Interactive comment on “Trace elements in mussel shells from the Brazos River, Texas: environmental and biological control” by Alexander A. VanPlantinga and Ethan L. Grossman

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Anonymous Referee #1 Received and published: 16 October 2019 **Author refers to line numbers in the Track Changes document.** This was a helpful review. Thank you so much for your time and insight. Your review helped make this a better paper. We feel it is a big step closer to being publication-worthy. Review of the manuscript “Trace elements in mussel shells from the Brazos River, Texas...” The paper addresses environmentally important question potentially suitable for Biogeoosciences. The title is not correct: this work is about Mn essentially, rather than trace elements Many references are incomplete Good point. The title is now revised to be more specific to the novel finding of the shell Mn/Ca-discharge relationship. L10: does it simply mean that Sr correlated with Mn in shells? Yes Introduction: The novelty of this study and motivation behind this work are unclear. Why river Mn flux is important at all? Indirect assessment of this flux via shells is not the easiest way... Good point. Now the novelty is stated on lines 15, 64, 260-265. Methods: How the samples were processes after dissolution; were they filtered? Was the dissolution complete? Now line 101 makes clear that shell sample dissolution was complete in the 2% nitric acid ICP-MS solutions. Eqn 1-3: Unclear why this information is needed The equations have been removed. This frees up space. Sampling (L149-150): The water samples were not filtered and acidified. As such, metal concentration (except probably Ca and Sr) in river water could not be measured and distribution coefficients do not make sense. Moreover, the whole main motivation of this study - reconstruction of Mn flux in the river - becomes compromised. As such, the distribution coefficients oven in Table 3 may not be usable. Now lines 110-112 clarify that the samples were not acidified immediately but were brought to 2% nitric for ICP-MS analysis. They were never filtered. While the VanPlantinga et al. (2017) paper discusses broad relationships between major dissolved ions that are consistent with our data, there are indeed risks of preservation problems in this study for the manganese concentration measurements. Therefore the presentation of dissolved manganese concentrations has been removed. The partition coefficient estimates for Mn/Ca in this study are given an asterisk in Table 3 where the water Mn concentration is assumed to be the median value for Brazos River water from a reliable study, Keeney-Kennicutt and Presley (1986).


In Fig 3C, use log scale for discharge. How good is this correlation? What about cor-
relation with temperature? Done L254-259: Another issue is what is Mn concentration in the lake hypolimnion? If the lake is seasonally stratified, then, during the overturn, the bottom Mn-rich waters can feed the river thus dramatically increasing the Mn concentration in the river water. Lines 287-291 now discuss this issue in the “point source theory” part of the discussion. L257-258: The argument is unclear. In Fig. 3E, Mn/Ca is not inversely related to Sr/Ca. Please show the relationships. This section was weak and needed to be revised. Thank you for directing my attention here. L270-271: The low flow may provide enhanced Mn2+ input from the riparian and hyporheic zone. We now include a reference to the relevant surface-groundwater interaction (Rhodes et al., 2017), which builds on concepts in VanPlantinga et al. (2017). The tracers for bank storage (high [Mg2+ + Ca2+ + HCO3-] relative to [Na+ + Cl-]) are prominent during the 1-2 day period following a rain storm, when bank storage quickly discharges. The idea that the Brazos River is a gaining stream in times of low flow, thus possibly changing the redox related dissolved ion chemistry such as Mn/Ca, is not supported by these studies. Rhodes, K.A., Proffitt, T., Rowley, T., Knappett, P.S., Montiel, D., Dimova, N., Tebo, D. and Miller, G.R.: The importance of bank storage in supplying baseflow to rivers flowing through compartmentalized, alluvial aquifers. Water Resources Research, 53(12), pp.10539-10557, 2017.

L277: notice here that the maximal suspended load is usually observed at high discharge. Yes, you read that correctly. However, there is a big emphasis on inorganic particles, being at higher concentrations in more turbid conditions which the mussels are less likely to feed on because this is a strong environmental stressor for them. As our study finds, the shell Mn/Ca is inversely related to log of discharge, so it cannot be the inorganic Mn-bearing particles that the mussels are eating. L288: Chl a of mg/L concentration is really high. May be a misprint here and the concentrations are in µg/L? This line now specifies that it is water column chlorophyll in mg x L-3 and benthic chlorophyll in mg x L-2. L293-295: As a conclusion to section 3.5, this is extremely discouraging. It looks like one cannot yet discuss the sources of Mn for shells, so this section is useless... We feel that calling for future research into spatial and temporal scales of manganese flux in rivers such as the Brazos River is appropriate. The research from Roach (2014) mentioned in this section gives us a basis to argue our hypothesis that the environmental Mn is ingested by mussels as organic particle bound Mn.

L312 Owen1996 is not in the ref list. This has been fixed. Thank you. L325-329: May be place this information in the Introduction. Again, this sentence is very discouraging: how is it related to particulate case analyzed in this work? What is more important, according to authors, in Brazes River: physiological mechanisms or environmental factors? The relative contributions to shell trace element chemistry from physiological factors such as metabolism, ion channels, reproduction vs. environmental factors such as river chemistry is the backdrop of this research. The first paragraph of the introduction covers this issue. I added a “does not necessarily…” here. Rewrite L 347-348. This sentence in the conclusions has now been revised. L349-350: This is not sufficiently discussed and the whole story of DMn can be compromised by inadequate sampling. The partition coefficient estimates for Mn/Ca in this study are given an asterisk in Table 3 where the water Mn concentration is assumed to be the median value for Brazos River water from a reliable study, Keeney-Kennicutt and Presley (1986).

Trace elements in mussel shells from the Brazos River, Texas: environmental and biological control

Abstract.

In sclerochronology, understanding the drivers of shell chemistry is necessary in order to use shells to reconstruct environmental conditions. We measured the Mg, Ca, Sr, Ba, and Mn contents in water samples and in mussel shells (Cyrtomonas tampicoensis) from the Brazos River, Texas. Sr/Ca correlated with Mn/Ca, while Mg/Ca and Ba/Ca did not correlate significantly with Mn/Ca. High Mn/Ca values were used to assess discharges in the Brazos River, Texas. High Mn/Ca values were correlated inversely with the log of river discharge. This study establishes with stable and clumped isotopes and by growth rate (Izumida, 2005). A major advantage of using Mg/Ca and Ba/Ca as the geologic past, but problems remain in understanding the relationship between mollusk shell chemistry and the ecosystems.

Introduction: The novelty of this study and motivation behind this work are unclear. The novelty is stated on lines 15, 64, 260-265.

The equations have been removed. This frees up space.

Fig. 1. responses in bold

Fig. 2. track changes
Mussel shell Mn/Ca as a novel proxy for discharge in the Brazos River, Texas

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Abstract. In sclerochronology, understanding the drivers of shell chemistry is necessary in order to use shells as environmental archives. We measured the Mg, Ca, Sr, Ba, and Mn contents in water samples and in the shells of two freshwater mussels (Amblema plicata and Cyrtonaias tampicoensis) from the Brazos River, Texas to test their reliability as environmental archives. Shells were analyzed along growth increments using age models established with stable and clumped isotopes. Shells were also examined with cathodoluminescence (CL) microscopy to map Mn/Ca distribution patterns. In the shells, Sr/Ca correlated with Mn/Ca, while Mg/Ca and Ba/Ca showed no clear trends. Mn/Ca correlated inversely with the log of river discharge. Because suspended chlorophyll concentration is high during low flow and suspended inorganic particles (turbidity) is high during high flow, peak Mn/Ca values may come from elevated feeding or metabolic rates related to the abundance or suspended particulate organic matter. For the first time, shell Mn/Ca values were used to reconstruct river discharge patterns, which, to our knowledge, has previously only been performed with shell chemistry using oxygen isotopes.

Copyright Statement

1 Introduction

Sclerochronology is the study of the physical and chemical properties of invertebrate hard parts and the temporal context in which they grew. It is useful in marine paleoecology, but can also be applied to freshwater ecosystems. There is great potential for using mollusks to reconstruct environmental conditions in the present and in the geologic past, but problems remain in understanding the relationship between shell chemistry and the ambient environment (da Fonseca et al., 2010). For example, shell Sr/Ca can record temperature as a reflection of local seawater temperature variations opposite what is thermodynamically predicted (e.g., Hedges, 1992; Colbath, 2001; Carr et al., 2006; Simmons et al., 2010; Geary et al., 2010). Shell Mg/Ca can record temperature (Peterson et al., 2008), and shell Ba/Ca sometimes correlates with bioturbation productivity (Yamada et al., 2010; Laurenzi et al., 2007), but it can also be controlled by growth rate (Zimmer et al., 2014). Mollusk soft tissue reflects variations in metal concentrations by organ and by element (Arifin and Bendell-Young, 2000; Chale, 2002; Ravera et al., 2003; Silva et al., 2006; Bellotto and Mieckeley, 2007). Soft tissue

Fig. 3. draft without track changes