

1 **Past and present platinum contamination of a major European fluvial-estuarine system:**  
2 **insights from river sediments and estuarine oysters**

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10

11 **ABSTRACT**

12 Platinum Group Metals (PGM) are modern, technology relevant elements for which (i) the  
13 anthropogenic cycle has outcompeted the natural cycles and (ii) environmental behaviour, fate  
14 and impact are still widely unknown. Improvement of signal processing in stripping  
15 voltammetry allowed for accurate determinations of platinum (Pt) in historical records of river  
16 sediments and estuarine oysters from the Gironde fluvial-estuarine continuum (SW France)  
17 comprising the Lot River. Sediment cores from the Lot River dated from 1952 to 2001,  
18 showed past Pt contamination due to former industrial (smelter) activities in the Lot River  
19 watershed. These samples revealed the phasing-out of a historical Pt contamination with  
20 Thorium (Th) - normalized values of  $11 \cdot 10^{-5} \pm 0.79 \cdot 10^{-5}$  for the deepest part of the core which  
21 is clearly greater than the regional geochemical background value ( $\text{Pt/Th} \sim 1.9 \cdot 10^{-5} \pm 0.39 \cdot 10^{-5}$ ).  
22 Wild oyster samples from the mouth of the Gironde Estuary collected from 1981 to 2013  
23 showed Pt concentrations ranging from  $0.80 \pm 0.01 \text{ pmol.g}^{-1}$  to  $3.10 \pm 0.14 \text{ pmol.g}^{-1}$ . Oyster  
24 samples have recorded the phasing-out of the smelter-related historical industrial Pt  
25 contamination and empirical modelling suggests the recent rise of a new source of Pt to the  
26 system. Temporal variations of Pt in oysters attributed to this recent source reflect the  
27 exponential increase of Pt demand for car catalytic converters, pointing towards the increasing  
28 importance of this emerging source to the aquatic system. Estuarine oysters prove to be  
29 suitable bioindicators for Pt contamination providing sensitive monitoring of emission  
30 variations over time. Furthermore, oysters may bioconcentrate Pt (Bioconcentration Factor,  
31  $\text{BCF} \sim 10^3$ ) and transfer this metal contamination to the higher food chain. These findings  
32 highlight the need for deeper understanding of environmental Pt contamination, processes and  
33 possible adverse effects to biota.

34 Highlights:

- 35 • Historical Pt records of both river sediment cores and estuarine wild oysters reflect  
36 past and present anthropogenic sources and subsequent contamination in the  
37 watershed
- 38 • Wild oysters are sensitive biomonitors of Pt contamination because they  
39 bioconcentrate Pt
- 40 • Anthropogenic Pt releases related to car catalytic converters emissions may  
41 profoundly affect watershed Pt budget

42 Keywords:

43 Platinum, sediments, wild oysters, bioaccumulation, PGM

44

45 **INTRODUCTION**

46

47 Platinum (Pt), one of the rarest elements in the Earth's crust with a typical  
48 concentration of  $0.5 \text{ ng.g}^{-1}$  (Rudnick and Gao, 2003), is a strategic commodity for industries  
49 in many countries (Reith et al., 2014, Cobelo-García et al., 2015) since its physical (density,  
50 resistance to corrosion...) and chemical (e.g. catalyst) properties serve in many applications  
51 such as laboratory and medical equipment or (medical) drugs. The most extended application  
52 is the use of Pt-based vehicle catalytic converters which contain about 1.5 g of Pt (Zereini et  
53 al., 1997) representing more than 70% of the total European Pt demand in 2013 (Johnson  
54 Matthey, 2014). Those devices are recognized as a major source of Pt to the environment and  
55 together with the burning of fossil fuels, mining and other industrial uses has lead to a  
56 complete disturbance of the global Pt cycle (Sen and Peucker-Ehrenbrink, 2012). The  
57 significant recent increase of Pt concentrations in Antarctic snow (Soyol-Erdene et al., 2011)  
58 suggests large-scale atmospheric transport of Pt (Barbante et al., 2001) implying its global  
59 contamination. Major concerns on ecosystems and biota contamination arose few years after  
60 introducing car catalyst technology in Europe (e.g. Schäfer et al., 1999) and today  
61 anthropogenic Pt enrichment is recorded in all Earth compartments: atmosphere, water,  
62 sediments, and soils (e.g. Pawlak et al., 2014). Accordingly, Pt is considered as an “emerging  
63 pollutant” for which it is necessary to develop innovative techniques providing reliable  
64 quantitative estimates of environmental pathways, loads, and concentrations (Rodrigues et al.,

65 2009). To date, however, there is still a lack of data on environmental Pt concentrations  
66 mostly due to the relative difficulty to measure this element at low ambient levels.

67         Recent work on Pt behavior in the Gironde Estuary has shown that estuarine reactivity  
68 along the salinity gradient is crucial for both the Pt distribution in the estuary and dissolved Pt  
69 export to the global ocean (Cobelo-García et al., 2014a). The net dissolved Pt addition due to  
70 estuarine mixing results in a higher export of dissolved Pt to the ocean than expected from the  
71 riverine input (Cobelo-García et al., 2014a). However, Pt sources and possible contamination  
72 of this system are still unknown. The present work aims at identifying past and present Pt  
73 contamination and sources by combining the first historical records of Pt in river sediments  
74 and estuarine oysters from the Gironde fluvial-estuarine system.

75

## 76 **MATERIAL AND METHODS**

### 77 **Study area**

78         The Gironde Estuary (about 170 km length), draining a 80 000 km<sup>2</sup> watershed, is a  
79 major European estuary considered a model for physical, hydrological and geochemical  
80 studies especially on trace element transport and reactivity in impacted watersheds (e.g.  
81 Lancelot et al., 2011). The Lot-Garonne-Gironde fluvial-estuarine system is affected by  
82 multi metal pollution originating from a common main point source being a former Zn-ore  
83 mining/metallurgic industry (e.g. 1842-1987: Cd, Zn, Cu, Pb; Audry et al., 2004a) on the  
84 Riou-Mort River near Decazeville and active from 1842 to 1987, lead to metal concentration  
85 enrichment of a small tributary, the Riou-Mort River (**Figure 1**). After transport, trace metals  
86 can settle down and be deposited in river sediments where they accumulate under favorable  
87 hydraulic conditions provided by natural and reservoir lakes (Audry et al., 2004a). Succeeding  
88 a relatively short time period, sediments form a “closed” system that no longer exchanges  
89 with components of the free water column (Callender, 2000) and represent archives of  
90 environmental conditions corresponding to a certain period in the past (Von Gunten et al.,  
91 1997). In 2001, two continuous sediment cores of about 1.4 m-long were collected using a  
92 manual corer consisting of a 10x10 cm rectangular Plexiglas tube. Sampling was realized in  
93 two hydroelectric reservoirs of the Lot River: the reservoirs of Marcenac and Cajarc located  
94 respectively upstream and downstream the Riou-Mort River i.e. the hypothetical Pt pollution  
95 source (**SI, Figure S1**). The sediment cores were sliced in thin horizontal sections at 1 cm  
96 resolution from the surface to 25 cm. The lower part was sampled with a 5 cm resolution.

97 Immediately after recovery, each sliced section was centrifuged in order to remove pore  
98 waters and then sealed in sampling-bags under nitrogen. Sediment samples were dried at 50°C  
99 to constant weight and then powdered and homogenized with an agate mortar (Audry et al.,  
100 2004a). The second set of samples consisted in a historic series of wild oysters which, as  
101 suspension feeders, are exposed to both dissolved metals and metals bound to mineral  
102 particles, phytoplankton and organic matter (Lanceleur et al., 2011) and therefore represent  
103 good bioindicators of their environment (Gunther et al., 1999). A time series (1981-2013) of  
104 mature (2 years old) wild-growing *Crassostrea gigas* Japanese oyster samples was extracted  
105 from the National Network for the Observation of Marine Environment Quality  
106 (RNO/ROCCH; i.e. the French Mussel-Watch; [www.ifremer.fr/deltn/pages/rno.htm](http://www.ifremer.fr/deltn/pages/rno.htm))  
107 specimen bank. Winter (February) oyster samples were chosen for the present work in order  
108 to avoid dilution of metal concentration due to variable soft-body weight during reproduction  
109 periods (Enríquez-Díaz et al., 2009). Individuals selected for this study originated from the  
110 mid-salinity range of the Gironde Estuary, at the La Fosse sampling site (salinity 15-20; **SI**,  
111 **Figure S1**), where highest trace metal concentrations are recorded in the same set of oyster  
112 samples (e.g. Cd and Ag; Lanceleur et al., 2011). A pool of fifteen individuals for each winter  
113 have been selected, lyophilized and grinded.

114

## 115 **Analytical Procedure**

116

117 Samples were ashed in quartz crucibles at 800°C during 3h according to the heating  
118 scheme described by Nygren et al. (1990) and then acid-digested using 5 mL concentrated  
119 hydrochloric acid HCl and 3 mL concentrated nitric acid HNO<sub>3</sub> (both Suprapur®, Merck)  
120 followed by 1 mL sulphuric acid H<sub>2</sub>SO<sub>4</sub> (TraceSELECT®, Fluka). After evaporation on a  
121 time-temperature controlled Teflon-coated hot plate, cooled contents were then diluted with  
122 0.1M HCl. Sediment samples were syringe-filtered using PFA syringe (Savillex®) and 25  
123 mm polyethersulfone membranes of 0.45 µm pore size (VWR®) prior to analyses. Platinum  
124 measurements were carried out by means of catalytic adsorptive cathodic stripping  
125 voltammetry. Laboratory analyses were performed in a laminar flow bench (ISO-5) housed in  
126 an ISO-7 laboratory. Platinum voltammetric determinations were carried out using a µAutolab  
127 Type III potentiostat (Metrohm® Autolab B.V.) connected to a polarographic stand  
128 (Metrohm® 663 V.A.) equipped with three electrodes: i) a hanging mercury drop electrode  
129 (HMDE; the working electrode), ii) a Ag/AgCl reference electrode, and iii) a glassy carbon  
130 auxiliary electrode. A polytetrafluoroethylene (PTFE) voltammetric cell served in all

131 experiments and the potentiostat was controlled using the GPES v. 4.9 software (EcoChemie  
132 B.V.). Aliquots of 8 mL of acid-digested sample were pipetted into the voltammetric cell, and  
133 two reagents, 3.3 mM formaldehyde (Riedelde-Haën), and 0.45 mM hydrazine sulphate  
134 (Fluka) were added directly to the solution and allowed for the detection of Pt in the acidic  
135 media (see details in Cobelo-García et al., 2014b). Sample solution was first deaerated by 5  
136 min of purging with humidified nitrogen (99.999% ALPHAGAZ™ 1, Air Liquide).  
137 Accumulation on the HMDE was then initiated with a potential set up at -0.3 V for 90 s, while  
138 the solution was stirred at 3000 rpm with a PTFE rod. After an equilibration time without  
139 stirring, a cathodic stripping scan was carried out by changing the potential from -0.5 V to -  
140 1.1 V in the differential pulse mode with a step potential of 4 mV, at a scan rate of 20 mV.s<sup>-1</sup>,  
141 a modulation time of 0.04 s, an interval time of 0.2 s, and a modulation amplitude of 25 mV.  
142 Before applying any derivative transformation, the original voltammogram was smoothed,  
143 with a smoothing factor of 2 and according to the Savitsky-Golay algorithm. The  
144 determination of Pt concentrations was achieved by standard addition method and signal was  
145 processed by second derivative transformation (applied after data smoothing) as described in  
146 Cobelo-García et al., (2014b). The improvement in the peak detection and quantification  
147 applying the second derivative signal allows for the acquisition of a well-defined peak for Pt  
148 at low accumulation times. Second derivative was selected as it is more efficient in  
149 eliminating the background interferences than the first derivative, while keeping good peak-  
150 shaped transformed signals and better signal-to-noise ratio than higher derivative orders  
151 (Cobelo-García et al., 2014b).

152 For typical masses of 200 mg for sediment and 40 mg for biological samples the  
153 detection limits (calculated as three times the standard deviation of blank measurements) were  
154 respectively of 0.11 pmol.g<sup>-1</sup> and 0.44 pmol.g<sup>-1</sup>. For sediments, accuracy was checked by the  
155 analysis of river sediment certified reference material (CRM; JSd-2; Geological Survey of  
156 Japan) with recoveries of about 90% and precision (%RSD) of about 5% (n=3). Since no  
157 CRM existed for Pt in biological matrices, precision of the method was tested on certified  
158 dogfish muscle (DORM) resulting in low relative standard deviation between replicates of  
159 about 5% (n=4).

160 Cadmium concentrations in oysters were measured by quadrupole ICP-MS (Inductively  
161 Coupled Plasma Mass Spectrometry) and typically differed by less than 15% from the data  
162 provided by RNO/ROCCH for aliquots of the same samples analyzed by Graphite Furnace  
163 Atomic Absorption Spectrometry ([www.ifremer.fr/deltn/pages/rno.htm](http://www.ifremer.fr/deltn/pages/rno.htm)). Cadmium and  
164 Thorium concentrations in sediment cores were also measured by ICP-MS (Audry et al.,

165 2004a). Accuracy was checked by analysis of CRM (CRM 320; BCR) and recoveries were  
166 about 95% and precision was generally better than 5% for concentrations 10 times higher than  
167 detection limits.

## 168 **RESULTS**

169

### 170 **Platinum concentrations in sediment cores**

171 Platinum concentrations in the Marcenac core samples were low and constant from the  
172 surface (4.5cm) to the bottom (122cm) of the core with a mean concentration of about 0.78  
173  $\text{pmol.g}^{-1} \pm 0.23$  (n=3; **Figure 2, A**). With concentrations ranging from about 1  $\text{pmol.g}^{-1}$  to 7  
174  $\text{pmol.g}^{-1}$ , Cajarc sediments exhibit relatively high Pt concentration variations with values  
175 clearly higher than the concentrations in the Marcenac core until approximately 40 cm depth  
176 (**Figure 2, A**). Maximum concentration occurred at the very bottom of the core, i.e. 123 cm  
177 depth representing about 10 times Marcenac core concentration. Between the surface and 40  
178 cm depth an almost flat profile can be observed with rather low and constant Pt  
179 concentrations. Platinum values finally almost reach Marcenac concentration in the topmost  
180 Cajarc sample (2cm depth) exhibiting a minimal concentration of 0.88  $\text{pmol.g}^{-1}$ . Besides, in  
181 most areas, hydraulic and mineralogical (chemical) particle fractionations result in increasing  
182 heavy metal concentration with decreasing sediment grain sizes making it essential to  
183 normalize for grain size effects on natural, lithogenic metal variability before assessing  
184 anthropogenic inputs (Loring and Rantala, 1992). Thorium which is a conservative, lithogenic  
185 element in sedimentary cores (Krachler and Shotyk, 2004) and which does not originate from  
186 any anthropogenic inputs in our study area served as a normalizing element. Platinum profile  
187 is smoothed by Th normalization, suggesting that grain size effects play a minor but visible  
188 role in the peak shape of the Pt record in the Cajarc core, i.e. Pt is predominantly enriched in  
189 the fine particles (**Figure 2, A**). However, except from the attenuation of some peaks,  
190 normalized Pt profile displays the same positive anomalies as the original Pt concentration  
191 profile and confirms the Pt enrichment of Cajarc sediments comparing to Marcenac core.  
192 Considering the low values and the low variability of Marcenac sediment core Pt  
193 concentrations, Marcenac sampling site may serve as a reference site for Pt pollution of the  
194 study area. Located upstream the industrial activity area, this site appears as not contaminated  
195 in numerous heavy metals such as Zn, Ag, Cd or Pb, and has therefore been considered as a

196 reference site for metal pollution of the Lot watershed in several previous studies (e.g.  
197 Lancelleur et al., 2011).

198

### 199 **Platinum concentrations in wild oysters**

200 Total Pt concentrations in oyster samples, expressed as  $\text{ng.g}^{-1}$  dry weight (dw) of  
201 oyster tissue, ranged from 0.80 to 3.1  $\text{pmol.g}^{-1}$  (**Figure 2, B**). From 1981 to 2000, Pt  
202 concentrations in oysters were constant with a mean value of about 1.8  $\text{pmol.g}^{-1}$  ( $\pm 0.19$   
203  $\text{pmol.g}^{-1}$ ). Between 2001 and 2008, Pt concentrations increased to a maximum in 2006 being  
204 almost 2-fold higher than the previous mean value. Following this peak, Pt concentrations  
205 decrease abruptly to a minimum of 0.80  $\text{pmol.g}^{-1}$  in 2012. Last measurement corresponding to  
206 the year 2013 displays however, a higher value, reaching again the mean concentration of the  
207 1981-2000 period.

208

## 209 **DISCUSSION**

210

### 211 **Past industrial Pt contamination in river sediments**

212

213 Considering Marcenac sampling site as a reference site, regional background Pt  
214 concentration, corresponding to mean Pt concentration of the core, is of about 0.78  $\text{pmol.g}^{-1}$ .  
215 Reservoir sediments from the Lot River appear to be impoverished regarding Upper  
216 Continental Crust (UCC) Pt content (2.6  $\text{pmol.g}^{-1}$ ; Rudnick and Gao, 2003), probably due to  
217 the geological composition of the Lot River watershed which mainly consists of Jurassic and  
218 Cretaceous marine calcareous sedimentary rocks (Audry, 2003). In such rocks, typical Pt  
219 concentrations are rather low, i.e., with typical concentrations lower than 2.6  $\text{pmol.g}^{-1}$  and  
220 often around 1  $\text{pmol.g}^{-1}$  in ordinary chert beds (Hori et al., 2007). Marcenac Pt concentrations  
221 were also low compared to other estuarine or coastal environment systems such as pre-  
222 anthropogenic sediments from the Massachusetts Bay (3  $\text{pmol.g}^{-1}$ ; Tuit et al., 2000) or  
223 Portuguese coastal unpolluted sediments (2.9  $\text{pmol.g}^{-1}$ ; Cobelo-García et al., 2011). Regional  
224 geochemical background for Pt in the Lot River watershed obtained from mean Th-  
225 normalized Pt concentrations in the reference study site of Marcenac is  $\text{Pt/Th} \sim 1.9 \cdot 10^{-5}$ .

226 In order to assess the extent of Pt enrichment of Cajarc sediments compared to  
227 background natural values, the Enrichment Factors (EF) were calculated as following:

228 
$$EF = (Pt/Th)_{Cajarc} / (Pt/Th)_{Marcenac} \quad (1)$$

229 Mean Pt/Th ratio of Marcenac sediments was selected as background value instead of crustal  
230 content in order to estimate the Riou-Mort River pollution impact. Enrichment factors were  
231 interpreted according to the scale established by Birth (2003) as detailed in Essien et al.  
232 (2009).

233 When comparing Th-normalized profiles of both Cd and Pt, positive anomalies occur at  
234 the same depths. This co-variation along the sediment core suggests a common source and  
235 transport of Cd and Pt metal inputs to the Lot River. Cadmium input variations in the Lot  
236 watershed were related to the history of the treatment of Zn-extraction residuals and were  
237 time-resolved according to radiochronology of  $^{137}\text{Cs}$  (Audry et al., 2004a). Accordingly, the  
238 historical Pt records in Cajarc sediments also closely reflect the evolution of the industrial  
239 activity in the Decazeville basin including changes in the treatment process of Zn residuals  
240 inducing variations of metal concentrations in river sediments. Bottom part of the core, dated  
241 from 1952, displays high Pt concentrations corresponding to moderately severe Pt enrichment.  
242 At that period residuals were stocked as sludge and subject to leaching during rainfalls.  
243 Elevated Pt/Th and Cd/Th values at a depth of 85 cm co-occurred reflecting the accidental  
244 seepage of 1986 which had its origins in the breach of the settling tank pipe draining waters  
245 used to leach the spoil tips (Audry, 2003). After this accidental event in 1986, Cd and Pt  
246 normalized profiles displayed a slight decrease and then constant, relatively low ratios, with  
247 Pt/Th ratios close to the background value at the Marcenac sampling site ( $Pt/Th \sim 1.5 \cdot 10^{-5}$ )  
248 and Pt EF showing an overall decreasing trend. For Cd this decrease was related to the  
249 cessation of Zn production in 1986 and subsequent remediation actions: treatment of  
250 groundwater tables and the containment of spoil tips by clay covering (Audry, 2003). The  
251 recent decrease of both Cd/Th and Pt/Th towards background values suggests that the  
252 remediation of the Decazeville site successfully reduced Cd and Pt releases from the former  
253 industrial area. In this context, early 1990's sediments indicate minor enrichment in Pt with  
254  $EF < 3$ . Sediment cores already served as indicators of Pt pollution sources in other systems  
255 such as an urban lake near Boston, Massachusetts. In these urban sediments the increasing Pt  
256 concentrations were clearly related to the introduction of automobile catalysts in the United  
257 States with Pt flux being approximately ten times higher than before (Rauch and Hemond,  
258 2003). Influence of anthropogenic Pt emissions originating from car catalytic converters can  
259 be neglected in Lot River sediment cores since no important urban area is located upstream  
260 from the sediment sampling sites and population density is low ( $\sim 33$  inhabitants/km<sup>2</sup>;



261 cartesfrance.fr). Recent works (2013 field campaign) established the Pt concentrations of  
262 surface Suspended Particulate Matter (SPM) from a Gironde Estuary tributary, the Garonne  
263 River, upstream (Port-Sainte-Marie sampling site) and downstream (La Réole sampling site;  
264 **Figure 1**) the Lot River confluence. Contemporary SPM displayed mean Th-normalized Pt  
265 values of  $\sim 6.5 \cdot 10^{-5}$  (Cobelo-García et al., 2014a) which are considerably higher than the most  
266 recent values in the Cajarc sediment core. At these sampling sites, the Garonne River drains  
267 the atmospherically deposited Pt pollution originating from highly urbanized areas such as the  
268 Toulouse and Agen urban agglomerations. This diffuse source must account for Pt enrichment  
269 of the Garonne watershed. The Garonne river draining a basin comprising two important  
270 urban areas Toulouse and Bordeaux agglomerations (both more than 1M inhabitants; **Figure**  
271 **1**), is the main Gironde Estuary tributary. The Gironde Estuary is therefore submitted to  
272 anthropogenic pressure concerning automobile exhaust catalyts and Pt pollution.  
273

#### 274 **Post-1990 exponential increase of car catalytic converters**

275  
276 As suspension feeder organisms, oysters, and especially the *C.gigas* species, have  
277 already served as bioindicators for trace metals contamination (e.g. Claisse et al., 1989). The  
278 Decazeville basin is known as the primary source of Cd in the Gironde watershed (Audry et  
279 al., 2004b), where chronic Cd pollution has led to prohibition of bivalve production and  
280 consumption since 1996. Mass balances at the watershed scale, showed that even 13-16 years  
281 after the termination of the Zn ore treatment (i.e. 1999-2002), the Decazeville basin  
282 contributed more than 61% - 92% of total Cd fluxes into the Gironde Estuary (Masson et al.,  
283 2006). This is further supported by i) historical records of Cd in estuarine freshwater  
284 sediments reflecting the industrial activity in the Decazeville watershed (Grousset et al., 1999)  
285 and ii) mass balances at the estuary scale, suggesting that intra-estuarine sources (e.g. the  
286 Bordeaux agglomeration) are negligible, compared to the main source (e.g. Schäfer et al.,  
287 2002). Knowing the major source of Cd inputs to the system, elementary ratio between Cd  
288 and Pt served to determine Pt source of contamination. Cajarc sediments revealed a  
289 characteristic, relatively constant Cd/Pt value close to 200 for the Zn-ore treatment period  
290 from 1952 to 1978. During the mid-1980s and early 1990s Cd/Pt ratios in Cajarc sediments  
291 were clearly higher and reached typical values of  $\sim 400$  suggesting that during the 1986  
292 pollution accident and the following years, Cd release was extremely dominant. Although  
293 estuarine transformation and bioaccumulation uptake processes may be different, similar

294 Cd/Pt values and variations occurred in wild oysters where Cd/Pt ratios were also of about  
295 200 in the early 1980s, and then increased from 1985 to 1989 to about 300 which best  
296 characterize the ultimate state of the Decazeville pollution source. Those findings support the  
297 co-evolution trend of the two trace metals Cd and Pt in the Gironde wild oysters as observed  
298 in the Cajarc sediment core, and therefore, their common source and parallel transport along  
299 the fluvial-estuarine system, i.e. from the industrial site to the coastal ocean. Given that  
300 industrial Pt demand was low before the 1990s (Johnson-Matthey, 2014), and in the absence  
301 of other reported Pt sources in the watershed, we assumed that this ratio would reflect the  
302 oyster response to the sum of Pt exclusively derived from both, natural sources and the  
303 historic waste reservoirs of the Decazeville industry. Based on elementary Cd/Pt ratios and  
304 assuming that during the whole observation period nearly all Cd in oysters was derived from  
305 the metal point source, we estimated respective theoretical Pt concentrations in oysters over  
306 time (**Figure 3**). Before 1988, estimated and measured Pt concentrations were very close  
307 which suggests that Pt in the oysters mostly derived from the industrial site. In contrast,  
308 increasing measured Pt concentrations and the gap appearing with estimated values after 1988  
309 were attributed to increasing contributions by other sources. Platinum demand and use for the  
310 majority of application sectors in Europe was constant over time, (Johnson Matthey, 2014),  
311 resulting in relatively constant inputs from the watershed. However, recent Pt demand in  
312 Europe for autocatalysts is an exception. In fact, from 1981 to 1999 Pt demand for catalytic  
313 converters in Europe has increased by 30 times and from 1981 to 2007 even by 100 times  
314 (**Figure 3**; Johnson Matthey, 2014). Despite the impossibility to access to Pt emission data in  
315 France, European Pt demand for autocatalysts seems to be a good proxy for Pt use in catalytic  
316 converters and therefore Pt emissions. In this sector, Pt use is almost simultaneous with  
317 demand since cars are built and sold in a short period of time in answer to current demand.  
318 Furthermore, emission data show that the majority of Pt particle emissions occur during the  
319 first thousands kilometers of the car (Artelt et al., 1999) resulting in a short delay between Pt  
320 demand and Pt emission. Historical measurements show that Pt concentrations rise in oyster  
321 samples until reaching a maximum value in 2006, then sharply decrease, probably reflecting a  
322 break-down in Pt demand in many sectors due to difficult economic conditions during 2008-  
323 2010 (Johnson Matthey, 2010). In fact, the largest fall in automobile Pt demand occurred in  
324 Europe, where gross car catalytic converters Pt demand decreased by 50% in average  
325 (Johnson Matthey, 2014). Recently, increasing Pt concentrations in oysters might result from  
326 a new strong European Pt demand for catalytic converters, which started to increase again  
327 since 2010 (Johnson Matthey, 2014). Increase in Pt emissions by cars is recorded by the wild

328 oysters, assuming a time-lag of 2-4 years. This response time can be explained by (i) transport  
329 time from the source to the estuary mouth (~ 400 km), (ii) estuarine particle residence time (~  
330 2 years; Jouanneau and Latouche, 1982), (iii) estuarine Pt transformation processes (Cobelo-  
331 García et al., 2014a) and (iv) the age of wild oysters at the sampling time (2 years old). As  
332 well as wild oysters, time-series analysis of mussels from an urban beach revealed excess (or  
333 anthropogenic) Pt related to its use in car catalytic converters and car sales in Spain and  
334 Portugal (Neira et al., 2015). Temporal trends of Pt accumulation in both wild oysters and  
335 mussels from urbanized aquatic system indicate the change in Pt use over time. Accordingly,  
336 the data suggest that, the historical metal pollution source in the Decazeville area was the  
337 major Pt source to the Gironde oysters in the past (before 1990), but that Pt emissions from  
338 cars have become increasingly dominant in the two past decades.

339

#### 340 **Platinum bioconcentration in wild oysters**

341

342 Experimental studies showed that traffic-related Pt is uptaken by biota such as plants  
343 (e.g. Schäfer et al., 1998) or aquatic animals under different exposure pathways (e.g. water  
344 containing road dust; Zimmermann et al., 2002). Field studies analyzed Pt uptake of aquatic  
345 organisms such as isopods or amphipods (e.g. Rauch and Morrison, 1999, Haus et al., 2007),  
346 and more recently bivalves (e.g. Essumang et al., 2010; Ruchter and Sures, 2015; Neira et al.,  
347 2015). In order to estimate the Pt uptake by wild oysters, bioconcentration factor (BCF) which  
348 refers to uptake of a chemical substance from water via respiratory surface and/or skin (Arnot  
349 and Gobas, 2006), was estimated as:

$$350 \quad \text{BCF} = C_B / C_{WD} \quad (2)$$

351 Where  $C_B$  is the chemical concentration in the organism ( $\text{mg.kg}^{-1}$ ) and  $C_{WD}$  the freely  
352 dissolved chemical concentration in the water ( $\text{ng.L}^{-1}$ ; Arnot and Gobas, 2006). We used  
353 dissolved Pt concentrations assuming that dissolved metals are generally potentially more  
354 bioavailable than their particulate forms (e.g. Lekhi et al., 2008). This statement is supported  
355 by preliminary results on Pt uptake pathways with the study of Pt organ distribution in *C.*  
356 *gigas* revealing higher Pt concentrations in gills suggesting the dominance of direct  
357 contamination pathway, i.e. uptake by the gill epithelium of the dissolved metal from the  
358 water column. Maximal dissolved trace metal concentration served to calculate the BCF that  
359 is known as being the minimal estimation. This concentration was measured recently in the

360 Gironde estuarine system at 0.62 pM, i.e.,  $1.2 \cdot 10^{-4}$  ng.g<sup>-1</sup> in the mid-salinity range (Cobelo-  
361 García et al., 2014a). Considering 2013 mean Pt concentration in oysters from the La Fosse  
362 site of 0.334 ng.g<sup>-1</sup>, dw, minimum BCF is of about  $3 \cdot 10^3$ . Similar values ( $\sim 5 \cdot 10^3$ ) were  
363 observed in wild mussels from the Samil urban beach (Spain; Neira et al., 2015). In  
364 comparison, for Cd and Ag respective minimum BCF were estimated at  $2 \cdot 10^5$  and  $6 \cdot 10^6$  in the  
365 same system (Lanceleur et al., 2011) suggesting that bioconcentration of Pt in wild oysters is  
366 lower. A study on aquatic macroinvertebrates proved that, although Pt concentrations are  
367 relatively low in aquatic habitats, high bioconcentration factors, close to those of essential  
368 elements, can occur in biota (Haus et al., 2007). Thus, bioconcentration and uptake of trace  
369 metals depend on several factors including the feeding behavior of the organism or the trace  
370 metal speciation. For instance, Ruchter and Sures (2015) attributed the low concentrations of  
371 traffic related metals in clam tissues to active avoidance of the soluble metal forms and  
372 particles in the water column. Furthermore, uptake mechanisms depend also on the Pt form  
373 present in the environment, Pt(IV) being more likely to be taken up at a higher rate than Pt(II)  
374 (Rauch and Morrison, 1999). The speciation and partitioning of Pt are highly dependent of the  
375 residence time of the metal in the water column (Cobelo-García et al., 2008) and Pt  
376 partitioning between the particulate and dissolved phase in the Gironde Estuary suggests  
377 complex behavior with no clear salinity dependence (Cobelo-García et al., 2014a).  
378 Discrepancies between measurements of Pt uptake in biota and other parameters such as the  
379 speciation and phase distribution might be related to a number of oversimplifications. More  
380 data are needed on Pt biogeochemical cycle, behavior and speciation since all those  
381 parameters vary according to the system. Thus, a recent comparison between current and 20  
382 years old dissolved Pt concentrations profiles shows that anthropogenic Pt has little effect on  
383 dissolved Pt in the open oceans (Suzuki et al., 2014). Our study suggests that coastal waters  
384 are more affected by atmospherically-derived anthropogenic Pt.

385 Even though large Pt inputs must originate from car catalytic converters other urban  
386 sources of Pt contamination should be considered. In fact surface waters draining hospital  
387 wastewaters which contain patient excretion of Pt-based anticancer drugs display Pt  
388 concentrations which could exceed natural inputs (Vyas et al., 2014) and have a significantly  
389 higher toxicological and cancerogenic impact than catalyst-borne inorganic Pt (Lenz et al.,  
390 2007). Recent works revealed that particle adsorption of Pt-based drugs (cisplatin and  
391 carboplatin) as well as the reactivity of their respective degradation products decreased from  
392 river water to estuarine water (Turner and Mascorda, 2015).

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## 396 **Conclusion**

397           Historical records of Pt in sediment cores and biota samples have allowed the  
398 identification of the continental sources that contribute to Pt pressure in the Gironde fluvial-  
399 estuarine continuum. The results clearly show the succession of two major sources: a former  
400 point source originating from industrial activities in the Lot watershed and a recent diffuse  
401 source related to the exponentially increasing Pt use in vehicle catalytic converters. Data on Pt  
402 levels in wild oysters suggest that (i) Pt in estuaries is bioavailable to bivalves, (ii) oysters are  
403 suitable biomonitors of Pt contamination in the environment, and (iii) oysters from the  
404 Gironde Estuary have recorded the succession of different Pt sources in the Gironde  
405 watershed, covering the past ~ 35 years (1981-2013). The recent evolution and dominance of  
406 catalytic converters derived Pt recorded in wild oysters and the widespread use of this  
407 technology all over the world clearly suggest that other watersheds also undergo profound  
408 changes in their Pt budget. The forecast increase in population density in coastal areas (UN,  
409 2007) will probably strongly enhance Pt pressure in coastal environments. Future research  
410 should account for Pt behavior and speciation in estuaries and other marine systems in order  
411 to accurately evaluate its bioavailability to marine organisms and the associated toxicity. All  
412 these information would allow better assessment of potential Pt adverse effects on living  
413 organisms and ecosystems.

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419 ISOGIRE, and the COST Action TD1407.

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562 Figures:

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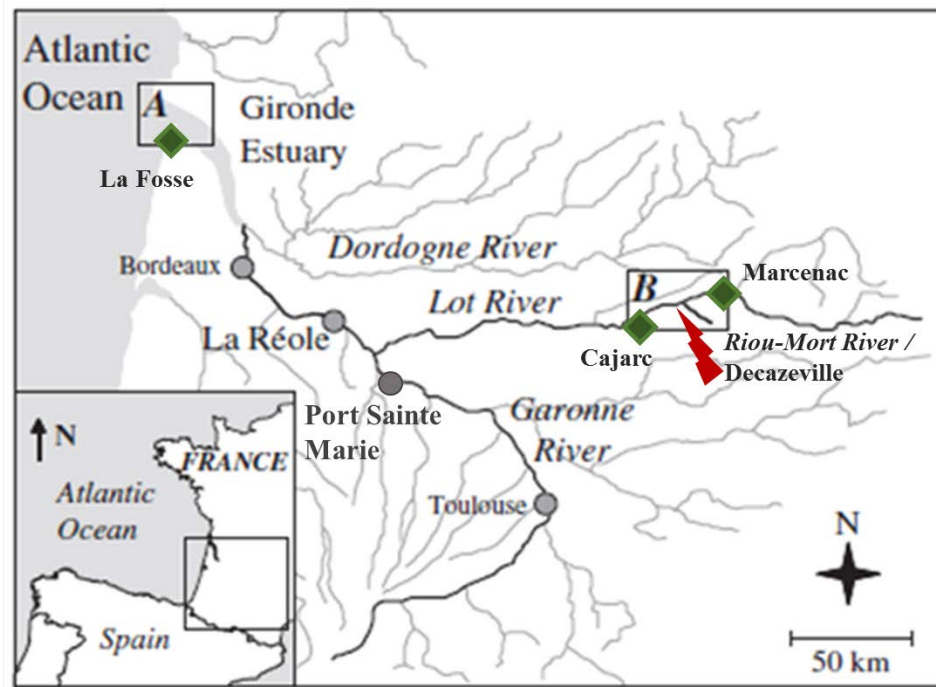
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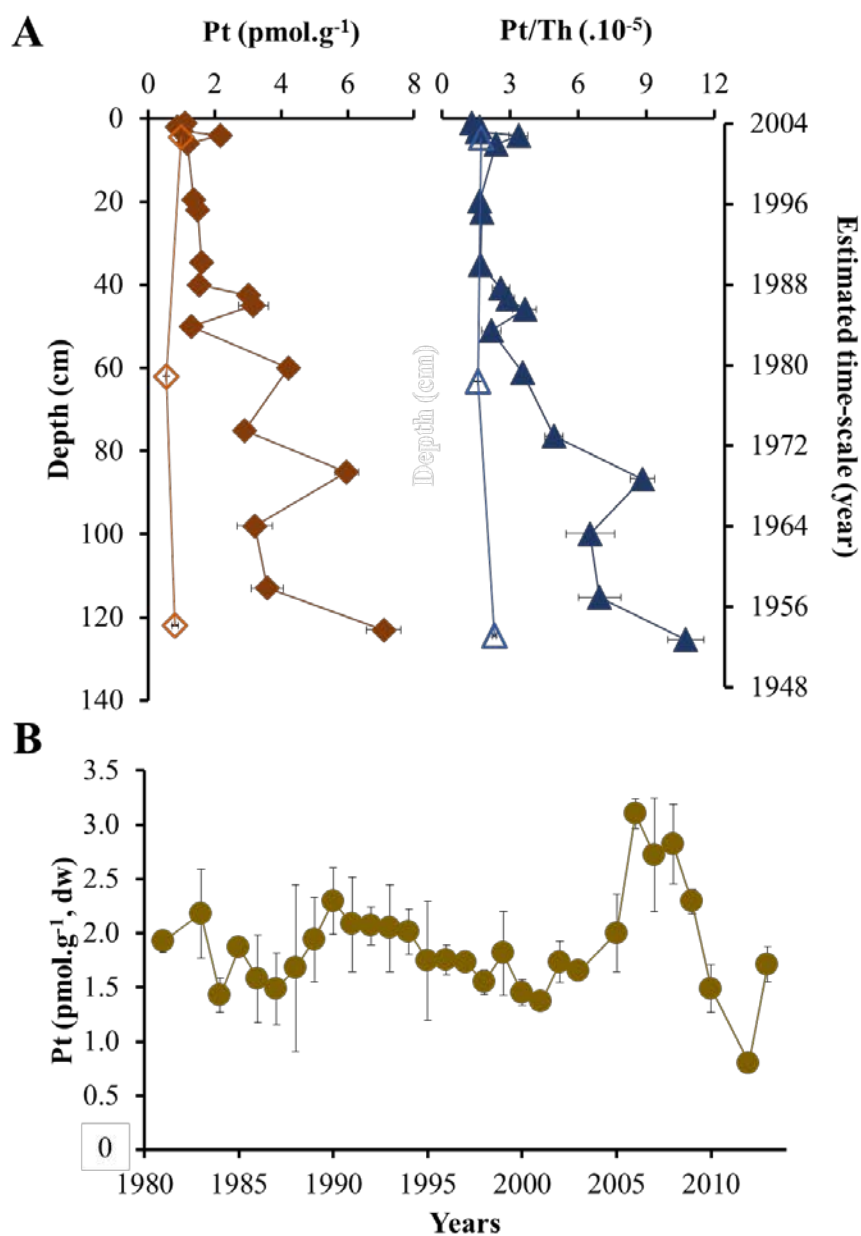
**Figure 1:** The Gironde Estuary (SW France) with sampling locations of (A) wild oysters and (B) sediment cores of the present study (diamonds)

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**Figure 2:** Historical records of Pt concentrations in sediment cores from the Lot River (A) and wild oysters from the Gironde Estuary (B).

(A) Depth profiles of the Pt concentrations (ng.g<sup>-1</sup>; diamonds) and Th-normalized Pt concentrations (triangles) for the Marcenac (empty symbols) and the Cajarc (filled symbols) sediment cores. Estimated time-scale from the <sup>137</sup>Cs profile (Audry et al., 2004a).

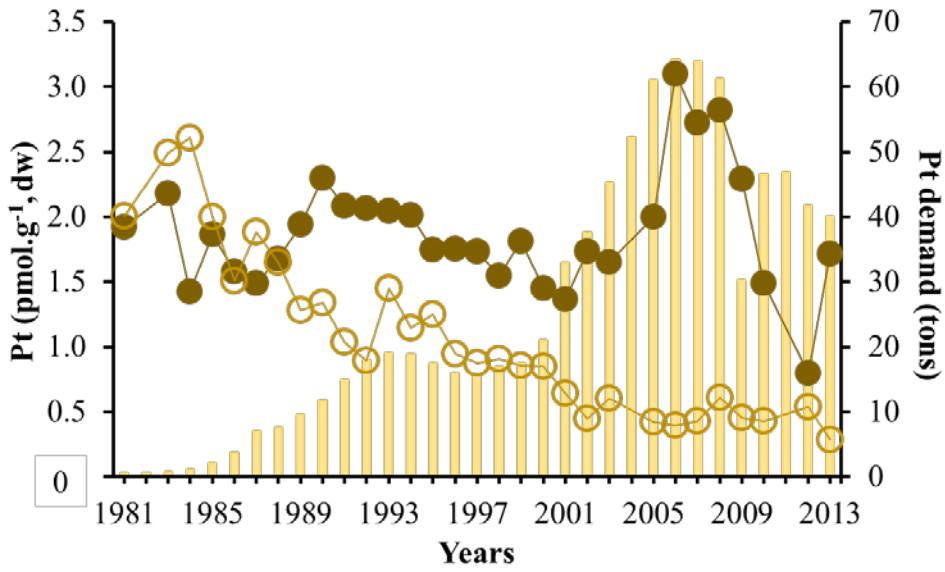
(B) Platinum concentrations in total oysters (ng.g<sup>-1</sup>, dry weight) from the La Fosse sampling site from 1981 to 2013.

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**Figure 3:** Time variations of Pt concentrations in wild oysters (circles) and European Pt demand for catalytic converters (bars; after Johnson Matthey, 2014). Platinum concentrations were measured (full circles) and estimated (open circles) from Cd/Pt ratio in oysters.

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605 Graphical abstract:

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