**Behaviour of Platinum During Estuarine Mixing
(Pontevedra Ria, NW Iberian Peninsula)**

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Abstract

The concentrations of Pt in sediments, water and suspended particulate matter (SPM) were determined in the Lérez river estuary (Pontevedra Ria, NW Iberian Peninsula) on two sampling dates in 2008 and 2011, by means of catalytic adsorptive stripping voltammetry. Average concentrations in sediments ($1.2 \pm 0.5 \text{ ng g}^{-1}$; $n=13$) corresponded to an enrichment factor of 2-4 compared to background values, and were in the range of those found in the SPM during the 2011 sampling ($2.1 \pm 2.4 \text{ ng g}^{-1}$; $n=15$), but significantly lower than in 2008 SPM ($8.0 \pm 4.4 \text{ ng g}^{-1}$; $n=15$). Higher dissolved Pt concentrations were also found in 2008 (0.21 and 0.62 pM in the freshwater and seawater end-member) compared to the 2011 campaign (0.03 – freshwater – and 0.40 pM – seawater end-member). Concentrations in the seawater end-members exceed those of typical North Atlantic waters, suggesting inputs of this element within the estuary. The extremely low value for the freshwater end-member in 2011 appears to be among the lowest Pt concentrations ever reported in the literature. Non-conservative behaviour of Pt during estuarine mixing was observed on both sampling dates. Particle-water distribution coefficients (K_d) show a decrease with salinity, in agreement with speciation calculations, which predict a transfer from neutral Pt(II) (as $\text{Pt}(\text{OH})_2$) in freshwater to negatively charged Pt(IV) (as $\text{PtCl}_5(\text{OH})^{2-}$) species in seawater. Such behaviour during estuarine mixing can play an important role in Pt mobilization from contaminated particles discharged into estuaries and coasts.

Keywords

Platinum, Estuaries, Particle-water interactions, Chemical speciation, Pontevedra Ria, NW Iberian Peninsula

1. Introduction

The geochemical behaviour of Pt in the aquatic environment is not yet fully understood, despite recent scientific efforts in this matter initiated after the introduction of catalytic converters in cars - containing Pt and other platinum group elements (Pd, Rh) - during the late 70's in the USA and late 80's in Europe (Rauch and Morrison 2008). Apart from the emission derived from catalytic converters, hospitals also represent a source of platinum into the environment, though to a lesser extent (Ravindra et al. 2004), due to the use of several platinum compounds as anti-tumor drugs. The available studies so far have shown: (i) elevated Pt concentrations well above background values in sediments, water bodies and biota at sites under vehicular traffic pressure (Ravindra et al. 2004); (ii) that emitted particles containing Pt - mainly as elemental or oxide forms - are subject to mobilization through interaction with natural organic and inorganic ligands and bacterial activity (Dahlheimer et al. 2007), and (iii) evidence for a long-range transport of Pt from the emission sources (Barbante et al. 2001).

The vast majority of the studies on the geochemistry of platinum in the aquatic environment have focused on freshwater urban systems, leaving an important gap in our current knowledge on Pt concentrations and behaviour in marine systems. Values of dissolved Pt have been reported for the Pacific (Goldberg et al. 1986), Indian (Jacinto and van den Berg 1989) and Atlantic (Colodner et al. 1993) oceans, with concentrations ranging from 0.2 to 1.6 pM. In these studies, concentrations invariant with depth in the North Atlantic (Colodner et al. 1993) were reported; a scavenged-type profile in the Indian Ocean (Jacinto and van den Berg, 1989) was observed, whereas for the Pacific the two available studies show discrepant behaviour: recycled-type (Goldberg et al. 1986) and conservative (Colodner 1991). As noted by other authors (e.g. Donat and Bruland 1995), the behaviour of platinum derived from these studies is not oceanographically consistent with respect to their basin-to-basin variation, suggesting the possibility of error in some of the data. No further studies have been carried out since then with the aim of resolving this apparent anomaly. Regarding estuarine and coastal systems, the data available are mainly restricted to the sedimentary contamination of Pt in areas subject to anthropogenic pressure (e.g. Tuit et al. 2000; Cobelo-García et al. 2011). The works by Turetta et al. (2003) and Obata et al. (2006) constitute the only existing studies to date reporting dissolved Pt values in estuarine waters; in their study, they found concentrations of dissolved Pt in two estuaries of the Tokyo area (Japan) and in the lagoon of Venice (Italy) that were 1-2 orders of magnitude greater than those reported for oceanic waters. However, the few data available impedes the characterization of the factors controlling the behaviour of Pt during estuarine mixing and its particle-water interactions and therefore its transport and fate in the coastal ocean.

To this aim, we report here the concentrations of dissolved and particulate Pt in samples collected during two estuarine transects in the Lérez Estuary (Pontevedra Ria, NW Iberian Peninsula). Results are discussed in terms of characterizing (i) the behaviour of Pt in an estuarine system subject to anthropogenic influence; and (ii) particle-water interactions and their implication for the mobility of Pt in coastal systems. Speciation calculations using thermodynamic data will be given to aid interpretation of the results.

2. Material and Methods

2.1 Study Site

The estuary of the Lérez River is situated in the innermost area of the Pontevedra Ria (NW Iberian Peninsula; Figure 1), with a watershed lithology dominated by granites (Carral et al. 1995). The Lérez River has an extension of 57 km and occupies a drainage basin of 500 km². In the Lérez River basin there is a population of approximately 17,900 inhabitants,

flowing into the city of Pontevedra with a population of 74,900 (www.ine.es). The mean Lerez River flow ranges from 2 to 80 m³ s⁻¹, following a pattern similar to the rainfall: high flows from December to March with a maximum in February and minimum in September. The river presents a mean flow of 21.2 m³ s⁻¹ and an average flow per unit area of 47 L s⁻¹ km⁻² (Ibarra & Prego, 1997). The estuary ranges from the Lerez River outflow (freshwater end-member) at the ria head to approximately around the Tambo island representing the saline end-member (Figure 1). Note that the high-salinity region of the estuary is situated well inland in the inner part of the ria, as is typical for the Galician ria systems (Cobelo-García et al. 2003).

The existing data (Antelo, 1992) indicate that the Lerez River, before the outflow at the city of Pontevedra, is a non-contaminated river with respect to both biological quality and physico-chemical characteristics. However, after the river outflow there are several urban and industrial sewage inputs to the estuary, leading to an increase in metal concentrations within the estuary, especially in the high-salinity region (Cobelo-García et al. 2003; Cobelo-García and Prego 2003).

2.2 Sampling

Sampling in the Lerez Estuary (Pontevedra Ria, NW Iberian Peninsula; Figure 1) was done at high tide on 16th April 2008 and 6th May 2011 onboard a rubber boat. For the analysis of Pt, surface (<0.5 m depth) samples were collected using 1L LDPE bottles (Nalgene), which were previously acid-washed using established trace metal clean protocols (e.g. EPA Method-1669, 1996). For the determination of dissolved organic carbon (DOC) and particulate organic carbon and nitrogen (POC and PON), samples were collected in 1-2 L glass bottles with PTFE flat liner caps (Aldrich). Glass bottles were previously acid washed (HCl 10%), rinsed with MQ and combusted at 450 °C for 12 h, and then double-bagged. Salinity, temperature and pH were measured in-situ using calibrated sensors (WTW Multiline P4 and Mettler Toledo SevenGo pH).

All sample processing was carried out in a laminar flow bench (ISO-5) housed inside an ISO-7 lab. Samples for Pt determination were filtered using an acid-cleaned Nalgene filtration unit and acid clean 0.2 µm polycarbonate (PC) membranes (Millipore). Filtered samples were acidified to pH 1.0 using HCl (Fluka, Trace Select) and filters stored frozen in plastic Petri dishes. Aliquots for DOC analysis were obtained by syringe filtration (glass syringe, Aldrich) using 25 mm GF/F filters (Acrodisc) and collected in acid-washed and combusted 30 mL glass vials with PTFE-lined caps (Aldrich). These aliquots were acidified to pH 2 (HCl Trace Select, Fluka) and frozen pending analysis. For POC and PON analysis, samples were filtered using a pre-combusted glass filtration unit (Sigma-Aldrich) and pre-combusted 47 mm GF/F filters (Whatman). Filters were stored frozen in plastic Petri dishes. Blank samples for all measurements were obtained using the same procedures.

Surface sediment samples of the estuarine area were collected in 2011 using a van Veen grab sampler at the stations indicated in Figure 1, wet-sieved through a 63 µm mesh and dried at 60°C until constant weight.

2.3 Analysis

Dissolved Pt was analyzed by means of catalytic adsorptive cathodic stripping voltammetry (Cat-AdCSV) using a modification of the method proposed by van den Berg and Jacinto (1988). Since this method may underestimate to some extent the Pt concentrations if organic matter is not properly decomposed by UV irradiation before analysis (Obata et al. 1996), the efficiency of Pt recovery using our 125-W high-pressure mercury lamp was checked at several digestion times (Figure 2) using a water sample from the Vigo Ria (NW Iberian Peninsula; 42°13'45"N; 08°46'01"W; Salinity ~ 32) with a DOC concentration of approx. 85 µM. Here we obtained a plateau in Pt concentrations after 2-h irradiation (Figure 2); this is lower than the 4-h irradiation time reported by Obata et

al. (2006) using a 400-W low-pressure lamp for waters of Tokyo Bay estuaries, but higher than the 30-min irradiation time necessary for a complete Pt recovery in urban waters using a 400-W high-pressure mercury lamp (Monticelli et al. 2010).

In this study, therefore, samples were UV irradiated in capped silica tubes for 2 hours using a 125-W high-pressure mercury lamp. After digestion, sulphuric acid (final concentration 0.5 M; Trace Select, Fluka), formaldehyde (final concentration 3.5 mM; Riedel-de-Haen) and hydrazine sulphate (final concentration 0.45 mM; Fluka) were added. Samples were then transferred to a PTFE voltammetric cell and a deposition potential of -0.3 V (vs. Ag/AgCl) was applied for 5-30 minutes depending on platinum concentrations. After a quiescence of 10 s, the potential was scanned to -1.1 V in the differential pulse mode and the Pt peak at about -0.90 V quantified. A Metrohm 663 VA polarographic stand (Herisau, Switzerland), equipped with a HMDE (working electrode), a Ag/AgCl (reference electrode) and a glassy carbon rod (auxiliary electrode) was used. The detection limit of the technique, expressed as three times the standard deviation of the blanks, was 0.02 pM. Given that there is no water reference material for Pt at present, the accuracy of the analytical procedure was checked by means of the analysis of spiked river, estuarine and oceanic waters; being aware of the slow reaction kinetics of Pt, spiked samples were allowed to equilibrate for a week before digestion and analysis. Concentrations obtained in the spiked samples (Table 1) show complete Pt recovery.

The determination of platinum in the 0.2 μm PC filters was also undertaken by means of Cat-AdCSV after combustion of the filter followed by acid digestion according to the methodology described in Cobelo-García et al. (2011). A typical detection limit of 0.5 ng g⁻¹ (expressed as 3xSD of the blank) was obtained for a suspended particulate matter (SPM) mass of 1 mg. A similar approach was used for the analysis of sediments (Cobelo-García et al. 2011). The accuracy was checked using river sediment (JSd-2; Geological Survey of Japan) and tunnel dust (BCR-723) certified reference materials, obtaining recoveries higher than 80% (JSd-2) and 95% (BCR-723).

The analysis of DOC, POC and PON was carried out using standard procedures as described in Gago et al. (2005). Dissolved Fe was determined using a voltammetric procedure similar to that described in Obata and van den Berg (2001).

3. Results and Discussion

3.1 Ancillary parameters

The variation of pH with salinity shows an increase from the freshwater end-member – pH = 6.6-6.8, which is typical of unpolluted streams draining granitic watersheds (Meybeck and Helmer 1989) – reaching a plateau of pH = 8.0-8.2 from mid-salinities to the seawater end-member (Figure 3a). The SPM recorded in the freshwater end-member (5.7 mg L⁻¹ in 2008 and 0.1 mg L⁻¹ in 2011, Table 2) corresponds to the low-end values for pristine streams (Meybeck and Helmer 1989). In the 2008 data, an exponential decrease of SPM with salinity is observed, whereas in 2011 there is no trend with salinity and the SPM remains generally below 1.5 mg L⁻¹ (Figure 3b). The higher SPM load in the 2008 sampling probably reflects a higher terrestrial runoff contribution due to the rainfall recorded in the previous week, which was absent on the 2011 sampling date (Figure S1). This is also suggested by the higher freshwater particulate C:N ratios in the 2008 sampling, which decrease towards saline waters; in 2011 no such elevation in the freshwater C:N ratios was observed (Figure 3f).

The remarkably low freshwater end-member DOC concentrations (around 60 μM ; Table 2), which are characteristic of the rivers draining into the Galician Rias (e.g. Gago et al. 2005), produce a pattern where DOC values increases towards more saline (and productive) waters (Figure 3d); such behaviour is opposite to most of the World estuaries fed by more organic-rich rivers (World DOC average of 400 μM ; Sedell and Dahm 1990).

Similarly to DOC, POC – in μM – increases down-estuary being especially evident in the 2008 transect (Figure 3e). Analysis of photosynthetic pigments revealed diatom predominance in the planktonic community of the seawater end-member (J.L. Garrido, pers. comm.).

Dissolved Fe (Figure 3c) decreases to some extent from the freshwater end-member to salinities of about 10-15, but its distribution is clearly affected by inputs at higher salinities (15-30). The inputs at high salinities in this estuary have been reported for other metals (e.g. Cobelo-García and Prego 2003) as a result of a greater influence of anthropogenic pressure in the lower part of the estuary.

3.2 Levels of platinum in water, suspended particulate matter and sediments

Platinum is one of the least abundant elements on Earth, with typical concentrations in the upper continental crust of about 0.5 ng g^{-1} (Rudnick and Gao 2003). In estuarine and coastal sediments, background values on the order of $0.3\text{-}0.6 \text{ ng g}^{-1}$ have been reported for Massachusetts Bay (USA; Tuit et al. 2000) and the Tagus Estuary and Prodelta (Portugal; Cobelo-García et al. 2011). The values of Pt in sediments of the Lérez Estuary found in this study show, in general, a clear enrichment compared to these background values (Figure 4), with an average concentration ($1.2 \pm 0.5 \text{ ng g}^{-1}$; $n=13$) which corresponds to an enrichment factor of 2-4. Sediment Pt concentrations are in the range of those found in the SPM during the 2011 sampling ($2.1 \pm 2.4 \text{ ng g}^{-1}$, $n=15$), but significantly lower than in 2008 SPM ($8.0 \pm 4.4 \text{ ng g}^{-1}$, $n=15$; Table 2). Higher dissolved Pt concentrations (Figure 5) were also found in 2008 (0.21 and 0.62 pM in the freshwater and seawater end-member, respectively) compared to the 2011 campaign (0.03 – freshwater – and 0.40 pM – seawater end-member; Table 2). Despite of elevated values of particulate platinum, it accounts on average for only $33 \pm 17 \%$ and $15 \pm 13 \%$ of total platinum (dissolved + particulate; Figure 5) due to low SPM in the estuary – which is generally below 2 mg L^{-1} (Figure 3b).

The extremely low value for the freshwater end-member in 2011 – which is close to the detection limit of the technique used – appears to be among the lowest Pt concentrations ever reported in the literature (Table 3). Accordingly, values of dissolved Pt of the order of the ones found for river water in this study have only been reported in pre-industrial (7260-7760 BP) Greenland ice cores ($0.04 - 0.08 \text{ pM}$; Barbante et al. 1999), in rain samples from the Seoul metropolitan area ($0.01\text{-}0.34 \text{ pM}$; Soyol-Erdene et al. 2011) and in the lower limit of rain samples collected in the suburban Tokyo area (range: $<0.15 - 2.9 \text{ pM}$; Shimamura et al. 2007) and in Greenland recent (1969-1988) snow core samples (range: $<0.04 - 3.2 \text{ pM}$; average: $0.87 \pm 0.97 \text{ pM}$; Barbante et al. 1999). Also, Soyol-Erdene and Huh (2012) have recently reported dissolved Pt concentrations in major rivers of East Asia, finding average concentrations down to 0.18 pM and for some samples values below 0.1 pM .

These estuarine dissolved Pt values are, however, 1-2 orders of magnitude lower than those obtained in the estuaries of the Tama and Ara rivers in Tokyo and in the lagoon of Venice (Obata et al. 2006; Turetta et al. 2003; Table 3) – which constitute the only reported data of dissolved Pt in estuarine waters to date – reflecting the considerably higher anthropogenic emissions compared to our study area.

3.3 Estuarine behaviour of dissolved and particulate Pt

Non-conservative behaviour of Pt during estuarine mixing (Figure 5) was observed on both sampling dates. Concentrations in the seawater-end members exceed those of typical North Atlantic waters, suggesting inputs of this element within the estuary (as observed also for dissolved Fe; Figure 3c). The higher terrestrial runoff contribution in the 2008

sampling, indicated by the amount of suspended particles and C/N ratios as explained in section 3.1, agrees with the systematically higher Pt concentrations observed compared to 2011. The clear dissolved Pt removal found in the low-salinity (<2 ppt) region in 2008 is, surprisingly, not accompanied by an increase in Pt particulate concentrations (as ng g⁻¹; Figure 5). Conversely, however, the Pt concentration in the suspended particles follows the same decreasing trend, which indicates the absence of a net transfer of Pt from the dissolved form to the SPM, suggesting a flocculation and sedimentation mechanism of a major fraction of the dissolved and particulate matter in which Pt is contained. The lack of a similar behaviour in the 2011 transect and the unknown estuarine behaviour in other World areas precludes, however, a generalization of a removal mechanism(s) in the low-salinity region of estuarine systems.

Particle-water interactions of Pt during estuarine mixing were quantified in terms of a distribution coefficient, K_D (L kg⁻¹), defined as the ratio of particulate metal on a w/w basis to aqueous metal on a w/v basis (Cobelo-Garcia et al. 2008). Note that we use a cutoff of 0.2 μ m to discriminate phases and therefore, relatively large, colloidal-sized Pt may be encompassed in the aqueous phase by this parametrization (Schijf and Zoll 2011). Particle-water distribution coefficients shows a decrease with salinity in both transects (Figure 5), but especially evident in the 2011 transect; here the relationship between K_D and salinity (S) was modeled using the simple power law (Turner et al. 2004): $K_D^{SW} = K_D^{FW}(S + 1)^{-b}$, where K_D^{FW} and K_D^{SW} are the distribution coefficients in fresh water and saline water, respectively, and b is a data-fitted constant. The lack of such a relationship in the 2008 transect is unclear but may be induced by the higher proportion of anthropogenic material in the suspended load – as evidenced by the elevated Pt particulate concentrations – presenting different particle-water partitioning. To this aim, further work on other World estuaries with varying anthropogenic pressure is planned, to fully characterize Pt partitioning during estuarine mixing.

The decrease in Pt particle-reactivity during estuarine mixing observed in both transects requires an increase in the proportion of negatively charged Pt species that have relatively little affinity for the negatively-charged particle surface. Here, we have calculated Pt speciation in natural waters derived from the available thermodynamic data in the literature to check whether it is in agreement with the observed estuarine behaviour. In natural waters, Pt may be present in two oxidation states (II and IV). In seawater, the dominant inorganic forms of Pt(II) and Pt(IV) are $PtCl_4^{2-}$ and $PtCl_5(OH)^{2-}$, respectively (Cosden and Byrne 2003; Gammons 1996). The equilibrium between Pt(II) and Pt(IV) can then be described by:

In order to obtain the stability constant for reaction (1), the standard Gibbs free energy of formation (ΔG_f^0) for $PtCl_4^{2-}$ and $PtCl_5(OH)^{2-}$ were calculated from (4) and (5) using the data reported by Ginstrup (1972), Shelimov et al. (1999), Elding (1978) and Nikolaeva et al. (1965):

resulting in a ΔG_f^0 ($PtCl_5(OH)^{2-}$) = -137.8 kcal mol⁻¹ and ΔG_f^0 ($PtCl_4^{2-}$) = -90.4 kcal mol⁻¹. Using these values, we obtain a ΔG_r^0 for reaction (1) of -16 kcal mol⁻¹. The stability constant for (1) is then derived from:

$$\log K = -\Delta G_r^0/2.3RT \quad (6)$$

resulting in a $\log K_1 = 11.7$ and

$$\log([PtCl_5(OH)^{2-}]/[PtCl_4^{2-}]) = 11.7 + \log[Cl^-] - 1/2\log fO_2 - pH \quad (7)$$

In typical seawater conditions ($fO_2 = 0.2$ atm and $[Cl^-] = 0.56$ M), this ratio becomes:

$$\log([PtCl_5(OH)^{2-}]/[PtCl_4^{2-}]) = 11.1 - pH \quad (8)$$

indicating that at typical seawater pH (7.5-8.4), Pt(IV) predominates over Pt(II). This thermodynamic prediction on the redox chemistry of Pt in seawater is also supported by the work of Cosden et al. (2003), who observed the partial rapid (~1 hour) oxidation of Pt(II) spiked to seawater to Pt(IV) in the presence of the macroalgae *Ulva lactuca* L.

In freshwater, the thermodynamic data available (Wood et al. 1989; Kalabina 1983) indicates that the dominant forms of Pt are $Pt(OH)_2$ for Pt(II) and $Pt(OH)_5^-$ for Pt(IV). Here, the equilibrium between these two species is given by:

The stability constant for reaction (9) was obtained from the ΔG^0_f for $Pt(OH)_2$ and $Pt(OH)_5^-$ calculated from (10) and (11) using the data reported by Ginstrup (1972), Kalabina (1983) and Wood et al. (1989):

resulting in a $\Delta G^0_f (Pt(OH)_5^-) = -161.6$ kcal mol⁻¹ and $\Delta G^0_f (Pt(OH)_2) = -59.5$ kcal mol⁻¹. Using these values, we obtain a ΔG^0_r for reaction (9) of 11.3 kcal mol⁻¹ and a $\log K_9 = -8.3$; therefore the ratio (at $fO_2 = 0.2$ atm):

$$\log([Pt(OH)_2]/[Pt(OH)_5^-]) = 8.7 - pH \quad (12)$$

indicates that for typical freshwater pH, $Pt(OH)_2$ predominates over $Pt(OH)_5^-$. It appears, therefore, that during estuarine mixing the shift in the chemical speciation of Pt involves both the transfer from neutral to negatively charged species, in accordance with the estuarine behaviour observed in this study, but also a change in its redox state. It has to be noted, however, that there is a significant uncertainty in the available stability constants (e.g. hydroxide complexes of Pt(IV); Kalabina 1983) so these speciation calculations should be considered provisional at best.

The decrease of Pt particle-reactivity with salinity was also observed in a previous study using water samples from the Tugela river estuary (South Africa; Cobelo-Garcia et al. 2008), although the magnitude of K_D values reported in the present study is around two orders of magnitude greater. Such differences may be explained by (i) a different chemical reactivity of particles in these two systems and/or (ii) the different experimental approach used in Cobelo-Garcia et al. (2008), where K_D 's were obtained after equilibration for 48 h of samples spiked with Pt(IV); accordingly, owing to the slow reaction kinetics of Pt (e.g. Cosden and Byrne 2003), the K_D values reported in Cobelo-Garcia et al. (2008) may have been underestimated due to incomplete equilibration of the added Pt with particles at the end of the incubation period.

The observed behaviour of Pt is similar to that of other elements (e.g. Cd) whose predominant chemical forms become less reactive during estuarine mixing (Turner et al.

2004). These elements are commonly observed to desorb from suspended particles as they cross the estuarine interface (Comans and van Dijk 1988), and this may be the case for Pt in estuaries, especially in those fed by anthropogenically-impacted freshwater inputs, provided that it is held sufficiently loosely (and exchangeable) at the particle surface. This would explain, for example, the mid-estuarine peaks of dissolved Pt that have been reported in estuarine samples of Tokyo Bay (Obata et al. 2006).

4. Conclusions

The marine chemistry of platinum is one of the least understood among those of the trace metals, and its oceanic budget is poorly constrained. Continental runoff is supposed to have a significant influence on the global Pt budget in the oceans – especially linked to the current anthropogenic emissions – but the paucity of studies reporting its concentrations in rivers and the processes influencing its transport, transformation and fate in estuaries and coastal systems impedes an appropriate estimation of fluxes across the land-ocean interface.

The results presented in this study provide new and valuable information regarding the concentrations of Pt and its chemical speciation and reactivity in estuaries. Accordingly, (i) the concentrations reported for the Lézé river estuary (0.03-0.62 pM) are about two orders of magnitude lower than those previously available for estuarine waters, indicating a significant variability – due to natural and/or anthropogenic factors – of its concentrations at a global scale; (ii) this study, the first determining ambient dissolved and particulate Pt concentrations, confirms the decrease in Pt particle-reactivity across the salinity gradient. The transfer from neutral Pt(II) ($\text{Pt}(\text{OH})_2$) to Pt(IV) negatively charged ($\text{PtCl}_5(\text{OH})^{2-}$) forms predicted by speciation calculations, assuming the available stability constants in the literature for Pt(II) and Pt(IV) complexes are correct, agrees with the experimentally observed particle-reactivity. Such a decrease in particle-reactivity during estuarine mixing can play an important role in Pt mobilization from contaminated particles discharged into estuaries and coasts, provided that it is held sufficiently loosely, thereby increasing the inputs of dissolved Pt into the oceans.

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FIGURE CAPTIONS

Figure 1. Map showing the location of the estuary of the Lérez River in the Pontevedra Ria (NW Iberian Peninsula). Dots and numbers in the expanded map indicate the stations where sediment samples were collected.

Figure 2. Effect of the UV irradiation time using a 125W high pressure mercury lamp on platinum concentration obtained in a sample taken in the Vigo Ria, NW Iberian Peninsula ($42^{\circ}13'45''\text{N}$; $08^{\circ}46'01''\text{W}$; $S \sim 32$, $\text{DOC} \sim 85 \mu\text{M}$).

Figure 3. Variation of pH (a), suspended particulate matter (SPM; b), dissolved Fe (c), dissolved organic carbon (DOC; d), particulate organic carbon (POC; e), and particulate C/N ratios (f) accros the salinity gradient in the 2008 (filled circles) and 2011 (empty circles) sampling dates.

Figure 4. Platinum concentrations in surface sediments taken on 05/06/2011 at the stations indicated in Figure 1. The shaded area represents the background platinum concentrations range obtained from Massachusetts Bay and the Tagus Estuary (Tuit et al. 2000; Cobelo-García et al. 2011), whereas the dashed line indicates the average platinum crustal abundance (Rudnick and Gao, 2003).

Figure 5. Variation of dissolved ($<0.2\mu\text{m}$) and total (dissolved + particulate) Pt (upper row), particulate Pt (ng g^{-1} ; middle row) and particle-water distribution coefficients (lower row) during estuarine mixing for the 2008 (left column) and 2011 (right column) sampling dates. Average dissolved Pt concentrations in the North Atlantic from Colodner (1991).

Supporting Information

Figure S1. Recorded precipitation during the month prior to each sampling date, indicated by arrows (taken from www.meteogalicia.es)

Table 1. Results of the recovery experiments. The river water sample corresponds to the freshwater end-member of the Lérez river estuary collected in the 2011 sampling of this study. The estuarine water was collected in the Vigo Ria (NW Iberian Peninsula; 42°13'45"N; 08°46'01"W; S ~ 32) and the Oceanic water at the North Atlantic BATS Station (31°46'N, 64°05'W).

Sample	Ambient Pt (pM)	Spiked Pt (pM)	Obtained Pt (pM)	Recovery (%)
River Water	~0.03	0.21	0.23 ± 0.01	96 ± 4
Estuarine Water	0.52 ± 0.03	0.52	1.09 ± 0.05	105 ± 4
Oceanic Water	0.15 ± 0.01	0.55	0.71 ± 0.07	101 ± 10

Table 2. Concentrations of suspended particulate matter (SPM), dissolved and particulate organic carbon (DOC & POC) and dissolved (<0.2 μm ; Pt_D) and particulate (>0.2 μm ; Pt_P) Pt found in the Lrez River estuary.

	Salinity	SPM (mg L^{-1})	DOC (μM)	POC (μM)	Pt_D (pM)	Pt_P (ng g^{-1})
<i>16th April 2008</i>						
	0.0	5.7	58.7	18.1	0.21	9.6
	0.1	4.9	58.8	18.7	0.23	5.3
	0.2	2.4	59.1	14.9	0.19	4.6
	0.5	2.4	63.3	21.2	0.04	3.2
	1.0	2.9	59.3	15.3	~0.02	3.1
	1.7	1.1	64.5	15.0	~0.03	1.5
	3.0	2.9	74.8	14.1	0.06	4.1
	4.4	1.5	70.9	14.8	0.18	15.7
	4.8	1.4	85.2	14.7	0.21	10.8
	6.7	1.0	82.2	20.9	0.18	11.5
	8.7	1.1	76.3	19.8	0.16	8.2
	10.6	2.0	83.1	25.6	0.13	9.0
	16.5	0.7	83.4	51.2	0.18	15.1
	27.4	1.1	87.2	40.1	0.49	6.9
	32.0	0.8	86.1	28.4	0.62	12.2
<i>6th May 2011</i>						
	0.0	0.1	56.8	8.8	~0.03	7.8
	0.2	0.7	-	11.8	0.05	0.7
	0.4	0.5	55.8	10.1	~0.01	0.7
	0.8	0.9	-	-	0.04	8.1
	2.4	0.7	52.6	9.2	~0.02	0.9
	3.0	0.8	-	-	~0.03	1.4
	3.3	1.0	62.7	34.1	~0.03	1.1
	4.4	0.6	-	-	~0.02	1.9
	6.2	0.8	58.9	16.5	~0.02	1.0
	8.5	0.6	-	-	0.10	1.6
	12.1	1.1	67.1	19.0	0.16	0.8
	15.0	1.0	-	-	0.13	1.2
	17.8	2.5	74.7	18.8	0.07	1.4
	21.0	1.3	-	19.4	0.26	1.1
	29.2	0.8	77.9	20.0	0.40	1.5

Table 3. Comparison of dissolved average Pt concentrations found in this study with literature values reported for different water matrices. Numbers in brackets indicate the range of values.

Type of sample		Number of samples	Pt (pM)	Reference
<i>Snow and Ice</i>	Greenland ice (7260-7760 years BP)	2	0.05 (0.04-0.08)	Barbante et al. (1999)
	Greenland recent snow (years 1969-1988)	22	0.87 ± 0.97	Barbante et al. (1999)
	Antarctic surface snow (years 1969-1995)	5	4.2 ± 1.8	Barbante et al. (1999)
<i>Rain</i>	Rain from suburban Tokyo (Japan)	20	0.7 ¹ (<0.15-2.9)	Shimamura et al. (2007)
	Rain from Seoul metropolitan area (Korea)	20	0.10 (0.01-0.34)	Soyol-Erdene et al. (2011)
<i>River water</i>	Lérez River (Pontevedra, Spain)	2	0.12 (0.03-0.21)	This study
	Major rivers of East Asia	200	0.36 (<0.1-5.8)	Soyol-Erdene and Huh (2012)
	Tama and Ara Rivers (Tokyo, Japan)	2	20 (9-31)	Obata et al. (2006)
	Urban channel (Como, Italy)	6	7.6 ± 3.8	Monticelli et al. (2010)
<i>Fountains</i>	Urban fountains (Madrid, Spain)	3	17 ± 5	Moldovan et al. (2003)
<i>Sewage</i>	Sewage effluents (Munich, Germany)	20	113 ± 106	Laschka and Nachtwey (1997)
<i>Estuarine water (S>20)</i>	Estuaries of the Tama and Ara rivers (Tokyo, Japan)	3	6.5 ± 2.8	Obata et al. (2006)
	Lérez River estuary (Pontevedra, Spain)	4	0.44 ± 0.15	This study
	Lagoon of Venice (Italy)	3	1.2 (1.0-1.5)	Turetta et al. (2003)
<i>Oceanic water</i>	North Atlantic (BATS Station ²) 0-4000 m	19	0.26 ± 0.08	Colodner (1991)

¹median; ²32°10'N, 64°30'W

Figure(s)

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