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Evidence of increased anthropogenic emissions of platinum: Time-series analysis of mussels (1991–2011) of an urban beach

Patricia Neira [a], Antonio Cobelo-García [a,*], Victoria Besada [b], Juan Santos-Echeandía [a], Juan Bellas [b]

[a] Grupo de Bioxeoquímica Mariña, Instituto de Investigacións Mariñas (IIM-CSIC), Eduardo Cabello 6, 36208 Vigo, Galicia, Spain
[b] Instituto Español de Oceanografía, Centro Oceanográfico de Vigo, Subida a Radio Faro 50, 36390 Vigo, Galicia, Spain

HIGHLIGHTS

- Platinum (0.30 to 0.68 ng g^{-1}) was determined in time-series (1991–2011) samples of wild mussels from an urban beach
- Platinum concentrations followed a statistically significant temporal trend
- The excess of Pt in mussels over the 1991–2011 period was correlated with the Pt autocatalyst demand and car sales
- A bioaccumulation factor of ~ 5 10^3 was derived, greater than those previously calculated for Pt from exposure experiments

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ABSTRACT

The anthropogenic emissions of Pt to the environment have increased significantly over the past decades, especially after the introduction of the catalytic converters in motor vehicles. In order to check whether this is affecting the levels of this trace metal on living organisms, time-series analysis of freeze-dried soft tissue material of wild mussels (*Mytilus galloprovincialis*) covering the period from 1991 to 2001 and collected at an urban beach in the city of Vigo (NW Iberian Peninsula) was conducted. Concentrations ranged from 0.30 to 0.68 ng g^{-1} with an average concentration of 0.47 ± 0.10 ng g^{-1} ($n = 21$); these concentrations were higher than those obtained for samples collected at a control location away from anthropogenic pressure (0.31 ± 0.10 ng g^{-1}; $n = 5$). Platinum concentrations followed a statistically significant temporal trend (at the 0.020 level), and the excess of Pt in mussels over the 1991–2011 period compared to the control location were correlated with the European Pt autocatalyst demand ($p = 0.0006$) and, especially, the car sales in Spain ($p = 0.0001$). A bioaccumulation factor of ~$5 \cdot 10^3$ was derived, which is greater than those previously calculated for Pt from exposure experiments, but 1–2 orders of magnitude lower than other trace elements (e.g. Zn, Cu, Pb, Cd).

1. Introduction

The natural environmental concentrations of platinum in the biosphere are extremely low, with average crustal abundance of 0.5 ng g^{-1} (Rudnick and Gao, 2003). However, Pt concentrations are currently increasing in the environment due to its use in a variety of anthropogenic activities, the most important including the use of this element in automobile catalytic converters and the manufacture of jewellery, representing 43% and 31%, respectively, of the total Pt demanded during the last decade (Johnson Matthey, 2013). The anthropogenic disturbance of the cycle of Pt at the Earth's surface is such that it has been estimated that more than 80% of the Pt flux is derived from anthropogenic activities (Sen and Peucker-Ehrenbrink, 2012).

As a result of the Pt emissions from catalytic converters in motor vehicles, this element currently represents a new category of traffic related trace metal contaminant in the environment (Haus et al., 2007). Accordingly, elevated Pt concentrations have been reported in areas and environmental compartments subject to vehicular traffic pressure such as road dust, roadside soils, sewage sludge and sediments of urban rivers and harbour basins (Schäfer et al., 1999; Ely et al., 2001; Fritsche and Meisel, 2004; Lésniewska et al., 2004; Zimmermann and Sures, 2004); also, evidence for a long range transport and global platinum environmental perturbation has been given (Soyol-Erdene et al., 2011).

The bioavailability and uptake of Pt emitted from catalytic converters and from soluble Pt species were demonstrated in exposure studies using different aquatic organisms, including freshwater isopods (Moldovan et al., 2001), European eels (Zimmermann et al., 2004), zebra mussels (Sures and Zimmermann, 2007), or common periwinkles (Mulholland and Turner, 2011). However, to date only few studies have been carried out reporting ambient concentrations of Pt in biological matrices. Among these, (i) Jensen et al. (2002) analysed the contamination of feathers from raptor species showing an increased temporal

* Corresponding author.
E-mail address: acobelo@iim.csic.es (A. Cobelo-García).

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trend of Pt concentrations reflecting the introduction of automobile catalytic converters; also, (ii) Haus et al. (2007) demonstrated the bioavailability of traffic-borne Pt in field samples of freshwater crustaceans from the Ruhr district (Germany) showing bioaccumulation factors in the range of other traffic related metals.

In this study we report Pt concentrations in time-series samples (1991–2011) of wild mussels (*Mytilus galloprovincialis*) collected in an urban beach of the Vigo Ria (NW Iberian Peninsula; Fig. 1). Mussels are ideal organisms for use as bio-indicators because as filtering organisms they tend to accumulate dissolved substances in the environment (e.g. Goldberg, 1986; Soto et al., 1997; Bellas et al, 2014) and have been widely used in the study area for biomonitoring of metal contamination (Besada et al., 2002, 2011). The main aim of this study is therefore to determine the temporal variation of Pt biological uptake in an urban beach during the past two decades and results will be discussed in terms of the potential link between the temporal variation of Pt accumulation in mussels and the anthropogenic use of this element from the early 1990's.

2. Material and methods

2.1. Sampling area

Wild mussels (*M. galloprovincialis*) were collected manually and during low tides, in the period of September–November, which corresponds to the second prespawning period in this area (Caceres-Martinez and Figueras, 1998) in order to minimize variations caused by differences in the mussel physiology and therefore minimize seasonal environmental variations. Sampling strategies during this two decade long program are described elsewhere (Besada et al., 2014).

Mussels were collected at Samil beach in the Vigo Ria, an urban beach located in the city of Vigo (Fig. 1) which holds a population of approx. 300,000 inhabitants; an urban stream (Lagares, mean annual flow of ~4 $m^3 s^{-2}$; Perez-Arlucea et al., 2005) discharges at the western part of the beach. For comparison purposes, mussel samples from a control point (Oia, Fig. 1) located around 40 km southward and far from any significant contamination influence were analysed for selected years (1991, 1995, 2000, 2005, 2010). The excess Pt fraction in the Samil beach samples was calculated subtracting the concentrations obtained from the control point.

2.2. Pretreatment

Each sample of mussels was prepared from 50 or more individuals representing the available size range (35–60 mm) existing in the sampling location. Soft tissues were separated from the shells, triturated with Ultraturrax and freeze-dried. An aliquot of the liophilized sample was withdrawn to calculate its water percentage (drying at 105 °C for 24 h, until constant weight). After a freeze-drying process, samples were homogenised again with a mixer mill and stored in acid-washed glass vials at room temperature until analysis.

2.3. Pt analysis

Platinum analysis was performed by means of catalytic adsorptive cathodic stripping voltammetry after appropriate digestion (Cobelo-García et al., 2014); briefly, around 100 mg of sample was ashed up to 800 °C in quartz crucibles in order to eliminate refractory organic material that may interfere during the voltammetric determination. Once cooled, a mixture of 3 mL of HCl and 1 mL of HNO_3 was added to the crucible and allowed to rest for at least 1 h. Then, the acid mixture was transferred to uncapped 30 mL PFA vials (Savillex) and placed on a Teflon-coated hot plate at 195 °C and allowed to evaporate until near dryness. After cooling down, 1 mL of H_2SO_4 was added to the vials and placed again on the hot plate until no fumes were observed (only sulphuric acid was present). After cooling, samples were diluted with 0.1 M HCl and transferred to 25 mL polypropylene volumetric flasks pending analysis. Typically, 3 independent digestions were performed for each sample and the relative standard deviation (RSD%) was generally below 15%.

In order to avoid contamination of samples, sample pretreatment and manipulation were performed in a laminar flow bench (ISO-5) housed inside and ISO-7 lab. Voltammetric determinations were carried out using a μAutolab Type III potentiostat (Metrohm Autolab B.V.) connected to a polarographic stand (Metrohm model 663VA). Details of the voltammetric procedure for the Pt determination are given in

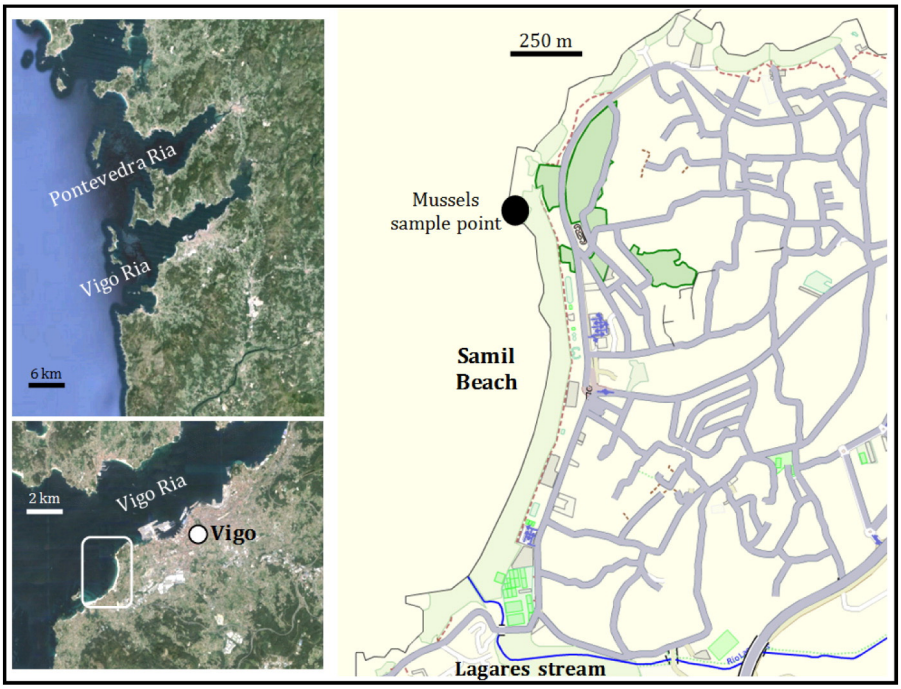

Fig. 1. Sampling location of mussels in the Samil beach (42°13.177 N, 08°46.604 W) of the Vigo Ria (NW Iberian Peninsula).