



Unionid shells (*Hyriopsis cumingii*) record manganese cycling at the sediment-water interface in a shallow eutrophic lake in China (Lake Taihu)



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ABSTRACT

Aquatic eutrophication is becoming a serious environmental problem throughout the world. The utility of bivalves as bio-filters to improve water quality and reduce algal blooms has been widely acknowledged, but the potential usefulness of bivalve shells as retrospective monitors of eutrophication-induced environmental change has received little attention. Here, we present the first multi-year, high-resolution Mn/Ca_{shell} records of the freshwater mussel, *Hyriopsis cumingii* (Lea, 1852) from a shallow eutrophic lake (Lake Taihu, China). Mn/Ca_{shell} time-series of the two studied shells exhibit a high degree of synchrony after being placed in a precise temporal context by means of growth pattern analysis. There is a large inter-annual variability of Mn/Ca_{shell} records during 2011–2015, with the highest value occurring in 2013. Mn/Ca_{shell} also displays a pronounced intra-annual variability with maxima consistently occurring during late spring/early summer. The high reproducibility of Mn/Ca_{shell} time-series among contemporaneous specimens highlights the existence of strong environmental rather than biological control on the incorporation of Mn into the shells. In particular, the striking feature of late spring/early summertime Mn/Ca_{shell} maxima is synchronous with the occurrence of reducing conditions beneath the sediment-water interface (SWI). The latter results in substantial increases of biologically available Mn²⁺ in the sediment pore water and organic particles, the element being rapidly taken up from these sources by the mussels with subsequent incorporation of Mn into their shells. Therefore, Mn/Ca_{shell} can potentially serve as a high-resolution proxy of the mobility of Mn at the SWI. As demonstrated by the present study, documenting and understanding geochemical properties of bivalve shells can help to retrospectively monitor eutrophication-induced environmental change in aquatic ecosystems.

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1. Introduction

Manganese is a naturally abundant and widely distributed metal in aquatic sediments where it is present primarily as insoluble MnO₂ (Pedersen and Price, 1982). However, MnO₂ is highly susceptible to the redox state of the sediment and is readily reduced to soluble Mn²⁺ ion when reducing conditions prevail (Pedersen and Price, 1982). Since Mn²⁺ is less readily oxidized back to MnO₂ and has a high affinity for organic matter (Wilson, 1980), extremely high levels of Mn²⁺ are often found in the sediment pore water and organic material (e.g., Aguilar and Nealson, 1998; Gao et al., 2006; Tao et al., 2012; Giles et al., 2016). Dissolved Mn²⁺ can also easily diffuse across the sediment-water interface (SWI) into the overlying water, where it can remain in the dissolved form for periods of days (Tebo, 1991; Pakhomova et al., 2007) and/or be removed from the water column by abiogenic and microbial oxidation (Richardson et al., 1988; Aguilar

and Nealson, 1998) and taken up by bacteria and phytoplankton (Sunda and Huntsman, 1985; Schoemann et al., 1998). Under intense reducing conditions, a substantial release of Mn²⁺ from the sediment would likely exert a dominant influence on the partitioning of Mn between dissolved and particulate phases in the overlying water column. Furthermore, the reductive dissolution of MnO₂ can greatly promote the release of elemental nutrients (N and P) and trace metals (Co, Zn, Cd, Ba, Pb, etc.) from the sediment which are preferentially associated with MnO₂ (Balistrieri and Murray, 1986; Pearce et al., 2013; Giles et al., 2016). Therefore, continuous monitoring of the release of Mn²⁺ at the SWI would provide valuable information regarding the geochemical behavior of Mn and many other elements in aquatic environments as well as eutrophication caused by the surplus of nitrogen and phosphorus.

Several studies have demonstrated the feasibility of using bivalve shells to investigate temporal changes of biologically available manganese from dissolved and/or particulate sources (e.g., Nyström et al., 1996; Vander Putten et al., 2000; Markich et al., 2002; Lazareth et al., 2003; Freitas et al., 2006; Langlet et al., 2007; Barats et al., 2008;

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