Short-term variations of platinum concentrations in contrasting coastal environments: the role of primary producers

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Abstract

Short-term variations of Pt concentrations and primary production indicators were compared in three contrasting coastal sites during spring bloom: (i) the Gironde Estuary mouth (SW France), (ii) the semi-enclosed Arcachon Bay (SW France), and (iii) the urbanized Genoa Harbor (NW Italy). At each site, surface seawater sampling and physical-chemical measurements were combined to study diel cycles (over 25 hours) of dissolved Pt concentrations in seawater (Pt_D) and master variables reflecting primary production activity (chlorophyll-a, phaeopigments, and particulate organic carbon, POC concentrations). Plankton nets were used in all sites, providing for the first time plankton Pt concentrations (Pt_{PK}) over a whole diel cycle (Gironde Estuary mouth) and spot sampling (Arcachon Bay and Genoa Harbor) in the coastal zone. Bivalves (wild oysters or mussels), reflecting organisms at higher trophic levels, were also collected at all sites. The POC/Chl-a ratios in the collected particulate material suggested high contribution of phytoplankton to the particulate matter in the productive Gironde Estuary mouth. At this site, phytoplankton activity partly controlled Pt cycling and particle/dissolved Pt partitioning during daytime. During the night, zooplankton grazing may release Pt into the dissolved phase. These processes are partly masked by external factors such as tide or local Pt sources, especially in more confined and/or urbanized coastal water bodies such as the Arcachon Bay and the Genoa Harbor. Platinum levels in plankton and bivalves from these contrasting sites along the Atlantic and Mediterranean coasts tended to reflect the general Pt levels in seawater. These results clearly suggest that (i) Pt contamination of coastal waters and marine organisms has become a common feature in urbanized sites and (ii) Pt transfer to the marine food chain starts at the basic level of primary producers. By concentrating Pt (Bioconcentration Factor: BCF ~ 10^4), phytoplankton may serve as a biomonitor to assess Pt contamination in coastal environments.

Keywords: Technology Critical Element, seawater, phytoplankton, bioconcentration

Declarations of interest: none

1. Introduction

Platinum (Pt) is a Technology Critical Element (TCE) for which there is an increasing need for accurate assessment of environmental impacts and natural dynamics (Cobelo-García et al., 2015). This emerging metallic contaminant belonging to the Platinum Group Elements (PGE) has been increasingly used in various applications over few decades, including vehicle catalytic converters and Pt-based anticancer drugs. Such emissions induce a general increase in Pt concentrations in all Earth compartments, with anthropogenic activities accounting for more than 80 % of Pt fluxes at the Earth's surface (Sen and Peucker-Ehrenbrink, 2012). Catalytic converters efficiently reduce gaseous pollutant emissions from car exhaust, but thermal and mechanical abrasions during vehicle functioning lead to PGE release into the environment (Artelt et al., 1999; Rauch et al., 2004a). Urban runoff and atmospheric deposition transport Pt emissions to the aquatic environment and ultimately to the coastal area and the sea. In addition, anti-cancer chemotherapy has been applying Pt-based compounds for decades (e.g. Lenz et al., 2007) and surface waters draining both effluents from hospitals with oncology ward and domestic wastewater receive excretion of Pt-based anticancer drugs from patients and outpatients at home (Vyas et al., 2014), which may lead to increasing Pt levels in urban sewage. Consequently, dissolved Pt concentrations in open ocean seawater (Colodner et al., 1993; Suzuki et al., 2014) or pristine estuaries (Pađan et al., 2019) are generally far below seawater concentrations near urbanized coastal or estuarine systems (Abdou et al., 2019; Cobelo-García et al., 2013; Mashio et al., 2017, 2016; Obata et al., 2006). Coastal environments facing ever-growing human pressure (~ 40 % of world's population live within 100 km of the coast; UN, 2017) therefore receive increasing anthropogenic Pt inputs from these various sources (Ruchter et al., 2015). Despite the crucial need for accurate assessment of the extent of Pt contamination and for the understanding of Pt biogeochemical cycles in coastal systems, so far only very few field studies address this issue.

Platinum bioavailability to living organisms and especially to marine biota is non-negligible. In fact, the limited environmentally relevant information available in the literature include Pt concentrations in marine macroalgae (Hodge et al., 1986), in marine bivalves (Abdou et al., 2019, 2016; Neira et al., 2015), and in dolphins (Essumang, 2008). There is even less information on the possible transfer mechanisms controlling Pt accumulation throughout the

aquatic trophic chain. At the base of this marine trophic chain, numerous algal species are able to sequestrate considerable amounts of trace elements from the dissolved phase, exerting a control on trace metal concentrations and cycling in marine systems (González-Dávila, 1995). As decaying and settling particles, phytoplankton cells also represent an important vehicle for the vertical transport of contaminants in the water column in marine environments through cell sinking into deeper waters and/or ingestion by consumers in surface waters (González-Dávila, 1995; Shams et al., 2014). Although phytoplankton communities may play a key role in the geochemical cycling of trace metals in coastal ecosystems (Caetano and Vale, 2003; Cloern, 1996), no study has reported yet on Pt concentrations in phytoplankton and the potential influence of this marine biological compartment on Pt cycling.

Based on sampling at ~ 1 h resolution covering diel cycles, as performed for the first time in the Gironde Estuary mouth, the Arcachon Bay and the Genoa Harbor, this study focuses on Pt cycles under different hydrological conditions and anthropogenic pressure. The objectives of the present work are (i) to identify potential relations in short-term (hourly timescale) Pt concentrations with phytoplankton production/degradation cycles, (ii) to assess the possible transfer of Pt through the aquatic trophic chain, and (iii) to investigate the potential use of phytoplankton material as a geochemical tool for biomonitoring Pt contamination in coastal systems. The outcomes of the present work are a part of the PhD thesis by Abdou (2018).

2. Material and Methods

2.1. Study area and sample collection

Study site characteristics

The Gironde Estuary (~170 km in length; 80,000 km² watershed area) is a major European estuary located in southwest France (Fig. 1A), considered a model system for physical, hydrological and geochemical studies, especially on trace element transport and reactivity in anthropogenically-impacted watersheds (Lanceleur et al., 2011). Its most important hydrodynamic characteristics are the semi-diurnal, meso- to macro-tidal regime, and the maximum turbidity zone (MTZ; > 1 $g.L^{-1}$ of suspended particulate matter), varying seasonally with river flow and exported occassionally to the Atlantic Ocean (Castaing and Allen, 1981; Doxaran et al., 2009). The Gironde Estuary drains the urban area of Bordeaux (1,190,000 inhabitants), located ~ 100 km upstream from the estuary mouth. Sampling was performed in the Gironde Estuary mouth on-board the Research Vessel (R/V) Thalia (TGIR FOF) at a fixed sampling site (45°40'00.2"N, 1°10'33.0"W, Fig. 1A). This site is located on the western

channel lying to the north, with a bottom depth varying between 10 and 30 m and a width between 2 and 4 km. This channel was artificially created by dredging in 1935 (Allen, 1971). Sampling took place in June 2017 (22^{nd}-23^{rd}) during low discharge conditions (Q ~ 235 $m^3.s^{-1}$, DIREN, public agency), over 29 hours (18 samples). This sampling period was characterized by the beginning of spring tide and tidal coefficients from 81 to 92 (tidal amplitudes varying from 3.80 m to 4.35 m). In addition, wild oyster samples (*Crassostrea gigas*; 15 organisms, ~ 9 cm shell length) were collected at the La Fosse sampling site (45°28'23.4"N, 0°59'50.9"W; Fig. 1A).

The Arcachon Bay is a meso-tidal lagoon in southwest France, ~ 100 km to the south of the Gironde Estuary mouth (Fig. 1B) and represents an important breeding ecosystem for regional seafood production, especially oysters. The sampling site (Comprian), located in a main current channel of the bay, receives inputs from the Leyre River, several cities surrounding the site (~ 90,000 inhabitants), and seawater from the Atlantic Ocean. In May 2015 (21^{st} – 22^{nd}), hourly sampling over a diel cycle of 31 hours was performed on board R/V Planula IV (TGIR FOF) at a fixed sampling site (Comprian site, 44°40.823'N, 1°05.902'W, Fig. 1B). The end of spring tide characterized our sampling period with tidal coefficients from 89 to 72 (tidal amplitudes varying from 3.10 m to 3.70 m). Wild oysters (*C. gigas*; 10 organisms, ~ 9 cm shell length) were collected manually on a bank near the Comprian site during low tide.

The Genoa Harbor is an artificial harbor in the northwest coast of Italy (Ligurian Sea, Fig. 1C) and one of the most important ports of the Mediterranean Sea. The area is exposed to anthropogenic pollution originating from sea-based (ferries, shipyards, marinas…) and land-based activities of the city of Genoa (580,000 inhabitants). The innermost part of the Genoa Harbor is the Old Port hosting a ferry terminal, several marinas and receiving urban sewage effluents (Ruggieri et al., 2011). Outside the Old Port a wide, less confined area protected by artificial breakwaters extends to the east and to the west, hosting diverse industrial activities and receiving discharges from a coal-fired power plant, treated urban wastewater and untreated surface run-off (Ruggieri et al., 2011). In April 2016 (19^{th} – 20^{th}), hourly sampling covering a diel cycle of 25 hours was performed inside the Genoa Harbor at the CNR platform (National Research Council, 44º23'44"N, 08º55'53"E, Fig. 1C). At this site, very small tidal amplitude of ~ 0.2 m was monitored. At the platform, wild mussels (*Mytilus galloprovincialis*, 10 organisms, ~ 7 cm shell length) were also collected manually.

Sample collection and processing

At all sites, surface seawater (~ 2 to 5 m depth) was pumped using an electric pumping system connected to Teflon tubing. Seawater samples for dissolved Pt (Pt_D) analysis were immediately filtered through 0.2 µm polycarbonate filters (Nucleopore®) using a filter-syringe (Sartorius®) and placed in pre-cleaned 60 mL Teflon FEP bottles (Nalgene®), previously rinsed with filtrate. Samples were acidified to pH = 1 (36.5 – 38 % HCl Baker® Instra) and stored in the dark at 4 °C pending analysis. Suspended Particulate Matter (SPM) and Particulate Organic Carbon (POC) concentrations in surface water were determined by filtration of precise water volumes through pre-combusted and pre-weighed filters (Whatman® GF/F, 0.7 µm; Etcheber et al., 2007). The filters were rinsed with MilliQ water to remove salts and were then oven dried to constant weight at 50 °C, weighed again, and kept in the dark at room temperature pending analysis. Furthermore, particulate samples were collected for determination of chlorophyll-a and phaeopigments by filtering seawater (Whatman® GF/F, 0.7 µm) and deep-freezing the filters (- 80 °C) pending analysis. For qualitative and quantitative analyses of phytoplankton, seawater samples were fixed with 2 % seawater-buffered formalin solution and kept in the dark at 4 °C pending analysis.

Material for plankton Pt (Pt_{PK}) analysis was collected, every 1 to 2 hours, by surface horizontal (~ 1m depth) sampling at the fix sampling station during the diel cycle of the Gironde Estuary. In the other sites, plankton material was collected at variable times during daytime in the Arcachon Bay (n = 3; Comprian station) and the Genoa Harbor (n = 5). Given the strong tidal currents and the related suspension of silts and fine-grained sand in the Gironde Estuary, we used sampling nets with nominal cut-off of 200 µm for the Gironde Estuary mouth; whereas the cut-off for the other sampling sites was 20 µm. Seawater containing concentrated plankton cells was retrieved from the collector and centrifuged at 1,500 rpm. The supernatant was removed and the collected residue was deep-frozen, freeze-dried, and kept in the dark at room temperature pending analysis.

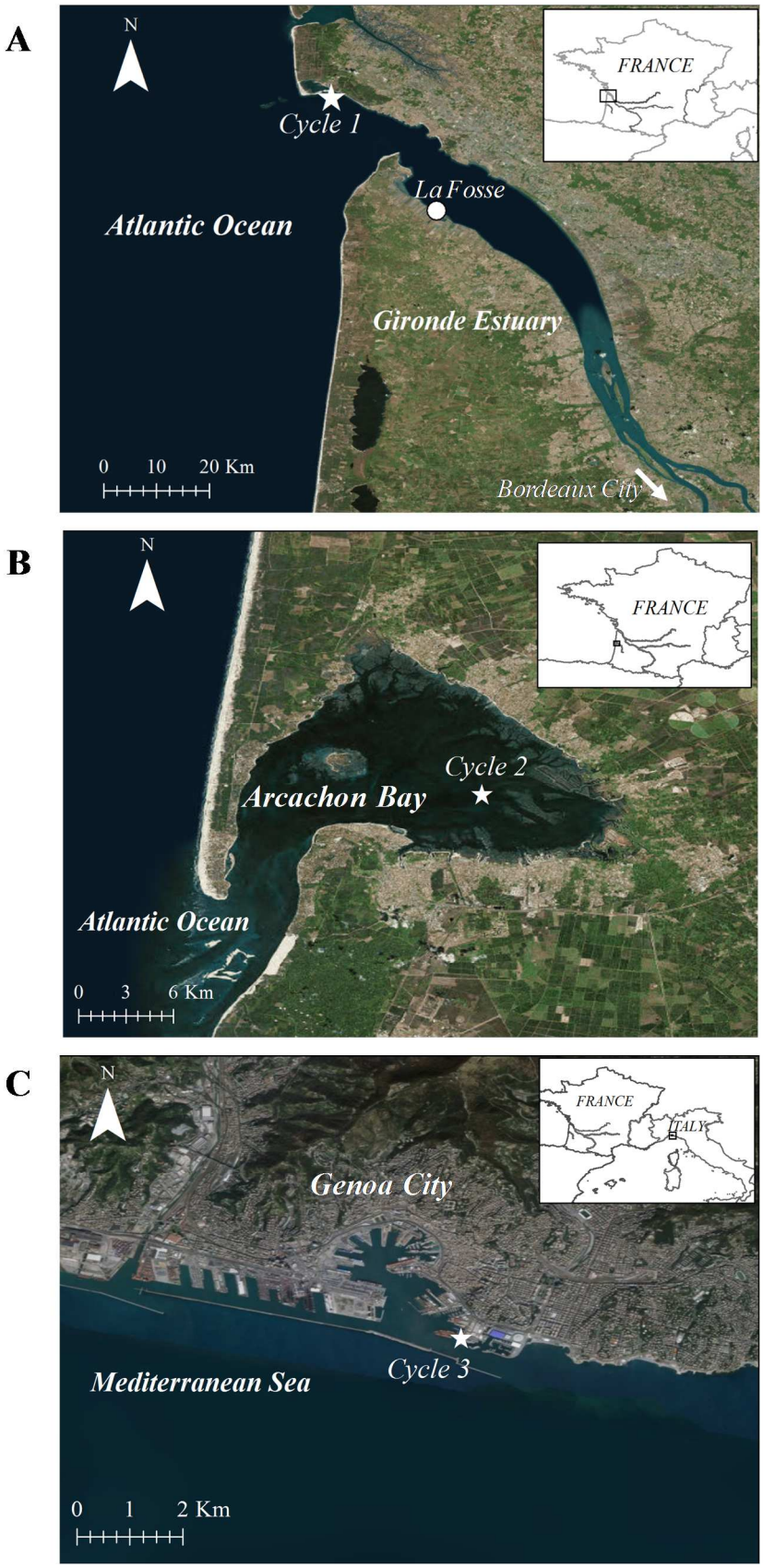

Fig. 1: Study areas with sampling sites (white stars). A: Gironde Estuary (Cycle 1), B: Arcachon Bay (Cycle 2), C: Genoa Harbor (Cycle 3). Wild bivalve samples were collected at La Fosse (oysters) site in the Gironde Estuary and at the "cycle" sampling sites for the Arcachon Bay (Comprian; oysters) and the Genoa Harbor (mussels).

After manual collection of wild bivalves, organisms were cleaned and depurated under oxygenation by bubbling air in seawater during 48 hours. The organisms were dissected and soft tissues were placed in acid-cleaned polypropylene (PP) tubes (DigiTUBEs, SCP SCIENCE®). Samples were then deep-frozen, freeze dried, grinded in an agate mortar and kept in the dark at room temperature pending analysis.

At all sites, physical-chemical parameters including temperature, salinity, and O_2 saturation level (O_2%) were measured *in situ* with a portable TetraCon 96® probe (PROFILINE, WTW), and pH with a Sentix 41® probe (PROFILINE, WTW). On site, average bottom depth of the Gironde Estuary was of ~ 14 m, while it was of ~ 5 m for both the Arcachon Bay and the Genoa Harbor. Information on solar radiation (irradiance) was obtained from the "Meteo France" and "Infoclimat" databases for the SW of France and from "DICCA" (Dipartimento di Ingegneria Civile, Chimica e Ambientale, University of Genoa) for the Genoa Harbor. We retrieved tidal information from the website maree.info and mareografico.it; and river discharges in the Gironde Estuary from the National Hydrographic Databank (DIREN).

2.2. Analytical methods

Platinum in seawater

The total dissolved Pt concentration in the filtered seawater samples was analyzed by Adsorptive Cathodic Stripping Voltammetry (AdCSV) as described in Cobelo-García et al. (2014b). Measurements were carried out using a μAutolab Type III potentiostat (Metrohm®) connected to a polarographic stand (Metrohm® 663 VA stand) equipped with three electrodes: (i) a hanging mercury drop electrode (HMDE, the working electrode), (ii) a silver/silver-chloride (Ag/AgCl) as reference electrode, and (iii) a glassy carbon auxiliary electrode. A polytetrafluoroethylene (PTFE) voltammetric cell was used in all experiments and the potentiostat was controlled using the NOVA 2.1 software. Elimination of organic matter by UV oxidation was performed by placing sample aliquots in capped Teflon FEP tubes with overnight irradiation using two 64 W UV lamps (NIQ 60/35 XL, Heraeus) under a fume hood. Aliquots (10 mL) of UV-digested sample were pipetted into the voltammetric cell together with 30 μL of 3.3 mM formaldehyde (37–41 % Analytical Reagent Grade, Fisher Chemical®), and 30 μL of 0.45 mM hydrazine sulfate (Analytical Reagent Grade, Fisher Chemical®). Platinum concentrations were quantified by the standard addition method, adding a controlled amount of a Pt stock solution prepared daily from a mono-elementary Pt

199 standard solution (1000 µg.mL^{-1} PLASMACAL, SCP Science®). We applied a deposition
200 time of 300 s and experimental parameters described elsewhere (Cobelo-García et al., 2014b).

201 The detection limit for Pt_D measured by AdCSV (calculated as 3 x blank standard deviation,
202 n = 20) was estimated to 0.15 pmol.L^{-1}. In the absence of Certified Reference Material
203 (CRM) for dissolved Pt in seawater, analytical quality of the voltammetric procedure was
204 evaluated by determination of Pt spiked CRM seawater (CASS-6, NRCC) giving recoveries
205 > 80% and precision expressed as Relative Standard Deviation (RSD) of ~ 15 % (n = 3) at the
206 2.5 pmol.L^{-1} range.

207 *Platinum in biological samples: plankton material and bivalves*

208 Ashing was applied as a pre-concentration method for Pt content in biological material (e.g.
209 Schäfer et al., 1998). Dry plankton or bivalve material (~ 1 g) was weighed and ashed in acid-
210 cleaned porcelain crucibles at 800 °C during 3 hours according to the heating scheme
211 described by Nygren et al. (1990). Ashed samples were weighed again to determine the
212 organic matter percentage (loss on ignition, L.O.I. technique) and samples were then
213 transferred into PP tubes, and digested at 110 °C for 3 hours with 2 mL HCl and 1 mL HNO_3
214 (30 % HCl and 65 % HNO_3 Suprapur, Merck®) as described in Abdou et al. (2018). Cooled
215 digestates were then diluted in 10 mL MilliQ® water and centrifuged at 4000 rpm for 10 min
216 (20 °C). The supernatant was stored in acid-cleaned PP tubes at 4 °C in the dark pending
217 analysis.

218 Platinum concentrations in plankton material (Pt_{PK}) or bivalves (Pt_{BV}) were determined by
219 Triple Quadrupole-Inductively Coupled Plasma Mass Spectrometry (TQ-ICP-MS, Thermo®
220 iCAP TQ), using standard addition method, as described previously for AdCSV. Hafnium-
221 oxide ions (HfO^+) interfere with all Pt isotopes making Pt accurate quantification by ICP-MS
222 difficult in environmental samples (Djingova et al., 2003). Platinum concentrations in natural
223 biological samples were measured by ICP-MS after mathematical correction of the HfO^+
224 interference using ^{194}Pt / ^{195}Pt natural ratio (assuming that HfO^+ is the dominant spectral
225 interference on those selected isotopes; Abdou et al., 2018). The detection limit for Pt levels
226 in biota measured by TQ-ICP-MS (calculated as 3 x blank standard deviation, n = 10) was
227 estimated to 0.15 pmol.g^{-1} for a nominal ashed sample mass of 50 mg and 0.005 pmol.g^{-1} for
228 typical biological sample mass of 1.5 g.

229 Since no CRM for Pt in biological matrices is available, aliquots of plankton net material
230 were analyzed in parallel using both ICP-MS and AdCSV, i.e. two independent measurement
231 techniques. They provided, as observed for bivalve samples in a previous study (Abdou et al.,
232 2018), similar results between both methods (RSD ~ 15 %, n = 5). Quality control was also

performed using available CRMs for Pt concentrations in solid matrices: Jsd-2 sedimentary rocks (indicative value from Geological Survey of Japan) and BCR®-723 road dust (IRMM). Analyses of Jsd-2 and BCR®-723 gave satisfactory results with precision of ~ 15 % and respective recovery values of 65% and > 80 % (n = 3) applying the same interference corrections as for biological samples.

Phytoplankton analysis

Phytoplankton assemblages in water were identified in four samples of the Gironde cycle (three samples collected during daytime on the first day at 8 am, 2 pm and 7 pm and one sample retrieved during the night of the second day at 1 am), in the Arcachon Bay (diel cycle in May 2017; eight samples) and the Genoa Harbor (three samples). In all cases, fixed phytoplankton cells were counted according to the Utermöhl method (Utermöhl, 1958). This technique applies the combined use of an inverted-microscope and a special counting chamber, where phytoplankton has been gathered through a sedimentation cylinder (Hasle, 1978). This method allows for the identification of the main taxa of autotrophic microplankton (in particular species of diatoms, dinoflagellates –mainly armored) and coccolithophorids. However, this method is not recommended for other flagellates that may possibly be damaged during the fixation process nor for pico-nanoplankton, due to the very small dimensions of the cells (Zingone et al. 2010).

Chlorophyll-a, phaeopigments, and POC

Chlorophyll a (Chl-a) was extracted in 90 % acetone and determined by spectrofluorometry (Trilogy, Turner, Strickland and Parsons, 1972). Dilutions of a solution of Chl-a (Anacystis nidulans, 1 $mg.L^{-1}$; C-6144; Sigma-Aldrich®) was used to calibrate the fluorimeter. Phaeopigments (phaeo) were also determined using the same analysis (after acidification, HCl 3M). Detection limit of the technique was 0.1 $\mu g.L^{-1}$ while precision was ~ 15 %. Due to sampling logistics, Chl-a and phaeo data in the Genoa Harbor are only available for daytime period. Particulate Organic Carbon (POC) was analyzed with a LECO© CS-125 after carbonate elimination with 2M HCl as described elsewhere (Etcheber et al., 2007). Analytical quality was checked by measuring CRMs (e.g. LECO 501–503). Accuracy was within 5 % of the certified values and the analytical error generally < 5 % (% RSD).

2.3. Data treatment

Bioconcentration factors

Bioconcentration factors (BCF; Arnot and Gobas, 2006) were determined according to the following Equation 1:

$$BCF = \frac{Pt_{biota}}{Pt_D} \times 10^3 \quad (1)$$

With Pt_{biota}: the Pt concentration in biota sample (corresponding to Pt_{PK} or Pt_{BV} in this study), Pt_D: the dissolved Pt concentration, and 10^3 a correcting factor for units.

Particulate organic matter content

Plankton material collected with nets may contain lithogenic material such as mineral(-oxide) particles (e.g. silicates, iron(Fe)-oxides etc...), as well as non-living organic aggregates and phytodetritus. Accordingly, the attribution of Pt content in the samples to phytoplankton material alone may be wrong, implying the need to account for abiotic particles and non-living organic matter that may complex Pt ions as other trace metals (Twining et al., 2011). Existing field studies often analyze bulk particulate matter under conditions where authors can assume low lithogenic and detrital contributions for a range of trace metals (Twining and Baines, 2013 and references therein). In order to evaluate the proportion of organic material in our samples, we used the loss on ignition technique (*Section 2.2*) providing the percentage of organic matter present in the particulate material (Particulate Organic Matter: POM) from plankton nets. We also evaluated POC/SPM ratio (POC%) in order to have the proportion of organic material in the SPM collected on filters (0.7 µm mesh size). Results from those two methods are shown in the Supporting Information (SI). Finally, we determined the POC/Chl-a ratio (filters 0.7 µm mesh size) in order to evaluate qualitatively the contribution of living phytoplankton to the organic material (Savoye et al., 2003).

3. Results

3.1. Physical-chemical parameter variations

Gironde Estuary

Tide height variations are presented in Fig. 2A. Master physical-chemical parameters monitored over the Cycle 1 (Fig. 2B) showed variations of SPM concentration from ~ 5 to 60 $mg.L^{-1}$. Two maximum values occurred the first day at 10 am and during the night (> 40 $mg.L^{-1}$). The pH and salinity measurements followed the same trend with variations from 8.06 to 8.20 and from 30 to 32.5, respectively (Fig. 2B). Those parameters were related to tidal regimes with higher salinity, pH and lower SPM concentrations at high tide. Solar radiation varied from 0 to 300 $J.cm^{-2}$, showing two maxima (at 11:30 am on the first day and at 1 pm on the second day; Fig. 2C). Oxygen saturation levels varying from ~ 100 to 110 % coincided with high tide at 5 pm on the first day (Fig. 2C). During the night, O_2% levels are at their minimum, coinciding with low salinity. In the middle of the nighttime, O_2% increased only slightly, fully displaying the second O_2% maximum during the second day at 11:30 am during low tide. Temperature values varied between 19.2 and 20.2 °C (Fig. 2C). Lower temperatures partly co-occurred with highest salinity (especially on the second day) and slightly higher values were monitored during the second day (11:30 am). Chlorophyll-a values ranged between ~ 4 and 8 $\mu g.L^{-1}$ while phaeopigments varied between ~ 2 and 10 $\mu g.L^{-1}$ (Fig. 2D). Chlorophyll-a concentrations showed an overall decreasing trend from the beginning of sampling until 7 am on the second day though increasing and reaching a maximum at 11:30 am. Phaeopigments seemed to follow SPM concentrations and showed a maximum at 11:30 am alike Chl-a levels. Calculated POC/Chl-a ratio variations showed values between ~ 50 and 300 (Fig. 2D).

Arcachon Bay

Results from Cycle 2 (Arcachon Bay) showed tide-related physical-chemical parameters (Fig. 3A, B, and C). The pH measurements follow the salinity trend oscillating at high and low tide, between 8.02 and 7.84 and between 32 and 22, respectively (maxima at 9 pm and 9 am; Fig. 3B). In general, SPM concentrations ranged from ~ 10 to 50 $mg.L^{-1}$ and followed tidal dynamics. Oxygen saturation levels varied from 75 to 85 % (i.e., always below the 100% saturation observed in the Gironde Estuary mouth; Fig. 3C). Temperature showed opposite variations (between 15.2 °C and 17.5 °C; Fig. 3C). Solar radiation reached maximum values (~ 300 $J.cm^{-2}$) at 2 pm on the first day and 1 pm on the following day (Fig. 3C).

Chlorophyll-a concentrations showed little variations between ~ 1 and 3.5 µg.L^{-1} while phaeopigments varied from ~ 0.5 to 3.5 µg.L^{-1} (Fig. 3D). Lower values of Chl-a occurred during nighttime compared to daytime concentrations. Pigment levels seemed to co-vary with POC/Chl-a ratio (ranging from 200 to 700; Fig. 3D) and with SPM concentrations.

Genoa Harbor

Results from the CNR Platform in the Genoa Harbor were very different from those in the previous sites. Salinity was constantly at ~ 37.2 as no tidal variation of similar amplitude occurred at this site (Fig. 4A and B). The pH values were also constant and close to ~ 8.3 while SPM concentrations varied little from ~ 2 to 8 mg.L^{-1} (i.e. 6-fold lower than in the Atlantic sites; Fig. 4B). Oxygen saturation levels (O_2%) were between 96 % and 100 %, i.e. between those observed in the Gironde Estuary mouth (minimum 100%) and in the Arcachon Bay, showing higher values during the day (Fig.4 C). Temperature variations seemed to follow a similar trend with values between 16.3 °C and 17.4 °C. Solar radiation varied from 0 to 350 J.cm^{-2} with a maximum occurring at 11 am (Fig.4 C).

Pigment concentrations showed increasing trends during the second day with values ranging between ~ 0.8 and 1.4 µg.L^{-1} and 0.4 and 0.5 µg.L^{-1} for Chl-a and phaeopigments, respectively (Fig. 4D). The POC/Chl-a ratio was nearly constant with average values of ~ 130 (Fig. 4D).

3.2. Phytoplankton composition

Gironde Estuary

Microscope observations showed phytoplankton abundance varying between ~ 36,000 and 58,000 cells.L^{-1}. Average percentages for daytime (three samples) showed ~ 80% contribution of Bacillariophyceae, mostly represented by *Pseudonitzschia spp.*, *Chaetoceros spp.*, *Asterionellopsis spp.*, and *Odontella spp.* Dinophyceae composed ~ 10% of the phytoplankton (*Ceratium fusus* and armoured dinoflagellates) and the last 10% was Prymnesiophyceae. Samples collected at 2 pm and 7 pm featured the association between the Bacillariophyceae *Thalassiosira sp.* and the coccolithophorid *Reticulofenestra sessilis*. During nighttime (one sample), slightly higher proportion of Bacillariophyceae occurred (~ 85%), while Primnesiophyceae became more abundant over Dinophyceae (15% against 2%, respectively). This phytoplankton composition was characteristic of this study site (REPHY, 2019).

Arcachon Bay

Phytoplankton composition was studied in water samples collected in Comprian in spring 2017. The abundance varied between ~ 19,000 and 40,000 cells.L^{-1}. Results showed that as for the Gironde Estuary, Bacillariophyceae was the main class represented in the phytoplankton assemblage (83.6-96.5 % over the cycle), despite showing a shift in the dominant class with tidal variations. At this site, long-term monitoring data and previous studies confirmed that in spring this class represented ~ 80% of the total phytoplankton abundances and were mainly composed during high tide of *Leptocylindrus danicus*, *Pseudonitzschia* spp., *Chaetoceros* spp., *Dactyliosolen fragilissimus* and *Asterionella glacialis* (REPHY, 2019; Ifremer/ODE/LITTORAL/LERAR, 2017; Glé et al., 2007).

Genoa Harbor

During the Genoa Harbor diel cycle, abundance of phytoplankton cells varied between ~ 60,000 and 167,000 cells.L^{-1}. Bacillariophyceae were as well the most abundant taxonomic group (80-98.2 %). This group was mainly composed of *Chaetoceros spp.*, *Leptocylindrus spp.*, *Pseudonitzchia spp.*, *Thalassiosira spp.*, or *Lauderia spp.* Another field campaign in spring 2017 also confirmed the dominance of Bacillariophyceae during diel cycle (72.0-97.5 %). This composition is typical for the season in the coastal Gulf of Genoa (Carli et al., 1994).

3.3. Platinum concentrations in seawater and plankton material

Gironde Estuary

Hourly measured Pt_D concentrations ranged from 0.23 to 0.58 pmol.L^{-1} showing alternating trends (Fig. 2E). Three main peaks occurred: (i) one on the first day at 2 pm (0.56 pmol.L^{-1}), followed by a decrease down to 0.27 pmol.L^{-1}, (ii) a small peak close to the night at 9 pm, and (iii) a third peak of 0.58 pmol.L^{-1} at 9 am on the second day. During the Cycle 1, Pt_{PK} concentrations ranged from 0.27 to 6.84 pmol.g^{-1} (Fig. 2E). Visual examination of plankton net material suggested that samples were mainly composed of phytoplankton during the day and zooplankton during the night. Plankton Pt concentrations displayed a generally decreasing trend on the first day from 8 am to 9 pm. During the nighttime, minimum values occurred in between two slight increases at 11 pm and 1 am. The following day, Pt_{PK} showed increasing levels from the early morning to maxima of ~ 7 pmol.g^{-1} at 9 am and 11:30 am.

Arcachon Bay

Dissolved Pt_D concentrations varied from 0.25 to 0.75 pmol.L^{-1} (Fig. 3E) on the first day and during nighttime. In the morning of the second day (from 8 am onwards), Pt_D levels tended to increase towards a high tide maximum at ~ 11 am and thereafter showed a clear decrease towards minimum values at 6 pm. The Pt_{PK} concentrations monitored at the Comprian site varied between 8.65 and 16.49 pmol.g^{-1} (Fig. 3E).

Genoa Harbor

No clear trend occurred for Pt_D concentrations (variations between 0.37 pmol.L^{-1} and 0.83 pmol.L^{-1}), although a general decreasing trend seemed to occur on the second day between 9 am and 8 pm (Fig. 4E). Nighttime Pt_D concentrations showed minimal values. The Pt_{PK} levels measured at this site varied between 15 and 34 pmol.g^{-1} (Fig. 4E).

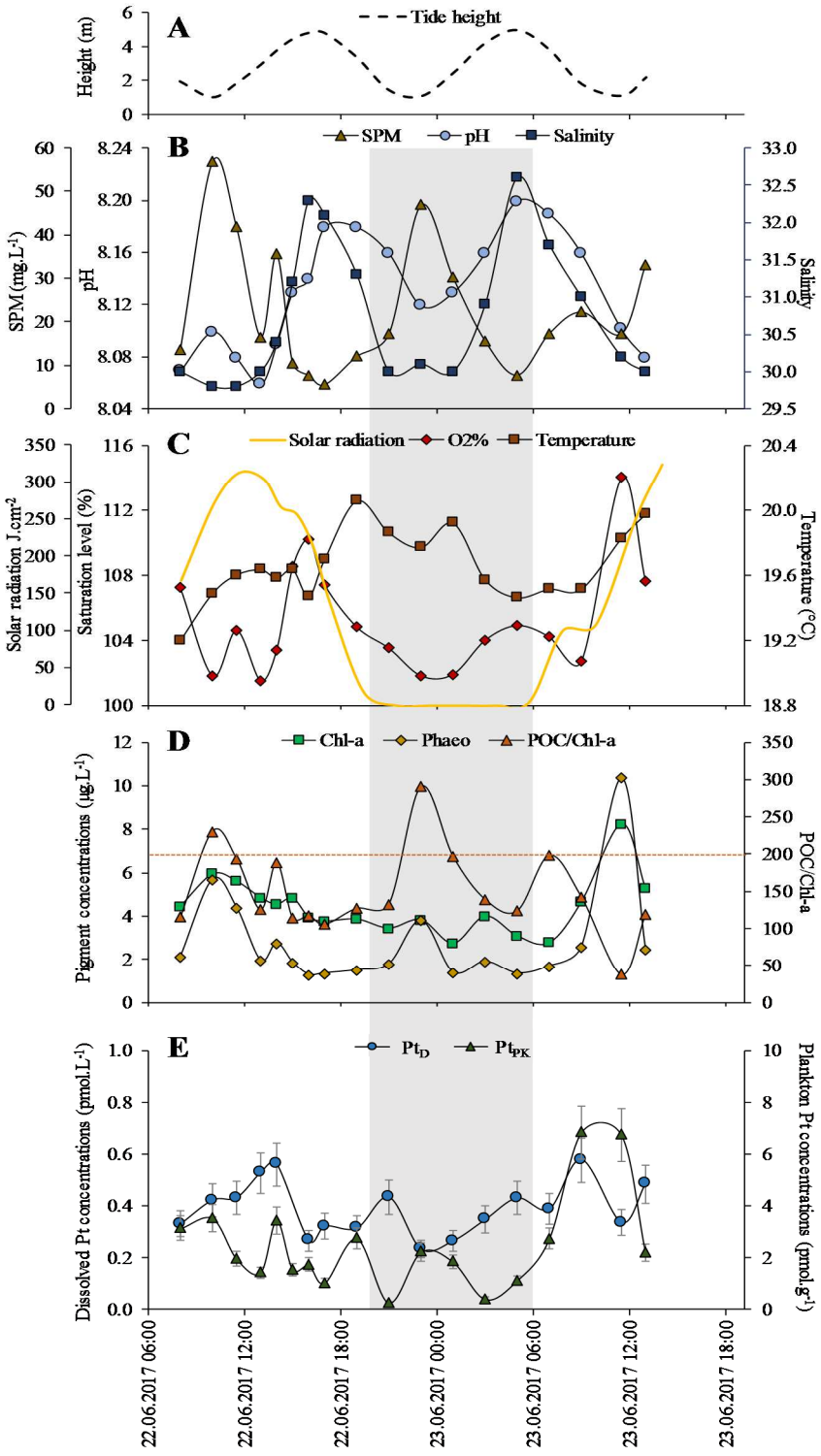

Fig. 2: Short-term variations in physical-chemical variables, algal pigments and Pt concentrations in seawater and plankton material from the Gironde Estuary in June 2017. A: Tide height (m, dashed line) B: Suspended Particulate Matter (SPM, $mg.L^{-1}$, triangles), pH (circles), and Salinity (squares); C: Solar radiation ($J.cm^{-2}$, solid line), Dissolved oxygen saturation levels (O_2%, diamonds), and Temperature (°C, squares); D: Chlorophyll-a (Chl-a, $\mu g.L^{-1}$, squares), Phaeopigments (Phaeo, $\mu g.L^{-1}$, diamonds), and Particulate Organic Carbon / Chlorophyll-a ratio (POC/Chl-a, triangles), the dashed line represents the limit for dominance of living phytoplankton in POM (Savoye et al., 2003); E: Dissolved Pt (Pt_D,

pmol.L^{-1}, circles), and plankton Pt (Pt_{PK}, pmol.g^{-1}, triangles) concentrations. The gray strip represents nighttime (Abdou, 2018).

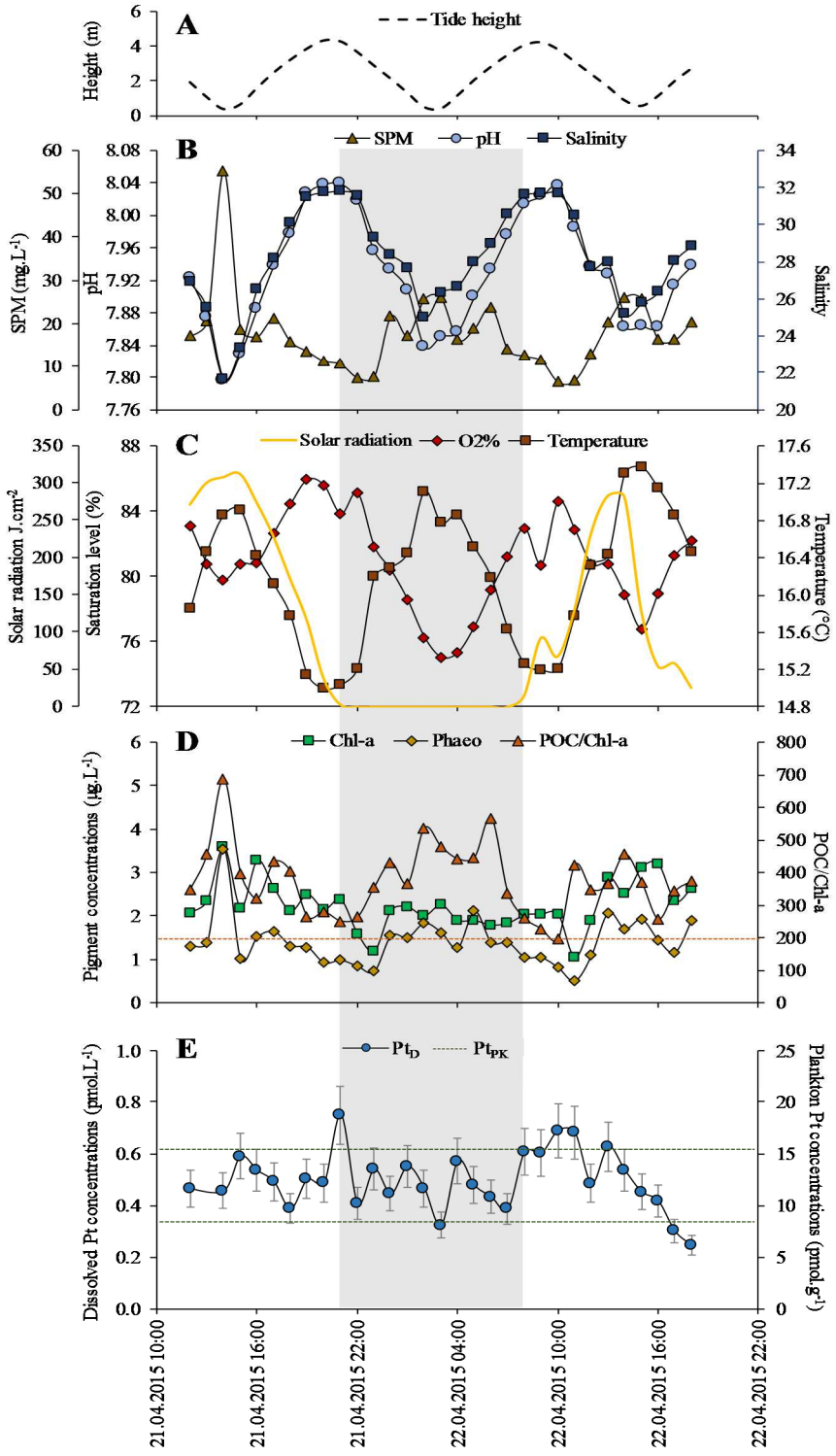

Fig. 3: Short-term variations in physical-chemical variables, algal pigments and Pt concentrations in seawater and plankton material from the Arcachon Bay in April 2015. A: Tide height (m, dashed line); B: Suspended Particulate Matter (SPM, mg.L^{-1}, triangles), pH (circles), and Salinity (squares); C: Solar radiation (J.cm^{-2}, solid line), Dissolved oxygen saturation levels (O_2%, diamonds), and Temperature (°C, squares); D: Chlorophyll-a (Chl-a, µg.L^{-1}, squares), Phaeopigments (Phaeo, µg.L^{-1}, diamonds), and Particulate Organic Carbon / Chlorophyll-a ratio (POC/Chl-a, triangles), the dashed

409 line represents the limit for dominance of living phytoplankton in POM (Savoye et al., 2003); E:
410 Dissolved Pt (Pt_D,
411 $pmol.L^{-1}$, circles) and range of plankton Pt (Pt_{PK}, $pmol.g^{-1}$, dashed line) concentrations. The gray strip
412 represents nighttime (Abdou, 2018).

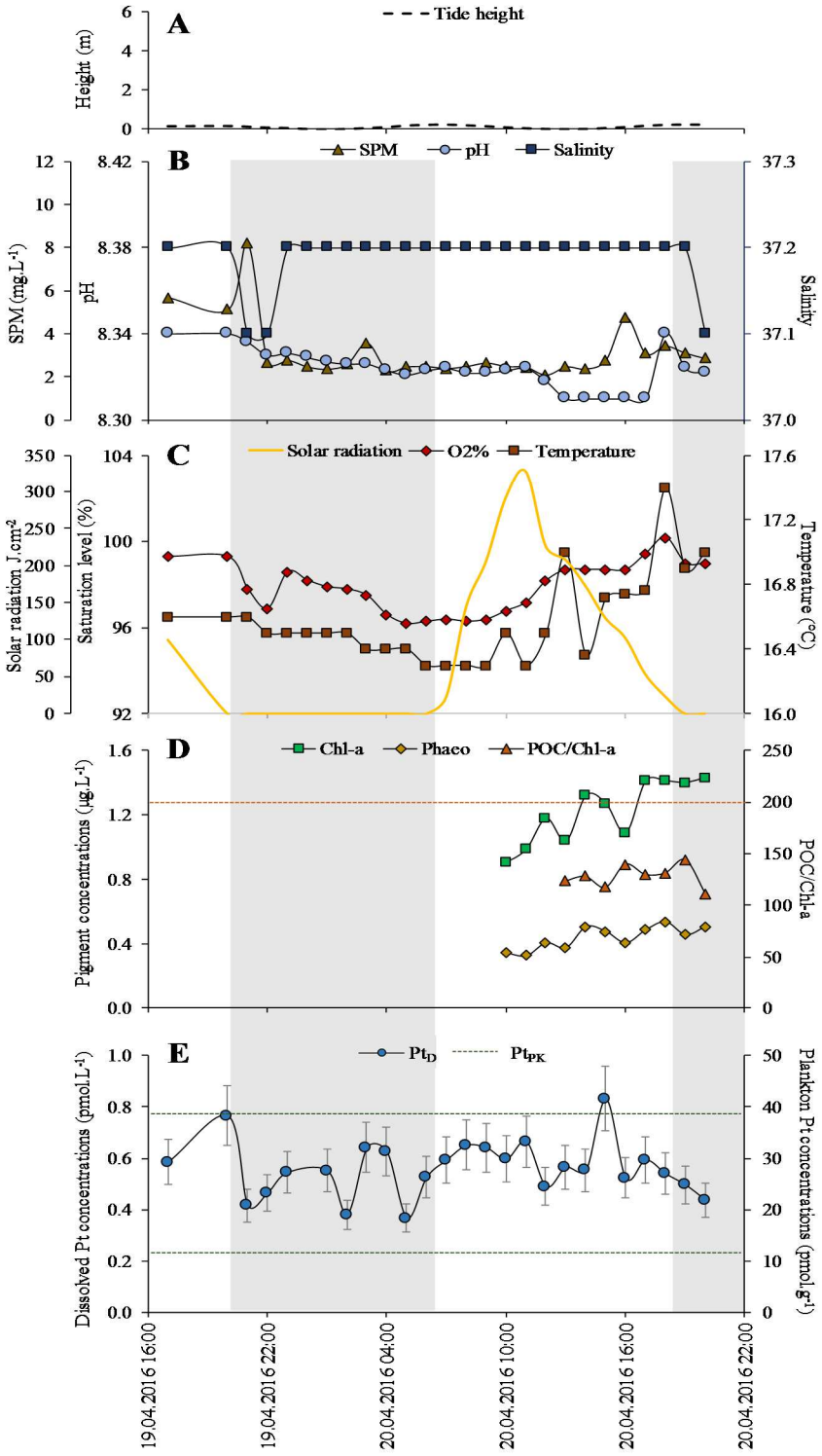

Fig. 4: Short-term variations in physical-chemical variables, algal pigments and Pt concentrations in seawater and plankton material from the Genoa Harbor in April 2016. A: Tide height (m, dashed line); B: Suspended Particulate Matter (SPM, mg.L^{-1}, triangles), pH (circles), and Salinity (squares); C: Solar radiation (J.cm^{-2}, solid line), Dissolved oxygen saturation levels (O_2%, diamonds), and Temperature (°C, squares); D: Chlorophyll-a (Chl-a, µg.L^{-1}, squares), Phaeopigments (Phaeo, µg.L^{-1}, diamonds), and Particulate Organic Carbon / Chlorophyll-a ratio (POC/Chl-a, triangles), the dashed line represents the limit for dominance of living phytoplankton in POM (Savoye et al., 2003); E: Dissolved Pt (Pt_D,

422 pmol.L^{-1}, circles) and range of plankton Pt (Pt_{PK}, pmol.g^{-1}, dashed line) concentrations. The gray strip
423 represents nighttime (Abdou, 2018).

3.4. Platinum concentrations and bioconcentration factors in plankton and bivalves from the three contrasting sites

Table 1 shows average Pt_D concentrations for the three sites with values of 0.38, 0.48, and 0.56 pmol.L^{-1} for the Gironde, the Arcachon Bay, and the Genoa Harbor, respectively. In order to compare Pt_{PK} in plankton material from the three sites, we report only daytime average Pt_{PK} concentrations of the Gironde Estuary mouth. At this site, Pt_{PK} was 3.01 pmol.g^{-1}, while in the Arcachon Bay and the Genoa Harbor, Pt_{PK} were clearly higher, i.e. ~ 12 and 24 pmol.g^{-1}, respectively (Table 1).

Platinum concentrations in bivalves (Pt_{BV}) were 1.69 pmol.g^{-1} in wild oysters (*C. gigas)* from the La Fosse site, i.e. slightly greater than in the Arcachon Bay (1.01 pmol.g^{-1}; Table 1). Wild mussels (*M. galloprovincialis*) from the Genoa Harbor showed Pt_{BV} of 2.44 pmol.g^{-1}.

The resulting BCF (Equation 1) for plankton (BCF_{PK}) ranged from 7.75 x 10^3 to 4.23 x 10^4 at the different sites, whereas BCF for bivalves (BCF_{BV}) varied from 2.09 x 10^3 to 2.27 x 10^4.

Table 1: Platinum concentrations in seawater (Pt_D; pmol.L^{-1}), plankton (Pt_{PK}; pmol.g^{-1}) and bivalves (Pt_{BV}; pmol.g^{-1}) from three study sites, and the associated bioconcentration factors (BCF, calculated from Equation (1); BCF_{PK} and BCF_{BV}; Abdou, 2018).

Sampling site	**$[Pt]_D$ (pmol.L^{-1})**			**$[Pt]_{PK}$ (pmol.g^{-1})**			**$[Pt]_{BV}$ (pmol.g^{-1})**			**BCF_{PK}**	**BCF_{BV}**
	Mean	*SD*	*n*	*Mean*	*SD*	*n*	*Mean*	*SD*	*n*	(x 10^3)	(x 10^3)
Gironde Estuary	0.38	0.15	18	3.01	1.78	13	1.69	0.15	5	7.75	22.73
Arcachon Bay	0.48	0.11	30	11.76	3.40	3	1.01	0.28	10	24.43	2.09
Genoa Harbor	0.56	0.11	25	23.77	9.48	5	2.44	0.69	10	42.30	4.35

4. Discussion

4.1. Tidal regimes and Pt concentrations in three contrasting sites

Gironde Estuary

Platinum concentrations in estuaries can both derive from natural sources including rock leaching and weathering (Upper Continental Crust Pt content of 2.6 pmol.g^{-1}; Rudnick and Gao, 2003); and from anthropogenic sources that include industrial activities, sewage effluents or Pt-bearing particles emitted by car catalytic converters. In this study, Pt concentrations were monitored at the very external part of the Gironde Estuary mouth under low discharge conditions (Q ~ 235 m^3.s^{-1}). Average Pt_D levels of this northeastern Atlantic Ocean coastal site (0.38 ± 0.15 pmol.L^{-1}) confirm previous North Atlantic Ocean Pt_D values (~ 0.1 - 0.3 pmol.L^{-1}, Colodner, 1991; López-Sánchez et al. 2019). Variations of Pt_D from 0.33 pmol.L^{-1} to 0.58 pmol.L^{-1} over the cycle may be partly due to mixing of estuarine waters with ocean water. The range of Pt_D values were in line with Pt_D addition along the Gironde Estuary salinity gradient as reported for similar discharge conditions (Q ~ 410 m^3.s^{-1} following a 3 month period with Q ~ 240 m^3.s^{-1}), resulting in Pt_D of 0.41 pmol.L^{-1} at salinity of 28.1 (Cobelo-García et al., 2014a).

The limited available information on Pt speciation in seawater suggests that Pt(IV) under the form $PtCl_5(OH)^{2-}$ dominates, while Pt(II) as the species $Pt(OH)_2$ dominates in freshwater (Cobelo-García et al., 2014a, 2013; Gammons, 1996; Pađan et al., 2019). Estuarine particle-water interactions along the salinity gradient are likely controlled by electrostatic interactions between SPM surface and inorganic aqueous species (Cobelo-Garcia et al., 2008; Cobelo-García et al., 2014a). Accordingly, elevated Pt_D concentrations with increasing salinity (Pt desorption from SPM) were studied in the Krka Estuary (Pađan et al., 2019) and partially observed along the Gironde salinity gradient (Cobelo-García et al., 2014a). The present Cycle 1 site being located at a very external part of the estuary mouth, with rather low SPM concentrations compared to the inner estuary, the variations of Pt concentrations do not clearly reflect such processes despite potential influence of SPM tidal variations.

The small amplitude in salinity values ~ 30 and 32.5 (Fig. 2B) recorded the tidal regime and the influence of freshwater expulsion during ebb tide (Fig. 2A). High tide occurred at 5 pm the first day and 5 am on day two, fitting salinity and pH measurements (Fig. 2A and B). Under these conditions, waters were generally colder and more oxygenated compared to low tide conditions. However, those parameters also featured correlations with day/night cycle as well as pigment concentrations (Fig. 2D and C; see *Section 4.2.*). Suspended Particulate

Matter (SPM) concentrations generally followed tidal regime with higher levels reached at low tides (10 am, 11 pm, and 1 pm; Fig. 2A and B). Considering that the majority of Pt contamination in the estuary may originate from continental sources, such as urban-impacted riverine inputs (e.g. Ruchter et al., 2015), one would expect higher Pt levels co-occurring with low tide events. Cobelo-García et al. (2014a) found that inside the Gironde Estuary, Pt_D levels may reach 0.84 pmol.L^{-1} in the low salinity range (S = 5.4) suggesting that this system is not extensively contaminated by Pt but still represents a net source of Pt_D to the coastal ocean. This idea is in line with the present observations for Pt_D levels during daytime (Fig. 2E) suggesting an increase of Pt_D concentrations on the first day from 8 am to 2 pm together with ebb tide, while on the second day the last measurement seemed to feature a new increase. One would need more data to confirm the influence of riverine pollution, also considering that during nighttime Pt_D levels are at the lowest under low tide conditions.

Plankton Pt concentration profile suggested no direct correlation with tidal regimes (Fig. 2E) but seemed to relate to day/night cycle as discussed in *Section 4.2*. However, some exceptions occurred during the sampling cycle. During the fortnightly cycle of varying tidal ranges, important changes in sediment resuspension and transport may take place. Accordingly, during neap to spring phase, tidal ranges vary from 1.5 m to 5.5 m at the estuary mouth together with increasing current velocity (Castaing and Allen, 1981; Sottolichio and Castaing, 1999). Our sampling campaign was carried out at the initiation of spring tide (average tidal range of 4 m; Fig. 2A) with tidal coefficients of 81 on the first day and 92 on the second (maximum salinity value higher during the second day, Fig. 2B). Under these conditions and resulting currents, large-scale sediment resuspension may take place with increased sediment concentrations in surface water (Castaing and Allen, 1981) especially at mid-tide. This is partly visible from increasing SPM concentrations on the first day at 2 pm at mid-flow tide (Fig. 2A and B). At the same time, slightly higher phaeopigment concentrations occurred together with higher POC/Chl-a ratio (Fig. 2D). In fact, in shallow systems or in deeper sites close to the shore, benthic POM may contribute to the POM pool of surface water through resuspension of microphytobenthos or decaying macrophytes (Irigoien and Castel, 1997; Liénart et al., 2017). These phytobenthic layers are potential metal carriers and their tidal suspension may influence metal cycles in coastal systems (Strady et al., 2011). Slight increases in Pt_{PK} levels on the first day at 2 pm and 7 pm may result from such processes. Although no SPM concentrations increase occurred at 7 pm on day one, microscopic observations of those samples revealed the association of *Reticulofenestra sessilis* with *Thalassiosira sp.*, which is a typical association of deep photic layers (e.g. Frada et al., 2010) with *Thalassiosira sp.* representing more than 15% of the total diatoms. Those findings

therefore support the hypothesis of increasing concentrations of particulate Pt related to phytobenthos transport in surface seawater under energetic tidal conditions.

Arcachon Bay

The position of the sampling site in the Arcachon Bay (Comprian Channel) allowed for more amplitude in the salinity variations and more influence of freshwater inputs (salinity range from 22 to 32; Fig. 3B). The pH variations followed the tidal regime as well as SPM concentrations with more turbid waters at low tide and a range of values similar to those of the Gironde Estuary. This field campaign also took place during spring tide with tidal coefficient of ~ 100. Contrary to the Gironde Estuary cycle, temperature co-varied strictly with the tidal regimes, rather than with solar radiation (Fig. 3A and C). Tide, and solar radiation/primary production to a lesser extent, seemed to control O_2 saturation level, since relatively higher O_2 saturation minima occurred during the day than during the night under low tide conditions (Fig. 3A and C). At this site, pigment concentrations were positively correlated with SPM concentrations suggesting that Chl-a and phaeopigments were tide-related with higher concentrations at low tide (Fig.3A, B and D).

Comprian sampling site, in this semi-enclosed bay, is located closer to urban/industrial activities (Arcachon agglomeration) than the Gironde Estuary mouth. This suggests potentially greater influences of Pt inputs from the surrounding urban areas, including surface run off and sewage from the urban agglomerations around the Arcachon Bay. Despite no significant differences between Pt_D levels in the two sites, such urban sources existing in the Arcachon Bay may explain the slightly higher average value recorded for Pt_D concentrations compared to the Gironde Estuary mouth (0.48 ± 0.11 pmol.L^{-1} and 0.38 ± 0.15 pmol.g^{-1}, respectively; Table 1). The major part of sewage discharge (draining hospital effluents and domestic wastewaters) from Arcachon City itself and the closest surroundings takes place into the open ocean at ~ 40 km to the south of the Bay inlet. One cannot exclude that such sewage release may partly move back towards the bay with coastal waters which might contribute to the highest Pt_D levels occurring at high tide at 9 pm on the first day and 11 am on the second one (Fig. 3E). Nevertheless, the monitored Pt_D profile did not show a clear tidal cycle. Potential sediment resuspension and microphytobentic sources may also be important factors in this shallow site under energetic tidal conditions as supported by the fact that at this site the contribution of benthic POM may account for ~ 20% (Liénart et al., 2017).

Genoa Harbor

The Genoa Harbor featured very different conditions since no tidal regimes similar to the previous sites occurred. Tide is generally less than 30 cm inside the harbor (Capello et al.,

2016). This explains the constant salinity of 37.2 and pH values of 8.3 (Fig. 4B). Moreover, sampling took place at ~ 5 m depth that is below the main influence of freshwater torrents (Capello et al., 2016) and no rainfall occurred during the sampling month. Our salinity records therefore mainly reflect seawater influence. However, freshwater inputs from both natural torrents such as the Bisagno River or other urban/industrial discharges take place in the harbor area (e.g. Ruggieri et al., 2011). Small variations in salinity values could be related to temporary freshwater inputs occurring twice at the beginning of the nighttime (9 pm on the first day and 8 pm on the second). However, similar to the Arcachon Bay, in the semi-enclosed Genoa Harbor, no clear trends in Pt_D occurred (Fig. 4E). This suggests, that the observed variations probably reflect changing inputs and biogeochemical recycling of anthropogenic Pt in this heavily urbanized and industrialized harbor. Dissolved Pt levels during daytime (0.60 ± 0.08 pmol.L^{-1}) were generally higher than 0.42 ± 0.01 pmol.L^{-1}, i.e. the typical value of the open Mediterranean Sea surface water (Ligurian Current; Abdou et al., 2019). Lowest Pt_D concentrations occurred during the night, which may support a decrease in Pt inputs related to daily human activities. Platinum sources including urban sewage typically show greater values during the day due to excretion of anticancer drugs (Kümmerer and Helmers, 1997) both from oncologic inpatients in hospitals and from outpatients at home (Lenz et al., 2007; Vyas et al., 2014). A great contribution can also derive from urban heavy traffic roads, including a major highway surrounding the harbor area. Automobile catalyst emissions are an important source of Pt to urban aquatic systems (Rauch et al., 2004a). Considering potential short-range atmospheric deposition (López-Sánchez et al., 2019), traffic-related Pt source may be considerably reduced during the nighttime. Other Pt sources include industrial effluents and emissions that are present in the harbor area (e.g. coal and oil industries; Finkelman and Aruscavage, 1981; Peavy, 1958).

4.2. Platinum cycles and primary production

The attribution of Pt concentrations to phytoplankton implies the identification of the composition of the collected particulate material. Literature reports POC/Chl-a ratios in the range of 20 to 200 for estuarine phytoplankton-dominated POM in estuary mouths during summer-fall (Cifuentes et al., 1988; Savoye et al., 2003). Especially, ratios of 80 ± 20 are typical of newly produced, living phytoplankton (Savoye et al., 2012). Ratios higher than 200 could result from detrital or degraded POM that dominates in the upper estuary. Other authors differentiate POC/Chl-a ratios lower than 200 for autotrophic and higher than 200 for mixo/heterotrophic organisms or detrital matter predominance (Bentaleb et al., 1998).

Gironde Estuary

Previous studies conducted in the Gironde Estuary report that limited phytoplankton primary production is possible in this turbid estuary with pigment levels probably explained by inputs of riverine or seaward phytoplankton (David et al., 2005; Irigoien and Castel, 1997). However, primary production and associated phytoplankton uptake of trace metals occur upstream from the MTZ (e.g. Cu; Petit et al., 2013). The present study site is located in a more external part of the Gironde Estuary mouth where intense primary production occurred. In fact, relatively high Chl-a levels (daytime average of 5 $\mu g.L^{-1}$) support productivity occurring at the estuary mouth together with POC % (daytime average 4 %; Table S1, SI) being clearly higher than in the inner, more turbid part of the estuary (1.5 % in the MTZ without seasonal variation; Etcheber et al., 2007). Low levels of POC/Chl-a ratios i.e. below 200, suggested a dominance of living phytoplankton in POM (Fig. 2D; Savoye et al., 2003). These conditions go along with a general oxygen oversaturation of the water mass (lowest O_2 saturation levels of > 100 %). These values were generally in phase with temperature, with increasing values during daytime and low levels during nighttime. Similar daily variations were already reported in the Gironde Estuary mouth (Baudrimont et al., 2005). The combination of summer conditions including high irradiance and low river discharge ($Q \sim 235\ m^3.s^{-1}$, upstream position of the MTZ) might therefore play a role in the development of phytoplankton cells. During this cycle, POC/Chl-a ratios followed the SPM concentration variations, with higher value at high tide and decreasing values during the flow until the beginning of the second day. Relatively high ratios exceeding 200 during ebb tide on the first day might be related to the transport of detrital material in freshwater. Similar phaeopigment variations, which are representative of degraded cells, support this hypothesis.

Chlorophyll-a followed SPM variations to a certain extent but more generally showed a decreasing trend during the first day and the night. The fact that Chl-a variations do not match tidal regimes may be explained by an on-site production of algal cells (autochthonous phytoplankton) rather than a transport of phytoplankton to the estuary mouth (allochthonous phytoplankton). Accordingly, out of the MTZ, increasing light penetration in the water column allows for autochthonous phytoplankton addition to POM (Savoye et al., 2012). Primary production may be light-driven rather than nutrient-limited, as Chl-a concentrations co-vary with irradiance during the daytime, which is in accordance with predictions on light-limited phytoplankton growth (Goosen et al., 1999; Irigoien and Castel, 1997). However, in the Gironde Estuary mouth, the general decreasing trend of Chl-a concentrations could still be related to nutrient depletion and to a potentially declining phase of phytoplankton bloom (Platt et al., 1992). Considering primary production relationship with light, on the first day

limitation may occur owing to relatively high SPM concentrations that could reduce light penetration in the water column (Castelle et al., 2009) and therefore photosynthetic processes. During the first day and nighttime, the decreasing trend of Chl-a concentrations suggests that no intensive, continuous autochthonous primary production took place, after the highest levels of the day reached at 10 am under maximal solar radiation.

Decreasing trend in Chl-a concentrations co-varied with similar, generally decreasing Pt_{PK} concentrations. At the same time, increasing trends occurred for Pt_D variations inducing a clear shift in Pt partitioning. Various biogeochemical processes in coastal waters (e.g. desorption, adsorption, dissolution/precipitation, bio- uptake or release) may transfer metals between the dissolved and the particulate phases (e.g. Turner, 2007). Decaying phytoplankton cells associated with Pt may lead to decreasing Pt_{PK} concentrations through cell lysis and/or vertical cell sinking. Although exact transfer mechanisms explaining exchanges of Pt between different carrier phases are widely unknown, the observed variations in Pt_D and Pt_{PK} may be either due to (i) internal transfer processes or (ii) external source/sinks releasing or sequestrating Pt_D from the estuarine water column. Internal transfer processes imply equilibrated mass balance, whereas non-equilibrated mass balances would suggest an open system involving external sources or sinks. Since no information was available on algal cell abundance in our plankton material, we did not perform mass balance calculations nor assess internal transfer. External transfer through cell sinking may also explain differences observed between Pt_{PK} decrease and Pt_D variations. Biogenic particles can sink more or less rapidly (depending on algal species; e.g. Luoma et al., 1998) and oscillate in the water column due to sediment resuspension cycles, especially in high-energy systems such as the Gironde Estuary. Accordingly, physical mechanisms may mask biogeochemical exchanges of Pt between the dissolved and the particulate phases by (i) sequestrating Pt-bearing particles in sediments or (ii) releasing Pt_{PK} and/or Pt_D from temporary sinks/sources including micro-phytobenthos mats and increasing Pt_{PK} levels as discussed in *Section 4.1*.

During the night and low tide, decreasing Chl-a levels suggest, together with low salinity, that in the downward part of the estuarine maximum turbidity zone degradation of phytoplankton occurs. Chlorophyll-a being degraded faster than the whole POM, increasing POC/Chl-a levels arose during phytoplankton degradation (Cifuentes et al., 1988; Savoye et al., 2003). Low tide phases bringing detrital material could also cause this increase in the POC/Chl-a ratio. Another possible explanation is the dominance of zooplankton organisms that perform nocturnal vertical migration for feeding (Daro, 1988), favoring a higher POC/Chl-a ratio (heterotroph organisms; Bentaleb et al., 1998). Such explanation is supported by higher POM obtained during the nighttime, whereas the ratio was almost constant for the daytime (Table

S1; SI). Thus, Pt_{PK} observed during nighttime may reflect Pt levels in zooplankton organisms with two higher values at 11 pm and 1 am (2.23 and 1.85 $pmol.g^{-1}$, respectively). Nighttime phytoplankton cell lysis through phytoplankton grazing could result in the increasing Pt_D values. As for other trace elements incorporated or adsorbed by phytoplankton, Pt might remain in the particulate phase until cell lyses and remineralization takes place (Sanders and Abbe, 1987; Sanders and Riedel, 1998).

The second day was more productive since much lower POC/Chl-a levels occurred (38 at 11:30 am), which clearly reflect the dominance of living phytoplankton (Savoye et al., 2012). Those cells are active suggesting more intense primary production took place together with increasing solar radiation and lower SPM concentrations. Dissolved O_2 saturation levels were much higher and not correlated with tide. A peak of pigment concentrations also arose at 11:30 am. Interestingly, increasing Pt_{PK} concentrations occurred together with this intensified primary production. Although the degree of surface complexation with organic matter remains unknown, laboratory experiments have shown that Pt adsorption kinetics onto estuarine sediments is greatest for those with relatively high total carbon contents (Couceiro et al., 2007). The clear increase of Pt_{PK} and the evaluation of the POM as fresh living phytoplankton support the hypothesis that phytoplankton ad or absorb Pt. Such complexation seems more likely to take place with newly produced phytoplankton cells. This could be explained either because absorption mechanisms through the active uptake of living cells is the principal pathway or because Pt is more likely to complex and adsorb on "fresh" organic material. Concomitant increase in both, Pt_D and particulate Pt on the second day, implied an additional Pt source from upstream (i.e., end of ebb tide, Fig 2A).

Arcachon Bay and Genoa Harbor

In the Arcachon Bay, Chl-a values were two-fold lower than in the Gironde Estuary suggesting lower productivity, probably related to the fact that this field campaign occurred in April while the one for the Gironde Estuary was in June. Lower O_2 saturation levels also suggest lower production and/or higher consumption in the riverine channels of the Arcachon Bay. In fact, POC/Chl-a ratios followed the SPM variations that were tide-dependent. Ebb tides therefore brought particulate material, which can be considered as detritic or degraded plankton cells considering the rather high POC/Chl-a ratios (< 400). Phaeopigments perfectly correlate with SPM concentrations, supporting this hypothesis. Microscopic observations during a following field campaign (Castellano M., personal communication) displayed major changes in phytoplankton composition associated to the tidal regime, suggesting that direct transport of phytoplankton (allochthonous production) and debris can play a dominant role. We also should consider the potential importance of anthropogenic POM (e.g. from urban

682 sewage; Liénart et al., 2017) in this urbanized semi-enclosed system (relatively high average
683 POC% of 6%; Table S1, SI).

684 Since no Pt_{PK} data were available for the whole cycle in Arcachon, in contrast to the Gironde
685 Estuary mouth, the variations in Pt_D cannot be clearly attributed to diel cycles in relation with
686 phytoplankton production and degradation. Phytoplankton sorption might therefore not
687 entirely explain the average Pt_{PK} concentrations of 11.76 ± 3.40 $pmol.g^{-1}$ of this site showing
688 dominance of non-living organisms or detrital particulate matter. Under such conditions, one
689 should also consider Pt complexation with inorganic particulate phases, including silt and
690 clay, also containing Fe- and manganese-(Mn)-oxy/hydroxides, which are potentially
691 important Pt carrier phases (Colodner et al., 1992; Jean-Soro et al., 2013; Lustig et al., 1996).
692 The general decreasing trend in Pt_D concentrations on the second day (from 11 am to 6 pm)
693 could yet be related to increasing primary production and subsequent Pt sequestration by
694 phytoplankton cells.

695 In the Genoa Harbor, POC/Chl-a ratios were constant as SPM concentrations, with values
696 below 200 suggesting the dominance of living phytoplankton. Increasing pigment
697 concentrations featured increasing primary production during daytime that is further
698 supported by increasing O_2 saturation levels. Despite the lack of significant differences
699 between values through time, the daytime Pt_D profile suggested an overall decreasing trend.
700 As for the Arcachon Bay, increasing primary production and the presence of active living
701 phytoplankton cells may have led to intensified Pt removal from the dissolved phase and
702 subsequent algal sorption.

703

704 ### 4.3. Platinum sorption by phytoplankton and accumulation in marine biota

705 *Transfer to phytoplankton*

706 Phytoplankton cells are efficient scavengers of trace elements, accumulating high
707 concentrations from the surrounding medium (Sanders and Riedel, 1998). Both active and
708 passive mechanisms can be involved in trace element sorption and the relative importance of
709 different sorption pathways depend on the target element (Sanders and Riedel, 1998).
710 Therefore, the observed Pt sorption by phytoplankton may reveal either: (i) active uptake of Pt
711 by phytoplankton cells with/without relevant biological functioning (e.g., mimicking other
712 bio-elements), (ii) passive adsorption of Pt on cell surface, or (iii) adsorption on organic
713 ligands produced by algal cells. Extracellular production of organic ligands by phytoplankton
714 can indeed play a major role in trace metal-organic interactions (González-Dávila, 1995). For

715 marine algae, element chemical speciation and the presence of other ions or chelators able to
716 regulate speciation are of major importance for bioavailability (Sanders and Riedel, 1998;
717 Sunda, 1989). Laboratory experiments showed linear increase of freshwater periphyton Pt
718 uptake following exposure to dissolved Pt(II) and Pt(IV) (Rauch et al., 2004b). Under longer
719 exposure time needed for Pt cellular absorption in natural environments, Pt toxicity is not
720 excluded (Rauch et al., 2004b). Accordingly, laboratory data report that for marine algae, both
721 adsorption and internalization are related to slow kinetics and are considerably constrained
722 (Cosden et al., 2003; Shams et al., 2014; Turner et al., 2007). However, another study on
723 accumulation of organic Pt species (cisplatin) by the marine macroalga *Ulva lactuca* showed
724 greater Pt interactions at the algal surface in seawater than expected by thermodynamic or
725 kinetic considerations (Easton et al., 2011). Considering the smaller size of marine microalgae
726 collected through phytoplankton nets, higher surface area and therefore higher metal sorption
727 is expected compared to sorption by macroalgae. In addition, despite their crucial importance,
728 laboratory results obtained under controlled conditions, not considering simultaneous
729 variations of various environmental factors affecting trace element distribution (e.g. trace
730 metal concentrations and speciation, light, temperature, water column stability), may not be
731 directly applicable to natural systems (Twining et al., 2011). The present study reflects, for
732 the first time, under natural conditions, that phytoplankton might play an important role in Pt
733 partitioning in productive coastal systems. Couceiro et al. (2007) reported that only small
734 quantities of Pt adsorbed on POM-rich cohesive sediments is further desorbed (< 1.5 %) in
735 chlorinated water, meaning that Pt is somewhat irreversibly adsorbed. Platinum sorption by
736 phytoplankton could therefore control Pt budget in productive coastal zones. Such
737 biogeochemical behavior characterizes other trace metals such as silver (Ag) for which no
738 desorption occurs along estuarine salinity gradients when it is associated to phytoplankton
739 (Sanders and Abbe, 1987). Silver ab- or adsorption therefore increases its retention in the
740 estuary, reducing its transport rate. Accordingly, short-term processes including diel cycles of
741 primary production showed their importance for other trace metals considered as biologically
742 essential (e.g. Fe, copper: Cu, or cobalt: Co), and anthropogenic metals (e.g. lead: Pb, Pinedo-
743 Gonzalez et al., 2014). Diel changes in such biological activity may therefore be critical for Pt
744 cycling in coastal systems.

745 *Consequences of Pt accumulation for the marine trophic chain*

746 Little information exists regarding Pt toxicity on algae. Although no significant toxicity was
747 reported, a linear decrease of the algal photosynthetic activity in freshwater periphyton
748 occurred under Pt exposure (Rauch et al., 2004b). Easton et al. (2011) showed no measurable
749 reduction of efficiency in marine macroalga *U. lactuca* exposed to cisplatin in seawater. Same

750 authors predict greater uptake by *U. lactuca* when sewage effluents discharge directly Pt-
751 based drugs into coastal waters than indirectly into fresh waters. Platinum-based complexes
752 directly released into coastal waters are indeed more reactive than after indirect discharge
753 allowing for estuarine mixing and the gradual conversion of these complexes back to the
754 parent drug (Easton et al., 2011). In addition, data also report greater sorption of inorganic
755 Pt(II) and Pt(IV) ions than cisplatin by the marine alga.

756 Phytoplankton cells are the first link in the marine trophic chain. Despite uncertainties in
757 potential adverse effects on these cells, transfer to and accumulation in higher organisms
758 cannot be excluded. Phytoplankton can accumulate relatively high concentrations of trace
759 elements from their environment with BCF of up to 10^6 (Fisher, 1986). Few studies report
760 environmental trace metal concentrations in algae, and therefore few BCF are available for
761 other trace elements. The marine macroalga *U. lactuca* showed BCF of ~ 10^3 to 10^4 for Cd,
762 Cr, Cu, Pb, or Zn (Conti and Cecchetti, 2003). These results reflect that, with similar BCF
763 (Table 1), Pt is as biogeochemically reactive to algae as other essential and anthropogenic
764 trace elements of concern that have been monitored for decades in coastal environments. In
765 wild bivalves, BCF of ~ 10^3 also occurred, which are similar to levels observed in wild
766 mussels from the Samil urban beach (Spain; Neira et al., 2015). However, in the Gironde
767 Estuary, Cd and Ag show BCF of 10^5 and 10^6, respectively (Lanceleur et al., 2011),
768 suggesting that Pt uptake from seawater by bivalves is lower compared to these trace metals.

769 Since bivalve feed on algal cells, Pt uptake may also occur through the trophic pathway after
770 phytoplankton filtration. Bivalves may also filter mineral particles included in suspended bulk
771 material. This would be especially the case in turbid systems such as the inner Gironde
772 Estuary. At this site, average Pt concentrations of 3.68 ± 1.89 pmol.g^{-1} are quantified in bulk
773 particulate material (SPM; Cobelo-García et al., 2014a) and their passage through the
774 digestive system may contribute to Pt levels measured in bivalve tissues. Zooplankton
775 organisms, which dominated during nighttime of Cycle 1, are also phytoplankton consumers.
776 Assuming that Pt_{PK} concentrations measured in nighttime samples mainly originate from
777 zooplankton organisms, lower Pt concentrations in those organisms (2.04 ± 0.19 pmol.g^{-1};
778 Fig.2 E) and in wild oysters (1.69 ± 0.15 pmol.g^{-1}; Table 1) than in phytoplankton, suggest
779 that biomagnification of Pt concentrations did not occur at these trophic levels. These higher
780 organisms may readily excrete Pt forms accumulated through phytoplankton consumption as
781 observed for other trace metals (e.g. Ag, Cd; Wang and Fisher, 1998). In addition, it is
782 possible that the dissolved phase remains the dominant uptake pathway in both bivalves and
783 zooplankton. Accordingly, other field studies associated the absence of metal

784 biomagnification to biodilution related to higher body mass of organisms from higher trophic
785 levels (Chernova and Lysenko, 2019; Liu et al., 2019).

786 Apart from direct feeding, sorption of Pt phytoplankton may regulate Pt forms and availability
787 to other marine biota. Phytoplankton biotransformation may alter (enhance or reduce)
788 contaminant toxicity to other organisms and associated adverse biological effects (Sanders
789 and Riedel, 1998). In addition, Pt sequestration by phytoplankton cells and potential cell
790 sinking in the water column may reduce its availability to other phytoplankton species or to
791 higher trophic levels (e.g. Sanders and Riedel, 1998).

792

793 *Plankton as a biomonitor of Pt contamination*

794 In both urbanized sites, the Arcachon Bay and the Genoa Harbor, Pt_{PK} concentrations were 4
795 to 8 times higher than in the Gironde Estuary mouth, respectively. Platinum levels in bivalves
796 did not show such differences since they were similar in oysters from the French Atlantic
797 coastal sites and only twice higher in mussels from the Genoa Harbor. Platinum plankton
798 concentrations may therefore reflect the levels of anthropogenic pressure found in these three
799 contrasting sites, with the phytoplankton from the Gironde Estuary reflecting coastal ocean
800 conditions, whereas the Arcachon Bay and, to a greater extent, the Genoa Harbor Pt_{PK} levels
801 feature urban/industrial human activities and associated Pt emissions. One should also
802 consider that different plankton net mesh sizes were used in the study to retrieve plankton
803 material for Pt analysis, i.e. 20 µm in the Arcachon Bay and Genoa Harbor and 200 µm in the
804 Gironde Estuary. The analyzed plankton communities may be different in relation with the
805 sampling, potentially biasing the Pt_{PK} comparison between sites. Moreover, if adsorption on
806 phytoplankton cells represents an important pathway for Pt bioconcentration, the relative
807 surface area available for Pt adsorption could have been therefore smaller in the Gironde
808 Estuary than in the other sites due to the net mesh size. This could contribute to the lower Pt
809 concentrations recorded in the Gironde Estuary samples. Furthermore, the relative importance
810 of the main genera varied among the sites, as algal communities undergo species succession
811 and changes in dominant species in different sites and seasons (Cobelo-Garcia et al. 2012).
812 This change in the phytoplankton composition potentially induces variation in trace metal
813 sorption. In the urbanized Arcachon Bay and the Genoa Harbor, Pt concentrations in
814 phytoplankton were ~ 10 times greater than in bivalves, whereas in the Gironde Estuary
815 mouth there were only ~ two-fold higher (Table 1). This difference in Pt_{PK} / Pt_{BV} ratio could
816 be related to the inner-estuary conditions of the La Fosse site, while the phytoplankton
817 samples originated from the open coastal zone (Fig. 1A). Despite common feeding and

818 filtering mechanisms, one should also consider potential differences in trace metal uptake and
819 accumulation that may occur between mussels and oysters, which are different bivalve species
820 (e.g. Ruelas-Inzunza and Páez-Osuna, 2000). Sampling of the two species in the same
821 sampling site will help to confirm our hypotheses. Higher BCF in plankton than in bivalves
822 from the same site shows the high potentiality provided by this marine biological fraction for
823 the monitoring of coastal metallic contamination. Given the short lifetime of phytoplankton,
824 these cells could be a promising biomonitor for contaminant pressure at short time scales.
825 More data would be necessary to evaluate the potential transfer of Pt from phytoplankton to
826 different zooplankton and bivalve species. This should be done with respect to accumulation
827 from ambient seawater as a prerequisite for reliable multi-species biomonitoring of Pt
828 contamination, as reported in other coastal environments with different contaminants (Conti
829 and Cecchetti, 2003). Potential irreversible Pt adsorption onto organic-rich particles (Couceiro
830 et al., 2007) and potentially onto phytoplankton cells as previously discussed, suggest that this
831 biological fraction could be used as tracer of Pt contamination and transport in coastal waters.
832 More importantly, considering the rapid Pt uptake or complexation on “fresh” living
833 phytoplankton cells (concomitant with cell production), phytoplankton could provide an early
834 signal of Pt contamination in productive coastal systems. Phytoplankton showed great ability
835 of accumulating this emerging contaminant several thousand times over the concentrations
836 quantified in seawater, as other commonly used marine bioindicator species for various
837 pollutants (e.g. Conti and Cecchetti, 2003).

5. Conclusions and perspectives

Results obtained from the three contrasting sites suggest that short-term processes, such as primary production may help understanding the marine biogeochemistry of Pt. In less urbanized sites with high primary productivity, algal Pt sorption and release appear as determinant factors in the Pt biogeochemical cycle. Through biological processes including Pt fixation by adsorption, absorption, sequestration as well as chemical biotransformation, phytoplankton can change trace metal biological reactivity and toxicity, and strongly alter Pt transport and fate. Such results are therefore valuable to shed further light on the controls of phytoplankton on the under-documented Pt reactivity in the marine environment. In contrast, in more confined and/or urbanized coastal water bodies, such biogeochemical signals may be masked by the dynamics of Pt inputs from diverse sources, such as wastewater, run off or urban aerosols. By reflecting the general state of Pt contamination of three contrasting sites comprising open coastal area and urbanized, semi-enclosed sites, and showing relatively high bioconcentration factors (up to 10^4), marine algae should be considered a relevant biomonitor of coastal short-term Pt distribution.

Knowing that trace metals may induce biological alterations to communities at higher trophic levels (Sanders and Riedel, 1998), there is a crucial need for more information on potential adverse effects of Pt on primary producers, i.e. the basis of the marine trophic chain. Results of this study clearly highlight the importance of considering changes occurring at hourly time-scales, when establishing sampling strategies for field campaigns on such bioreactive trace metals, as a prerequisite for obtaining representative results as already recommended in previous studies (Pinedo-Gonzalez et al., 2014). It is important to develop monitoring of Pt and other PGE in the phytoplankton fraction, including rhodium (Rh) which is predicted to participate in biological removal and transport processes in marine systems to a greater extent (Shams et al., 2014). Determination of Pt concentrations in the different functional groups and plankton classes would help understanding its cycles in the marine food chain (Twining et al., 2011). Further investigations are required in order to understand and estimate the extent of Pt sorption in phytoplankton cells, given that their potential complexation capacity could influence marine Pt cycling.

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877

878 **References**

879 Abdou, M., Schäfer, J., Gil-Díaz, T., Tercier-Waeber, M.-L., Catrouillet, C., Massa, F.,
880 Castellano, M., Magi, E., Povero, P., Blanc, G., 2019. Spatial variability and sources
881 of platinum in a contaminated harbor – tracing coastal urban inputs. Environ. Chem.
882 https://doi.org/10.1071/EN19160
883 Abdou, M., 2018. Platinum biogeochemical cycles in coastal environments. PhD thesis,
884 University of Bordeaux. 292pp.
885 Abdou, M., Dutruch, L., Schäfer, J., Zaldibar, B., Medrano, R., Izagirre, U., Gil-Díaz, T.,
886 Bossy, C., Catrouillet, C., Hu, R., Coynel, A., Lerat, A., Cobelo-García, A., Blanc, G.,
887 Soto, M., 2018. Tracing platinum accumulation kinetics in oyster Crassostrea gigas, a
888 sentinel species in coastal marine environments. Science of The Total Environment
889 615, 652–663. https://doi.org/10.1016/j.scitotenv.2017.09.078
890 Abdou, M., Schäfer, J., Cobelo-García, A., Neira, P., Petit, J.C.J., Auger, D., Chiffoleau, J.-F.,
891 Blanc, G., 2016. Past and present platinum contamination of a major European
892 fluvial–estuarine system: Insights from river sediments and estuarine oysters. Marine
893 Chemistry, 13th International Estuarine Biogeochemistry Symposium (IEBS) -
894 Estuaries Under Anthropogenic Pressure 185, 104–110.
895 https://doi.org/10.1016/j.marchem.2016.01.006
896 Abdou, M., Schäfer, J., Hu, R., Gil-Díaz, T., Garnier, C., Brach-Papa, C., Chiffoleau, J.-F.,
897 Charmasson, S., Giner, F., Dutruch, L., Blanc, G., 2019. Platinum in sediments and
898 mussels from the northwestern Mediterranean coast: Temporal and spatial aspects.
899 Chemosphere 215, 783–792. https://doi.org/10.1016/j.chemosphere.2018.10.011
900 Allen, G.P., 1971. Relationship between grain size parameter distribution and current patterns
901 in the Gironde estuary (France). Journal of Sedimentary Research 41, 74–88.
902 https://doi.org/10.1306/74D721EE-2B21-11D7-8648000102C1865D
903 Arnot, J.A., Gobas, F.A., 2006. A review of bioconcentration factor (BCF) and
904 bioaccumulation factor (BAF) assessments for organic chemicals in aquatic
905 organisms. Environ. Rev. 14, 257–297. https://doi.org/10.1139/a06-005
906 Artelt, S., Kock, H., König, H.P., Levsen, K., Rosner, G., 1999. Engine dynamometer
907 experiments: platinum emissions from differently aged three-way catalytic converters.
908 Atmospheric Environment 33, 3559–3567. https://doi.org/10.1016/S1352-
909 2310(99)00109-0
910 Baudrimont, M., Schäfer, J., Marie, V., Maury-Brachet, R., Bossy, C., Boudou, A., Blanc, G.,
911 2005. Geochemical survey and metal bioaccumulation of three bivalve species
912 (Crassostrea gigas, Cerastoderma edule and Ruditapes philippinarum) in the Nord
913 Médoc salt marshes (Gironde estuary, France). Science of The Total Environment
914 337, 265–280. https://doi.org/10.1016/j.scitotenv.2004.07.009
915 Bentaleb, I., Fontugne, M., Descolas-Gros, C., Girardin, C., Mariotti, A., Pierre, C., Brunet,
916 C., Poisson, A., 1998. Carbon isotopic fractionation by plankton in the Southern
917 Indian Ocean: relationship between δ13C of particulate organic carbon and dissolved
918 carbon dioxide. Journal of Marine Systems 17, 39–58. https://doi.org/10.1016/S0924-
919 7963(98)00028-1
920 Caetano, M., Vale, C., 2003. Trace-element Al composition of seston and plankton along the
921 Portuguese coast. Acta Oecologica, Proceedings of the Plankton Symposium, Espinho,
922 Portugal 24, S341–S349. https://doi.org/10.1016/S1146-609X(03)00024-9
923 Capello, M., Cutroneo, L., Ferretti, G., Gallino, S., Canepa, G., 2016. Changes in the physical
924 characteristics of the water column at the mouth of a torrent during an extreme rainfall
925 event. Journal of Hydrology, Flash floods, hydro-geomorphic response and risk
926 management 541, 146–157. https://doi.org/10.1016/j.jhydrol.2015.12.009

927 Carli, A. (Genoa U. (Italy) I. di S.A.M., Pane, L., Romairone, V., 1994. A study of
928 phytoplankton populations of the Riva Trigoso Bay (Gulf of Genoa) in relation to
929 eutrophication features of the water. MAP Technical Reports Series (UNEP).
930 Castaing, P., Allen, G.P., 1981. Mechanisms controlling seaward escape of suspended
931 sediment from the Gironde: A macrotidal estuary in France. Marine Geology, Estuary
932 \3- Shelf Interrelationships 40, 101–118. https://doi.org/10.1016/0025-3227(81)90045-
933 1
934 Castelle, S., Schäfer, J., Blanc, G., Dabrin, A., Lanceleur, L., Masson, M., 2009. Gaseous
935 mercury at the air–water interface of a highly turbid estuary (Gironde Estuary,
936 France). Marine Chemistry, 10th International Estuarine Biogeochemistry Symposium
937 - "Estuaries in a Changing World" 117, 42–51.
938 https://doi.org/10.1016/j.marchem.2009.01.005
939 Chernova, E.N., Lysenko, E.V., 2019. The content of metals in organisms of various trophic
940 levels in freshwater and brackish lakes on the coast of the sea of Japan. Environ Sci
941 Pollut Res 26, 20428–20438. https://doi.org/10.1007/s11356-019-05198-8
942 Cifuentes, L.A., Sharp, J.H., Fogel, M.L., 1988. Stable carbon and nitrogen isotope
943 biogeochemistry in the Delaware estuary. Limnology and Oceanography 33, 1102–
944 1115. https://doi.org/10.4319/lo.1988.33.5.1102
945 Cloern, J.E., 1996. Phytoplankton bloom dynamics in coastal ecosystems: A review with
946 some general lessons from sustained investigation of San Francisco Bay, California.
947 Reviews of Geophysics 34, 127–168. https://doi.org/10.1029/96RG00986
948 Cobelo-García, A., Bernárdez, P., Leira, M., López-Sánchez, D.E., Santos-Echeandía, J.,
949 Prego, R., Pérez-Arlucea, M., 2012. Temporal and diel cycling of nutrients in a
950 barrier–lagoon complex: Implications for phytoplankton abundance and composition.
951 Estuarine, Coastal and Shelf Science, Coastal Lagoons in a changing environment:
952 understanding, evaluating and responding 110, 69–76.
953 https://doi.org/10.1016/j.ecss.2012.03.015
954 Cobelo-García, A., Filella, M., Croot, P., Frazzoli, C., Du Laing, G., Ospina-Alvarez, N.,
955 Rauch, S., Salaun, P., Schäfer, J., Zimmermann, S., 2015. COST action TD1407:
956 network on technology-critical elements (NOTICE)—from environmental processes to
957 human health threats. Environ Sci Pollut Res 22, 15188–15194.
958 https://doi.org/10.1007/s11356-015-5221-0
959 Cobelo-García, A., López-Sánchez, D.E., Almécija, C., Santos-Echeandía, J., 2013. Behavior
960 of platinum during estuarine mixing (Pontevedra Ria, NW Iberian Peninsula). Marine
961 Chemistry 150, 11–18. https://doi.org/10.1016/j.marchem.2013.01.005
962 Cobelo-García, A., López-Sánchez, D.E., Schäfer, J., Petit, J.C.J., Blanc, G., Turner, A.,
963 2014a. Behavior and fluxes of Pt in the macrotidal Gironde Estuary (SW France).
964 Marine Chemistry, Estuarine Biogeochemistry 167, 93–101.
965 https://doi.org/10.1016/j.marchem.2014.07.006
966 Cobelo-García, A., Santos-Echeandía, J., López-Sánchez, D.E., Almécija, C., Omanović, D.,
967 2014b. Improving the Voltammetric Quantification of Ill-Defined Peaks Using Second
968 Derivative Signal Transformation: Example of the Determination of Platinum in
969 Water and Sediments. Anal. Chem. 86, 2308–2313. https://doi.org/10.1021/ac403558y
970 Cobelo-Garcia, A., Turner, A., Millward, G.E., 2008. Fractionation and Reactivity of
971 Platinum Group Elements During Estuarine Mixing. Environ. Sci. Technol. 42, 1096–
972 1101. https://doi.org/10.1021/es0712118
973 Colodner, D., 1991. The Marine Geochemistry of Rhenium, Iridium and Platinum (No.
974 WHOI-91-30). WOODS HOLE OCEANOGRAPHIC INSTITUTION MA.
975 Colodner, D.C., Boyle, E.A., Edmond, J.M., 1993. Determination of rhenium and platinum in
976 natural waters and sediments, and iridium in sediments by flow injection isotope

977 dilution inductively coupled plasma mass spectrometry. Anal. Chem. 65, 1419–1425.
978 https://doi.org/10.1021/ac00058a019
979 Colodner, D.C., Boyle, E.A., Edmond, J.M., Thomson, J., 1992. Post-depositional mobility of
980 platinum, iridium and rhenium in marine sediments. Nature 358, 402–404.
981 https://doi.org/10.1038/358402a0
982 Conti, M.E., Cecchetti, G., 2003. A biomonitoring study: trace metals in algae and molluscs
983 from Tyrrhenian coastal areas. Environmental Research 93, 99–112.
984 https://doi.org/10.1016/S0013-9351(03)00012-4
985 Cosden, J.M., Schijf, J., Byrne, R.H., 2003. Fractionation of Platinum Group Elements in
986 Aqueous Systems: Comparative Kinetics of Palladium and Platinum Removal from
987 Seawater by Ulva lactuca L. Environ. Sci. Technol. 37, 555–560.
988 https://doi.org/10.1021/es0259234
989 Couceiro, F., Turner, A., Millward, G.E., 2007. Adsorption and desorption kinetics of
990 rhodium (III) and platinum (IV) in turbid suspensions: Potential tracers for sediment
991 transport in estuarine flumes. Marine Chemistry, 9th International Estuarine
992 Biogeochemistry Symposium Estuaries and Enclosed Seas under Changing
993 Environmental Conditions 107, 308–318.
994 https://doi.org/10.1016/j.marchem.2007.02.010
995 Daro, M.H., 1988. Migratory and Grazing Behavior of Copepods and Vertical Distribution of
996 Phytoplankton [WWW Document]. URL
997 https://www.ingentaconnect.com/content/umrsmas/bullmar/1988/00000043/00000003
998 /art00028 (accessed 9.25.19).
999 David, V., Sautour, B., Chardy, P., Leconte, M., 2005. Long-term changes of the zooplankton
1000 variability in a turbid environment: The Gironde estuary (France). Estuarine, Coastal
1001 and Shelf Science 64, 171–184. https://doi.org/10.1016/j.ecss.2005.01.014
1002 Djingova, R., Heidenreich, H., Kovacheva, P., Markert, B., 2003. On the determination of
1003 platinum group elements in environmental materials by inductively coupled plasma
1004 mass spectrometry and microwave digestion. Analytica Chimica Acta 489, 245–251.
1005 https://doi.org/10.1016/S0003-2670(03)00716-5
1006 Doxaran, D., Froidefond, J.-M., Castaing, P., Babin, M., 2009. Dynamics of the turbidity
1007 maximum zone in a macrotidal estuary (the Gironde, France): Observations from field
1008 and MODIS satellite data. Estuarine, Coastal and Shelf Science 81, 321–332.
1009 https://doi.org/10.1016/j.ecss.2008.11.013
1010 Easton, C., Turner, A., Sewell, G., 2011. An evaluation of the toxicity and bioaccumulation of
1011 cisplatin in the marine environment using the macroalga, Ulva lactuca. Environmental
1012 Pollution 159, 3504–3508. https://doi.org/10.1016/j.envpol.2011.08.018
1013 Essumang, D.K., 2008. Bioaccumulation of platinum group metals in dolphins, Stenella sp.,
1014 caught off Ghana. African Journal of Aquatic Science 33, 255–259.
1015 https://doi.org/10.2989/AJAS.2008.33.3.8.620
1016 Etcheber, H., Taillez, A., Abril, G., Garnier, J., Servais, P., Moatar, F., Commarieu, M.-V.,
1017 2007. Particulate organic carbon in the estuarine turbidity maxima of the Gironde,
1018 Loire and Seine estuaries: origin and lability. Hydrobiologia 588, 245–259.
1019 https://doi.org/10.1007/s10750-007-0667-9
1020 Finkelman, R.B., Aruscavage, P.J., 1981. Concentration of some platinum-group metals in
1021 coal. International Journal of Coal Geology 1, 95–99. https://doi.org/10.1016/0166-
1022 5162(81)90006-9
1023 Fisher, N.S., 1986. On the reactivity of metals for marine phytoplankton. Limnology and
1024 Oceanography 31, 443–449. https://doi.org/10.4319/lo.1986.31.2.0443

Frada, M., Young, J., Cachão, M., Lino, S., Martins, A., Narciso, Á., Probert, I., Vargas, C. de, 2010. A guide to extant coccolithophores (Calcihaptophycidae, Haptophyta) using light microscopy.

Gammons, C.H., 1996. Experimental investigations of the hydrothermal geochemistry of platinum and palladium: V. Equilibria between platinum metal, Pt(II), and Pt(IV) chloride complexes at 25 to 300°C. Geochimica et Cosmochimica Acta 60, 1683–1694. https://doi.org/10.1016/0016-7037(96)00048-8

Glé, C., Del Amo, Y., Bec, B., Sautour, B., Froidefond, J.-M., Gohin, F., Maurer, D., Plus, M., Laborde, P., Chardy, P., 2007. Typology of environmental conditions at the onset of winter phytoplankton blooms in a shallow macrotidal coastal ecosystem, Arcachon Bay (France). J Plankton Res 29, 999–1014. https://doi.org/10.1093/plankt/fbm074

González-Dávila, M., 1995. The role of phytoplankton cells on the control of heavy metal concentration in seawater. Marine Chemistry 48, 215–236. https://doi.org/10.1016/0304-4203(94)00045-F

Goosen, N.K., Kromkamp, J., Peene, J., van Rijswijk, P., van Breugel, P., 1999. Bacterial and phytoplankton production in the maximum turbidity zone of three European estuaries: the Elbe, Westerschelde and Gironde. Journal of Marine Systems 22, 151–171. https://doi.org/10.1016/S0924-7963(99)00038-X

Hasle, R., 1978. The inverted microscope method. Phytoplankton manual 88–96.

Hodge, Vern., Stallard, Martha., Koide, Minoru., Goldberg, E.D., 1986. Determination of platinum and iridium in marine waters, sediments, and organisms. Anal. Chem. 58, 616–620. https://doi.org/10.1021/ac00294a029

Ifremer/ODE/LITTORAL/LERAR (2017). Qualité du Milieu Marin Littoral. Bulletin de la surveillance 2016. Départements: Gironde, Landes, Pyrénées Atlantiques. ODE/LITTORAL/LERAR/17-004. https://archimer.ifremer.fr/doc/00388/49893/

Irigoien, X., Castel, J., 1997. Light Limitation and Distribution of Chlorophyll Pigments in a Highly Turbid Estuary: the Gironde (SW France). Estuarine, Coastal and Shelf Science 44, 507–517. https://doi.org/10.1006/ecss.1996.0132

Jean-Soro, L., Oleron-Hamdous, A., Béchet, B., Legret, M., 2013. Evaluation of platinum distribution between different soil components. J Soils Sediments 13, 569–574. https://doi.org/10.1007/s11368-012-0491-3

Kümmerer, K., Helmers, E., 1997. Hospital effluents as a source for platinum in the environment. Science of The Total Environment 193, 179–184. https://doi.org/10.1016/S0048-9697(96)05331-4

Lanceleur, L., Schäfer, J., Chiffoleau, J.-F., Blanc, G., Auger, D., Renault, S., Baudrimont, M., Audry, S., 2011. Long-term records of cadmium and silver contamination in sediments and oysters from the Gironde fluvial–estuarine continuum – Evidence of changing silver sources. Chemosphere 85, 1299–1305. https://doi.org/10.1016/j.chemosphere.2011.07.036

Lenz, K., Koellensperger, G., Hann, S., Weissenbacher, N., Mahnik, S.N., Fuerhacker, M., 2007. Fate of cancerostatic platinum compounds in biological wastewater treatment of hospital effluents. Chemosphere 69, 1765–1774. https://doi.org/10.1016/j.chemosphere.2007.05.062

Liénart, C., Savoye, N., Bozec, Y., Breton, E., Conan, P., David, V., Feunteun, E., Grangeré, K., Kerhervé, P., Lebreton, B., Lefebvre, S., L'Helguen, S., Mousseau, L., Raimbault, P., Richard, P., Riera, P., Sauriau, P.-G., Schaal, G., Aubert, F., Aubin, S., Bichon, S., Boinet, C., Bourasseau, L., Bréret, M., Caparros, J., Cariou, T., Charlier, K., Claquin, P., Cornille, V., Corre, A.-M., Costes, L., Crispi, O., Crouvoisier, M., Czamanski, M., Del Amo, Y., Derriennic, H., Dindinaud, F., Durozier, M., Hanquiez, V., Nowaczyk, A., Devesa, J., Ferreira, S., Fornier, M., Garcia, F., Garcia, N., Geslin, S., Grossteffan,

E., Gueux, A., Guillaudeau, J., Guillou, G., Joly, O., Lachaussée, N., Lafont, M., Lamoureux, J., Lecuyer, E., Lehodey, J.-P., Lemeille, D., Leroux, C., Macé, E., Maria, E., Pineau, P., Petit, F., Pujo-Pay, M., Rimelin-Maury, P., Sultan, E., 2017. Dynamics of particulate organic matter composition in coastal systems: A spatio-temporal study at multi-systems scale. Progress in Oceanography 156, 221–239. https://doi.org/10.1016/j.pocean.2017.03.001

Liu, J., Cao, L., Dou, S., 2019. Trophic transfer, biomagnification and risk assessments of four common heavy metals in the food web of Laizhou Bay, the Bohai Sea. Science of The Total Environment 670, 508–522. https://doi.org/10.1016/j.scitotenv.2019.03.140

López-Sánchez, D.E., Cobelo-García, A., Rijkenberg, M.J.A., Gerringa, L.J.A., de Baar, H.J.W., 2019. New insights on the dissolved platinum behavior in the Atlantic Ocean. Chemical Geology 511, 204–211. https://doi.org/10.1016/j.chemgeo.2019.01.003

Luoma, S.N., Geen, A. van, Lee, B.-G., Cloern, J.E., 1998. Metal uptake by phytoplankton during a bloom in South San Francisco Bay: Implications for metal cycling in estuaries. Limnology and Oceanography 43, 1007–1016. https://doi.org/10.4319/lo.1998.43.5.1007

Lustig, S., Zang, S., Michalke, B., Schramel, P., Beck, W., 1996. Transformation behaviour of different platinum compounds in a clay-like humic soil: speciation investigations. Science of The Total Environment 188, 195–204. https://doi.org/10.1016/0048-9697(96)05172-8

Mashio, A.S., Obata, H., Gamo, T., 2017. Dissolved Platinum Concentrations in Coastal Seawater: Boso to Sanriku Areas, Japan. Arch Environ Contam Toxicol 73, 240–246. https://doi.org/10.1007/s00244-017-0373-1

Mashio, A.S., Obata, H., Tazoe, H., Tsutsumi, M., Ferrer i Santos, A., Gamo, T., 2016. Dissolved platinum in rainwater, river water and seawater around Tokyo Bay and Otsuchi Bay in Japan. Estuarine, Coastal and Shelf Science 180, 160–167. https://doi.org/10.1016/j.ecss.2016.07.002

Neira, P., Cobelo-García, A., Besada, V., Santos-Echeandía, J., Bellas, J., 2015. Evidence of increased anthropogenic emissions of platinum: Time-series analysis of mussels (1991–2011) of an urban beach. Science of The Total Environment 514, 366–370. https://doi.org/10.1016/j.scitotenv.2015.02.016

Nygren, Olle., Vaughan, G.T., Florence, T.Mark., Morrison, G.M.P., Warner, I.M., Dale, L.S., 1990. Determination of platinum in blood by adsorptive voltammetry. Anal. Chem. 62, 1637–1640. https://doi.org/10.1021/ac00214a020

Obata, H., Yoshida, T., Ogawa, H., 2006. Determination of picomolar levels of platinum in estuarine waters: A comparison of cathodic stripping voltammetry and isotope dilution-inductively coupled plasma mass spectrometry. Analytica Chimica Acta 580, 32–38. https://doi.org/10.1016/j.aca.2006.07.044

Pađan, J., Marcinek, S., Cindrić, A.-M., Layglon, N., Garnier, C., Salaün, P., Cobelo-García, A., Omanović, D., 2019. Determination of sub-picomolar levels of platinum in the pristine Krka River estuary (Croatia) using improved voltammetric methodology. Environ. Chem. https://doi.org/10.1071/EN19157

Peavy, C.C., 1958. The Importance of Platinum in Petroleum Refining [WWW Document]. URL https://www.ingentaconnect.com/content/matthey/pmr/1958/00000002/00000002/art00003 (accessed 9.26.19).

Petit, J.C.J., Schäfer, J., Coynel, A., Blanc, G., Deycard, V.N., Derriennic, H., Lanceleur, L., Dutruch, L., Bossy, C., Mattielli, N., 2013. Anthropogenic sources and biogeochemical reactivity of particulate and dissolved Cu isotopes in the turbidity

gradient of the Garonne River (France). Chemical Geology 359, 125–135. https://doi.org/10.1016/j.chemgeo.2013.09.019
Pinedo-Gonzalez, P., West, A.J., Rivera-Duarte, I., Sañudo-Wilhelmy, S.A., 2014. Diel Changes in Trace Metal Concentration and Distribution in Coastal Waters: Catalina Island As a Study Case. Environ. Sci. Technol. 48, 7730–7737. https://doi.org/10.1021/es5019515
Platt, T., Sathyendranath, S., Ulloa, O., Harrison, W.G., Hoepffner, N., Goes, J., 1992. Nutrient control of phytoplankton photosynthesis in the Western North Atlantic. Nature 356, 229–231. https://doi.org/10.1038/356229a0
Rauch, S., Hemond, H.F., Peucker-Ehrenbrink, B., 2004a. Recent Changes in Platinum Group Element Concentrations and Osmium Isotopic Composition in Sediments from an Urban Lake. Environ. Sci. Technol. 38, 396–402. https://doi.org/10.1021/es0347686
Rauch, S., Paulsson, M., Wilewska, M., Blanck, H., Morrison, G.M., 2004b. Short-Term Toxicity and Binding of Platinum to Freshwater Periphyton Communities. Arch Environ Contam Toxicol 47, 290–296. https://doi.org/10.1007/s00244-004-3197-8
REPHY – French Observation And Monitoring Program For Phytoplankton And Hydrology In Coastal Waters, 2019. REPHY dataset - French Observation and Monitoring program for Phytoplankton and Hydrology in coastal waters. 1987-2018 Metropolitan data. https://doi.org/10.17882/47248
Ruchter, N., Zimmermann, S., Sures, B., 2015. Field Studies on PGE in Aquatic Ecosystems, in: Zereini, F., Wiseman, C.L.S. (Eds.), Platinum Metals in the Environment, Environmental Science and Engineering. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 351–360. https://doi.org/10.1007/978-3-662-44559-4_22
Rudnick, R.L., Gao, S., 2003. Composition of the Continental Crust. Treatise on Geochemistry 3, 659. https://doi.org/10.1016/B0-08-043751-6/03016-4
Ruelas-Inzunza, J.R., Páez-Osuna, F., 2000. Comparative bioavailability of trace metals using three filter-feeder organisms in a subtropical coastal environment (Southeast Gulf of California). Environmental Pollution 107, 437–444. https://doi.org/10.1016/S0269-7491(99)00157-8
Ruggieri, N., Castellano, M., Capello, M., Maggi, S., Povero, P., 2011. Seasonal and spatial variability of water quality parameters in the Port of Genoa, Italy, from 2000 to 2007. Marine Pollution Bulletin 62, 340–349. https://doi.org/10.1016/j.marpolbul.2010.10.006
Sanders, J.G., Abbe, G.R., 1987. The role of suspended sediments and phytoplankton in the partitioning and transport of silver in estuaries. Continental Shelf Research, Dynamics of Turbid Coastal Environments 7, 1357–1361. https://doi.org/10.1016/0278-4343(87)90040-9
Sanders, J.G., Riedel, G.F., 1998. Metal accumulation and impacts in phytoplankton, in: Langston, W.J., Bebianno, M.J. (Eds.), Metal Metabolism in Aquatic Environments. Springer US, Boston, MA, pp. 59–76. https://doi.org/10.1007/978-1-4757-2761-6_4
Savoye, N., Aminot, A., Tréguer, P., Fontugne, M., Naulet, N., Kérouel, R., 2003. Dynamics of particulate organic matter δ15N and δ13C during spring phytoplankton blooms in a macrotidal ecosystem (Bay of Seine, France). Marine Ecology Progress Series 255, 27–41. https://doi.org/10.3354/meps255027
Savoye, N., David, V., Morisseau, F., Etcheber, H., Abril, G., Billy, I., Charlier, K., Oggian, G., Derriennic, H., Sautour, B., 2012. Origin and composition of particulate organic matter in a macrotidal turbid estuary: The Gironde Estuary, France. Estuarine, Coastal and Shelf Science, ECSA 46 Conference Proceedings 108, 16–28. https://doi.org/10.1016/j.ecss.2011.12.005

1173 Schäfer, J., Hannker, D., Eckhardt, J.-D., Stüben, D., 1998. Uptake of traffic-related heavy
1174 metals and platinum group elements (PGE) by plants. Science of The Total
1175 Environment 215, 59–67. https://doi.org/10.1016/S0048-9697(98)00115-6
1176 Sen, I.S., Peucker-Ehrenbrink, B., 2012. Anthropogenic disturbance of element cycles at the
1177 Earth's surface. Environ. Sci. Technol. 46, 8601–8609.
1178 https://doi.org/10.1021/es301261x
1179 Shams, L., Turner, A., Millward, G.E., Brown, M.T., 2014. Extra- and intra-cellular
1180 accumulation of platinum group elements by the marine microalga, Chlorella
1181 stigmatophora. Water Research 50, 432–440.
1182 https://doi.org/10.1016/j.watres.2013.10.055
1183 Sottolichio, A., Castaing, P., 1999. A synthesis on seasonal dynamics of highly-concentrated
1184 structures in the Gironde estuary. Comptes Rendus de l'Académie des Sciences -
1185 Series IIA - Earth and Planetary Science 329, 795–800. https://doi.org/10.1016/S1251-
1186 8050(00)88634-6
1187 Strady, E., Blanc, G., Baudrimont, M., Schäfer, J., Robert, S., Lafon, V., 2011. Roles of
1188 regional hydrodynamic and trophic contamination in cadmium bioaccumulation by
1189 Pacific oysters in the Marennes-Oléron Bay (France). Chemosphere 84, 80–90.
1190 https://doi.org/10.1016/j.chemosphere.2011.02.051
1191 Strickland, J.D.H., Parsons, T.R., 1972. A practical handbook of seawater analysis. Fisheries
1192 Research Board of Canada.
1193 Sunda, W.G., 1989. Trace Metal Interactions with Marine Phytoplankton. Biological
1194 Oceanography 6, 411–442. https://doi.org/10.1080/01965581.1988.10749543
1195 Suzuki, A., Obata, H., Okubo, A., Gamo, T., 2014. Precise determination of dissolved
1196 platinum in seawater of the Japan Sea, Sea of Okhotsk and western North Pacific
1197 Ocean. Marine Chemistry 166, 114–121.
1198 https://doi.org/10.1016/j.marchem.2014.10.003
1199 Turner, A., 2007. Particle–water interactions of platinum group elements under estuarine
1200 conditions. Marine Chemistry 103, 103–111.
1201 https://doi.org/10.1016/j.marchem.2006.08.002
1202 Turner, A., Lewis, M.S., Shams, L., Brown, M.T., 2007. Uptake of platinum group elements
1203 by the marine macroalga, Ulva lactuca. Marine Chemistry 105, 271–280.
1204 https://doi.org/10.1016/j.marchem.2007.02.009
1205 Twining, B.S., Baines, S.B., 2013. The Trace Metal Composition of Marine Phytoplankton.
1206 Annual Review of Marine Science 5, 191–215. https://doi.org/10.1146/annurev-
1207 marine-121211-172322
1208 Twining, B.S., Baines, S.B., Bozard, J.B., Vogt, S., Walker, E.A., Nelson, D.M., 2011. Metal
1209 quotas of plankton in the equatorial Pacific Ocean. Deep Sea Research Part II: Topical
1210 Studies in Oceanography, Plankton Dynamics and Carbon Cycling in the Equatorial
1211 Pacific 58, 325–341. https://doi.org/10.1016/j.dsr2.2010.08.018
1212 United Nations, 2017. Factsheet: People and Oceans. The Ocean Conference, New York, 5-9
1213 June 2017.
1214 Utermöhl, H., 1958. Methods of collecting plankton for various purposes are discussed. SIL
1215 Communications, 1953-1996 9, 1–38.
1216 https://doi.org/10.1080/05384680.1958.11904091
1217 Vyas, N., Turner, A., Sewell, G., 2014. Platinum-based anticancer drugs in waste waters of a
1218 major UK hospital and predicted concentrations in recipient surface waters. Science of
1219 The Total Environment 493, 324–329. https://doi.org/10.1016/j.scitotenv.2014.05.127
1220 Wang, W.-X., Fisher, N.S., 1998. Excretion of trace elements by marine copepods and their
1221 bioavailability to diatoms [WWW Document].
1222 https://doi.org/info:doi/10.1357/002224098765213649

1223 Zingone, A., Totti, C., Sarno, D., Cabrini, M., Caroppo, C., Giacobbe, M.G., Luglio, A.,
1224 Nuccio, C., Socal, G., 2010. Fitoplancton: metodiche di analisi quali-quantitativa.
1225 Manuali e Linee Guida 56/2010 213–237.
1226