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Platinum in sediments and mussels from the northwestern Mediterranean coast: temporal and spatial aspects

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Abstract

Platinum (Pt) is considered a Technology Critical Element (TCE) and an emerging metallic contaminant with increasing release into the environment. Gaps in knowledge and understanding of environmental levels, fate and effects of Pt still exist, especially in the marine environment. This work presents Pt concentrations in the northwestern Mediterranean coast including: (i) temporal variability from sediment cores and farmed mussels in the Toulon Bay (historically affected by intense human activities) and (ii) spatial distribution from recent wild mussels collected along ~ 300 km coastline with contrasting ecosystems (including natural reserves), quantified using voltammetry and inductively coupled plasma-mass spectrometry. The historical (> 100 years) record of Pt in sediments from the Toulon Bay suggests the existence of non-negligible Pt sources older than those related to vehicle

emission devices, such as petrol industry and coal-fired activities. A strong Pt increase in more recent sediments (from ~ 12 to 16 ng.g^{-1}) and mussels (8-fold increase from ~ 0.12 to 0.80 ng.g^{-1}) covering the past 25 years reflect the overall evolution of Pt demand in Europe (~ 20 -fold increase for vehicle catalysts in 20 years). Spatial biomonitoring of Pt in mussels along the northwestern Mediterranean coast is assumed to reflect inter-sites differences of Pt exposure (0.09 to 0.66 ng.g^{-1}) despite seasonal effect on tissue development. This study highlights the need for thorough and regular monitoring of Pt levels in sediments and biota from urbanized coastal areas in order to better assess the environmental impact of this TCE, including potential risks for marine organisms.

Keywords: Platinum; sediments; mussels; biomonitoring; Mediterranean coast

1. Introduction

Platinum is a Technology Critical Element (TCE) and an emerging metallic contaminant for which there is a growing need for accurate assessment of environmental distribution and impacts (Cobelo-García et al., 2015). This element is increasingly used in various applications due to its high chemical resistance and excellent catalytic properties. Anthropogenic activities account for more than 80 % of Pt fluxes at the Earth surface (Sen and Peucker-Ehrenbrink, 2012). Today, the most extended application is the use of Pt in vehicle catalytic converters to control air pollution by cars, trucks, motorcycles and non-road mobile machinery, accounting for more than 70 % of the European Pt demand (Johnson Matthey, 2017).

Increasing Pt emissions from automobile exhaust catalytic converters have led to an increase in Pt concentration in many environmental compartments including atmosphere, soils, sediments, interstitial waters, and seawater with anomalies occurring even in very remote, supposedly pristine areas such as the Antarctic snow (e.g. Alméjida et al., 2015; Obata et al., 2006; Rauch et al., 2004, 2006; Schäfer et al., 1999; Schäfer and Puchelt, 1998; Soyol-Erdene et al., 2011). Increasing Pt concentrations are also recorded in aquatic organisms comprising plants, bivalves, and marine mammals which prove to bioaccumulate this element (Abdou et al., 2016; Alméjida et al., 2016; Essumang, 2008; Neira et al., 2015). In spite of growing efforts to improve the understanding of biogeochemical Pt cycles, there is still a lack of relevant environmental data. This is particularly the case in marine environments, mainly due to analytical challenges when analyzing Pt at ultra-trace levels in complex environmental matrices (i.e. seawater, sediments and biota). In fact, only few field studies report on Pt levels, distribution and geochemical behavior in coastal ecosystems. Coastal areas are considered as vulnerable sites due to their anthropogenic socio-economic roles, hosting ~ 70 % of the urban populations and economic activities worldwide (Small and Nicholls, 2003). This pressure implies the risk of serious environmental consequences (McGranahan et al., 2007) such as

trace metal contamination and possible transfer to the marine food web. Evidence of measurable anthropogenic Pt inputs into the coastal environment are especially based on the analysis of sediment cores (e.g. Rauch et al., 2004; Tuit et al., 2000). The few papers reporting on Pt in coastal seawater suggest that supposedly uncontaminated surface seawater shows dissolved Pt concentrations in the range of 0.05 - 0.1 ng.L⁻¹ (e.g. Cobelo-García et al., 2014a; Goldberg et al., 1986). The even more limited number of field studies reporting on Pt concentrations in marine organisms prove Pt bioavailability and relatively high potential for Pt bioconcentration, especially in marine bivalves (Abdou et al., 2016; Neira et al., 2015). Accordingly, these organisms appear as suitable biomonitors to assess Pt levels in marine environments (Abdou et al., 2018).

The Mediterranean Sea is a semi-enclosed system with ever growing anthropogenic pressure along its northwestern coast (Durrieu de Madron et al., 2011; Martín et al., 2009) that comprises several highly populated cities with extensively urbanized and industrialized areas. The progressive urbanization of this coastal area and the possible changes of seawater chemistry due to additional anthropogenic inputs have already been reported in previous studies addressing environmental quality of the Mediterranean coast. Indeed, evidences exist on heavy metal pollution (e.g. Oursel et al., 2013; Tessier et al., 2011), metal-organic components (e.g. organotin; Pougnet et al., 2014) and nutrients (Ruggieri et al., 2011), especially at historically exposed sites and major harbors, such as the Toulon Bay or the Genoa Harbor. The United Nations Environment Program (UNEP) has implemented the Program for the Assessment and Control of Marine Pollution in the Mediterranean (MED POL) among other environmental initiatives. Among the sources of pollution monitored are important shipping industry, oil, gas and chemical industries that are widely developed in the NW Mediterranean coast (UNEP, 2017).

The present work aims at providing an assessment of Pt levels in: (i) historical samples (sediment cores and farmed mussels) from an industrial and strongly urbanized Mediterranean harbor (Toulon Bay, France), and (ii) wild mussels from selected, contrasting sites along 300 km of the northwestern Mediterranean coast, including industrial sites supposedly influenced by Pt-releasing anthropogenic activities.

2. Material and Methods

2.1. Study area, sampling sites, and sample collection

The northwestern Mediterranean coast is characterized by high urbanization and numerous harbors, with areas that have faced centuries of intense anthropogenic pressure due to urban and industrial emissions, trade, war material spills, navigation, dredging and fishery among other activities. Progressive intense urbanization has led to a general anthropogenically-derived chronic pollution by multiple contaminants of various origins (e.g. trace metals, Oursel et al., 2013). Different sets of samples were collected at contrasting sites in France and Italy, covering a coastline of ~ 300 km in the northwestern Mediterranean (Fig. 1).

The Toulon Bay

Long-term evolution of Pt in a harbor affected by strong multi-component pollution was studied in sediment cores and farmed mussels from the Toulon Bay (TB, Fig. 1). The Toulon Bay is divided into two parts by an artificial embankment, forming the Large Bay and the Small Bay (LB and SB, respectively; Fig. 1) and receives urban inputs from Toulon city (~ 600,000 inhabitants, Tessier et al., 2011). The Toulon Bay has been strongly polluted by anthropogenic wastes originating from both historic (bombardments and fleet scuttling during World War II: one hundred ships destroyed and sunk, mainly in the Small Bay) and ongoing

activities (French Navy, commercial traffic, urban raw sewage release, industry, tourism; Dang et al., 2015; Tessier et al., 2011). Accordingly, high levels of inorganic and organic pollutants are accumulated in sediments from the Toulon Bay (e.g. Dang et al., 2015; Pougnet et al., 2014; Tessier et al., 2011). Both sediment cores and mussels were sampled in the SB characterized by a semi-closed shape with a surface of $\sim 9.8 \text{ km}^2$ where the morphology and the artificial barrier limit water circulation favoring accumulation of sediment and associated contaminants (Fig. 1, Tessier et al., 2011).

The sediment cores were sampled by the laboratory PROTEE from November 2008 to June 2009 in the context of a wider survey on sediment quality in the Toulon Bay (Tessier et al., 2011). The two sediment cores analyzed in this study were collected at sampling site TB1 located in the eastern part of SB, close to a former Navy submarine base and in the main navigation channel; and at site TB2 located in the western part of SB, close to a fish/mussel farming area (Fig. 1). The sediment cores were processed as previously described in Tessier et al. (2011). Briefly, 10 cm diameter and 1 m long (Interface Corer, Plexiglas® tube) sediment cores were transported to the laboratory PROTEE directly after sampling and sliced (2 cm resolution) under inert atmosphere (N_2) to preserve redox conditions. The sliced sediment samples were pooled and homogenized (Teflon spoon), placed into pre-cleaned 1 L high-density polyethylene (HDPE) bottles and deep frozen (-18°C). All frozen samples were subsequently freeze-dried (within one month) and sieved (2 mm).

Farmed mussels (35 - 65 mm, *Mytilus galloprovincialis*) were sampled annually since 1984 at the sampling site TB2 (Fig. 1) by the RNO-ROCCH mussel watch program (IFREMER). Freeze-dried soft tissues (pooled total soft bodies of more than 30 individuals) from the National Mussel Watch sample bank (storage at room temperature and in the dark) were selected, covering the period from 1984 to 2014 at 3-years intervals.

131 *Mediterranean coastline*

132 Wild mussels (*M. galloprovincialis*) were sampled at contrasting sites along the northwest
133 Mediterranean coastline: in Banyuls-sur-Mer, Sète, Saintes-Marie-de-la-Mer, Faraman, and
134 Toulon Bay (respectively BM, ST, SMM, FM, TB; Fig. 1) and in the South of the Corsica
135 Island (Bonifacio, BF, Fig. 1) by the IRSN (French Institute for Radioprotection and Nuclear
136 Safety) within a regular monitoring program (2016-2017). In addition, wild mussels from the
137 Genoa Harbor were collected (GH, Fig. 1) during a field campaign held in April 2016. After
138 manual collection, mussels (~ 7 cm) were cleaned, opened, and soft tissue and shells were
139 weighed separately. This sampling scheme cover a great diversity of expected pollution levels
140 (industrialized and preserved sites). Accordingly the sampling sites Banyuls-sur-Mer, Sète,
141 Faraman, and Bonifacio are located in natural preserved area with no expected source of
142 pollution. The sampling site Saintes-Marie-de-la-Mer is in a leisure harbor and therefore
143 potentially more affected by pollution whereas the sites Toulon Bay and Genoa Harbor
144 represent two major harbors of the NW Mediterranean Coast. Several pollution source are
145 expected since they are characterized by petroleum, industrial fumes and urban runoff
146 pollution (Baumard et al., 1998). The Condition Indices (CI = Visceral Content, wet
147 weight / Shell, wet weight; Strady et al., 2011) were determined for all the samples. For
148 samples collected along the French coastline, each sampling corresponded to the collection of
149 ~ 240 individuals that were pooled. For samples collected in the Genoa Harbor, 10 organisms
150 were processed individually. Mussel tissues were then oven-dried at 80 °C to constant weight
151 and dried tissues were kept at room temperature in the dark pending analysis.

152 Seasonal trace metal level variations have been observed in *M. galloprovincialis* related to
153 variable soft-body weight during reproduction periods (e.g. Charmasson et al., 1999, Erk et
154 al., 2018). Accordingly, in Spring, Summer, and early Fall, gonads contain developing and
155 mature gametes and represent up to 35 % of the total body weight, while Autumn and early

Winter correspond to the period of gametogenic quiescence and associated lower metabolic rate (Widdows, 1978). In order to observe the seasonality of Pt concentrations, mussel samples from Winter (December – February) were analyzed together with mussels from Spring and Summer / Fall (July – October) from the same site, when both sets of samples were available. For the sampling sites Banyuls-sur-Mer, Bonifacio, and Genoa Harbor, only mussel samples from dates within the reproduction cycle were analyzed (July 2016, October 2016, and April 2016 respectively).

2.2. Analytical methods

Sediment

Platinum concentrations in sediment core samples were determined by Adsorptive Cathodic Stripping Voltammetry (AdCSV) as described in Cobelo-García et al. (2014b). Measurements were carried out using a μ Autolab Type III potentiostat (Metrohm® Autolab B.V.) connected to a polarographic stand (Metrohm® 663 V.A.) equipped with three electrodes: (i) a hanging mercury drop electrode (HMDE, the working electrode), (ii) a silver/silver-chloride (Ag/AgCl) reference electrode, and (iii) a glassy carbon auxiliary electrode. A polytetrafluoroethylene (PTFE) voltammetric cell served in all experiments and the potentiostat was controlled using the NOVA 2.1 software. According to the protocol for sediment treatment described by Cobelo-García et al. (2011), about 50 mg of sediment samples were ashed in porcelain crucibles at 800 °C during 3 h (removal of Organic Matter, OM). Ashed samples were transferred into 30 mL perfluoroalkoxy (PFA) vessels with screw caps (Savillex®) and acid-digested at 195 °C for 4 h using 5 mL HCl and 3 mL HNO₃ (30 % HCl and 65 % HNO₃ Suprapur, Merck®). After this step, vessel caps were removed and the acids evaporated at 195 °C until near dryness. The residue was re-dissolved using 1 mL of

sulfuric acid (H_2SO_4 , 93 – 98 % Trace metal grade, Fisher Chemical®) at 195 °C. Cooled contents were diluted using 0.1 M HCl, centrifuged at 4000 rpm for 10 min (20 °C), and made up to 25 mL in pre-clean Teflon bottles (Nalgene®).

Aliquots of acid-digested sample (dilution 1:1 with MilliQ water®) were pipetted into the voltammetric cell together with 30 μL of 3.3 mM formaldehyde (37–41 % Analytical Reagent Grade, Fisher Chemical®), 30 μL of 0.45 mM hydrazine sulfate (Analytical Reagent Grade, Fisher Chemical®), and 300 μL of H_2SO_4 . Platinum concentrations were determined by standard addition method (adding mono-elementary Pt standard solution 1000 $\mu\text{g}\cdot\text{mL}^{-1}$ PLASMACAL, SCP Science®) using a deposition time of 90 s and experimental parameters as described elsewhere (Cobelo-García et al., 2014b).

Mussels

A previous inter-method comparison using two completely independent digestion and measurement techniques (Inductively Coupled Plasma-Mass Spectrometry: ICP-MS and AdCSV) has shown that Pt concentrations in natural biological samples (oysters) can be reliably measured by ICP-MS when sufficient sample mass (i.e. ~ 0.25 g dry weight, 0.13 ng Pt) is available (Abdou et al., 2018). Indeed, hafnium-oxides (HfO^+) interferences that may prevent correct analysis of Pt in biological matrices (Godlewska-Żyłkiewicz, 2004; Pyrzynska, 2015) can be mathematically corrected using the ^{193}Ir (iridium) signal that is highly interfered by HfO^+ (Abdou et al. 2018, Djingova et al., 2003). The ICP-MS method can therefore be an alternative to AdCSV for detection of Pt in biological samples. Due to relatively low sample mass available for farmed mussels from the Toulon Bay, these samples were analyzed by AdCSV applying the same procedure as for sediment cores, using a deposition time of 180 s. In contrast, sufficient sample mass was available for the wild mussel samples from the Mediterranean coastline, allowing for the time saving analysis using ICP-MS (ICP-MS, Thermo, X Series II). About 1.5 g of sample was ashed at 800 °C in porcelain

crucibles. After cooling, ashed residues were transferred into acid-cleaned polypropylene (PP) tubes (DigiTUBE[®], SCP SCIENCE[®]), and digested at 110 °C for 3 h with 2 mL HCl and 1 mL HNO₃ (30 % HCl and 65 % HNO₃ Suprapur, Merck[®]) as described in Abdou et al. (2018) for environmental samples. Cooled contents were then diluted in 10 mL MilliQ water[®], centrifuged at 4000 rpm for 10 min (20 °C). Analyses were performed applying the standard addition method (using mono-elementary Pt standard solution 1000 µg.mL⁻¹ PLASMACAL, SCP Science[®]).

Quality control

Quality control was performed using the only Certified Reference Materials available for Pt being the BCR[®]-723 road dust (IRMM) and the Jsd-2 sedimentary rocks (indicative value from GSJ). Platinum quantification by AdCSV provided satisfactory recovery of 89% for BCR[®]-723 and 98% for Jsd-2 (n = 3) as well as ICP-MS analyses giving recovery values of 87% and 101% respectively. Uncertainty of the analysis, expressed as Relative Standard Deviation (RSD%), was below 10% using both methods. In addition, in the absence of any biological CRM for Pt, a previous study inter-compared ICP-MS and AdCSV as different, independent analytical method. Results for similar sample masses as applied in the present study allowed for reproducible and similar (< 3 % difference in average) results for both methods indicating good accuracy. The detection limit for particulate (sediment and biota) Pt measured by AdCSV (calculated as 3 x blank standard deviation, n = 5) was estimated to 0.03 ng.g⁻¹ for typical mass of 50 mg. The detection limit for Pt measured in biological samples by ICP-MS (n = 10 blanks) was estimated to 0.003 ng.g⁻¹ for typical biological sample masses of ~ 1.5 g.

3. Results

3.1. Historical record of Pt concentrations in sediments and mussels from the Toulon Bay

Platinum concentrations in the two sediment cores TB1 and TB2 ranged from 6 ng.g⁻¹ to 15 ng.g⁻¹ (Fig. 2A). Samples in the TB1 core showed relatively constant Pt levels of ~ 10 ng.g⁻¹, with only a small variation at 5 cm depth showing Pt concentration of ~ 7 ng.g⁻¹. In contrast, the core TB2 showed a general trend of Pt concentrations decreasing with depth, i.e. the highest concentrations occurred in the top of the core and the lowest values in the bottom (Fig. 2A). Overall, the Pt concentrations tended to be lower in the core TB1 than in TB2. When comparing sediment samples from different depths or different cores, one has to exclude that the observed variations are due to grain size effects because particle size fractionation may lead to increasing trace metal concentrations with decreasing grain size (Loring and Rantala, 1992). Accordingly, grain size effects on natural, lithogenic trace metal variability must be corrected by normalization over a grain size dependent lithogenic element before assessing anthropogenic inputs (Loring and Rantala, 1992). Aluminum (Al) has been chosen as the normalization element for the Toulon Bay and many other systems (e.g. Ho et al., 2012; Pougnet et al., 2014; Tessier et al., 2011), as Al contents are influenced by natural sedimentation and the effects of enhanced erosion, but not by pollution (Li and Schoonmaker, 2003; Luoma and Rainbow, 2008). In fact, correlation ($R^2 = 0.94$) between potassium (K) and Al concentrations in surface and deep sediment showed the close relationship between Al and clay minerals, supporting the pertinence of Al-normalization (Tessier et al., 2011). In both cores, Al-normalization did not modify the profiles, suggesting that grain size effects on spatial (horizontal and vertical) Pt distribution are negligible (Fig. 2B). These results suggest that in the sediment core TB2 (i) nearly all layers are enriched in Pt compared to the core TB1

and (ii) there is a clear increasing trend in Pt enrichment from the bottom to the top of the core (3-fold; Fig. 2).

Platinum concentrations in farmed mussels from the Toulon Bay ranged from 0.10 to 0.79 ng.g⁻¹, in the 1984 to 2014 period (Fig. 3). Platinum concentrations were relatively low and constant (~ 0.15 ng.g⁻¹) from 1984 to 1990, followed by a clearly increasing trend over time towards a maximum value of 0.79 ng.g⁻¹ in 2014, which is ~ 8 times greater than the levels of the 1980's. In the same period, the European Pt gross demand for car catalytic converters evolved from 1-2 tons.y⁻¹ in the late 1980s to ~ 40 tons.y⁻¹ from 2010 to 2014 (Fig. 3).

3.2. Platinum concentrations in mussels from the northwestern Mediterranean coast

Platinum concentrations in wild mussels from contrasting sites, expressed in ng.g⁻¹ dw ranged from ~ 0.09 to 0.66 ng.g⁻¹ (Fig. 4). Winter mussels were compared to Spring and Summer / Fall mussels, whenever possible as described in section 2.1.

Winter mussel Pt concentrations varied from ~ 0.33 to 0.55 ng.g⁻¹ (black bars; Fig. 4). For those mussels, Pt concentrations at the different sites tended to increase from the western to the eastern sites along the coast (Sète to Toulon Bay). Winter mussels from Sète sampling site showed the lowest Pt levels, while highest concentrations occurred in mussels from Faraman site and from the Toulon Bay.

Summer / Fall mussel Pt concentrations ranged from ~ 0.09 to 0.66 ng.g⁻¹ (white bars; Fig. 4), with mussels from Sète showing the lowest concentrations at a given sampling period, while highest concentrations occurred in mussels from the Toulon Bay. Platinum concentrations were also determined in wild mussels collected in the Genoa Harbor in April 2016. Ten individuals were analyzed separately, providing an average Pt concentration of

0.48 ± 0.14 ng.g⁻¹ (Genoa Harbour, Fig. 4). Condition Indices varied from 17 to 47 between sites and sampling periods. Spring and Summer / Fall individuals showed CI ranging from 21 to 47 with a mean value of 31, while it varied from 17 to 23 with a mean value of 20 in Winter organisms.

4. Discussion

4.1. Historical records of Pt concentrations in the Toulon Bay

Two complementary approaches to study the temporal evolution of Pt in the Toulon Bay rely on the analysis of environmental archives: sediment cores and mussel samples from a historical sample bank, implying different time scales and resolution.

Historical record in sediments

Average sedimentation rate in the Toulon Bay sediments was estimated from the vertical distribution of ²¹⁰Pb activity in the sediment cores in previous work (Tessier et al., 2011), suggesting an average sedimentation velocity of 0.21 ± 0.05 cm.y⁻¹. Accordingly, the studied sediment cores cover the period ~ 1890 - 2008 and the top 10 cm layer would reflect ~ 50 years of history (Tessier et al., 2011). As Al-normalization performed to correct for variations in sediment nature and grain size (Sageman and Lyons, 2003) did not modify the Pt profiles in the Toulon Bay sediments (Fig. 2B), the observed variations are attributed to anthropogenic inputs, rather than lithogenic processes, as described elsewhere (e.g. Almécija et al., 2016).

The assessment of the degree of contamination in a given environmental sample requires the establishment of references representing “uncontaminated” conditions in comparable sample types. Classically, authors have compared their results with average values of the Upper Continental Crust (UCC, e.g. Abdou et al., 2016; Cobelo-García et al., 2011; Rauch et al., 2004). This first approach may suggest that the Pt concentrations in the Toulon Bay sediments

are clearly higher (up to 30 fold) than the UCC average (0.5 ng.g^{-1} , Rudnick and Gao, 2003). More representative reference samples may be locally identified either in (i) remote areas, presumably not affected by the contaminant (spatial approach) or in (ii) samples representing conditions during periods before the contaminant release (temporal approach). Given the high spatial variability in (i) Pt global contaminant dispersion, measurable even in remote sites (e.g. polar ice, Soyol-Erdene et al., 2011) and (ii) heterogeneous sediment nature at a large spatial scale, we have considered to apply the temporal approach to reliably determine the contamination degree of Pt in the Toulon Bay.

In fact, Pt concentrations in the bottom layers of the sediment cores, i.e. $\sim 10 \text{ ng.g}^{-1}$ in core TB1 and $\sim 6 \text{ ng.g}^{-1}$ in core TB2, supposedly dating from the early 20th century, could serve as the local reference level for relatively uncontaminated sediment. These values may appear high, compared to background values reported for ancient sediments in the Tagus Estuary ($0.2 - 0.3 \text{ ng.g}^{-1}$, Cobelo-García et al., 2011) or for the UCC Pt content. They are, however, similar in magnitude as Pt records from marine pristine sediment cores (~ 1 up to 5 ng.g^{-1} in Atlantic abyssal pelagic sediment; Colodner et al., 1992) and other pelagic sediments from a variety of locations in the Pacific ocean (0.4 to 22 ng.g^{-1} , Koide et al., 1991), both sampled before the recent emergence of Pt as a global contaminant. Furthermore, pre-anthropogenic coastal sediments from the Massachusetts Bay showed similar Pt levels than bottom layers from the Toulon Bay ($\sim 5 \text{ ng.g}^{-1}$, Tuit et al., 2000). These observations together with high Pt levels in South Pacific pelagic sediment ($\sim 30 \text{ ng.g}^{-1}$, Lee et al., 2003) and in marine manganese nodules (up to 900 ng.g^{-1} , Koide et al., 1991) tend to suggest that relatively high Pt concentrations in coastal sediments may, at least partly, be attributed to the presence of marine particles and not necessarily derive from terrigenous and/or anthropogenic sources. Accordingly, the Toulon Bay bottom sediments may be considered as the local, pre-industrial reference (especially core TB2). In fact, the Toulon Bay receives water from the open

Mediterranean Sea via the Ligurian Current flowing from east to west including deep water areas (Duffa et al., 2011), transporting particles of marine origin into the bay. These findings highlight the need for better knowledge of marine particle baseline Pt concentrations in the Mediterranean Sea and worldwide, as a prerequisite to accurately evaluate anthropogenic contamination in coastal particles and sediments by distinguishing geochemical background from anthropogenic signals.

The Pt/Al values suggest increasing concentrations from the bottom to the top in the core TB2 (~3-fold increase from the bottom to the top layers; Fig. 2B). However, the relatively small recent increase in Pt/Al values (~ 20 % in the period ~ 1984-2008) combined with the relatively high values in the bottom of the core TB1 may be due to its position in the eastern part of the SB, more exposed to the marine incoming water than the site TB2 (counterclockwise circulation in the Toulon Bay; Duffa et al., 2011). In addition, the site TB1 is located close to a main navigation channel, thus, one cannot fully exclude post-depositional Pt redistribution of the sediment. Post-depositional Pt redistribution processes might include both physical mixing (e.g. navigation, dredging...) and chemical redistribution related to diagenesis processes (Almécija et al., 2015; Tuit et al., 2000). Chemically-driven Pt mobility was already observed in other coastal sediments showing maximum Pt enrichment at the base of the surface mixed layer after scavenging at the oxic/anoxic boundary (Cobelo-García et al., 2011). Furthermore, a sediment core from the Boston Harbor also showed chemical mobility of Pt, implying Pt remobilization in sediments at short time scales (Tuit et al., 2000). According to Colodner et al. (1992), a fraction of Pt in marine sediments is labile, suggesting that Pt may be scavenged from seawater into both Fe-Mn oxyhydroxide minerals and organic-rich sediments, so that these phases might dominate the Pt distribution in sediments. Previous work has compared trace metal (Cu, Hg, Pb, and Zn) distributions in the same cores from the

349 Toulon Bay showing some evidence of partial mixing in the core TB1 (Dang et al., 2015;
350 Tessier et al., 2011).

351 In contrast, the position of the core TB2 in a shallow zone with low water regeneration
352 (Tessier et al., 2011) and less impacted by currents, ship traffic and/or dredging, suggests that
353 no major sediment reworking occurred. In this core, the continuous increase of Pt/Al over the
354 past century before the mid-1980s cannot be explained by the relatively new technology of
355 car catalytic converters, implying additional, yet less reported anthropogenic Pt sources to the
356 marine environment. In fact, Pt concentrations in surface sediments from the Boston Harbor
357 dating from 1978 (i.e. integrating Pt emissions before the introduction of car catalysts)
358 showed a 17-fold enrichment of Pt concentrations relative to background values (i.e. up to
359 12.5 ng.g^{-1} , Tuit et al., 2000). This observation suggests that, despite the higher Pt release
360 rates of the early catalytic converters and considering the relatively low number of catalyst-
361 equipped cars at that time, other, probably industrial sources may have affected the Pt levels
362 in harbor sediments (Tuit et al., 2000). Older Pt emissions might be related to the use of Pt in
363 several industrial applications, since Pt played an important role in various catalytic processes
364 (e.g. catalytic cracking of crude petroleum) applied for the production of the very high octane
365 fuels required for aircraft and automobile engines during World War II (Peavy, 1958). After
366 the war, Pt catalyst reforming processes, introduced to the refining industry in 1949, produced
367 huge amounts of lower octane fuels for automobile engines, and industrial / home heating
368 fuels. Accordingly, the years 1950 to 1960 were considered as the industry's "platinum
369 period" (Peavy, 1958). In addition, emissions from intense coal industry during the first half
370 of the 20th century, may have contributed to elevated Pt concentrations, since high Pt
371 concentrations were reported for coal samples ($\sim 5 \text{ ng.g}^{-1}$, Finkelman and Aruscavage, 1981;
372 up to 70 ng.g^{-1} , Dai et al., 2003). As a result of the scuttling of the French Navy fleet during
373 WWII (November 1942, Tessier et al., 2011), huge amounts of industrial coal are still present

374 in the surface sediments inside the Toulon Bay with the area of the core TB2 being the coal
375 loading dock (Dang et al., 2018). Although the Pt concentrations in this coal are unknown,
376 given the range of values reported in the literature, industrial coal and/or fly ashes could
377 partly explain the Pt accumulation in the core TB2, with a stronger increasing trend before
378 ~ 1960, and a period of weaker increase during ~ 1960 – 1990.

379 Recent increase of Pt concentrations (~ 50 % increase in ~ 24 years in core TB2; Fig. 2) is
380 consistent with observations in other coastal environments, such as the Tagus Estuary. In this
381 system, Pt values at the top of the sediment core (up to 9.5 ng.g^{-1} , Cobelo-García et al., 2011)
382 representing ~ 30 - 40 times the local background are observed. Platinum concentrations in
383 saltmarsh sediments impacted by high traffic in the same estuary showed a surface peak value
384 exceeding 40 ng.g^{-1} (Almécija et al., 2015). This recent contamination has been clearly
385 attributed to increasing Pt demand, use and emission related to the introduction of car exhaust
386 catalytic converters since the early 1990's (Rauch and Morrison, 2008). Considering Pt
387 concentration originating from catalysts of $\sim 4 \text{ ng.g}^{-1}$ for the topmost samples in sediment
388 core TB2, Pt deposition rates are estimated to $\sim 15 \text{ g Pt.y}^{-1}$ based on an annual sedimentation
389 rate of $\sim 0.2 \text{ cm.y}^{-1}$, a density of wet sediment of 0.64 g.cm^{-3} and a porosity of 0.7, as well as
390 a SB surface of 9.8 km^2 (Tessier et al., 2011). A rough estimation of Toulon Bay catalyst
391 emission of ~ 10 to 20 g Pt.y^{-1} is obtained assuming $\sim 200,000$ vehicles equipped with
392 catalysts with an average yearly mileage of $1,000 \text{ km.vehicle}^{-1}$ and an average emission rate
393 ranging between 50 and $100 \text{ ng Pt.km}^{-1}$ (based on values from Rauch and Peucker-
394 Ehrenbrink, 2015). As observed on a global scale in Rauch et al. (2005), the difference
395 between emission and deposition rates may originate from several factors including over-
396 /underestimated emission rates which is influenced by the age and the type of vehicle (e.g.
397 Moldovan et al., 2002) or the occurrence of recent additional sources (e.g. wastewaters and Pt
398 from anticancer-drugs, Vyas et al., 2014). Literature reports that Pt emissions from cars are

mainly deposited at a distance of less than 20 m from the edge of the road (e.g. Fritsche and Meisel, 2004; Schäfer and Puchelt, 1998). Over-estimation of Pt inputs may also originate from the transfer of Pt emissions to seawater that is surely influenced by several factors including prevailing wind direction (Schäfer and Puchelt, 1998) and road runoff. Exportation of fine-grained urban particles towards the outer bay or the open sea by currents and/or potential partial Pt dissolution from urban particles in contact with seawater may also occur (Cobelo-García et al., 2014a). In addition, dissolved Pt will probably be diluted and exported rather than accumulated in sediments. Despite potential errors in the estimations, calculated Pt emission rates from car catalysts in the SB are generally in good agreement with recent Pt deposition rates in sediment core TB2 and might therefore explain a large fraction of total Pt deposition in the area.

Historical record in mussels

The temporal evolution of Pt concentrations in mussels farmed close to the site of core TB2 (Fig. 1) reflected a ~ 8-fold increase over the 1984 to 2014 period, especially since the mid-1990s (Fig. 3). Together with the ~ 20-fold increase in European Pt demand for car catalysts over the same period, this observation suggests that vehicle-emitted Pt has been introduced into the coastal ecosystem of the Toulon Bay with an effective transfer to living marine organisms. These first results for Pt in Mediterranean bivalves are in line with increasing Pt/Al values in the TB2 core from the same site and with previous work on wild oysters and mussels from the French and the Spanish (Galician) Atlantic coast (oysters, Abdou et al., 2016; mussels, Neira et al., 2015). Given the fact, that biomonitoring organisms are sampled on a regular basis, sediment-specific uncertainties due to physical or chemical disturbance of the historical record are excluded and, therefore, the use of sentinel organisms from sample banks may provide reliable information on trends in ambient contaminant pressure over time.

In fact, the recent Pt increase in mussels goes along with a decrease in Pb as observed in the same mussel samples from the Toulon Bay (Dang et al., 2015) and in Galician Mussels (Neira et al., 2015). These opposite trends may be explained by the successive ban of leaded gasoline (leading to decreasing Pb emissions) in parallel to the growing deployment of catalyst-equipped vehicles, since leaded gasoline damages the catalysts and thus is not compatible with this modern technology (Schäfer and Puchelt, 1998). The apparent baseline Pt concentration (0.1 ng g^{-1} ; Fig. 3) in Toulon Bay mussels could reflect either natural Pt background although one cannot exclude that these concentrations partly result from other historic Pt contamination as recorded in the sediment.

4.2. Biomonitoring of Pt in mussels along the northwestern Mediterranean coast

Spatial distribution of Pt concentrations in mussels from contrasting sites along the Mediterranean coast seemed to roughly follow an increasing gradient from western to eastern sites, reflecting inter-site differences in terms of urbanization and supposed Pt inputs. Generally, in order to avoid trace metal variations related to seasonality, including reproduction, leading to “biological dilution” of gonads (Regoli and Orlando, 1994), Winter organisms are used for comparison. In those mussels, the lowest Pt concentrations occurred at the sampling site Sète. Low Pt concentrations also occurred in mussels available from sites Banyuls-sur-Mer (Natural Reserve of Cerbère-Banyuls) and Bonifacio (Summer / Fall mussels). All those three sites are located in supposedly less exposed areas, i.e. far from major urban areas. Slightly higher Pt concentrations ($\sim 0.4 \text{ ng.g}^{-1}$) measured in Winter mussels from sampling site Saintes-Maries-de-la-Mer cannot be explained by intense urban pressure, yet, mussel sampling was performed inside the leisure harbor. Even though the sampling site Faraman is located in a non-urbanized area (Natural Regional Park of Camargue), relatively high Pt concentrations ($\sim 0.5 \text{ ng.g}^{-1}$) in wild Winter mussels suggest contamination of this site, possibly by seawater draining pollution from La-Fos-sur-Mer city. In fact, in the late

1980's, the Gulf of Fos was considered as one of the most polluted neritic areas in Europe with important metal pollution (Cu, Pb, Cd, Zn; Benon et al., 1978). This area hosts important oil industries that might be a source of Pt to the marine environment as previously discussed (section 4.1.). Other studies report high trace metal contamination in native and caged mussels *M. galloprovincialis* from areas close to major urban and industrial centers such as La-Fos-sur-Mer (Andral et al., 2004), with a battery of biomarkers indicating disturbed health in mussels (Zorita et al., 2007) from the most impacted zones including the La-Fos-sur-Mer Harbor. In addition the sampling site Faraman is directly under the influence of the Rhône outflow (Charmasson et al., 1999) which may drain all the pollution originating from the urbanized watershed. Similar Pt concentrations occurred in mussels from sampling site TB2 in the Toulon Bay (Seyne sur Mer), showing the highest Pt level (0.55 ng.g^{-1}) of the studied sites. This value is somewhat lower than the 2014 value ($\sim 0.8 \text{ ng.g}^{-1}$) in farmed mussels from the same area in the Toulon Bay. Platinum concentration range in mussels from the Genoa Harbor, marked by industrial / urban water pollution (Ruggieri et al., 2011), is similar to levels observed in the Toulon Bay (Fig. 4). These observations suggest that Pt accumulation in mussels from the different sites may reflect the supposed exposure from anthropogenic pressure, similarly to other trace metals, showing strong gradients between mussels from less populated areas or regions with no major river inputs (e.g. Sète) and those from heavily populated and industrialized port areas (Fowler and Oregioni, 1976).

Few field studies report on Pt levels in biota from coastal marine environments. Recent samples of wild mussels *M. galloprovincialis* from an urban beach in Vigo (Spain) revealed Pt concentrations of $\sim 0.45 \text{ ng.g}^{-1}$ (2011 value, Neira et al., 2015), while wild oysters (*Crassostrea gigas*) from the moderately contaminated Gironde Estuary mouth contained $\sim 0.33 \text{ ng.g}^{-1}$ (2013 value, Abdou et al., 2016). Accordingly, Pt levels in mussels from the Mediterranean sites are similar in magnitude to those in wild bivalves from the Atlantic coast,

but with clearly higher values in confined harbor sites with relatively high urban/industrial pressure. Bioconcentration factors (BCF), comparing Pt accumulation in tissues to ambient seawater concentrations were determined as $BCF = Pt_B / Pt_D$, where Pt_B is the Pt concentration in the organism ($ng.g^{-1}$, dw) and Pt_D the dissolved Pt concentration in seawater ($ng.L^{-1}$, Arnot and Gobas, 2006) for the Genoa Harbor mussels (no Pt_D data available for the other sites). Average BCF in the Genoa Harbor mussels was $\sim 4 \times 10^3$, i.e. similar to values reported for wild mussels *M. galloprovincialis* from an urban beach ($\sim 5 \times 10^3$; Neira et al., 2015) and for wild oysters from the Gironde Estuary ($\sim 3 \times 10^3$, Abdou et al., 2016). These values show that marine bivalve bioconcentrate Pt ambient signal reflecting: (i) the presence of natural bioavailable Pt species and (ii) their suitable use for Pt monitoring in coastal systems. Although it is assumed that dissolved metals are potentially more bioavailable than their particulate forms (e.g. Lekhi et al., 2008), filter-feeders such as mussels are able to absorb metals, and more particularly PGEs, in dissolved and particulate forms (Zimmermann and Sures, 2018). Given that Pt emissions from car exhaust systems mainly occur as very small particles (from micrometers down to nanometric size; Folens et al., 2018; Rauch et al., 2001), more work is necessary to characterize the behavior of such particles in the marine environment and understand their role in Pt transfer to living organisms.

Physiological status including growth and reproductive state may impact metal concentrations in bivalves, due to ‘dilution’ effects by rapid tissue growth or weight increase during gonad development (Casas et al., 2008; Couture et al., 2010). Therefore, contaminant concentrations in tissues reflect ambient concentrations, but also food availability or seasonal reproduction cycles (Andral et al., 2004; Charmasson et al., 1999; Dang et al., 2015). Inter-site comparison may require adjustment of raw concentration data from different sites with reference to a standard Condition Index to limit the risk of miss-interpretation, as shown from a mussel caging study, where site-dependent growth differences occurred at relatively short timescales

(Andral et al., 2004). Comparison of Pt concentrations in the soft bodies of mussels sampled in Winter and in Spring and Summer/Fall from four of the seven studied sites clearly suggests that Pt concentrations undergo seasonal fluctuations (Fig. 4). The Condition Indices in the different mussel samples ranged from 17 to 47 with higher CI for Spring and Summer/Fall samples than for Winter samples, when comparison was available (Fig. 4). This result is expected supposing higher soft tissue mass during the reproduction season than during Winter. Indeed, during gametogenesis, the penetration of gonadic tissues into the digestive gland may biologically dilute metal concentrations in mussel total soft tissues (Regoli and Orlando, 1994). At three sites, the Winter concentrations are greater than the respective Summer values, as expected, whereas at the Toulon Bay site, Pt concentrations were higher in Summer, despite higher CI (Fig. 4). The latter observation might reflect environmental Pt exposure related with either site-specific changes in bio-transfer or temporarily higher local Pt inputs (e.g. tourism related). However, these hypotheses cannot be validated with the available dataset. The observed seasonal fluctuations do not change the order of supposed Pt exposure between the studied sites (Sète to Toulon Bay; Fig. 1), suggesting that the uncertainties discussed above do not invalidate the spatial biomonitoring approach, yet warranting an optimized sampling strategy to limit potential biases.

5. Conclusions

Historical records of both sediment cores and mussels collected in a severely polluted site, the Toulon Bay, suggest the existence of former (non-vehicle related) sources of Pt in the system. They also revealed the impact of recent contamination related to increasing Pt emissions through car catalytic converters that may be of major importance in this area under high anthropogenic pressure. Biomonitoring in mussels from contrasting areas along the

523 northwestern Mediterranean coastline suggests a relation between the degree of exposure and
524 the Pt concentrations in mussel tissues. Mussels could therefore be considered as a potential
525 good bioindicator of Pt levels in marine environments. Considering the relatively high Pt
526 concentrations in some sampling sites, systematic (bio-)monitoring programs should therefore
527 be run in such coastal environments marked by historical and current Pt contamination.
528 Continuous metal inputs to the coastal zone may lead to increasing pollution in these already
529 highly contaminated areas with the risk of Pt export to the marine environment. Further
530 investigations are therefore of major importance to accurately determine biogeochemical Pt
531 distribution, reactivity and fate in marine waters.

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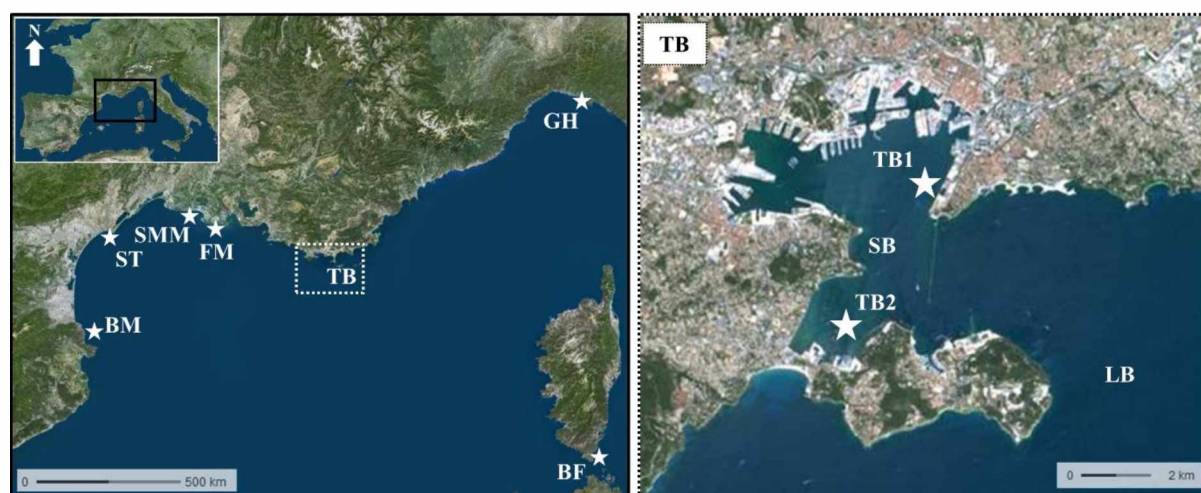


Fig. 1: Sampling sites along the northwestern Mediterranean coast. From east to west BM: Banyuls-sur-Mer, ST: Sète, SMM: Saintes-Maries-de-la-Mer, FM: Faraman, TB: Toulon Bay with the two sampling sites TB1 and TB2 (zoom on the right panel; SB: Small Bay, LB: Large Bay), BF: Bonifacio, and GH: Genoa Harbor, Italy. Source: geoportail.gouv.fr

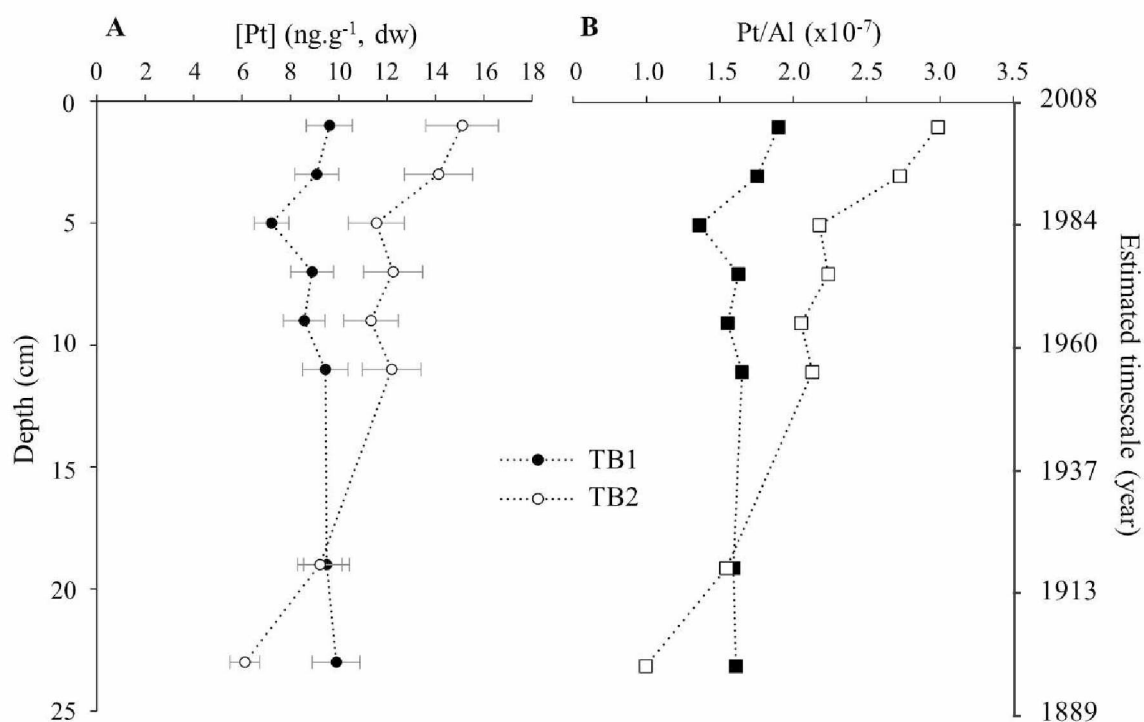


Fig. 2: Depth profiles of Pt concentrations (A) and Al-normalized Pt concentrations (B) in sediment cores from the Toulon Bay. Sediment cores were collected at site TB1 (filled symbols) and TB2 (empty symbols). A: Platinum concentrations (ng.g⁻¹, dw: dry weight, circles), B: Aluminum-corrected Pt concentrations (x 10⁻⁷, squares). Aluminum concentrations are from Tessier et al. (2011). Error bars correspond to analytical uncertainty (RSD%).

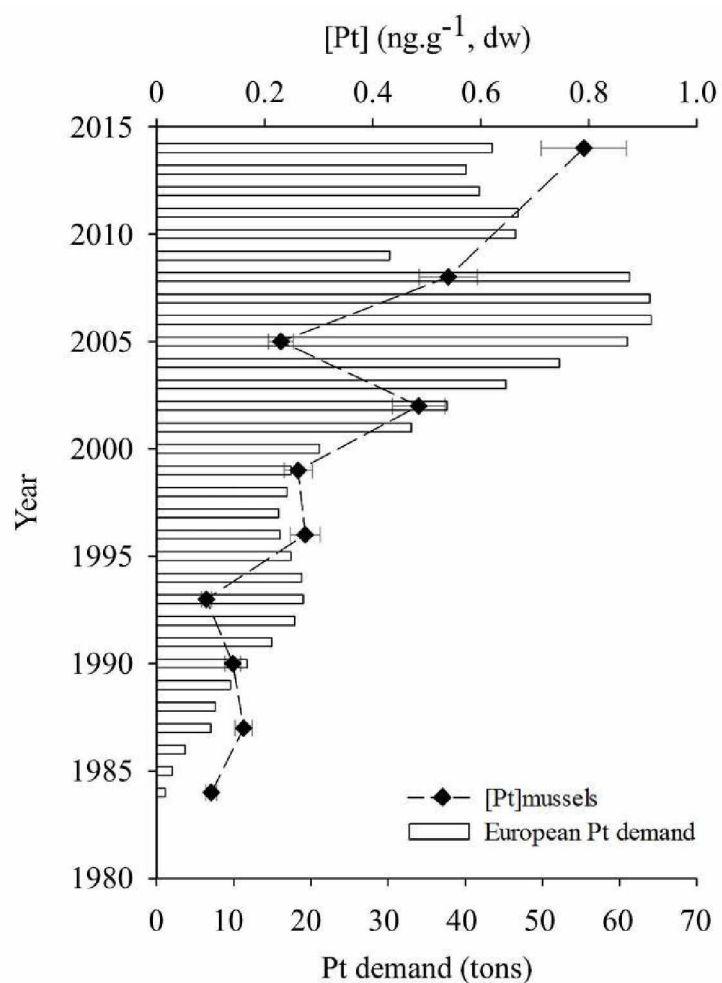


Fig. 3: Platinum concentrations in farmed mussels from the Toulon Bay (ng.g⁻¹, dw; sampling site TB2) and European Pt gross demand (metric tons, after Johnson Matthey, 2017) for car catalytic converters during the 1984-2014 period. Error bars correspond to analytical uncertainty (RSD%).

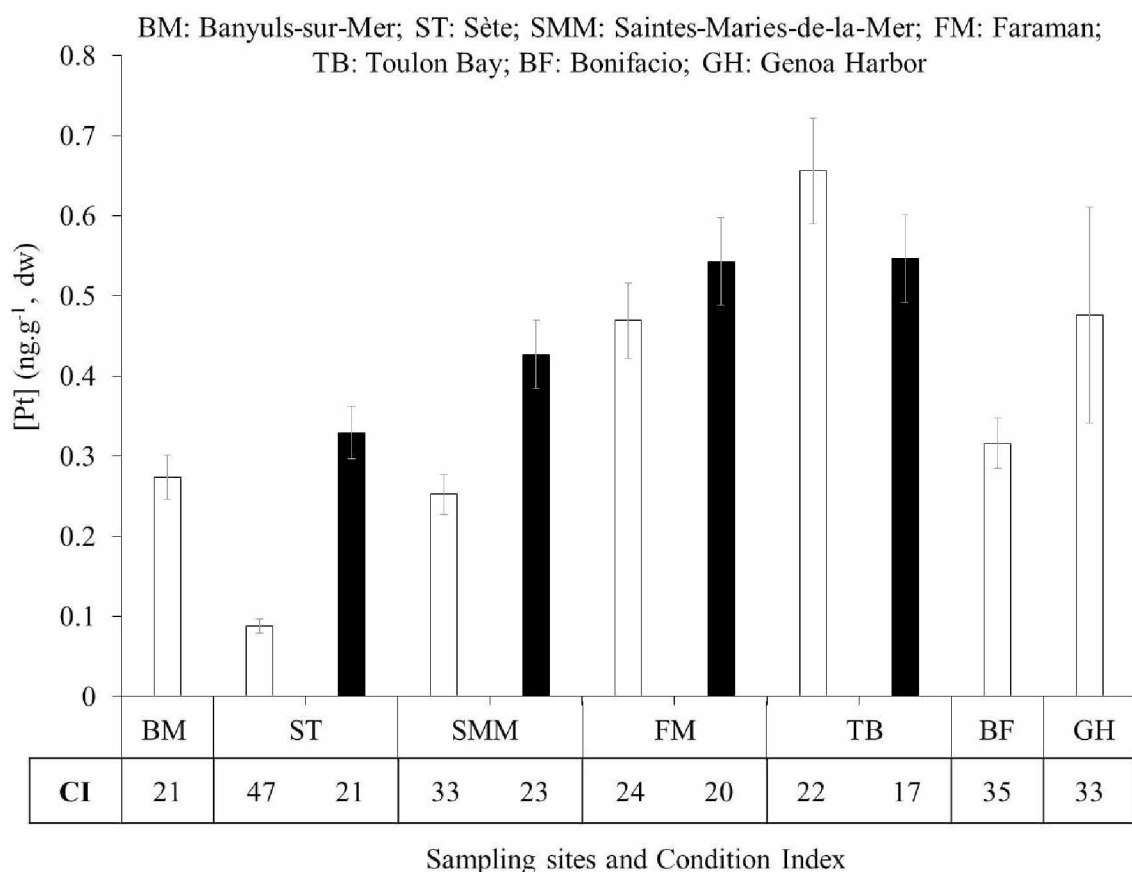


Fig. 4: Platinum concentrations (ng.g^{-1} , dry weight: dw) in wild mussels sampled along the northwestern Mediterranean coast. Winter, Spring and Summer / Fall mussels were analyzed for the same sampling sites when possible. Black bars correspond to sample collection during Winter, whereas white bars correspond to sample collection during reproductive season (Spring and Summer / Fall); CI: average Condition Index of the mussel pools for the French coastline ($n \sim 240$) and of the 10 individuals from the Genoa Harbor. Error bars correspond to analytical uncertainty (RSD%).