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Tracing platinum accumulation kinetics in oyster *Crassostrea gigas*, a sentinel species in coastal marine environments

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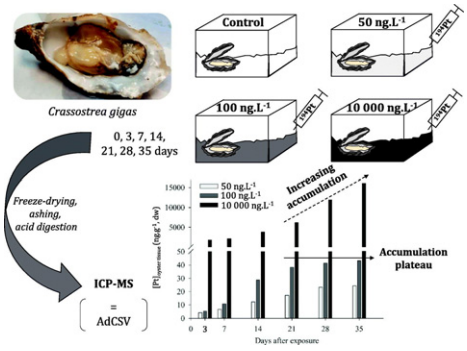
HIGHLIGHTS

- Suitable biota mass (after ashing) provides accurate Pt determination with ICP-MS.
- Oysters show high (concentration independent) Pt accumulation potential.
- Correlation exists between Pt levels in wild oysters and ambient seawater.

GRAPHICAL ABSTRACT



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ABSTRACT

Platinum Group Elements (PGEs) are extremely scarce in the Earth's Crust and of strong interest for high-end technologies due to their specific properties. They belong to the Technology Critical Elements (TCEs) for which use is forecast to increase, implying growing emissions into the environment in the following years. In particular, with the intensive use of platinum (Pt) in car catalytic converters, the anthropogenic geochemical cycle of this element has surpassed the natural cycle. Yet, environmental Pt levels are still in the sub picomolar range, making its analytical detection a challenge. Few studies cover the behavior of Pt in marine waters in terms of speciation, reactivity and possible transfer to the biota. In this study, oysters (*Crassostrea gigas*) from an unpolluted estuary were exposed to the stable isotope ^{194}Pt in seawater at a range of concentrations during 35 days. Seawater was renewed daily and spiked to three nominal Pt concentrations (50, 100, and 10,000 ng·L^{-1}) for two replicate series. In addition, control conditions were monitored. Five oysters from each tank were dissected after 3, 7, 14, 21, 28, 35 days of Pt exposure, and analyzed by ICP-MS. Accuracy of this analytical method applied to biological matrix was checked by an inter-method comparison with a voltammetrical technique. A concentration-dependent accumulation of Pt in oysters increasing with exposure time occurred. After 28 days, oyster Pt accumulation from low and intermediate exposure conditions reached a plateau. This was not the case of the highest exposure condition for which oyster tissues showed increasing concentrations until the last day of the experiment. A linear

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correlation exists between seawater concentrations and Pt content in oysters for low and intermediate exposure concentrations i.e. closer to environmental concentrations. By showing high Pt accumulation potential, oysters may serve as sentinels, ensuring biomonitoring of Pt concentrations in marine coastal waters.

1. Introduction

With the ongoing changes in resource use and technological progression, many elements undergo major disturbance of their geochemical cycles. This is the case of a group of elements named Technology Critical Elements (TCEs). These trace elements have the particularity of being scarce at the Earth surface but have a great interest in terms of economy since they offer peculiar characteristics applied to modern technologies. In this group, the Platinum Group Elements (PGEs) draw attention since their Earth's surface anthropogenic fluxes exceed their natural geochemical fluxes (Sen and Peucker-Ehrenbrink, 2012). In particular, platinum (Pt) is used for jewelry and anti-cancer drugs. However, the major demand for Pt is for automobile catalytic converters. Catalytic properties of Pt are used to reduce vehicle emissions representing >50% of the end use market for PGEs (Bossi and Gediga, 2017).

Regularly introduced in cars from the early 1990's, different environmental compartments have recorded this ongoing change in Pt use. Accordingly, in highly urbanized areas, very high concentrations of Pt are found in road-dusts and roadside soils (Schäfer and Puchelt, 1998). Yet environmental records of Pt increase include also airborne particulate matter such as in Mexico or Germany where elevated Pt concentrations were attributed to automobile catalysts (Rauch et al., 2006; Zereini et al., 2001). Increasing Pt concentrations are also observed in sedimentary cores from (i) an urban lake showing a major increase in Pt accumulation rates from the 1990's to the 2000's (Rauch and Hemond, 2003), (ii) urban estuaries that record strong anthropogenic Pt sources (Mashio et al., 2016) and (iii) even very remote areas such as Antarctica (Soyol-Erdene et al., 2011) since airborne particles are not only present in areas close to emissions but can be transported over longer distances (Zereini et al., 2001). Beyond those abiotic environmental archives, organisms have also been studied to assess environmental changes of trace metal concentrations. This is particularly the case of bivalves that are sedentary sentinel organisms for many trace elements, especially in coastal environments (e.g. Goldberg et al., 1978). Bivalves have already been used to detect Pt contamination in aquatic ecosystems (Abdou et al., 2016; Neira et al., 2015; Ruchter and Sures, 2015). Those studies have shown that wild bivalves (respectively oysters *Crassostrea gigas* and mussels *Mytilus edulis*, and freshwater clams *Corbicula* sp.) seem to be suitable biomonitors for Pt contamination reflecting emission variations over time. Such organisms may bioconcentrate Pt up to a factor of $5 \cdot 10^3$ (Neira et al., 2015). This is a very valuable feature, considering the analytical challenge that represents Pt analysis in samples (e.g. water, particles, and organisms) from natural aquatic environments. Concentrations are very low in such natural samples (i.e. in the $ng \cdot L^{-1}$ range) and often close to detection limits whatever the analytical technique. The strong and complex matrix of coastal waters implies additional analytical limitations, which may explain why only few studies report Pt levels in seawater and coastal environments. Currently, two methods for Pt determination in seawater are described in previous publications: Adsorptive Cathodic Stripping Voltammetry (AdCSV) and Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (ID-ICP-MS) with respective detection limits (expressed as three times the standard deviation of blank measurements) for seawater of $3.9 \cdot 10^{-3}$ $ng \cdot L^{-1}$ and $2.9 \cdot 10^{-3}$ $ng \cdot L^{-1}$ Pt (Cobelo-García et al., 2014a; Mashio et al., 2016). For the second technique, pre-concentration of Pt on an anion exchange resin is required to concentrate Pt and remove sea-salt and interfering metals present in seawater matrix (Obata et al., 2006). Platinum concentrations in biological materials collected in the field are most commonly analyzed by voltammetry (Ruchter and Sures, 2015; Neira et al., 2015; Abdou et al., 2016). Matrix effects (spectral interferences with Hafnium Oxygen: HfO^+ particularly) and generally low content of Pt analyte may lead to analytical difficulties when using quadrupole ICP-MS (Godlewska-Żyłkiewicz, 2004; Pyrzynska, 2015). However, this technique presents several advantages compared to voltammetrical techniques that is in particular interfered by the presence of organic matter and other interfering trace metals (Cobelo-García et al., 2014b). Advantages of ICP-MS method include the fact that this analytical technique is less time consuming in terms of i) sample preparation (organic matter elimination not compulsory, no evaporation required, single-use vessel) and ii) sample analysis (automated sample injection, rapid measurement etc.). In this study, determination of Pt concentrations in biota was done by ICP-MS analyses after an ashing step of the samples. Accuracy of Pt determination was cross-checked by an inter-method comparison between ICP-MS and voltammetry, as no appropriate Certified Reference Material (CRM) is available.

There is still a lack of knowledge concerning Pt speciation in coastal environments. Literature reports that in seawater, the inorganic equilibrium speciation of Pt(II) and Pt(IV) is dominated by $PtCl_4^{2-}$ and $PtCl_5(OH)^{2-}$, respectively (Gammons, 1996) with Pt(IV) being the most important oxidation state (Cobelo-García et al., 2013). Yet, metal source or metal speciation can considerably influence biological availability (Zimmermann et al., 2015) and several exposure studies have proved the potentiality of Pt to accumulate in aquatic organisms. Literature reports that soluble Pt is more bioavailable to zebra mussels than particle-bound Pt (Sures and Zimmermann, 2007). Platinum uptake by the freshwater isopod *Asellus aquaticus* was found to be higher for Pt(IV) than for Pt(II) (Rauch and Morrison, 1999) while the reverse was observed for other freshwater organisms (e.g. Zimmermann et al., 2002). Other aquatic organisms exposed to dissolved Pt include fish species such as eel *Anguilla anguilla* (Zimmermann et al., 2004), or chub *Squalius cephalus* (Ruchter, 2012) reporting the accumulation capacity of these freshwater animals. Mulholland and Turner (2011) addressed for the first time Pt accumulation in natural seawater in an aquatic organism, the gastropod *Littorina littorea*. Accumulation of Pt from dissolved form uptake and diet was studied and suggested that Pt is mainly accumulated from the aqueous phase. This paper is to the best of our knowledge the first addressing Pt accumulation kinetics in a marine bivalve by exposing wild oysters (*Crassostrea gigas*) to isotopically-labelled Pt (^{194}Pt) in seawater for 35 days. Platinum uptake kinetics were investigated in oysters using a wide range of Pt concentrations including environmentally relevant concentrations. Previous studies have already proved the ability of wild oysters to accumulate trace metals integrating and amplifying the environmental signal (e.g. Baudrimont et al., 2005; Lanceleur et al., 2011). More particularly *C. gigas* species already served as monitors to study historical records of recent Pt contamination in an estuary (Abdou et al., 2016). This species represents therefore a promising Pt accumulating sentinel for biomonitoring studies. This work aims at determining the rate and kinetics of dissolved Pt accumulation in soft tissues of oysters. In addition, results will help to determine the potentiality of using wild oysters as sentinel organisms for Pt in marine coastal environments.

2. Material and methods

All the laboratory material in contact with the samples was soaked in an acid bath (HCl 65% J.T. Baker 10% v/v or HNO_3 65% Honeywell 10% v/