

## Behavior and fluxes of Pt in the macrotidal Gironde Estuary (SW France)

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## Abstract

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3 Dissolved and particulate platinum ( $Pt_D$  and  $Pt_P$ , respectively) have been measured  
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5 along the salinity gradient in surface water of the Gironde Estuary during two  
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7 contrasting hydrological regimes; namely, moderate discharge (November 2012) and  
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9 high discharge (March 2013). During both sets of conditions,  $Pt_D$  concentrations  
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11 displayed maxima but at different locations along the salinity gradient. These  
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13 observations are attributed to the addition of Pt from suspended particles traversing the  
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15 estuary, an effect that is kinetically constrained and sensitive to discharge conditions. A  
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17 minimum in  $Pt_D$  concentration in the low salinity range observed under high discharge  
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19 conditions also suggests that Pt removal may occur in the maximum turbidity zone  
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21 (MTZ). Particulate Pt also exhibited mid-estuarine maxima, an effect attributed to the  
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23 presence of anthropogenic Pt in this region, but no clear trend for  $Pt_P/Pt_D$  distribution  
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25 coefficients was evident during either sampling.  
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33 Estimated daily gross dissolved ( $Pt_D$ ) and particulate Pt ( $Pt_P$ ) fluxes at La Réole, the  
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35 main fluvial entry to the Gironde Estuary, were  $0.018\text{--}0.11\text{ mole day}^{-1}$  ( $3.6\text{--}22\text{ g day}^{-1}$ )  
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37 and  $0.001\text{--}0.18\text{ mole day}^{-1}$  ( $0.21\text{--}35\text{ g day}^{-1}$ ) in November and March, respectively.  
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41 **Using Boyle's method**, the daily net  $Pt_D$  fluxes from the Gironde Estuary to the coastal  
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43 ocean were estimated at  $0.03\text{ mole day}^{-1}$  ( $6.5\text{ g day}^{-1}$ ) for moderate discharge and  $0.17$   
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45  $\text{mole day}^{-1}$  ( $34\text{ g day}^{-1}$ ) during high discharge, reflecting the regime-dependent  
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47 magnitude of Pt remobilisation along the salinity gradient. The findings of the study  
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49 suggest that estuarine reactivity is of major importance for both the distributions of Pt in  
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51 estuaries and its export to the global ocean.  
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57 Keywords: platinum; reactivity; Gironde Estuary; desorption; fluxes  
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## 1 Introduction

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3 Platinum (Pt), one of the most abundant of the Platinum Group Elements (PGE), is  
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5 **amongst the rarest elements in the Earth's crust**, with an average concentration of about  
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7 2.6 pmol g<sup>-1</sup> (or 0.5 ng g<sup>-1</sup> ; Rudnick and Gao, 2003). High chemical resistance and  
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9 excellent catalytic properties for chemical reactions make Pt an increasingly important  
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11 component for many technical applications in the chemical, electrical and petroleum  
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13 industries (Johnson Matthey 2013). Platinum is also used in catalysts for gasoline and  
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15 diesel vehicles and is currently being investigated as a potential catalyst in fuel cells of  
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17 electric cars (APS and MRS 2011). Additionally, Pt is a component of many cytotoxic  
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19 anticancer drugs due to the capacity of certain Pt complexes to inhibit cell reproduction  
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21 by interaction with DNA molecules (Remon et al. 2013). The growing use of Pt and the  
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23 release of a diversity of chemical forms of the metal, including anthropogenic metallic  
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25 and oxidic nanoparticles emitted from vehicles along roads and anticancer metabolites  
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27 emitted from hospitals and in the home, make Pt an emerging transition metal  
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29 contaminant of particular concern (Schäfer et al. 1999; Curtis et al. 2010; Cobelo-García  
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31 et al. 2011). Forecasts of increasing release into terrestrial and aquatic systems, coupled  
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33 with long-distance transport to remote and sensitive areas (e.g. Greenland and Antarctic  
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35 Ice; Barbante et al. 2001; Soyol-Erdene et al. 2011) warrant closer monitoring and a  
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37 better understanding of the anthropogenic Pt cycle. With respect to the latter, current  
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39 estimates suggest that around 85% of the **total flux of Pt at the Earth's surface is derived**  
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41 from human activities (Sen and Peucker-Ehrenbrink 2012).  
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52 Because urbanized and industrialized areas are hot-spots of Pt use and emission they  
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54 represent major sources of the metal to the surrounding aquatic environment via run-off  
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56 and wastewater release (Ravindra et al. 2004). Once emitted to aquatic systems,  
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1 however, little is understood about the transport, behavior and fate of Pt or its  
2 compounds. In particular, there is a lack of information on the behavior of Pt in  
3 estuaries (e.g. Turner, 2007; Turner and Mascorda, 2014) where the nature, fluxes and  
4 concentrations of contaminants are often modified by a variety of chemical and  
5 biological reactions. To this end, the present work provides the first measurements of  
6 dissolved and particulate Pt for a major European estuary (Gironde, SW France). The  
7 data form the basis of both an examination of the partitioning and geochemical behavior  
8 of the metal along the salinity gradient and estimates of its flux from land to ocean  
9 under different hydrological conditions.  
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## 26 2 Material and Methods

### 27 2.1 Study Area

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34 The Gironde Estuary, France (~170 km length, ~80 000 km<sup>2</sup> watershed surface  
35 area; Fig. 1) is a major European estuary in terms of size and material transport from  
36 continent to ocean. Various studies on its physical, hydrological and chemical  
37 functioning, including anthropogenically modified trace element cycles, have made it a  
38 model fluvial-estuarine system (e.g. Sottolichio and Castaing, 1999, Schäfer et al.,  
39 2002). The Gironde Estuary is a meso- to macrotidal estuary and has a mean annual  
40 freshwater discharge of ~1000 m<sup>3</sup> s<sup>-1</sup>. Asymmetrical progression of the tidal wave  
41 towards the upstream estuary induces a pronounced maximum turbidity zone (MTZ),  
42 with concentrations of suspended particulate matter (SPM) exceeding 1 g L<sup>-1</sup> in surface  
43 water and several hundreds of g L<sup>-1</sup> in bottom water. The MTZ typically resides in the  
44 low salinity region and migrates up and down estuary with seasonal river flow  
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1 variations (Sottolichio and Castaing, 1999). These hydrological and sedimentary  
2 features result in typical water and particle residence times of ~20–90 days and ~1–2  
3 years, respectively (Castaing and Jouanneau, 1979).  
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## 7 8 *2.2 Sampling* 9

10 River water and SPM samples were collected in January 2013 at the La Réole (the  
11 major fluvial entry of the Gironde Estuary; freshwater discharge into the Gironde ~2500  
12 m<sup>3</sup> s<sup>-1</sup>) and Port St Marie sites (upstream of the Garonne River and Lot River  
13 confluence) in January 2013. The La Réole site integrates material transport from the  
14 major of the watersheds and is located in the freshwater reaches upstream of the limit of  
15 the dynamic tide (Schäfer et al. 2002). River water and SPM samples (for analyses of  
16 dissolved and particulate platinum, Pt<sub>D</sub> and Pt<sub>P</sub>, respectively) were collected using a  
17 telescopic arm fitted with an electric pumping system at ~ 1 m from the riverbank and at  
18 ~ 0.2 m depth; samples were taken after pumping at least 10 L. Water samples were  
19 filtered immediately through 0.2 µm polycarbonate filters (Nucleopore®) and filtrates  
20 were collected in acid-washed polypropylene (PP) bottles previously rinsed with an  
21 aliquot of the filtrate, acidified to pH=1 (12 M HCl, Baker Instra) and stored in the dark  
22 at 4°C pending analysis.  
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43 Estuarine water and SPM samples were collected along the salinity gradient of  
44 the Gironde Estuary during two contrasting freshwater regimes in November 2012  
45 (~410 m<sup>3</sup> s<sup>-1</sup>) and March 2013 (~2000 m<sup>3</sup> s<sup>-1</sup>) **onboard the RV “Côtes de la Manche”**  
46 (INSU). Sampling of surface water (1.5 m depth) was performed with Niskin Bottles,  
47 thoroughly rinsed with estuarine water from the site. The sample transfer from the  
48 Niskin Bottle into the filtration equipment was performed directly in order to prevent  
49 possible sample contamination due to contact with silicone tubing.  
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1 The samples were immediately filtered through pre-weighed cellulose acetate  
2 filters (Sartorius®, 0.2 µm porosity). Aliquots for Pt<sub>D</sub> measurements were transferred  
3 into 125 ml acid-cleaned PP bottles, acidified to pH = 1 (12 M HCl, Baker Instra) and  
4 stored in the dark at 4°C. The filters containing surface SPM from the estuarine salinity  
5 gradient were dried to constant weight (50°C, 48 h), re-weighed and stored in the dark  
6 pending digestion and analysis. Samples of bottom SPM (including unconsolidated  
7 sediment or fluid mud) were collected along the salinity gradient of the Gironde Estuary  
8 during the GIMERCAD (March 2007) cruise using a peristaltic pump with PP-tubing  
9 and collected by centrifugation (Westfalia; 12,000 g) as described elsewhere (Schäfer et  
10 al., 2002). This technique is considered a practicable and reliable method for  
11 representative SPM sampling in all hydrologic situations (Schäfer et al., 2002). The  
12 particulate samples were dried (50°C, 48 h), powdered and homogenized with an agate  
13 pestle and mortar and stored in sealed PP containers pending digestion and analysis.  
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### 32 *2.3 Freshwater discharge and SPM concentrations*

33 Fluvial freshwater discharges into the Gironde Estuary are equivalent to the sum of the  
34 daily flows in the Garonne and the Dordogne Rivers (Figure 1). The data on daily  
35 average freshwater discharges were obtained from the national service responsible for  
36 measuring river water discharges in France (HYDRO). Determination of SPM  
37 concentrations was performed at all stations by the filtration of precise volumes of  
38 river/estuary water through dry, pre-weighed filters (Durrieu glass-fibre, 0.7 µm  
39 porosity) as described elsewhere (Schäfer et al. 2002). The filters were dried to constant  
40 weight at 45°C, and re-weighed.  
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### 59 *2.4 Dissolved and particulate platinum analyses*

1 The determination of platinum was achieved by means of catalytic adsorptive cathodic  
2 stripping voltammetry as outlined by Van den Berg and Jacinto (1988) and using the  
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4 second derivative signal transformation (Cobelo-García et al. 2014). All laboratory  
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6 work was performed in a laminar flow bench (ISO-5) housed inside an ISO-7  
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8 laboratory. Voltammetric analyses were carried out using a  $\mu$ Autolab Type III  
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10 potentiostat (Metrohm Autolab BV) connected to a polarographic stand (Metrohm  
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12 model 663VA) equipped with a hanging mercury drop electrode (HMDE, working  
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14 electrode), a Ag/AgCl (reference electrode) and a glassy carbon rod (counter electrode).  
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16 A PTFE voltammetric cell was used in all experiments and solutions in the  
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18 voltammetric cell were stirred using a rotating PTFE rod with the highest rotation speed  
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20 (3000 rpm) selected. Mercury used was specifically for analysis and polarography  
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22 (EMSURE<sup>®</sup>, Merck) and the largest drop size possible (0.52 mm<sup>2</sup>) was employed. The  
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24 potentiostat was controlled using GPES v.4.9 software (EcoChemie BV).  
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36 *Procedure for the determination of dissolved Pt.* The breakdown of organic matter in  
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38 the water samples, necessary for the determination of Pt<sub>D</sub>, was achieved by means of  
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40 UV oxidation; samples were placed in capped quartz tubes and irradiated for two hours  
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42 using a 125-W high-pressure mercury lamp placed in a fume hood located inside the  
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44 ISO-7 laboratory (Cobelo-García et al., 2013). A 10 mL aliquot of UV-digested sample  
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46 was pipetted into a Teflon<sup>®</sup> voltammetric cell. Aliquots of 300  $\mu$ L of 17.7 M H<sub>2</sub>SO<sub>4</sub>  
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48 ( $\geq 95\%$ ; TraceSELECT<sup>®</sup>, Fluka), 65  $\mu$ L of 1.46% formaldehyde (36.5%, Riedel-de-  
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50 Haën) and 95  $\mu$ L of 50 mM hydrazine sulfate (Fluka) (all diluted in Millipore Milli-Q  
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52 water and stored in 30 mL PFE Nalgene bottles) were added directly to the sample  
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54 resulting in final concentrations of the reagents as follows: 0.5 M H<sub>2</sub>SO<sub>4</sub>, 3.3 mM  
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1 formaldehyde and 0.45 mM hydrazine. The sample solution was then deaerated by  
2 purging with humidified N<sub>2</sub> (99.999%; Alphagaz<sup>TM</sup> 1, Air Liquide) for 5 minutes prior  
3 to analysis. A new mercury drop was extruded and the potential was set at -0.3 V for a  
4 deposition time of 300 s while the solution was stirred at 3000 rpm with the PTFE rod.  
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6 Stirring was then stopped and, after a quiescence period of 10 s, a stripping scan was  
7 performed from -0.5V to -1.1V in the differential pulse (DP) mode at a scan rate of 20  
8 mV s<sup>-1</sup> and using a modulation time of 0.04 s, an interval time of 0.2 s, a modulation  
9 amplitude of 25 mV and a step potential of 4 mV. The determination of Pt<sub>D</sub>  
10 concentrations was achieved by the method of standard additions using the second  
11 derivatives of the voltammetric scans after smoothing the data points according to the  
12 Savitsky-Golay algorithm using a smoothing factor of 2 (Cobelo-García et al. 2014).  
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27 *Procedure for the determination of Pt in SPM and sediments.* Suspended particulate  
28 matter and sediment samples were ashed in quartz crucibles, and acid-digested using 30  
29 mL screw-capped PFA vials (Savillex) on a time-temperature controlled Teflon-coated  
30 hot plate (SFH 5013 HD & TR 1040 PicoTrace GmbH). Prior to the acid digestion,  
31 sediments were ashed at 800°C for 3 hours, following the heating scheme given by  
32 Nygren et al. (1990), in order to remove refractory organics that may interfere during  
33 the voltammetric determination. Ashed SPM and sediments were digested using a  
34 mixture of 5mL concentrated HCl and 3mL concentrated HNO<sub>3</sub> (both Suprapur<sup>®</sup>,  
35 Merck) at 195°C for 4 hours. Digests were allowed to cool down, caps were removed  
36 and the acid was evaporated until near dryness. The residue was then redissolved by  
37 adding 1 mL of concentrated HCl and 1 mL of H<sub>2</sub>SO<sub>4</sub>, and heated again until only  
38 H<sub>2</sub>SO<sub>4</sub> was present. Cooled contents were then diluted with 0.1 M HCl, syringe-filtered  
39 using a PFA syringe (Savillex) and 25 mm polyethersulfone membranes of 0.45 µm  
40 pore size (VWR) and taken up into 25 mL PP volumetric flasks (Nalgene). The  
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voltammetric determination of Pt<sub>P</sub> in the diluted digests was carried out using the same procedure for water samples but without UV-irradiation.

The detection limit for Pt<sub>D</sub> (expressed as 3sd of blank measurements) was 0.02 pM, whereas for Pt<sub>P</sub> a detection limit of 0.14 pmol g<sup>-1</sup> (0.1 ng g<sup>-1</sup>) was obtained for a typical dry sample mass of 10 mg. The relative standard deviation (RSD) of the determination for both Pt<sub>D</sub> and Pt<sub>P</sub> was generally below 10%. The accuracy of the Pt<sub>P</sub> determination, checked against digests of river sediment (JSd-2; Geological Survey of Japan) and tunnel dust (BCR-723) certified reference materials, revealed recoveries greater than 80% and 95%, respectively. Since there is no certified reference material for Pt<sub>D</sub> in water, the accuracy of the voltammetric procedure was evaluated by means of the analysis of spiked river and estuarine waters; recoveries of greater than 95% were attained by this approach (Cobelo-García et al. 2013).

## 2.5 Thorium analyses

In order to account and correct for potential variations in grain size, chemical normalization of Pt<sub>P</sub> concentrations were performed with respect to particulate thorium, Th<sub>P</sub>, an immobile, insoluble element unaffected by anthropogenic inputs (Larrose et al., 2010). Thorium measurements were performed on fine, ground and homogenized samples of sediment and SPM. Between 0.02 and 0.04 g of precisely weighted aliquots were digested using 3 mL HF (suprapur 22 mol L<sup>-1</sup>), 1.5 mL HCl (suprapur 12 mol L<sup>-1</sup>) and 0.5 mL HNO<sub>3</sub> (suprapur 15 mol L<sup>-1</sup>) in closed 50 ml PP digiprep tubes on a digiprep temperature controlled digestion system for 3 h at 110°C. Digests were evaporated to dryness and redissolved in 3% HNO<sub>3</sub> at 65°C for 45 min and repeatedly

1 ultrasonicated. Thorium analyses were performed by Q-ICPMS (Thermo X7 series II,  
2 ThermoScientific). Thorium counts were always higher than 5000 times those of the  
3 procedural blanks (digestion and analysis; 0.67 pmol L<sup>-1</sup>), which represented less than  
4 0.05 % of the measured Th concentrations in the samples. Replicate measurements ( $n =$   
5 2 or 3) of several samples always agreed within 5 % rsd. Accuracy was verified with the  
6 digestion and analysis of a certified sediment (NCSDC311, certified value of Th = 37  
7 nmol g<sup>-1</sup>), returning a concentration of 36 nmol g<sup>-1</sup> and corresponding to a recovery of  
8 97%.

## 24 *2.6 Flux estimates*

27 Daily gross Pt<sub>D</sub> and Pt<sub>P</sub> fluxes were estimated by multiplying the respective  
28 concentrations in the fluvial Gironde Estuary sampled during January 2013 with daily  
29 freshwater discharge and SPM data, as described elsewhere (Lanceleur et al. 2011).  
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35 Total Pt daily gross fluxes were estimated as the sum of gross Pt<sub>D</sub> and Pt<sub>P</sub> fluxes.  
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38 Daily net fluxes of Pt<sub>D</sub> **transferred to the coastal ocean were estimated using Boyle's**  
39 **method; that is, by assuming conservative mixing in the high salinity range and**  
40 **extrapolating the theoretical conservative mixing line over the whole salinity gradient**  
41 **(Boyle et al. 1974).**  
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## 53 3 Results

### 57 *3.1 River discharges and SPM concentrations*

1 During the November 2012 sampling, the estimated freshwater discharge into the  
2 Gironde Estuary was  $\sim 410 \text{ m}^3 \text{ s}^{-1}$  but followed a long lasting ( $\sim 3$  month) period with  
3 low freshwater discharges ( $\sim 240 \text{ m}^3 \text{ s}^{-1}$  on average). Suspended particulate matter  
4 concentrations ranged from  $\sim 20 \text{ mg L}^{-1}$  at salinity ( $S$ ) = 28 to  $2400 \text{ mg L}^{-1}$  at  $S = 2$  and  
5 in the MTZ. Under these conditions the MTZ was well-developed and restricted to the  
6 very low salinity range, as SPM concentrations decreased and remained below values of  
7  $< 500 \text{ mg L}^{-1}$  at  $S \geq 3$  (Figure 2).  
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18 During the January and March 2013 sampling, freshwater discharge into the Gironde  
19 Estuary was relatively high ( $2500 \text{ m}^3 \text{ s}^{-1}$  and  $2000 \text{ m}^3 \text{ s}^{-1}$ , respectively; Table 1) and  
20 SPM concentrations ranged from  $85 \text{ mg L}^{-1}$  ( $S = 22$ ) to  $850 \text{ mg L}^{-1}$  ( $S = 0.9$ ). By  
21 comparison, the freshwater discharge during the March 2007 GIMERCAD cruise, when  
22 bottom SPM was sampled, was  $2600 \text{ m}^3 \text{ s}^{-1}$  and the MTZ was well-developed with SPM  
23 concentrations in surface water of up to  $1600 \text{ mg L}^{-1}$  in the low salinity range and  
24 average values of  $\sim 300 \text{ mg L}^{-1}$  at  $8 < S < 25$  (Dabrin et al. 2009). Bottom water SPM  
25 concentrations were up to  $66\,000 \text{ mg L}^{-1}$  during the GIMERCAD cruise (Table 1), or in  
26 the typical  $20\,000$  to  $100\,000 \text{ mg L}^{-1}$  range for this region based on observations near/in  
27 the fluid mud zone (Robert et al. 2004).  
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### 47 *3.2 Dissolved and particulate Pt concentrations*

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51 The distributions of  $\text{Pt}_D$  ( $< 0.2 \mu\text{m}$ ) and  $\text{Pt}_P$  ( $> 0.2 \mu\text{m}$ ) are shown for the two sampling  
52 campaigns in Figure 2. Annotated are the distributions of SPM and, for  $\text{Pt}_D$ , the  
53 theoretical dilution line adjoining the river end members and an Atlantic Ocean end-  
54 member, based on average measurements of  $\text{Pt}_D$  in the North Atlantic Ocean (Colodner  
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1991). Also shown in Figure 2 are sediment-water distribution coefficients,  $K_{Ds}$  ( $L\ kg^{-1}$ ), defining the concentration ratios of  $Pt_P$  to  $Pt_D$ :

$$K_D = \frac{[Pt_P]}{[Pt_D]} \cdot 10^3 \quad (1)$$

Freshwater  $Pt_D$  concentrations (i.e. at  $S = 0$ ) were 0.53 pM in January 2013; along the salinity gradients, concentrations at the lowest salinities were 0.54 pM ( $S = 1.2$ ) in November 2012 and 0.60 pM ( $S = 0.2$ ) in March 2013. Concentrations of  $Pt_D$  obtained in this study for the Gironde Estuary ranged from 0.35 to 0.84 pM overall, with average ( $\pm$  one sd) values of  $0.54 \pm 0.14$  pM ( $n = 15$ ) in November 2012 and  $0.50 \pm 0.06$  pM ( $n = 11$ ) in March 2013 (Figure 2; Table 1). Minimum  $Pt_D$  concentrations in both profiles were  $\sim 0.4$  pM and maximum  $Pt_D$  concentrations reached 0.84 pM at  $S = 5$  in November 2012 and 0.62 pM at  $S = 17$  in March 2013.

Average concentrations of  $Pt_P$  in SPM were similar on both sampling dates; namely,  $3.68 \pm 1.89$  pmol  $g^{-1}$  (November 2012) and  $3.49 \pm 1.38$  pmol  $g^{-1}$  (March 2013). Minimum and maximum  $Pt_P$  concentrations in SPM were 1.03 pmol  $g^{-1}$  ( $S = 27.0$ ) and 8.97 pmol  $g^{-1}$  ( $S = 9.9$ ) in November 2012, and 1.28 pmol  $g^{-1}$  ( $S = 0.5-0.9$ ) and 5.18 pmol  $g^{-1}$  ( $S = 0.2$ ) in March 2013 (Figure 3; Table 1). Platinum concentrations in bottom SPM ( $Pt_S$ ) across the salinity gradient during March 2007 ranged from 1.69 pmol  $g^{-1}$  ( $S = 0.4$ ) to 4.46 pmol  $g^{-1}$  ( $S = 8.5$ ), with an average concentration of  $3.03 \pm 0.87$  pmol  $g^{-1}$  (Figure 3; Table 1).

Distribution coefficients were very similar during both samplings, averaging  $6850 \pm 3040$   $L\ kg^{-1}$  and  $6950 \pm 3220$   $L\ kg^{-1}$  for November and March, respectively, and with

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respective ranges of 2670 to 13,700 L kg<sup>-1</sup> and 2640 to 12,000 L kg<sup>-1</sup>. The highest values of  $K_D$  occurred at  $S = 9.9$  and  $6.3$  for the November and March samplings, respectively, while the lowest values occurred at  $S \sim 27$  and  $0.9$ , respectively (Figure 3).

### 3.3 Thorium concentrations and Pt enrichment factors

Average particulate Th concentrations ( $Th_P$ ) were  $0.0485 \pm 0.0068 \mu\text{mol g}^{-1}$  ( $n=23$ ) and close to its crustal abundance of  $0.0453 \pm 0.0043 \mu\text{mol g}^{-1}$  (Rudnick and Gao, 2003).

Particulate Th concentrations in bottom SPM (March 2007) and surface SPM (November 2012 and March 2013) were not significantly different, suggesting a rather constant granularity for all samples.

In order to correct for potential grain size variability on  $Pt_P$  distributions, concentrations were normalized with respect to  $Th_P$  and thence to a Th-normalised baseline

$$EF_{Pt} = \frac{\left(\frac{Pt_P}{Th_P}\right)_{\text{sample}}}{\left(\frac{Pt_P}{Th_P}\right)_{\text{reference}}} \quad (2)$$

Here,  $EF_{Pt}$  is an enrichment factor and the reference in the denominator is based on the crustal abundances of Pt ( $=2.6 \text{ pmol g}^{-1}$ ) and Th ( $=0.0453 \mu\text{mol g}^{-1}$ ) reported by Rudnick and Gao (2003).

Platinum enrichment factors varied from depleted values ( $EF_{Pt}<1$ ) of 0.41 to enriched values ( $EF_{Pt}>1$ ) of 2.41, with an average of  $1.18 \pm 0.54$  ( $n = 22$ ). November SPM samples exhibited higher  $EF_{Pt}$  values compared with those of March 2013 and March 2007, with respective averages of  $1.58 \pm 0.76$  ( $n = 6$ ),  $0.92 \pm 0.47$  ( $n = 6$ ) and  $1.09 \pm 0.34$  ( $n = 9$ ).

## 4 Discussion

### 4.1 Comparison of Pt concentrations with those from previous studies

Platinum in estuaries is derived from both natural and anthropogenic sources. Aqueous forms are derived from the leaching of rocks, waste inputs from hospitals and municipal sewage, and the dissolution of the metal from catalytic converter particulates.

Particulate forms are delivered via weathering of rocks in the catchment, from the input of vehicular catalytic particulates and through the adsorption of aqueous forms to SPM.

The number of studies reporting the concentrations of Pt<sub>D</sub> in natural waters is rather limited, with values ranging from tens of fmol L<sup>-1</sup> to tens of pmol L<sup>-1</sup> (Cobelo-García et al. 2013). For example, a study of Pt<sub>D</sub> distribution in eleven large pristine rivers in East Asia by Soyol-Erdene and Huh (2012), spanning 198 samples returned an overall average concentration of 0.38 ± 0.13 pM (mean ± one sd of median values for the eleven rivers). Obata et al. (2006) first reported Pt<sub>D</sub> concentrations in estuarine waters and obtained concentrations in the range of 5 to 35 pM around Tokyo Bay (Japan). Relatively high concentrations were attributed to various anthropogenic emissions within the extensively urbanized area. Considerably lower estuarine concentrations of Pt<sub>D</sub> (~0.02–0.62 pM, with a mean ± one sd of 0.20 ± 0.16 pM and 0.09 ± 0.11 pM for two independent sampling campaigns) were recently reported for a small urban system (Lérez Estuary –Pontevedra Ria) fed by a pristine river in NW Spain (Cobelo-García et al. 2013). Concentrations of Pt<sub>D</sub> obtained in the present study for the Gironde Estuary (ranging from 0.35 to 0.84 pM) provide further evidence of the typical sub-picomolar Pt concentrations in natural waters that are not extensively perturbed by urbanization.

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Dissolved Pt concentrations along the salinity gradient of the Gironde Estuary are clearly higher than the average North Atlantic value of 0.26 pM (Figure 2); specifically, concentrations of  $Pt_D$  in the river end-member are approximately double the Atlantic end-member value. Thus, while the Gironde does not appear to be extensively contaminated by Pt, the estuary is nevertheless a net source of dissolved Pt to the coastal ocean.

As with the dissolved phase, average  $Pt_P$  concentrations in surface SPM were similar during both samplings; namely,  $3.69 \pm 1.79$  (November 2012) and  $3.49 \pm 1.38$  pmol  $g^{-1}$  (March 2013). The average crustal Pt abundance is about 2.6 pmol  $g^{-1}$  (Peucker–Ehrenbrink and Jahn 2001; Rudnick and Gao 2003) and, consistent with this figure,  $Pt_P$  background concentrations in estuarine and coastal sediments on the order of 1.5 to 3 pmol  $g^{-1}$  have been reported for Massachusetts Bay USA, (Tuit et al. 2000), and the Tagus Estuary and prodelta, Portugal (Cobelo–García et al. 2011). Average concentrations of  $Pt_P$  in bottom SPM ( $3.03 \pm 0.87$  pmol  $g^{-1}$ ) are slightly lower than the corresponding averages in the SPM and closer to typical crustal–background concentrations.

The only published study reporting  $Pt_P$  concentrations in estuarine SPM is that of Cobelo–García et al. (2013) for the Lérez Estuary. Here, concentrations of  $10.8 \pm 12.3$  pmol  $g^{-1}$  ( $n=15$ ) and  $41.0 \pm 22.6$  pmol  $g^{-1}$  ( $n=15$ ) were reported for sampling dates during April 2008 and May 2011, respectively. Average  $Pt_P$  concentrations obtained in the present study for the Gironde Estuary are considerably lower, and, as a consequence of these discrepancies, values of  $K_D$  are significantly higher in the Lérez, exceeding  $10^5$  L  $kg^{-1}$  in some cases (Cobelo–García et al. 2013).

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These differences may result from the different turbidities and hydrodynamics in the two systems. Thus, while typical SPM concentrations in the Lérez are no greater than a few mg per liter (generally around  $1 \text{ mg L}^{-1}$ ; Cobelo-García et al. 2013), the Gironde Estuary is highly turbid and SPM concentrations of hundreds of mg per liter are usually present throughout most of its axis. Higher estuarine turbidities are often characterized by systems of greater energy and suspended particles of larger mean diameters than estuaries of low turbidity (Turner and Millward, 2002). Since larger particles have lower surface areas, they have less propensity to adsorb metal ions, including those of Pt, from the aqueous phase. Additionally, because of its urbanized shoreline, the smaller Lérez estuary may contain a higher proportion of  $\text{Pt}_p$  in vehicular catalytic form. Because Pt in this form is relatively insoluble compared with other forms of (e.g. adsorbed)  $\text{Pt}_p$ , the net  $\text{Pt}_p$ - $\text{Pt}_d$  partitioning of the metal would be elevated compared with that observed in the Gironde.

#### 4.2. $\text{Pt}_p$ enrichment based on $\text{Th}_p$ normalization

When the particulate Pt data are normalized with respect to Th and enrichment factors calculated (equation 2), the values obtained indicate, on average, low to null enrichment in March 2013 surface SPM ( $\text{EF}_{\text{Pt}} = 0.92 \pm 0.47$ ;  $n = 6$ ) and March 2007 bottom SPM ( $\text{EF}_{\text{Pt}} = 1.09 \pm 0.34$ ;  $n = 9$ ), and a moderate enrichment in November 2012 estuarine surface SPM ( $\text{EF}_{\text{Pt}} = 1.58 \pm 0.76$ ;  $n = 6$ ).

Assuming that particulate Pt in SPM mainly originates from soil erosion and runoff from urban/road surfaces, this observation suggests that during high discharge periods, or periods of high precipitation in the watershed (as in March 2007 and March 2013),



1 the  $Pt_P/Th_P$  ratios in SPM from the Gironde Estuary subsurface waters reflect typical  
2 watershed signatures. Thus, after long periods of rainfall (i) urban surfaces are likely to  
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4 have been washed out, conferring a low stock of Pt-rich particles available for runoff,  
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6 and (ii) intense erosion of soil surfaces in the rural regions of the watershed provides a  
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8 large flux of particles with baseline catchment signatures (especially in early spring,  
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10 when the fields are free of intense vegetative cover).  
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15 Conversely, in November 2012 and following a long period (~ 4 months) of low  
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17 freshwater discharge into the Gironde Estuary, conditions favor a greater urban  
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19 signature in the estuary since the relative contribution of fresh urban particles and  
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21 wastewater to gross fluxes is at maximum (Deycard et al, accepted). The transport of  
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23 Pt-rich particles into the Gironde by runoff during short, small-scale rain events in the  
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25 Bordeaux urban region and adjacent industrial areas could also explain locally increased  
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27  $Pt_P/Th_P$  ratios in SPM. Specifically, **the Bec d'Ambes industrial area at the confluence**  
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29 of the Garonne and the Dordogne Rivers (Figure 1) hosts several chemical industries  
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31 and petrol/gas storage and distribution facilities where Pt may be employed because of  
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33 its excellent catalytic properties (Johnson-Matthey 2013).  
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41 The observed  $EF_{Pt}$  values in the mid-salinity range of the Gironde Estuary during both  
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43 November (2012) and March (2013) also allow us to derive a first-order estimate of the  
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45 relative contributions of natural and anthropogenic particulate Pt in the system. Thus,  
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47 assuming an average  $Pt_P$  concentration of  $3.0 \text{ pmol g}^{-1}$  in samples without measurable  
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49 anthropogenic enrichment ( $0.9 < EF_{Pt} < 1.2$ ), the  $EF_{Pt}$  values in the mid-salinity range  
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51 ( $1.8 \pm 0.1$ ) suggest that roughly one third of the  $Pt_P$  ( $\sim 1.2 \text{ pmol g}^{-1}$ ) in these samples is  
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53 of anthropogenic origin. Given that (i) the estimated mass of the SPM stock is 4–5  
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55 million tons, and (ii) average particle residence time in the Gironde Estuary is 1–2 years,  
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1 we estimate that the average anthropogenic particulate Pt contribution to the Gironde  
2 Estuary Pt budget is around 2–6 mol yr<sup>-1</sup> (400–1200 g yr<sup>-1</sup>).  
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#### 5 4.3. Fractionation of Pt in the estuarine water column 6 7

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9 In order to examine, quantitatively, the partitioning and fractionation of Pt in the water  
10 column of the Gironde Estuary, the fraction of Pt in the particulate phase was computed  
11 as follows (Turner and Millward, 2002):  
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$$16 \text{Pt}_p \text{ fraction} = 1 - \frac{1}{1 + K_D \cdot \text{SPM}/10^6} \quad (3)$$

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23 The results of the calculations are shown in Figure 4 as a function of SPM concentration  
24 and with lines of equal  $K_D$  annotated for reference. Also shown for comparison are  
25 results arising from two surveys undertaken in the Lérez Estuary and as described above  
26 (Cobelo-García et al. 2013). In the Gironde, and for both samplings, the fraction of  $\text{Pt}_p$   
27 ranges from about 0.1 to 0.9, and the data are close to the isopleth of  $K_D = 10^4 \text{ L kg}^{-1}$ .  
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29 This reflects a relatively uniform partitioning of Pt in the estuary, regardless of salinity  
30 or hydrological conditions, and indicates that fractionation is governed largely by the  
31 concentration of SPM in the water column. In the Lérez Estuary, however, the fraction  
32 of  $\text{Pt}_p$  ranges from about 0.02 to 0.7 and the data are more widely distributed over a  
33 range of  $K_D$ s (between about  $10^4$  and  $10^6 \text{ L kg}^{-1}$ ); here, therefore, fractionation is more  
34 sensitive to both  $K_D$  and concentration of SPM. Thus, despite concentrations of SPM  
35 that are orders of magnitude greater in the Gironde than in the Lérez, the  $\text{Pt}_p$   
36 fractionation between the two estuaries is not that dissimilar. As suggested above, it is  
37 likely that particles in the Lérez are smaller and of higher surface area, resulting in a  
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1 greater propensity for the adsorption of Pt, and contain a higher proportion of relatively  
2 unreactive (immobile) catalytic Pt.  
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#### 9 *4.4 Estuarine reactivity of Pt and its relation to likely speciation*

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12 The  $Pt_D$  distribution in surface water along the estuarine gradient of the Gironde  
13 suggests addition of the metal throughout the estuary during the November sampling  
14 but only towards the outer estuary, and removal in the upper estuary during March  
15 (Figure 2). These distributions are not accompanied by equivalent and opposite changes  
16 in the distributions of  $Pt_P$ , which shows a bell-shape distribution across the salinity  
17 gradient with maximum values and  $EF_{Pt}$  at mid salinities and depletion in the low  
18 salinity zone (Figure 3). This results in complex distributions of  $K_D$  with no clear  
19 salinity dependence, although highest  $K_{DS}$  are consistently found at mid-salinities.  
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33 There is only limited thermodynamic information relevant to the speciation of Pt  
34 in estuaries (or end-members thereof). Available data suggest that, in sea water, the  
35 inorganic equilibrium speciation of Pt(II) and Pt(IV) is dominated by  $PtCl_4^{2-}$  and  
36  $PtCl_5(OH)^{2-}$ , respectively (Gammons, 1996), and that, in freshwater, speciation of Pt(II)  
37 and Pt(IV) is dominated by  $Pt(OH)_2$  and  $Pt(OH)_5^-$ , respectively (Kalabina, 1983).  
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39 Moreover, calculations undertaken by Cobelo-García et al. (2013) indicate that Pt(IV) is  
40 the more important oxidation state in sea water, but that Pt(II) is more important in  
41 freshwater. Since the relative abundance of the free ion is vanishingly small in aqueous  
42 solution (Cosden and Byrne, 2003), interactions of Pt with particulate matter are,  
43 therefore, likely to be restricted to negatively charged or neutral complexes. Because the  
44 negative charge of the dominant complexes is predicted to increase with increasing  
45 salinity and given that SPM bears a net negative charge across the estuarine gradient  
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1 (Loder and Liss, 1985), there will be an increasing repulsion between the SPM surface  
2 and Pt species with increasing salinity; in other words, a reduction in Pt adsorption or  
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4  $K_D$  is predicted along the estuarine gradient. This effect has been demonstrated for  
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6 Pt(IV) by Turner (2007) under laboratory conditions using natural sediment.  
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9 More specifically, in anticancer drugs, Pt(II) occurs as a series of complexes  
10 (cisplatin, carboplatin and oxaliplatin) which are relatively stable when administered in  
11 chloride solution, but become highly reactive (as positively charged, aquated  
12 metabolites) in an environment of low chloride concentration (i.e. within the cell;  
13 Verstraede et al., 2001; Curtis et al., 2010). The metabolites of the drugs, therefore,  
14 remain reactive once discharged into fresh water but become progressively less reactive  
15 as the chloride concentration (or salinity) of the environment increases. Consequently,  
16 and as above, Pt in these forms exhibits a reduction in its tendency to adsorb to  
17 suspended particles along the estuarine gradient (Curtis et al., 2010; Turner and  
18 Mascorda, 2014).  
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33 These descriptions of Pt speciation are partly consistent with the observations on  
34 the distributions and partitioning of Pt in the Gironde. Thus, although no clear reduction  
35 in  $K_D$  with salinity is evident, the broad maximum in  $Pt_D$  recorded during November is  
36 consistent with remobilisation of the metal from SPM traversing the salinity gradient as  
37 species become more negative and less particle-reactive. In March, there is evidence for  
38 remobilisation in the lower estuary but removal from the aqueous phase in the upper  
39 estuary. In neither survey, however, does the change in  $Pt_D$  reflect an equivalent but  
40 opposite change in  $Pt_P$ , presumably because of the sheer stock of mobile particulate  
41 matter in the sedimentary reservoir and the fact that Pt exists in particulate form bound  
42 in different forms of differing labilities.  
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Clearly, discrepancies between measurements of Pt in the estuary and the speciation considerations above reflect a number of oversimplifications. Thus, firstly we have neglected any interactions of Pt with dissolved or colloidal organic matter. Obata et al. (2006) detected significant fractions of electrochemically-inactive organically-complexed Pt species in estuarine waters and these forms have the potential to be flocculated and sedimented from the water column, an effect that is consistent with the minimum in  $Pt_D$  at low salinities that we observed during the March sampling. Secondly, reactions involving Pt are kinetically controlled because of the slow rearrangements of the coordination spheres of Pt(II) and Pt(IV) (Cosden et al., 2003) and this effect is known to constrain the rates of both the complexation and adsorption of aqueous Pt (Turner et al., 2006; Shams et al., 2014). Thirdly,  $Pt_P$  in catalytic form is relatively unreactive and unlikely to undergo mobilisation readily, and fourthly, we have not considered the potential for benthic fluxes of the metal from tidally disturbed sediment and pore waters. With respect to the latter, previous work on early diagenesis and metal behavior at the sediment-water interface of the Gironde estuary has shown that benthic diffusive metal fluxes are relatively small compared to metal transfer induced by tidally resuspended sediments and/or dredging, and that benthic metals probably equilibrate very efficiently with the abundant the overlying water column (Audry et al. 2007b; Audry et al. 2006; Robert et al. 2004; Audry et al. 2007a).

The differences in Pt distributions and partitioning between the two surveys of the Gironde Estuary may be related to different hydrodynamic regimes and their constraints on Pt reactivity. In March, under high river discharge and the presence of a broad MTZ and when we have inferred a relatively high proportion of non-anthropogenic Pt in the system, the maximum in  $Pt_D$  is relatively small and restricted to the upper half of the

1 salinity range. In November, and under moderate river discharge and the presence of a  
2 more distinct MTZ in the upper estuary, the maximum in  $Pt_D$  is greater and broader,  
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4 occurring throughout the estuary. Having reasoned the tendency for different forms of  
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6  $Pt$  to undergo remobilisation on thermodynamic principles, it is predicted that the extent  
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8 of desorption is dependent on the concentration of SPM, the amount and nature of  $Pt$   
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10 held on these particles and the flushing time of the estuary. Given that the concentration  
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12 of  $Pt_P$  is similar between the two samplings, the longer flushing times in November (by  
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14 factors of three to four, as estimated from freshwater discharges according to Castaing  
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16 and Jouanneau, 1979; November 2012: 70–80 days; March 2013: 20–30 days) allow  
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18 greater timescales for the remobilisation of  $Pt$  within the estuary. During March,  
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20 remobilisation may occur to the same extent but is likely to be constrained to the outer  
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22 estuary and into the adjacent coastal zone. Given that aqueous forms of metal are  
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24 generally more bioavailable than particulate forms to a wider variety of organisms  
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26 (Kramer, 1994), the region in which remobilisation occurs may have an impact on the  
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28 types of organism that accumulate  $Pt$ . The oyster production areas in the Marennes–  
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30 Oléron Bay, for example, may be exposed to greater quantities of  $Pt$  during periods of  
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32 high discharge and short residence times and when  $Pt$ -bearing particles are forced  
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34 further downestuary. Further studies are required to elucidate the extent and impacts of  
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36  $Pt$  accumulation by estuarine and coastal wildlife.  
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#### 51 *4.5 Gross and net Pt fluxes*

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54 From the concentrations of  $Pt$  in the fresh water end-member sampled in January 2013,  
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56 total gross  $Pt$  fluxes from the watershed into the Gironde Estuary were estimated at  
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58  $0.02\text{--}0.29 \text{ mole day}^{-1}$  ( $3.8\text{--}57 \text{ g day}^{-1}$ ), with gross  $Pt_D$  fluxes ranging from  $0.018\text{--}0.11$   
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1 mole day<sup>-1</sup> (3.6–22 g day<sup>-1</sup>), and gross Pt<sub>P</sub> fluxes from 0.001–0.18 mole day<sup>-1</sup> (0.21–35 g  
2 day<sup>-1</sup>). The net Pt<sub>D</sub> fluxes exported to the coastal Atlantic Ocean during the two  
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4 sampling campaigns were estimated at 0.03 to 0.17 mole day<sup>-1</sup> (6.5 to 34 g day<sup>-1</sup>). The  
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6 removal of Pt<sub>D</sub> observed at low salinities in March 2013 has a minor but not negligible  
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8 impact on the exported flux, with a decrease of about 10–15% (5 g day<sup>-1</sup>). The overall  
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10 gross Pt<sub>D</sub> specific yield from the watershed into the Gironde Estuary is estimated to be  
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12 between 0.023 and 0.14 × 10<sup>-5</sup> mole km<sup>-2</sup> day<sup>-1</sup> (4.5 to 28 × 10<sup>-5</sup> g km<sup>-2</sup> day<sup>-1</sup>). This  
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14 estimation compares well with the Pt<sub>D</sub> yield reported for eleven large pristine rivers in  
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16 East Asia covering mean discharges from 220 to 29,500 m<sup>3</sup> s<sup>-1</sup>; here, Soyol–Erdene and  
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18 Huh (2012) obtained a discharge-weighted mean of 0.04 × 10<sup>-5</sup> mole km<sup>-2</sup> day<sup>-1</sup> (8 × 10<sup>-5</sup>  
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20 g km<sup>-2</sup> day<sup>-1</sup>), with values in the range of 0.01 to 8.13 × 10<sup>-5</sup> mole km<sup>-2</sup> day<sup>-1</sup> (2 to 24  
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22 × 10<sup>-5</sup> g km<sup>-2</sup> day<sup>-1</sup>). Also, values of between 0.015 and 0.077 × 10<sup>-5</sup> mole km<sup>-2</sup> day<sup>-1</sup> have  
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24 been estimated from the data of Cobelo–García et al. (2013) for the Lézé Estuary  
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26 (average discharge of 21 m<sup>3</sup> s<sup>-1</sup>). Although data are unavailable for other world rivers,  
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28 results presented in this study lend support to a global riverine gross Pt<sub>D</sub> flux into  
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30 estuaries of 0.036 × 10<sup>3</sup> mole day<sup>-1</sup> (7 × 10<sup>3</sup> g day<sup>-1</sup>), obtained assuming a mean global  
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32 riverine value of 0.36 pM for Pt<sub>D</sub> and a global river runoff of 1025 × 10<sup>8</sup> m<sup>3</sup> day<sup>-1</sup>  
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34 (Soyol–Erdene and Huh 2012).  
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45 The non-conservative behavior of Pt<sub>D</sub> in the present study, with net addition over a  
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47 range of salinities, results in an enhanced export of Pt to the Atlantic Ocean waters  
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49 relative to the input of Pt<sub>D</sub> via rivers. Accordingly, the calculated net specific Pt<sub>D</sub> fluxes  
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51 from the Gironde Estuary to the ocean are between 0.04 and 0.22 × 10<sup>-5</sup> mole km<sup>-2</sup> day<sup>-1</sup>  
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53 (8 to 42 × 10<sup>-5</sup> g km<sup>-2</sup> day<sup>-1</sup>), or roughly double the gross Pt<sub>D</sub> flux from the watershed.  
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57 The estuarine remobilisation of Pt<sub>D</sub> has important implications for the estimation of the  
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59 Pt oceanic budget and its residence time. For example, an oceanic residence time of 24  
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1  $\times 10^3$  years was derived by Soyol-Erdene and Huh (2012) assuming no release or uptake  
2 of  $Pt_D$  in estuaries; the authors indicated, however, that a 50% release in estuaries would  
3 modify this value to  $16 \times 10^3$  years. Based on the observations of the present study in the  
4 Gironde Estuary, the latter value would appear to be a more accurate estimate.  
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## 10 11 12 13 14 5. Conclusions and perspectives 15 16

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18 This work provides the first measurements and flux estimates of  $Pt_D$  and  $Pt_P$  for a major  
19 European estuary. Overall concentrations of  $Pt_D$  and  $Pt_P$  ranged from 0.35 to 0.84 pM  
20 and from 1.02 to 8.97 pmol  $g^{-1}$ , respectively. The behavior of  $Pt_D$  during estuarine  
21 mixing was non-conservative during two sampling campaigns, with minimum  
22 concentrations observed in the low salinity range on one occasion and net addition over  
23 a range of salinities observed during both campaigns. Addition was attributed to the  
24 thermodynamic drive for the remobilization of various forms of Pt from suspended  
25 particles traversing the salinity gradient. The gross  $Pt_D$  yield from the watershed into the  
26 Gironde Estuary agrees well with values reported for other world rivers, and reinforces  
27 current estimates of the global riverine Pt flux to estuaries. The net  $Pt_D$  addition on  
28 estuarine mixing results in a 2-fold increase in the export of Pt to the ocean compared  
29 with the riverine input, with consequent implications for estimates of the Pt oceanic  
30 mass balance and residence time. More data for a wider range of systems, including  
31 both pristine environments and estuaries whose catchments are intensively urbanized,  
32 are needed to verify whether the behavior of Pt observed in the Gironde is a general  
33 trait.  
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1 Although our understanding of the biogeochemical behaviour of Pt in the marine  
2 environment has advanced in the past decade, there are still a number of issues that have  
3 not been adequately addressed. These include the determination of the mobility and  
4 bioavailability of particle-bound Pt in estuaries, an estimation of Pt fluxes prior to the  
5 introduction of catalytic converters through the analysis of SPM sample archives and/or  
6 sediment cores, and measurement of the bioaccumulation of Pt in estuarine biota used  
7 for human consumption (e.g. oysters, cockles). Moreover, no field studies have been  
8 carried out thus far on the estuarine behavior of the other PGE: Pd and Rh. As with Pt,  
9 these elements are present in catalytic converters and their **fluxes at the Earth's surface**  
10 are also dominated by human activities (Sen and Peucker-Ehrenbrink 2012). Given the  
11 perturbation of their geochemical cycles and their relatively high bioavailability  
12 observed in terrestrial systems (especially Pd; Schäfer et al. 1998), further studies on  
13 these metals are called for.

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2 Figure Captions  
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5 Figure 1. Map of the Gironde Estuary and fluvial reaches of the Garonne and Dordogne  
6 Rivers, with sampling points along the salinity gradient ( $KP > 20$ ) and at La Réole ( $KP =$   
7  $-70$ ).  
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12 Figure 2. Figure 2. Variation of  $Pt_D (< 0.2 \mu m)$  during estuarine mixing for the November  
13 2012 (a) and March 2013 (b) sampling dates. Theoretical dilution lines are shown  
14 adjoining the dissolved river end-member concentrations and the average dissolved Pt  
15 concentration in the North Atlantic (open symbol) from Colodner (1991). The irregular  
16 solid lines represent the distributions of suspended particulate matter.  
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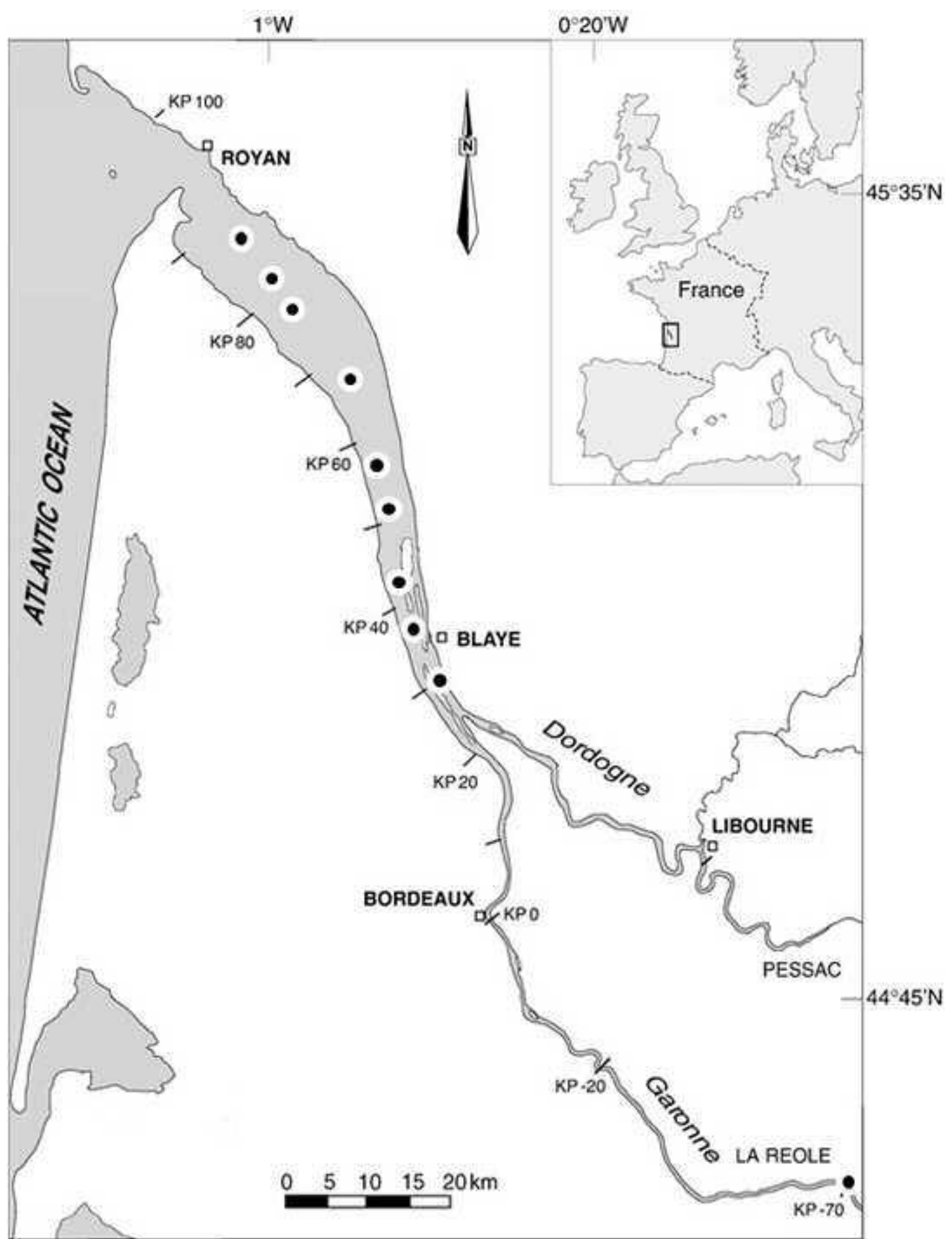
23 Figure 3. Variation of (a)  $Pt_p (> 0.2 \mu m)$ , (b) particle-water distribution coefficients and  
24 (c) enrichment factors (EF) during estuarine mixing for the November 2012 (closed  
25 circles) and March 2013 (open circles) estuarine samplings. Also included are data for  
26 the January 2013 river sampling (squares) and March 2007 bottom SPM sampling (open  
27 triangles). Enrichment factors were calculated using equation 2; see text for further  
28 information.  
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36 Figure 4. **Figure 4: Fractionation of Pt in the Gironde Estuary (November, ■; March, ▲)**  
37 **and in the Lérez Estuary (April 2008, ○; May 2013, ◇) as a function of the concentration**  
38 **of suspended particulate matter, SPM, and as calculated according to equation 2.**  
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Table 1. Salinities, concentrations of suspended particulate matter (SPM), dissolved Pt and particulate Pt (Pt<sub>D</sub> and Pt<sub>P</sub>, respectively), and Th<sub>P</sub> concentrations and Pt enrichment factors (EF<sub>Pt</sub>) in the Gironde system.

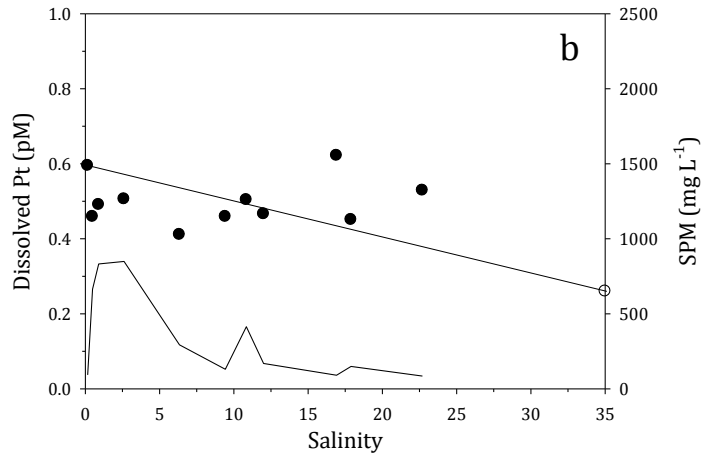
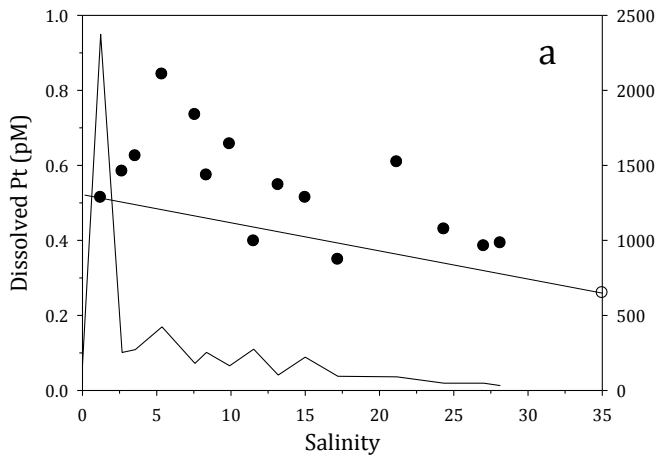
		SPM	S	Pt <sub>D</sub>	Pt <sub>P</sub>	Th <sub>P</sub>	EF <sub>Pt</sub>	
		(mg L <sup>-1</sup> )		(pM)	(pmol g <sup>-1</sup> )	(μmol g <sup>-1</sup> )		
<i>River samples</i>								
<i>(surface SPM)</i>								
<i>January 2013</i>	Port St Marie	163	0.0	0.53	3.74			
	La Réole	168	0.0	0.53	3.64	0.0562	1.16	
<i>Estuarine samples</i>								
<i>(Surface SPM)</i>								
<i>November 2012</i>		2373	1.2	0.51	3.13	0.0537	1.03	
		253	2.7	0.58	3.43	0.0455	1.33	
		272	3.6	0.63	3.28			
		424	5.4	0.84	4.31	0.0471	1.61	
		180	7.6	0.74	3.33			
		254	8.4	0.57	4.51			
		164	9.9	0.66	8.97	0.0545	2.91	
		275	11.5	0.40	3.02			
		103	13.2	0.55	4.77			
		222	15.0	0.51	5.13			
		94	17.2	0.35	4.36	0.0420	1.83	
		91	21.2	0.61	1.95	0.0447	0.76	
		48	24.3	0.43	2.51			
		48	27.0	0.39	1.03			
		21	28.1	0.39	1.44			
	<i>March 2013</i>		93	0.2	0.60	5.18		
			664	0.5	0.46	1.28	0.0554	0.41
		832	0.9	0.49	1.28	0.0493	0.46	
		849	2.6	0.51	2.36	0.0480	0.87	
		293	6.3	0.41	4.97			
		130	9.4	0.46	4.36			
		414	10.8	0.50	3.08	0.0544	0.99	
		169	12.0	0.47	4.36	0.0449	1.71	
		91	16.9	0.62	2.87	0.0462	1.09	
		149	17.9	0.45	4.15			
		85	22.7	0.53	4.56			
<i>Estuarine samples</i>								
<i>(bottom SPM)</i>								
<i>March 2007</i>		1640	0.0		2.61	0.0397	1.16	
		23600	0.4		1.69	0.0493	0.61	
		59300	3.8		3.08	0.0470	1.16	
		32200	4.8		2.87	0.0519	0.98	
		4300	7.4		4.36	0.0445	1.73	
		51400	6.9		2.92	0.0440	1.17	
		66100	8.5		4.46	0.0646	1.22	
		22100	13.1		2.97	0.0522	1.00	
		134	21.6		2.36	0.0532	0.78	

Figure(s)  
[Click here to download high resolution image](#)

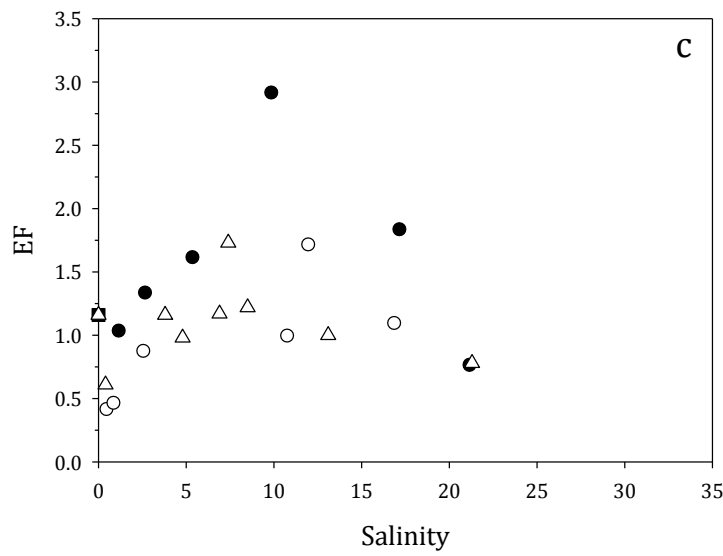
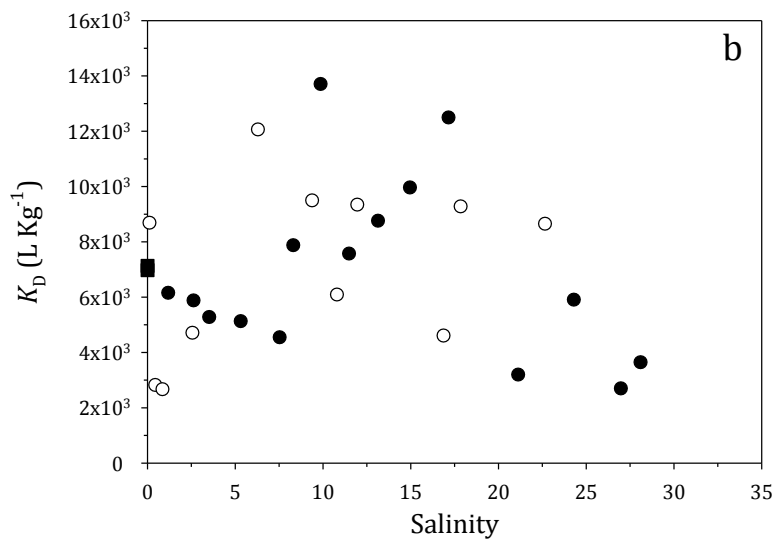
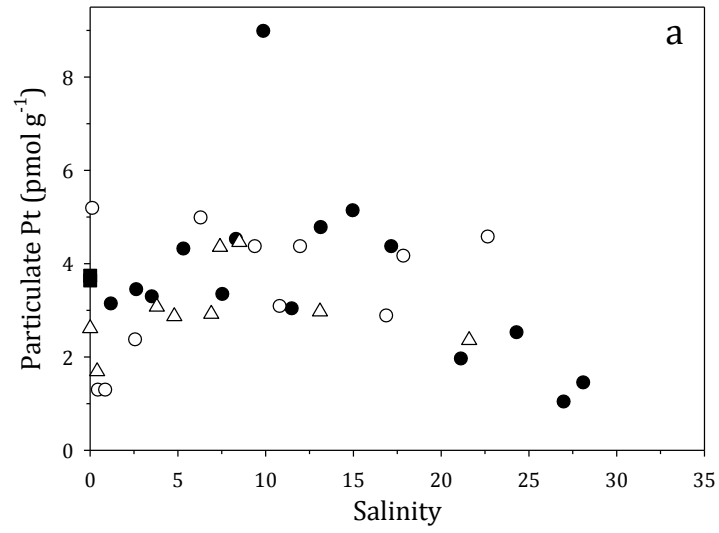




Figure(s)



Figure(s)





**Highlights**

- Dissolved and particulate platinum have been measured along the salinity gradient in surface water of the Gironde Estuary
- Dissolved and particulate platinum concentrations displayed maxima but at different locations along the salinity gradient
- No clear trend for particle-water distribution coefficients was evident
- Estuarine reactivity is of major importance for both the distributions of Pt in estuaries and its export to the global ocean