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Lead accumulation in oyster shells, a potential tool for environmental monitoring

Elsa Cariou*, Christèle Guivel, Carole La, Laurent Lenta, Mary Elliot

Laboratoire de Planétologie et Géodynamique (LPG), UMR CNRS 6112, Nantes University, 2 rue de la Houssinière BP92208, 44322 Nantes Cedex 3, France

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ABSTRACT

Pb/Ca profiles were measured on ten live collected *Ostrea edulis* from three sites characterized by different levels of lead content. Intra-shell and inter-shell reproducibility were tested comparing several Pb/Ca profiles measured by LA-ICP-MS within a specimen, and within specimens from the same site. Results indicate that signals recorded are reproducible and mean shell Pb/Ca values are site-dependent. Second order variability is explained either by smoothing effects, biological effects or micro-environmental heterogeneities in lead distribution. Mean Pb contents measured in marine bivalve shells are reviewed here. Ranging from 0 to 50 ppm, they show a strong relationship with the environmental level of local lead contamination, and do not appear species-dependent. Our measurements show a linear relationship between mean shell Pb/Ca and surface sediment Pb concentrations, making marine bivalves and particularly *O. edulis* a potential accurate bio-monitoring tool able to monitor bioavailable lead along European coasts since Mesolithic, with an annual resolution.

1. Introduction

With mercury and cadmium, lead (Pb) is one of the most frequent and toxic contaminant in our environment. Lead is naturally introduced in marine environments by forest fires, volcanic activity and erosion and transport processes. It is supplied to water by gas exchanges, precipitations or fall-out of particles (Clark, 2001). Drained by rivers, it is transported dissolved as carbonate, hydroxide or chloride complexes (Libes, 1992). Tending to adsorb on organic matter particles, and being stocked in sediments under this particulate form, lead residence time is estimated to be less than five years in the surface waters (Veron et al., 1987; Wu and Boyle, 1997). However, in sediments and soils, its geochemical half-life is estimated about seven centuries (Semlali et al., 2004). Stocked in the soft surface sediments, lead can easily be remobilized and its remnant toxicity can poison the environment over millenniums.

Lead was extensively used during the Antiquity, in water supply systems or cooking utensils, having severe consequences on the health of the population (Harrison and Laxen, 1981). Smelters' activities locally contributed to lead supply in the sediments. Anthropogenic lead in the sediments of some antique harbors also reveals the impact of ore extraction and utilization for domestic purposes (Delile et al., 2014). High latitude ice-cores and high altitude varved lake deposits also show lead increases for this period, testifying the global environmental impact of lead use during Antiquity (Boutron et al., 2004; Guyard et al., 2007). Later, the industrial revolution marks the first major global increase in lead fluxes to the ocean (Clark, 2001). A second increase coincides with the 1930–1970 period, and the atmospheric dispersal of residues from leaded gasoline (Boyle et al., 1986; Harrison and Laxen, 1981). Since this period, lead inputs into coastal environments have been decreasing, but local resuspension events are frequent, protracting the adverse environmental effects of these anthropogenic lead inputs (Lazareth et al., 2000; Gillikin et al., 2005). Locally, additional lead supplies can originate from dumping and opening-closing of ore mines in the watershed of coastal rivers (Richardson et al., 2001; Liehr et al., 2005).

Unlike copper or iron, lead is not a biologically essential metal. Its toxicity is conferred by its charge and ionic radius, which allow lead to imitate and substitute some major elements, and cross most biological barriers without being detected (Taylor and Maher, 2012). Though, it accumulates in most of organisms, causing severe neurological, cardiovascular or calcification troubles. Despite this bioaccumulation displays many negative effects on the health of organisms, it is also useful to detect lead environmental contaminations and assess temporal and spatial variations in its bioavailability (Schintu et al., 2010; Søndergaard et al., 2014). In coastal environments the lead content in the organs of shell mollusks like bivalves is extensively used to evaluate and monitor the environmental effects of local anthropogenic lead inputs (Søndergaard et al., 2014; Rainbow, 1995; Wang et al., 1996). A retrospective environmental monitoring is possible measuring lead

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* Corresponding author.
E-mail address: elsa.cariou@univ-nantes.fr (E. Cariou).

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content in the sedimentary deposits. However, such measurements are submitted to important biases (sediment remobilization, chemical diffusion, bioturbation…), and generally present a low time-resolution. A network of observations along the French coasts has been set up since 1974 and provides information about lead concentrations in surface sediments every 6 to 8 years. Such a spatial and time resolution is good enough to provide information about mid-term changes in lead concentrations but is insufficient to detect ancient lead contaminations as well as to trace the evolution of detailed (weekly to monthly) lead concentrations.

Bivalve shells are made of calcite or aragonite and are usually well preserved in the fossil record. Trace elements are incorporated into the successive layers of carbonate and can reflect the physic-chemical environment in which it was secreted (Elliot et al., 2009; Schöne and Gillikin, 2013). In bivalve shells, lead is substituted to calcium in the carbonate lattice (Bourgoin, 1987; Ramos et al., 2004). For a few filter-feeding species (*Mytilus edulis*, *Mya arenaria*, and *Crassostrea gigas*), relationships were observed between shell lead content and either suspended particulate lead concentration (Bourgoin, 1990) or dissolved lead concentration in the seawater (Pitts and Wallace, 1994; Almeida et al., 1998). However, Vander Putten et al. (2000) observed no direct correlation between the lead content of the calcite outer layer of *M. edulis* and either dissolved or particulate lead concentrations in the Netherlands estuaries, highlighting that the different layers of bivalve shells might respond differentially to environmental concentrations. Recently, two studies tracing the lead content along the growth increments of the long-lived bivalve *Arctica islandica* highlighted the possibility of building chronologies and visualizing ancient environmental lead concentrations (and thus anthropogenic lead inputs) over the last millennium through lead shells content (Krause-Nehring et al., 2012; Holland et al., 2014). These studies illustrate how marine bivalve shells can be precious environmental archives, and how identifying target promising species (widely distributed, well-known physiology…) and shell layers (with solid relationships with environmental concentrations) is required, before definitely endorsing bivalve' shells as retrospective environmental bio-monitoring tools.

Ostrea edulis is an interesting species to target. This flat oyster is a filter-feeder bivalve that occupies subtidal and lower intertidal zones of rocky and silty shores. It displays a wide pan-European distribution (living from Mediterranean Sea to Norway, at temperatures between 5 °C and 25 °C), a longevity up to 20 years, and adult shells generally exceed 10 cm in diameter and 1 cm in thickness. Richardson et al. (1993) and Milner (2001) investigated the shell growth in live specimens from several locations around the British Isles. They showed that shell growth is mainly affected by temperature, salinity and food supply and slows down in colder months (February – March), forming annual growth lines and clefts at the boundary between the shell and the ligostracum, identifiable under the microscope.

This study aims to evaluate a potential tool for environmental monitoring, comparing variations in lead content recorded in ten flat oyster shells collected in three sites along the French Atlantic coasts. Each site was chosen as it is differentially affected by lead environmental inputs and monitored. One of them is supposed to be mainly impacted by atmospheric lead inputs, while the two others are differentially affected by riverine inputs of lead-rich sediments, from ancient mining activities. In order to evaluate the ability of *O. edulis* to monitor retrospectively the lead content of its environment, shell lead content was measured by LA-ICP-MS in the foliated calcite of the hinges of 3–4 specimens from each site. The mean lead content of shells was first compared between shells within the same site and then between different sites. The reproducibility of Pb/Ca signals recorded within a shell and between the different shells from a same site was initially investigated. Finally, confrontation of mean values measured in the surface sediments and mean values of Pb/Ca recorded in shells of each site allowed to propose and discuss the existence of a close relationship between shell lead content and environmental lead concentrations, making of *O. edulis* a key species for retrospective environmental bio-monitoring.

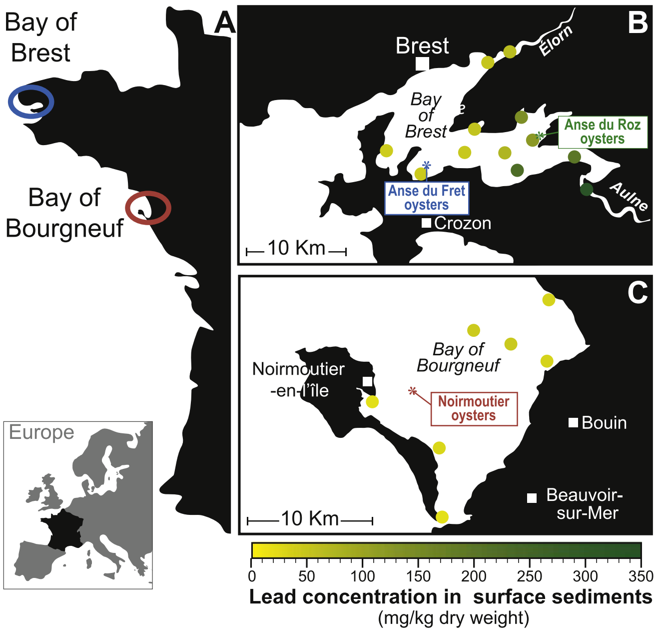

Fig. 1. A) Location of the Bay of Brest and the Bay of Bourgneuf along the French Atlantic coasts. B & C) Location of the sampled specimens and distribution of mean Pb concentration in the surface sediments between 2000 and 2015, according to the Quadrige database (IFREMER).

2. Material and methods

2.1. Sampling locations and environmental data

In January 2015, 20 samples of *Ostrea edulis* were collected alive in the Bay of Brest (Fig. 1), in the Anse du Fret (48°17′30″N; 4°28′39″O) and the Anse du Roz (48°19′27″N; 4°20′4″O), respectively. Specimens were collected by scuba diving, within a radius of 100 m. Oysters were 8–10 cm long and specialists of oyster fishing in the bay estimated their age around 8–10 years old, on the basis of size and growth rings visible on the shells. In November 2015, 5 live specimens were collected around the “La Chausse” shoal (Fig. 1), near the harbour of Noirmoutier-en-l'île, in the Bay of Bourgneuf (46°59′32″N; 2°11′12″O), within a radius of 200 m. Ranging from 11 to 14 cm in length, those oysters were estimated to be around 10–12 years old by professionals of oyster fishing in the Bay of Bourgneuf. Soft tissues were removed immediately after collection for all oysters.

The Bay of Bourgneuf and the Bay of Brest were specifically chosen because flat oysters show similar growth rates. Water temperature and salinity are monitored sub-monthly by the REPHY network (Réseau de surveillance du Phytoplancton et des Phycotoxines) of the French Research Institute for Exploitation of the Sea (IFREMER). In the two areas, mean ranges of annual water temperatures are similar (13.5 °C ± 7 °C). In the Bay of Brest, salinity generally fluctuates between 35 and 33‰ (PSU). Low salinity values are more frequent in the Bay of Bourgneuf but rarely fall below 28‰ (PSU). In the two bays, metal concentrations in surface sediments (Fig. 1) are also monitored in several sites by IFREMER (Quadrige database, *Réseau d'Observation de la Contamination Chimique*). Measurements were done in 2008 and 2014 in the Bay of Bourgneuf and in 2001, 2009 and 2015 in the Bay of Brest.

The Bay of Bourgneuf is largely opened to the Atlantic Ocean and partly protected by the peninsula of Noirmoutier. No major river drains into the bay but it is surrounded by large marshes, drained by dozens of creeks. The main known sources of Pb are atmospheric inputs and local draining (Amiard-Triquet, 1987). Pb concentrations measured in the