Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2019-323-AC1, 2019

Biogeosciences
Discussions
Open Access

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

Alexander A. VanPlantinga and Ethan L. Grossman

acvanp@gmail.com

Received and published: 4 December 2019

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 Brazor River, Texas..." The paper addresses environmentally important question potentially suitable for Bio- geosciences. 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).

Keeney-Kennicutt, W.L. and Presley, B.J.: The geochemistry of trace metals in the Brazos River estuary. Estuarine, Coastal and Shelf Science, 22(4), pp.459–477, 1986.

VanPlantinga, A.A., Grossman, E.L. and Roark, E.B.: Chemical and isotopic tracer evaluation of water mixing and evaporation in a dammed Texas river during drought. River Research and Applications, 33(3), pp.450–460, 2017.

In Fig 3C, use log scale for discharge. How good is this correlation? What about correlation 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 hy- porheic 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 chlorophyl 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 com- promised 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).

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2019-323, 2019.

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 Brazor River, Texas..."

The paper addresses environmentally important question potentially suitable for Biogeosciences.

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

Fig. 1. responses in bold

Mussel shell Mn/Ca as a novel proxy for discharge in the Brazos River, Texas~~Trace elements in mussel shells from the Brazos River, Texas: environmental and biological control~~

Authors: Alexander A. VanPlantinga[1] and Ethan L. Grossman[1]
[1]Department of Geology and Geophysics, Texas A&M University, College Station, Texas, USA 77843-3115

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 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 ~~dissolved and inorganic particulate sources of manganese are low~~ 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, s~~S~~hell 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 paleoclimatology, 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 mollusk shell chemistry and the ambient environment (Immenhauser et al., 2016). For example, shell Sr/Ca can record temperature as a reflection of mollusk metabolic response to seasonal temperature variation opposite what is thermodynamically predicted for aragonite (Wheeler, 1992; Gillikin et al., 2005; Carré et al., 2006; Sosdian et al., 2006; Gentry et al., 2008). Shell Mg/Ca can record temperature (Freitas et al., 2006), and shell Ba/Ca sometimes correlates with diatom primary productivity (Vander Putten et al., 2000; Lazareth et al., 2003), but it can also be controlled by growth rate (Izumida

1

Fig. 2. track changes

Mussel shell Mn/Ca as a novel proxy for discharge in the Brazos River, Texas

Authors: Alexander A. VanPlantinga[1] and Ethan L. Grossman[1]
[1]Department of Geology and Geophysics, Texas A&M University, College Station, Texas, USA 77843-3115

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 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 paleoclimatology, 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 mollusk shell chemistry and the ambient environment (Immenhauser et al., 2016). For example, shell Sr/Ca can record temperature as a reflection of mollusk metabolic response to seasonal temperature variation opposite what is thermodynamically predicted for aragonite (Wheeler, 1992; Gillikin et al., 2005; Carré et al., 2006; Sosdian et al., 2006; Gentry et al., 2008). Shell Mg/Ca can record temperature (Freitas et al., 2006), and shell Ba/Ca sometimes correlates with diatom primary productivity (Vander Putten et al., 2000; Lazareth et al., 2003), but it can also be controlled by growth rate (Izumida et al., 2011). Mollusk soft tissue reflects variations in metal bioaccumulation 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

1

Fig. 3. draft without track changes