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Marine Pollution Bulletin 50 (2005) 1530–1540
MARINE POLLUTION BULLETIN
www.elsevier.com/locate/marpolbul

Inter- and intra-annual variations of Pb/Ca ratios in clam shells (*Mercenaria mercenaria*): A record of anthropogenic lead pollution?

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Abstract

In this study, we re-assess the use of bivalve shells as a proxy of lead pollution. Previous studies have stressed that shells display little variability compared to soft tissues and thus are better for pollution biomonitoring. However, in this manuscript we illustrate that there is large inter- and intra-annual Pb variability between shells of the clam *Mercenaria mercenaria* collected in North Carolina, USA. Therefore, year to year, as well as intra-annual variations in Pb/Ca ratios should be interpreted with caution. Despite this variability, we were able to obtain an annual Pb chronology from 1949 to 2002 using 11 shells collected at different times which clearly exhibited the late 1970's peak in Pb from leaded gasoline use. This indicates that when enough specimens are pooled together, bivalve shells can be used to reconstruct large, long term changes in environmental Pb concentrations. Our data compare well with other studies of aragonite clams from sites with low regional lead pollution. From this we conclude that the Cape Lookout region of North Carolina has not received extensive pollution over the 1949–2002 period. The Pb concentration in shells growing in the 1949–1976 period was not significantly different from those growing in the 1982–2002 period, although other proxies suggest that the 1949–1976 period should be considerably higher. Therefore, our data suggest that there is still a modern low-level source of Pb in the coastal North Carolina environment.

Keywords: Lead; Anthropogenic pollution; Proxy record; Metals; Mollusk; Coastal sediments; North Carolina

1. Introduction

Coastal and estuarine environments are important natural resources supporting recreational activities and commercial fishing as well as providing a host of ecological services. The pollution of these regions can have serious adverse effects and thus has been closely monitored in the past several decades. The Mussel Watch program, where soft tissues of bivalves have been used to monitor pollution in the coastal zone (e.g., Goldberg, 1975; Claisse, 1989), has been monumental in this regard. Nevertheless, pre-1970 data are scarce (Cantillo, 1998) and data are limited to certain estuaries. For example, there are currently only seven Mussel Watch sites along the entire North Carolina (USA) coast (Lauenstein et al., 2002). Although new Mussel Watch sites could be started in other estuaries, it would require several years of monitoring to determine temporal

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0025-326X/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2005.06.020

pollution trends and would not allow reconstruction of past Pb concentration levels. There are other substrates that can retrospectively extend the record back through time and into other locations, which would not require extensive monitoring, such as sediments (e.g., Chillrud et al., 2003; Cooper et al., 2004; Kim et al., 2004), tree rings (e.g., Watmough et al., 1999) and biogenic carbonates (e.g., Shen and Boyle, 1987; Pitts and Wallace, 1994; Lazareth et al., 2000); each with its own advantages and drawbacks. For instance, sediments may be bioturbated and often provide low resolution profiles (e.g., Sharma et al., 1987; Cooper et al., 2004). On the other hand, biogenic carbonates can provide high-resolution profiles and once incorporated the proxy remains more or less stable as long as diagenetic processes do not occur. However, the biology of the animal may affect the record (Vander Putten et al., 2000). Both corals and sclerosponges have been shown to accurately trace anthropogenic Pb inputs in tropical and subtropical waters (Shen and Boyle, 1987; Lazareth et al., 2000; Swart et al., 2002; Ramos et al., 2004), but long term chronologies (>50 years) based on bivalve shells have not been attempted.

Similar to sclerosponges, bivalve carbonate may be a superior recorder of Pb because bivalves accumulate higher Pb concentrations in their skeletons. Sclerosponge skeletons contain 10–35 times more Pb than corals (based on the 1970's Pb peak; Shen and Boyle, 1987; Lazareth et al., 2000; Swart et al., 2002). Bivalve shell Pb/Ca ratios from polluted sites have been reported to be higher than 7 μmol/mol (Price and Pearce, 1997), whereas corals from polluted sites can have Pb/Ca ratios reaching only 0.23 μmol/mol (Fallon et al., 2002).

There have been many studies on trace metal concentrations in bivalve shells. However, many of these studies did not include Pb due to its low levels (Szefer et al., 2002; Nicholson and Szefer, 2003; Cravo et al., 2004). Of the studies that did measure Pb, many analyzed whole shells (Koide et al., 1982; Yap et al., 2003), thus averaging several years of shell growth and including the outer layer of the shell which may exchange with the external medium. Other studies, which did sample only the most recently formed shell material have shown that shell Pb concentrations are linearly related to tissue, particulate and dissolved Pb concentrations (Bourgoin, 1990; Pitts and Wallace, 1994). However, Bourgoin (1990) analyzed the inner nacreous shell layer and Pitts and Wallace (1994) analyzed the last formed section of the shell (the outer layer). This could effect the Pb levels they measured because Pb concentrations have been shown to vary by a factor of more than 10 between inner and outer shell layers (Fuge et al., 1993; Raith et al., 1996). Richardson et al. (2001) analyzed Pb concentrations in *Modiolus modiolus* shells from a polluted and non-polluted site covering 10 years of growth. They found elevated levels in shells from the polluted site, as well as a decrease of concentrations through time, which they attributed to the decline in pollution at the polluted site. However, they could not deconvolve age and time, and age has been shown to influence Pb concentrations in some mollusks (e.g., Hirao et al., 1994). Despite the large interest in using bivalve shells as records of past pollution, there has not been an attempt to create a continuous chronology back through time. Although bi- valves are commonly short-lived, several shells can be strung together to form a master chronology, much longer than any one individual's lifespan (Schöne, 2003).

The general objective of this study was to test if indeed bivalve shells can provide a long term record of anthropogenic Pb pollution. To reach this objective we first attempt to obtain pristine background Pb/Ca ratios from a fossil Pliocene *Mercenaria mercenaria* shell in order to have a baseline to compare the modern shells to. Secondly, the intra-annual Pb/Ca variation is assessed by sampling three shells across several annual growth increments at a high resolution. Finally, by analyzing Pb/Ca ratios of the annual growth increments in eleven *M. mercenaria* shells collected at different times we can construct a chronology back through time at an annual resolution. Using shells collected at different dates and of different ages also allows us to assess any effect of age on the records. As no data are available on environmental Pb concentrations at our collection sites, we compare our measured Pb/Ca profile with an expected Pb profile based on published data from biogenic carbonates and total national US Pb emissions.

2. Materials and methods

2.1. Sample collection, preparation and analysis

Living *M. mercenaria* were collected from the Cape Lookout region of North Carolina, USA (Fig. 1) at about 1 m water depth in 1980 ($n = 2$), 1982 ($n = 3$), 2002 ($n = 3$) and 2003 ($n = 3$) (full data are listed in Table 1). More data on environmental conditions can be found in Peterson et al. (1985), Peterson (1986, 2002), and Gillikin et al. (2005a). Additionally, a Pliocene shell (∼3.2 million years old) was collected from the Duplin formation in South Carolina (1.5 km northwest of Timmonsville) in order to determine a shell Pb/Ca baseline. Elliot et al. (2003) have shown that *M. mercenaria* precipitate aragonite shells. Sections of the shells were cut with a diamond saw along the axis of maximal growth, rinsed with deionised water, air dried and mounted on microscopic slides. Clams were aged by counting the internal growth lines (Fig. 2), which have been proven to be annual (Peterson et al., 1985) and calendar years were assigned by back-dating from the time of collection. Considering that the inner