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

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23 emission devices, such as petrol industry and coal-fired activities. A strong Pt increase in
24 more recent sediments (from ~ 12 to 16 ng.g^{-1}) and mussels (8-fold increase from ~ 0.12 to
25 0.80 ng.g^{-1}) covering the past 25 years reflect the overall evolution of Pt demand in Europe
26 (~ 20 -fold increase for vehicle catalysts in 20 years). Spatial biomonitoring of Pt in mussels
27 along the northwestern Mediterranean coast is assumed to reflect inter-sites differences of Pt
28 exposure (0.09 to 0.66 ng.g^{-1}) despite seasonal effect on tissue development. This study
29 highlights the need for thorough and regular monitoring of Pt levels in sediments and biota
30 from urbanized coastal areas in order to better assess the environmental impact of this TCE,
31 including potential risks for marine organisms.

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

33

34 **1. Introduction**

35 Platinum is a Technology Critical Element (TCE) and an emerging metallic contaminant for
36 which there is a growing need for accurate assessment of environmental distribution and
37 impacts (Cobelo-García et al., 2015). This element is increasingly used in various applications
38 due to its high chemical resistance and excellent catalytic properties. Anthropogenic activities
39 account for more than 80 % of Pt fluxes at the Earth surface (Sen and Peucker-Ehrenbrink,
40 2012). Today, the most extended application is the use of Pt in vehicle catalytic converters to
41 control air pollution by cars, trucks, motorcycles and non-road mobile machinery, accounting
42 for more than 70 % of the European Pt demand (Johnson Matthey, 2017).

43 Increasing Pt emissions from automobile exhaust catalytic converters have led to an increase
44 in Pt concentration in many environmental compartments including atmosphere, soils,
45 sediments, interstitial waters, and seawater with anomalies occurring even in very remote,
46 supposedly pristine areas such as the Antarctic snow (e.g. Almécija et al., 2015; Obata et al.,
47 2006; Rauch et al., 2004, 2006; Schäfer et al., 1999; Schäfer and Puchelt, 1998; Soyol-Erdene
48 et al., 2011). Increasing Pt concentrations are also recorded in aquatic organisms comprising
49 plants, bivalves, and marine mammals which prove to bioaccumulate this element (Abdou et
50 al., 2016; Almécija et al., 2016; Essumang, 2008; Neira et al., 2015). In spite of growing
51 efforts to improve the understanding of biogeochemical Pt cycles, there is still a lack of
52 relevant environmental data. This is particularly the case in marine environments, mainly due
53 to analytical challenges when analyzing Pt at ultra-trace levels in complex environmental
54 matrices (i.e. seawater, sediments and biota). In fact, only few field studies report on Pt levels,
55 distribution and geochemical behavior in coastal ecosystems. Coastal areas are considered as
56 vulnerable sites due to their anthropogenic socio-economic roles, hosting ~ 70 % of the urban
57 populations and economic activities worldwide (Small and Nicholls, 2003). This pressure
58 implies the risk of serious environmental consequences (McGranahan et al., 2007) such as

59 trace metal contamination and possible transfer to the marine food web. Evidence of
60 measurable anthropogenic Pt inputs into the coastal environment are especially based on the
61 analysis of sediment cores (e.g. Rauch et al., 2004; Tuit et al., 2000). The few papers
62 reporting on Pt in coastal seawater suggest that supposedly uncontaminated surface seawater
63 shows dissolved Pt concentrations in the range of 0.05 - 0.1 ng.L⁻¹ (e.g. Cobelo-García et al.,
64 2014a; Goldberg et al., 1986). The even more limited number of field studies reporting on Pt
65 concentrations in marine organisms prove Pt bioavailability and relatively high potential for
66 Pt bioconcentration, especially in marine bivalves (Abdou et al., 2016; Neira et al., 2015).
67 Accordingly, these organisms appear as suitable biomonitors to assess Pt levels in marine
68 environments (Abdou et al., 2018).

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

83 The present work aims at providing an assessment of Pt levels in: (i) historical samples
84 (sediment cores and farmed mussels) from an industrial and strongly urbanized Mediterranean
85 harbor (Toulon Bay, France), and (ii) wild mussels from selected, contrasting sites along
86 300 km of the northwestern Mediterranean coast, including industrial sites supposedly
87 influenced by Pt-releasing anthropogenic activities.

88

89 **2. Material and Methods**

90 2.1. Study area, sampling sites, and sample collection

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

98 *The Toulon Bay*

99 Long-term evolution of Pt in a harbor affected by strong multi-component pollution was
100 studied in sediment cores and farmed mussels from the Toulon Bay (TB, Fig. 1). The Toulon
101 Bay is divided into two parts by an artificial embankment, forming the Large Bay and the
102 Small Bay (LB and SB, respectively; Fig. 1) and receives urban inputs from Toulon city
103 (~ 600,000 inhabitants, Tessier et al., 2011). The Toulon Bay has been strongly polluted by
104 anthropogenic wastes originating from both historic (bombardments and fleet scuttling during
105 World War II: one hundred ships destroyed and sunk, mainly in the Small Bay) and ongoing

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

113 The sediment cores were sampled by the laboratory PROTEE from November 2008 to June
114 2009 in the context of a wider survey on sediment quality in the Toulon Bay (Tessier et al.,
115 2011). The two sediment cores analyzed in this study were collected at sampling site TB1
116 located in the eastern part of SB, close to a former Navy submarine base and in the main
117 navigation channel; and at site TB2 located in the western part of SB, close to a fish/mussel
118 farming area (Fig. 1). The sediment cores were processed as previously described in Tessier et
119 al. (2011). Briefly, 10 cm diameter and 1 m long (Interface Corer, Plexiglas® tube) sediment
120 cores were transported to the laboratory PROTEE directly after sampling and sliced (2 cm
121 resolution) under inert atmosphere (N_2) to preserve redox conditions. The sliced sediment
122 samples were pooled and homogenized (Teflon spoon), placed into pre-cleaned 1 L high-
123 density polyethylene (HDPE) bottles and deep frozen ($-18 \text{ }^\circ\text{C}$). All frozen samples were
124 subsequently freeze-dried (within one month) and sieved (2 mm).

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

130

131 *Mediterranean coastline*

132 Wild mussels (*M. galloprovincialis*) were sampled at contrasting sites along the northwestern
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

156 Winter correspond to the period of gametogenic quiescence and associated lower metabolic
157 rate (Widdows, 1978). In order to observe the seasonality of Pt concentrations, mussel
158 samples from Winter (December – February) were analyzed together with mussels from
159 Spring and Summer / Fall (July – October) from the same site, when both sets of samples
160 were available. For the sampling sites Banyuls-sur-Mer, Bonifacio, and Genoa Harbor, only
161 mussel samples from dates within the reproduction cycle were analyzed (July 2016, October
162 2016, and April 2016 respectively).

163

164 2.2. Analytical methods

165 *Sediment*

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

180 sulfuric acid (H₂SO₄, 93 – 98 % Trace metal grade, Fisher Chemical®) at 195 °C. Cooled
181 contents were diluted using 0.1 M HCl, centrifuged at 4000 rpm for 10 min (20 °C), and made
182 up to 25 mL in pre-clean Teflon bottles (Nalgene®).

183 Aliquots of acid-digested sample (dilution 1:1 with MilliQ water®) were pipetted into the
184 voltammetric cell together with 30 µL of 3.3 mM formaldehyde (37–41 % Analytical Reagent
185 Grade, Fisher Chemical®), 30 µL of 0.45 mM hydrazine sulfate (Analytical Reagent Grade,
186 Fisher Chemical®), and 300 µL of H₂SO₄. Platinum concentrations were determined by
187 standard addition method (adding mono-elementary Pt standard solution 1000 µg.mL⁻¹
188 PLASMACAL, SCP Science®) using a deposition time of 90 s and experimental parameters
189 as described elsewhere (Cobelo-García et al., 2014b).

190 *Mussels*

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

205 crucibles. After cooling, ashed residues were transferred into acid-cleaned polypropylene (PP)
206 tubes (DigiTUBEs, SCP SCIENCE®), and digested at 110 °C for 3 h with 2 mL HCl and
207 1 mL HNO₃ (30 % HCl and 65 % HNO₃ Suprapur, Merck®) as described in Abdou et al.
208 (2018) for environmental samples. Cooled contents were then diluted in 10 mL MilliQ
209 water®, centrifuged at 4000 rpm for 10 min (20 °C). Analyses were performed applying the
210 standard addition method (using mono-elementary Pt standard solution 1000 µg.mL⁻¹
211 PLASMACAL, SCP Science®).

212 *Quality control*

213 Quality control was performed using the only Certified Reference Materials available for Pt
214 being the BCR®-723 road dust (IRMM) and the Jsd-2 sedimentary rocks (indicative value
215 from GSJ). Platinum quantification by AdCSV provided satisfactory recovery of 89% for
216 BCR®-723 and 98% for Jsd-2 (n = 3) as well as ICP-MS analyses giving recovery values of
217 87% and 101% respectively. Uncertainty of the analysis, expressed as Relative Standard
218 Deviation (RSD%), was below 10% using both methods. In addition, in the absence of any
219 biological CRM for Pt, a previous study inter-compared ICP-MS and AdCSV as different,
220 independent analytical method. Results for similar sample masses as applied in the present
221 study allowed for reproducible and similar (< 3 % difference in average) results for both
222 methods indicating good accuracy. The detection limit for particulate (sediment and biota) Pt
223 measured by AdCSV (calculated as 3 x blank standard deviation, n = 5) was estimated to
224 0.03 ng.g⁻¹ for typical mass of 50 mg. The detection limit for Pt measured in biological
225 samples by ICP-MS (n = 10 blanks) was estimated to 0.003 ng.g⁻¹ for typical biological
226 sample masses of ~ 1.5 g.

227 3. Results

228 3.1. Historical record of Pt concentrations in sediments and mussels from the 229 Toulon Bay

230 Platinum concentrations in the two sediment cores TB1 and TB2 ranged from 6 ng.g⁻¹ to
231 15 ng.g⁻¹ (Fig. 2A). Samples in the TB1 core showed relatively constant Pt levels of
232 ~ 10 ng.g⁻¹, with only a small variation at 5 cm depth showing Pt concentration of ~ 7 ng.g⁻¹.
233 In contrast, the core TB2 showed a general trend of Pt concentrations decreasing with depth,
234 i.e. the highest concentrations occurred in the top of the core and the lowest values in the
235 bottom (Fig. 2A). Overall, the Pt concentrations tended to be lower in the core TB1 than in
236 TB2. When comparing sediment samples from different depths or different cores, one has to
237 exclude that the observed variations are due to grain size effects because particle size
238 fractionation may lead to increasing trace metal concentrations with decreasing grain size
239 (Loring and Rantala, 1992). Accordingly, grain size effects on natural, lithogenic trace metal
240 variability must be corrected by normalization over a grain size dependent lithogenic element
241 before assessing anthropogenic inputs (Loring and Rantala, 1992). Aluminum (Al) has been
242 chosen as the normalization element for the Toulon Bay and many other systems (e.g. Ho et
243 al., 2012; Pougnet et al., 2014; Tessier et al., 2011), as Al contents are influenced by natural
244 sedimentation and the effects of enhanced erosion, but not by pollution (Li and Schoonmaker,
245 2003; Luoma and Rainbow, 2008). In fact, correlation ($R^2 = 0.94$) between potassium (K) and
246 Al concentrations in surface and deep sediment showed the close relationship between Al and
247 clay minerals, supporting the pertinence of Al-normalization (Tessier et al., 2011). In both
248 cores, Al-normalization did not modify the profiles, suggesting that grain size effects on
249 spatial (horizontal and vertical) Pt distribution are negligible (Fig. 2B). These results suggest
250 that in the sediment core TB2 (i) nearly all layers are enriched in Pt compared to the core TB1

251 and (ii) there is a clear increasing trend in Pt enrichment from the bottom to the top of the core
252 (3-fold; Fig. 2).

253

254 Platinum concentrations in farmed mussels from the Toulon Bay ranged from 0.10 to
255 0.79 ng.g^{-1} , in the 1984 to 2014 period (Fig. 3). Platinum concentrations were relatively low
256 and constant ($\sim 0.15 \text{ ng.g}^{-1}$) from 1984 to 1990, followed by a clearly increasing trend over
257 time towards a maximum value of 0.79 ng.g^{-1} in 2014, which is ~ 8 times greater than the
258 levels of the 1980's. In the same period, the European Pt gross demand for car catalytic
259 converters evolved from 1-2 tons.y^{-1} in the late 1980s to $\sim 40 \text{ tons.y}^{-1}$ from 2010 to 2014
260 (Fig. 3).

261

262 3.2. Platinum concentrations in mussels from the northwestern Mediterranean coast

263 Platinum concentrations in wild mussels from contrasting sites, expressed in $\text{ng.g}^{-1} \text{ dw}$ ranged
264 from ~ 0.09 to 0.66 ng.g^{-1} (Fig. 4). Winter mussels were compared to Spring and
265 Summer / Fall mussels, whenever possible as described in section 2.1.

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

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

276 $0.48 \pm 0.14 \text{ ng.g}^{-1}$ (Genoa Harbour, Fig. 4). Condition Indices varied from 17 to 47 between
277 sites and sampling periods. Spring and Summer / Fall individuals showed CI ranging from 21
278 to 47 with a mean value of 31, while it varied from 17 to 23 with a mean value of 20 in
279 Winter organisms.

280 **4. Discussion**

281 4.1. Historical records of Pt concentrations in the Toulon Bay

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

285 *Historical record in sediments*

286 Average sedimentation rate in the Toulon Bay sediments was estimated from the vertical
287 distribution of ^{210}Pb activity in the sediment cores in previous work (Tessier et al., 2011),
288 suggesting an average sedimentation velocity of $0.21 \pm 0.05 \text{ cm.y}^{-1}$. Accordingly, the studied
289 sediment cores cover the period $\sim 1890 - 2008$ and the top 10 cm layer would reflect
290 ~ 50 years of history (Tessier et al., 2011). As Al-normalization performed to correct for
291 variations in sediment nature and grain size (Sageman and Lyons, 2003) did not modify the Pt
292 profiles in the Toulon Bay sediments (Fig. 2B), the observed variations are attributed to
293 anthropogenic inputs, rather than lithogenic processes, as described elsewhere (e.g. Almécija
294 et al., 2016).

295 The assessment of the degree of contamination in a given environmental sample requires the
296 establishment of references representing “uncontaminated” conditions in comparable sample
297 types. Classically, authors have compared their results with average values of the Upper
298 Continental Crust (UCC, e.g. Abdou et al., 2016; Cobelo-García et al., 2011; Rauch et al.,
299 2004). This first approach may suggest that the Pt concentrations in the Toulon Bay sediments

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

308 In fact, Pt concentrations in the bottom layers of the sediment cores, i.e. $\sim 10 \text{ ng.g}^{-1}$ in core
309 TB1 and $\sim 6 \text{ ng.g}^{-1}$ in core TB2, supposedly dating from the early 20th century, could serve as
310 the local reference level for relatively uncontaminated sediment. These values may appear
311 high, compared to background values reported for ancient sediments in the Tagus Estuary
312 ($0.2 - 0.3 \text{ ng.g}^{-1}$, Cobelo-García et al., 2011) or for the UCC Pt content. They are, however,
313 similar in magnitude as Pt records from marine pristine sediment cores (~ 1 up to 5 ng.g^{-1} in
314 Atlantic abyssal pelagic sediment; Colodner et al., 1992) and other pelagic sediments from a
315 variety of locations in the Pacific ocean (0.4 to 22 ng.g^{-1} , Koide et al., 1991), both sampled
316 before the recent emergence of Pt as a global contaminant. Furthermore, pre-anthropogenic
317 coastal sediments from the Massachusetts Bay showed similar Pt levels than bottom layers
318 from the Toulon Bay ($\sim 5 \text{ ng.g}^{-1}$, Tuit et al., 2000). These observations together with high Pt
319 levels in South Pacific pelagic sediment ($\sim 30 \text{ ng.g}^{-1}$, Lee et al., 2003) and in marine
320 manganese nodules (up to 900 ng.g^{-1} , Koide et al., 1991) tend to suggest that relatively high
321 Pt concentrations in coastal sediments may, at least partly, be attributed to the presence of
322 marine particles and not necessarily derive from terrigenous and/or anthropogenic sources.
323 Accordingly, the Toulon Bay bottom sediments may be considered as the local, pre-industrial
324 reference (especially core TB2). In fact, the Toulon Bay receives water from the open

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

331 The Pt/Al values suggest increasing concentrations from the bottom to the top in the core TB2
332 (~3-fold increase from the bottom to the top layers; Fig. 2B). However, the relatively small
333 recent increase in Pt/Al values (~ 20 % in the period ~ 1984-2008) combined with the
334 relatively high values in the bottom of the core TB1 may be due to its position in the eastern
335 part of the SB, more exposed to the marine incoming water than the site TB2
336 (counterclockwise circulation in the Toulon Bay; Duffa et al., 2011). In addition, the site TB1
337 is located close to a main navigation channel, thus, one cannot fully exclude post-depositional
338 Pt redistribution of the sediment. Post-depositional Pt redistribution processes might include
339 both physical mixing (e.g. navigation, dredging...) and chemical redistribution related to
340 diagenesis processes (Almécija et al., 2015; Tuit et al., 2000). Chemically-driven Pt mobility
341 was already observed in other coastal sediments showing maximum Pt enrichment at the base
342 of the surface mixed layer after scavenging at the oxic/anoxic boundary (Cobelo-García et al.,
343 2011). Furthermore, a sediment core from the Boston Harbor also showed chemical mobility
344 of Pt, implying Pt remobilization in sediments at short time scales (Tuit et al., 2000).
345 According to Colodner et al. (1992), a fraction of Pt in marine sediments is labile, suggesting
346 that Pt may be scavenged from seawater into both Fe-Mn oxyhydroxide minerals and organic-
347 rich sediments, so that these phases might dominate the Pt distribution in sediments. Previous
348 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 e 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

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

410

411 *Historical record in mussels*

412 The temporal evolution of Pt concentrations in mussels farmed close to the site of core TB2
413 (Fig. 1) reflected a ~8-fold increase over the 1984 to 2014 period, especially since the mid-
414 1990s (Fig. 3). Together with the ~20-fold increase in European Pt demand for car catalysts
415 over the same period, this observation suggests that vehicle-emitted Pt has been introduced
416 into the coastal ecosystem of the Toulon Bay with an effective transfer to living marine
417 organisms. These first results for Pt in Mediterranean bivalves are in line with increasing
418 Pt/Al values in the TB2 core from the same site and with previous work on wild oysters and
419 mussels from the French and the Spanish (Galician) Atlantic coast (oysters, Abdou et al.,
420 2016; mussels, Neira et al., 2015). Given the fact, that biomonitoring organisms are sampled
421 on a regular basis, sediment-specific uncertainties due to physical or chemical disturbance of
422 the historical record are excluded and, therefore, the use of sentinel organisms from sample
423 banks may provide reliable information on trends in ambient contaminant pressure over time.

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

433 4.2. Biomonitoring of Pt in mussels along the northwestern Mediterranean coast

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

449 1980's, the Gulf of Fos was considered as one of the most polluted neritic areas in Europe
450 with important metal pollution (Cu, Pb, Cd, Zn; Benon et al., 1978). This area hosts important
451 oil industries that might be a source of Pt to the marine environment as previously discussed
452 (section 4.1.). Other studies report high trace metal contamination in native and caged mussels
453 *M. galloprovincialis* from areas close to major urban and industrial centers such as La-Fos-
454 sur-Mer (Andral et al., 2004), with a battery of biomarkers indicating disturbed health in
455 mussels (Zorita et al., 2007) from the most impacted zones including the La-Fos-sur-Mer
456 Harbor. In addition the sampling site Faraman is directly under the influence of the Rhône
457 outflow (Charmasson et al., 1999) which may drain all the pollution originating from the
458 urbanized watershed. Similar Pt concentrations occurred in mussels from sampling site TB2
459 in the Toulon Bay (Seyne sur Mer), showing the highest Pt level (0.55 ng.g^{-1}) of the studied
460 sites. This value is somewhat lower than the 2014 value ($\sim 0.8 \text{ ng.g}^{-1}$) in farmed mussels from
461 the same area in the Toulon Bay. Platinum concentration range in mussels from the Genoa
462 Harbor, marked by industrial / urban water pollution (Ruggieri et al., 2011), is similar to
463 levels observed in the Toulon Bay (Fig. 4). These observations suggest that Pt accumulation
464 in mussels from the different sites may reflect the supposed exposure from anthropogenic
465 pressure, similarly to other trace metals, showing strong gradients between mussels from less
466 populated areas or regions with no major river inputs (e.g. Sète) and those from heavily
467 populated and industrialized port areas (Fowler and Oregioni, 1976).

468 Few field studies report on Pt levels in biota from coastal marine environments. Recent
469 samples of wild mussels *M. galloprovincialis* from an urban beach in Vigo (Spain) revealed
470 Pt concentrations of $\sim 0.45 \text{ ng.g}^{-1}$ (2011 value, Neira et al., 2015), while wild oysters
471 (*Crassostrea gigas*) from the moderately contaminated Gironde Estuary mouth contained
472 $\sim 0.33 \text{ ng.g}^{-1}$ (2013 value, Abdou et al., 2016). Accordingly, Pt levels in mussels from the
473 Mediterranean sites are similar in magnitude to those in wild bivalves from the Atlantic coast,

474 but with clearly higher values in confined harbor sites with relatively high urban/industrial
475 pressure. Bioconcentration factors (BCF), comparing Pt accumulation in tissues to ambient
476 seawater concentrations were determined as $BCF = Pt_B / Pt_D$, where Pt_B is the Pt
477 concentration in the organism ($ng.g^{-1}$, dw) and Pt_D the dissolved Pt concentration in seawater
478 ($ng.L^{-1}$, Arnot and Gobas, 2006) for the Genoa Harbor mussels (no Pt_D data available for the
479 other sites). Average BCF in the Genoa Harbor mussels was $\sim 4 \times 10^3$, i.e. similar to values
480 reported for wild mussels *M. galloprovincialis* from an urban beach ($\sim 5 \times 10^3$; Neira et al.,
481 2015) and for wild oysters from the Gironde Estuary ($\sim 3 \times 10^3$, Abdou et al., 2016). These
482 values show that marine bivalve bioconcentrate Pt ambient signal reflecting: (i) the presence
483 of natural bioavailable Pt species and (ii) their suitable use for Pt monitoring in coastal
484 systems. Although it is assumed that dissolved metals are potentially more bioavailable than
485 their particulate forms (e.g. Lekhi et al., 2008), filter-feeders such as mussels are able to
486 absorb metals, and more particularly PGEs, in dissolved and particulate forms (Zimmermann
487 and Sures, 2018). Given that Pt emissions from car exhaust systems mainly occur as very
488 small particles (from micrometers down to nanometric size; Folens et al., 2018; Rauch et al.,
489 2001), more work is necessary to characterize the behavior of such particles in the marine
490 environment and understand their role in Pt transfer to living organisms.

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

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

516

517 **5. Conclusions**

518 Historical records of both sediment cores and mussels collected in a severely polluted site, the
519 Toulon Bay, suggest the existence of former (non-vehicle related) sources of Pt in the system.
520 They also revealed the impact of recent contamination related to increasing Pt emissions
521 through car catalytic converters that may be of major importance in this area under high
522 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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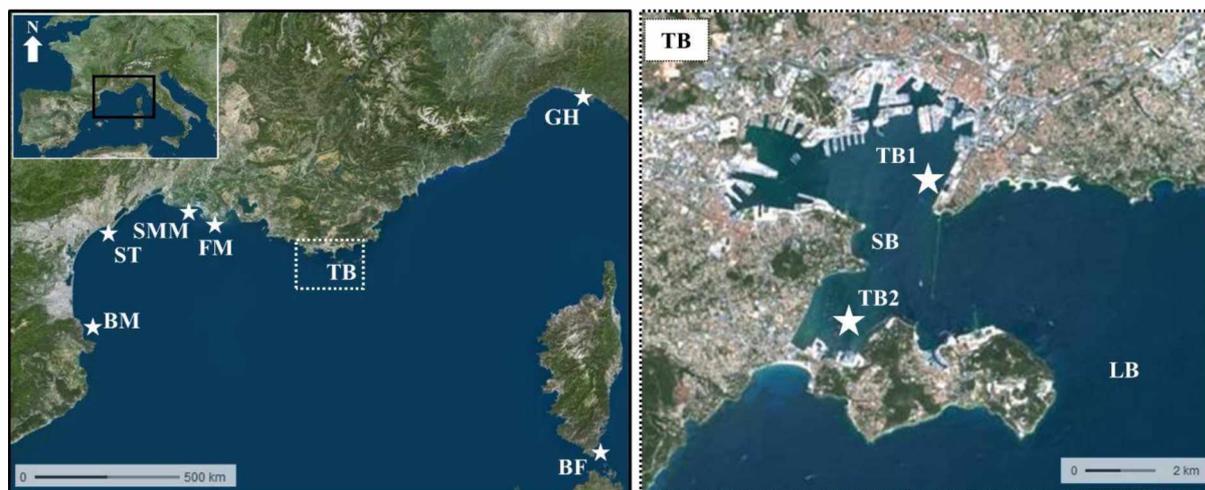


Fig. 1: Sampling sites along the northwestern Mediterranean coast. From east to west BM: Banyuls-sur-Mer, ST: Sète, SMM: Saintes-Maries-de-la-Mer, FM: Faraman, TB: Toulon Bay with the two sampling sites TB1 and TB2 (zoom on the right panel; SB: Small Bay, LB: Large Bay), BF: Bonifacio, and GH: Genoa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

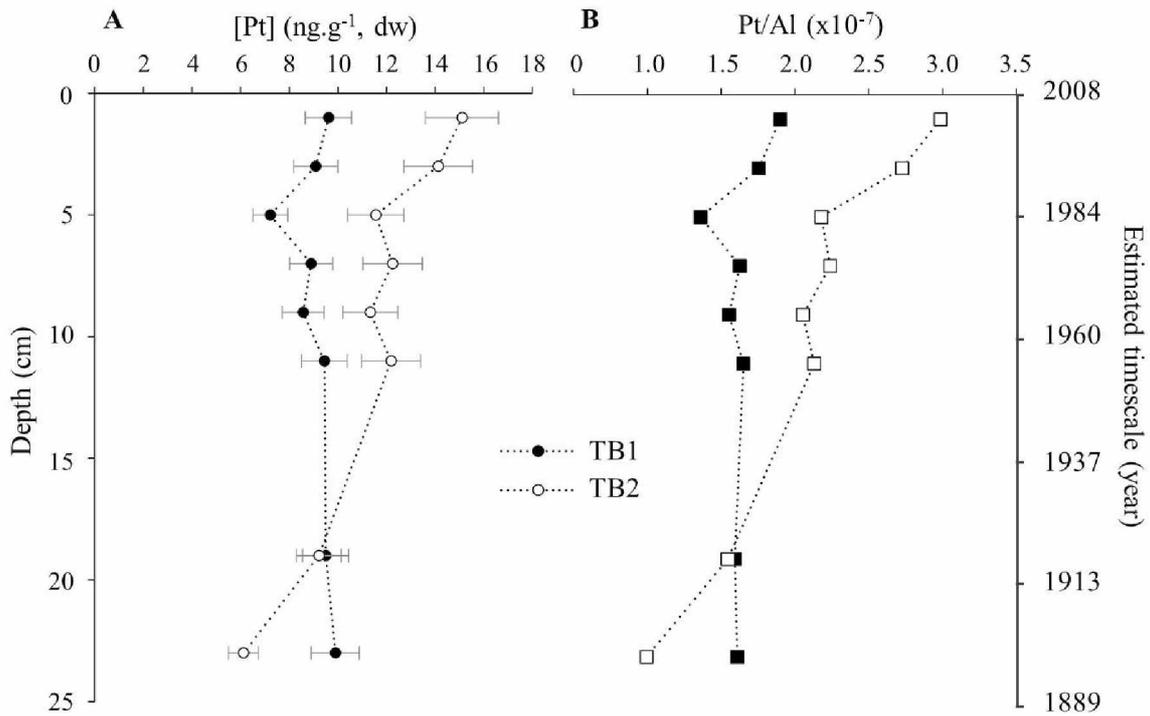


Fig. 2: Depth profiles of Pt concentrations (A) and Al-normalized Pt concentrations (B) in sediment cores from the Toulon Bay. Sediment cores were collected at site TB1 (filled symbols) and TB2 (empty symbols). A: Platinum concentrations (ng.g⁻¹, dw: dry weight, circles), B: Aluminum-corrected Pt concentrations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

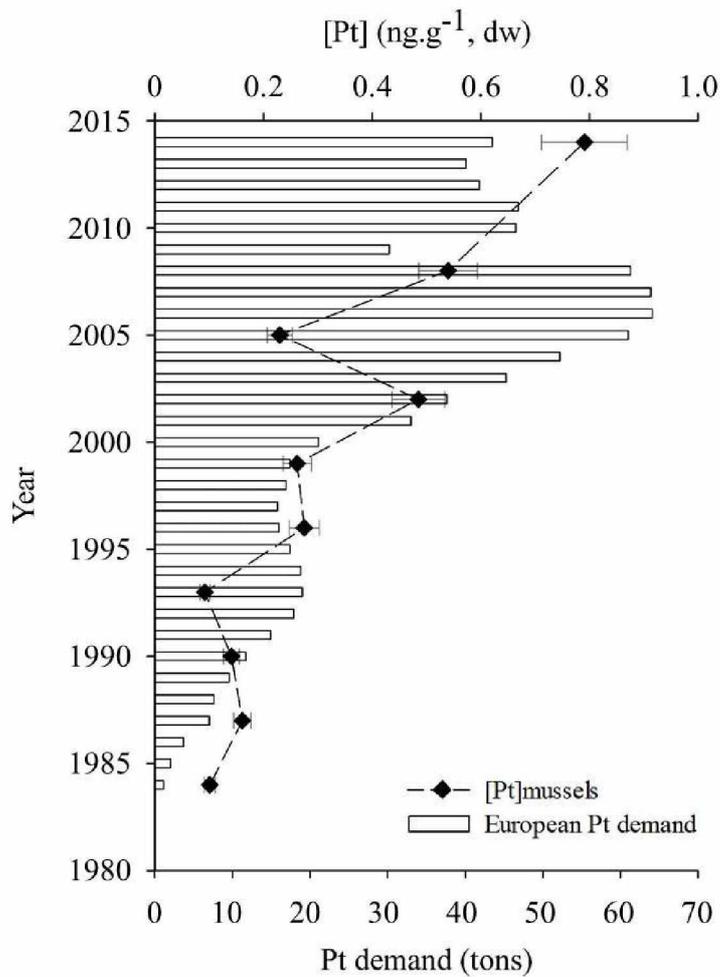
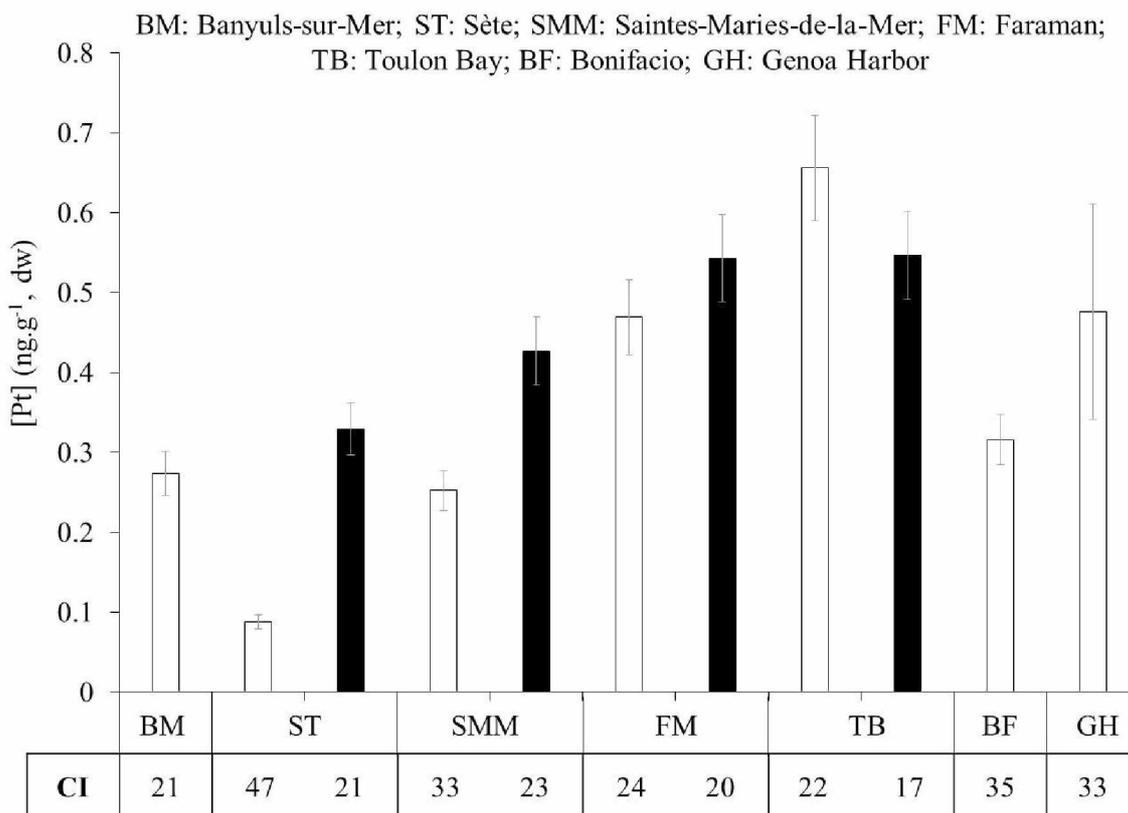


Fig. 3: Platinum concentrations in farmed mussels from the Toulon Bay ($\text{ng}\cdot\text{g}^{-1}$, dw; sampling site TB2) and European Pt gross demand (metric tons, after Johnson Matthey, 2017) for car catalytic converters during the 1984-2014 period. Error bars correspond to analytical uncertainty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



Sampling sites and Condition Index

Fig. 4: Platinum concentrations ($\text{ng}\cdot\text{g}^{-1}$, 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%).