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

Abdou Melina^{1,*}, Schäfer Jörg¹, Hu Ruoyu¹, Gil-Díaz Teba¹, Garnier Cédric²,
Brach-Papa Christophe³, Chiffolleau Jean-Francois³, Charmasson Sabine⁴, Giner Franck⁴,
Dutruch Lionel¹, Blanc Gerard¹

¹ University of Bordeaux, UMR CNRS 5805 EPOC, 33615 Pessac Cedex, France

² Laboratoire PROTEE, Université du Sud Toulon-Var, BP 20132, 83957 La Garde, France

³ IFREMER, LBCM, Centre Atlantique, Rue de l'Île d'Yeu, 44311 Nantes, France

⁴ IRSN, PSE-ENV/SRTE/LRTA, CEA CADARACHE, 13115 Saint Paul Lez Durance, France

* Corresponding author : Melina Abdou, email address : melina.abdou@u-bordeaux.fr

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.

Highlights

► Platinum levels were monitored in contrasting sites of the NW Mediterranean coast ► Historical sediments reflect non-vehicle related, old Pt anthropogenic sources ► Past 25-years sediments and mussels show recent vehicle related Pt contamination ► Biomonitoring mussels reflect the degree of Pt contamination in coastal environment

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

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

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

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

82 The present work aims at providing an assessment of Pt levels in: (i) historical samples
83 (sediment cores and farmed mussels) from an industrial and strongly urbanized Mediterranean

84 harbor (Toulon Bay, France), and (ii) wild mussels from selected, contrasting sites along
85 300 km of the northwestern Mediterranean coast, including industrial sites supposedly
86 influenced by Pt-releasing anthropogenic activities.

87

88 **2. Material and Methods**

89 2.1. Study area, sampling sites, and sample collection

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

97 *The Toulon Bay*

98 Long-term evolution of Pt in a harbor affected by strong multi-component pollution was studied
99 in sediment cores and farmed mussels from the Toulon Bay (TB, Fig. 1). The Toulon Bay is
100 divided into two parts by an artificial embankment, forming the Large Bay and the Small Bay
101 (LB and SB, respectively; Fig. 1) and receives urban inputs from Toulon city (~ 600,000
102 inhabitants, Tessier et al., 2011). The Toulon Bay has been strongly polluted by anthropogenic
103 wastes originating from both historic (bombardments and fleet scuttling during World War II:
104 one hundred ships destroyed and sunk, mainly in the Small Bay) and ongoing activities (French
105 Navy, commercial traffic, urban raw sewage release, industry, tourism; Dang et al., 2015;
106 Tessier et al., 2011). Accordingly, high levels of inorganic and organic pollutants are

107 accumulated in sediments from the Toulon Bay (e.g. Dang et al., 2015; Pougnet et al., 2014;
108 Tessier et al., 2011). Both sediment cores and mussels were sampled in the SB characterized
109 by a semi-closed shape with a surface of $\sim 9.8 \text{ km}^2$ where the morphology and the artificial
110 barrier limit water circulation favoring accumulation of sediment and associated contaminants
111 (Fig. 1, Tessier et al., 2011).

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

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

129

130 *Mediterranean coastline*

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

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

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

162

163 2.2. Analytical methods

164 *Sediment*

165 Platinum concentrations in sediment core samples were determined by Adsorptive Cathodic
166 Stripping Voltammetry (AdCSV) as described in Cobelo-García et al. (2014b). Measurements
167 were carried out using a μ Autolab Type III potentiostat (Metrohm® Autolab B.V.) connected
168 to a polarographic stand (Metrohm® 663 V.A.) equipped with three electrodes: (i) a hanging
169 mercury drop electrode (HMDE, the working electrode), (ii) a silver/silver-chloride (Ag/AgCl)
170 reference electrode, and (iii) a glassy carbon auxiliary electrode. A polytetrafluoroethylene
171 (PTFE) voltammetric cell served in all experiments and the potentiostat was controlled using
172 the NOVA 2.1 software. According to the protocol for sediment treatment described by Cobelo-
173 García et al. (2011), about 50 mg of sediment samples were ashed in porcelain crucibles at
174 800 °C during 3 h (removal of Organic Matter, OM). Ashed samples were transferred into
175 30 mL perfluoroalkoxy (PFA) vessels with screw caps (Savillex®) and acid-digested at 195 °C
176 for 4 h using 5 mL HCl and 3 mL HNO₃ (30 % HCl and 65 % HNO₃ Suprapur, Merck®). After
177 this step, vessel caps were removed and the acids evaporated at 195 °C until near dryness. The
178 residue was re-dissolved using 1 mL of sulfuric acid (H₂SO₄, 93 – 98 % Trace metal grade,

179 Fisher Chemical®) at 195 °C. Cooled contents were diluted using 0.1 M HCl, centrifuged at
180 4000 rpm for 10 min (20 °C), and made up to 25 mL in pre-clean Teflon bottles (Nalgene®).

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

188 *Mussels*

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

204 digested at 110 °C for 3 h with 2 mL HCl and 1 mL HNO₃ (30 % HCl and 65 % HNO₃
205 Suprapur, Merck®) as described in Abdou et al. (2018) for environmental samples. Cooled
206 contents were then diluted in 10 mL MilliQ water®, centrifuged at 4000 rpm for 10 min
207 (20 °C). Analyses were performed applying the standard addition method (using mono-
208 elementary Pt standard solution 1000 µg.mL⁻¹ PLASMACAL, SCP Science®).

209 *Quality control*

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

223 3. Results

224 3.1. Historical record of Pt concentrations in sediments and mussels from the
225 Toulon Bay

226 Platinum concentrations in the two sediment cores TB1 and TB2 ranged from 6 ng.g⁻¹ to
227 15 ng.g⁻¹ (Fig. 2A). Samples in the TB1 core showed relatively constant Pt levels of ~ 10 ng.g⁻¹,
228 with only a small variation at 5 cm depth showing Pt concentration of ~ 7 ng.g⁻¹. In contrast,
229 the core TB2 showed a general trend of Pt concentrations decreasing with depth, i.e. the highest
230 concentrations occurred in the top of the core and the lowest values in the bottom (Fig. 2A).

231 Overall, the Pt concentrations tended to be lower in the core TB1 than in TB2. When comparing
232 sediment samples from different depths or different cores, one has to exclude that the observed
233 variations are due to grain size effects because particle size fractionation may lead to increasing
234 trace metal concentrations with decreasing grain size (Loring and Rantala, 1992). Accordingly,
235 grain size effects on natural, lithogenic trace metal variability must be corrected by
236 normalization over a grain size dependent lithogenic element before assessing anthropogenic
237 inputs (Loring and Rantala, 1992). Aluminum (Al) has been chosen as the normalization
238 element for the Toulon Bay and many other systems (e.g. Ho et al., 2012; Pougnet et al., 2014;
239 Tessier et al., 2011), as Al contents are influenced by natural sedimentation and the effects of
240 enhanced erosion, but not by pollution (Li and Schoonmaker, 2003; Luoma and Rainbow,
241 2008). In fact, correlation ($R^2 = 0.94$) between potassium (K) and Al concentrations in surface
242 and deep sediment showed the close relationship between Al and clay minerals, supporting the
243 pertinence of Al-normalization (Tessier et al., 2011). In both cores, Al-normalization did not
244 modify the profiles, suggesting that grain size effects on spatial (horizontal and vertical) Pt
245 distribution are negligible (Fig. 2B). These results suggest that in the sediment core TB2 (i)
246 nearly all layers are enriched in Pt compared to the core TB1 and (ii) there is a clear increasing
247 trend in Pt enrichment from the bottom to the top of the core (3-fold; Fig. 2).

248

249 Platinum concentrations in farmed mussels from the Toulon Bay ranged from 0.10 to
250 0.79 ng.g⁻¹, in the 1984 to 2014 period (Fig. 3). Platinum concentrations were relatively low
251 and constant (~ 0.15 ng.g⁻¹) from 1984 to 1990, followed by a clearly increasing trend over time
252 towards a maximum value of 0.79 ng.g⁻¹ in 2014, which is ~ 8 times greater than the levels of
253 the 1980's. In the same period, the European Pt gross demand for car catalytic converters
254 evolved from 1-2 tons.y⁻¹ in the late 1980s to ~ 40 tons.y⁻¹ from 2010 to 2014 (Fig. 3).

255

256 3.2. Platinum concentrations in mussels from the northwestern Mediterranean coast

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

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

265 Summer / Fall mussel Pt concentrations ranged from ~ 0.09 to 0.66 ng.g⁻¹ (white bars; Fig. 4),
266 with mussels from Sète showing the lowest concentrations at a given sampling period, while
267 highest concentrations occurred in mussels from the Toulon Bay. Platinum concentrations were
268 also determined in wild mussels collected in the Genoa Harbor in April 2016. Ten individuals
269 were analyzed separately, providing an average Pt concentration of 0.48 ± 0.14 ng.g⁻¹ (Genoa
270 Harbour, Fig. 4). Condition Indices varied from 17 to 47 between sites and sampling periods.
271 Spring and Summer / Fall individuals showed CI ranging from 21 to 47 with a mean value of
272 31, while it varied from 17 to 23 with a mean value of 20 in Winter organisms.

273 4. Discussion

274 4.1. Historical records of Pt concentrations in the Toulon Bay

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

278 *Historical record in sediments*

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

287 The assessment of the degree of contamination in a given environmental sample requires the
288 establishment of references representing “uncontaminated” conditions in comparable sample
289 types. Classically, authors have compared their results with average values of the Upper
290 Continental Crust (UCC, e.g. Abdou et al., 2016; Cobelo-García et al., 2011; Rauch et al.,
291 2004). This first approach may suggest that the Pt concentrations in the Toulon Bay sediments
292 are clearly higher (up to 30 fold) than the UCC average (0.5 ng.g^{-1} , Rudnick and Gao, 2003).
293 More representative reference samples may be locally identified either in (i) remote areas,
294 presumably not affected by the contaminant (spatial approach) or in (ii) samples representing
295 conditions during periods before the contaminant release (temporal approach). Given the high
296 spatial variability in (i) Pt global contaminant dispersion, measurable even in remote sites (e.g.

297 polar ice, Soyol-Erdene et al., 2011) and (ii) heterogeneous sediment nature at a large spatial
298 scale, we have considered to apply the temporal approach to reliably determine the
299 contamination degree of Pt in the Toulon Bay.

300 In fact, Pt concentrations in the bottom layers of the sediment cores, i.e. $\sim 10 \text{ ng.g}^{-1}$ in core TB1
301 and $\sim 6 \text{ ng.g}^{-1}$ in core TB2, supposedly dating from the early 20th century, could serve as the
302 local reference level for relatively uncontaminated sediment. These values may appear high,
303 compared to background values reported for ancient sediments in the Tagus Estuary (0.2 -
304 0.3 ng.g^{-1} , Cobelo-García et al., 2011) or for the UCC Pt content. They are, however, similar
305 in magnitude as Pt records from marine pristine sediment cores (~ 1 up to 5 ng.g^{-1} in Atlantic
306 abyssal pelagic sediment; Colodner et al., 1992) and other pelagic sediments from a variety of
307 locations in the Pacific ocean (0.4 to 22 ng.g^{-1} , Koide et al., 1991), both sampled before the
308 recent emergence of Pt as a global contaminant. Furthermore, pre-anthropogenic coastal
309 sediments from the Massachusetts Bay showed similar Pt levels than bottom layers from the
310 Toulon Bay ($\sim 5 \text{ ng.g}^{-1}$, Tuit et al., 2000). These observations together with high Pt levels in
311 South Pacific pelagic sediment ($\sim 30 \text{ ng.g}^{-1}$, Lee et al., 2003) and in marine manganese nodules
312 (up to 900 ng.g^{-1} , Koide et al., 1991) tend to suggest that relatively high Pt concentrations in
313 coastal sediments may, at least partly, be attributed to the presence of marine particles and not
314 necessarily derive from terrigenous and/or anthropogenic sources. Accordingly, the Toulon Bay
315 bottom sediments may be considered as the local, pre-industrial reference (especially core
316 TB2). In fact, the Toulon Bay receives water from the open Mediterranean Sea via the Ligurian
317 Current flowing from east to west including deep water areas (Duffa et al., 2011), transporting
318 particles of marine origin into the bay. These findings highlight the need for better knowledge
319 of marine particle baseline Pt concentrations in the Mediterranean Sea and worldwide, as a
320 prerequisite to accurately evaluate anthropogenic contamination in coastal particles and
321 sediments by distinguishing geochemical background from anthropogenic signals.

322 The Pt/Al values suggest increasing concentrations from the bottom to the top in the core TB2
323 (~3-fold increase from the bottom to the top layers; Fig. 2B). However, the relatively small
324 recent increase in Pt/Al values (~ 20 % in the period ~ 1984-2008) combined with the relatively
325 high values in the bottom of the core TB1 may be due to its position in the eastern part of the
326 SB, more exposed to the marine incoming water than the site TB2 (counterclockwise circulation
327 in the Toulon Bay; Duffa et al., 2011). In addition, the site TB1 is located close to a main
328 navigation channel, thus, one cannot fully exclude post-depositional Pt redistribution of the
329 sediment. Post-depositional Pt redistribution processes might include both physical mixing (e.g.
330 navigation, dredging...) and chemical redistribution related to diagenesis processes (Almécija
331 et al., 2015; Tuit et al., 2000). Chemically-driven Pt mobility was already observed in other
332 coastal sediments showing maximum Pt enrichment at the base of the surface mixed layer after
333 scavenging at the oxic/anoxic boundary (Cobelo-García et al., 2011). Furthermore, a sediment
334 core from the Boston Harbor also showed chemical mobility of Pt, implying Pt remobilization
335 in sediments at short time scales (Tuit et al., 2000). According to Colodner et al. (1992), a
336 fraction of Pt in marine sediments is labile, suggesting that Pt may be scavenged from seawater
337 into both Fe-Mn oxyhydroxide minerals and organic-rich sediments, so that these phases might
338 dominate the Pt distribution in sediments. Previous work has compared trace metal (Cu, Hg,
339 Pb, and Zn) distributions in the same cores from the Toulon Bay showing some evidence of
340 partial mixing in the core TB1 (Dang et al., 2015; Tessier et al., 2011).

341 In contrast, the position of the core TB2 in a shallow zone with low water regeneration (Tessier
342 et al., 2011) and less impacted by currents, ship traffic and/or dredging, suggests that no major
343 sediment reworking occurred. In this core, the continuous increase of Pt/Al over the past century
344 before the mid-1980s cannot be explained by the relatively new technology of car catalytic
345 converters, implying additional, yet less reported anthropogenic Pt sources to the marine
346 environment. In fact, Pt concentrations in surface sediments from the Boston Harbor dating

347 from 1978 (i.e. integrating Pt emissions before the introduction of car catalysts) showed a 17-
348 fold enrichment of Pt concentrations relative to background values (i.e. up to 12.5 ng.g^{-1} , Tuit
349 et al., 2000). This observation suggests that, despite the higher Pt release rates of the early
350 catalytic converters and considering the relatively low number of catalyst-equipped cars at that
351 time, other, probably industrial sources may have affected the Pt levels in harbor sediments
352 (Tuit et al., 2000). Older Pt emissions might be related to the use of Pt in several industrial
353 applications, since Pt played an important role in various catalytic processes (e.g. catalytic
354 cracking of crude petroleum) applied for the production of the very high octane fuels required
355 for aircraft and automobile engines during World War II (Peavy, 1958). After the war, Pt
356 catalyst reforming processes, introduced to the refining industry in 1949, produced huge
357 amounts of lower octane fuels for automobile engines, and industrial / home heating fuels.
358 Accordingly, the years 1950 to 1960 were considered as the industry's "platinum period"
359 (Peavy, 1958). In addition, emissions from intense coal industry during the first half of the 20th
360 century, may have contributed to elevated Pt concentrations, since high Pt concentrations were
361 reported for coal samples ($\sim 5 \text{ ng.g}^{-1}$, Finkelman and Aruscavage, 1981; up to 70 ng.g^{-1} , Dai et
362 al., 2003). As a result of the scuttling of the French Navy fleet during WWII (November 1942,
363 Tessier et al., 2011), huge amounts of industrial coal are still present in the surface sediments
364 inside the Toulon Bay with the area of the core TB2 being the coal loading dock (Dang et al.,
365 2018). Although the Pt concentrations in this coal are unknown, given the range of values
366 reported in the literature, industrial coal and/or fly ashes could partly explain the Pt
367 accumulation in the core TB2, with a stronger increasing trend before ~ 1960 , and a period of
368 weaker increase during $\sim 1960 - 1990$.

369 Recent increase of Pt concentrations ($\sim 50\%$ increase in ~ 24 years in core TB2; Fig. 2) is
370 consistent with observations in other coastal environments, such as the Tagus Estuary. In this
371 system, Pt values at the top of the sediment core (up to 9.5 ng.g^{-1} , Cobelo-García et al., 2011)

372 representing ~ 30 - 40 times the local background are observed. Platinum concentrations in
373 saltmarsh sediments impacted by high traffic in the same estuary showed a surface peak value
374 exceeding 40 ng.g⁻¹ (Almécija et al., 2015). This recent contamination has been clearly
375 attributed to increasing Pt demand, use and emission related to the introduction of car exhaust
376 catalytic converters since the early 1990's (Rauch and Morrison, 2008). Considering Pt
377 concentration originating from catalysts of ~ 4 ng.g⁻¹ for the topmost samples in sediment core
378 TB2, Pt deposition rates are estimated to ~ 15 g Pt.y⁻¹ based on an annual sedimentation rate of
379 ~ 0.2 cm.y⁻¹, a density of wet sediment of 0.64 g.cm⁻³ and a porosity of 0.7, as well as a SB
380 surface of 9.8 km² (Tessier et al., 2011). A rough estimation of Toulon Bay catalyst emission
381 of ~ 10 to 20 g Pt.y⁻¹ is obtained assuming ~ 200,000 vehicles equipped with catalysts with an
382 average yearly mileage of 1,000 km.vehicle⁻¹ and an average emission rate ranging between 50
383 and 100 ng Pt.km⁻¹ (based on values from Rauch and Peucker-Ehrenbrink, 2015). As observed
384 on a global scale in Rauch et al. (2005), the difference between emission and deposition rates
385 may originate from several factors including over-/underestimated emission rates which is
386 influenced by the age and the type of vehicle (e.g. Moldovan et al., 2002) or the occurrence of
387 recent additional sources (e.g. wastewaters and Pt from anticancer-drugs, Vyas et al., 2014).
388 Literature reports that Pt emissions from cars are mainly deposited at a distance of less than 20
389 m from the edge of the road (e.g. Fritsche and Meisel, 2004; Schäfer and Puchelt, 1998). Over-
390 estimation of Pt inputs may also originate from the transfer of Pt emissions to seawater that is
391 surely influenced by several factors including prevailing wind direction (Schäfer and Puchelt,
392 1998) and road runoff. Exportation of fine-grained urban particles towards the outer bay or the
393 open sea by currents and/or potential partial Pt dissolution from urban particles in contact with
394 seawater may also occur (Cobelo-García et al., 2014a). In addition, dissolved Pt will probably
395 be diluted and exported rather than accumulated in sediments. Despite potential errors in the
396 estimations, calculated Pt emission rates from car catalysts in the SB are generally in good

397 agreement with recent Pt deposition rates in sediment core TB2 and might therefore explain a
398 large fraction of total Pt deposition in the area.

399

400 *Historical record in mussels*

401 The temporal evolution of Pt concentrations in mussels farmed close to the site of core TB2
402 (Fig. 1) reflected a ~ 8-fold increase over the 1984 to 2014 period, especially since the mid-
403 1990s (Fig. 3). Together with the ~ 20-fold increase in European Pt demand for car catalysts
404 over the same period, this observation suggests that vehicle-emitted Pt has been introduced into
405 the coastal ecosystem of the Toulon Bay with an effective transfer to living marine organisms.
406 These first results for Pt in Mediterranean bivalves are in line with increasing Pt/Al values in
407 the TB2 core from the same site and with previous work on wild oysters and mussels from the
408 French and the Spanish (Galician) Atlantic coast (oysters, Abdou et al., 2016; mussels, Neira
409 et al., 2015). Given the fact, that biomonitoring organisms are sampled on a regular basis,
410 sediment-specific uncertainties due to physical or chemical disturbance of the historical record
411 are excluded and, therefore, the use of sentinel organisms from sample banks may provide
412 reliable information on trends in ambient contaminant pressure over time. In fact, the recent Pt
413 increase in mussels goes along with a decrease in Pb as observed in the same mussel samples
414 from the Toulon Bay (Dang et al., 2015) and in Galician Mussels (Neira et al., 2015). These
415 opposite trends may be explained by the successive ban of leaded gasoline (leading to
416 decreasing Pb emissions) in parallel to the growing deployment of catalyst-equipped vehicles,
417 since leaded gasoline damages the catalysts and thus is not compatible with this modern
418 technology (Schäfer and Puchelt, 1998). The apparent baseline Pt concentration (0.1 ng g^{-1} ;
419 Fig. 3) in Toulon Bay mussels could reflect either natural Pt background although one cannot
420 exclude that these concentrations partly result from other historic Pt contamination as recorded
421 in the sediment.

422 4.2. Biomonitoring of Pt in mussels along the northwestern Mediterranean coast

423 Spatial distribution of Pt concentrations in mussels from contrasting sites along the
424 Mediterranean coast seemed to roughly follow an increasing gradient from western to eastern
425 sites, reflecting inter-site differences in terms of urbanization and supposed Pt inputs.
426 Generally, in order to avoid trace metal variations related to seasonality, including reproduction,
427 leading to “biological dilution” of gonads (Regoli and Orlando, 1994), Winter organisms are
428 used for comparison. In those mussels, the lowest Pt concentrations occurred at the sampling
429 site Sète. Low Pt concentrations also occurred in mussels available from sites Banyuls-sur-Mer
430 (Natural Reserve of Cerbère-Banyuls) and Bonifacio (Summer / Fall mussels). All those three
431 sites are located in supposedly less exposed areas, i.e. far from major urban areas. Slightly
432 higher Pt concentrations ($\sim 0.4 \text{ ng.g}^{-1}$) measured in Winter mussels from sampling site Saintes-
433 Maries-de-la-Mer cannot be explained by intense urban pressure, yet, mussel sampling was
434 performed inside the leisure harbor. Even though the sampling site Faraman is located in a non-
435 urbanized area (Natural Regional Park of Camargue), relatively high Pt concentrations
436 ($\sim 0.5 \text{ ng.g}^{-1}$) in wild Winter mussels suggest contamination of this site, possibly by seawater
437 draining pollution from La-Fos-sur-Mer city. In fact, in the late 1980’s, the Gulf of Fos was
438 considered as one of the most polluted neritic areas in Europe with important metal pollution
439 (Cu, Pb, Cd, Zn; Benon et al., 1978). This area hosts important oil industries that might be a
440 source of Pt to the marine environment as previously discussed (section 4.1.). Other studies
441 report high trace metal contamination in native and caged mussels *M. galloprovincialis* from
442 areas close to major urban and industrial centers such as La-Fos-sur-Mer (Andral et al., 2004),
443 with a battery of biomarkers indicating disturbed health in mussels (Zorita et al., 2007) from
444 the most impacted zones including the La-Fos-sur-Mer Harbor. In addition the sampling site
445 Faraman is directly under the influence of the Rhône outflow (Charmasson et al., 1999) which
446 may drain all the pollution originating from the urbanized watershed. Similar Pt concentrations

447 occurred in mussels from sampling site TB2 in the Toulon Bay (Seyne sur Mer), showing the
448 highest Pt level (0.55 ng.g^{-1}) of the studied sites. This value is somewhat lower than the 2014
449 value ($\sim 0.8 \text{ ng.g}^{-1}$) in farmed mussels from the same area in the Toulon Bay. Platinum
450 concentration range in mussels from the Genoa Harbor, marked by industrial / urban water
451 pollution (Ruggieri et al., 2011), is similar to levels observed in the Toulon Bay (Fig. 4). These
452 observations suggest that Pt accumulation in mussels from the different sites may reflect the
453 supposed exposure from anthropogenic pressure, similarly to other trace metals, showing strong
454 gradients between mussels from less populated areas or regions with no major river inputs (e.g.
455 Sète) and those from heavily populated and industrialized port areas (Fowler and Oreioni,
456 1976).

457 Few field studies report on Pt levels in biota from coastal marine environments. Recent samples
458 of wild mussels *M. galloprovincialis* from an urban beach in Vigo (Spain) revealed Pt
459 concentrations of $\sim 0.45 \text{ ng.g}^{-1}$ (2011 value, Neira et al., 2015), while wild oysters (*Crassostrea*
460 *gigas*) from the moderately contaminated Gironde Estuary mouth contained $\sim 0.33 \text{ ng.g}^{-1}$ (2013
461 value, Abdou et al., 2016). Accordingly, Pt levels in mussels from the Mediterranean sites are
462 similar in magnitude to those in wild bivalves from the Atlantic coast, but with clearly higher
463 values in confined harbor sites with relatively high urban/industrial pressure. Bioconcentration
464 factors (BCF), comparing Pt accumulation in tissues to ambient seawater concentrations were
465 determined as $\text{BCF} = \text{Pt}_B / \text{Pt}_D$, where Pt_B is the Pt concentration in the organism (ng.g^{-1} , dw)
466 and Pt_D the dissolved Pt concentration in seawater (ng.L^{-1} , Arnot and Gobas, 2006) for the
467 Genoa Harbor mussels (no Pt_D data available for the other sites). Average BCF in the Genoa
468 Harbor mussels was $\sim 4 \times 10^3$, i.e. similar to values reported for wild mussels *M.*
469 *galloprovincialis* from an urban beach ($\sim 5 \times 10^3$; Neira et al., 2015) and for wild oysters from
470 the Gironde Estuary ($\sim 3 \times 10^3$, Abdou et al., 2016). These values show that marine bivalve
471 bioconcentrate Pt ambient signal reflecting: (i) the presence of natural bioavailable Pt species

472 and (ii) their suitable use for Pt monitoring in coastal systems. Although it is assumed that
473 dissolved metals are potentially more bioavailable than their particulate forms (e.g. Lekhi et al.,
474 2008), filter-feeders such as mussels are able to absorb metals, and more particularly PGEs, in
475 dissolved and particulate forms (Zimmermann and Sures, 2018). Given that Pt emissions from
476 car exhaust systems mainly occur as very small particles (from micrometers down to
477 nanometric size; Folens et al., 2018; Rauch et al., 2001), more work is necessary to characterize
478 the behavior of such particles in the marine environment and understand their role in Pt transfer
479 to living organisms.

480 Physiological status including growth and reproductive state may impact metal concentrations
481 in bivalves, due to 'dilution' effects by rapid tissue growth or weight increase during gonad
482 development (Casas et al., 2008; Couture et al., 2010). Therefore, contaminant concentrations
483 in tissues reflect ambient concentrations, but also food availability or seasonal reproduction
484 cycles (Andral et al., 2004; Charmasson et al., 1999; Dang et al., 2015). Inter-site comparison
485 may require adjustment of raw concentration data from different sites with reference to a
486 standard Condition Index to limit the risk of miss-interpretation, as shown from a mussel caging
487 study, where site-dependent growth differences occurred at relatively short timescales (Andral
488 et al., 2004). Comparison of Pt concentrations in the soft bodies of mussels sampled in Winter
489 and in Spring and Summer/Fall from four of the seven studied sites clearly suggests that Pt
490 concentrations undergo seasonal fluctuations (Fig. 4). The Condition Indices in the different
491 mussel samples ranged from 17 to 47 with higher CI for Spring and Summer/Fall samples than
492 for Winter samples, when comparison was available (Fig. 4). This result is expected supposing
493 higher soft tissue mass during the reproduction season than during Winter. Indeed, during
494 gametogenesis, the penetration of gonadic tissues into the digestive gland may biologically
495 dilute metal concentrations in mussel total soft tissues (Regoli and Orlando, 1994). At three
496 sites, the Winter concentrations are greater than the respective Summer values, as expected,

497 whereas at the Toulon Bay site, Pt concentrations were higher in Summer, despite higher CI
498 (Fig. 4). The latter observation might reflect environmental Pt exposure related with either site-
499 specific changes in bio-transfer or temporarily higher local Pt inputs (e.g. tourism related).
500 However, these hypotheses cannot be validated with the available dataset. The observed
501 seasonal fluctuations do not change the order of supposed Pt exposure between the studied sites
502 (Sète to Toulon Bay; Fig. 1), suggesting that the uncertainties discussed above do not invalidate
503 the spatial biomonitoring approach, yet warranting an optimized sampling strategy to limit
504 potential biases.

505

506 **5. Conclusions**

507 Historical records of both sediment cores and mussels collected in a severely polluted site, the
508 Toulon Bay, suggest the existence of former (non-vehicle related) sources of Pt in the system.
509 They also revealed the impact of recent contamination related to increasing Pt emissions
510 through car catalytic converters that may be of major importance in this area under high
511 anthropogenic pressure. Biomonitoring in mussels from contrasting areas along the
512 northwestern Mediterranean coastline suggests a relation between the degree of exposure and
513 the Pt concentrations in mussel tissues. Mussels could therefore be considered as a potential
514 good bioindicator of Pt levels in marine environments. Considering the relatively high Pt
515 concentrations in some sampling sites, systematic (bio-)monitoring programs should therefore
516 be run in such coastal environments marked by historical and current Pt contamination.
517 Continuous metal inputs to the coastal zone may lead to increasing pollution in these already
518 highly contaminated areas with the risk of Pt export to the marine environment. Further
519 investigations are therefore of major importance to accurately determine biogeochemical Pt
520 distribution, reactivity and fate in marine waters.

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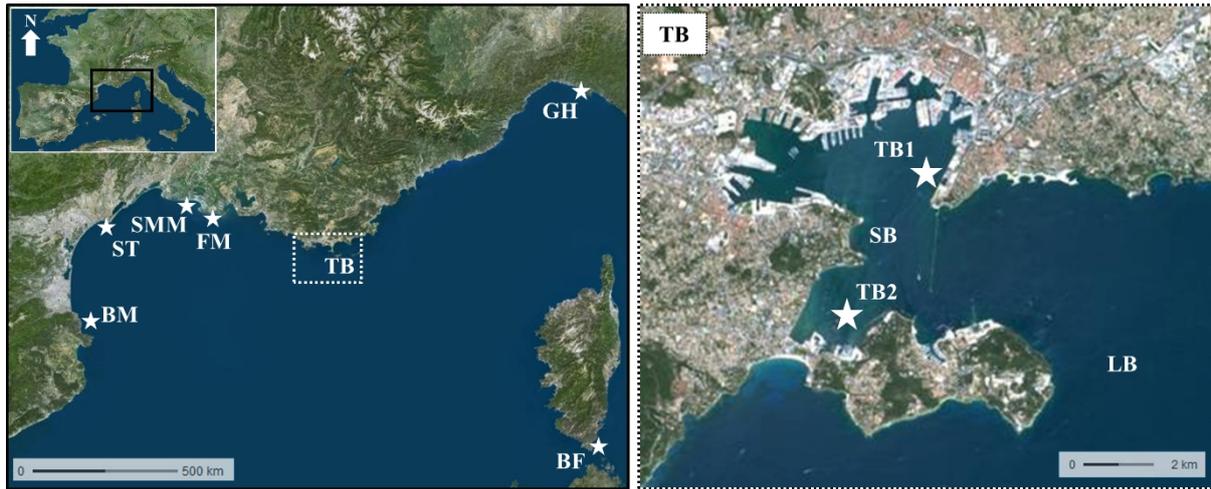


Fig. 1: Sampling sites along the northwestern Mediterranean coast. From east to west BM: Banyuls-sur-Mer, ST: Sète, SMM: Saintes-Maries-de-la-Mer, FM: Faraman, TB: Toulon Bay with the two sampling sites TB1 and TB2 (zoom on the right panel; SB: Small Bay, LB: Large Bay), BF: Bonifacio, and GH: Genoa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

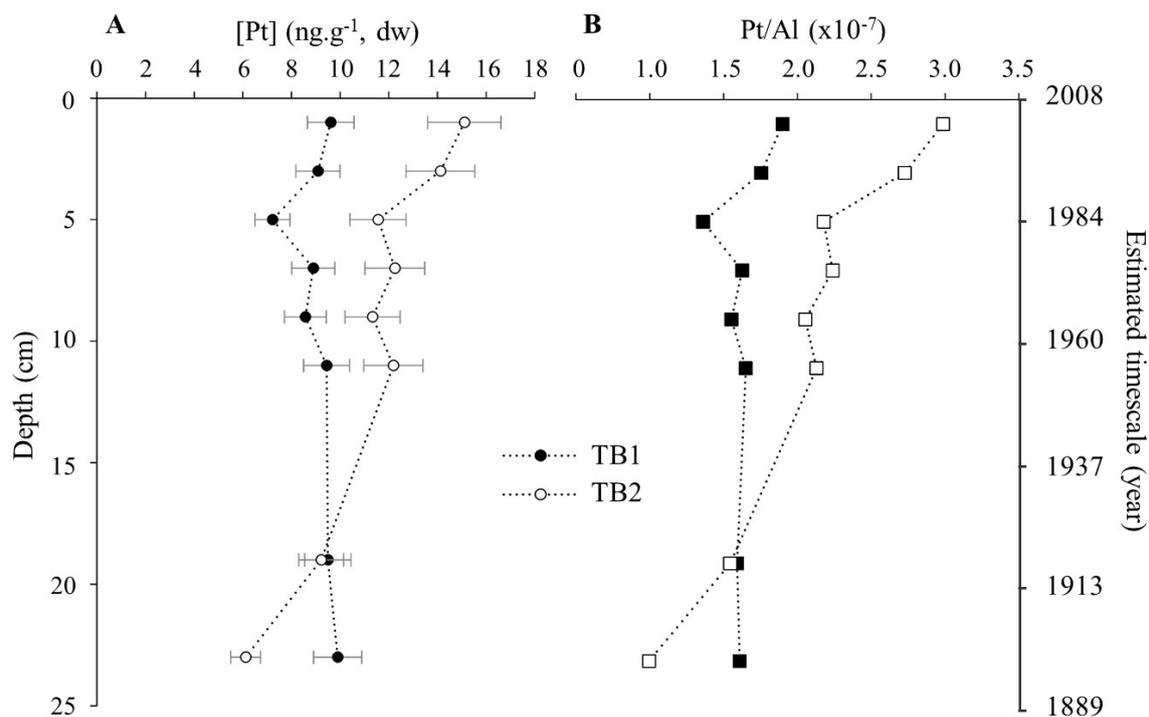


Fig. 2: Depth profiles of Pt concentrations (A) and Al-normalized Pt concentrations (B) in sediment cores from the Toulon Bay. Sediment cores were collected at site TB1 (filled symbols) and TB2 (empty symbols). A: Platinum concentrations (ng.g^{-1} , dw: dry weight, circles), B: Aluminum-corrected Pt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

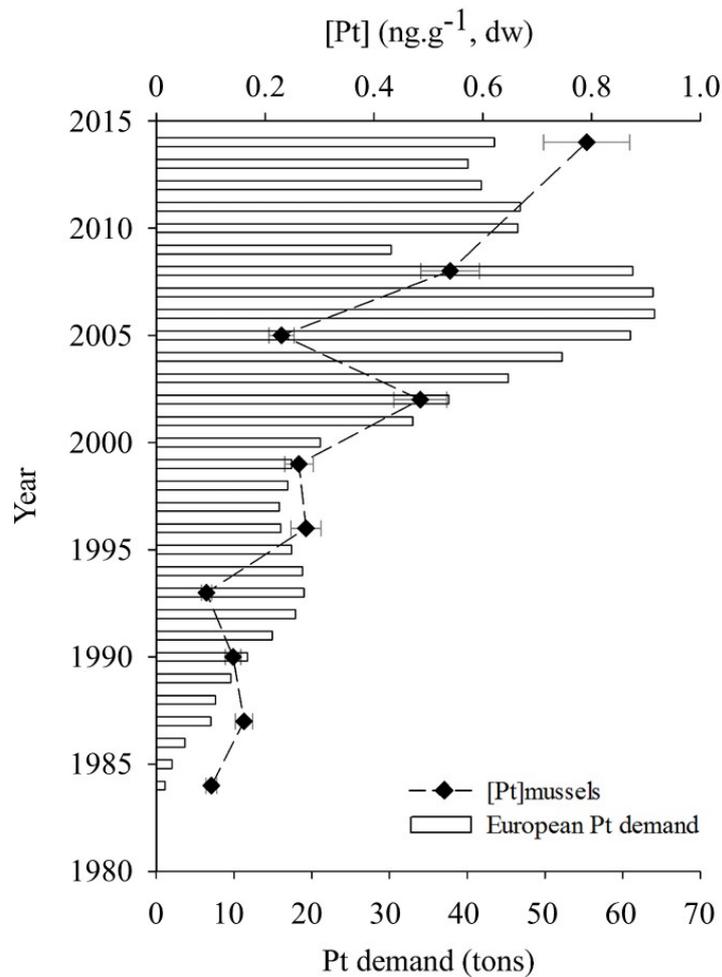


Fig. 3: Platinum concentrations in farmed mussels from the Toulon Bay (ng.g⁻¹, dw; sampling site TB2) and European Pt gross demand (metric tons, after Johnson Matthey, 2017) for car catalytic converters during the 1984-2014 period. Error bars correspond to analytical uncertainty (RSD%).

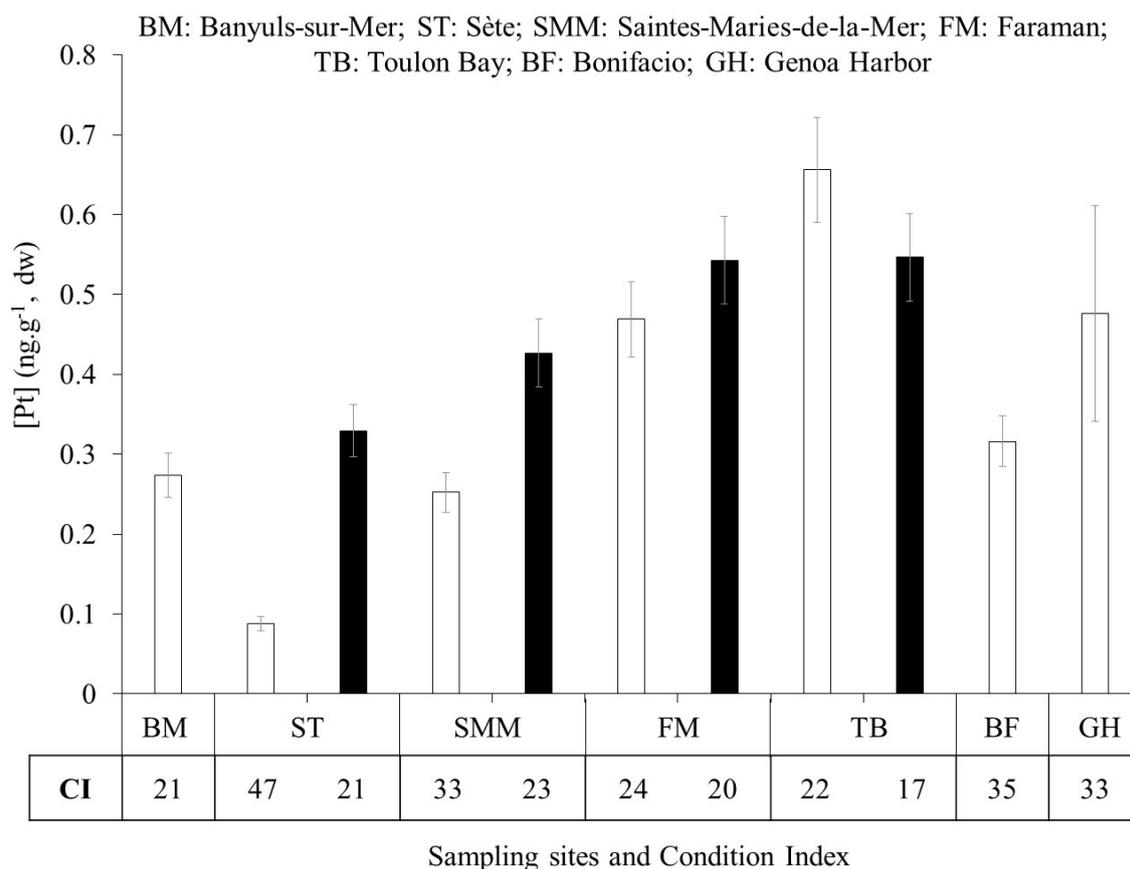


Fig. 4: Platinum concentrations ($\text{ng}\cdot\text{g}^{-1}$, dry weight: dw) in wild mussels sampled along the northwestern Mediterranean coast. Winter, Spring and Summer / Fall mussels were analyzed for the same sampling sites when possible. Black bars correspond to sample collection during Winter, 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%).