



History of bioavailable lead and iron in the Greater North Sea and Iceland during the last millennium – A bivalve sclerochronological reconstruction



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ABSTRACT

We present the first annually resolved record of biologically available Pb and Fe in the Greater North Sea and Iceland during 1040–2004 AD based on shells of the long-lived marine bivalve *Arctica islandica*. The iron content in pre-industrial shells from the North Sea largely remained below the detection limit. Only since 1830, shell Fe levels rose gradually reflecting the combined effect of increased terrestrial runoff of iron-bearing sediments and eutrophication. Although the lead gasoline peak of the 20th century was well recorded by the shells, bivalves that lived during the medieval heyday of metallurgy showed four-fold higher shell Pb levels than modern specimens. Presumably, pre-industrial bivalves were offered larger proportions of resuspended (Pb-enriched) organics, whereas modern specimens receive fresh increased amounts of (Pb-depleted) phytoplankton. As expected, metal loads in the shells from Iceland were much lower. Our study confirms that bivalve shells provide a powerful tool for retrospective environmental biomonitoring.

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1. Introduction

As a marginal sea bordered by the most densely populated and highly industrialized countries, the North Sea is severely impacted by human activities (Weichart, 1973). Aside from overfishing, oil and gas exploitation, modification of the sea floor by dredging, bottom trawling, and removal of sand and gravel, pollution constitutes a major threat to the biota inhabiting the North Sea. Main sources of organic (e.g., PCB, PAH, DDT) and inorganic contaminants (heavy metals, radionuclides, REEs) include rivers, coastal industries, dumping and the atmosphere (Schlünzen et al., 1997). Some of these pollutants are water-soluble and can directly deteriorate the water quality (OSPAR, 2000, 2009b), whereas others accumulate in the sediment. Remobilization of such substances occurs during changes in the biological activity in the water column, in the sediment or near the sediment surface (e.g., enhanced downward transport of organic matter following phytoplankton blooms, increased rates of bioturbation, etc.) and associated changes in pH and DO and can result in secondary pollution effects (Kersten, 1988; Kersten et al., 1994).

To determine baseline levels of biologically available contaminants in the North Sea prior to intensified human perturbation,

distinguish natural from anthropogenic environmental disturbances, and identify periods of intensified remobilization of potentially harmful substances at the sea floor, it is crucial to know how pollutant levels changed through time. Such information is indispensable for management purposes and predicting future threads of anthropogenic pollution. For this purpose, numerous sediment cores have been retrieved from various localities in the North Sea during the last decades (Förstner and Reineck, 1974; Behre et al., 1985; Irion and Müller, 1990; Irion, 1993). Results clearly indicate rising heavy metal loads toward more recently deposited strata. The major disadvantage of sedimentary deposits, however, is poor temporal resolution and dating control. Bioturbation results in significant time-averaging and obscures short-term cycles. Furthermore, continuous and undisturbed sediment records are absent in large parts of the North Sea as a result of repeated sediment reworking and re- sedimentation in these shallow-water settings (Kersten et al., 1988; Irion and Müller, 1990; Irion, 1993). Many records only cover the last one or two centuries or so (Förstner and Reineck, 1974; Behre et al., 1985; Irion, 1993). In addition, sediment records alone can barely provide information on levels of biologically available contaminants close to the sediment water interface where many benthic organisms are dwelling. Such data is particularly relevant from ecotoxicological perspective.

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Skeletal hard parts of animals, in particular bivalve mollusks, serve as powerful archives of pollution. Shells of bivalves grow by periodic accretion of calcium carbonate and contain distinct annual and daily growth lines and increments (portions between consecutive growth lines). These growth patterns can be used to temporally contextualize each shell portion. If the date of death, and thus the date of the last shell formation is known, a precise calendar date can be assigned to each growth increment. Changes in the physico-chemical environment are recorded in the shell in the form of variable growth increment widths and chemical properties. For example, oxygen isotope values ($\delta^{18}\text{O}$) can provide information on ambient water temperature during shell formation. Likewise, increased heavy metal loads in the water are reflected in elevated levels of these elements in the shells (e.g., Carriker et al., 1982; Price and Pearce, 1997; Richardson et al., 2001; Gillikin et al., 2005; Liehr et al., 2005; Pearce and Mann, 2006). Respective values in fossil shells have previously been used to determine heavy metal loads in the environment prior to major anthropogenic disturbance (e.g., Bourgoin and Risk, 1987; Pitts and Wallace, 1994), but such studies only provided snapshots into the climatic past lacking absolute temporal alignment of the data. Gillikin et al. (2005) presented the first, well-dated, long-term (53-year) record of lead contamination off the coast of North Carolina, USA, based on eleven contemporaneous shells of *Mercenaria mercenaria*. Despite differences in Pb/Ca ratios among contemporaneous specimens, the increasing use of leaded gasoline during the 1970s was clearly recorded by the shells. Krause-Nehring et al. (2012) analyzed the Pb/Ca history in the North Sea, Iceland and off the coast of Virginia between the late 18th century and modern times based on LA-ICP-MS (laser ablation – inductively coupled plasma – mass spectrometry) analysis of three shells of *Arctica islandica*, a species that can live for several hundred years (Schöne et al., 2005a; Butler et al., 2013). While the shells from the North Sea and the US coast confirmed the findings by Gillikin et al. (2005), the shell from Iceland, a much less polluted habitat, showed significantly lower Pb/Ca ratios.

Since shell growth is governed to a large degree by environmental variables, growth curves (or so-called sclerochronologies) of contemporaneous specimens show similar patterns. By stringing together increment chronologies based on synchronous changes in interannual shell growth (cross-dating) it is possible to construct a stacked sclerochronology covering centuries to millennia and many generations of bivalves, a method very similar to dendrochronology (e.g., Witbaard et al., 1997; Butler et al., 2013; Lohmann and Schöne, 2013). In combination with heavy metal data of the shells, cross-dating can open new avenues in retrospective environmental biomonitoring (Gillikin et al., 2005).

Here, we present the first high-resolution, multi-regional heavy metal record of the North Sea covering the last millennium. The focus of this study is on Pb/Ca and Fe/Ca ratios. Specifically, we studied (1) how Pb/Ca and Fe/Ca levels fluctuated through time (focus on interannual and lower time-scales) and space, (2) how these element levels varied among contemporaneous specimens from the same habitat and (3) to what degree diagenesis and biological factors may have obscured the data. Contrary to existing studies of this kind in which the metal load in discrete shell portions was determined (discrete spot analysis), we employed the so-called line-scan method that enabled us to obtain uninterrupted heavy metal chronologies from each shell. We will demonstrate the advantage of this method for shell-based retrospective environmental monitoring.

1.1. Anthropogenically emitted Pb and Fe in the ocean, transport mechanisms

In modern, industrial times, a significant portion of Pb in the ocean is derived from the combustion of leaded gasoline. For

example, in the North Sea, Pb from atmospheric emissions accounts for up to ca. 70% of the total lead input (Irion and Müller, 1987; Duce, 1991; Schlünzen et al., 1997; Irion, 1993; Injuk et al., 1998). Among other organic substances, tetraethyl lead has been added to gasoline as an antiknock agent which reacts to highly volatile Pb chlorides and Pb bromides during combustion that are emitted to the atmosphere as aerosols. This resulted in a significant increase in Pb fluxes to the oceans between 1923 and the 1980s (e.g., Schaule and Patterson, 1981; Flegal and Patterson, 1983; Nriagu, 1990; Wu and Boyle, 1997; Hoffman et al., 2003). In preindustrial times, however, lead was mostly released to the environment during mining and smelting (Settle and Patterson, 1980; Nriagu, 1983; Hong et al., 1994; de Calatay, 2005). As indicated by peat bogs from England, for example, atmospheric lead pollution reached an all-time maximum at ca. 1200 and was excessively high between 1150 and 1500 (Le Roux et al., 2004). Whereas particulate lead is transported through rivers and accumulates in the sediment (Balls, 1985; Irion, 1993), lead from atmospheric emissions becomes soluble in surface waters and is re-adsorbed to biological particles (Wu and Boyle, 1997) which sink to the sea floor and can be ingested and digested by benthic organisms (e.g., Kröncke, 1987; Prosi, 1989; Fisher et al., 1996; Darriba and Sánchez-Marín, 2013). Pb is toxic to most organisms (e.g., Eisler, 1988; WHO, 2000; Verma and Dubey, 2003), inter alia because it mimics other biologically essential metals (substitution of Ca^{2+} , Mg^{2+} , Fe^{2+} , Zn^{2+} , and Na^{+} ; Lidsky and Schneider, 2003; Flora et al., 2012).

The main iron contributors are hyper-arid terrestrial areas, anthropogenic and volcanic sources (Jickells et al., 2005). Anthropogenically released iron largely comes from combustion, (coal) mining and smelting activities (e.g., Tiwary and Dhar, 1994; Vuori, 1995; Rösner, 1997; Chuang et al., 2005; Guieu et al., 2005). The majority of iron reaches coastal and shelf waters in the form of insoluble iron oxides (detrital iron, e.g., goethite) through riverine input and, to a lesser extent, through the atmosphere in the form of aerosols (e.g., mineral dust particles; Duce and Tindale, 1991; Wells et al., 1995; Jickells et al., 2005; Spolaor et al., 2013). The latter react with surface waters and release water-soluble Fe^{II} which is more bioavailable than Fe^{III} (Shaked et al., 2005; Baker and Croot, 2010; Spolaor et al., 2013). Dissolved iron is an essential and limiting nutrient for marine phytoplankton that stimulates primary productivity (e.g., Martin and Fitzwater, 1988; Boyd et al., 2007; Smetacek et al., 2012). However, it is readily oxidized to Fe^{III} . Residence times for dissolved iron in oxygenated water are on the order of several hours (Salomons and Förstner, 1984; Dehairs et al., 1989; Millero and Sotolongo, 1989; González-Dávila et al., 2006; Baker and Croot, 2010) to nearly three years (de Jong et al., 2007). Due to their poor solubility, detrital iron (III) oxides sink to the sea floor where they become incorporated into the sediment (Wells et al., 1995; Shaked et al., 2005; Baker and Croot, 2010; Spolaor et al., 2013). When reducing conditions prevail in the sediment or near the sediment surface, Fe^{III} can be converted to the water-soluble, biologically available form.

2. Material and methods

Fourteen shells of *A. islandica* were collected in the Greater North Sea (Dogger Bank, German Bight, Norwegian Sea) and NE Iceland (Fig. 1; Table 1). One specimen from the Dogger Bank and German Bight and the two specimens from Iceland were collected alive, the remaining ten shells were single subfossil valves. One specimen (ICE14-A01L) was collected by scuba diving; all other shells were obtained by dredging (Table 1). To identify possible effects of water depth and substrate type, a broad range of shells from different settings were analyzed. Shells from a supposedly pristine habitat

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