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Mn/Ca in shells of *Arctica islandica* (Baltic Sea) – A potential proxy for ocean hypoxia?

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ABSTRACT

Oxygen depletion threatens an increasing number of shallow water environments, specifically habitats below the seasonal halocline in coastal settings of the Baltic Sea. To understand the natural variations of dissolved oxygen levels on seasonal and inter-annual time-scales prior to the instrumental era, high-resolution archives are urgently required. The present study evaluates the potential use of Mn/Ca values in shells of the bivalve, *Arctica islandica* to infer concentrations of past dissolved oxygen concentrations. This study is based on laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) data of six contemporaneous specimens and demonstrates that background variations of shell Mn/Ca are inversely linked to dissolved oxygen concentrations in the water column ($r = -0.68$; $R^2 = 0.46$, $p < 0.0001$), which in turn are coupled to the amount of dissolved Mn. The regular seasonal changes were superimposed by sharp Mn/Ca peaks, most likely resulting from the ingestion of a large amount of Mn-rich organic particles. The availability of such particles can increase due to the resuspension of food particles by strong bottom currents or alternatively, result from increased particle flux from surface waters after major river discharges and subsequent phytoplankton blooms. Besides sharp Mn/Ca peaks, often accompanied by sharp Ba/Ca peaks and increased shell growth rate. In addition, after exceptional major barotropic inflows from the North Sea, the biogeochemical steady-state conditions remained disturbed for up to ca. two years, because the redox-sensitive elements were removed from the water column by oxygenated waters, and it took time for them to build up again in the water column. Therefore, subsequent to such Major Baltic Inflows (MBIs), dissolved Mn levels and shell Mn/Ca values were strongly reduced despite summertime low-oxygen conditions. As demonstrated here, Mn/Ca data of *A. islandica* shells can potentially serve as a proxy for dissolved oxygen levels in the water column. To further develop this proxy, a set of additional environmental and physiological proxies such as shell Ba/Ca values and growth rate should be critically assessed and used in combination with shell Mn/Ca.

1. Introduction

Oxygen depletion threatens an increasing number of nearshore shallow-water ecosystems (Vaquer-Sunyer and Duarte, 2008). Severe and prolonged low-oxygen conditions can be lethal for aquatic organisms and destroy benthic communities (Karlson et al., 2002; Diaz and Rosenberg 2008) with repercussions for the entire food web (Zillén et al., 2008). Low levels of dissolved oxygen (DO) can also alter the biogeochemical cycles of nutrients by enhancing the release of phosphorus and nitrogen from the sediment into the overlying water column which promotes eutrophication and amplifies oxygen undersaturation (Österblom et al., 2007). Despite significant differences in low-oxygen tolerance among species, the threshold of DO below which most marine organisms greatly suffer or perish is, on average, approx. 2.3 mg/L (corresponding to 1.6 mL/L or 72.2 μmol/L) (Vaquer-Sunyer and Duarte, 2008). This concentration delimits normoxic from hypoxic

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