in the Methods section that our measurements could be considered as "dissolved" even though the EPA method actually detects total recoverable analytes. In our revised manuscript, we will remove the term "dissolved," wherever it may cause confusion.

4. Many of the concentrations are reported to four significant figures, which seems an unlikely level of precision.

[AUTHOR'S RESPONSE] We agree and will round up the concentrations to the nearest decimal of the corresponding detection limits.

5. Much of the correlation analysis (Table 3) is not particularly useful in helping understand the geochemistry. Demonstrating that specific conductivity and salinity are highly correlated is simply stating the obvious. Likewise, the results section contains obvious statements of trends in the data that are unlikely to be helpful for a reader and aren't really used in the discussion.

[AUTHOR'S RESPONSE] We appreciate the reviewer for the thorough review and helpful comments. We agree that the two parameters are closely related and will exclude specific conductivity in the correlation analysis in our revised manuscript.

6. In the beginning of the discussion, the authors use gram units for concentration while elsewhere they use mole units. This is unnecessarily confusing.

[AUTHOR'S RESPONSE] Thanks for catching the inconsistency. We will change the gram units to mole units in our revised manuscript.

7. Overall, the discussion is vaguely descriptive and speculative. As mentioned above, much of the prior work on estuarine chemistry of these elements (especially Ba) is uncited. Consultation with that literature might provide the authors with insight not only to the geochemistry of their system but also as to what questions remain unanswered in studies of the estuarine behavior of these elements.

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[AUTHOR'S RESPONSE] Thanks very much for the critiques. As mentioned above, our study and the studies of Jong & Shiller and Xu & Marcantonio have different research focuses, and were conducted in different riverine/estuarine environments. We believe the three studies complement one another in geochemistry research in rivers that enter the Northern Gulf of Mexico. We assure that the point made by the reviewer here is well taken. We will do our best to improve the quality of the discussion in our revised manuscript, and will include citations to the two suggested articles. Finally, we would like again to sincerely thank the reviewer for the helpful comments and suggestions.

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

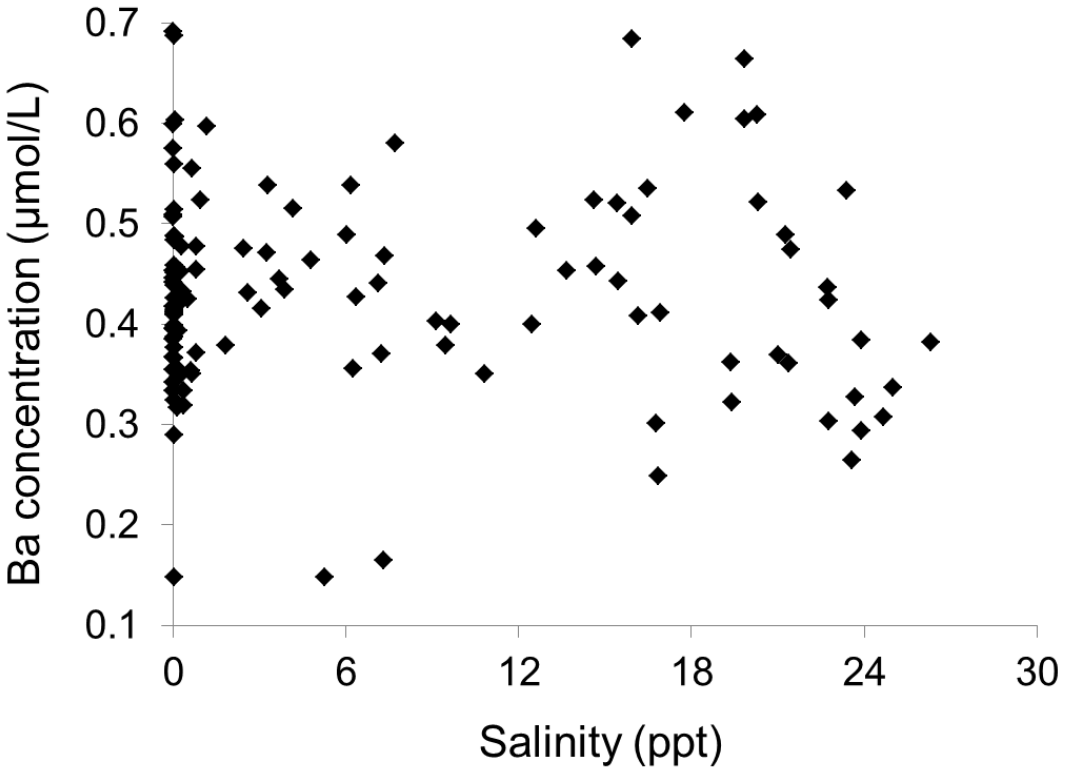

Fig. 1.

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