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

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1   **Platinum in sediments and mussels from the northwestern Mediterranean coast:**

2   **temporal and spatial aspects**

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12   **Abstract**

13   Platinum (Pt) is considered a Technology Critical Element (TCE) and an emerging metallic

14   contaminant with increasing release into the environment. Gaps in knowledge and

15   understanding of environmental levels, fate and effects of Pt still exist, especially in the

16   marine environment. This work presents Pt concentrations in the northwestern Mediterranean

17   coast including: (i) temporal variability from sediment cores and farmed mussels in the

18   Toulon Bay (historically affected by intense human activities) and (ii) spatial distribution

19   from recent wild mussels collected along ~ 300 km coastline with contrasting ecosystems

20   (including natural reserves), quantified using voltammetry and inductively coupled plasma-

21   mass spectrometry. The historical (> 100 years) record of Pt in sediments from the Toulon

22   Bay suggests the existence of non-negligible Pt sources older than those related to vehicle

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

1. Introduction

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

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

3

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 ~ 9.8 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 °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

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 μAutolab 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 HNO_3 (30 %

178   HCl and 65 % HNO_3 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 (H_2SO_4, 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 H_2SO_4. 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 ^{193}Ir (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 HNO$_3$ (30 % HCl and 65 % HNO$_3$ 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®).

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.

3. Results

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

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

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 (~ 0.15 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 ~ 40 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 ng.g^{-1} 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 ± 0.14 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 ± 0.05 cm.y^{-1}. Accordingly, the studied

289 sediment cores cover the period $\sim$ 1890 - 2008 and the top 10 cm layer would reflect

290 $\sim$ 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

13

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. ~ 10 ng.g^{-1} in core

309 TB1 and ~ 6 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 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 (~ 5 ng.g^{-1}, Tuit et al., 2000). These observations together with high Pt

319 levels in South Pacific pelagic sediment (~ 30 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

14

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 (~ 5 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 ~ 4 $ng.g^{-1}$ for the topmost samples in sediment

388 core TB2, Pt deposition rates are estimated to ~ 15 g $Pt.y^{-1}$ based on an annual sedimentation

389 rate of ~ 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

390 a SB surface of 9.8 km² (Tessier et al., 2011). A rough estimation of Toulon Bay catalyst

391 emission of ~ 10 to 20 g $Pt.y^{-1}$ is obtained assuming ~ 200,000 vehicles equipped with

392 catalysts with an average yearly mileage of 1,000 $km.vehicle^{-1}$ and an average emission rate

393 ranging between 50 and 100 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 (~ 0.4 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 (~ 0.5 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 (~ 0.8 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 ~ 0.45 ng.g^{-1} (2011 value, Neira et al., 2015), while wild oysters

471   (*Crassostrea gigas*) from the moderately contaminated Gironde Estuary mouth contained

472   ~ 0.33 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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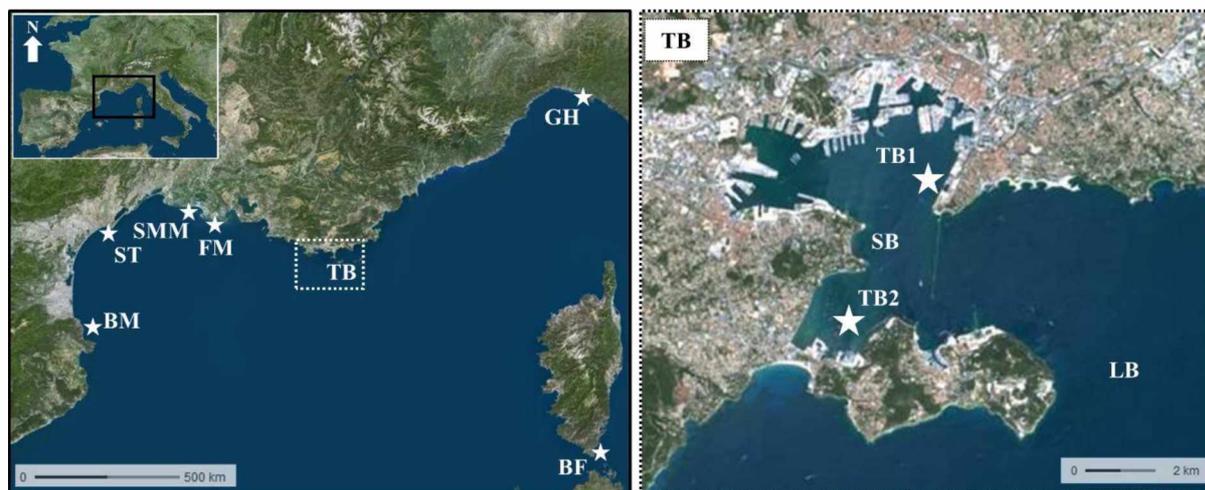
Fig. 1: Sampling sites along the northwestern Mediterranean coast. From east to west BM: Banyuls-sur-Mer, ST: Sète, SMM: Saintes-Maries-de-la-Mer, FM: Faraman, TB: Toulon Bay with the two sampling sites TB1 and TB2 (zoom on the right panel; SB: Small Bay, LB: Large Bay), BF: Bonifacio, and GH: Genoa Harbor, Italy. Source: geoportail.gouv.fr
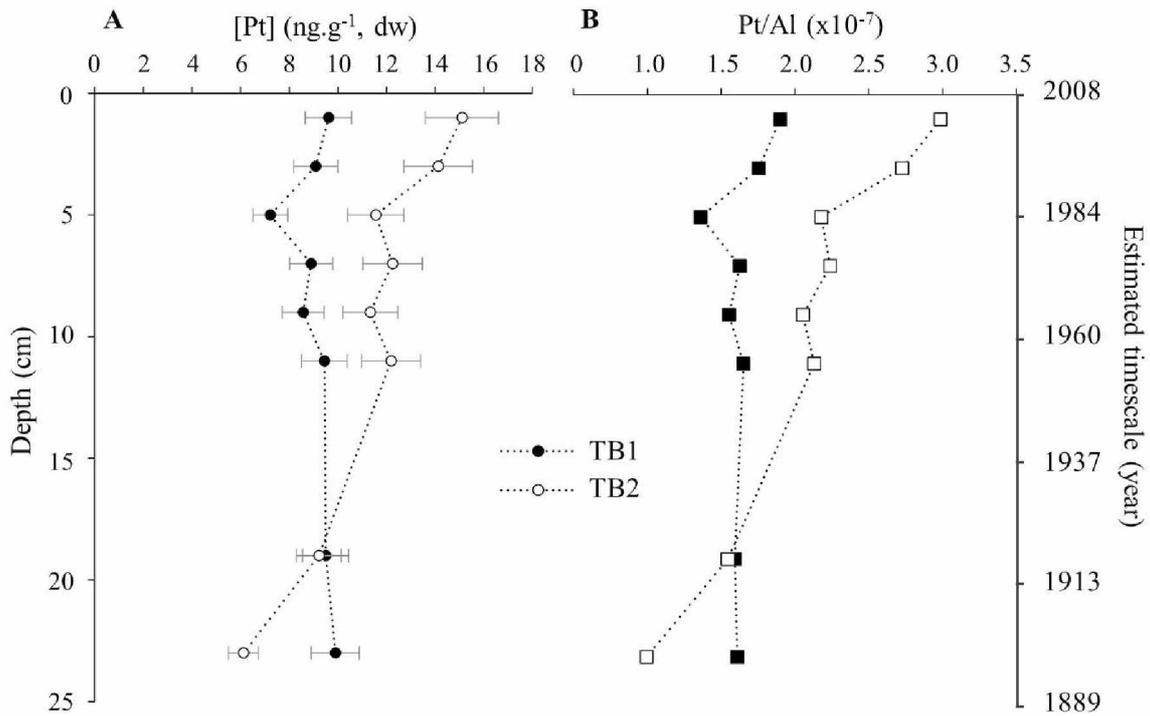
Fig. 2: Depth profiles of Pt concentrations (A) and Al-normalized Pt concentrations (B) in sediment cores from the Toulon Bay. Sediment cores were collected at site TB1 (filled symbols) and TB2 (empty symbols). A: Platinum concentrations (ng.g^{-1}, dw: dry weight, circles), B: Aluminum-corrected Pt concentrations (x 10^{-7}, squares). Aluminum concentrations are from Tessier et al. (2011). Error bars correspond to analytical uncertainty (RSD%).
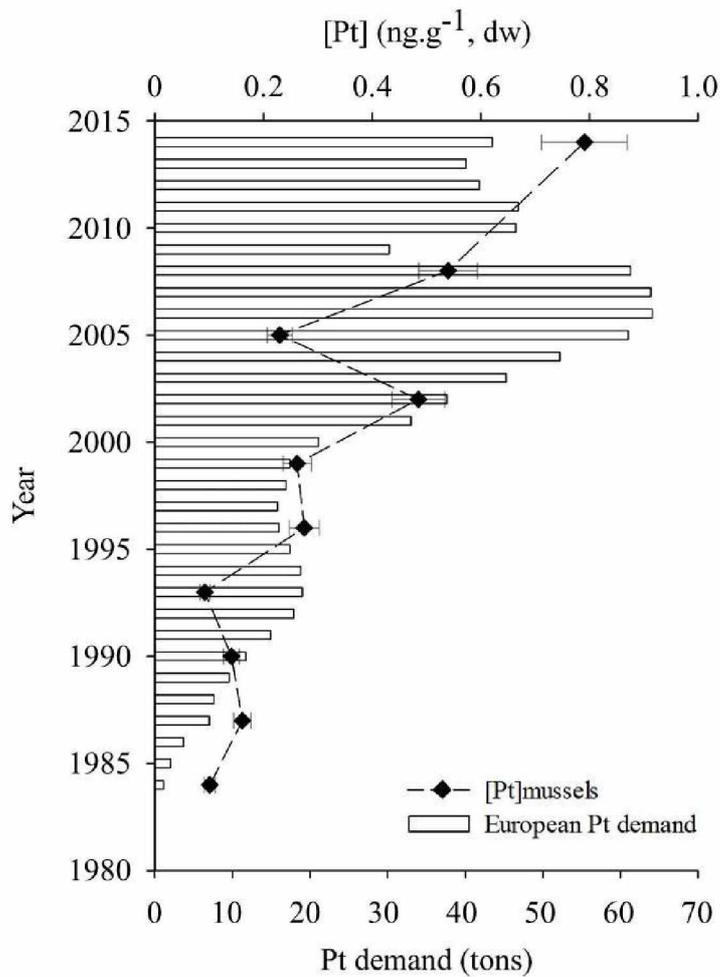
Fig. 3: Platinum concentrations in farmed mussels from the Toulon Bay (ng.g^{-1}, dw; sampling site TB2) and European Pt gross demand (metric tons, after Johnson Matthey, 2017) for car catalytic converters during the 1984-2014 period. Error bars correspond to analytical uncertainty (RSD%).
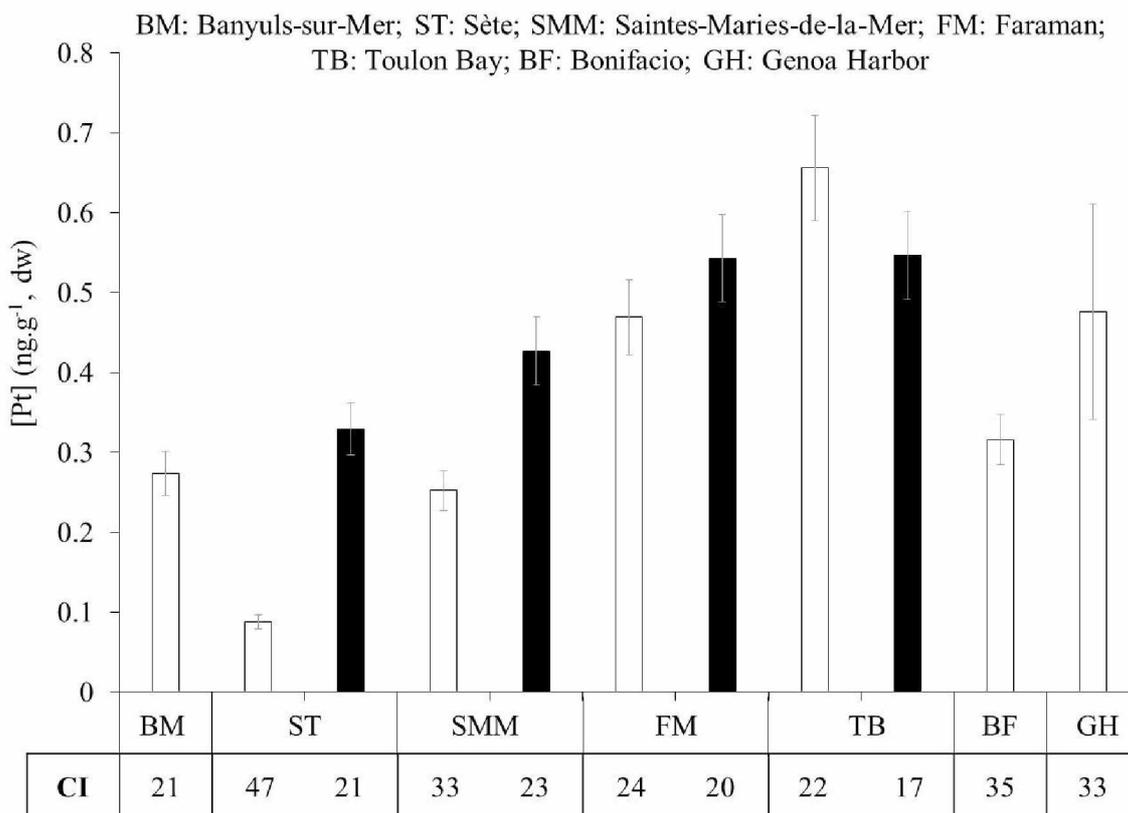
Fig. 4: Platinum concentrations (ng.g^{-1}, dry weight: dw) in wild mussels sampled along the northwestern Mediterranean coast. Winter, Spring and Summer / Fall mussels were analyzed for the same sampling sites when possible. Black bars correspond to sample collection during Winter, whereas white bars correspond to sample collection during reproductive season (Spring and Summer / Fall); CI: average Condition Index of the mussel pools for the French coastline (n ~ 240) and of the 10 individuals from the Genoa Harbor. Error bars correspond to analytical uncertainty (RSD%).