Osmium and Platinum Decoupling in the Environment: Evidences in Intertidal Sediments (Tagus Estuary, SW Europe)

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ABSTRACT:

Catalytic converters in automobiles have significantly increased the input of platinum group elements (PGEs) to the environment and their coupled geochemical behavior has been proposed. To check this hypothesis, Pt and Os concentrations and $^{187}Os/^{188}Os$ ratios were determined in sediment cores and interstitial waters from the Tagus Estuary (SW Europe) affected by different traffic pressure.

Platinum concentration in surface sediments nearby the high traffic zone (up to 40 $ng \cdot g^{-1}$) indicated severe contamination. Although lower than Pt, Os enrichment was also observed in surface sediments, with lower $^{187}Os/^{188}Os$ ratios than in deeper layers. Dissolved Pt and Os in interstitial waters, 0.1-0.7 pg g^{-1} and 0.03-0.10 pg g^{-1} respectively, were higher than in typical uncontaminated waters. Results indicate two sources of Pt and Os into the Tagus Estuary salt marshes: a regional input associated with industrial activities, fossil fuel combustions and regional traffic; and a local source linked to nearby traffic density emissions. Estimations of Os and Pt released by catalytic converters support this two-source model. Differences in geochemical reactivity and range of dispersion from their sources lead to a decoupled behavior of Os and Pt, questioning the use of Os isotopes as proxies of PGE sources to the environment.

1. INTRODUCTION

Platinum group elements (PGE: ruthenium, rhodium, palladium, osmium, iridium and platinum) are amongst the least abundant elements in the upper continental crust, where their typical concentrations range from 20 pg g^{-1} (Ir) to 500 pg g^{-1} (Pt, Pd)[1]. These elements are relatively enriched in the Earth's mantle, and mantle-derived rocks host some of the largest PGE deposits in the World (e.g. Bushveld Complex[2] and Noril'sk[3]). The use of PGE in several human activities is increasing their environmental concentrations[4,5]; accordingly, it has been estimated that 86-98% of PGE total flux at Earth's surface derives from anthropogenic activities[6]. One of the main application of PGE (especially Pt, Pd and Rh) is their use in automobile catalytic converters in order to reduce the emissions of CO, NO_x and SO_2[7]. This industrial application has been greatly responsible for an exponential increase of the PGE demand over the past 40 years[8]. A catalytic converter emits during its lifetime microparticles (1-63 μm[9]) covered by tiny fragments (<0.3 μm down to the nanoparticle size[10]) of Pt, Pd, and Rh as active components[11], and include smaller amounts of Os, Ir, and Ru as impurities[12]. As a result, elevated PGE concentrations are generally found in areas close to high traffic density, especially within ~2 m near the road[12–16]. Evidence for a global scale PGE contamination has also been observed in ice from Greenland and Antarctica[17,18].

Several studies have characterized the anthropogenic contribution of PGE in the environment using the Os isotope signature ($^{187}Os/^{188}O$)[19–24] taking advantage of the $^{187}Os/^{188}Os$ ratio as a tracer of a variety of anthropogenic and natural sources[1,19,20,25,26]. For example, the typical $^{187}Os/^{188}Os$ ratios of the PGE ores associated with mantle-derived rocks, like the Bushveld complex[2], are 0.10 - 0.20[27] while ratios from the upper continental crust are 1.05 ± 0.23[1], allowing the estimation of the Os anthropogenic

63 fraction in environmental samples[23,25,25,26]. Assuming that Os and other PGE derive
64 from the same anthropogenic sources, the Os isotopic composition has been used to
65 estimate the anthropogenic fraction of Pt, Pd, and Rh, mainly in urban
66 environments[19,21,22,24]. It has been suggested, however, that the anthropogenic Os
67 source(s) to the environment may be decoupled from the sources affecting other PGE
68 mainly due to the volatility of Os tetraoxide[26]. Therefore, the Pt, Pd, and Rh estimation
69 of anthropogenic contribution may be erroneously based on Os isotope signature[26]. A
70 recent example of this decoupling is seen in the samples of PM_{10} aerosols from Cape
71 Cod (USA)[5] displaying Ir/Os ratios that are much greater than a natural ratio of ~1.

72 This study was designed to investigate the extent to which Pt is decoupled from Os in
73 natural environments, especially in such complex systems like salt marshes, a transition
74 environment between the continent and the ocean, where important physico-chemical
75 processes occur. Besides, salt marshes systems are particularly vulnerable to global
76 change and the sea level rise, and their characterization is taking an especial relevance.
77 We studied salt marsh sediments from the Tagus Estuary (SW Europe) that are subject
78 to different degrees of traffic influence[13] and where the geochemistry of other trace
79 elements has been well-characterized[28–30]. The main aims of this research are: (1) to
80 better understand the geochemical behavior of Pt and Os in salt marshes; (2) quantify
81 the anthropogenic source of Pt and Os in sediments and interstitial waters from salt
82 marshes affected by different traffic impact; and (3) assess the coupling/decoupling
83 behavior of anthropogenic Pt and Os.

84 **2. MATERIAL AND METHODS**

85 ***2.1. Study area***

The Tagus Estuary, Portugal (SW Europe; Figure 1) is one of the largest estuaries in Europe, with an extension of 320 km^2 and a volume of 1900 Hm^3. The estuary is a mesotidal system, where tidal water inundates large extensions of salt marshes on a semidiurnal scale. Intertidal areas, including salt marshes, comprise around 40% of the estuary. The Lisbon city is located at the northern margin but the whole estuary is subjected high human pressure with around 3 million inhabitants living in this area, several industries (chemicals, petrochemicals, fertilizers and pesticides) settled in the margins[31].

Cores were collected from two stations in the intertidal salt marshes at the southern bank of Tagus Estuary, with different traffic pressure (Figure 1). High Traffic Station – *Samouco* salt marsh– is located nearby a 17.2 km long motorway bridge that has been operational since April 1998 with a daily average of 50,000 vehicles[32]. Past anthropogenic activities in the area were negligible. Low Traffic Station –*Rosario* salt marsh– is located nearby an important industrial area in the past, the Barreiro Chemical Complex; this was one of the first heavy chemical plant industries in Portugal, established around 1900 and its contaminating effects have been previously reported[33,34]. The highest industrial activity in this complex was between 1940's and 1970's. The world crises in the 1980's lead to the closure of some industries while other were transformed for optimization purposes[34]. In the last period a pyrite roasting plant operated in the complex (1990[34]), attempted to implement a method to extract Pt, Au and Ag but the industrial processes were in an early stage of development and the low yield make it a failure. Waste water treatments only started to be build up in the 1990's and the most recent one, which covers this area (from Barreiro to Moita) did not start until 2013. Thus in the last 2 decades no activity related with pyrite roasting operated in

110 the chemical complex of the Tagus estuary. Furthermore, the traffic pressure nearby the
111 Rosario salt marsh (Low Traffic Station) area is low.

112 ***2.2. Sampling***

113 Several 20 cm long cores were sampled in the intertidal area of both salt marshes in
114 March 2011 (Low Traffic Station) and September 2011 (High Traffic Station).
115 Sediment cores were sectioned in situ every 2 cm in the first 10 cm and every 3 cm
116 between 10 and 20 cm depth. Each sample was stored in acid-clean high-density
117 polyethylene bottles avoiding the air presence inside to minimize sediment oxidation.
118 Bridge-gullypot sediment, representing automobile dust, including dust from catalytic
119 converters, was also sampled at the High Traffic Station (Figure 1). Interstitial waters
120 were extracted by centrifugation at 8000 rpm for 30 minutes at +4°C, filtered through
121 0.45 µm polycarbonate membranes, stored in acid-clean low-density polyethylene
122 bottles and acidified using Suprapur©(Merck) HCl (pH≈1). A refractometer (Atago
123 S/Millα 0-100‰) was used to measure salinity in porewater. Sediment samples were
124 oven-dried (<60 °C) until constant weight and ground in an agate mortar. All materials
125 used were acid-cleaned and sample handling was done inside laminar flow hoods.
126 Procedural blanks were prepared using Milli-Q (Millipore) water.

127 ***2.3. Analytical methods***

128 Platinum was determined in sediments and interstitial waters by means of catalytic
129 adsorptive cathodic stripping voltammetry (catalytic AdCSV)[13,35,36]. For interstitial
130 waters, and in order to remove organic matter that may severely interfere during the
131 voltammetric determination of Pt, diluted (1:10) samples were UV-digested for 4 h as
132 described earlier[35] (see Figure S-1 for further details) in the presence of 22 mM H_2O_2

(TraceSelect© Ultra, Fluka). For interstitial waters, we obtained blanks of 0.003 ± 0.003 pg g^{-1} ($\overline{x} \pm SD$; *n=13*) and a detection limit ($x_{blank} + 3 \times SD_{blank}$) of 0.013 pg g^{-1} (Table 1). For sediments, the removal of organic matter was achieved by ashing the sediments (around 200 mg) at 800 °C in quartz crucibles[13]. Samples were then transferred to 30 mL Teflon® vessels with screw caps (Savillex) for digestion with 5 mL of concentrated HCl and 3 mL of concentrated HNO_3 (Merck Suprapur) at 195 °C (hot plate temperature) for 4 h. Following digestion, the vessel caps were removed and the acids evaporated at 195 °C to near dryness. The residue was re-dissolved with 1 mL of concentrated HCl and 1 mL of concentrated H_2SO_4 (Fluka Trace Select), evaporated at 195 °C until no fumes were observed and a near constant volume, comprising mostly H_2SO_4, was attained. This procedure removes remnant HNO_3 which interferes with the catalytic AdCSV Pt determination. Samples were cooled, diluted with 0.1 M HCl, syringe-filtered (0.45 µm) and made up to 25 mL in polypropylene volumetric flasks (see Figure S-1 for further details). The detection limit ($x_{blank} + 3 \times SD_{blank}$) for a typical mass of 200 mg of sediment was 37 pg g^{-1} (Table 1); the average blank value was 24 ± 4 pg g^{-1} (*n=10*). The accuracy was checked using road dust certified reference material (BCR-723[37]) and good agreement was obtained with the certified concentrations (Table 1).

Osmium concentration and isotopic composition in sediments and interstitial water were determined using negative thermal ionization mass spectrometry (N-TIMS) using previously established procedures at Dartmouth Radiogenic Isotope Geochemistry Laboratory for water [26,38,39] and for silicates [40,41]. For interstitial waters the procedure is described in brief as follows and outlined in the supporting information (Figure S-2). About 30 to 50 g water was weighed in a quartz glass tube ("Carius tube") and spiked

157 with ^{190}Os tracer solution. The sample was then frozen at −20 °C and placed in a High
158 Pressure Asher (HPA-S, Anton-Paar) immediately after adding 500 µL of *Jones*
159 *Reagent* ($Cr^{IV}O_3$ dissolved in 6 M H_2SO_4,) and heated to 300 °C with a confining
160 pressures of 128 bar for 16 hours. This step allows Os in the sample to equilibrate with
161 tracer Os via conversion to a common oxidation state (OsO_4). Once the sample cooled it
162 was removed from HPA-S and OsO_4 (boiling point = 135 °C) separated by distillation
163 and trapped in ice-chilled HBr. This step reduces OsO_4 to hexabromoosmate, which is
164 further purified by microdistillation[42]. Blank for this procedure was found to be 0.0013
165 ± 0.0006 pg g^{-1} ($\bar{x} \pm SD$) with an $^{187}Os/^{188}Os$ ratio of 0.368 ± 0.044 ($n=2$) (Table 1).

166 For determination of Os concentration and isotope composition of sediments, we
167 followed the method described by Chen *et al.* 2006[40] and Wu et al. 2013[41]. Briefly, ~0.5
168 g of rock powder was spiked with ^{190}Os tracer solution in a Carius tube and attacked
169 with reverse *aqua-regia* (3 mL HCl plus 5 mL HNO_3) into the HPA-S (300 °C, 128
170 bars, 16h). This procedure leaches out Os from the silicates and equilibrates it with
171 tracer Os by converting both a common oxidation state (OsO_4). Osmium tetraoxide is
172 then separated from bulk solution by solvent extraction with Br_2 (liquid) and purified
173 using microdistillation. Around 65 % of the Os is recovered by this procedure[40]. Blanks
174 were found to be 0.19 ± 0.07 pg g^{-1} with $^{187}Os/^{188}Os$ ratio of 0.288 ± 0.003 ($n=2$).

175 The Os fraction of the sample in 0.5 µL of HBr was loaded on the pre-cleaned Pt side
176 filament using a fine polypropylene tubing fitted on a Hamilton microsyringe and dried
177 at 0.8 A. The typical load was centered and 1–2 mm of the filament length. Three drops
178 of fresh $Ba(OH)_2$ emitter solution were loaded on top of the sample and dried. The
179 filament was then heated to 1.2 A for 6 s. Osmium isotopes were measured as OsO_3^- on
180 a Triton thermal ionization mass spectrometer (TIMS) using the double filament

geometry developed by Chen and Sharma (2009)[38]. The data were corrected for oxygen isotope composition, mass fractionation and [Os] estimated by isotope dilution. Repeated (n=20) measurements of 1 pg laboratory standard (Max Planck Institute Os-1 standard) gave an average $^{187}Os/^{188}Os$ =0.1067±0.1% (2σ RSD), which is within uncertainty of the established isotope value of 0.1069 for this standard. All reported $^{187}Os/^{188}Os$ ratios in this paper have a 2σ uncertainty of 2%. Table 1 provides some values of Os concentration and $^{187}Os/^{188}Os$ ratios for road dust reference materials[37] and compares our values with previous results[43] due to the absence of certified values.

Aluminum was determined by graphite furnace atomic absorption spectroscopy, after microwave digestion using a mixture of HCl, HNO_3 and HF[44]. Blanks, detection limit and reference materials for Al analysis[45] are given in Table 1.

2.4. Estimation of enrichment factors and anthropogenic fractions of osmium and platinum:

Enrichment factors for Os (EF_{Os}) and Pt (EF_{Pt}) with respect to local background levels (Table 2) were calculated using the following equation:

$$EF_{Pt\ or\ Os} = \frac{([Pt\ or\ Os]/[Al])_{sample}}{([Pt\ or\ Os]/[Al])_{local\ background}} \quad (1)$$

The anthropogenic fraction of Pt (AF_{Pt}, %) was calculated normalizing by Pt/Al instead of using Pt/Os ratios[25] to avoid the influence of coupled/decoupled behavior of Os and Pt by means of:

$$AF_{Pt}(\%) = \left(1 - \frac{([Pt]/[Al])_{local\ background}}{([Pt]/[Al])_{sample}}\right) x100 = \left(1 - \frac{1}{EF_{Pt}}\right) x100 \quad (2)$$

The equation proposed by Rauch[23,25] was used to calculate the anthropogenic fraction of Os (AF_{Os}, %), based on the isotopic compositions, but using local background levels instead of the average $^{187}Os/^{188}Os$ of the eroded upper continental crust[1] (Table 2).

$$AF_{Os}\ (\%) = \frac{\left(\frac{^{187}Os}{^{188}Os}\right)_{local\ background} - \left(\frac{^{187}Os}{^{188}Os}\right)_{sample}}{\left(\frac{^{187}Os}{^{188}Os}\right)_{local\ background} - \left(\frac{^{187}Os}{^{188}Os}\right)_{anthropogenic}} \times 100 \qquad (3)$$

Natural and anthropogenic concentrations of Os and Pt were calculated applying this *AF* (%) to the total concentrations[25].

3. RESULTS

3.1. Sedimentary background

Sediments from both stations are composed by fine grained sedimentary material. The Al_2O_3 content ranged from 9 to 23%, with values increasing with depth at both sites (Table 2). Organic matter content ($LOI_{550\ ^{o}C}$, %) in sediments was 6.8 ± 3.3% and 6.6 ± 2.7 % at Low and High Traffic Station (except for the upper 4 cm at High Traffic Station where values up to 23% were found, Figure S-3). The oxygen penetration depth was very low at both sites (Figure S-3). At High Traffic Station, oxygen saturation was below the detection limit even in the uppermost layers; at Low Traffic Station, oxygen was present in the upper 20 cm (3.1 ± 4.5 %), and below detection limit at higher depths. No macrofauna were found in the collected sediments. This sediment characteristics are in line with results obtained by Caetano et al. (2008; 2012)[28,29] in several marshes from the Tagus estuary. Other parameters analyzed in interstitial waters (Eh, salinity, dissolved Fe, Mn and total reduced sulfur species) are showed in the supporting information (Figure S-3).

3.2. Concentrations of Pt and Os in sediment

Platinum concentrations in sediments cores from both stations showed a surface peak; the concentration at the High Traffic Station (40100 pg g^{-1}) is about 15 times higher than that at the Low Traffic Station (2750 pg g^{-1}; Figure 2, Table 2; for the complete dataset see Table S-1). Platinum concentration decreases with depth, reaching similar average background values below 5 cm (Figure 2, Table 2): 670 ± 89 (High Traffic Station; $\bar{x} \pm SD$, n=5) and 682 ± 240 pg g^{-1} (Low Traffic Station; n=4). Osmium concentrations ranged from 25 to 68 pg g^{-1}, but no trend with depth was observed (Figure 2, Table 2): surface Os concentrations were 47 and 51 pg g^{-1} for the High Traffic Station and Low Traffic Station, respectively, whereas the average concentrations for the deeper layers (>5cm depth) were 36 ± 6.8 pg g^{-1} (High Traffic Station) and 62 ± 6.7 pg g^{-1} (Low Traffic Station). The sample from the motorway bridge gullypot at High Traffic Station, which is representative of the road runoff source[46], contained 157000 pg g^{-1} of Pt and 114 pg g^{-1} of Os (Table 2).

3.3. Concentrations of Pt and Os in overlying and interstitial waters

To the knowledge of the authors, the data of dissolved Pt and Os for interstitial waters obtained in this study (Figure 2; Table S-1) are the first reported in the literature. The values obtained for Pt ranged from 0.14 to 0.66 pg g^{-1} (with the exception of a 2.5 pg g^{-1} peak at Low Traffic Station) and between 0.028 and 0.11 pg g^{-1} for Os. The average dissolved concentrations of Pt (0.21 ± 0.07 pg g^{-1}) and Os (0.037± 0.011 pg g^{-1}) at the Low Traffic Station were, in general, lower than at High Traffic Station (0.55 ± 0.07 pg g^{-1} for Pt and 0.074 ± 0.027 pg g^{-1} for Os). In the overlying water, Pt and Os concentrations were 0.164 pg g^{-1} and 0.019 pg g^{-1}, respectively, being lower than those found in interstitial waters for Os.

3.4. $^{187}Os/^{188}Os$ ratios in sediments and interstitial waters

The $^{187}Os/^{188}Os$ ratios in the sediments ranged from 0.91 to 1.18, while in interstitial waters values varied between 0.85 and 1.07 and in the overlying water the ratio was 0.92 (Figure 2, Table 2, complete dataset in Table S-1). Gullypot sediment exhibits the highest $^{187}Os/^{188}Os$ ratio, 1.26. Profiles of $^{187}Os/^{188}Os$ ratios in interstitial waters and sediments had a similar trend at High Traffic Station, i.e., decreasing towards the surface. Ratios in sediments and interstitial waters from Low Traffic Station were similar in the upper 8 cm, but values in sediments increased markedly towards the bottom at a higher extent than in interstitial waters.

DISCUSSION

4.1 The anthropogenic impact on Pt and Os

Previous studies have reported typical Pt and Os concentrations for continental crust (Pt= 510 pg g^{-1}, Os = 31 pg g^{-1}) and contaminated sediments (Pt = 10^3-10^5 pg g^{-1}, Os = $4x10^1$-$8x10^2$ pg g^{-1}, more information in Table S-2[12,15,16,19,20,22,23,46–53]). Platinum found in the upper layers (<4 cm) from the two salt marshes, as well as in the gullypot, were elevated in comparison to background values (Table 2). The enrichment factor for Pt (EF_{Pt}, equation 1) was 119 in the upper sediments (<2 cm) of High Traffic Station, but decreased sharply to 8 at 2 - 4 cm depth. In the Low Traffic Station, the enrichment was much lower and restricted to the surface layer (<2cm, EF_{Pt} = 4); for deeper layers, the calculated enrichment were within the typical natural variability of background sediments (Table 2). Noteworthy, the EF_{Os} in sediments from both High and Low Traffic Stations suggest minor to null anthropogenic input. At Low Traffic Station a EF_{Os} close to 1 (i.e. no enrichment) was obtained despite the higher Os concentrations

compared to High Traffic Station. The calculated anthropogenic fractions (*AF*; equations 2-3) in the upper layer of High Traffic Station showed that 99 % of Pt (39700 pg g^{-1}) was from anthropogenic origin but only 15 % of Os (7 pg g^{-1}). In the Low Traffic Station the anthropogenic contribution was 77 % for Pt (2120 pg g^{-1}) and 18 % for Os (9 pg g^{-1}) in the surface sediments. Significantly, both stations have similar Os contribution from anthropogenic sources, but a 20-fold difference for Pt.

The deposition rates of anthropogenic Pt were calculated for the layers where the anthropogenic fraction (AF_{Pt}, Table 2) was found to be greater than 50% (using the sedimentation rates reported earlier[54] for both stations, see Figure S-4 for a detailed explanation of the calculations); these are the upper 4 and 2 cm at the High and Low Traffic Station, respectively. The average estimated deposition rates are 6,600 ng Pt m^{-2} y^{-1} at the Low Traffic Station (0 - 2 cm) and comparable to a deposition rate of a) 8,400 ng Pt m^{-2} y^{-1} in urban environments of Germany[55], and b) 9,000 ± 5,000 ng Pt m^{-2} y^{-1} for the period 1992-2002 in an urban lake in USA[22]. In contrast, the Pt deposition rates at the High Traffic Station are 310,000 ng Pt m^{-2} y^{-1} (0 - 2 cm) and 17,000 ng Pt m^{-2} y^{-1} (2 - 4 cm) indicating a substantially larger anthropogenic input of Pt at this site.

Since the automobile traffic over the motorway bridge is the most relevant activity at the High Traffic Station, we evaluated whether this source alone may explains the Pt input. The estimation of the Pt input from catalytic converters was made based on the following information: (i) 50,000 vehicles per day passing through the bridge[32]; (ii) an estimation of 37 % of vehicles with gasoline engine and 63 % with diesel[56]; (iii) a release of 400 - 800 ng Pt Km^{-1} and 108 - 150 ng Pt Km^{-1} for new (less than 1 year) and old (more than 1 year) diesel vehicles, respectively, from laboratory measurements[11] ; (iv) a release of 100 ng Pt Km^{-1} and 6-8 ng Pt Km^{-1} for new and old gasoline vehicles,

293 respectively, from laboratory measurements[11]; (v) a release of 270 ng Pt Km^{-1} for every
294 car, as an alternative based on environmental estimations[51,55]; (vi) the bridge is 17.2 Km
295 long; (vii) 4928 days have passed since the bridge started to operate (April 1998) until
296 the sampling (September 2011). Based on these, the bridge car traffic has resulted in a
297 release of 450 or 1140 g of Pt to the environment (following laboratory measurements[11]
298 or environmental estimations[51,55]; see Figure S-5 and Table S-3 for further information
299 on this estimation).

300 Given that (i) almost all the Pt contamination is in the top 4-cm sediment layer based on
301 the AF_{Pt} obtained for the top 4 cm (Table 2), and (ii) a sediment deposition of 3.9 cm
302 since the bridge was open in 1998 (Figure S-4) is derived using the sedimentation rates
303 reported previously[54], the estimated Pt enrichment in the vicinity of the motorway
304 bridge may be calculated taking into account the dispersion range of the emitted
305 particles from catalytic converters. If a 2-m dispersion is taken into consideration based
306 on studies in roadside soil[12,49,52], an enrichment of 61,000-160,000 pg g^{-1} of Pt would be
307 expected in the vicinity of the road bridge (depending on the model of emissions[11,51,55]).
308 However, this estimated range of enrichment is higher than the concentration found in
309 the sediments from the High Traffic Station (40,000 pg g^{-1}). The difference may be due
310 to higher dispersion of particles from the bridge than from a regular road. Accordingly,
311 and using the estimations above, a particle dispersion of 16 m would be needed to
312 explain the enrichment found at High Traffic Station (or 6 m following laboratory
313 measurements[11]; more information in Figure S-5 and Table S-3).

314 The release of Os from traffic at High Traffic Station was estimated following the
315 previous assumptions (number of vehicles, length of bridge, etc) and with (i) the release
316 of almost all the Os from catalytic converters is during the first year of vehicle life

(approximately first 20,000 Km) due to its volatile character[57]; and (ii) catalytic converters contain 6 - 228 pg g^{-1} of Os[57]. On this basis, an estimation of 1.7 mg input of Os to the roadside was found (further information Figure S-5 and Table S-3). This value could explain an input of 0.24 pg g^{-1} (2 m dispersion) or 0.03 pg g^{-1} (15 m, using the dispersion calculated for Pt) in the first 4 cm of the sediment, and a deposition of 1.8 ng m^{-2} y^{-1} or 0.24 ng m^{-2} y^{-1} (depending on 2 or 15 m of dispersion). On the top of that, considering that Os is released as the gaseous OsO_4 species, it is expected that the dispersion is well higher than that considered for Pt –which is released as particles– and therefore the Os inputs here indicated are an upper limit estimation, minimizing its local deposition even further. These calculations show that the Os supply from nearby traffic is significantly lower than the typical regional atmospheric deposition; accordingly, Rauch *et al.* 2010[20] estimated an atmospheric deposition during the last 40 years around 30 ng m^{-2} y^{-1} of Os from a peat bog located in the NW Iberian Peninsula. Assuming this deposition rate in High Traffic Station sediments, an increase of 3.9 pg g^{-1} of Os would be expected in the top 4-cm sediment layer, i.e., which is 16 - 160 times higher than the Os that nearby traffic may supply.

The surface sediments have low $^{187}Os/^{188}Os$ ratios compared to the background. The presence of a less radiogenic source in the surface is consistent with the surface anthropogenic Os contribution at both stations (Table 2). The $^{187}Os/^{188}Os$ ratios against the inverse of Os concentrations are plotted in Figure 3. Four potential sources − fossil fuels (radiogenic, Os = 210 pg g^{-1}, $^{187}Os/^{188}Os$ = 3.7)[58,59]; Iberian pyrite belt (radiogenic, Os = 330 pg g^{-1}, $^{187}Os/^{188}Os$ = 9.7)[53]; PGE ores (unradiogenic, Os = 3 10^5 pg g^{-1}, $^{187}Os/^{188}Os$ = 0.2)[20,60,61] and eroded continental crust (Os = 31 pg g^{-1}, $^{187}Os/^{188}Os$ = 1.05)[1]– have been identified (triangles, Figure 3) to help explain the Os isotope

compositions in the sediment core samples. Sediments from High Traffic Station (diamonds, Figure 3) fall close to the eroded continental crust endmember, but PGE ores appear to influence surface samples. Interestingly, the interpretation of $^{187}Os/^{188}Os$ ratios in sediments from Low Traffic Station (dots, Figure 3) is more complex. Surface sediments show an isotopic composition similar to High Traffic Station, pointing a link to the PGE ores source. However, deeper sediments show a higher influence of a more radiogenic source(s) like fossil fuels and the Iberian Pyrite Belt. The higher industrial activity of Barreiro Chemical Complex due to a pyrite roasting (that processed pyrite from Iberian Pyritic Belt) and a smelter from a steel factory, all of them using fossil combustibles to perform their activity, may explain the fossil fuels and the pyrite belt contribution. Moreover, the gullypot sediment sample also shows an important contribution of this more radiogenic source(s), being within the mixing line of fossil fuels and PGE ores; thus, anthropogenic sources (fossil fuels, pyrite belt and PGE ores) influence the deeper sediment isotopic values at Low Traffic Station. Rauch *et al.* 2010[20] defined similar sources to explain the isotopic composition of a peat bog in the NW Iberian Península where their effect was detected for the last 50 years, including the Iberian Pyritic Belt mining activities, although geographically their study area was farther from the mining area than our study area.

Concentrations of Pt and Os in interstitial waters (Pt: 0.14 - 0.66 pg g^{-1}, Os: 0.028 - 0.11 pg g^{-1}) were higher than typical values for oceanic waters (0.04 - 0.3 and 0.008 pg g^{-1} for Pt and Os, respectively[62]), and for estuarine waters (S=30 ‰; 0.08 - 0.11 pg g^{-1} for Pt[35] and 0.01 pg g^{-1} for Os[63]). Using North Atlantic waters[35,38] as a reference for interstitial waters the Os enrichment was higher than Pt enrichment, suggesting a lower mobility of Pt compared to Os, which appears to be easily mobilized in the interstitial

365 water. Accordingly, the similar Os isotopic composition in interstitial waters and
366 sediments suggest the existence of quasi-equilibrium conditions between both phases,
367 indicating fast reaction kinetics for this element in contrast with the well-known
368 chemical inertness of Pt in surface environments. The dissolved Os profiles in
369 interstitial waters, with concentrations increasing with depth, support the idea of
370 diffusive fluxes from the sediments to the overlying water. Interestingly, the isotopic
371 composition of overlying water shows almost the same ratios than open oceanic waters
372 (0.95[64] for the North Atlantic) suggesting that salt marshes may act as a source of Os to
373 the ocean. Nevertheless, the export of Os would deplete the pool in sediments if not
374 balanced by equivalent inputs, therefore requiring an import to the sediment by
375 atmospheric deposition. Also, the sediment-water partition of Os – and eventually the
376 diffusive fluxes – appears to be affected by the amount of organic matter and/or
377 sulfides, as indicated by the increase in the sediment/water partition coefficients with
378 these two variables (see Figure S-6, supporting information).

379 ***4.2 Os-Pt decoupling in the environment***

380 The Pt/Os ratios of sediments show a wide range of values (Figure 2, Table 2). Ratios of
381 Pt/Os for background sediments at High (19 ± 5) and Low Traffic Stations (11 ± 5)
382 were comparable to average eroded continental crust (16.5[1], Figure 2). However, ratios
383 in surface sediments near the bridge (High Traffic Station) were ~45 times higher than
384 background levels and 5 times the background at the Low Traffic Station. The highest
385 Pt/Os ratio was found in the gullypot sediment, which was twice the value in surface
386 sediments at High Traffic Station. In addition, if Pt and Os were derived only from
387 anthropogenic sources, ratios (calculated using the amount of Pt and Os and applying
388 them the AF_{Pt} and AF_{Os}) would be 5600 and 220 in High and Low Traffic Station,

389 respectively. Thus, the regional common source indentified in the Low Traffic Station
390 (Pt sedimentation rate 6,600 ng m^{-2} y^{-1}), has a Pt/Or ratio of 220. The other local source
391 (Pt sedimentation rate 300,000 ng m^{-2} y^{-1}) that is related to vehicular traffic emissions
392 (High Traffic Station) had Pt/Os ratio ~ 5600, which is in agreement with the elevated
393 ratios for the particles emitted from catalytic converters ($4x10^6$-$2x10^8$ [11,12,57]).

394 In interstitial waters Pt/Os ratios are lower and within a narrow range of 5 - 12 in all the
395 profiles (Figure 2), which are close to ratios for North Atlantic waters (Pt/Os = 5, Figure
396 2, light blue straight line; Table 2), except for ratio for the Pt peak at Low Traffic
397 Station (Pt/Os = 57; 14.5 cm). The absence of a surface peak in Pt/Os agrees with the
398 lower reactivity of Pt respect to Os. The results obtained suggest different post-
399 depositional processes for anthropogenic Pt and Os: while most of Pt remains within the
400 sediment (mainly as particles), Os appears to reach equilibrium between the sediment
401 and the interstitial waters and eventually exported to the estuary.

402 Our results point to the existence of two different anthropogenic sources of Pt and Os to
403 the salt marshes at Tagus Estuary:

404 -a regional source, with Pt/Os ~220 linked to human activities around Lisbon
405 area including large scale traffic[22,55] and industrial effects with emphasis to fossil fuels
406 as a relevant source.

407 -a local source, linked to nearby traffic emissions and affected by the degree of
408 dispersion (e.g. bridge>regular road).

409 These results support the hypothesis of a decoupled behavior between Pt and Os in the
410 environment relative to both sources and mechanisms of release and dispersion, as well
411 as their different reactivity and mobility. Accordingly, Pt is dispersed as solid and non-

412 reactive particulates, whereas Os is emitted as gaseous OsO_4 and when settled displays
413 a higher mobility. This should be taken into consideration when using the Os isotope
414 ratios for the reconstruction of the sources and contamination of platinum group
415 elements in environmental matrices.

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424

425 **Supporting information available:** Schemes for detailed processes of Pt and Os
426 analysis in interstitial waters and sediments; supplementary methods of analysis for
427 auxiliary parameters (Eh, O_2, salinity, loss on ignition, dissolved Fe, Mn and total
428 reduced sulfur species); correlation between the partition coefficient of Os in sediments
429 and interstitial waters vs. loss on ignition and sulfur species; a further explanation for
430 the sedimentation rates and deposited thickness calculated for each station and
431 calculations for the Pt and Os release by catalytic converters. The complete dataset is
432 also included, as well as some values of Pt and Os in natural con contaminated
433 sediments. This information is available free of charge via the Internet at
434 http://pubs.acs.org.

435

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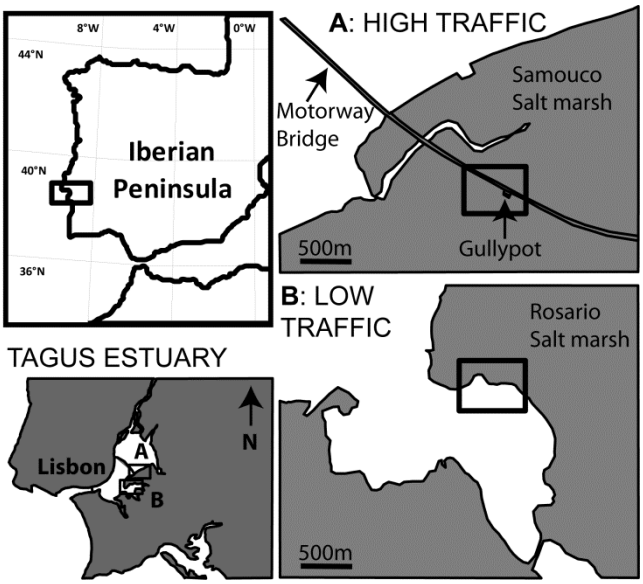

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623

624 Figure 1: Map of study area location in the south bank of the Tagus Estuary (A: High
625 Traffic Station, B: Low Traffic Station).

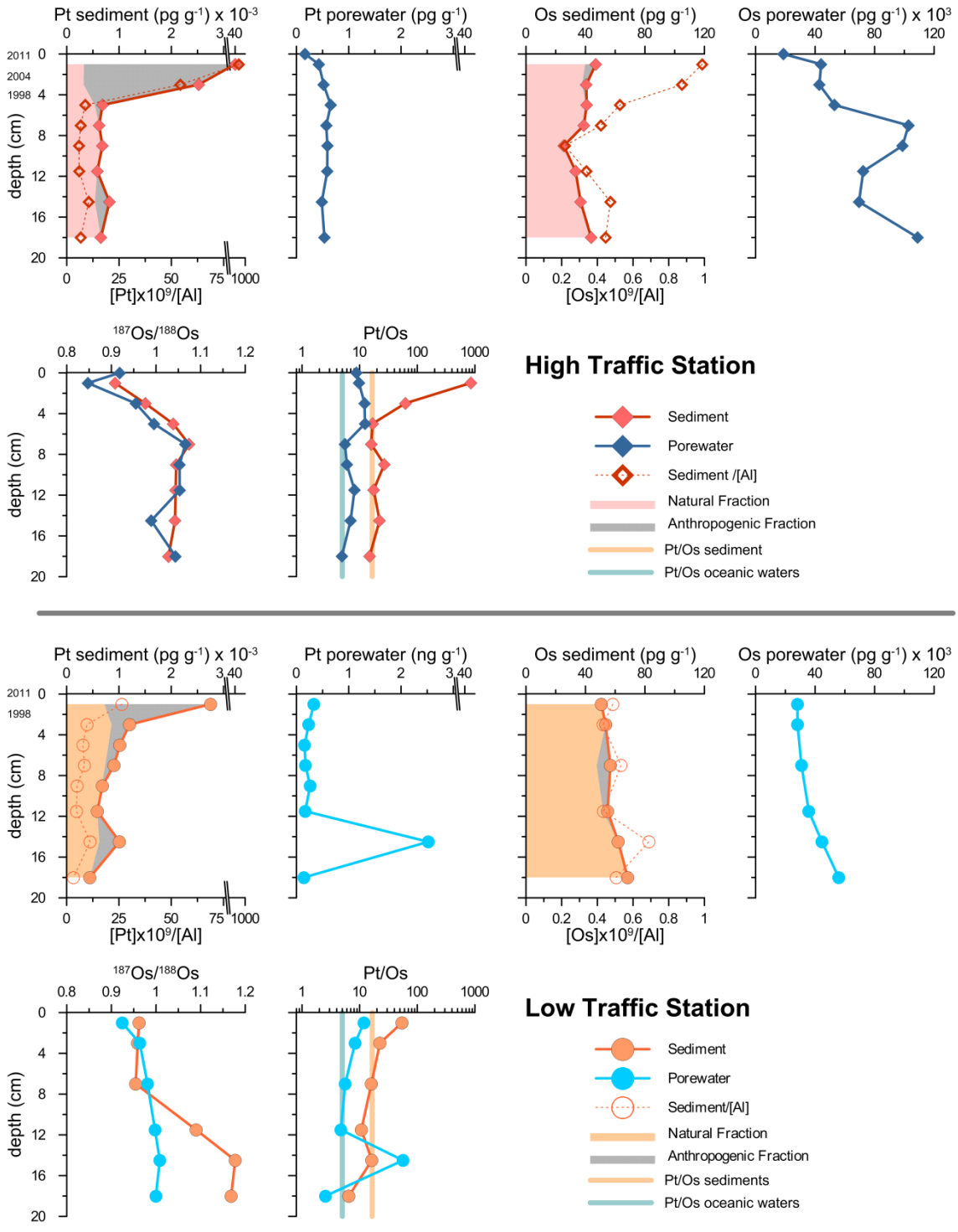
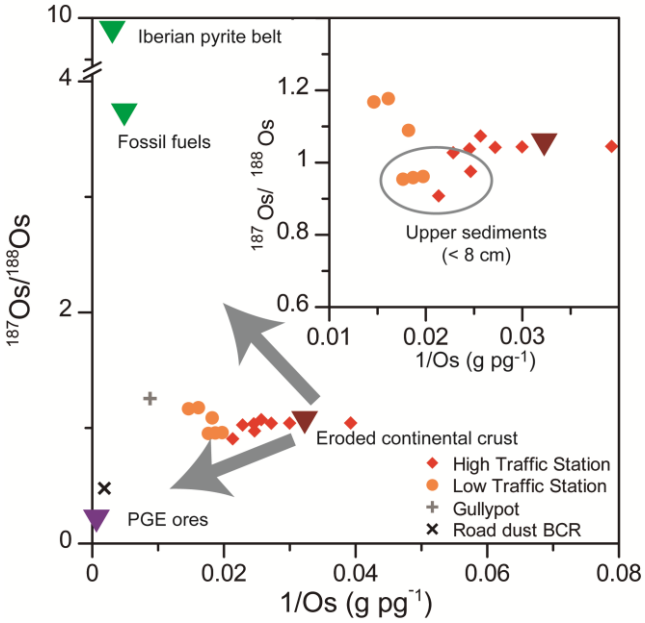


Figure 2: Pt concentration in sediment and porewater (pg g^{-1}) -concentrations normalized by Al in dashed lines-, Os concentration in sediment and porewater (pg g^{-1}), $^{187}Os/^{188}Os$ ratio and Pt/Os ratios. Natural and anthropogenic contributions for Pt and Os in sediments are shown as different areas in the total concentration. Mean Pt/Os ratios in oceanic waters (North Atlantic[35,38]) and sediment[1] are indicated as vertical lines in Pt/Os, blue and orange, respectively.



633

634 Figure 3: $^{187}Os/^{188}Os$ vs. $1/[Os]_{total}$ (g pg^{-1}) in High Traffic Station and Low Traffic

635 Station sediments, bridge gullypot and road dust reference material for this study. Fossil

636 fuels[58,59], Iberian pyrite belt[53], PGE ores[20,60,61] and eroded continental crust[1] define the

637 potential Os sources. The plot shows two tendencies of anthropogenic impact (grey

638 arrows).

639

Table 1: Blanks, detection limits (blank + 3xSD) and reference materials for the study: BCR-723 road dust reference material[37], PACS-2 marine sediment reference material[45].

Sediment sample	Pt (pg g^{-1})	Os (pg g^{-1})	$^{187}Os/^{188}Os$	Al (%)
Blank	24 ± 4 (*n=10*)	0.19 ± 0.07 (*n=2*)	0.288 ± 0.003 (*n=2*)	0.0004 ± 0.0001
DL	37	0.40	-	0.0007
BCR-723 (road dust)	81500 ± 6300 (*n=7*)	457	0.53	-
		635	0.43	-
	(cert. 81300 ± 2500)	(cert. 460 ± 20)*		
PACS-2 (marine sediment)	-	-	-	6.78 ± 0.75 (*n=4*) (cert. 6.63 ± 0.32)

Porewater sample	Pt (pg g^{-1})	Os (pg g^{-1})	$^{187}Os/^{188}Os$	
Blank	0.003 ± 0.003 (*n=13*)	0.0013 ± 0.0006 (*n=2*)	0.368 ± 0.044 (*n=2*)	-
DL (porewater)	0.013	0.0031	-	-

Values: mean value ± SD; number of replicates in brackets.
Sediment blanks for typical sediment mass of 200 and 500 mg for Pt and Os respectively.
Interstitial water blanks for 2 and 40 mL of sample for Pt and Os respectively.
*No certify value of Os in IRMM, value from Meisel el at. 2003[43].

Table 2: Sediment sample values of Al_2O_3 (% weight), Pt and Os concentrations (pg g^{-1})and $^{187}Os/^{188}Os$ used for calculations of anthropogenic fraction for Pt and Os, in sediments of High Traffic Station core and gullypot, Low Traffic Station core, road dust reference material BCR-723, eroded continental crust[1,65], range of oceanic waters[51] and water from North Atlantic[35,38,64].Anthropogenic fractions for Os (AF_{Os}) are calculated by Rauch et al. 2004 and 2006[23,25] method (using isotopic rates) and anthropogenic fractions for Pt (AF_{Pt}) normalizing with Pt/Al ratios of background (normalization by Pt/Os ratios of eroded continental crust values (Rauch´s method[23,25]) or Pt/Os ratios of local background were calculated did not show important differences).

sample	Season	Depth (cm)	Al_2O_3 (%)	[Pt] pg g^{-1}	EF_{Pt}	AF_{Pt} (%)	[Os] pg g^{-1}	EF_{Os}	$^{187}Os/^{188}Os$	AF_{Os} (%)	Pt/Os
High Traffic 0-2	Summer	0-2	9.0	40100	119	99	46.9	2.6	0.908	15	854
High Traffic 2-4		2-4	8.8	2520	7.6	87	40.6	2.3	0.976	7	62
High Traffic 4-6		4-6	14.6	683	1.2	19	40.8	1.4	1.038	0	17
High Traffic background		6-20	18.3 ± 2.6^1	670 ± 89^1	1.0 ± 0.3^1	6 ± 14^1	35.7 ± 6.8^1	1.0 ± 0.3^1	1.047 ± 0.008^1	0 ± 0^1	19 ± 5^1
Low Traffic 0-2	Spring	0-2	19.7	2750	4	77	50.7	0.9	0.962	18	54
Low Traffic 2-4		2-4	23.4	1200	1.6	38	53.5	0.8	0.959	19	22
Low Traffic 6-8		6-8	24.7	906	1.4	29	56.7	1.0	0.954	19	16
Low Traffic background		8-20	23.1 ± 4.1^2	682 ± 240^2	1.1 ± 0.7^2	15 ± 27^2	61.8 ± 6.7^3	1.0 ± 0.2^3	1.145 ± 0.048^3	2 ± 3^3	11 ± 5^3
High Traffic Gullypot	-	-	18.3	157000	256	100	114	3	1.257	-	1380
Road Dust ref BCR-723	-	-	-	81500 ± 6300	160	99	457, 635	15, 21	0.531, 0.429	58, 69	128, 178
Eroded continental crust	-	-	15.2	510	-	-	31	-	1.05 ± 0.23	-	16
Oceanic waters		-	-	0.04-0.3	-	-	0.003-0.011	-	0.95	-	-
North Atlantic waters		-	-	0.05	-	-	0.010	-	1.05	-	5

Values: mean value ± SD Number of replicates[1]n=5; [2]n=4;[3]n=3