GEOCHEMICAL BEHAVIOUR AND SOURCES OF PLATINUM GROUP ELEMENTS IN ANTHROPOGENICALLY-IMPACTED SEDIMENTS

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Ph.D. Thesis 2015

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Clara Almécija Pereda

para optar ao **título de Doutora con Mención Internacional** pola Universidade de Vigo co título:

Geochemical behaviour and sources of Platinum Group Elements in anthropogenically-impacted sediments

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e ca titoría da **Dra. Marta Pérez Arlucea** do Dpto. Xeociencias Mariñas e O.T. da Facultade de Ciencias do Mar, Universidade de Vigo

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AUTORIZACIÓN DA TESE

O **Dr. Antonio Cobelo García** e o **Dr. Juan Santos Echeandía** pertencentes ao Grupo de Bioxeoquímica Mariña (Departamento de Oceanografía) do Instituto de Investigacións Mariñas IIM-CSIC, en calidade de directores da tese doutoral titulada:

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presentada pola doutoranda **Clara Almécija Pereda** para optar ao título de Doutora con Menición Internacional pola Universidade de Vigo, autorizan a presentación da citada tese dado que reúne as condicións necesarias para a súa defensa.

En Vigo, a 7 de Abril de 2015

Juan Santos

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AUTORIZACIÓN DA TESE

A **Dra. Marta Pérez Arlucea** do Departamento de Xeociencias Mariñas e O.T., da Universidade de Vigo, titora da presente memoria de tese doutoral titulada:

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Marta Pérez

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Resumen

La biogeoquímica de los elementos traza tiene por objetivo la caracterización y comprensión de sus ciclos así como su distribución a gran escala (y la de sus isótopos), ya que actualmente, la falta de conocimiento sobre sus fuentes, sumideros, ciclo interno o especiación química limitan su aplicabilidad. Además, la identificación y cuantificación de los procesos que controlan la distribución de los elementos traza es clave para evaluar su vulnerabilidad al cambio global, predecir su comportamiento ante un cambio de las condiciones ambientales y evaluar la correcta gestión frente a ellos. El océano y sus diferentes ambientes de transición son regiones que despiertan un interés especial debido a la gran complejidad de los mismos y el escaso conocimiento que sobre ellos existe. En este contexto surge la idea de realizar esta tesis doctoral, con el fin de ahondar en el conocimiento de la geoquímica sedimentaria de los elementos del grupo de platino.

Capítulo 1. Introducción general y objetivos

En este capítulo se hace una breve introducción sobre la caracterización de los elementos del grupo del platino, sus usos industriales y las implicaciones ambientales que esos usos conllevan. Además se incluye un breve resumen de las técnicas analíticas que se emplean para su determinación y de la capacidad de determinar su origen. Finalmente se expone un hipótesis de trabajo, se enuncian unos objetivos para verificarla y se justifica la elección de las áreas de estudio para llevarlo a cabo.

Elementos del grupo del platino: Los elementos del grupo del platino (EGPs) es un conjunto de elementos químicos que comprande 6 elementos: rutenio (Ru), rodio (Rh), paladio (Pd), osmio (Os), iridio (Ir) y platino (Pt), y que presentan propiedades catalíticas especiales, de resistencia al ataque químico o propiedades eléctricas estables. Los EGPs son elementos altamente siderófilos, con una afinidad extrema al hierro, y, por lo tanto, se estima que el 99.8% de lo EGPs de la Tierra residen en el núcleo, quedando el manto superior claramente empobrecido en ellos. Las concentraciones en el núcleo varían desde 0.4 µg g^{-1} del Rh hasta 5.5 µg g^{-1} del Pt, mientras que en la corteza superior continental presentan concentraciones medias entre los 22 pg g^{-1} del Ir y los 520 pg g^{-1} del Pd, lo que significa un enriquecimiento en el núcleo entre 1,000 y 100,000 veces, dependiendo del elemento considerado. Así, los EGPs forman parte de los elementos más escasos en el medio ambiente, con concentraciones ultra-traza (<1 ng g^{-1}), y cualquier interacción humana en su ciclo superficial implicará una perturbación importante del equilibrio natural. No obstante, existen fuentes naturales tales como emisiones volcánicas, polvo cósmico o plumas hidrotermales que originan depósitos ricos en EGPs como los nódulos de Fe-Mn o los emplazamientos magmáticos. De hecho, es la intrusión en la corteza de cuerpos magmáticos diferenciados, junto con unos mecanismos excepcionales de segregación y concentración, lo que provocan la formación de depósitos minerales ricos en EGPs económicamente muy rentables, como el famoso *Bushveld Igneous Complex* (Sudáfrica), con aproximadamente el 80% de las reservas mundiales, o el yacimiento *Norilsk (*Rusia*)*.

Usos industriales y consecuencias medioambientales: Debido a sus propiedades singulares los EGPs son muy demandados para diversos usos industriales, especialmente en los últimos 40 años donde ha habido un aumento exponencial de su demanda. Los catalizadores de los vehículos, desarrollados para reducir las emisiones de gases tóxicos del motor y transformarlos en gases más inocuos, son su principal aplicación, constituyendo hasta el 70% del Pt que se demanda en Europa. Las industrias química, eléctrica, biomédica (el Pt es un componente fundamental de los compuestos para quimioterapias), o del vidrio y la joyería, son otras actividades que emplean EGPs. Además, dado su elevado valor económico también se emplean como activo para inversión económica. De esta manera, el empleo de EGPs en todas estas actividades humanas está generando un aumento de su concentración en el medio ambiente, siendo de origen humano entre un 86 y un 98% del flujo de EGPs en la superficie terrestre. Varios estudios previos han señalado un enriquecimiento en los sedimentos superficiales en las zonas urbanas y otras zonas de influencia humana, pero también se han documentado en ambientes remotos. Las concentraciones exhiben un amplio rango de valores, dependiendo de las concentraciones naturales locacles en cada zona. Así, si las emisiones antropogénicas de EGPs están vinculadas con su uso industrial, cualquier industria que los utilice se convierte en una posible fuente de EGPs para el medio ambiente.

Los catalizadores de los vehículos a motor emiten, a lo largo de su vida, partículas de EGPs durante su funcionamiento, especialmente Pt, Pd y Rh, que son los componentes activos principales. Como resultado de estas emisiones, se encuentran concentraciones elevadas de EGPs generalmente adyacentes a las carreteras con alta densidad de tráfico (dentro de los 2 primeros metros), aunque el viento, la escorrentía y la topografía pueden condicionan su distribución. Las actividades mineras y metalúrgicas son otra fuente de EGPs debido a la alta cantidad de polvo y partículas que producen, afectado fundamentalmente a la calidad del aire. Algunos estudios han detectado concentraciones elevadas de EGPs en las áreas circundantes a minas, incluyendo hierba, suelos y líquenes; aunque las tasas de emisión no están cuantificadas, una necesidad importante para la evaluación y gestión de las actividades mineras. También los efluentes de hospitales son una importante fuente de EGPS al ambiente, debido al contenido de EGPs de terapias contra el cáncer y que los pacientes eliminan principalmente por la orina, así como el uso de EGPs en compuestos para reparación odontológica o del Os para tinción de tejidos.

Determinación analítica: Uno de los temas más delicados a la hora de estudiar la geoquímica de los EGP reside en la dificultad de la determinación analítica, debido a su baja concentración, que precisa del empleo de técnicas que permitan medir EGPs con precisión en matrices contaminadas, pero también sus niveles naturales o de fondo. Además, la recogida de muestras, separación y almacenamiento de las mismas pueden afectar sustancialmente la fiabilidad de los resultados; es necesario el uso de técnicas limpias ya que una manipulación incorrecta durante cualquier paso del proceso podría causar contaminación, elevando las concentraciones entre 10 y 1,000 veces. Esto hace que la determinación de EGPs precise de técnicas de alta sensibilidad y selectividad, fundamentalmente la espectrometría de masas con plasma acoplado inductivamente (ICP-MS) o la voltametría adsortiva de redisolución catódica (AdCSV). El empleo del ICP-MS se caracteriza por la rapidez, simplicidad y capacidad multi-elemental, aunque las interferencias isobáricas pueden causar importantes inexactitudes, más notables en las concentraciones ultra-trazas de los EGPs. Varios estudios han demostrado que la AdCSV es una alternativa adecuada para la determinación de EGPs, debido a la alta exactitud, la precisión, la selectividad y sensibilidad, así como bajos límites de detección y el coste económico. Por lo tanto, el desarrollo y mejora de las técnicas de análisis son uno de los principales retos dentro del campo de la geoquímica de contaminantes emergentes.

Trazabilidad: Es importante hacer mención especial a una de las características más interesantes dentro del estudio de EGPs, que es el uso de los isótopos de Os para la caracterización de su origen: natural o antropogénico. El Os exhibe una amplia gama de composición isotópica según su origen y litología debido a la variación de la proporción del ^{187}Os, el isótopo radiogénico que se deriva de la desintegración radiactiva de ^{187}Re. Por lo tanto, las relaciones de ^{187}Os/^{188}Os trazan una variedad de orígenes: las proporciones típicas ^{187}Os/^{188}Os de los yacimientos de los que proceden los EGPs de uso industrial, como *Bushveld Complex* (que supone el 80% de la producción mundial), es de 0.1-0.2, mientras que las relaciones de la corteza continental superior son 1.05±0.23. Esta notable diferencia permite estimar la contribución antropogénica de Os en muestras ambientales, y, suponiendo que el resto de EGPs derivan de las mismas fuentes, se estima también la fracción antropogénica del Pt, Pd y Rh en entornos urbanos. Sin embargo, la aplicación de esta herramienta en entornos naturales es casi inexistente y está limitado al estudio de algunas turberas, afectadas exclusivamente por deposición atmosférica, siendo inexistentes los estudios de sistemas naturales más complejos.

Hipótesis de trabajo, objetivos y justificación: Estudios previos han concluido que existe una perturbación antropogéncia en entornos urbanos causada por la liberación de EGPs al medio ambiente. Sin embargo también han formulado preguntas que quedan aún sin respuesta, como ¿Cuál es el destino de los EGPs cuando llegan a ambientes naturales? ¿Cómo es su comportamiento sedimentario? ¿Siguen siendo inertes? ¿Se disuelven? ¿Existen en una forma biodisponible siendo asimilados por las plantas y entrando en la cadena alimentaria? Ante estas incógnitas nace la hipótesis de trabajo de esta tesis doctoral:

> *¿Cómo es el comportamiento geoquímico de los elementos del grupo del platino en los sedimentos afectados por emisiones de origen antropogénico? ¿Cuáles son sus principales fuentes?*

y se plantean los siguientes objetivos para obtener su respuesta:

-desarrollo y/o mejora de los métodos para la determinación de las concentraciones ultra-traza de EGPs en diferentes matrices naturales, incluyendo niveles de fondo

-mejora del conocimiento de su comportamiento sedimentatio y los procesos postdeposicionales que les afectan

-evaluación del papel que desempeña la presencia de vegetación en los sedimentos dentro del ciclo biogeoquímico de los EGPs

-determinación de la transferencia de EGPs desde los sedimentos a compartimentos biológicos y su posible bioacumulación siendo incorporados en la cadena alimentaria

-cuantificación de la contribución antropogénica a la totalidad de EGPs presentes en los sedimentos y aguas intersticiales, en función del impacto del tráfico circundante

-valoración del acoplamiento real de los EGPs según sus fuentes antropogénicas y su comportamiento

-descripción del papel de las marismas en el ciclo de los EGPs y cuantificación de la exportación (o importación) de EGPs al estuario y al mar

-evaluación del impacto de las actividades mineras de EGPs en los ambientes naturales circundantes

Para llevar a cabo este estudio se seleccionan dos áreas de trabajo por sus características particulares:

a) El río Hex (Rustenburg, Sudáfrica) que drena la zona minera del *Bushveld Igneous Complex*, el mayor yacimiento de EGPs, donde se llevan a cabo actividades mineras intensas

b) Las marismas del estuario del Tajo (W Península Ibérica), bajo diferentes niveles de tráfico, donde el comportamiento de otros elementos traza (Pb, Cr, Zn, Ni, Cu, As, Cd, Co) ha sido bien caracterizado, y el papel de las marismas en los ciclos biogeoquímicos de los mismos, condicionado por los diferentes procesos físicos, químicos y microbiológicos, es conocido

Capítulo 2. Mejora de la determinación voltamétrica del rodio a concentraciones ultra-traza aplicado a muestras naturales mediante el empleo de la transformación de la señal

El rodio (Rh) está presente en la superficie terrestre en concentraciones ultra-traza (60 pg g^{-1}). Sin embargo, su uso en catalizadores de los vehículos a motor ha aumentado su emisión y concentración en zonas con alta densidad de tráfico. Así mismo, en los últimos años se ha incrementado el interés en las técnicas analíticas para su determinación con el fin de poder medir dicho incremento con respecto a los niveles naturales de manera precisa. En este estudio se propone una mejora para la determinación de Rh por AdCSV (voltametría adsortiva de redisolución catódica) aplicando la transformación de la señal voltamétrica mediante la segunda derivada.

La optimización de los parámetros experimentales que afectan al análisis voltamétrico se llevó a cabo utilizando muestras de sedimento. Dicha optimización incluye la cantidad de muestra utilizada, las concentraciones de ácido clorhídrico y de formaldehido en la disolución final, el tiempo de equilibrio y deposición y el potencial de trabajo para dicha deposición. El uso de la transformación por segunda derivada proporciona picos bien definidos debido a la minimización de las interferencias de fondo de la matriz, y conlleva una disminución significativa en los límites de detección. En consecuencia, se obtuvieron unos límites de detección de 23 fM Rh en la celda y de 1.6 pg g^{-1} de Rh por 200 mg de sedimento.

La metodología optimizada se aplicó al análisis de Rh en un testigo de sedimento recogido cerca de un puente de la autopista del Estuario del río Tajo (Lisboa, Portugal). Aquí, las concentraciones de Rh variaron desde 0.06 hasta 0.47 ng g^{-1}, mostrando un enriquecimiento superficial de Rh vinculado al tráfico, lo cual es consistente con un pico superficial de Pt. También han sido analizados materiales de referencia, como el polvo de carretera (BCR-723) y el sedimento fluvial (JSd-2), y los valores obtenidos concuerdan con las concentraciones certificadas y publicadas.

Capítulo 3. Platino en sedimentos de marisma: comportamiento y asimilación biológica

El platino (Pt) es uno de los elementos químicos más escasos en la corteza terrestre, siendo su concentración media de 0.5 ng g^{-1}. Sin embargo el uso del Pt en diversas actividades humanas, especialmente en catalizadores de vehículos, está incrementando su concentración en sedimentos superficiales. Estudios previos han evaluado el comportamiento sedimentario del Pt en las zonas urbanas; pero los sistemas naturales han sido escasamente estudiados.

Este trabajo tiene como objetivo caracterizar el comportamiento sedimentario del Pt liberado en ambientes costeros y determinar el papel que la vegetación típica de marisma tiene dentro del ciclo biogeoquímico del Pt. Se muestrearon varios testigos de sedimento en la marisma del estuario del Tajo (colonizada y sin colonizar por *Sarcocornia fruticosa*), bajo diferentes condiciones de tráfico vehicular. La concentración de Pt se analizó por voltametría adsortiva de redisolución catódica en sedimento, agua intersticial y diferentes tejidos de *Sarcocornia Fruticosa* –raíces, tallos y hojas–. Otros parámetros auxiliares se analizaron en agua intersticial –potencial redox, oxígeno disuelto, sulfuros totales, salinidad o Fe y Mn disueltos– y también se determinaron otros elementos químicos en las muestras de sedimentos (Fe, Mn, Al, Cd, V, Zn, Pb).

Aunque se ha encontrado un enriquecimiento superficial de Pt en los sedimentos de la estación de muestreo de Bajo Tráfico (2.8 ng g^{-1}), el mayor enriquecimiento ha sido descrito en la estación de Alto Tráfico donde la concentración de Pt alcanza, en algunos casos, hasta 40 ng g^{-1}, apuntando a la alta densidad de vehículos en la zona como la causa principal. Sin embargo, el Pt disuelto presente en el agua intersticial no muestra un pico superficial de Pt, mostrando perfiles bastante homogéneos (0.26-0.66 ng L^{-1} en sedimentos vegetados y de 0.14-0.70 ng L^{-1} en sedimentos sin vegetar), lo que indica una baja reactividad de Pt del sedimento, a excepción de dos picos ricos en Pt en las zonas más profundas, que alcanzan hasta 2.5 ng L^{-1} y que podría estar relacionados con cambios en las condiciones redox. Estos picos aparecen también en la concentración de Pt en las raíces (0.9±0.6 ng g^{-1}), que no muestran un enriquecimiento respeto a la concentración de Pt en el sedimento ni en el agua intersticial, y por lo tanto la bioacumulación y el trasporte a las partes subaéreas de la planta son bajas (la concentración de Pt media en tallos y hojas es 0.04±0.05 ng g^{-1}). Además, se han encontrado comportamientos acoplados entre Pt y el Mn disuelto que podría condicionar la formación de diferentes especies de Pt (apareciendo especies más biodisponibles en la estación de Bajo Tráfico).

Por lo tanto, el papel que juega la vegetación es fundamental para la geoquímica sedimentaria del Pt, ya que controla las condiciones redox del sedimento y por lo tanto la presencia de especies de Pt más o menos biodisponibles.

Capítulo 4. Desacoplamiento de platino y osmio en el medio ambiente: evidencias en sedimentos intermareales (Estuario del Tajo, SO Europa)

El uso de catalizadores en los automóviles ha provocado un aumento significativo en la liberación de los elementos del grupo del platino al medio ambiente. Trabajos previos han concluido que el origen de todos los elementos del grupo del platino es común, así como el comportamiento geoquímico que controla su distribución ambiental. Para comprobar la validez de esta hipótesis se muestrearon testigos de sedimento en dos estaciones de la marisma del estuario del Tajo (SO de Europa), afectadas por diferente presión del tráfico. Así, se determinaron las concentraciones de platino (Pt) –por voltametría adsortiva de redisolución catódica (AdCSV)– y osmio (Os) y la relación isotópica $^{187}Os/^{188}Os$ –por espectrometría de masas de ionización térmica negativa (N-TIMS)– en sedimentos y agua intersticial. La concentración de Pt en los sedimentos superficiales cerca de la zona de Alto Tráfico (que alcanza valores de 40 ng g^{-1}) indicó contaminación severa. Sin embargo, los sedimentos superficiales no mostraron enriquecimiento en Os. Las relaciones $^{187}Os/^{188}Os$, que comprenden valores desde 0.908 hasta 1.178, señalaron la existencia de otras fuentes además de los vehículos. Las concentraciones de Pt y de Os disueltos en aguas intersticiales, 0.1-0.7 ng L^{-1} para Pt y 0.03-0.10 ng L^{-1} para Os (reportados por primera vez en la literatura), fueron más altos que los valores típicos para las aguas no contaminadas. En base a los resultados obtenidos se identificaron dos fuentes de Pt y Os en las marismas del estuario del Tajo: una entrada regional vinculada con las actividades industriales donde se utilizan gran cantidad de combustibles fósiles y con el tráfico a escala regional; y una fuente local asociada con una alta densidad del tráfico en las inmediaciones de la zona de muestreo de Alto Tráfico. La cantidad estimada de Os y Pt liberados por los catalizadores de los coches apoyan este modelo de los dos orígenes. Además de las diferentes fuentes, la diferente capacidad de dispersión (el Pt se libera en forma de partículas y el Os como OsO_4 gaseoso) y diferente capacidad de disolución y movilización llevan a la conclusión de un comportamiento desacoplado entre el Pt y el Os. Como consecuencia, estos resultados cuestionan el uso de los isótopos de Os como trazador del origen de los otros elementos del grupo del platino en el medio ambiente.

Capítulo 5. Flujos difusivos de osmio y platino en sedimentos de marisma (Estuario del Tajo, SO Europa)

La cuantificación de flujos en ambientes costeros es una de las materias más importantes para la caracterización de los ciclos biogeoquímicos de los elementos impactados antropogénicamente. Los elementos del grupo del platino se encuentran entre estos contaminantes antropogénicos debido, principalmente, a su uso en los catalizadores de los coches, que liberan partículas al medio ambiente durante su uso. Por lo tanto el objetivo de este estudio es la estimación de los flujos difusivos de osmio (Os) y platino (Pt) en sedimentos de marisma para evaluar si dichas marismas están funcionando como sumideros o como fuentes de estos elementos a las aguas del estuario y al océano.

Se tomaron dos testigos de sedimento, con su correspondiente agua sobrenadante, en un punto de las marismas del estuario del Tajo, en marzo y septiembre de 2011, de los cuales se extrajo el agua intersticial. La concentración de Pt en el agua intersticial se analizó por AdCSV, mientras que la concentración de Os y su composición isotópica se determinó por N-TIMS. Para calcular los flujos difusivos se aplicó la primera ley de Fick modificada para sedimentos porosos, proporcional al gradiente de concentraciones de dichos elementos entre las aguas intersticiales y sobrenadantes. Además, se realizó una estimación teórica de los coeficientes de difusión de las especies químicas típicas del Os y del Pt en el agua salada (a 298 ºK) debido a la falta de valores experimentales en la literatura.

El Pt mostraba un comportamiento diferente en primavera y verano: las marismas retienen Pt durante la primavera (–370 ng m^{-2} y^{-1}) y exportan una pequeña cantidad de Pt en verano (49 ng m^{-2} y^{-1}), siendo un sumidero neto de Pt a lo largo del ciclo anual. En cualquier caso, la liberación/retención de Pt (1.6 g y 12 g, respectivamente) es insignificante en comparación con la entrada de Pt vinculado al tráfico. Sin embargo, las marismas se comportan como una fuente de Os al estuario, y posteriormente al océano, durante todo el año (primavera 0.71-1.4 ng m^{-2} y^{-1}, verano 1000-1900 ng m^{-2} y^{-1}, dependiendo de la especiación). Liberan 32-61 g de Os al estuario sólo en verano, lo que supone entre el 19 y 32% del Os que llega al estuario del Tajo en un año. Extrapolando estos resultados a todas las marismas del mundo, supondrían una liberación del 25-40% de la cantidad total de Os que llega anualmente a los océanos siendo un compartimento clave en el ciclo global del Os. Consideramos además que estos resultados apuntan de nuevo a un comportamiento desacoplado entre Os y Pt que es necesario tener en cuenta para futuras investigaciones, si bien es cierto que sería necesario un estudio en mayor profundidad para mejorar el conocimiento sobre el ciclo biogeoquímico de los estos elementos traza.

Capítulo 6. Elementos del grupo del platino en sedimentos fluviales de zonas mineras: el río Hex (*Bushveld Igneous Complex*, Sudáfrica)

La evaluación del impacto ambiental de las actividades mineras desde el punto de vista de los elementos del grupo del platino y otros elementos traza es fundamental para prevenir riesgos potenciales para la población. Este estudio evalúa las concentraciones de elementos del grupo del platino en sedimentos fluviales de cuatro zonas diferentes del río Hex, el cual drena la zona minera del *Bushveld Igneous Complex* (Sudáfrica). Se analizaron elementos mayoritarios y traza (Fe, Ca, Al, Mg, Mn, V, Cr, Zn, Cu, As, Co, Ni, Cd y Pb) por espectrometría de absorción atómica por llama y electrotérmica en partículas en suspensión y en diferentes fracciones de sedimento (<63, 63-500 y 500-2000 µm). Los elementos del grupo del platino –Pt, Pd, Rh e Ir– se midieron por ICP-MS después de la eliminación de elementos que pueden causar interferencias isobáricas, mediante el uso de una resina de intercambio catiónico DOWEX 50W-X8. Los valores fueron corregidos después de analizar y sustraer los blancos de procedimiento. Finalmente la exactitud se controló mediante el análisis de materiales de referencia. Elementos como Ni, Cr, Pt, Pd, Rh e Ir muestran concentraciones de 3-, 13-, 18-, 28-, 48- y 44- veces los niveles típicos en corteza continental superior, respectivamente, aunque sus concentraciones son menores que las analizadas en la roca madre local. Las concentraciones más elevadas se observaron más cerca de la zona minera, en la fracción <63 µm, y disminuyendo con la distancia. Por todo ello, es probable que procedan de la deposición atmosférica de partículas ricas en elementos del grupo del platino liberadas por las actividades mineras y de la escorrentía superficial que las redistribuye.

Por lo tanto, las actividades antropogénicas como la minería están causando cierta perturbación del ciclo geoquímico superficial de los elementos del grupo del platino, aumentando su presencia en la fracción fina de los sedimentos del río y por lo tanto la posible exposición de la población a los mismos, lo que representa un riesgo potencial. Proponemos que nuevos parámetros indicadores de contaminación tales como la calidad de las partículas que se emiten, que se depositan posteriormente en vegetación, suelos y otros ambientes, o la calidad de los sedimentos fluviales, se añadan a los protocolos que evalúan la sostenibilidad de las actividades mineras.

Capítulo 7. Síntesis y conclusiones generales

El trabajo comprendido en esta tesis doctoral supone un extenso estudio del comportamiento sedimentario de los elementos del grupo del platino (EGPs) en ecosistemas naturales y la evaluación de sus fuentes de emisión de origen humano.

Mejoras analíticas: Esta tesis supone un importante progreso en la determinación analítica de los diferentes EGPs. En consecuencia, se han podido analizar concentraciones naturales y contaminadas por actividades humanas mediante el uso de diversas metodologías complejas.

La AdCSV se ha utilizado para la determinación de platino en diferentes matrices, aplicando el método desarrollado por van den Berg y Jacinto (1988) y mejorado por Cobelo-García *et al.* (2011). Se han establecido además protocolos específicos de preparación de muestras y condiciones apropiadas de análisis para aguas intersticiales y los tejidos biológicos. Además, se ha propuesto un método nuevo para la determinación de rodio por voltametría, mediante la aplicación de la transformación por segunda derivada descrito por Cobelo-García et al., (2014). Se utilizó además el N-TIMS para la determinación de Os y de su composición isotópica, así como el ICP-MS para determinación simultánea de diversos EGPs tras el paso de la muestra por una columna de intercambio catiónico. En este método también se realizó la optimización del pretratamiento de la muestra (temperatura de muflado).

Se han publicado por primera vez datos de concentraciones de Pt y Os en aguas intersticiales, lo que hace de esta tesis (y de los artículos resultantes de la misma) una referencia científica para futuros estudios sobre los ciclos geoquímicos de EGPs. Por otra parte, las concentraciones de alguno de estos elementos no certificados en los materiales de referencia más comunes de EGPs como el polvo de carretera BCR-723 y el sedimento fluvial, JSd-2, son también dados (por ejemplo, Rh en JSd-2 por diferentes métodos).

El comportamiento sedimentario del platino precedente de catalizadores en zonas de marisma: El comportamiento de los diferentes EGPs (especialmente Pt y Os) se ha estudiado en las marismas del estuario del Tajo (SO Europa) bajo diferentes densidades de tráfico de vehículos. Allí, el papel de la vegetación es esencial para entender el comportamiento sedimentario del Pt, ya que las raíces de las plantas halófitas controlan la geoquímica del sedimento que las rodean (condiciones redox, presencia de O_2, degradación de la materia orgánica) determinando la formación de especies químicas en fase sólida o disuelta. Se ha encontrado una clara relación entre Pt y Mn disueltos en el agua intersticial de las marismas, similar a la relación Pt-Mn de las costras y nódulos de Fe-Mn que podría ser explicada por procesos de co-precipitación/adsorción/secuestro de Pt simultáneo a la formación de óxidos de Mn. La concentración de Pt en las raíces de S*arcocornia fruticosa*, que reflejan la concentración de Pt existente en cada momento en el agua intersticial, y el escaso transporte de Pt a los tejidos subaéreos de las plantas indican la inexistencia de una verdadera bioacumulación de Pt y de una incorporación efectiva de Pt a la cadena alimentaria.

Existen dos fuentes antropogénicas diferentes de EGPs en las marismas en Estuario del Tajo:

-una fuente de EGPs regional vinculada a las actividades humanas en todo el área de Lisboa, incluyendo actividades industriales o el tráfico a gran escala, que afecta a toda la marisma y que provoca un pequeño enriquecimiento en EGPs respecto a las concentraciones de fondo (Pt/Os~ 200)

-una fuente de EGPs local vinculados sólo a las emisiones del tráfico de vehículos, que provoca un enriquecimiento superficial de Pt (también Rh) y que afecta sólo cerca de la carretera/autopista (Pt/Os>> 200)

Por lo tanto, se observa un comportamiento desacoplado de los diferentes EGPs en el medio ambiente, especialmente de Os respecto a los otros EGPs, en relación tanto a sus fuentes como a sus mecanismos de liberación y dispersión o a su diferente reactividad y movilidad. El Pt permanece asociado a partículas en el sedimento (no reactivo), sin existir disolución importante del mismo en el agua intersticial. Así los sedimentos funcionan como un sumidero efectivo del Pt antropogénico. El Os, que se emite como OsO_4 gaseoso, muestra una mayor movilidad, exportándose al estuario y aguas oceánicas. De hecho, al menos el 20% del Os que llega cada año hasta el estuario del Tajo viene directamente de las marismas y se estima que el Os emitido por todas las marismas del planeta podría alcanzar hasta el 40% del Os oceánico, lo que convertiría las marismas en un compartimento clave en el ciclo geoquímico del Os. En consecuencia, el desacoplamiento Pt-Os debe tenerse en cuenta al utilizar las relaciones isotópicas de Os para la reconstrucción de fuentes de contaminación de los EGPs en matrices ambientales.

La influencia de las actividades de minería extractiva de elementos del grupo del platino en los ambientes acuáticos circundantes: Aunque las concentraciones elevadas de EGPs (y otros elementos traza) en los sedimentos de los ríos mineros corresponden principalmente a los altos niveles naturales, las actividades mineras causan perturbaciones del ciclo geoquímico superficial de los EGPs, como el aumento de sus concentraciones en la fracciones limo y arcilla (<63 µm) derivado de la deposición atmosférica y la escorrentía superficial. Por lo tanto, esta deposición atmosférica podría afectar a la vegetación local y cultivos y aumentar la exposición a EGPs de la población local.

Proponemos que indicadores ambientales como partículas en el aire, suelos o sedimentos fluviales deban ser consideradas en los protocolos que evalúan la sostenibilidad de las actividades mineras con el fin de mejorar la calidad del medio ambiente y proteger a la población local.

Como conclusión general, esta tesis trata de mejorar la comprensión de los ciclos biogeoquímicos de los elementos del grupo del platino y la perturbación que el desarrollo de las actividades humanas está causando en ellos. La variación que los ecosistemas están sufriendo en las últimas décadas respecto a sus condiciones naturales tiene aún más relevancia en las regiones costeras, especialmente vulnerables al cambio global. Por lo tanto, esperamos que todas las conclusiones alcanzadas en esta tesis puedan contribuir al progreso del conocimiento geoquímico así como a la mejora de la gestión ambiental.

Limiar

A bioxeoquímica dos elementos traza ten por obxectivo a caracterización e comprensión dos seus ciclos así como a súa distribución a grande escala (e a dos seus isótopos), xa que actualmente, a falla de coñecemento sobre a súas fontes, sumidoiros, ciclos internos ou especiación química limitan a súa aplicabilidade. Ademais, a identificación e cuantificación dos procesos que controlan a distribución dos elementos traza é clave para avaliar a súa vulnerabilidade á mudanza global, predicir o seu comportamento ante un cambio das condicións ambientais e avaliar a correcta xestión ante eles. O océano e os seus diferentes ambientes de transición son rexións que espertan un interese especial debido á grande complexidade dos mesmos e ao escaso coñecemento que sobre eles existe. Neste contexto agroma a idea de realizar esta tese de doutoramento, coa fin de afondar no coñecemento da xeoquímica sedimentaria dos elementos do grupo do platino.

Capítulo 1. Introdución xeral e obxectivos

Neste capítulo faise unha breve introdución sobre a caracterización dos elementos do grupo do platino, os seus usos industriais e as implicacións ambientais que de estes derivan. Ademais inclúese un breve resume das técnicas analíticas que se empregan para a súa determinación e a capacidade de determinar a súa orixe. Finalmente exponse unha hipótese de traballo, enúncianse uns obxectivos para verificala e xustifícase a elección das áreas de estudo para levalo a cabo.

Elementos do grupo do platino: Os elementos do grupo do platino (EGPs) é un conxunto de elementos químicos que comprende 6 elementos: rutenio (Ru), rodio (Rh), paladio (Pd), osmio (Os), iridio (Ir) e platino (Pt), e que presentan propiedades catalíticas especiais, de resistencia ao ataque químico ou propiedades eléctricas estábeis. Os EGPs son elementos altamente siderófilos, con unha afinidade extrema ao ferro, e, polo tanto, estímanse que o 99.8% dos EGPs da Terra residen no núcleo, quedando o mantos superior claramente empobrecido neles. As concentracións no núcleo varían dende 0.4 µg g^{-1} do Rh até 5.5 µg g^{-1} do Pt, mentres que na cortiza superior continental presentan concentración medias entre os 22 pg g^{-1} do Ir e os 520 pg g^{-1} do Pd, o que significa un enriquecemento no núcleo entre 1,000 e 100,000 veces, dependendo do elemento considerado. Así, os EGPs forman parte dos elementos máis escasos no medio ambiente, con concentración ultra-traza (<1 ng g^{-1}), e calquera interacción humana no seu ciclo superficial implicará unha perturbación importante do equilibrio natural. Non obstante, existen fontes naturais tales como as emisión volcánicas, polvo cósmico ou plumas hidrotermais que orixinan depósitos ricos en EGPs como nódulos de Fe-Mn ou os emprazamentos magmáticos. De feito, a intrusión na cortiza de corpos magmáticos diferenciados, xunto cuns mecanismos excepcionais de segregación e concentración, o que provoca a formación de depósitos minerais ricos en EGPs economicamente moi rendíbeis como o afamado *Bushveld Igneous Complex* (Sudáfrica), con aproximadamente o 80% das reservas mundiais, ou o xacemento *Norilsk (*Rusia*)*.

Usos industriais e consecuencias medioambientais: Debido ás súas propiedades singulares os EGPs son moi demandados para diversos usos industriais, especialmente nos derradeiros 40 anos onde houbo un aumento exponencial na súa demanda. Os catalizadores dos vehículos, desenvoltos para reducir as emisións de gases tóxicos do motor e transformalos en gases máis inocuos, son a súa principal aplicación, constituíndo até o 70% do PT que se demanda na Europa. A industria química, eléctrica, biomédica (o Pt é unha compoñente fundamental dos compostos para quimioterapias), ou do vidro e a xoiería, son outras das actividades que empregan EGPs. Ademais, dado o seu elevado valor económico tamén se empregan como activo para inversión económica. Deste xeito, o emprego de EGPs en todas as actividades humanas está xerando un aumento da súa concentración no medio ambiente, sendo de orixe humana entre un 86 e un 98% do fluxo de EGPs na superficie terrestre. Varios estudos previos sinalaron un enriquecemento nos sedimentos superficiais nas zonas urbanas e outras zonas de influencia humana, pero tamén foron documentados en ambientes remotos. As concentracións amosan un amplo rango de valores, dependendo das concentracións naturais locais de cada zona. Así, se as emisións antropoxénicas de EGPs están vinculadas co seu uso industrial, calquera industria que os use convértese nunha posíbel fonte de EGPs para o medio ambiente.

Os catalizadores dos vehículos a motor emiten, ao longo da súa vida, partículas de EGPs durante o seu funcionamento, especialmente Pt, Pd, y Rh, que son os compoñentes activos principais. Como resultados destas emisións, encóntranse concentracións elevadas de EGPs xeralmente adxacentes (dentro dos 2 primeiros metros) ás estradas con alta densidade de tráfico, aínda que o vento, a escorrentía e a topografía poden condicionar a súa distribución. As actividades mineiras e metalúrxicas son outra fonte de EGPs debido á alta cantidade de polvo e partículas que producen, afectado fundamentalmente á calidade do ar. Algúns estudos detectaron concentracións elevadas de EGPs nas áreas circundantes ás minas, incluíndo herba, chans e liques; aínda que as taxas de emisión non están cuantificadas, unha necesidade importante para a avaliación e xestión das actividades mineiras. Tamén os efluentes de hospitais son unha importante fonte de EGPs ao ambiente, debido ao contido do EGPs de terapias contra o cancro e que os doentes eliminan principalmente polos ouriños, así como o uso de EGPs en compostos para reparación odontolóxica ou do Os para tinxir os tecidos.

Determinación analítica: Un dos temas máis delicados á hora de estudar a xeoquímica dos EGP fica na dificultade da determinación analítica, debido á súa baixa concentración, que precisa do emprego de técnicas que permitan medir EGPs con precisión en matrices contaminadas, pero tamén os seus niveis naturais ou de fondo. Ademais, a recollida de mostras, separación e almacenaxe das mesmas pode afectar substancialmente á fiabilidades dos resultados; é necesario o uso de técnicas limpas xa que unha manipulación incorrecta durante calquera paso do proceso podería causar contaminación, elevando as concentracións entre 10 e 1,000 veces. Este feito fai que a determinación de EGPs precise de técnicas de alta sensibilidade e selectividade, fundamentalmente a espectrometría de masas con plasma axuntado indutivamente (ICP-MS) ou a voltametría adsortiva de redisolución catódica (AdCSV). O emprego do ICP-MS caracterízase pola rapidez, simplicidade e capacidade multi-elemental, aínda que as interferencias isobáricas poden causar importantes inexactitudes, máis notábeis nas concentracións ultra-trazas dos EGPs, debido á alta exactitude, á precisión, á selectividade e sensibilidade, así como aos baixos límites de detección e coste económico. Polo tanto, o desenvolvemento e mellora das técnicas de análise son uns dos principais retos dentro do campo da xeoquímica de contaminantes emerxentes.

Trazabilidade: É importante facer mención especial a unha das características máis interesantes dentro do estudo de EGPs, que é o uso dos isótopos de Os para a caracterización da súa orixe: natural ou antropoxénica. O Os amosa unha ampla gama de composición isotópica segundo a súa orixe e litoloxía debido á variación da proporción do ^{187}Os, o isótopo radioxénico que se deriva da súa desintegración radioactiva de ^{187}Re. Polo tanto, as relacións de ^{187}Os/^{188}Os trazan unha variedade de orixes: as proporcións típicas ^{187}Os/^{188}Os dos xacementos dos que proceden os EGPs de uso industrial, como *Bushveld Complex* (que supón o 80% da proporción mundial), é de 0.1-0.2, namentres que as relacións na cortiza continental superior son de 1.05±0.23. Esta notábel diferenza permite estimar a contribución antropoxénica de Os en mostras ambientais, e, supoñendo que o resto de EGPs derivan das mesmas fontes, estímase tamén a fracción antropoxénica do Pt, Pd e Rh en contornas urbanas. Sen embargo, a aplicación desta ferramenta en contornas naturais é case que inexistente e está limitado á o estudo de algunhas turbeiras, afectadas exclusivamente por deposición atmosférica, sendo inexistentes os estudos de sistemas naturais máis complexos.

Hipótese de traballo, obxectivos e xustificación: Estudos previos concluíron que existe unha perturbación antronpoxénica en contornas urbanas causada pola liberación de EGPs ao medio ambiente. Sen embargo tamén formularon preguntas que quedan aínda sen resposta, como cal é o destino dos EGPs cando chega a contornas naturais? Como é o seu comportamento sedimentario? Seguen a ser inertes? Disólvense? Existe nun xeito biodispoñíbel sendo asimilados polas plantas e entrando na cadea alimentaria? Ante estas incógnitas nace a hipótese de traballo desta tese de doutoramento.

> *Como é o comportamento xeoquímico dos elementos do grupo do platino nos sedimentos afectados por emisións de orixe antropoxénica? Cales son as súas principais fontes?*

e suscítanse os seguintes obxectivos para obter a súa respostas:

-desenvolvemento e mellora dos métodos para a determinación das concentracións ultra-traza de EGPs en diferentes matrices naturais, incluíndo niveles de fondo

-mellora do coñecemento do seu comportamento sedimentario e os procesos postdeposcionais que lles afectan

-avaliación do papel que desempeña a presenza de vexetación nos sedimentos dentro do ciclo bioxeoquímico dos EGPs

-determinación da transferencia de EGPs dende os sedimentos aos compartimentos biolóxicos e a súa posíbel bioacumulación sendo incorporados na cadea alimentaria

-cuantificación da contribución antropoxénica á totalidade de EGPs presentes nos sedimentos e augas intersticiais, en función do impacto do tráfico circundante

-valoración do axuste real dos EGPs segundo ás súas fontes antropoxénicas e o seu comportamento

-descrición do papel das marismas no ciclo dos EGPs e cuantificación da exportación (ou importación) de EGPs ao estuario e ao mar

-avaliación do impacto das actividades mineiras de EGPs nos ambientes naturais circundantes

Para levar a cabo este estudo seleccionáronse dúas áreas de traballo polas súas características particulares:

a) O río Hex (Rustenburg, Sudáfrica) que drena a zona mineira do *Bushveld Igneous Complex*, o meirande xacemento de EGPs, onde se levan a cabo actividades mineiras intensas

b) As marismas do estuario do Texo (W Península Ibérica), baixo diferentes niveis de tráfico, onde o comportamento de outros elementos traza (Pb, Cr, Zn, Ni, Cu, As, Cd, Co) foi ben caracterizado, así como o papel das marismas nos seus ciclos bioxeoquímicos dos mesmos, condicionado polos diferentes procesos físicos, químicos e microbiolóxicos é coñecido.

Capítulo 2. Mellora da determinación voltamétrica do rodio a concentración ultra-traza aplicado a mostras naturais mediante o uso da transformación do sinal

O rodio (Rh) está presente na superficie terrestre en concentración ultra-traza (60 pg g^{-1}). Sen embargo, o seu uso en catalizadores dos vehículos a motor aumentou a súa emisión e concentración en zonas de alta densidade de tráfico. Así mesmo, nos últimos anos, incrementouse o interese nas técnicas analíticas para a súa determinación ca fin de poder medir dito incremento con respecto aos niveis naturais dun xeito preciso. Neste estudo proponse unha mellora para a determinación de Rh por AdCSV (voltametría adsortiva de redisolución catódica) aplicando a transformación do sinal voltamético mediante o uso da segunda derivada.

A optimización dos parámetros experimentais que afecta ao análise voltamétrico levouse a cabo usando mostras de sedimento. Dita optimización inclúe a cantidade de mostra utilizada, as concentración de ácido clorhídrico e de formaldehido na disolución final, en tempo de equilibrio e deposición e o potencial de traballo para dita deposición. O uso da transformación por segunda derivada proporciona picos ben definidos debido a que se minimizan as interferencias de fondo da matriz, e leva unha disminución significativa nos límites de detección. En consecuencia, obtivéronse uns límites de detección de 23 fM Rh na cela e de 1.6 pg g^{-1} de Rh por 200 mg de sedimento.

Na metodoloxía optimizada aplicouse ao análise de Rh unha testemuña de sedimento recollida perto dunha ponte da autoestrada do Estuario do río Texo (Lisboa, Portugal). Aquí, as concentracións de Rh variaron dende 0.06 até 0.47 ng g^{-1}, amosando un enriquecemento superficial de Rh vinculado ao tráfico, o cal é consistente cun pico superficial de Pt. Tamén foron analizados materiais de referencia, como o polvo da estrada (BCR-723) e o sedimento fluvial (JSd-2), e os seus valores obtidos concordan cas concentración certificadas e publicadas.

Capítulo 3. Platino en sedimentos de marisma: comportamento e asimilación biolóxica

O platino (Pt) é un dos elementos químicos máis escasos na cortiza terrestre, sendo a súa concentración de 0.5 ng g^{-1}. Sen embargo o uso do Pt en diversas actividades humanas, especialmente en catalizadores de vehículos, está incrementando a súa concentración en sedimentos superficiais. Estudos previos avaliaron o comportamento sedimentario do Pt nas zonas urbanas; pero os sistemas naturais foron escasamente estudados.

Este traballo ten como obxectivo caracterizar o comportamento sedimentario do Pt liberado en ambientes costeiros e determinar o papel que a vexetación típica de marisma ten dentro do ciclo bioxeoquímico do Pt. Colléronse mostras de varias testemuñas de sedimento na marisma do estuario do Texo (colonizada e sen colonizar por *Sarcocornia fruticosa*), baixo diferentes condicións de tráfico vehicular. A concentración de Pt analizouse por voltametría adsortiva de redisolución catódica en sedimento, auga intersticial e diferentes tecidos de *Sarcocornia fruticosa* –raíces, talos e follas-. Outros parámetros auxiliares analizáronse na auga intersticial –potencial redos, osíxeno disolto, sulfuros totais, salinidade ou Fe e Mn disoltos- e tamén determináronse outros elementos químicos nas mostras de sedimentos (Fe, Mn, Al, Cd, V, Zn, Pb).

Aínda que se encontrou un enriquecemento superficial de Pt nos sedimentos da estación de mostraxe de Baixo Tráfico (2.8 ng g^{-1}), o meirande enriquecementos foi descrito na estación de Alto Tráfico onde a concentración de Pt acada, nalgúns casos, até 40 ng g^{-1}, apuntando á alta densidade de vehículos na zona como causa principal. Sen embargo, o Pt disolto presente na auga intersticial non amosa un pico superficial de Pt, amosando perfís bastante homoxéneos (0.26-0.66 ng L^{-1} en sedimentos vexetados e de 0.14-0.70 ng L^{-1} en sedimentos sen vexetar), o que indica unha baixa reactividade do Pt do sedimento, a excepción de dous picos en Pt nas zonas máis profundas, que acadan até 2.5 ng L^{-1} e que poderían estar relacionados con cambios nas condicións redox. Estes picos aparecen tamén na concentración de Pg nas raíces (0.9±0.6 ng g^{-1}), que non amosan un enriquecemento respecto á concentración de Pt no sedimento nin na auga intersticial, e polo tanto a bioacumulación e o transporte ás partes subaéreas da planta son baixas (a concentración de Pt media en talos e follas é 0.04±0.05 ng g^{-1}). Ademais, foron encontrados comportamentos axustados entre Pt e o Mn disolto que podería condicionar a formación de diferentes especies de Pt (aparecendo especies máis biodispoñíbeis na estación de Baixo Tráfico).

Polo tanto, o papel que xoga a vexetación é fundamental para a xeoquímica sedimentaria do Pt, xa que controla as condicións redox do sedimento e polo tanto a presenza de especies de Pt máis ou menos biodispoñíbeis.

Capítulo 4. Desaxuste de platino e osmio no medio ambiente: evidencias en sedimentos intermareais (Estuario do Texo, SO Europa)

O uso de catalizadores nos automóbeis provocou un aumento significativo na liberación dos elementos do grupo d platino ao medio ambiente. Traballos previos concluíron que a orixe de todos os elementos do grupo do platino é común, así como o comportamento xeoquímico que controla a súa distribución ambiental. Para comprobar a validez desta hipótese colléronse mostras de testemuñas de sedimento en dúas estacións da marisma do Texo (SO de Europa), afectadas por diferente presión de tráfico. Así, determináronse as concentracións de platino (Pt) –por voltametría adsortiva de redisolución catódica (AdCSV)– e osmio (Os) e a relación isotópica $^{187}Os/^{188}Os$ –por espectrometría de masas de ionización térmica negativa (N-TIMS)– en sedimentos e auga intersticial. A concentración de Pt nos sedimentos superficiais perto dazona de Alto Tráfico (que acada valores de 40 ng g^{-1}) indicou contaminación severa. Sen embargo, os sedimentos superficiais non amosaron un enriquecemento en Os. As relacións $^{187}Os/^{188}Os$, que comprenden valores dende 0.908 até 1.178, sinalaron a existencia de outras fontes ademais dos vehículos. As concentracións de Pt e de Os disoltos en augas superficiais, 0.1-0.7 ng L^{-1} para Pt e 0.03-0.10 ng L^{-1} para Os (reportados por primeira vez na literatura), foron máis altos que os valores típicos para as augas non contaminadas. En base aos resultados obtidos identificáronse dúas fontes de Pt e os nas marismas do estuario do Texo: unha entrada rexional vinculada cas actividades industriais onde se utilizan grande cantidade de comustíbeis fósiles e co tráfico a escala rexional; e unha fonte local asociada cunha alta densidade do tráfico nas inmendiacións da zona de mostraxe de Alto Tráfico. A cantidade estimada de Os e Pt liberados polos catalizadores dos coches apoian este modelo de dúas orixes. Ademais das diferentes fontes, a diferente capacidade de dispersión (o Pt libérase en forma de partículas e o Os como OsO_4 gaseoso) e diferente capacidade de disolución e mobilización levan a conclusión dun comportamento desaxustado entre o Pt e o Os. Como consecuencia, estes resultados cuestionan o uso dos isótopos de Os como trazador da orixe doutros elementos do grupo do platino no medio ambiente.

Capítulo 5. Fluxos difusivos de osmio e platino en sedimentos de marisma (Estuario do Texo, SO Europa)

A cuantificación de fluxos en ambientes costeiros é unha das materias máis importantes para a caracterización dos ciclos bioxeoquímicos dos elementos impactados antropoxénicamente. Os elementos do grupo do platino atópanse entre estes contaminantes antropoxénicos debido, principalmente, ao seu uso nos catalizadores dos coches, que liberan partículas ao medio ambiente durante o seu uso. Polo tanto o obxectivo deste estudo é a estimación dos fluxos difusivos de osmio (Os) e platino (Pt) en sedimentos de marisma para avaliar se ditas marismas están funcionando como sumidoiros ou como fontes destes elementos ás augas do estuario ao océano.

Tomáronse dúas testemuñas de sedimento, coa súa correspondente auga sobrenadante, no punto das marismas do estuario do Texo, en marzo e setembro de 2011, dos cales colleuse a auga intersticial. A concentración de Pt na auga intersticial analizouse por AdCSV, mentres que a concentración do Os e a súa composición isotópica determinouse por N-TIMS. Para calcular os fluxos difusivos aplicouse a primeira lei de Fick modificada para sedimentos porosos, proporcional ao gradiente de concentracións de ditos elementos entre as augas intersticiais e sobrenadantes. Ademais, realizouse unha estimación teórica dos coeficientes de difusión das especies químicas típicas do Os e Pt no auga salgada (a 298 ºK) debido á falta de valores experimentais na literatura.

O Pt amosaba un comportamento diferente en primavera e verán: as marismas reteñen Pt durante a primavera (–370 ng m^{-2} y^{-1}) e exportan unha pequena cantidade de Pt no verán (49 ng m^{-2} y^{-1}), sendo un sumidoiro neto de Pt ao longo do ciclo anual. En calquera caso, a liberación/retención de Pt Pt (1.6 g e 12 g, respectivamente) é insignificante en comparación coa entrada de Pt vinculada ao tráfico. Sen embargo, as marismas compórtanse como unha fonte de Os ao estuario, e posteriormente ao océano, durante todo o ano (primavera 0.71-1.4 ng m^{-2} y^{-1}, verán 1000-1900 ng m^{-2} y^{-1}, dependendo da especiación). Liberan 32-61 g de Os ao estuario só en verán, o que suón entre o 19 e o 32% do Os que chega ao estuario do Texo nun ano. Extrapolando estes resultados a todas as marismas do mundo, supoñerían unha liberación do 25-40% da cantidade total de Os que chega anualmente aos océanos sendo un comportamento chave no ciclo global do Os. Consideramos ademais que estres resultados apuntan de novo a un comportamento desaxustado entre Os e Pt que é necesario ter en conta para futuras investigación, se ben é certo que sería necesario un estudo en maior profundidade para mellorar o coñecemento sobre o ciclo bioxeoquímico destes elementos traza.

Capítulo 6. Elementos do grupo do platino en sedimentos fluviais de zonas mineiras: o río Hex (*Bushveld Igneous Complex*, Sudáfrica)

A avaliación do impacto ambiental das actividades mineiras dende o punto de vista dos elementos do grupo do platino e outros elementos traza é fundamental para previr os riscos potenciais para poboación. Este estudo avalía as concentración de elementos do grupo do platino en sedimentos fluviais de catro zonas diferentes do río Hex, o cal drena a zona mineira do *Bushveld Igneous Complex* (Sudáfrica). Analizáronse elementos maioritarios e traza (Fe, Ca, Al, Mg, Mn, V, Cr, Zn, Cu, As, Co, Ni, Cd e Pb) por espectrometría de absorción atómica por chama e electrotérmica en partículas en suspensión e en diferentes fraccións de sedimento (<63, 63-500 e 500-2000 µm). Os elementos do grupo do platino –Pt, Pd, Rh e Ir– medíronse por ICP-MS despois da eliminación de elemntos que poden causar interferencias isobáricas, mediante o uso dunha resina de intercambio catiónico DOWEX 50W-X8. Os valores foron corrixidos despois de analizar e subtraer os brancos de procedemento. Finalmente a exactitude controlouse mediante a análise de materiais de referencia. Elementos como Ni, Cr, Pt, Pd, Rh e Ir amosan concentracións de 3-, 13-, 18-, 28-, 48- y 44- veces os niveis típicos na cortiza continental superior, respectivamente, aínda que as súas concentracións son menores que as analizadas na rocha nai local. As concentracións máis elevadas observáronse máis perto da zona mineira, na fracción <63 µm e diminuíndo coa distancia. Por todo elo, é probábel que procedan da deposición atmosférica de partículas ricas en elementos do grupo do platino liberadas polas actividades mineiras e da escorrentía superficial que as redistribúe.

Polo tanto, as actividades antropoxénicas como a minería están causando unha certa perturbación do ciclo xeoquímico superficial dos elementos do grupo do platino, aumentando a súa presencia na fracción fina dos sedimentos do río e polo tanto a posíbel exposición da poboación aos mesmo, o que representa un risco potencial. Propoñemos que novos parámetros indicadores de contaminación tales como a calidade das partículas que se emiten, que se depositan posteriormente na vexetación, chans e outros ambientes, ou a calidade dos sedimentos fluviais, engádanse aos protocolos que avalían a sostenibilidade das actividades mineiras.

Capítulo 7. Síntese e conclusións xerais

O traballo comprendido nesta tese de doutoramento supón un extenso estudo do comportamento sedimentario dos elementos do grupo do platino (EGPs) en ecosistemas naturais e a avaliación das súas fontes de emisión de orixe humana.

Melloras analíticas: Esta tese supón un importante progreso na determinación dos diferentes EGPs. En consecuencia, puidéronse analizar concentracións naturais e contaminadas por actividades humanas mediante o uso de diversas metodoloxías complexas.

A AdCSV utilizouse para a determinación do platino en diferentes matrices, aplicando o método desenvolvido por van den Berg e Jacinto (1988) e mellorado por Cobelo-García *et al.* (2011). Establecéronse ademais protocolos específicos de preparación de mostras e condicións apropiadas de análise para augas intersticiais e os tecidos biolóxicos. Ademais, propúxose un método novo para a determinación do rodio por voltametría, mediante a aplicación da transformación por segunda derivada descrito por Cobelo-García et al., (2014). Utilizouse ademais o N-TIMS para a determinación de Os e da súa composición isotópica, así como o ICP-MS para a determinación simultánea de diversos EGPs tralo paso da mostra por unha columna de intercambio catiónico. Neste método tamén se realizou a optimización do pretratamento da mostra (temperatura de muflado).

Publicáronse por primeira vez datos de concentracións de Pt e Os en augas intersticiais, o que fai que esta tese (e os artigos resultantes da mesma) unha referencia científica para futuros estudos sobre os ciclos xeoquímicos de EGPs. Por outra parte, as concentración de algún destes elementos non certificados nos materiais de referencia máis comúns de EGPs como po da estrada BCR-723 e o sedimento fluvial, JSd-3, son tamén dados (por exemplo, Rh en JSd-2 por diferentes métodos).

O comportamento sedimentario do platino procedente de catalizadores en zonas de marisma: O comportamento dos diferentes EGPs (especialmente Pt e Os) estudouse nas marismas do estuario do Texo (SO Europa) baixo diferente densidades de tráfico de vehículos, Alí, o papel da vexetación é esencial para entender o comportamento sedimentario do Pt, xa que as raíces das plantas halófitas controlan a xeoquímica do sedimento que as rodean (condicións redox, presenza de O_2, degradación da materia orgánica) determinando a formación de especies químicas en fase sólida ou disolta. Atopouse unha clara relación entre Pt e Mn disoltos na auga intersticial das marismas, similar á relación Pt-Mn das costras e nódulos de Fe-Mn que podería ser explicada por procesos de co-precipitación/adsorción/secostro de Pt simultáneo á formación de óxidos de Mn. A concentración de Pt nas raíces de S*arcocornia fruticosa*, que reflexan a concentración de Pt existente en cada momento na auga intersticial, e o escaso transporte de Pt aos tecidos subaéreos das plantas indican a inexistencia dunha verdadeira bioacumulación de Pt e dunha incorporación efectiva de Pt á cadea alimentaria.

Existen dúas fontes antropoxénicas diferentes de EGPs nas marismas do Estuario do Texo:

> -unha fonte de EGPs rexional vinculada ás actividades humanas en toda a área de Lisboa, incluíndo actividades industriais ou o tráfico a grande escala, que afecta a toda a marsima e que provoca un pequeno enriquecemento en EGPs con respecto ás concentración de fondo (Pt/Os~ 200)
>
> -unha fonte de EGPs local vinculados só ás emisións do tráfico de vehículos, que provocan un enriquecemento superficial de Pt (tamén Rh) e que aecta só perto da estrada/autoestrada (Pt/Os>> 200)

Polo tanto, observase un comportamento desaxustado dos diferente EGPs no medio ambiente, especialmente de Os respecto a os outros EGPs, en relación tanto ás súas fontes como aos seus mecansimos de liberación e dispersión ou á súa diferente reactividade e mobilidade. O Pt permanece asociado a partículas no sedimento (non reactivo), sen existir disolución importante do mesmo na auga intersticial. Así os sedimentos funcionan como un sumidoiro efectivo de Pt antropoxénico. O Os, que se emite como OsO_4 gaseoso, amosa unha maior mobilidade, exportándose ao estuario e augas oceánicas. De feito, polo menos o 20% do Os que chega cada ano ao estuario do Texo vén directamente das marismas e estímase que o Os emitido por todas as marismas do planeta podería acadar até o 40% do Os oceánico, o que convertería as marismas nun compartimento chave no ciclo xeoquímico do Os. En consecuencia, o desaxuste Pt-Os debe terse en conta ao usar as relacións isotópicas do Os para a reconstrución de fontes de contaminación dos EGPs en matrices ambientais.

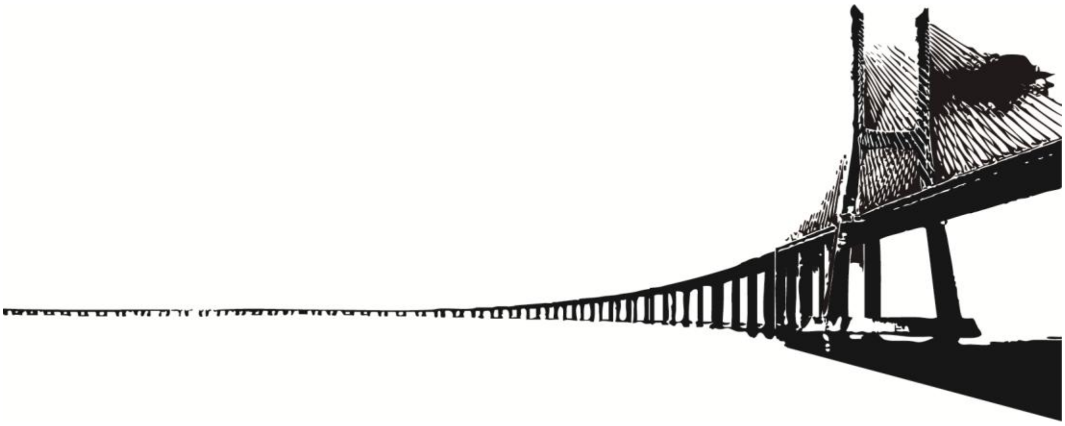
A influencia das actividades da minería extractiva de elementos do grupo do platino nos ambientes acuáticos circundantes: Aínda que as concentracións elevadas de EGPs (e outros elementos traza) nos sedimentos dos ríos mineiros corresponden principalmente aos altos niveis naturais, as actividades mineiras causan perturbacións do ciclo xeoquímico superficial dos EGPs, como o aumento das súas concentracións nas fracción limo e arxila (<63 µm) derivado da deposición atmosférico e a escorrentía superficial. Polo tanto, esta deposición atmosférica podería afectar á vexetación local de cultivos e aumentar a exposición a EGPs da poboación local.

Propoñemos que indicadores ambientais como partículas no ar, chans ou sedimentos fluviais deban de ser consideradas nos protocolos que avalían a sustentabilidade das actividades mineiras ca fin de mellorar a calidade do medio ambiente e protexer a poboación local.

Como conclusión xeral, esta tese trata de mellora a comprensión dos ciclos bioxeoquímicos os elementos do grupo do platino e a perturbación que o desenvolvemento das actividades humanas está causando neles. A variación que os ecosistemas están sufrindo nas últimas décadas respecto ás súas condicións naturais teñen aínda máis relevancia nas rexións costeiras, especialmente vulnerábeis á mudanza global. Polo tanto, agardamos que todas as conclusións acadadas nesta tese poidan contribuir ao progreso do coñecemento xeoquímico así como á mellora da xestión ambienta.

Chapter 1

Introduction and objectives



Introduction and objectives

1.1 Importance of trace elements geochemistry

Many studies carried out in the last years have been conducted to understand the biogeochemical cycles and distribution of trace elements and their isotopes in the environment. For many trace elements, however, their sources, sinks, internal cycling, isotopic behavior or chemical speciation are poorly constrained making it difficult to draw conclusions about their global biogeochemical cycles. Therefore, the identification and quantification of processes that control the distribution of trace elements (and their isotopes) is a key factor to assess their vulnerability to global change –including contamination– and to predict their behavior in response to changing environmental conditions.

The ocean and its different interfaces (i.e. land, sediments, atmosphere, Figure 1.1) are regions of special interests due to the high complexity and low understanding of their functioning. The biogeochemical cycles of trace elements involve the determination of their sources, sinks, and fluxes through different oceanic reservoirs (Santos Echeandía, 2009) which are influenced by biological, chemical and geological processes leading to a redistribution among the different environmental matrices (i.e. water, sediment and organisms). In addition, it should be noted that some trace elements are essential for life, while others may display toxic effects for marine organisms. As a result, the scientific community and several funding organisms concentrate significant efforts to cover the existing gaps about the knowledge of the biogeochemical cycles of trace elements. Some international programs like LOICZ (Land-Ocean Interactions in the Coastal Zone, www.loicz.org; Kremer et al., 2005) and, specially, GEOTRACES (An international study of Marine Biogeochemical cycles of Trace Elements in their isotopes, www.geotraces.org; Scientific Committee on Oceanic Research, 2006) were created to shed further light on the knowledge about biogeochemistry (Figure 1.2). GEOTRACES program considers some interesting goals for the study of the biogeochemical cycles of trace elements in the oceanic system that pursue: (i) to determine global ocean distributions of selected trace elements and isotopes and to evaluate the sources, sinks, and internal cycling to characterize all the processes that regulate their distributions (Figure 1.1), (ii) to understand the processes involved in oceanic trace-element cycles sufficiently well so that the response of these cycles to global change can be predicted and (iii) to understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column (Scientific Committee on Oceanic Research, 2006). The strategies to achieve the aims proposed are focused in different research fields related to fluxes and processes at ocean interfaces, internal cycling (a complex suite of transport and transformation processes in the ocean), and development of new proxies (Figure 1.1 and Figure 1.3).

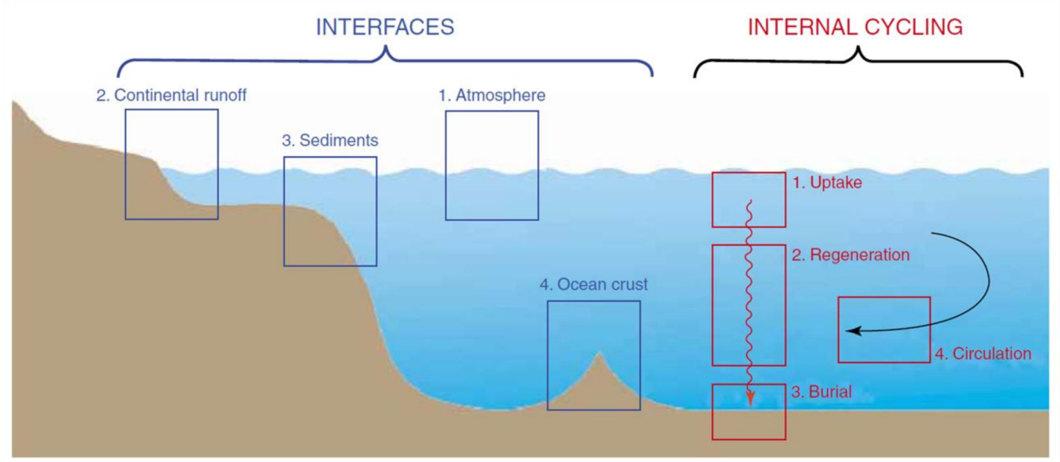


Figure 1.1: Scheme of the major influences on the trace elements cycles in the ocean, divided in: A) interfaces (blue): atmosphere, continental runoff, sediments and ocean crust; B) Internal cycling: uptake, regeneration, burial and circulation.

Figure 1.2: Logos of LOICZ and GEOTRACES programs (images taken from organisms web sites).

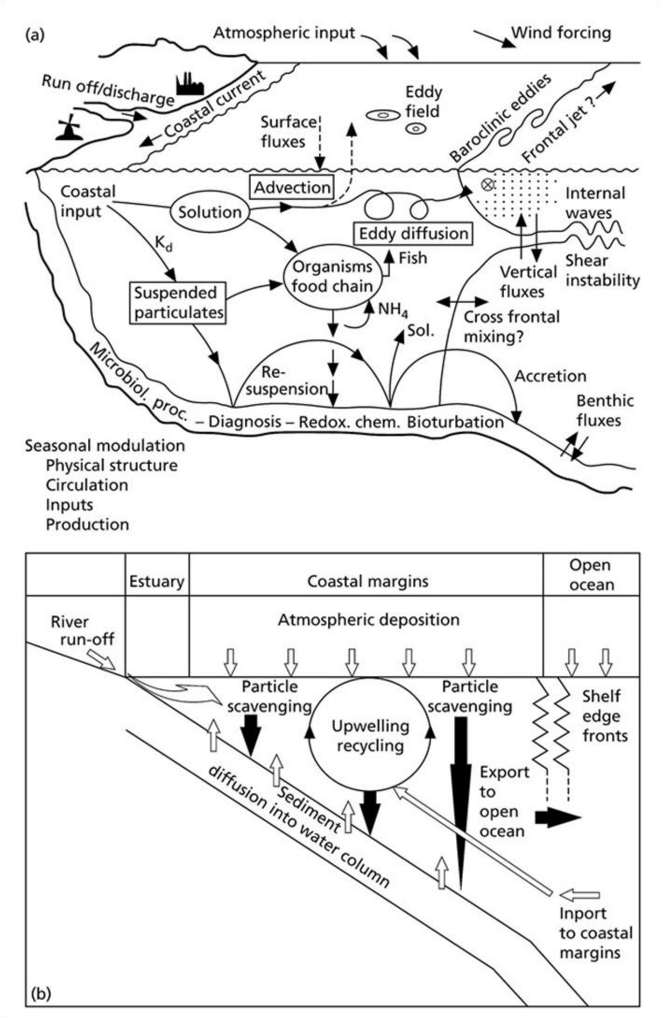


Figure 1.3: General processes that influence the fate of trace elements and pollutants in the coastal margins (a) and representation of trace elements pathways in the coastal margins (b) (from Trace Elements in the Oceans, Chester, 2012).

1.2 Platinum group elements (PGE)

1.2.1 Characterization

The platinum group elements (PGEs) is a group of 6 elements located in the transition metals region on the periodic table of the elements (Figure 1.4), 3 in the period V –ruthenium (Ru), rhodium (Rh) and palladium (Pd)– and 3 in the period VI –osmium (Os), iridium (Ir), and platinum (Pt)–. All these elements present similar characteristics like catalytic properties, resistance to chemical attack, excellent endurence to high-temperature, and stable electrical properties (USGS, 2015).

PGEs are highly siderophile elements –elements with an extreme affinity for iron that dissolve in it as solid solutions or in molten state–, and, as such, the bulk of Earth's PGE budget is thought to reside in the core, estimated to be more than 99.8% (Lorand et al., 2008), as evidenced by

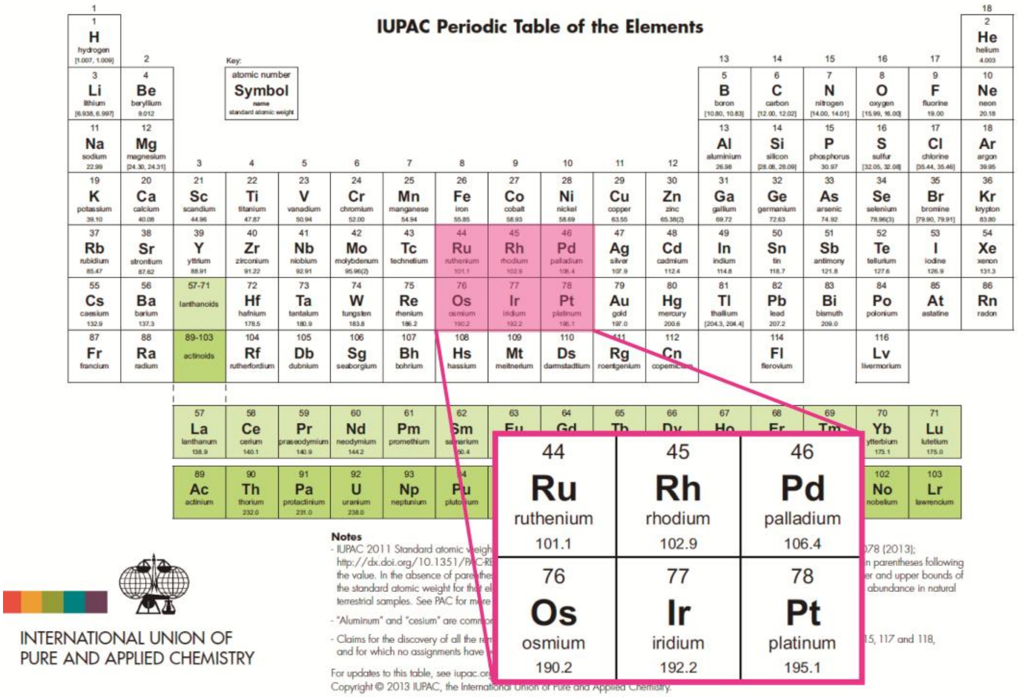


Figure 1.4: IUPAC Periodic Table of the elements where Platinum Group Elements are highlighted (from IUPAC, 2013).

the relative depletion of PGEs in Earth's upper mantle. Table 1.1 summarizes the concentrations of each PGEs in the Earth´s core (Lorand et al., 2008) and Upper Continental Crust (Wedepohl, 1995; Peucker-Ehrenbrink and Jahn, 2001) showing an evident enrichment from 1000 to 100,000 times in the core, depending on the element. Therefore, PGEs are amongst the rarest elements in the environment exhibiting ultra-trace concentrations at the Earth's surface (<1 ng g^{-1}) and any human interaction in the surface cycle of PGEs will likely result in the disturbance of their natural equilibrium. However, it is important to remark that some natural sources, like volcanic emissions (Soyol-Erdene et al., 2011), cosmic dust (Gabrielli et al., 2004), hydrothermal plumes (Cave et al., 2003) or mantle partial melts (Naldrett et al., 2008) entail the formation of high PGE deposits like for example Fe-Mn crusts (Burton et al., 1999) or mantle intrusions in the earth crust (Naldrett et al., 2008).

The development of a fractioning body of magma that intrudes into the crust, followed by particular mechanisms that serve to concentrate the PGEs (Naldrett et al., 2008), leads to the formation of economically viable PGE-rich deposits. Thus, different PGE ores are distributed along the world (Figure 1.5) in singular geological settlements that allow the formation of these unique deposits like the Bushveld Igneous Complex (South Africa), Noril'sk (Russia), Stillwater Complex (Montana, US) or Great Dyke (Zimbabwe) (Holwell and McDonald, 2010). The largest ore of platinum is the Bushveld Igneous Complex, which contains about 75%, 54%, and 82% of the world resources of Pt, Pd, and Rh, respectively; its reserves are large enough to meet the anthropogenic demand for decades (Cawthorn, 2010; Glaister and Mudd, 2010).

Table 1.1: Concentrations of the Platinum Group Elements in the Earth´s core (Lorand et al., 2008) and in the Upper Continental crust (Wedepohl, 1995; Peucker-Ehrenbrink and Jahn, 2001).

PGEs	Earth´s core (pg g^{-1})	Upper Continental Crust (pg g^{-1})	Earth´s core enrichment
Ru	2200000 - 4200000	210	10^4
Rh	400000 - 800000	60	10^3 - 10^4
Pd	1700000 - 3150000	520	10^3
Os	1000000 - 3000000	31	10^4 - 10^5
Ir	1000000 - 3000000	22	10^4 - 10^5
Pt	3300000 - 5500000	510	10^3 - 10^4

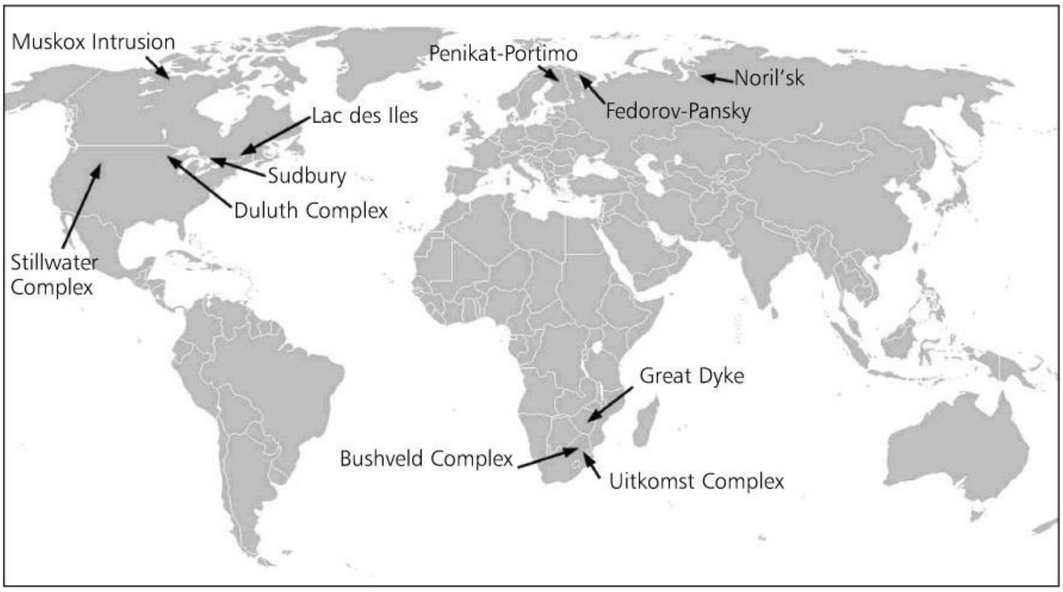


Figure 1.5: Global distribution of major magmatic platinum group elements sulfide deposits (Holwell and McDonald, 2010).

1.2.2 Human uses

Due to the unique properties of PGEs like chemical inertness, high melting point or the ability to catalyze chemical reactions (Brenan, 2008), PGEs have become extremely demanded for industrial uses, and the number of applications where PGEs are needed has significantly increased in the recent years (Rauch and Morrison, 2008), and, accordingly, an exponential increase of the PGE demand over the past 40 years (Johnson Matthey, 2013). Figure 1.6 shows the demand by uses of the PGEs during the present century (Johnson Matthey, 2013).

Catalytic converters for the automobile sector (autocatalyst in theFigure 1.6) is the main application demanding PGEs, especially Pt, Pd and Rh as active components in the catalytic converters of motor vehicles –diesel or gasoline– (Palacios et al., 2000), containing Ir, Ru and Os as impurities (Fritsche and Meisel, 2004). Catalytic converters were developed to treat engine exhaust emissions, transforming the noxious gases CO, NO_x or hydrocarbons into more harmless products like CO_2, N_2 and water (Farrauto and Heck, 1999; Böck, 2006). The introduction of catalytic converters started in the '70s in United States (Rauch et al., 2004a; Ravindra et al., 2004) and in the '80s-'90s in Europe (Fritsche and Meisel, 2004; Wiseman and

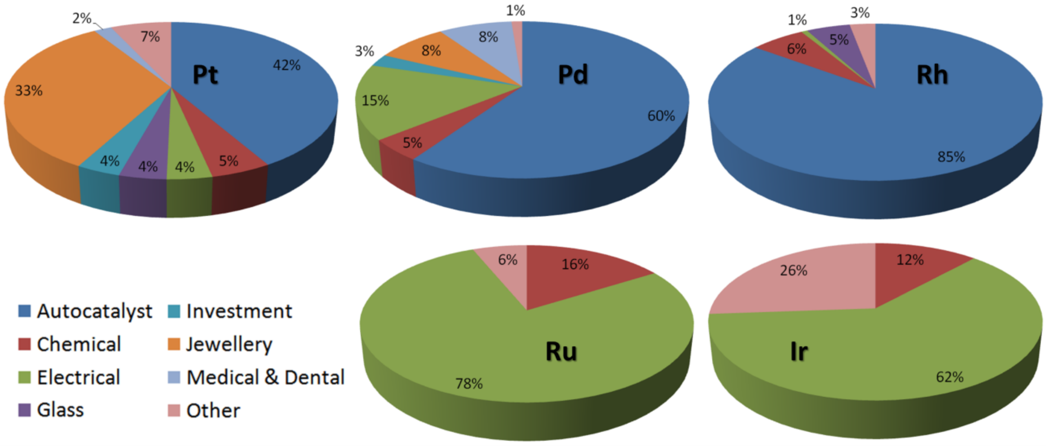


Figure 1.6: World demand by application of the different Platinum Group Elements during 2000-2013 for Pt, Pd, and Rh and 2005-2013 for Ir and Ru (data of Os are not available). Total demand in weight: Pt= 3300 tons, Pd= 3500 tons, Rh= 380 tons, Ru= 260 tons and Ir= 50 tons (Johnson Matthey, 2013).

Zereini, 2009). In fact, since the '80s, almost 70% of the European platinum demand has been used for manufacturing catalytic converters (Johnson Matthey, 2013).

But PGEs are being used in many other different activities like chemical, electrical, biomedical industries or glass and jewelry (Figure 1.6). The chemical industry uses a significant amount of Pt or Pt-Rh alloy in gauze-shape to catalyze the partial oxidation of ammonia to yield nitric oxide, used for fertilizers, explosives, and nitric acid. Besides, Pt, Ir and alloys are used as crucible materials for the growth of single crystals, especially oxides. Also, PGEs are important as catalysts in synthetic organic chemistry and in the refining of crude oil and other processes used in the petrochemical industry. In the electrical industry PGE alloys are used in low-voltage and low-energy contacts, film circuits, furnace components, and electrodes (USGS, 2015). Regarding to medical uses, Pt-containing drugs are used in the treatment of different forms of cancer (Rauch and Morrison, 2008), but also other PGEs are usually utilized with scientific-medical aims like stain fixative in electron microscopy applications for Os (Rauch and Morrison, 2008) or dentist alloys for Pd (Ravindra et al., 2004). On the other hand, the PGEs, specially Pt and Pd, are used in investment because of its expensive value that changes with the supply and demand.

1.2.3 Environmental relevance

The use of PGEs in the above-mentioned human activities is increasing their environmental concentrations (Rauch and Morrison, 2008; Sen et al., 2013); accordingly, it has been estimated that 86 - 98% of PGE total flux at the Earth's surface derives from anthropogenic activities (Sen and Peucker-Ehrenbrink, 2012): Ir~ 98%> Os> Ru> Pd> Pt> Rh~ 86% (Figure 1.7). Several previous studies have reported an enrichment in surface sediments and deposits linked to human activities, especially in urban areas or human-influenced environments (Schäfer and Puchelt, 1998; Tuit et al., 2000; Fritsche and Meisel, 2004; Rauch et al., 2004a; Whiteley and Murray, 2005; Sutherland et al., 2007) but also in remote environments (Barbante et al., 2001; Rauch et al., 2004b, 2005a, 2010; Soyol-Erdene et al., 2011; Sen et al., 2013). Table 1.2 shows data of Pt, Pd, Rh and Os concentrations from different types of sediments like peat bogs or road soils, contaminated and non-contaminated ranges (from several bibliographic sources:

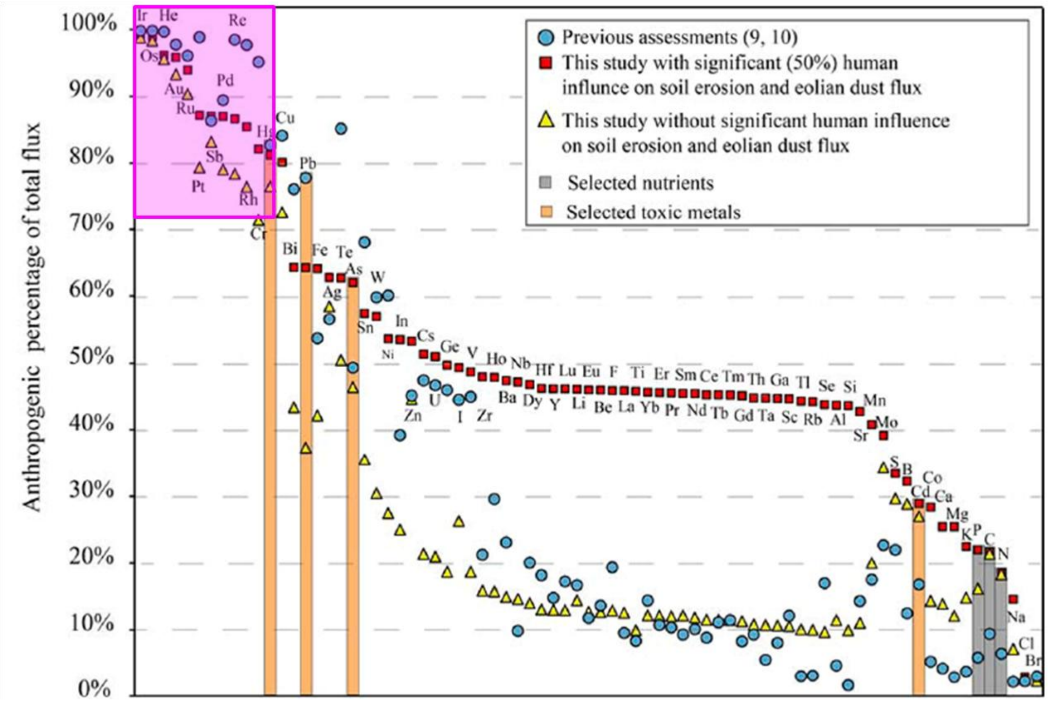


Figure 1.7: Comparison of relative human contribution (in %) to the total mobilization between the study of Sen and Peucker-Ehrenbrink (2012) where red squares: 50% human influence on soil erosion and eolian dust flux; yellow triangles: soil erosion and eolian dust fluxes are considered natural flows; blue circles: previous report (figure from Sen and Peucker-Ehrenbrink, 2012).

Table 1.2: Bibliographic Pt, Pd, Rh and Os concentrations in different sediments: contaminated and background values (Wedepohl, 1995; Schäfer and Puchelt, 1998; Peucker-Ehrenbrink and Jahn, 2001; Fritsche and Meisel, 2004; Rauch et al., 2004a, 2004b; Whiteley and Murray, 2005; Sutherland et al., 2007; Prichard et al., 2008).

Sediment	Authors	Pt ($pg\ g^{-1}$)		Pd ($pg\ g^{-1}$)		Rh ($pg\ g^{-1}$)		Os ($pg\ g^{-1}$)	
		contam.	backgr.	contam.	backgr.	contam.	backgr.	contam.	backgr.
Loess	Peucker/Wedepohl	-	510		520		60	-	31
Peat bog	Rauch *et al.*, 2004b	2700-290000	-	840-3100		280-710		6.9-24	-
Urban lake	Rauch *et al.*, 2004a	11000-30000	1000-1700	12000-26000	1600-4700	1600-3500	200	150	56-71
Urban watersheds	Sutherland *et al.*, 2007	57000-70000	-	16000-18000		5500-6200		-	-
Urban stream sed.	Prichard *et al.*, 2008	610000	2000	1100000	2000	210000	< 1000	-	-
Urban Infiltration	Whiteley-Murray, 2005	9000-100000	990	5400-61000	1600	1600-17000	290	-	-
Road side	Fritsche-Meisel, 2004	9100-130000	160-280	1500-21000	290-360	1100-13000	30-50	40-250	40-90
Road dust	Schäfer-Puchelt, 1998	12000-1100000	-	1500-200000	-	2000-200000	-	-	-
Road side soil	Schäfer-Puchelt, 1998	20000-200000	400-3000		< 400-1200		< 100-600	-	-

Wedepohl 1995; Schäfer and Puchelt 1998; Peucker-Ehrenbrink and Jahn 2001; Fritsche and Meisel 2004; Rauch et al. 2004a, 2004b; Whiteley and Murray 2005; Sutherland et al. 2007; Prichard et al. 2008). Concentrations exhibit a wide range of values, depending on the local background of the sampling area.

Thus, the anthropogenic PGE emissions are linked with the industrial use of these elements and any industry that manufactures PGE-containing products in susceptible to be a source of these elements to the environment.

1.2.3.1 PGE emission from catalytic converters

A catalytic converter emits during its lifetime microparticles with a size of 1-63 µm (Artelt et al., 1999) covered by tiny fragments (<0.3 µm) of PGEs (Prichard and Fisher, 2012), especially in the first 30,000 Km (Palacios et al., 2000); afterwards the release of PGE particles decreases. The quantification of the PGE release by catalytic converters has been an important topic among the scientific community, since PGE emissions depend on different aspects, including the type of engine and catalyst –catalytic converters composition has been changing depending on the market price and the engineering developments (Farrauto and Heck, 1999; Fritsche and Meisel, 2004)–, the vehicle speed or the driving conditions (Ravindra et al., 2004; Rauch and Morrison, 2008). Some authors, based on direct measurements (Palacios et al., 2000), reported that a gasoline catalyst releases 100, 250 and 50 ng Km^{-1} for Pt, Pd and Rh respectively in the first 30,000 Km, and 6-8, 12-16 and 3-12 ng Km^{-1} (Pt, Pd and Rh) after 30,000 Km, whereas a diesel catalysts reaches 400-800 and 108-150 ng Km^{-1} (Pt) before and after 30,000 Km, respectively. Other authors, based on environmental evidences, reported that the average release of Pt by vehicle is 270 ng Km^{-1} (Schäfer et al., 1999; Zereini et al., 2001a). Regarding Os, due to the volatility of OsO4, is completely released in the first year of the catalytic converter due to the high operating temperatures of the catalyst (Poirier and Gariépy, 2005). Several studies have analyzed airborne particles in urban areas concluding that catalytic converters are the source of such important contamination (Alt et al., 1993; Zereini et al., 2001b; Rauch et al., 2005b; Sen et al., 2013).

As a result of these emissions, elevated PGE concentrations are generally found in areas close to high traffic density within ~2 m near the road (Helmers and Mergel, 1998; Schäfer and Puchelt, 1998; Zereini et al., 2001a; Fritsche and Meisel, 2004), although the wind, runoff and topography may take control over their distribution (Schäfer and Puchelt, 1998).

1.2.3.2 PGE emission from mining and metal production

The mining and metal production activities are also an important source of PGE emissions due to the high amount of dust and particles that these industries produce during their activity resulting in airborne contamination. Some studies near mining areas and smelters have confirmed elevated Pt and Os concentrations in the surrounding areas, including grass, soils and lichens (Rodushkin et al., 2007; Rauch and Fatoki, 2013). However, emission rates, an important variable for the assessment and management of metal production activities, are not well quantified (Rauch and Morrison, 2008).

1.2.3.3 PGE emission from medical facilities

The Pt contained in the anti-cancer therapies is mostly removed by the urine of the patients (Alt et al., 1997; Krachler et al., 1998; Fragnière et al., 2005; Ruggiero et al., 2013) increasing Pt concentration in the sewage waters, as well as the Os used in staining processes (Esser and Turekian, 1993), the Pd used in dentist alloys (Ravindra et al., 2004) or other PGEs applied to the medical uses. Therefore, the effluents of hospitals and dental clinics are other important source of PGEs to the environment (Lenz et al., 2007; Rauch and Morrison, 2008) where Pt concentrations from 10 to 3500 ng L^{-1} have been reported (Kümmerer et al., 1999).

Although most of the existing studies have been focused on the PGE transport from the emission to deposition, some other studies have analyzed Pt concentration in biological natural samples (Hodge et al., 1986; Alt et al., 1988; Beinrohr et al., 1993; Alt et al., 1997; Pino et al., 2010) or food (Hoppstock et al., 1989; Alt et al., 1997; Fragnière et al., 2005) to have an idea about concentrations in different environmental matrices. Other studies have made significant advances in the research of the Pt uptake, designing tests where different organisms are grown in an artificial Pt-rich environments (Schäfer et al., 1998; Moldovan et al., 2001; Cosden et al., 2003; Zimmermann et al., 2004) or in natural contaminated areas (Rauch and Morrison, 1999; Moldovan et al., 2001; Haus et al., 2007; Orecchio and Amorello, 2010). Experimental investigations reveals a Pt uptake by terrestrial and aquatic plants (Zimmermann and Sures, 2004) in response to the environmental increase in Pt concentration in the last decades (Helmers and Mergel, 1998; Schäfer et al., 1998; Cosden et al., 2003), but there is a lack of studies to demonstrate bioaccumulation in plants for long exposure periods, in natural concentrations and real chemical species at natural waters.

1.2.4 Analytical methods for PGE determination

One of the major issues or limitations in the study of the geochemistry of PGEs is based in the difficulty of their analytical determination. The development of appropriate analytical methods to accurately measure PGEs in contaminated matrices, but also background concentrations is a major challenge. Besides, samples collection, separation and conservation can substantially affect the reliability of the results (Balcerzak, 2011) and trace-clean methodologies are required to avoid sample contamination; actually, an incorrect handling during the process could cause contamination leading to 10 to 1000 higher concentrations than the real sample (Santos Echeandía, 2009).

The determination of PGEs needs high sensitive and selective techniques like inductively coupled plasma mass spectrometry (ICP-MS) (Colodner et al., 1993; Meisel et al., 2003; De Boni et al., 2007), adsorptive voltammetry (AV) (van den Berg and Jacinto, 1988; Helmers and Mergel, 1998; Cobelo-García et al., 2014), electrothermal atomic absorption spectrometry (ET-AAS) (Hodge et al., 1986; Cantarero et al., 1994), neutron activation analysis (NAA) (Hoffman et al., 1978; Murali et al., 1990) or thermal ionization mass spectrometry (TIMS) (Sharma et al., 2007; Turekian et al., 2007). ICP-MS is characterized by rapidity, simplicity and multi-elementary capacity, although isobaric interferences –like $^{63}\mathrm{Cu}^{40}\mathrm{Ar}^{+}$ or $^{91}\mathrm{Zr}^{12}\mathrm{C}^{+}$ on Rh^{103}– may cause severe inaccuracies in the determination of PGEs (León et al., 1997), more noteworthy at the ultra-trace PGE concentrations of biological or environmental samples. Thus, the removal of interferences by means of cationic exchange resins is essential (Meisel et al., 2003; De Boni et al., 2007; Balcerzak, 2011); isotope dilution has also been used prior to ICP-MS determination (Meisel et al., 2003; Chen and Sharma, 2009; Rauch et al., 2010) but it is not suitable for monoisotopic elements like Rh. Several studies have showed that adsorptive voltammetry is a suitable alternative for PGE determination, due to high accuracy, precision, selectivity and sensitivity, as well as low detection limits and economical cost (Helmers and Mergel, 1998; Cobelo-García et al., 2014), although diverse difficulties and limitations related to the complexity of natural matrices and low natural concentrations also exist. Consequently, the development and improvement of analytical techniques, that provide higher sensitivity, higher precision and simplicity, is one of the main challenges to better understand the geochemistry of new emergent ultra-trace contaminants like PGEs.

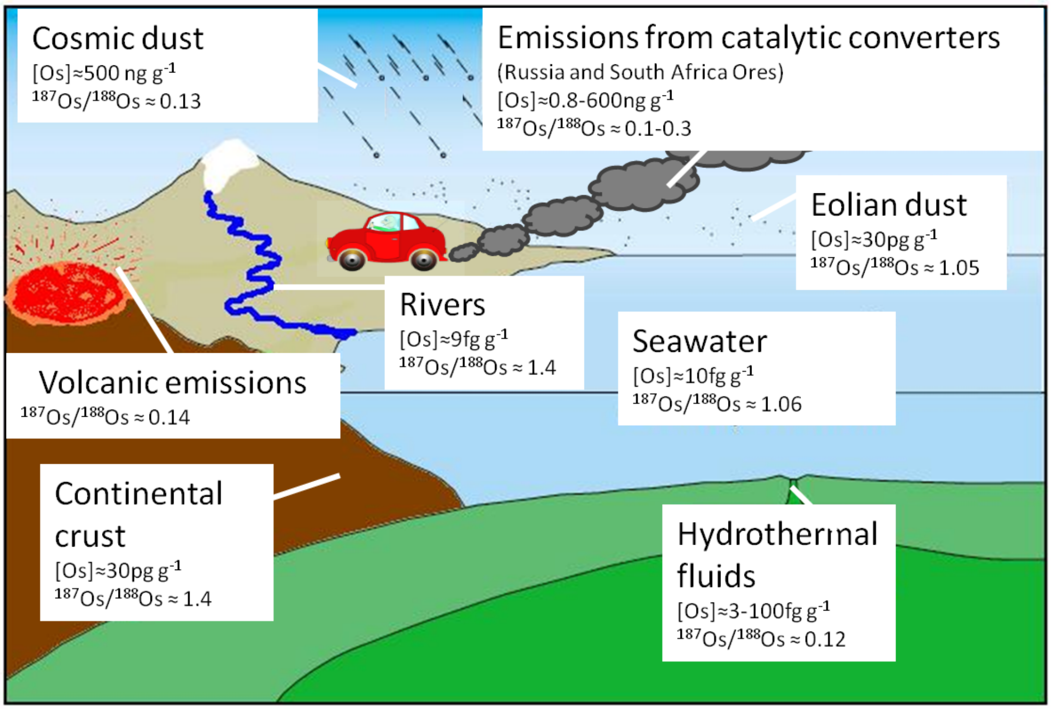


Figure 1.8: Superficial geochemical cycle of Os where each compartments show their Os concentrations and their ^{187}Os/^{188}Os ratio (data from Peucker-Ehrenbrink and Ravizza 2000 and Rauch et al. 2010).

1.2.5 Traceability

One of the most interesting PGE features is the use of Os isotopes for source characterization (Esser and Turekian, 1993; Ravizza and Bothner, 1996; Rauch et al., 2004a, 2004b, 2005b, 2010). Osmium exhibits a wide range of isotopic compositions due to the variation of radiogenic ^{187}Os, derived from radioactive decay of ^{187}Re ($T_{1/2}$≈ 42x10^9 years), in diverse sources and lithologies (Poirier and Gariépy, 2005). Hence, ^{187}Os/^{188}Os ratios trace a variety of anthropogenic and natural origins (Rauch et al., 2006; Sharma, 2011). The typical ^{187}Os/^{188}Os ratios of the PGE ores like the Bushveld complex (Naldrett et al., 2008), where around of 80% of the PGE resources are located (Cawthorn, 2010), are 0.10-0.20 (Schoenberg et al., 1999), while ratios from the upper continental crust are 1.05±0.23 (Peucker-Ehrenbrink and Jahn, 2001). This difference in ^{187}Os/^{188}Os allows the estimation of the Os anthropogenic fraction in environmental samples (Rauch et al., 2004b, 2006, 2010; Sharma, 2011). Anthropogenic Os shows ratios similar to ores 0.1-0.2, while the natural deposits are associated with upper

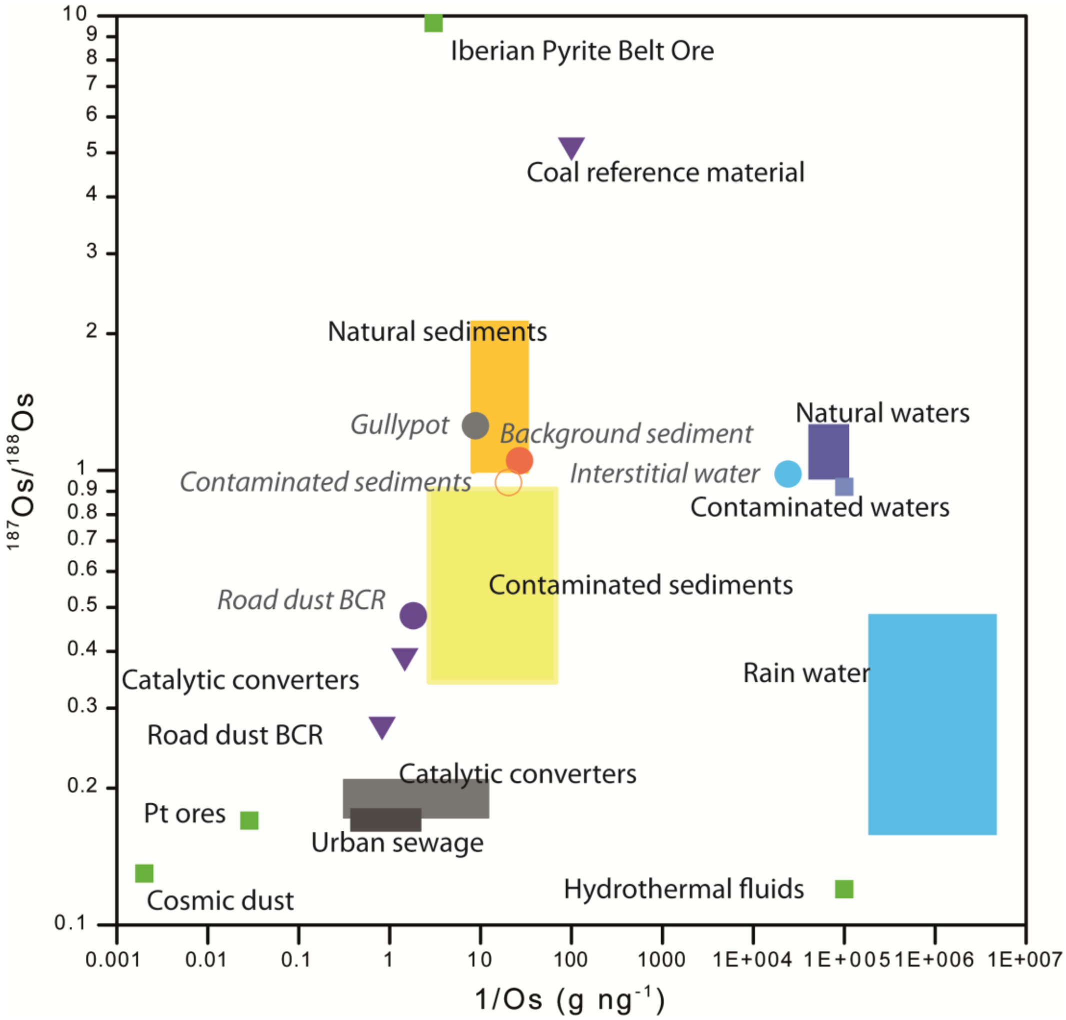


Figure 1.9: $^{187}Os/^{188}Os$ vs. 1/[Os]total in different matrices and environments (squares) and reference materials (triangles) (data from Esser and Turekian, 1993; Ravizza and Bothner, 1996; Burton et al., 1999; Mathur et al., 1999; Peucker-Ehrenbrink and Ravizza, 2000; Peucker-Ehrenbrink and Jahn, 2001; Fritsche and Meisel, 2004; Rauch et al., 2004a; Poirier and Gariépy, 2005; Rauch et al., 2005b; Rodushkin et al., 2007; Sharma et al., 2007; Turekian et al., 2007; Chen et al., 2009; Rauch et al., 2010) and our study in Chapter 4 (circles).

continental crust ratios 1.05±0.23 (Figure 1.8). Although several –albeit unusual– natural sources present $^{187}Os/^{188}Os$ ratios similar to the anthropogenic values, like cosmic dust or volcanic emissions, they are considered negligible compared to the earth crust pool. Assuming that Os and other PGEs derive from the same anthropogenic sources, the Os isotopic composition has been used to estimate the anthropogenic fraction of Pt, Pd, and Rh, mainly in urban environments (Esser and Turekian, 1993; Ravizza and Bothner, 1996: Rauch et al., 2004a, 2005b). However, natural systems are poorly characterized: only some ombrotrophic peat bogs, affected exclusively by atmospheric deposition, are well studied (Rauch et al., 2004b, 2010), but not other natural complex systems subject to different inputs.

Figure 1.9 shows ^{187}Os/^{188}Os ratios in natural sediments (Esser and Turekian, 1993; Ravizza and Bothner, 1996; Peucker-Ehrenbrink and Jahn, 2001; Fritsche and Meisel, 2004; Rauch et al., 2004a) and waters –sea, estuarine and riverine– (Sharma et al., 2007; Turekian et al., 2007; Chen et al., 2009; Rauch et al., 2010), with values of 1-2 and 1-1.3 respectively. However, contaminated matrices have less radiogenic signal, 0.3-0.9 for sediments (Esser and Turekian, 1993; Ravizza and Bothner, 1996; Fritsche and Meisel, 2004; Rauch et al., 2004a) and 0.9 for waters (Turekian et al., 2007; Chen et al., 2009). Human-activities derived products, like urban sewages (Ravizza and Bothner, 1996) or catalytic converters (Poirier and Gariépy, 2005; Rodushkin et al., 2007), exhibit values around 0.16-0.21, close to the ores signal (Rauch et al., 2010). However, there are other natural deposits (Burton et al., 1999; Mathur et al., 1999; Peucker-Ehrenbrink and Ravizza, 2000; Rauch et al., 2010) whose isotopic compositions are very different from mean value in continental crust like the Iberian Pyrite Belt or hydrothermal fluids. Besides, some important reference materials used in analytical chemistry to check the accuracy of the methods in different matrices –like road dust (Fritsche and Meisel, 2004), catalytic converters (Poirier and Gariépy, 2005), coal (Rodushkin et al., 2007)– are plotted in the Figure 1.9.

1.3 Hypothesis, objectives and justification

Previous studies have concluded that there is an anthropogenic disturbance in urban sediments caused by the PGEs released to the environment due to their anthropogenic use. However, they still have left several unanswered questions (Figure 1.10). What is the fate of PGEs when they arrive to natural environments? How is the sedimentary PGE geochemistry? Do they remain inert? Do they dissolve? Do they exists in a bioavailable form being assimilated by plants and entering the food chain?

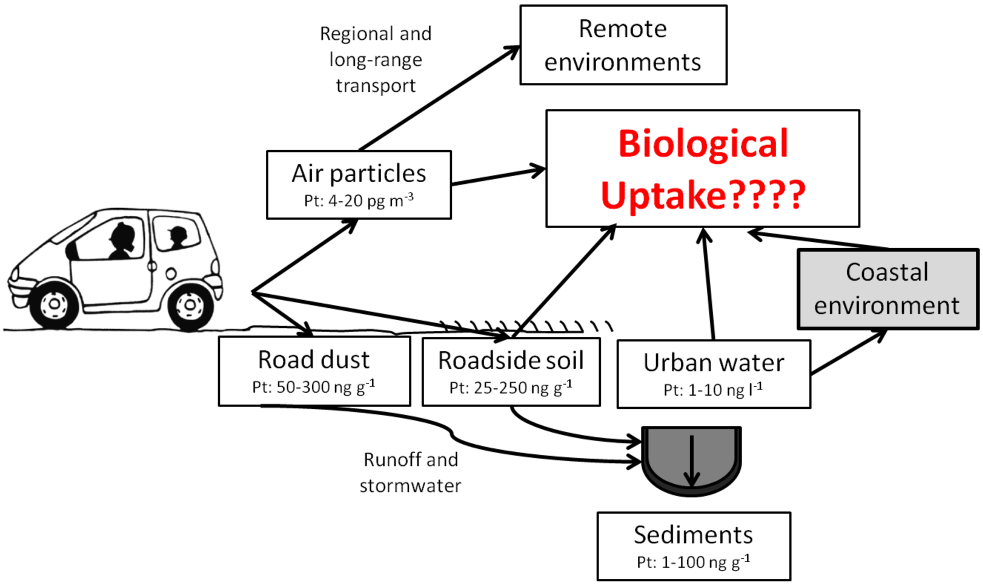


Figure 1.10: PGE-fate in urban environments from autocatalyts (modified from Rauch and Morrison, 2008).

Hence, this thesis is based on this working hypothesis:

> ***How is the geochemical behavior of platinum group elements in anthropogenically-impacted sediments? What are their main sources?***

and the following main objectives were proposed in order to shed light to the above questions:

-developing and/or improving methods to determine ultra-trace PGE concentrations in different natural matrices and background concentrations

-improving the knowledge about the sedimentary PGE geochemical behavior and postdepositional processes affecting these elements

-evaluating the role of vegetation in the biogeochemical cycle of PGEs in sediments

-ascertaining the transference of PGEs from sediment to biological compartments (bioaccumulation)

-determining the anthropogenic contribution of PGEs in sediments and interstitial waters affected by different traffic impact

-assessing the real coupled sources and behavior of PGEs from anthropogenic origin

-assessing the role of salt marshes in the PGE cycle and quantifying the exportation/importation of PGEs from these areas to estuaries and open ocean waters

-assessing the impact of PGE mining activities on the surrounding environments

To carry out all these aims, two study areas have been selected due to their particular characteristics:

a) The Hex river (Rustenburg, South Africa) that drains the mining area of the Bushveld Igneous Complex (Photography 1.1), the largest PGE resource in the world (Cawthorn, 2010) where intense mining activities are performed, and

b) The salt marshes of Tagus Estuary (W Iberian Peninsula), under different traffic pressures (Photography 1.2). The behavior of other trace elements (e.g. Pb, Cr, Zn, Ni, Cu, As, Cd, Co) have already been well-characterized in the area to improve the understanding of their biogeochemical cycles (Caçador et al., 1996; Caetano et al., 1997;

Photography 1.1: The Merensky Reef, the main PGE-rich deposit in Bushveld Igneous complex (South Africa). The black layers are the PGE-contain ones (from Johnson Matthey, 2013).

Falcão and Vale, 1998; Cabrita et al., 1999; Sundby et al., 2003, 2005; Caetano et al., 2007; Taillefert et al., 2007; Caetano et al., 2008; Deborde et al., 2008; Tanackovic et al., 2008; Caçador et al., 2009; Duarte et al., 2010; Santos-Echeandía et al., 2010; Caetano et al., 2012), conditioned by the different physical, chemical and microbial processes of salt marsh sediments (Taillefert et al., 2007). In this way, this previous information will serve to draw conclusions about PGE behaviour in the system. Besides, salt marsh plants present the ability of phytostabilizing contaminants by uptaking (Duarte et al., 2010) and some studies proposed their use with phytoremediation purposes (Caçador et al., 2009; González-Alcaraz et al., 2011).

Photography 1.2: Salt marshes of Tagus Estuary under a motorway bridge (Clara Almécija, March 2011).

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Chapter 2

Improvement of the ultra-trace voltammetric determination of Rh in environmental samples using signal transformation

Based on the work submitted to *Talanta*

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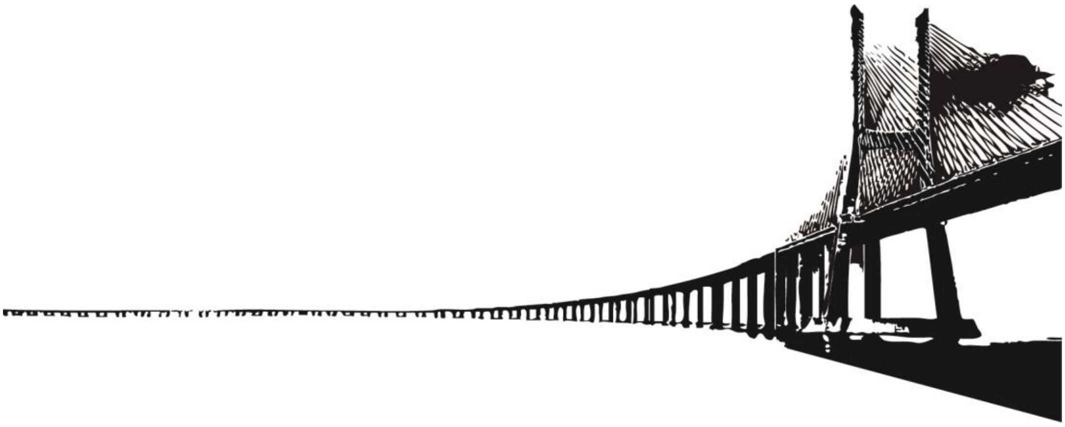

Improvement of the ultra-trace voltammetric determination of Rh in environmental samples using signal transformation

Abstract

Rhodium (Rh) is present at the Earth's surface at ultra-trace concentrations (0.06 ng g^{-1}); however, its use in catalytic converters has increased its deposition nearby traffic pressure and therefore the interest in analytical techniques for Rh determination has increased in the recent years. In this study we propose an improvement of Rh measurement by adsorptive voltammetry applying second-derivative signal transformation.

The optimization of experimental parameters affecting the voltammetric analysis were carried out using sediment samples; these include the amount of sample digest used, the hydrochloric and formaldehyde concentrations, equilibration time and deposition potential. The use of the second derivative transformation provides well-defined peaks due to the minimization of background interferences, and leads to a significant decrease in the detection limits. Accordingly, a detection limit of 23 fM Rh in the cell was obtained, which corresponds to 1.6 pg g^{-1} of Rh for 200 mg of sediments.

The optimized methodology was applied to the analysis of Rh in a sediment core collected close to a motorway bridge from Tagus Estuary (Lisbon, Portugal). Here, Rh concentrations ranged from 0.06 to 0.47 ng g^{-1}, showing a surface Rh-enrichment linked to traffic, which is consistent

with a Pt superficial peak. Reference materials have been also analyzed, including road dust (BCR-723) and river sediment (JSd-2), and values obtained are in agreement with certified concentrations and previously values reported in the literature.

2.1 Introduction

Rhodium (Rh) belongs to the Platinum Group Elements (PGEs) together with platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd) and ruthenium (Ru). As highly siderophile elements, the Earth's core sequesters about 99.8% of PGEs (Lorand et al., 2008) explaining their ultra-trace concentrations at the Earth's surface (<1 ng g^{-1}); accordingly, typical Rh concentration in the upper continental crust is 0.06 ng g^{-1} (Wedepohl, 1995). The use of several PGEs – especially Pt, Pd and Rh– as active components in the catalytic converters of motor vehicles, which were developed to transform exhaust emissions (CO, NO_x or hydrocarbons) into more harmless products (Böck, 2006), has increased their environmental concentrations close to traffic pressure (Whiteley and Murray, 2005; Sutherland, 2007); also, evidence for a global environmental perturbation has been given from samples collected in remote environments (Rauch et al., 2005a; Soyol-Erdene et al., 2011). Actually, in 2012 the world demand of Rh for catalytic converters was about 69% of its total demand (~14 tons) (Johnson Matthey, 2013).

Rhodium is still a challenging element from an analytical perspective due to its ultra-trace concentrations in the environment even at anthropogenically-impacted areas. Several previous works have applied and improved different techniques for Rh determination, including atomic absorption spectrometry (Hodge et al., 1986; Cantarero et al., 1994) or neutron activation analysis (Hoffman et al., 1978; Murali et al., 1990); however, inductive coupled plasma mass spectrometry ICP-MS (Colodner et al., 1993; Ely and Neal, 1999; Meisel et al., 2003; Barefoot, 2004; De Boni et al., 2007) and adsorptive voltammetry (van den Berg and Jacinto, 1988; León et al., 1997; Helmers and Mergel, 1998; Huszal et al., 2005; Locatelli, 2007; Orecchio and Amorello, 2010; Van Der Horst et al., 2012; Cobelo-García et al., 2014; Silwana et al., 2014) have become the most widely used method due to their higher sensitivity. Besides, some other studies have solved important issues (e.g. storage problems) (Balcerzak, 2011). ICP-MS is characterized by rapidity, simplicity and multi-elementary capacity (Ely and Neal, 1999; Meisel et al., 2003; Barefoot, 2004; De Boni et al., 2007), although isobaric interferences on Rh^{103} –like $^{63}Cu^{40}Ar^{+}$ or $^{91}Zr^{12}C^{+}$– may cause severe inaccuracies in the Rh quantification (León et al., 1997), more noteworthy at the ultra-trace concentrations of biological or environmental samples. Thus, the removal of interferences (e.g. cationic exchange resins) is essential (Meisel et al., 2003; Balcerzak, 2011); isotope dilution, usually performed to solve this drawback (Meisel et al., 2003), is not suitable for monoisotopic elements like Rh. In this scenario, several studies (Wang and Taha, 1991; León et al., 1997; Helmers and Mergel, 1998; Huszal et al., 2005; Locatelli, 2006; Dalvi et al., 2008; Orecchio and Amorello, 2010; Van Der Horst et al., 2012; Silwana et al., 2014) have showed that adsorptive voltammetry is a suitable alternative for Rh determination, due to high accuracy, precision, selectivity and sensitivity as well as low detection limits and economical cost (Monticelli et al., 2007).

However, voltammetry presents also some difficulties and limitations for Rh determination related to the complexity of natural matrices and low natural concentrations. Model lab-made samples are easily quantified (Wang and Taha, 1991; Monticelli et al., 2007), but environmental samples containing complicated matrices may cause severe interferences in the background baseline current, e.g. Zn-peak potential is similar to Rh-peak (León et al., 1997) resulting a ill-defined peak (Cobelo-García et al., 2014). Moreover, whereas determinations of Rh using voltammetry for biological tissues (León et al., 1997; Helmers and Mergel, 1998; Orecchio and Amorello, 2010) or anthropogenically-impacted road dust have been reported (Helmers and Mergel, 1998), the absence of Rh determination in sediments or waters is a constant due to the high detection limits compared to natural concentrations (Locatelli, 2006; Dalvi et al., 2008; Van Der Horst et al., 2012).

Consequently, revising the method for Rh determination by voltammetry is necessary to improve their applicability and efficiency, one of the main challenges in the geochemistry of new emergent ultra-trace contaminants. Therefore, in this study we present an improvement of Rh measurement by adsorptive voltammetry in sediment samples applying the second derivative transformation described as described earlier for Pt (Cobelo-García et al., 2014), leading to a faster method, with lower detection limits, and able to determine natural non-contaminated concentration. Besides, data of Rh concentration in a sediment core collected at a high-traffic area will be presented to reinforce the suitability of the new proposed method.

2.2 Material and methods

2.2.1 Instrumentation and reagents

A Metrohm model 663VA voltammetric stand, equipped with a hanging mercury drop electrode (HMDE) as the working electrode, a Ag/AgCl/KCl$_{sat}$ as the reference electrode and a glassy carbon rod as counter electrode, connected to a µAutolab Type III potentiostat (Metrohm Autoloab B.V.), was used to in the experimental work. The system was controlled by GPES v.4.9 software (EcoChemie B.V.). Samples in the polytetrafluoroethylene (PTFE) voltammetric cell were purged with humidified N_2 (99.9999%; Alphagaz1, Ari Liquide); stirring of the solution was attained using a PTFE rod (speed= 3000 rpm). Mercury used was for analysis and polarography (EMSURE, Merck), and a drop size of 0.52 mm^2 was selected.

Laboratory work was carried out in a laminar flow bench (ISO 5) housed inside an ISO 7 lab where temperature was controlled (25 °C). All the materials used during the experiments were acid pre-cleaned, rinsed with Milli-Q water (Millipore, 18.2 MΩ cm at 25 °C) and handled inside laminar flow hoods.

Reagents used in this study were HNO_3 65% and HCl 30% (Suprapur$^©$ Merck), formaldehyde (36.5%, Riedel-de-Haën), H_2SO_4 (≥95%; Trace-SELECT, Fluka) and hydrazine sulfate (Fluka). Solutions of formaldehyde (1.46%) and hydrazine (50 mM) were in Milli-Q water and stored in flourinated ethylene propylene bottles (FEP; Nalgene), being stables during several weeks. Rh and Pt atomic absorption standards (Fluka) were used to prepare weekly working solutions for standard addition.

2.2.2 Rhodium determination in sediment samples

100-250 mg of sediments were ashed in quartz crucibles up to 800 °C (3h) to remove organic matter. Ashed sediments were digested in a mixture of 3 mL concentrated HNO_3 and 5 mL concentrated HCl in 30 mL PFA bombs (Savillex) for 4h at 195 °C using a temperature-controlled Teflon-coated hot plate (PicoTrace). Then, samples were allowed to cool down, caps were removed, and the acid was evaporated until near dryness. Then 1 mL of concentrated HCl was added and evaporated again. Finally, 1 mL of concentrated HCl was added and allowed to redissolve the residue; then Milli-Q water was added and the digest was syringe-filtered using a PFA syringe (Savillex) and 25 mm polyethersulfone membranes with 0.45 µm pore size (Pall) and made up to 25 mL (final HCl concentration ~0.38 M) in a polypropylene volumetric flask

(Nalgene).

An aliquot of 2 mL of sample is diluted with 8 mL of Milli-Q water and 400µL of HCl (30%) and 200 µL of formaldehyde (1.46%) are added to get the optimized mix to measure in the voltammeter (for reference materials 0.5-1 mL of sample and 9-9.5 mL of Milli-Q water). After 5 minutes of stirring and purging (parameters described in the section above), HMDE is set at –0.7 V during 30 s with stirring to promote the Rh(III) adsorption on the mercury drop (León et al., 1997). After 10 seconds of equilibrium (without stirring) the voltammeter sweeps from –0.9 to –1.25 V (differential pulse mode) with a time interval of 0.2 s and amplitude interval of 0.025 V. The peak appearing at –1.12 to –1.18 V, at which Rh(III)/Rh(0) reduction takes place, is caused by the catalytically-promoted hydrogen reduction caused by the Rh(0) formed at the surface of the mercury drop. The intensity (A) of this hydrogen reduction (catalyzed by Rh) in the voltammogram is proportional to the Rh concentration in the sample. This Rh concentration is quantified by the method of standard additions.

We have applied to the Rh intensity signal the second derivative signal transformation described earlier by Cobelo-García *et al.* (2014) in order to improve the sensibility, resolution and detectability of the method. Besides, this methodology enhances the ability of removing the interferences by matrix and other elements. Using GPES v.4.9 software, the original current signal is smoothed, low-pass filter (smoothing factor of 2), to remove the noise whose presence could be amplified after first and second derivative. After smoothing, the second derivative signal transformation is applied and good-shaped-peak are obtained. The following equation (Eq 2.1) describes the transformation (Cobelo-García et al., 2014):

$$\frac{dI}{dE}(n) = 0.5\left(\frac{I(n)-I(n-1)}{E(n)-E(n-1)}\right) + 0.5\left(\frac{I(n+1)-I(n)}{E(n+1)-E(n)}\right) \qquad \text{[Eq. 2.1]}$$

were $I(A)$ is the current intensity, $E(V)$ the applied potential and n the data point. The height of the second derivative peak of intensity is recorded as measurement of Rh concentration. The height of the original scan peak is also measured to compare both methods.

2.2.3 Experiment design

Several variables affecting the sensitivity and accuracy of the Rh determination were optimized. These include: (a) equilibration time needed to reach a constant analytical signal, owing to the well-known slow reaction kinetics of Rh (Cobelo-García, 2013); (b) deposition time; (c) depositional potential; (d) HCl concentration in the cell, and (e) formaldehyde concentration in the cell. For carrying out this study a sediment sample has been used in all the experiments to perform the optimization in an environmental real matrix.

2.2.4 Samples

One sediment core was collected in September 2011 in the salt marsh area of the Tagus Estuary (Lisbon, W Iberian Peninsula), *Samouco Salt Marsh*. Sampling point was located by a 17.2 km long motorway bridge that was open in April 1998, with a daily average of 50,000 vehicles (Instituto de Intraestructuras Rodoviárias IP (Portugal), 2013). Previous anthropogenic pressure in this area was negligible. Table 2.1 shows procedural blanks and reference materials –road dust BCR-723 with Rh certified value (Institute of Reference Materials and Measurements, 2013) and stream sediment JSd-2 (Geological Survey of Japan)– used to check the accuracy and precision of the method.

2.2.5 Platinum determination

Platinum was determined in sediments and reference materials as an auxiliary parameter for Rh analysis. Briefly, 150 mg of sediment samples were ashed at 800 °C for 3 h to remove the

Table 2.1: Rh concentration in refecence materials –road dust BCR 723 (Institute of Reference Materials and Measurements, 2013) and river sediment JSd-2 (Geological Survey of Japan)– blanks and detection limits (3 SD blank) in this study and other reports (León et al., 1997; Helmers and Mergel, 1998; Hall and Oates, 2003; Orecchio and Amorello, 2010; Almécija et al., in revision a).

		Concentration (ng g^{-1})	Concentration in cell (fM)
BCR-723	certify value	12.8 ± 1.3	-
	this study (*n=3*)	12.9 ± 1.7	-
JSd-2	Hall and Oates, 2003	3.18 ± 1.04	-
	Almécija *et al.*, ICP-MS	2.6 ± 0.2	-
	this study (*n=3*)	2.91 ± 0.80	-
blank (*n=6*)	Sample	12 ± 0.5 (pg g^{-1})*	180 ± 8
detection limit	Sample	1.6 (pg g^{-1})*	23
	León 1997	-	54
	Helmers and Mergel 1998	-	1.5×10^{4}
	Orecchio y Amorello 2010	120 (pg g^{-1})*	-

Values: mean value ± SD

*Values calculated for 200 g of sample

organic matter and digested by a mixture of HCl (5 mL) and HNO_3 (3 mL) using a hot plate at 195 °C (4 h). After complete acid evaporation, 1 mL of HCl and 1 mL of H_2SO_4 were added to re-dissolve the residue and evaporated until no gases were released. Finally, the sediment sample is diluted in 0.1 M HCl, filtered and made up to 25 mL (section 2.2). For voltammetric determination of Pt by the method of standard additions and second derivative transformation (Cobelo-García et al., 2014), 2-4 mL of samples and Milli-Q water up to 10 mL, 65 µL of formaldehyde (1.46%) and 100 µL of hydrazine sulfate (50mM) were added in the cell. After purging and stirring, the deposition at –0.3 V was carried out and the sample was scanned from –0.5 to –1.1 V to measure the Pt peak (Cobelo-García et al., 2014). For reference materials, the samples digested for Rh were used, adding 300 µL of H_2SO_4 directly in the voltammetric.

2.3 Results and discussion

2.3.1 Second derivative transformation

Figure 2.1 shows the improvement in peak identification and resolution using the second derivative signal (A/V^2) in for the reference materials BCR-723 (road dust) and JSd-2 (river sediment). For the road dust sample, a shoulder-shaped peak is observed in the original voltammogram using the conditions detailed in Figure 2.1. The situation is however more complicated in the river sediment sample due to the lower Rh concentration (around 3 ng g^{-1} compared to 12.8 ng g^{-1} in the road dust) and a higher background current, resulting in an undetectable Rh signal in the original scan. The use of the second derivative transformation eliminates the background interference and a clear, well-defined quantifiable peak (Cobelo-García et al., 2014) is observed in both samples increasing proportionally with the successive standard additions.

2.3.2 Optimization of experimental parameters

200 mg of the sediment sample from 2-4 cm of the core (Rh concentration ~0.3 ng g^{-1}) were digested and used to optimize Rh analysis by voltammetry, in a final solution of ~6 ng L^{-1} (2 mL of sample +8 mL of Milli-Q water +30 µL of Rh-spike). Figure 2.2 plots each optimization step.

2.3.2.1 Equilibration time

Due to the well-known slow reaction kinetics of Rh (Cobelo-García, 2013), the second derivative voltammetric signal was monitored over a period of more than 2 h of equilibration time under stirring conditions (Figure 2.2a). It is shown that at least 30 min are required to reach a plateau in the signal for the sample, whereas the peak potential shifts to more negative values. The situation is different after Rh spikes: here, 5 min equilibration time is enough to get a constant signal.

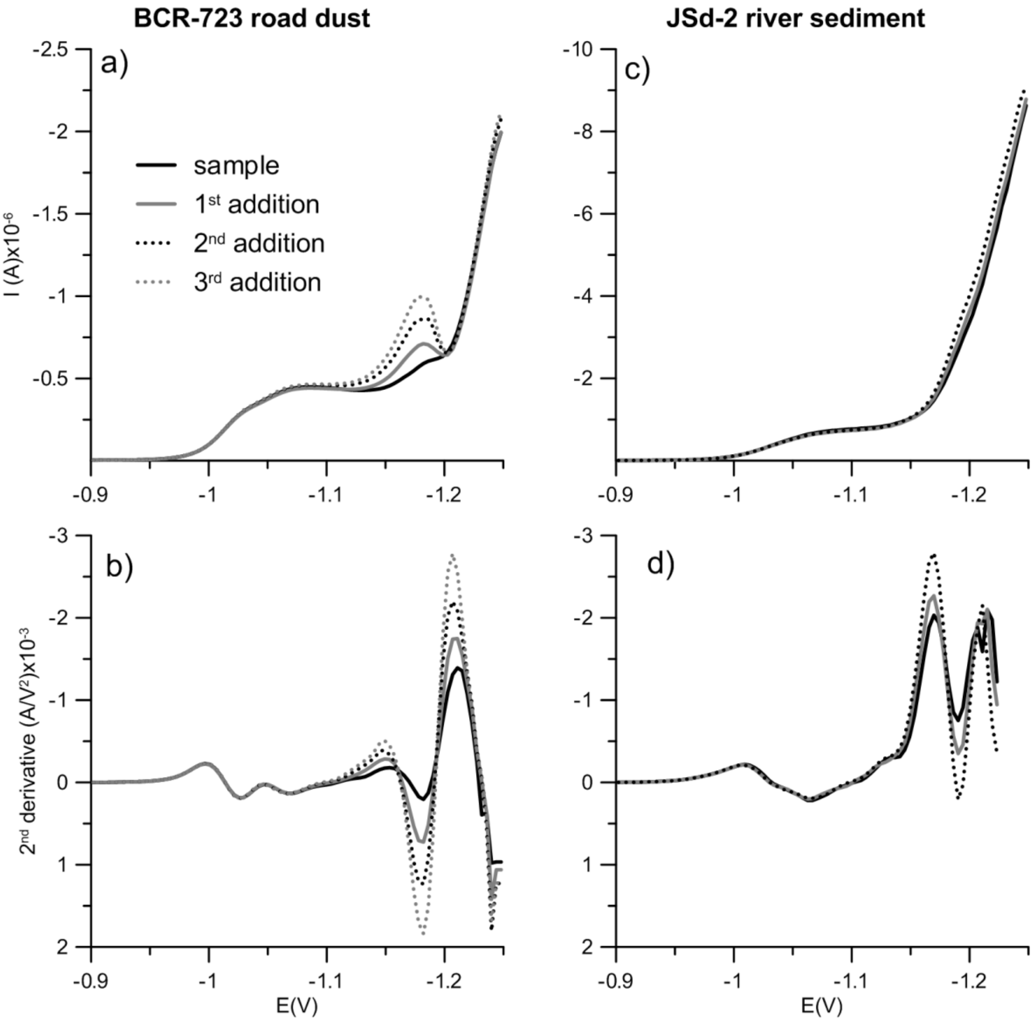

Figure 2.1: Original and second derivative voltammograms in road dust reference material (left, BCR-723) and river sediment (right, JSd-2) with several standard additions. Conditions: (i) BCR-723: 1 mL of sample digest +9 mL of MQ-water, initial Rh concentration ~37 pM, and +26.7 pM Rh spiked for each addition; JSd-2: 0.5 mL of sample digest +9.5 mL of MQ-water, initial Rh concenetration ~8 pM, and +4.5 pM Rh spiked for each addition; (ii) 0.42 M HCl; (iii) 0.022 M formaldehyde, (iv) 30 s deposition time, (v) –0.7 V deposition potential.

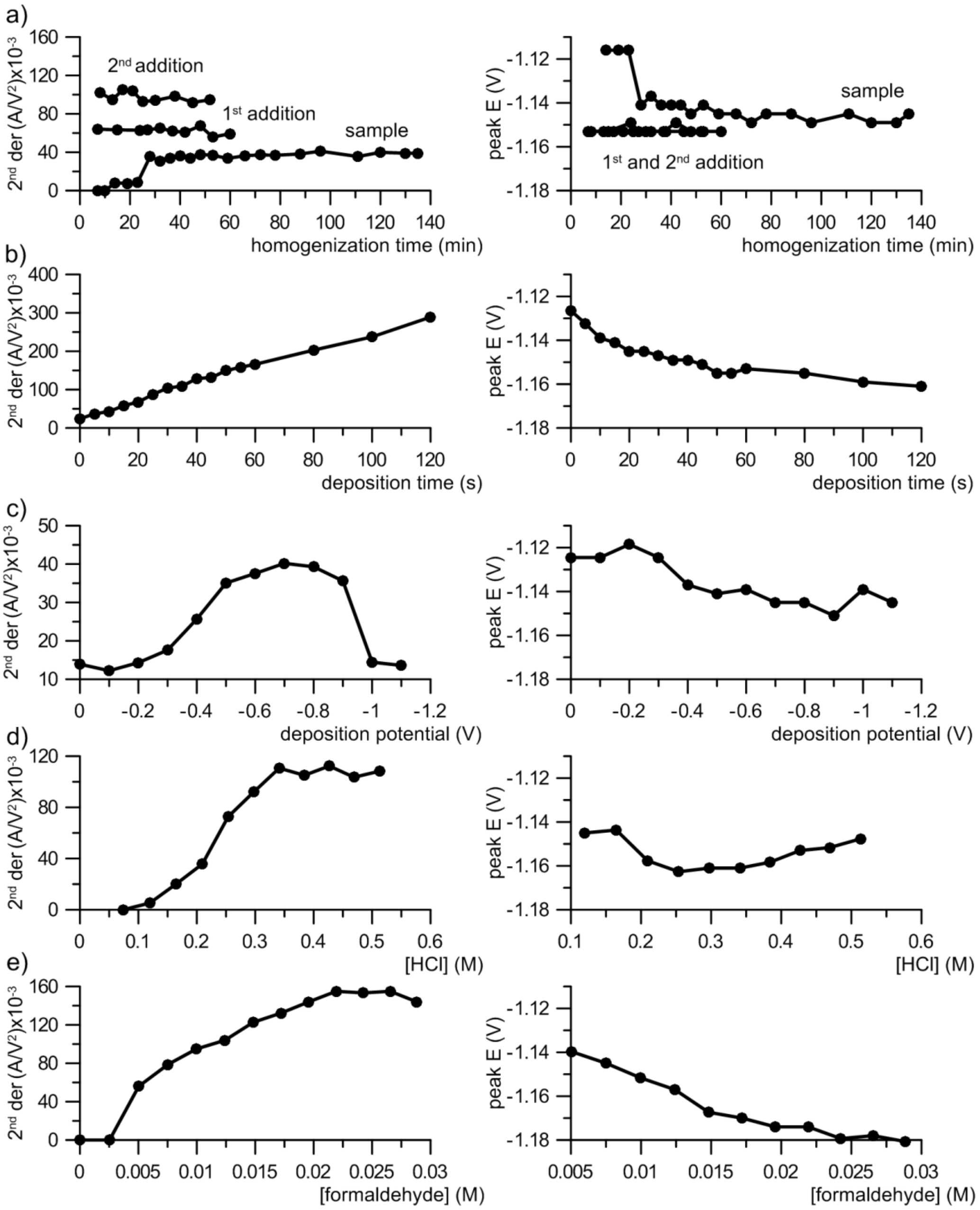

Figure 2.2: Variation of sensitivity of the second derivative peak (A/V^2x10^{-3}, left) and peak potential (V, right) with the optimization of the different parameters: a) homogenization time (min); b) deposition time (s); c) deposition potential (V); d) HCl concentration in the cell (mol L^{-1}) and e) formaldehyde concentration in the cell (mol L^{-1}). For each experiment the other parameters remain invariable: a) homogenization time= 30 minutes, b) deposition time 30 s, c) deposition potential –0.7 V, d) [HCl]= 0.43 M and e) [formaldehyde]= 0.022 M. (Rh concentration in sample 2-4 cm ~0.3 ng g^{-1} and in the cell ~6 ng L^{-1}).

2.3.2.2 Deposition potential and accumulation time

The dependence of the height of the Rh peak with the accumulation time was checked up to 120 seconds and it was found to increase linearly (Figure 2.2b), whereas the peak potential shifted to more negative values at higher accumulation periods. On the other hand, the highest sensitivity was obtained at deposition potentials from –0.5 to –0.9 V; a value of –0.7V was chosen for all subsequent determinations (Figure 2.2c).

2.3.2.3 Hydrochloric acid and formaldehyde concentrations

Hydrochloric acid is the optimum supporting electrolyte for the voltammetric determination of Rh (León et al., 1997). Figure 2.2d shows that sensitivity increases with the acid concentration in the cell until reaching a plateau at about 0.35 M HCl; an optimized HCl concentration of 0.40-0.45 M was chosen for the determinations. Similarly, a concentration at 0.022 M of formaldehyde (Figure 2.2e) was selected. The increase in HCl concentrations had no clear impact on Rh peak potential, whereas for formaldehyde the peak is shifted to more negative values at higher concentrations.

From these results, the best conditions to analyze Rh in natural sediment samples are the following: (i) mixture of 2 mL of digested sample, 8 mL of Milli-Q Water, HCl (30%, Suprapur© Merck) at a concentrations of 0.43 M (adding 400 µL of HCl), 200 µL of formaldehyde (1.46%) to obtain a concentration of 0.022 M; (ii) after 30 minutes of stirred equilibration, analyze the sample after 300 s of purging, 30 s of deposition at –0.7 V; (iii) sweeping from –0.9 to –1.25 V and (iv) second derivative transformation.

2.3.3 Accuracy, precision and detection limits

Selection of the type of baseline in the second derivative voltammograms is critical for the accuracy of the determination (Cobelo-García et al., 2014). Accordingly, Figure 2.3 shows the second derivative voltammogram for a BCR-723 (road dust; certified Rh concentration of 12.8±1.3 ng g^{-1}, Table 2.1) digest and three different baselines checked: (a) front-peak horizontal baseline, (b) peak-peak baseline and (c) rear-peak horizontal baseline. Using the method of standard additions, concentrations of 8.1, 12.1 and 14.8 ng g^{-1} were obtained by the different baseline methods (a, b and c, respectively); therefore, the peak-peak baseline was chosen for our determination since it provided the most accurate results. Analysis of three separate BCR-723 digests yielded an average Rh concentration of 12.9±1.7 ng g^{-1} (Table 2.1), indicating a complete recovery, and a relative standard deviation (%) of 13%. For the river

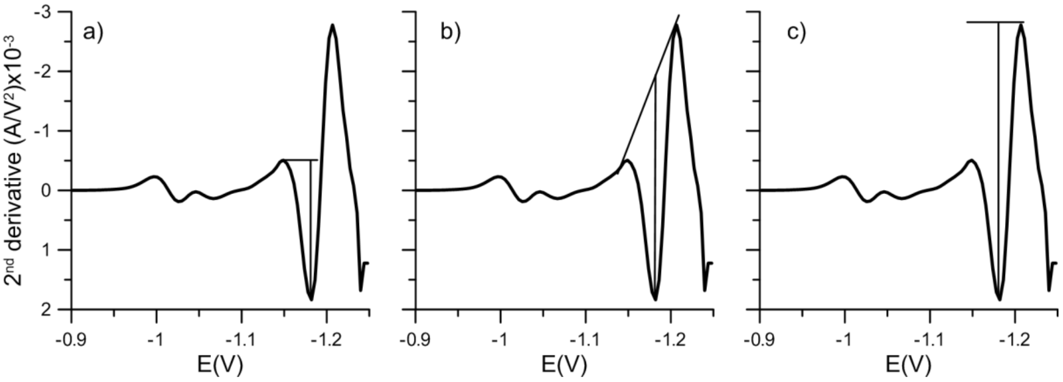

Figure 2.3: Second derivative voltammogram of road dust reference material were three different modes of baseline are shown: a) front-peak horizontal baseline, b) peak-peak baseline and c) rear-peak horizontal baseline. Final concentrations in dust calculated were 8.1, 12.1 and 14.8 ng g^{-1} respectively.

sediment reference material (JSd-2) a concentration of 2.9±0.8 ng g^{-1} was found (relative standard deviation 28%); this reference material lacks certified Rh concentration, but the value found here is in agreement with those previously reported by Hall and Oates, (2003) and the one obtained in our lab using ICP-MS for determination (Almécija et al., in revision a; Table 2.1), 3.2±1.0 ng g^{-1} and 2.6±0.2 ng g^{-1}, respectively.

Procedural blanks resulted in an average Rh concentration in the diluted digest in the voltammetric cell of 180±8 fM ($\bar{x} \pm SD$, *n=6*) which corresponds to a 12±0.5 pg g^{-1} for a typical sediment mass of 200 mg. Detection limit of 23 fM (1.6 pg g^{-1} for 200 mg of sediment), calculated as $3 \times SD$ of blanks is satisfactory for the analysis of Rh in uncontaminated sediments and soils (Table 2.1).

Several previous studies had reported optimal conditions to analyze Rh by adsorptive cathodic stripping voltammetry in natural samples (León et al., 1997; Helmers and Mergel, 1998; Orecchio and Amorello, 2010; Van Der Horst et al., 2012; Silwana et al., 2014). León *et al.* (1997) developed a method for the simultaneous detection and quantification of Pt and Rh. However, the detection limit for Rh obtained by León *et al.* (1997), 54 fM, is higher than the one obtained using our procedure (23 fM; calculated as $3 \times SD$ of blanks, Table 2.1). Also, Helmers and Mergel´s method (Helmers and Mergel, 1998), similar to ours in electrolyte concentration and deposition potential, needs a 4 times longer deposition time although their samples contain up to 160-fold higher Rh concentration. Besides, the detection limit reported is almost 650-fold our detection limit (1.5x10^4 fM, Table 2.1). Other authors (Orecchio and Amorello, 2010; Van Der Horst et al., 2012; Silwana et al., 2014) reported other modifications in the method, but not suitable for analyzing real natural concentrations due to too high detection limits.

2.3.4 Application of the method to sediment samples

Figure 2.4 shows the Rh and Pt profiles in a salt marsh sediment core in the Tagus Estuary. Concentrations ranged from 0.06 to 0.47 ng g^{-1} and from 0.58 to 40 ng g^{-1} for Rh and Pt, respectively. Both elements displayed maximum values at surface decreasing with depth where they reach concentrations similar to their upper continental crustal abundance, i.e. 0.06 ng g^{-1} for Rh (Wedepohl, 1995) and 0.51 ng g^{-1} for Pt (Peucker-Ehrenbrink and Jahn, 2001). The Pt/Rh ratios in the core were 8.7±3.9, similar to crustal values (8.5;Figure 2.4), with the exception of the surface sample (0-2 cm; Pt/Rh: 85).

The sample point in the salt marsh is located by a high-traffic motorway bridge with a daily average of 50,000 cars (Instituto de Intraestructuras Rodoviárias IP (Portugal), 2013); the observed surface enrichment linked to the use of Pt and Rh as active components of catalytic converters of motor vehicles has been extensively reported for diverse environmental compartments (Rauch et al., 2005a; Whiteley and Murray, 2005; Sutherland, 2007; Soyol-

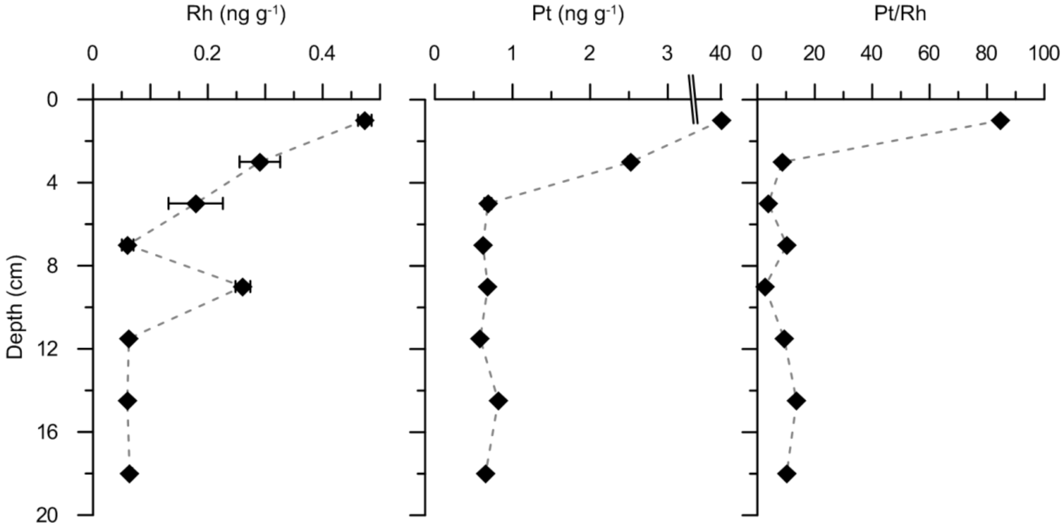

Figure 2.4: Rh and Pt profiles and the Pt/Rh from a sedimentary core at a salt marsh under high traffic pressure of the Tagus Estuary.

Erdene et al., 2011) but also in the study area (Cobelo-García et al., 2011; Almécija et al., in revision b). It is however surprising the elevated Pt/Rh (85) obtained for the most recent sediment layer, considering that typical Pt/Rh ratios in catalytic converters is around 5 (Fritsche and Meisel, 2004) and that other studies in traffic-impacted compartments also reported lower values (5-16; Ely et al., 2001; Zereini et al., 2001; Rauch et al., 2004, 2005b; Whiteley and Murray, 2005; Sutherland, 2007) including the road dust reference material BCR-723 (Institute of Reference Materials and Measurements, 2013). In spite of this difference in the Pt/Rh ratio, our surface Rh value is in the range of contaminated sediment (Zereini et al., 2001; Rauch and Morrison, 2008).

An important remarkable goal of this study is the almost complete lack of Rh data –analyzed by voltammetry– for sediment samples. Although several authors used sediments, soils or dust to check their methods (Locatelli, 2006; Van Der Horst et al., 2012) only Helmers and Mergel (1998) reported real Rh concentrations (9.7 and 75.1 ng g^{-1} in road dust samples), being this concentration 21 to 1300 times higher than our samples. This fact reinforces the idea of the challenge accepted and achieved by our analysis, able to measure contaminated but also non contaminated sediments (Rh concentration less than 0.1 ng g^{-1}), due to the improvement in the determination using second derivative signal transformation.

2.4 Conclusions

In this study we propose a new methodology to analyzed rhodium by catalytic adsorptive cathodic stripping voltammetry applying the second derivative transformation described by Cobelo-García *et al.* (2014) in a previous study. The higher rapidity in the analysis and the increase in sensitivity –due to minimization of baseline effects– improve the capability of the determination of Rh in natural samples. Besides, the analysis of sediments allows us to measure Rh in contaminated but also non-contaminated samples with natural background concentrations. Therefore, this study supports the second derivative method as a noteworthy alternative for Rh analysis, compatible with complementary analysis (like Pt) in the same decomposition procedure.

Acknowledgements

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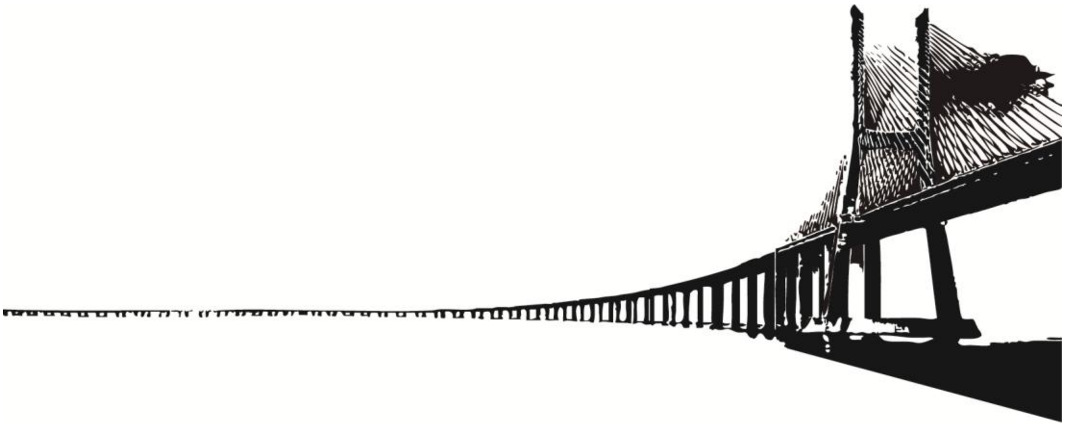
Chapter 3

Platinum in salt marsh sediments: behavior and plant uptake

Based on the work to be submitted to *Biogeochemistry* by

C. Almécija, A. Cobelo-García, M. Caetano and J. Santos-Echeanadía



Platinum in salt marsh sediments: behavior and plant uptake

Abstract

Platinum is one of the least abundant elements in the earth crust with an average concentration of 0.5 ng g^{-1}, but the use of Pt in several human activities (e.g. automobile catalytic converters) is increasing the concentration in surface sediments. Previous studies have assessed the sedimentary behaviour of Pt in urban areas, whereas natural systems are still poorly study.

This study is aimed to characterize the sedimentary behaviour of the platinum released in coastal environments and ascertain the role of vegetation on Pt sedimentary biogeochemistry. Several sediment cores were sampled in the salt marshes of the Tagus Estuary under different vehicular traffic pressure (in unvegetated and vegetated areas). Pt concentration was analysed in sediment, interstitial water and different tissues –roots, leaves and stem– of *Sarcocornia fruticosa*, a typical salt marsh plant, by catalytic adsorptive cathodic stripping voltammetry. Auxiliary parameters –e.g. redox potential, dissolved oxygen, total sulphides, salinity or dissolved Fe and Mn for interstitial waters– and several elements for sediments (Fe, Mn, Al, Cd, V, Zn, Pb) were also determined.

Although surface enrichment of Pt exists in the sediments at Low Traffic Station (2.8 ng g^{-1}), the highest enrichment was founded at High Traffic Station where Pt concentration is, in some cases, up to 40 ng g^{-1}. However, dissolved Pt in interstitial waters does not show this superficial

peak displaying quite homogeneous profiles (0.26-0.66 and 0.14-0.7 ng L^{-1} for unvegetated and vegetated sediments, respectively), indicating a low reactivity, except for two Pt-rich-peaks (up to 2.5 ng L^{-1}) that could be linked to redox changes. These peaks are also reflected in the Pt concentration of roots (0.9±0.6 ng g^{-1}), although roots lack an enrichment respect to sediments and interstitial waters, reflecting a low bioaccumulation and also low translocation to aerial parts (Pt mean value in stems and leaves is 0.04±0.05 ng g^{-1}). Besides, coupled behaviors between Pt and dissolved Mn have been found and could condition the formation of different Pt-species (higher Pt bioavailability exits at Low Traffic Station).

Therefore, the role of vegetation is fundamental on the geochemical sedimentary behavior of Pt, due to the control of the redox conditions by roots in the surrounding sediments and leading to Pt species of varying bioavailability.

3.1 Introduction

Platinum (Pt) is one of the least abundant elements is the earth crust, due to its extreme affinity to the core (Rauch and Morrison, 2008) where Pt concentration is about 4 orders of magnitude higher than in the upper continental crust (5.5 µg g^{-1} and 0.51 ng g^{-1} respectively, Peucker-Ehrenbrink and Jahn 2001; Lorand et al 2008).

Platinum has been used in many different activities like chemical, biomedical industries or jewelry, but catalytic converters, used for engine emission reduction, currently represents 40-45% of the world Pt demand (Brenan, 2008; Johnson Matthey, 2013). Actually, since the 80´s-90´s, when cars started to use catalytic converters in Europe, 70% of the Pt demand in Europe is for the manufacturing of catalytic converters (Johnson Matthey, 2013). Previous studies have reported an enrichment in superficial sediments and deposits linked to human activities in urban areas (Schäfer and Puchelt, 1998; Tuit et al., 2000; Fritsche and Meisel, 2004; Rauch et al., 2004a; Whiteley and Murray, 2005; Sutherland et al., 2007) but also in remote environments (Rauch et al., 2004b; Soyol-Erdene et al., 2011; Sen et al., 2013). However, understanding of the post-depositional reactivity of emitted Pt is necessary to assess its potential uptake and accumulation by living organisms and transfer through the food chain.

Some studies have analyzed Pt concentration in biological natural samples (Hodge et al., 1986; Alt et al., 1988; Beinrohr et al., 1993; Alt et al., 1997; Pino et al., 2010) or food (Hoppstock et al., 1989; Alt et al., 1997; Fragnière et al., 2005) to ascertain concentrations in different matrices; others have advanced in the research of the Pt uptake, designing tests where different organisms are grown in model Pt-rich environments (Schäfer et al., 1998; Moldovan et al., 2001; Cosden et al., 2003; Zimmermann et al., 2004) or in natural contaminated ones (Rauch and Morrison, 1999; Moldovan et al., 2001; Haus et al., 2007; Orecchio and Amorello, 2010). Experimental investigations revealed that Pt is effectively accumulated by terrestrial and aquatic plants and organisms (Zimmermann and Sures, 2004), reflecting an environmental increase in Pt concentration (Helmers and Mergel, 1998; Schäfer et al., 1998; Cosden et al., 2003; Neira et al., 2015); however, there is a lack of studies dealing with the long-term accumulation of Pt by plants under natural conditions.

The performance of salt marshes and, specially, of their dominant halophytic plant species, which have a strong capability to accumulate anthropogenic contaminants by their belowground biomass (e.g. Pb, Cr, Zn, Ni, Cu, As, Cd, Co), have been well-characterized to improve the understanding of the biogeochemical cycle of several trace elements (Caçador et al., 1996; Sundby et al., 2003, 2005; Caetano et al., 2007, 2008; Tanackovic et al., 2008; Caçador et al., 2009; Duarte et al., 2010; Santos-Echeandía et al., 2010). The ability of these plants to phytostabilize contaminants by their uptake is due to their high biomass production (Duarte et al., 2010), and this has entailed their use for phytoremediation purposes (Caçador et al., 2009; González-Alcaraz et al., 2011). Thus, in order to check a possible bioaccumulation or transfer to the biological compartments, this study analyzes Pt concentration in sediments impacted by Pt inputs (Cobelo-García et al., 2011; Almécija et al., in revision), rhizoconcretions, interstitial water and roots, stems and leaves of *Sarcocornia fruticosa;* to this aim, cores from the salt marshes of the Tagus Estuary (SW Europe) at two different sampling points, where daily traffic density is extremely different, were collected. The main objective of this work is, therefore, to investigate the role of the salt marsh plants in the biogeochemical cycle of Pt and its post-depositional mobility.

3.2 Study area

Tagus Estuary (Figure 3.1), with a extension of 320 Km^2 (40% are salt marshes), is one of the largest estuaries in Europe. The city of Lisbon (Portugal), with 3 million inhabitants, is located in the north bank of the Estuary (Valentim et al., 2013).

Two stations, under different traffic pressures, were chosen for sampling: *Samouco* Salt Marsh or High Traffic Station (Figure 3.1A) and *Rosario* Salt Marsh or Low Traffic Station (Figure 3.1B). High Traffic Station is located under a motorway bridge with a traffic density of 50,000 vehicles per day (Instituto de Intraestructuras Rodoviárias IP (Portugal), 2013). Before the bridge was opened in 1998, the human activities in the area were negligible. However, Low Traffic Station, where the traffic pressure is low, had an important human influence due to the presence of the Barreiro Chemical Complex in the surrounding area, whose contaminant effects, especially between the 40´s and the 70´s, have been reported in several studies (Caetano et al., 2007; Mil-Homens et al., 2013).

3.3 Material and methods

3.3.1 Sampling and treatment of samples

Sediment cores were sampled in the intertidal salt marsh area of the Tagus Estuary in March (spring) and September (summer) 2011. At High Traffic Station (Figure 3.1A) cores were collected in two different points, one colonized by the halophytic plant *Sarcocornia fruticosa*, typical in upper salt marshes, and the other without vegetation; at Low Traffic Station cores were taken only where *Sarcocornia fruticosa* grows (Figure 3.1B). Leaves and stems were also sampled at both stations and seasons. Besides, some rhizoconcretions that surrounded the roots of *Sarcocornia fruticosa*, formed by precipitation of Fe oxides in the pores of the sediment grains (Vale, 1990; Sundby et al., 1998, 2003), were collected in the Low Traffic Station (20-30 cm). Each core was sliced in situ and stored in acid-clean high-density polyethylene bottles, avoiding the air presence inside to minimize sediment oxidation (every 2 cm from 0 to 10 cm, every 3 cm from 10 to 20 cm, every 5 cm from 20 to the bottom of the core).

Sediment samples and rhizoconcretions were oven-dried (<60 °C) until constant weight, homogenized and ground in agate mortar. Alive roots (white color) of *Sarcocornia fruticosa* were sampled in the oxic part of the core, isolated from each slide of sediments using a magnifying glass and plastic tweezers. Roots, stems and leaves were rinsed and cleaned with Milli-Q© (Millipore) water to avoid the presence of dust or sediment particles, dried (<60 °C) until constant weight and ground. Interstitial waters (first 20 cm of the core) were extracted from the sediment by centrifugation at 8000 rpm for 30 minutes at +4°C, filtered through 0.45 μm polycarbonate membranes, stored in acid-clean low-density polyethylene bottles and acidified

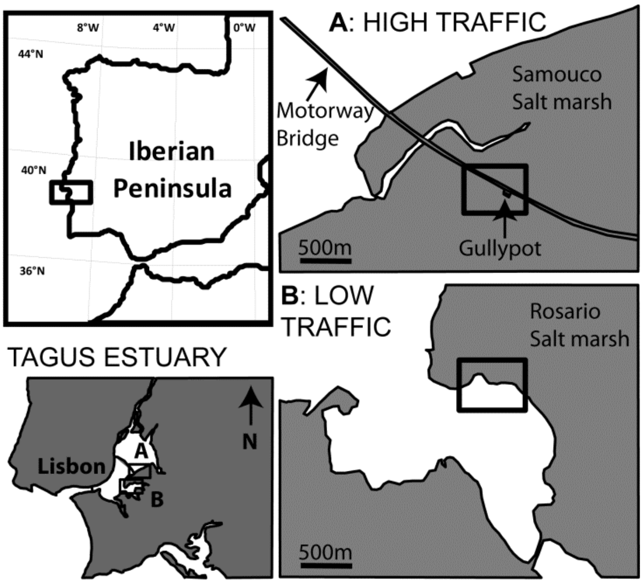


Figure 3.1: Map of the study area in the Tagus Estuary (Lisbon, SW Europe). Two sampling points were chosen: (A) High Traffic Station (Samouco), under a motorway highway bridge; and (B) Low Traffic Station (Rosario).

using Suprapur© (Merck) HCl (pH ~1). Besides, procedural blanks were prepared using Milli-Q© water. The Figure 3.2 summarizes the sample treatment procedure. All laboratory material was acid-cleaned prior to use and samples were manipulated inside laminar flow hoods.

3.3.2 Auxiliary parameters

Auxiliary parameters (redox potential, pH and oxygen saturation) were measured in duplicate cores using calibrated probes. A refractometer (Atago S/Millα 0-100‰) was used to measure salinity in porewater.

3.3.3 Analytical methods

3.3.3.1 Pt analysis by AdCSV in sediments, roots and interstitial water

Platinum was determined in sediments, concretions, roots, leaves and stems and interstitial waters by catalytic adsorptive cathodic stripping voltammetry (catalytic AdCSV) following the method described by van den Berg and Jacinto, (1988) and modified by Cobelo-García *et al.* (2013) (Figure 3.2).

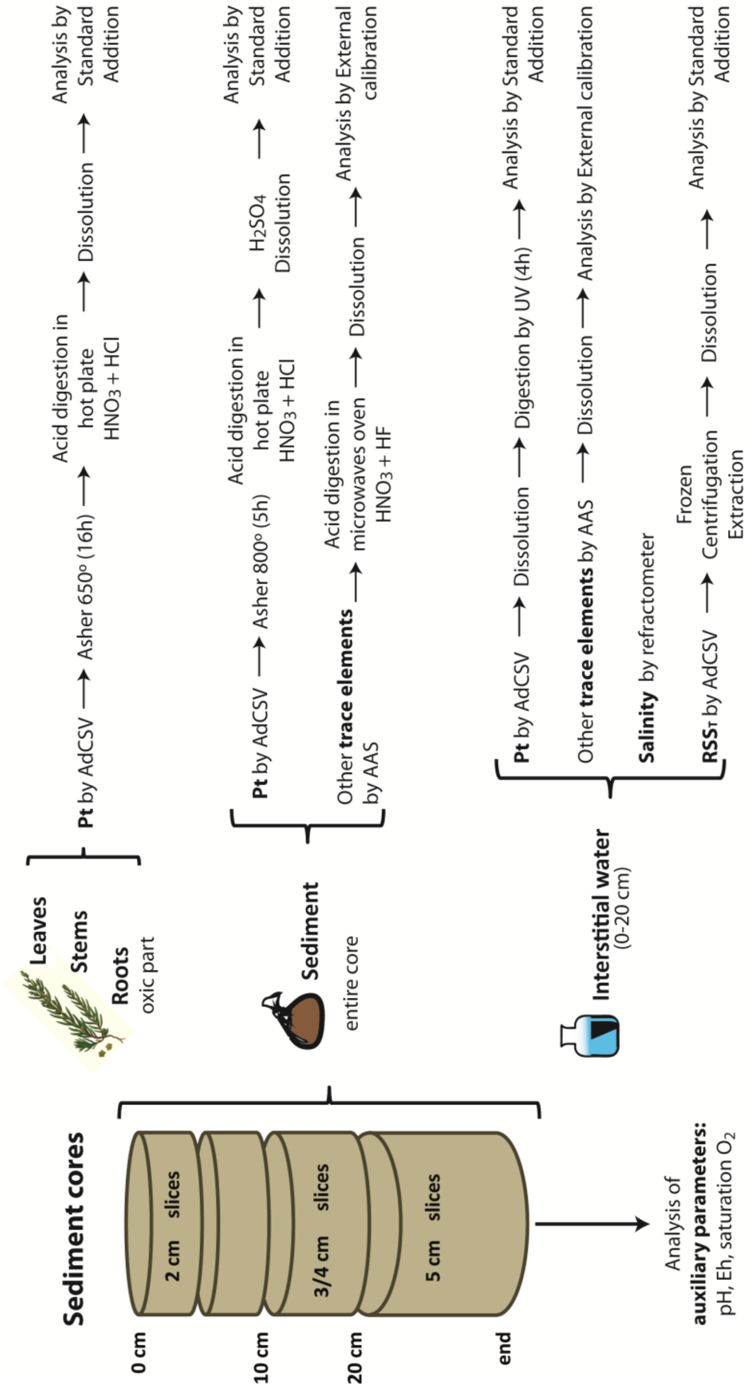


Figure 3.2: Scheme of sampling, pre-treatment and analysis of samples: AdCSV= adsorptive athodic stripping voltammetry; AAS= atomic absorption spectrometry; UV= ultraviolet radiation; RSS_T= total reduced sulfur species.

For sediments, around 200 mg of sample were ashed for 5 h at 800 ºC in quartz crucibles (Cobelo-García et al., 2011) to remove the organic matter that may severely interfere during the voltammetric determination of Pt. Then, samples were transferred to 30 mL Teflon® vessels with 5 mL concentrated HCl and 3 mL concentrated HNO_3 (Merck Suprapur) and digested on a Teflon-coated hot plate (Pico Trace, 195 ºC, 4 h). After digestion, vessel caps were removed and the acids were allowed to evaporate to near dryness; the residue was then re-dissolved with 1 mL concentrated HCl (Merck Suprapur) and 1 mL concentrated H_2SO_4 (Fluka Trace Select) and evaporated again until no fumes were observed (only H_2SO_4 remaining) to ensure that there was no HNO_3 remnant as it may interfere during the voltammetric determination. Samples were allowed to cool, diluted with 0.1 M HCl, syringe-filtered (0.45 µm) and made up to 25 mL in volumetric flasks. This method was also used for Pt determination in vegetal tissues, except for the ashing conditions; here, a temperature of 650 ºC for 16 h was chosen (800 ºC caused some problems with samples). Blanks and detection limits for Pt in sediments and roots are indicated in Table 3.1. The road dust certified reference material BCR-723 (Institute of Reference Materials and Measurements, 2013) was analyzed to check the accuracy of the analytical procedure, yielding a close agreement with the certified concentration (Table 3.1).

For interstitial waters, samples were diluted (1:11) and UV-digested (4 h) in the presence of 22 mM H_2O_2 (TraceSelect© Ultra, Fluka) to remove organic matter (Cobelo-García et al., 2013; Almécija et al., in revision). Blanks and detection limits are also included in Table 3.1. All the results given are blank-corrected.

Table 3.1: Blanks and detection limits (3xSD) for Pt determination in porewaters, sediments and roots. Results for the road dust reference material BCR-723 are also included.

	Porewater (ng L^{-1})	Sediment (ng g^{-1})	Roots (ng g^{-1})
Blank	0.003 ± 0.003 (*n=13*)	0.024 ± 0.004 (*n=10*)	0.057 ± 0.018 *(n=8)*
Detection Limit	0.01	0.013	0.054
Reference Material	-	81.5 ± 6.3 (*n=7*) (cert. 81.3 ± 2.5)	-

Values: mean value ± SD; number of replicates in brackets.

Blanks for Pt correspond to a typical mass of 200 mg of sediment and 100 mg of dried roots.

3.3.3.2 Determination of other trace elements

Trace elements were determined in sediments (Fe, Mn, V, Cd, Pb, and Zn) and interstitial waters (Fe and Mn) by electrothermal graphite furnace atomic absorption spectrophotometry (GFAA, Varian SpectrAA 220), whereas Al was measured by flame atomic absorption spectrophotometry (Varian SpectrAA 220FS). Sediment samples were acid digested using a microwave oven (MarsXpress, CEM) in Teflon® bombs using a 3:1 mixture of HNO_3 (Hiperpur© 69% Panreac) and HF (Suprapur© 40% Merck). Interstitial water samples were diluted before the analysis (Figure 3.2). One blank was run every ten samples and results were blank-corrected. The accuracy of the analytical methodology was checked using PACS-2 marine sediment reference material (National Researcher council Canada, 2013) and the results were in agreement with the certified values (Table 3.2).

3.3.3.3 Total reduced sulfur in interstitial water

Total reduced sulfur species (RSS_T) were determined in interstitial waters by means of cathodic stripping voltammetry (Figure 3.2) according to Bura-Nakic et al. (2009). This RSS_T fraction includes sulfides, polysulfides, organic thiols, polysulfanes and molecular S^0.

3.3.3.4 Biomass and loss on ignition (LOI)

Other parameters determined to help in the interpretation of the results were the biomass and loss on ignition (LOI). Biomass weight (%) was calculated following the equation:

$$Biomass\ (\%) = \frac{Weight_{roots\ slice}}{Weight_{slice}} \times 100 \qquad \text{[Eq 3.1]}$$

where $Weight_{roots\ slice}$ is the weight of the roots in each slice and $Weight_{slice}$ is the weight of the entire slice.

The loss on ingnition ($LOI_{550\,°C}$, %) was calculated following the method proposed by Heiri *et al.* (2001) to approximate the organic and carbonate content in sediments.

$$LOI_{550\,°C} = \frac{Dw_{105\,°C} - Dw_{550\,°C}}{Dw_{105\,°C}} \times 100 \qquad \text{[Eq 3.2]}$$

where $Dw_{105\,°C}$ is the weight of the sediment after 16h ashing at 105 °C, for achieving a constant dry weight of the sample, and $Dw_{550\,°C}$ is the weight of the same sample ashed again at 550 °C during 16h, to combust organic matter.

Table 3.2: Certified and measured values in reference material PACS-2 (marine sediment, National Researcher Council Canada 2013) analyzed by atomic absorption spectrometry.

	Fe ($g\ kg^{-1}$)	V ($mg\ kg^{-1}$)	Pb ($mg\ kg^{-1}$)	Mn ($mg\ kg^{-1}$)	Zn ($mg\ kg^{-1}$)	Cd ($mg\ kg^{-1}$)	Al ($mg\ kg^{-1}$)
This study	41.1 ± 1.9	127 ± 7	179 ± 16	449 ± 44	343 ± 32	2.20 ± 0.29	11.9 ± 1.2
Certified	41.2 ± 1.6	133 ± 5	183 ± 8	440 ± 19	364 ± 23	2.11 ± 0.15	12.6 ± 0.3

Values: mean value ± error (CI= 95%; n=6)

3.4 Results

3.4.1 Unvegetated samples

3.4.1.1 High Traffic Station

Figure 3.3 shows the results for the unvegetated sediment cores from High Traffic Station, in spring (upper pannel) and summer (lower pannel). Oxygen saturation was under the detection limit in both cores, except for upper 2 cm in spring where the saturation was up to 2%. Redox potential (Eh, mV vs. H^+) values showed a general trend to increase from top to bottom, between –66 and 210 mV (only summer data available). In spring, pH and salinity (not shown) presented values of 7.09±0.24 (*n=23*) and 22.8±5.4 (*n=8*) respectively, and in summer 6.95±0.29 (*n=21*) and 37.2±2.3 (*n=8*). For both seasons pH tends to decrease with depth while salinity showed the opposite behavior. The loss on ignition ($LOI_{550\ °C}$) had homgeneous values in spring (4.2±1.2%, *n=13*), whereas in summer, the profile showed an enrichment in the upper 4 cm (up to 23%) and a more saw-tooth profile (6.6±2.7 %, *n=14*, z> 4 cm). Fe, Mn and RSS_T profiles in interstitial waters presented peaks in the first 20 cm in both samplings, but peaks are softer in spring data for all these variables than in summer (Figure 3.3). Dissolved Fe ranged from 0.05 to 0.19 mg L^{-1} (peak at < 2 cm) in spring and 0.04 to 11.0 mg L^{-1} (peak depth in 5 cm) in summer. Dissolved Mn varied from 0.46 to 1.2 mg L^{-1} in spring and from 0.50 to 2.8 mg L^{-1} in summer (peak depth 7 cm and around 3 times the concentration of the spring peak). The highest difference appeared in RSS_T profiles, where spring and summer data ranged between 1.7-8.8 µg L^{-1} and 5.4-14000 to µg L^{-1} respectively, both showing surface peaks (all values can be found in Table 3.3 and Table 3.4, for spring and summer).

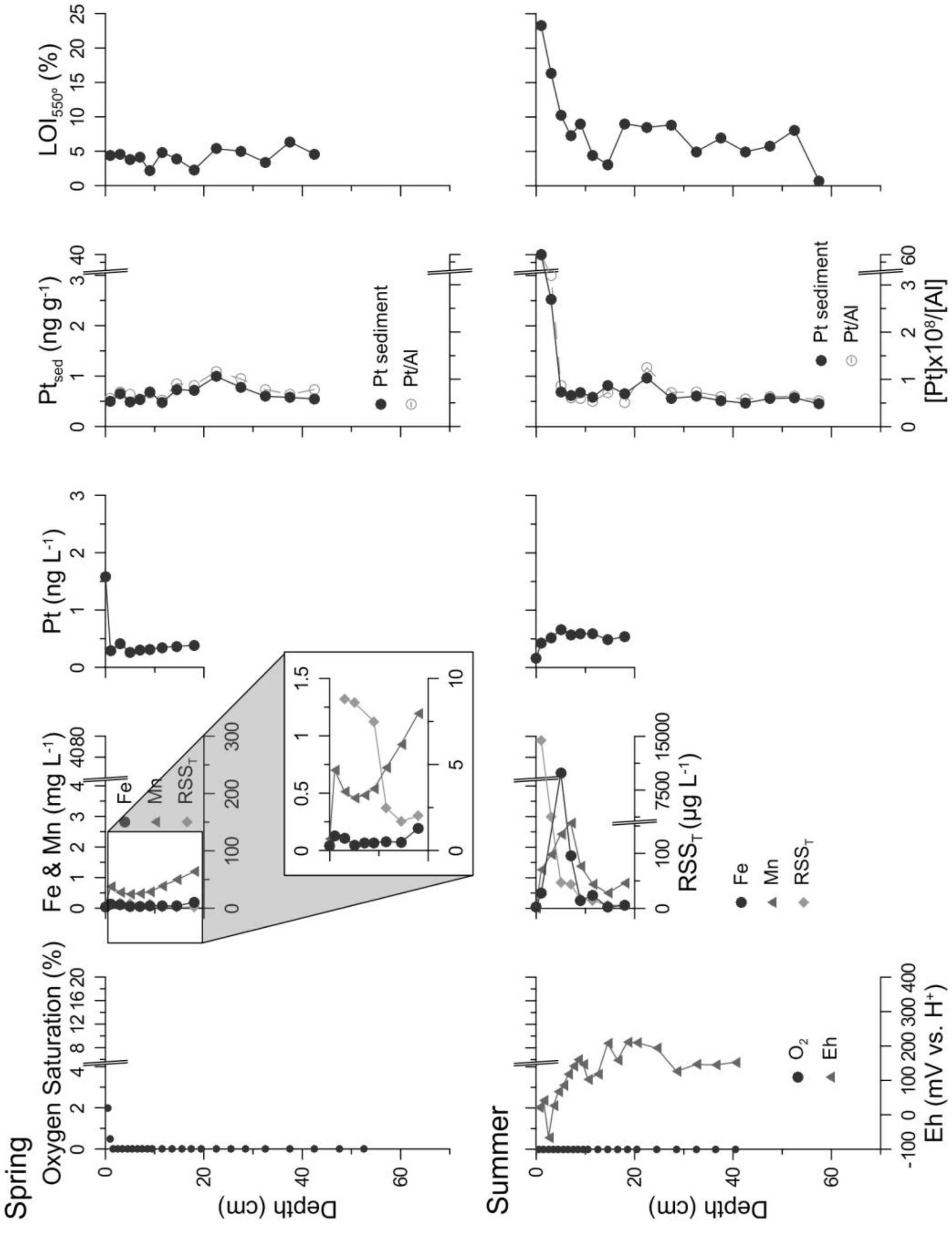


Figure 3.3: Spring and summer profiles of O_2, Eh in the cores; Fe, Mn, RSS_T (total reduced sulfur species) and Pt in interstitial water; Pt concentration in sediments and roots and biomass and LOI (%) in sediments for High Traffic Station unvegetated. The sample at depth= 0 corresponds to the overlaying water.

Table 3.3: Raw data of unvegetated core from High Traffic Station (Samouco Salt Marsh) in Spring (March 2011).

		Sediment								Roots	Interstitial Water				
	Depth	Pt	Fe	Mn	V	Cd	Pb	Zn	Al	Pt	Pt	Fe	Mn	RSS_T	
	(cm)	(ng g^{-1})	(mg g^{-1})	(µg g^{-1})	(µg g^{-1})	(µg g^{-1})	(µg g^{-1})	(µg g^{-1})	(mg g^{-1})	(ng g^{-1})	(ng L^{-1})	(mg L^{-1})	(mg L^{-1})	(µg L^{-1})	Sal.
HTS overlying	-	-	-	-	-	-	-	-	-	-	1.58	0.041	0.103	-	17
HTS 00-02	1	0.495	49.2	468	108	0.029	50.8	123	83.3	-	0.286	0.126	0.701	-	20
HST 02-04	3	0.646	41.5	344	103	0.038	58.5	128	89.2	-	0.410	0.106	0.511	8.82	19
HST 04-06	5	0.492	41.1	342	103	0.034	48.1	121	72.8	-	0.260	0.048	0.458	8.59	20
HST 06-08	7	0.530	45.5	320	106	0.032	37.9	109	91.2	-	0.297	0.066	0.482	-	20
HST 08-10	9	0.689	44.3	260	108	0.021	33.5	120	98.1	-	0.313	0.067	0.538	7.50	22
HST 10-13	11.5	0.471	43.0	276	108	0.042	35.7	114	84.7	-	0.346	0.079	0.721	2.48	24
HST 13-16	14.5	0.733	46.7	332	110	0.041	38.6	116	80.9	-	0.366	0.071	0.927	1.69	29
HST 16-20	18	0.713	48.4	326	111	0.028	36.2	120	82.0	-	0.383	0.194	1.200	2.02	34
HST 20-25	22.5	0.992	44.2	308	112	0.044	32.9	145	85.2	-	-	-	-	-	-
HST 25-30	27.5	0.780	44.5	262	110	0.110	32.6	145	77.4	-	-	-	-	-	-
HST 30-35	32.5	0.599	38.2	264	110	0.114	33.2	127	76.6	-	-	-	-	-	-
HST 35-40	37.5	0.576	46.0	296	105	0.143	32.9	139	85.0	-	-	-	-	-	-
HST 40-45	42.5	0.548	41.4	292	99.3	0.183	30.6	144	69.9	-	-	-	-	-	-

Table 3.4: Raw data of unvegetated core from High Traffic Station (Samouco Salt Marsh) in Summer (September 2011).

		Sediment								Roots	Interstitial Water				
	Depth (cm)	Pt (ng g^{-1})	Fe (mg g^{-1})	Mn (µg g^{-1})	V (µg g^{-1})	Cd (µg g^{-1})	Pb (µg g^{-1})	Zn (µg g^{-1})	Al (mg g^{-1})	Pt (ng g^{-1})	Pt (ng L^{-1})	Fe (mg L^{-1})	Mn (mg L^{-1})	RSS$_T$ (µg L^{-1})	Sal.
HTS overlying	-	-	-	-	-	-	-	-	-	-	0.164	0.046	0.013	-	34
HTS 00-02	1	40.1	30.2	542	59.2	0.248	51.8	177	69.1	-	0.429	0.494	1.260	14400	34.5
HST 02-04	3	2.52	31.5	518	68.4	0.236	63.2	155	78.9	-	0.520	4.880	1.750	3800	35
HST 04-06	5	0.683	31.6	639	72.2	0.093	73.7	169	78.3	-	0.656	10.700	2.430	47.2	35
HST 06-08	7	0.619	41.5	613	98.1	0.104	101	245	100	-	0.571	1.720	2.790	43.3	36
HST 08-10	9	0.682	45.7	356	100	0.045	74.8	125	115	-	0.592	0.254	1.380	17.2	38
HST 10-13	11.5	0.584	41.9	367	111	0.062	66.9	105	110	-	0.589	0.423	0.790	14.4	39
HST 13-16	14.5	0.816	42.0	313	112	0.179	46.7	106	113	-	0.484	0.039	0.497	5.35	40
HST 16-20	18	0.653	45.4	347	112	0.121	36.3	286	127	-	0.535	0.096	0.829	5.75	40
HST 20-25	22.5	0.968	43.6	397	112	0.091	31.6	96.5	77.7	-	-	-	-	-	-
HST 25-30	27.5	0.558	40.8	467	111	0.085	28.0	93.8	77.2	-	-	-	-	-	-
HST 30-35	32.5	0.605	41.2	366	104	0.045	28.6	96.1	82.3	-	-	-	-	-	-
HST 35-40	37.5	0.516	39.4	378	102	0.063	27.5	90.7	80.7	-	-	-	-	-	-
HST 40-45	42.5	0.466	40.3	278	98.2	0.062	31.4	88.5	80.2	-	-	-	-	-	-
HST 45-50	47.5	0.557	41.7	307	105	0.058	27.9	96.3	88.0	-	-	-	-	-	-
HST 50-55	52.5	0.572	41.1	303	105	0.051	29.6	97.9	88.5	-	-	-	-	-	-
HST 55-60	57.5	0.452	38.1	261	97.7	0.061	27.7	93.4	81.7	-	-	-	-	-	-

Pt concentrations in interstitial waters presented a increasing trend with depth in both cores, more progresive in spring, between 0.26 and 0.41 ng L^{-1} (0.33±0.05 ng L^{-1}, $\bar{x} \pm SD$, *n=8*), and concentrated in the first 6 cm in summer, ranging between 0.43 and 0.66 ng L^{-1} (0.55±0.07, *n=8*) (Figure 3.3, Table 3.3 and Table 3.4). The most remarkable fact is the divergence among Pt concentrations in overlaying water, exhibiting the highest concentration in spring, 1.6 ng L^{-1}, and the lowest in summer, 0.16 ng L^{-1}, 10 times lower.

In sediments, Pt concentrations ranged from 0.47 to 0.99 ng g^{-1} (0.64±0.15, *n=13)* and from 0.45 to 40 ng g^{-1} (0.64±0.13, *n=14*, at depths> 4cm) in spring and summer cores respectively (Figure 3.3, Table 3.3 and Table 3.4). Only the first 4 cm showed evident differences between both cores: homogeneous in spring and with a clear surface peak in summer (40 ng g^{-1} at < 2cm, 2.5 ng g^{-1} at 2-4 cm). Some other trace elements showed similar concentrations in both seasons like Pb or Zn (Figure 3.4 for spring sampling, Figure 3.5 for summer one; all data in Table 3.3 and Table 3.4). However, Cd presented a surface enrichment in summer, agreeing with Pt peak, while in spring, the concentrations increased with the depth. Fe and Mn in sediments revealed some minimum peaks in the first 25 cm for both samplings. These values were normalized by aluminum since Al is commonly used to normalize metal concentrations in order to minimize differences in concentrations associated with changes in particle nature and grain size (Windom et al., 1989; Sageman and Lyons, 2003).

3.4.2 Vegetated samples

3.4.2.1 High Traffic Station

Figure 3.7 shows the results for the vegetated cores from High Traffic Station in spring (upper pannel) and summer (lower pannel). Oxygen profiles showed clear distinctive conditions: saturations were up to 20% in spring (6±5%, $\bar{x} \pm SD$, *n=32*) but under the detection limit in summer throughout the core. Eh ranged from –100 to 180 mV (vs. H^{+}), but also showing an increasing trend with depth similar to that found for the unvegetated core in the same area (see above). The pH ranged between 6.63 and 7.07 (6.97±0.13, *n=22*) and 6.29 and 6.95 (6.53±0.16, *n=18*) in spring and summer, decreasing with depth. Salinity varied, from the top of the core to the bottom, from 17 to 26 (20.1±3.1, *n=8*) in spring and from 35 to 40 (37.3±1.9, *n=8*) in summer. $LOI_{550\ °C}$ and Biomass (%) displayed similar profiles in both samplings, especially in the summer one where the maximum of

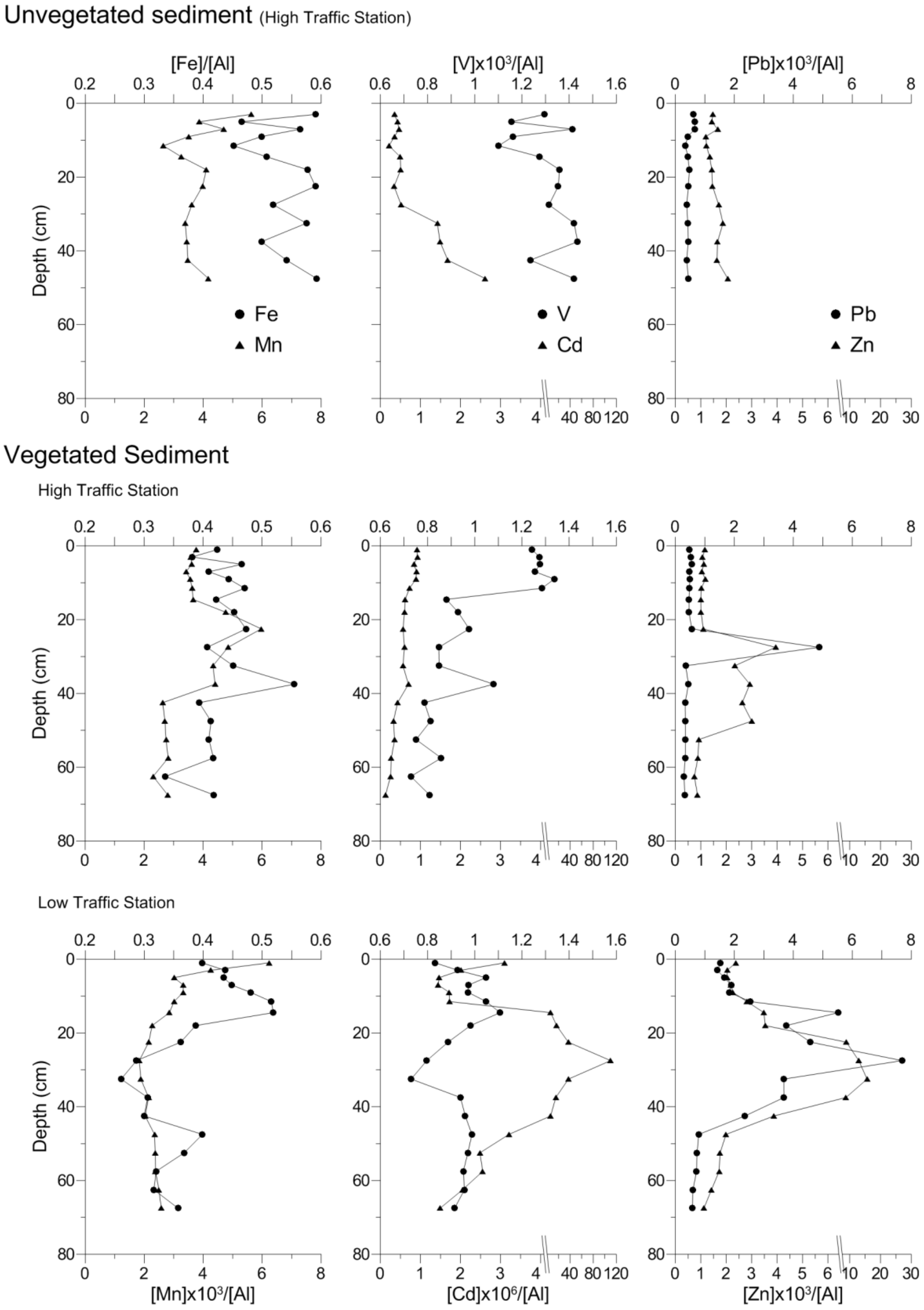
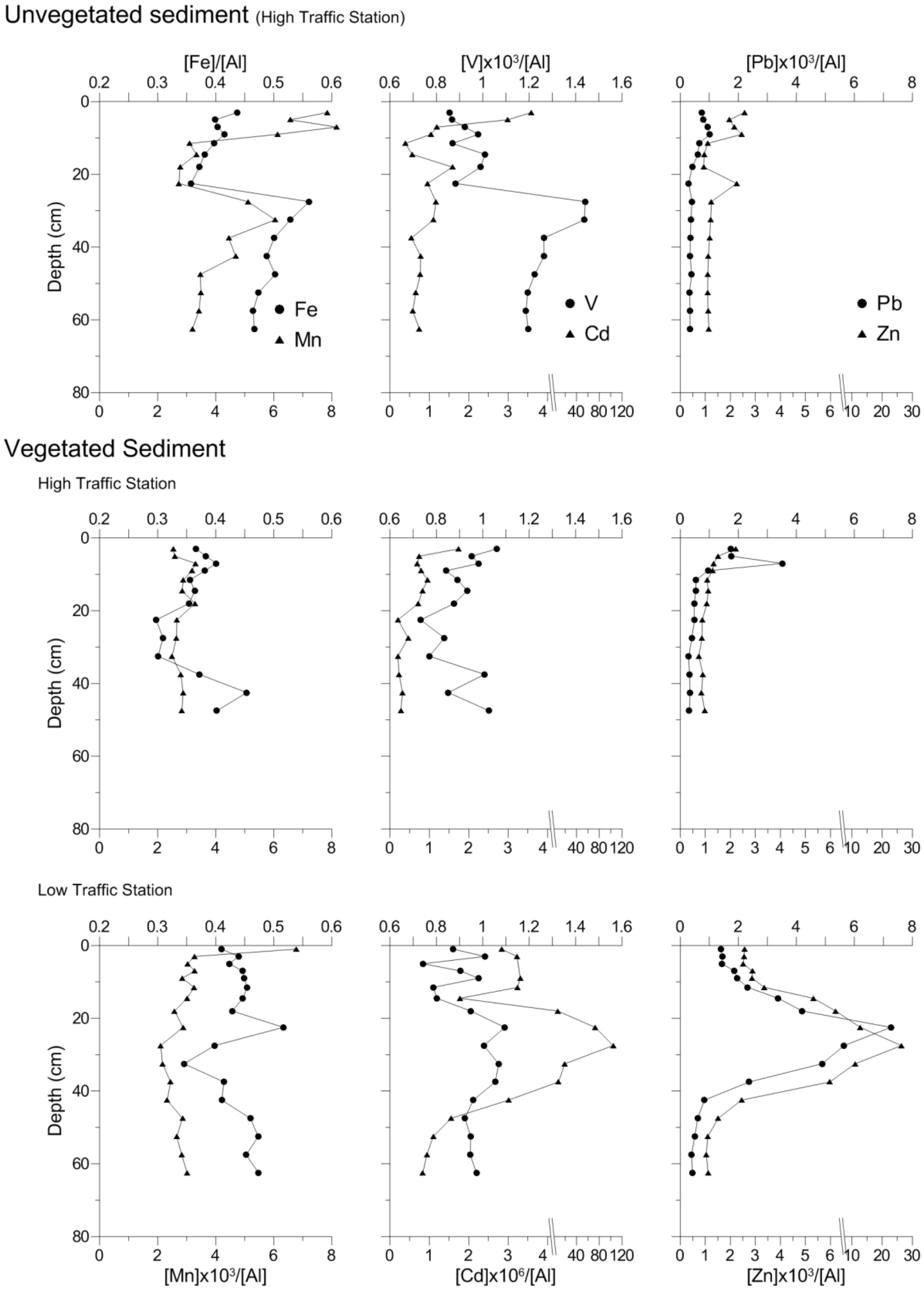


Figure 3.4: Spring profiles of other trace elements (Fe, V, Pb, Mn, Cd and Zn) for each sampling station.



Unvegetated sediment (High Traffic Station)

Vegetated Sediment

High Traffic Station

Low Traffic Station

Figure 3.5: Summer profiles of other trace elements (Fe, V, Pb, Mn, Cd and Zn) in each sampling station.

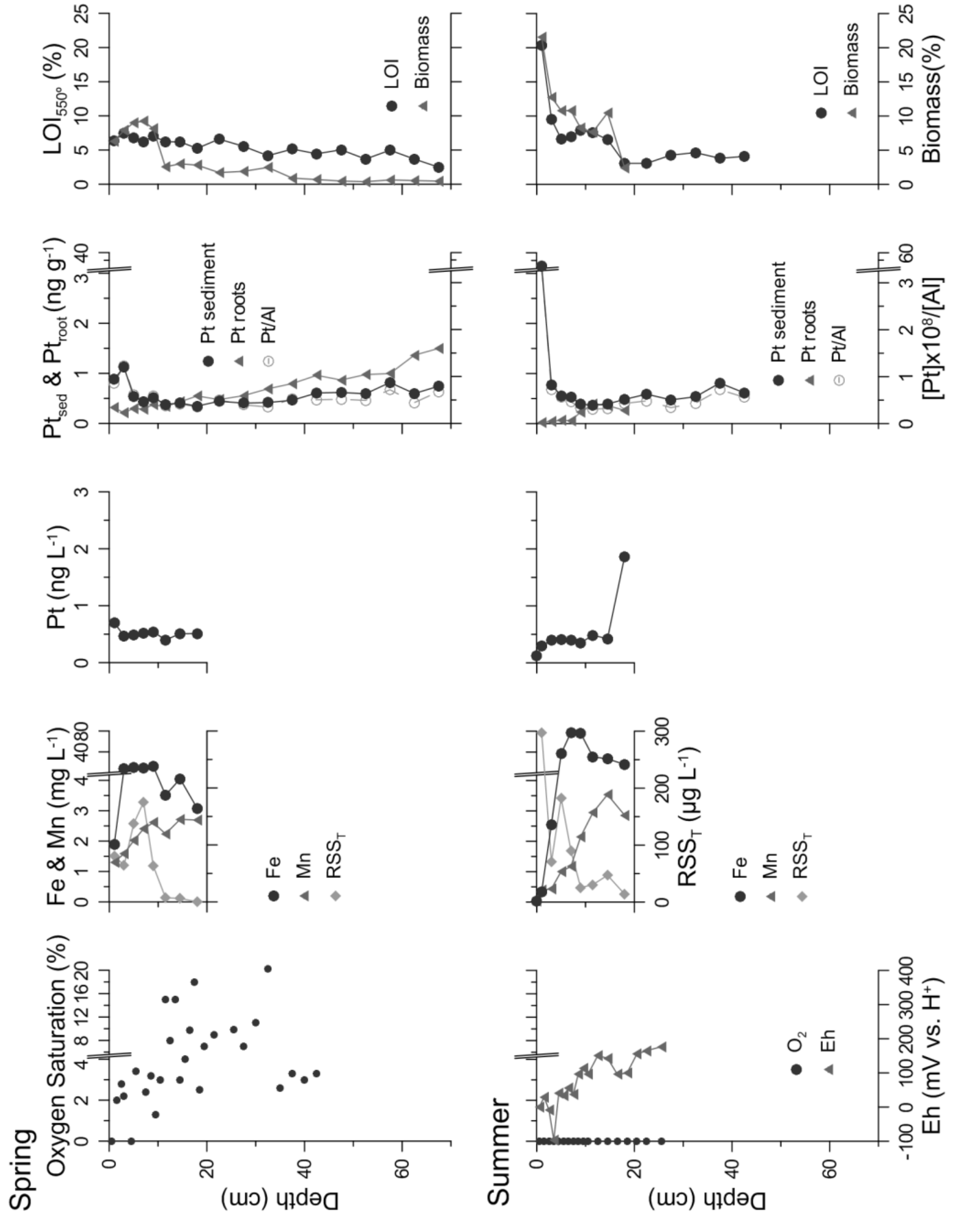


Figure 3.6: Spring and summer profiles of O_2, Eh in the cores; Fe, Mn, RSS_T (total reduced sulfur species) and Pt in interstitial water; Pt concentration in sediments and roots and biomass and LOI (%) in sediments for High Traffic Station where *Sarcocornia fruticosa* is growing. The sample at depth= 0 corresponds to the overlaying water.

biomass (22% < 2 cm) agreed with maximum of $LOI_{550\ °C}$ (20%). The main difference appeared in the samples deeper than 10 cm in the spring core, where LOI is usually 2 times the biomass.

Dissolved elements (Fe, Mn) in interstitial waters presented sub-surface peaks in both cores (Figure 3.7, Table 3.5 for spring and Table 3.6 summer). Fe concentration in interstitial waters were similar in spring and summer, ranging from 1.9 and 12.0 mg L^{-1} (peak centered at 7 cm depth) and 0.34 and 78.0 mg L^{-1} (maximum 9-11.5 cm), accordingly. Minimum values were observed at surface in both cores. In a similar manner, Mn profiles, whose concentrations were between 1.3-2.7 mg L^{-1} (spring) and 0.4-3.5 mg L^{-1} (summer), showed the minimum at surface and the maximum around 15 cm. RSS_T concentrations followed a similar pattern in both sampling: a surface maximum, followed by a minimum and another sub-surface maximum (spring: 1.0-180 µg L^{-1} and max. at 5 cm; summer: 14-300 µg L^{-1} and max. at 7 cm).

Dissolved Pt in the porewater presented similar concentrations for all the samples, 0.52±0.08 ng L^{-1} ($\bar{x} \pm SD$, *n=8*) and 0.40±0.06 ng L^{-1} ($\bar{x} \pm SD$, *n*=7) in spring and summer samplings respectively, except for a peak of 1.9 ng L^{-1} in the deepest sample in summer (18 cm). Overlying water for summer (no sample was collected in spring) showed the lowest Pt concentration in this study, 0.12 ng L^{-1}. With the exception of the peak at 18 cm in the summer core, both porewater profiles were similar than the observed for the unvegetated sediments.

For sediments, Pt averaged very similar in both samplings, 0.56±0.21 ng g^{-1} (*n=18*) in spring and 0.54±0.14 ng g^{-1} (*n=12*) in summer, excepting for the surface peaks. The highest concentrations were found at 2-4 cm (1.1 ng g^{-1}) in spring, a modest subsuperficial enrichment, and at 0-2 cm where Pt reached 5.5 ng g^{-1}, 10-fold the mean value. There was no marked trend in the rest of the core. Pt in roots showed concentrations from 0.21 to 1.5 ng g^{-1} in spring and 0.027 to 0.39 ng g^{-1} in summer, and were in the range of those for the surrounding sediments. Nevertheless, and contrarily to the sediment, roots revealed a clear increasing trend with depth (Figure 3.6, Table 3.5 and Table 3.6). Analysis of Pt for other tissues of *Sarcocornia fruticosa* resulted in very low concentrations (Table 3.7), in fact under the detection limit for some samples (0.054 ng g^{-1}, Table 3.1). Pt for leaves samples in spring (0.039 ng g^{-1}) is higher than in stem samples (0.015 ng g^{-1}) while in summer Pt was not detected in leaves and was similar to the previous sampling for stems

Table 3.5: Raw data of vegetated core (Sarcocornia fruticosa) from High Traffic Station (Samouco Salt Marsh) in Spring (March 2011).

		Sediment								Roots	Interstitial Water				
	Depth (cm)	Pt (ng g^{-1})	Fe (mg g^{-1})	Mn (µg g^{-1})	V (µg g^{-1})	Cd (µg g^{-1})	Pb (µg g^{-1})	Zn (µg g^{-1})	Al (mg g^{-1})	Pt (ng g^{-1})	Pt (ng L^{-1})	Fe (mg L^{-1})	Mn (mg L^{-1})	RSS$_T$ (µg L^{-1})	Sal.
HTS 00-02	1	0.879	43.7	388	128	0.094	49.3	119	103	0.317	0.698	1.890	1.300	81.0	17
HST 02-04	3	1.124	35.0	329	117	0.085	48.2	98.2	91.8	0.210	0.471	8.540	1.590	64.0	18
HST 04-06	5	0.543	41.2	320	113	0.074	49.0	98.5	88.5	0.300	0.491	9.940	2.020	138	18
HST 06-08	7	0.435	38.2	319	117	0.084	44.1	97.0	93.2	0.287	0.522	9.040	2.400	175	18
HST 08-10	9	0.519	39.5	317	119	0.079	44.1	105	89.0	0.374	0.540	12.10	2.610	63.0	20
HST 10-13	11.5	0.381	48.0	370	131	0.074	48.4	104	102	0.336	0.400	3.510	2.240	7.20	21
HST 13-16	14.5	0.405	41.5	360	86.5	0.061	45.8	98.7	98.3	0.431	0.506	4.050	2.720	6.02	23
HST 16-20	18	0.345	44.3	467	91.0	0.059	45.6	98.8	97.9	0.548	0.511	3.080	2.690	1.08	26
HST 20-25	22.5	0.443	41.8	528	86.3	0.050	48.8	97.0	88.4	0.476	-	-	-	-	-
HST 25-30	27.5	0.405	41.9	499	87.3	0.062	502	406	103	0.554	-	-	-	-	-
HST 30-35	32.5	0.417	53.7	516	101	0.067	41.4	278	119	0.691	-	-	-	-	-
HST 35-40	37.5	0.462	49.1	390	95.6	0.062	39.3	259	88.5	0.796	-	-	-	-	-
HST 40-45	42.5	0.608	47.6	318	95.2	0.052	40.3	318	121	0.960	-	-	-	-	-
HST 45-50	47.5	0.618	49.6	325	97.5	0.039	40.2	360	120	0.866	-	-	-	-	-
HST 50-55	52.5	0.591	49.6	332	90.9	0.043	41.1	112	121	0.975	-	-	-	-	-
HST 55-60	57.5	0.817	47.6	321	97.8	0.031	38.2	101	114	0.996	-	-	-	-	-
HST 60-65	62.5	0.596	45.0	309	97.7	0.034	38.4	100	134	1.363	-	-	-	-	-
HST 65-70	67.5	0.744	46.0	308	88.9	0.014	35.9	95.7	110	1.499	-	-	-	-	-

Table 3.6: Raw data of vegetated core (Sarcocornia fruticosa) from High Traffic Station (Samouco Salt Marsh) in Summer (September 2011).

		Sediment								Roots	Interstitial Water				
	Depth (cm)	Pt (ng g^{-1})	Fe (mg g^{-1})	Mn (µg g^{-1})	V (µg g^{-1})	Cd (µg g^{-1})	Pb (µg g^{-1})	Zn (µg g^{-1})	Al (mg g^{-1})	Pt (ng g^{-1})	Pt (ng L^{-1})	Fe (mg L^{-1})	Mn (mg L^{-1})	RSS_T (µg L^{-1})	Sal.
HTS overlying	-	-	-	-	-	-	-	-	-	-	0.120	0.037	0.038	-	34
HTS 00-02	1	5.50	29.3	203	84.9	0.139	140	177	80	0.027	0.295	0.344	0.387	298	35
HST 02-04	3	0.771	40.6	274	101	0.079	187	159	106	0.041	0.399	2.550	0.432	70.2	35
HST 04-06	5	0.558	39.9	328	97.8	0.069	350	133	99.5	0.064	0.406	36.900	1.010	182	36
HST 06-08	7	0.527	43.1	360	95.2	0.089	108	146	113	0.059	0.403	77.700	1.170	90.4	37
HST 08-10	9	0.389	42.7	346	107	0.115	65.5	129	120	0.229	0.351	76.100	2.150	25.4	37
HST 10-13	11.5	0.368	43.3	338	111	0.098	63.2	133	119	0.388	0.485	31.000	2.940	30.5	39
HST 13-16	14.5	0.391	43.2	401	107	0.088	58.7	130	122	0.362	0.423	26.900	3.540	46.9	39
HST 16-20	18	0.484	33.6	301	82.8	0.023	55.2	99.4	113	0.263	1.86	16.500	2.860	13.9	40
HST 20-25	22.5	0.587	37.4	320	101	0.056	48.1	105	121	-	-	-	-	-	-
HST 25-30	27.5	0.474	41.8	347	107	0.028	40.6	103	139	-	-	-	-	-	-
HST 30-35	32.5	0.535	46.1	347	125	0.029	39.0	112	124	-	-	-	-	-	-
HST 35-40	37.5	0.809	50.8	322	95.4	0.036	37.6	94.5	112	-	-	-	-	-	-
HST 40-45	42.5	0.614	43.8	309	112	0.030	33.7	107	109	-	-	-	-	-	-

(0.012 ng g^{-1}), but in any case, Pt concentrations in leaves and stems were lower than the Pt analyzed in the roots for each sample (Table 3.7).

Concentrations of other trace elements analyzed in sediments are plotted in Figure 3.4 (spring) and Figure 3.5 (summer). Pb peaks in both cores, at 25-30 cm in spring (coinciding with Zn peak) and at 5 cm in summer –and not so high as in spring–, is the most highlighting fact, as well as a Cd and V surface peaks in summer.

3.4.2.2 Low Traffic Station

The results of the cores taken at Low Traffic Station for both seasons are plotted in Figure 3.7. Oxygen was present in spring in the first 20 cm (0.5-18%), whereas in summer oxygen appeared from 5 to 20 cm (0.2-6.2%). The Eh behavior was quite similar in both samplings, i.e. highest values coinciding with the more oxygenated part of the cores (spring: 270±60 mV, *n=8*; summer: 270±36, *n=21*) and decreased when oxygen was depleted (spring: –53±28, *n=5*; summer: 86±33, *n=9*). The pH profile showed a decreasing trend in summer core, from 7.7 (z= 0.5 cm) to 6.71 (z= 24.5 cm) but the trend was not clear in the spring sampling (6.35±0.06, *n=30*). Salinity increased with depth in both cores, although it was higher in summer (from 22 to 32.5 in spring and 38 to 51 in summer). Again, the calculations of biomass and $LOI_{550\ °C}$ presented values similar in all the profile (spring; LOI= 7±3%, *n=18*, and biomass= 7±2%, *n=9*; summer: LOI= 7±2%, *n=17*, and biomass= 5±1%, *n=8*, data in Table 3.8 and Table 3.9).

All the auxiliary analysis of porewater exhibited a surface maximum concentration in the summer core (0.58 and 5.0 mg L^{-1} for Fe and Mn, and 76 µg L^{-1} for RSS_T), while in spring only Mn had a surface peak (6.3 mg L^{-1}); RSS_T reached a maximum at 2-4 cm (81 µg L^{-1}) whereas for Fe a maximum was observed at 14.5 cm (6.7 mg L^{-1}).

Dissolved Pt in interstitial waters had homogeneous profiles in both samplings (0.21 ± 0.07 ng L^{-1}, *n=7* in spring and 0.48 ± 0.09 ng L^{-1}, *n=8* in summer), except for a peak 12-fold the average concentration in spring (2.5 ng L^{-1}, 14.5 cm). The summer overlying water had, again, the lowest concentration in the profile (0.21 ng L^{-1}).

For sediments, Pt in both profiles decreased with depth down around 25 cm, where a minimum was reached. Concentrations ranged from 2.8 to 0.022 ng g^{-1} in spring and from 1.1 to 0.11 ng g^{-1} in summer (the highest concentrations is in the surface layer). Rhizoconcretions showed a distribution of Pt concentrations from inner to outer layer of 1.1

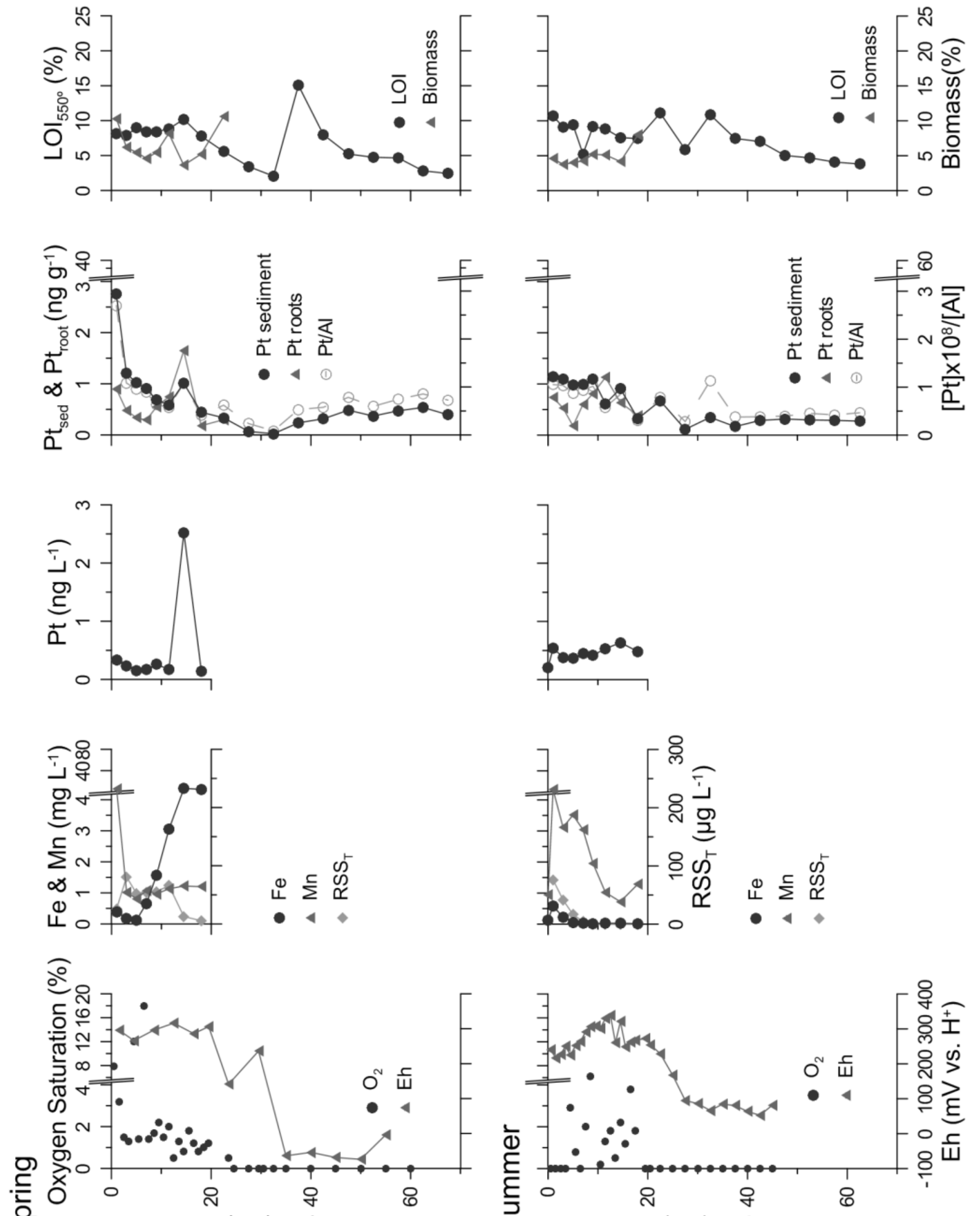


Figure 3.7: Spring and summer profiles of O_2, Eh in the cores; Fe, Mn, RSST (total reduced sulfur species) and Pt in interstitial water; Pt concentration in sediment and and roots and biomass and LOI (%) in sediments for Low Traffic Station where *Sarcocornia fruticosa* is growing. The sample at depth= 0 corresponds to the overlaying water.

Table 3.7: Platinum concentration (ng g^{-1}) in different tissues of *Sarcocornia fruticosa* in both sampling stations and seasons and Pt concentrations in different layers of rizhoconcrections from Low Traffic Station.

Sample		Pt (ng g^{-1}) High Traffic Station		Pt (ng g^{-1}) Low Traffic Station	
		Spring	Summer	Spring	Summer
Sarcocornia fruticosa	Roots	0.21 - 1.5	0.027 - 0.39	0.18 - 1.6	0.18 - 1.1
	Stems	0.015	0.012	0.086	UDL
	Leaves	0.039	UDL	0.13	UDL
Rizhoconcrections	Inner	-		1.12	
	Middle	-		0.71	
	Outer	-		0.87	

UDL= under detection limit

ng g^{-1}, 0.7 and 0.9 respectively (Table 3.7). Roots presented Pt concentrations ranging between 0.18 and 1.6 ng g^{-1} in spring, whose trend is decreasing with depth except for a peak at 15 cm, and between 0.18 and 1.1 ng g^{-1} in summer (Table 3.7, Table 3.8, Table 3.9 and Figure 3.7). Pt concentrations in stems and leaves of *Sarcocornia fruticosa* were lower than the concentrations measured in the roots: concentrations were 0.086 ng g^{-1} for stems and 0.13 ng g^{-1} for leaves in summer, but below the detection limit in summer sampling (Table 3.7).

For other trace elements in sediments the most noticeable feature are the sub-superficial peaks (20-30 cm) observed for Pb, Zn and Cd analysis in both samplings, spring (Figure 3.4) and summer (Figure 3.5). At the same depth a minimum of Fe, Mn and V is detected in spring (Figure 3.5) that did not appear in the summer core, with no clear trends. Mn presented a surface maximum in each season.

3.5 Discussion

3.5.1 Pt in sediments and interstitial waters: sediment/interstitial waters partitioning

Pt concentrations in sediments exhibit, in general, a surface enrichment (Figure 3.3, Figure 3.6 and Figure 3.7), previously described in the area by Cobelo-García *et al.* (2011), especially in

Table 3.8: Raw data of vegetated core (Sarcocornia fruticosa) from Low Traffic Station (Rosario Salt Marsh) in Spring (March 2011).

		Sediment								Roots	Interstitial Water				
	Depth (cm)	Pt (ng g^{-1})	Fe (mg g^{-1})	Mn (µg g^{-1})	V (µg g^{-1})	Cd (µg g^{-1})	Pb (µg g^{-1})	Zn (µg g^{-1})	Al (mg g^{-1})	Pt (ng g^{-1})	Pt (ng L^{-1})	Fe (mg L^{-1})	Mn (mg L^{-1})	RSS$_T$ (µg L^{-1})	Sal.
LTS 00-02	1	2.75	40.6	636	84.9	0.316	156.	242	102	0.896	0.334	0.389	6.300	26.0	25
LST 02-04	3	1.20	48.5	473	103	0.223	158	226	111	0.479	0.234	0.173	1.020	80.7	23
LST 04-06	5	1.02	46.5	322	112	0.157	177	218	107	0.336	0.156	0.125	0.812	52.1	22
LST 06-08	7	0.906	45.7	339	99.4	0.147	193	223	102	0.290	0.173	0.662	1.070	53.9	22
LST 08-10	9	0.684	51.4	355	104	0.184	196	242	107	0.544	0.262	1.560	0.966	55.2	23
LST 10-13	11.5	0.588	53.1	310	108	0.178	261	290	103	0.749	0.169	3.040	1.130	65.9	24
LST 13-16	14.5	1.01	48.7	268	104	0.604	518	327	93.9	1.64	2.524	6.720	1.220	12.5	27.5
LST 16-20	18	0.444	42.2	247	107	1.813	410	385	109	0.180	0.143	5.030	1.200	5.59	32.5
LST 20-25	22.5	0.334	19.5	116	47.8	1.987	247	481	53.9	0.298	-	-	-	-	-
LST 25-30	27.5	0.069	8.32	53.1	23.1	3.192	223	375	29.0	-	-	-	-	-	-
LST 30-35	32.5	0.022	6.86	49.6	19.209	0.978	96.8	411	26.3	-	-	-	-	-	-
LST 35-40	37.5	0.237	13.7	96.1	42.090	0.679	165	393	44.8	-	-	-	-	-	-
LST 40-45	42.5	0.315	16.4	111	52.498	0.342	129	212	54.7	-	-	-	-	-	-
LST 45-50	47.5	0.484	24.6	145	60.955	0.198	49.0	123	61.7	-	-	-	-	-	-
LST 50-55	52.5	0.369	22.8	147	60.175	0.154	45.6	109	62.0	-	-	-	-	-	-
LST 55-60	57.5	0.471	20.3	151	60.324	0.162	45.5	109	63.4	-	-	-	-	-	-
LST 60-65	62.5	0.537	19.9	157	60.148	0.129	37.6	89.3	62.9	-	-	-	-	-	-
LST 65-70	67.5	0.394	19.4	140	49.662	0.081	31.3	60.9	54.3	-	-	-	-	-	-

Table 3.9: Raw data of vegetated core (Sarcocornia fruticosa) from Low Traffic Station (Rosario Salt Marsh) in Summer (September 2011).

		Sediment								Roots	Interstitial Water				
	Depth (cm)	Pt (ng g^{-1})	Fe (mg g^{-1})	Mn (µg g^{-1})	V (µg g^{-1})	Cd (µg g^{-1})	Pb (µg g^{-1})	Zn (µg g^{-1})	Al (mg g^{-1})	Pt (ng g^{-1})	Pt (ng L^{-1})	Fe (mg L^{-1})	Mn (mg L^{-1})	RSS$_T$ (µg L^{-1})	Sal.
LTS overlying	-	-	-	-	-	-	-	-	-	-	0.205	0.122	0.937	-	39
LTS 00-02	1	1.14	44.3	731	94.3	0.306	151	277	108	0.735	0.540	0.581	5.030	76.0	38
LST 02-04	3	1.10	46.6	346	107	0.342	154	270	106	0.528	0.383	0.222	3.120	41.6	41
LST 04-06	5	0.981	47.4	340	83.3	0.489	160	281	112	0.178	0.367	0.058	3.510	16.4	45
LST 06-08	7	0.989	47.3	347	95.8	0.580	198	305	106	0.601	0.450	0.028	3.040	4.66	50
LST 08-10	9	1.10	48.5	307	106	0.357	211	310	108	0.810	0.420	0.015	1.960	UDL	51
LST 10-13	11.5	0.614	47.7	342	82.7	0.340	244	353	105	1.127	0.529	0.026	1.020	UDL	50
LST 13-16	14.5	0.907	47.8	322	85.8	0.190	361	569	107	0.637	0.635	0.026	0.721	UDL	48
LST 16-20	18	0.321	45.0	271	99.6	0.707	441	652	105	0.383	0.482	0.009	1.280	UDL	47
LST 20-25	22.5	0.671	43.7	243	92.6	6.16	614	1083	84.6	-	-	-	-	-	-
LST 25-30	27.5	0.112	15.8	83.4	39.9	4.14	224	1046	39.7	-	-	-	-	-	-
LST 30-35	32.5	0.347	10.6	66.5	32.8	0.595	150	341	30.7	-	-	-	-	-	-
LST 35-40	37.5	0.166	18.3	108	46.6	0.363	105	264	44.2	-	-	-	-	-	-
LST 40-45	42.5	0.287	30.7	174	71.7	0.225	62.0	183	74.8	-	-	-	-	-	-
LST 45-50	47.5	0.314	36.4	226	73.1	0.123	47.5	120	79.2	-	-	-	-	-	-
LST 50-55	52.5	0.296	31.0	174	62.1	0.072	32.6	71.9	65.5	-	-	-	-	-	-
LST 55-60	57.5	0.288	30.9	193	64.6	0.064	26.4	70.9	68.3	-	-	-	-	-	-
LST 60-65	62.5	0.273	27.8	177	57.1	0.049	24.5	65.3	58.7	-	-	-	-	-	-

High Traffic Station. The highest Pt concentration was obtained for the surface layer (40.1 ng g^{-1}) at the unvegetated core (Figure 3.3 summer), which is one order of magnitude higher than typical average continental crust abundance (0.51 ng g^{-1}; Peucker-Ehrenbrink and Jahn 2001). These high concentrations agree with surface enrichments linked with traffic-borne contamination that have been reported before in several locations like big harbors (Tuit et al., 2000), urban lakes (Rauch et al., 2004a), sediments nearby road soils (Schäfer and Puchelt, 1998; Zereini et al., 2001) and collectors of urban runoff and gullypots (Wei and Morrison, 1994; Schäfer and Puchelt, 1998; Fritsche and Meisel, 2004; Whiteley and Murray, 2005; Sutherland et al., 2007). In addition to Pt input by traffic, the presence of high biomass (biomass= 25%, summer, High Traffic Station, Figure 3.6) may favor the retention of contaminants.

However, although some profiles exhibited a slight increase of dissolved Pt with depth (Figure 3.3 spring, Table 3.7 summer), the surface Pt-enrichment in sediments is not reflected in the interstitial waters, suggesting a low reactivity of the anthropogenically emitted Pt, at least on a short-time scale. Concentrations of Pt in porewaters were within a narrow range (0.26-0.66 ng L^{-1} for unvegetated cores; 0.14-0.70 ng L^{-1} for vegetated cores), with the exception of two peaks (1.9 ng L^{-1} at 18 cm for summer and 2.5 ng L^{-1} at 14.5 cm for spring, at High and Low Traffic Station respectively, Figure 3.6 and Figure 3.7) found in the deeper part of the vegetates cores, that could be linked with redox changes that dissolve the solid Pt passing to the interstitial water (Figure 3.6 and Figure 3.7). Actually, the spring Pt peak at Low Traffic Station (Figure 3.7) agreed with Pt peaks in the sediment and in the roots, as well as the Fe reduction peak.

Dissolved Pt in interstitial waters for unvegetated and vegetated cores (from 0.14 to 2.5 ng L^{-1}) is higher than typical oceanic waters (0.02-0.08 ng L^{-1}, Colodner, 1991, Table 3.10). The Pt ratios between interstitial and oceanic waters are 2-125, although highly reactive elements, like Fe and Mn (Caetano et al., 1997; Santos-Echeandía et al., 2010), showed a several-orders difference between interstitial and oceanic waters, even for elements removed by roots (Cd, Zn, Cu). This low ratio may be due to the higher Pt mobility in saline environments, where the ligands that likely favor Pt dissolution are more abundant, specially Cl^- that forms different Pt-complexes (Colombo et al., 2008; Reith et al., 2014), being $PtCl_5(OH)^{2-}$ the assumed dominant species (Cobelo-García et al., 2013). At Low Traffic Station, where samples overtake typical salinity of seawater (35.2, Millero et al. 2008), reaching values of ~50 (Table 3.8 and Table 3.9), there is a clear significant relation between dissolved Pt and salinity (Figure 3.8, first column), not found in High Traffic Station were salinity was lower than 41 (Table 3.5 and Table 3.6).

Table 3.10: Values of trace elements concentration in pore water from previous studies in Low Traffic Station for unvegetated (Caetano et al. 1997, this study) and vegetated sediments under *Sarcocornia fruticosa* (Santos-Echeandía et al. 2010, this study), and typical oceanic waters values (Colodner, 1991; Bruland and Lohan, 2006).

element	interstitial water unvegetated (ng L^{-1})	interstitial water vegetated (ng L^{-1})	oceanic water (ng L^{-1})
Fe	140000 - 330000	9500 - 3600000	1.1 - 120
		9000 - 6700000*	
Mn	560000 - 13000000	320000 - 770000	3.3 - 290
		720000 - 6300000*	
Zn	-	78000 - 920000	3.3 - 620
Cu	-	1700 - 11000	34 - 300
Pb	-	6000 - 56000	1.0 - 33
Cd	-	30 - 6500	0.11 - 120
Pt	0.26 - 0.66*	0.14 - 2.5*	0.02 - 0.08

*data from this study

Figure 3.8 represents partition coefficients K_d (K_d= *[Pt]sediment/[Pt]porewater,* L Kg^{-1}), where *[Pt]sediment* is expressed in ng Kg^{-1} and *[Pt]porewater* in ng L^{-1}, against different parameters analyzed in porewater that have shown significant relationships with ($p< 0.01$), like salinity, and dissolved Mn. At High Traffic Station (upper panel, Figure 3.8) dissolved Mn shows an inverse relationship with K_d, and, as a result, direct relationship with dissolved Pt in interstitial waters. Some previous studies pointed to the possible co-precipitation, adsorption or sequestration of Pt simultaneously to the formation of Fe-Mn oxides and oxyhydroxides in ferromanganese nodules and crusts at the seafloor (Halbach et al., 1989; Koschinsky and Hein, 2003; Hein and Koschinsky, 2014) but also in sedimentary environments (Colodner et al., 1992; Wei and Morrison, 1994; Cobelo-García et al., 2011). Actually, the Pt-enrichment of ferromanganese crust and nodules has been reported in many studies (Halbach et al., 1989; Hein et al., 2000; Koschinsky and Hein, 2003; Asavin et al., 2009; Cabral et al., 2009; Hein and Koschinsky, 2014; Reith et al., 2014), especially those rich in Mn (Cabral et al., 2009; Reith et al., 2014), becoming Fe-Mn crusts to be considered as potential Pt ores, (average Pt concentration reaches 1-3 µg g^{-1}, Halbach et al. 1989; Hein et al. 2000; Asavin et al. 2009), and a potential significant source of Pt to the environment when they dissolve (Hein et al., 2000). Although the formation mechanism is still not well constrained, Halbach *et al.* (1989) formulated a chemical reaction that could explain this co-precipitation by the use of $PtCl_4^{2-}$ as the predominant Pt specie in seawater. Since posterior studies have concluded that the typical Pt species in seawater is $PtCl_5(OH)^{2-}$ (Cobelo-García et al., 2013), we have modified the equating to explain the Pt-Mn coprecipitation (Eq. 3.3):

$$3Mn^{2+} + [PtCl_5(OH)]^{2-} + 5H_2O \leftrightarrow Pt + 3MnO_2 + 5Cl^- + 11H^+ \qquad \text{[Eq 3.3]}$$

Thus, the anoxic environments with Eh> 100 mV described at High Traffic Station define the optimal conditions to require Mn^{4+} to oxidize organic matter (Hong et al., 1995) –Mn reduction peaks were shown in dissolved Mn profiles (Figure 3.3 and Figure 3.6), except for spring vegetated core–, favoring the Pt-enrichment in interstitial (and saline) waters.

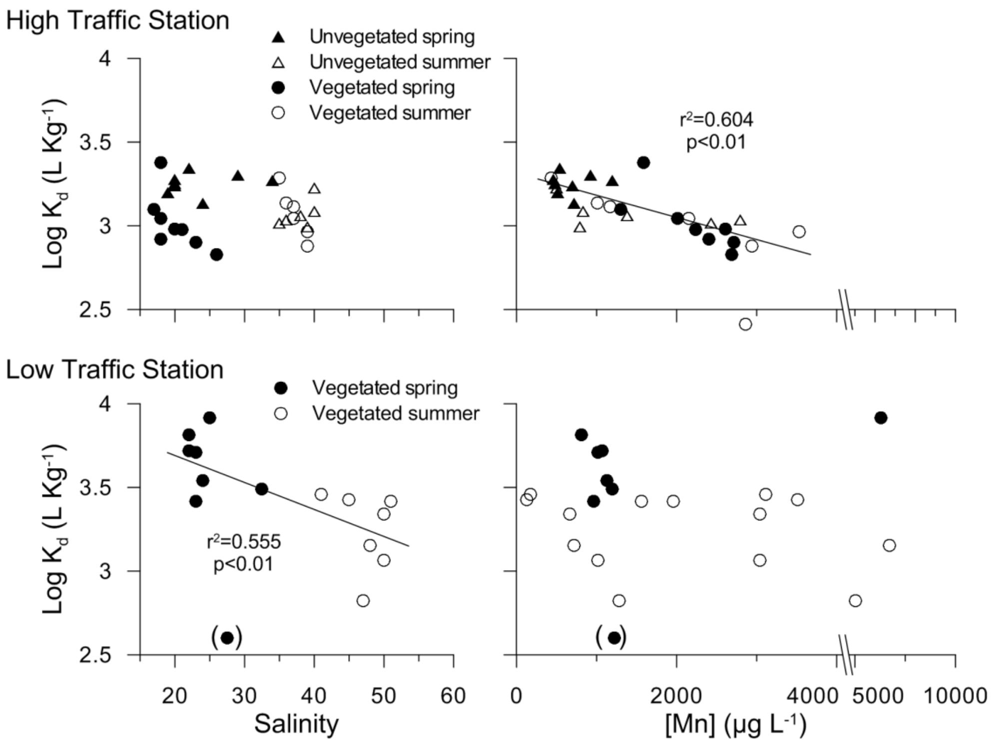


Figure 3.8: Correlation between the Pt solid-water partition coefficient (Kd) with Salinity and Mn, in interstitial waters at High Traffic Station (upper panel) and Low Traffic Station (lower panel): triangles= unvegetated, dot= vegetated, black= spring, white= summer. Data corresponding to Pt peaks (surface peaks in sediments and deeper peaks in interstitial waters) are not used for the correlations.

3.5.2 Pt in the belowground biomass: roots/sediment and roots/interstitial waters partitioning

The presence of vegetation (e.g. *Sarcocornia fruticosa*) may condition the behavior of Pt strengthening the role of salt marshes as efficient sinks for nutrients (Caetano et al., 2011). Some of these plants present the ability to concentrate anthropogenically-born elements in their belowground biomass (Caetano et al., 2008), exceeding the sediment levels (Figure 3.9), becoming roots essential for the biogeochemistry of the surrounding sediments (Sundby et al., 2003, 2005; Caetano et al., 2008).

Distribution of Pt concentration in the roots of High Traffic Station (Figure 3.6) and Low Traffic station (Figure 3.7) show similar trend with sediments, that are more concentrated in Pt, except for the deepest samples from spring (High Traffic Station, Figure 3.6 upper panel). The enrichment factor of Pt concentration in roots of *Sarcocornia fruticosa* respect to the sediments (enrichment factor= $[Pt]_{roots}/[Pt]_{sediment}$, Caetano et al. 2008) is 1.0±0.7 (*n=26*) and 0.7±0.5 (*n=17*) at High and Low Traffic Stations, respectively, with an overall mean of 0.9 ± 0.6 (*n=43*, Figure 3.9) Thus, there is no Pt-enrichment in roots of *Sarcocornia fruticosa*, whose enrichment

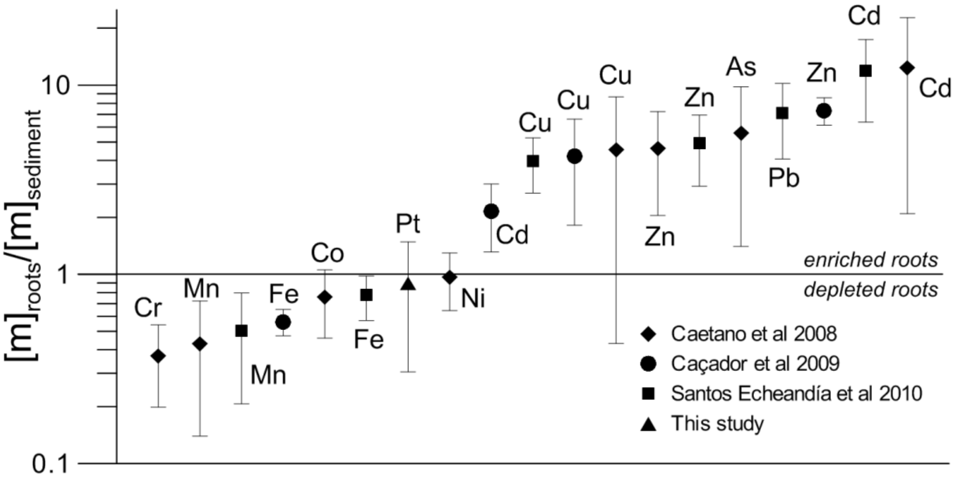


Figure 3.9: Enrichment factor in the concentration of some elements in roots of *Sarcocornia fruticosa* respect of their concentration in sediments ($[m]_{roots}/[m]_{sediment}$). Data have been taken from Caetano et al. 2008 (diamonds), Caçador et al. 2009 (dots), Santos-Echeandía et al. 2010 (squares) and this study (triangles). Values bellow the horizontal line indicate a depletion in roots and values above the horizontal line indicate an enrichment.

factor is relatively constant with respect to sampling areas or seasons. Also, roots of *Sarcocornia fruticosa* are depleted –respect to the sediment– in some elements like Cr, Mn, Co, Fe, Pt or Ni; but enriched in others like Cu, Zn, As, Pb or Cd (Caetano et al. 2008; Caçador et al. 2009; Santos-Echeandía et al. 2010, Figure 3.9). Besides, enrichment factors show very similar values for Fe and Pt (Figure 3.9).

However, the Pt peak in spring roots at 14 cm (Low Traffic Station, Figure 3.7 upper panel), that reaches 1.6 ng g^{-1}, is coincident with the Pt peak in interstitial water. Therefore, since roots are absorbing the surrounding porewater, the chemical perturbations that this water undergoes will be reflected in the uptake by roots, and accordingly, significant relationships between Pt in roots and interstitial waters ($p < 0.05$) have been found (Figure 3.10). However, dissolved Pt at Low Traffic Station appears to be more bioavailable than at High Traffic Station (for the same Pt concentrations in porewater, Pt in roots is higher in Low Traffic Station, Figure 3.10), suggesting that different Pt-species exist in each station, reflecting different oxygen saturation, salinity, pH, Eh and/or dissolved elements.

Previous several studies have tried to shed light to the Pt uptake by plants, the primary producers and, hence, the first step to be integrated into the food chain. Analysis in grass and weeds that grow nearby the roads showed values up to 300 times more concentrated that our roots (Hees et al., 1998; Helmers and Mergel, 1998; Schäfer et al., 1998; Djingova et al., 2003). However, most of them concluded that Pt-enrichment of the plants, as an uptake indicator, is

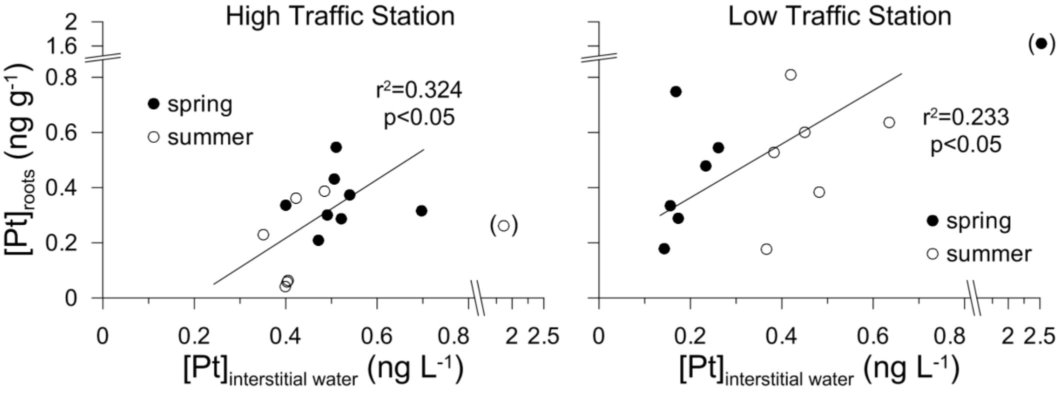


Figure 3.10: Correlation between dissolved Pt in interstitial water and concentrations in roots for High Traffic Station (left) and Low Traffic Station (right) in spring (black) and summer (white). Datapoints in brackets (peaks is porewater) are outliers not used for correlation calculations.

low and classified Pt as an immobile element, even though greenhouse experiments with high concentrations of Pt in the sediments had been performed (Hoppstock et al., 1989; Lustig et al., 1997; Schäfer et al., 1998; Orecchio and Amorello, 2010). Studies in seaweeds showed a higher bioaccumulation (e.g. *Ulva lactuca,* Cosden et al. 2003) due to the different Pt speciation when salinity increases, what agrees with the more bioavailable Pt form in Low Traffic Station (Figure 3.10), where salinity is always higher than in High Traffic Station (Figure 3.8 and Table 3.5, Table 3.6, Table 3.8 and Table 3.9). Some investigations have been done in typical aquatic organism, some of them, bioindicators of contamination. Despite *Asellus aquaticus*, a freshwater isopod, presented high concentrations of Pt in urban rivers (Zimmermann et al., 2002; Haus et al., 2007), after some hours of depuration levels decreased near no-contaminated samples, indicating no bioaccumulation (Rauch and Morrison, 1999; Moldovan et al., 2001). This removal of Pt can be compared to the Pt behavior in *Sarcocornia fruticosa* roots, that are able to reflect the Pt concentration for surrounding interstitial waters in each moment, being the Pt-enrichment a reversible state (no trace of the Pt-rich peak in spring cores has been found in summer one, Low Traffic Station, Figure 3.7).

3.5.3 Pt translocation in Sarcocornia Fruticosa tissues

Pt concentration in roots (0.9±0.6 ng g^{-1}, *n= 43,* using all the data, Table 3.11) is always higher than in stems and leaves (no significant differences between leaves and stems, Table 3.11) –in some cases 30 times higher– indicating that plants do not transport Pt efficiently through its tissues (Table 3.11). This low Pt translocation to the aerial parts of plants has been documented before in other species (Ravindra et al., 2004).

Salt marshes vegetation exhibit this behavior for other elements (Fitzgerald et al., 2003; Weis and Weis, 2004; Caçador et al., 2009; González-Alcaraz et al., 2011), probably due to their low solubility in the conditions of salt marshes (Sundby et al., 2005; Duarte et al., 2010;). In fact, previous studies in below and aboveground parts of *Sarcocornia fruticosa* found also this low translocation for other elements (Table 3.11, Caetano et al. 2008 and Caçador et al. 2009): all the elements exhibit a higher concentration in roots that in the other tissues (2-4 orders of magnitude), especially Fe, Ni, Cu, Zn, As or Cd. Therefore, the active part in biogeochemical cycle of these elements, as well as of Pt, happens in the belowground part (Duarte et al., 2010).

Nonetheless, although concentrations in roots are always higher than in aerial parts of *Sarcocornia fruticosa*, the concentration of some elements (e.g. Cu, Zn, Co or Cd) in the

Table 3.11: Values of several elements in the belowground and aboveground tissues of *Sarcocornia* fruticosa from bibliography (Caetano et al., 2008; Caçador et al., 2009) and this study. Values from Caetano et al. 2008 are averaged between the highest and the lowest concentrations given in this manuscript.

	Belowground tissues	Aboveground tissues		
element	Roots (μg g^{-1})	Stems (μg g^{-1})	Leaves (μg g^{-1})	Average(μg g^{-1})
Fe	3800000	-	-	9000
Mn	110	-	-	27
Zn	5600	-	-	45
	990 ± 560	28 ± 22	24 ± 18	26 ± 19
Cr	21	-	-	1.1
Ni	28	-	-	0.53
Cu	250	-	-	3.1
	290 ± 50	6.5 ± 2.2	5.9 ± 1.9	6.2 ± 2.0
As	650	-	-	0.79
Cd	23	-	-	0.021
	7.0 ± 2.8	0.31 ± 0.13	0.21 ± 0.14	0.26 ± 0.14
Co	16 ± 3	8.3 ± 3.2	6.6 ± 2.7	7.4 ± 2.9
Pt	0.9 ± 0.6* (1)	0.029 ± 0.039*	0.043 ± 0.061*	0.036 ± 0.048*
	(n=43)	*(n=4)*	*(n=4)*	*(n=8)*

* data in ng g^{-1}; (1) average concentration without considering adsorption data: 0.6 ± 0.4 (n=33)

aboveground biomass is not negligible (Caetano et al., 2008). The detritus that come from the aerial tissues, strongly variable with the seasons, could be an important source of contaminants before being buried, especially because these organic rests can be easily transported by wind and runoff to other parts (Caçador et al., 2009). However, the cycle of Pt is unaffected by this issue, due to small amount of Pt in the aerial parts.

3.6 Conclusions

The role of vegetation is primordial in the sedimentary behavior of Pt in salt marshes, because roots of halophytic plants control the geochemistry in the surrounding sediments (redox conditions, presence of O_2, organic matter degradation) that determine the chemical species in solid and dissolved phases.

A clear relationship between dissolved Pt and Mn has been found in the interstitial waters of salt marshes, similar to the Pt-Mn relation found in Fe-Mn crusts and nodules, that pinpoints to a co-precipitation/adsorbing/scavenging processes in the Mn-oxides formation.

The Pt concentration in roots, that reflects the Pt concentration in interstitial waters at every moment, and the low translocation of Pt to the aerial tissues, indicate the lack of a real Pt-bioaccumulation and the Pt incorporation to the food chain.

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Chapter 4

Osmium and platinum decoupling in the environment: evidences in intertidal sediments (Tagus Estuary, SW Europe)

Based on the work submitted to *Environmental Science and Technology*

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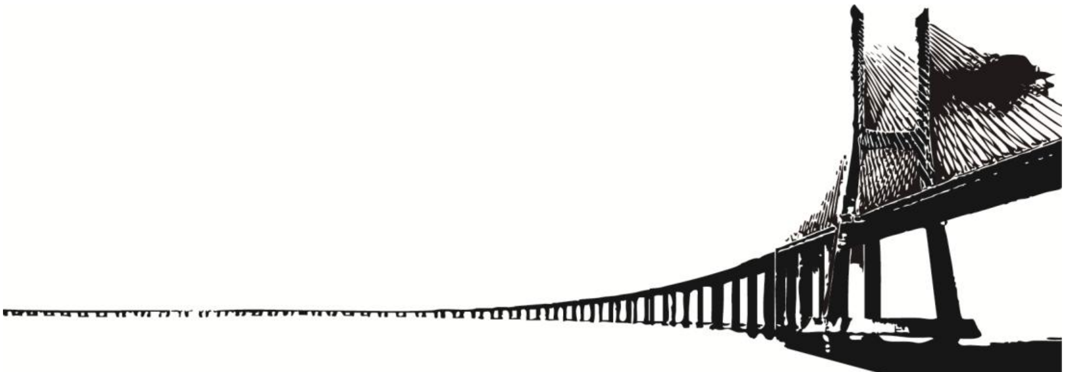


Osmium and platinum decoupling in the environment: evidences in intertidal sediments (Tagus Estuary, SW Europe)

Abstract

The use of catalytic converters in automobiles has significantly increased the release of platinum group elements to the environment. It has been invoked that common sources and similar geochemical behavior control the environmental distribution of these elements. In order to check this hypothesis intertidal salt marsh sediment cores were sampled in two sites of the Tagus Estuary (SW Europe) affected by different traffic pressure. Platinum and Os concentrations and $^{187}Os/^{188}Os$ isotopic ratios were determined in sediments and interstitial waters. Concentration of Pt in surface sediments nearby the high traffic zone (up to 40 ng·g^{-1}) indicated severe contamination. However, surface sediments did not show Os enrichment and $^{187}Os/^{188}Os$ ratios, ranging from 0.908 to 1.178, pointed to the existence of other sources besides vehicles. Concentrations of dissolved Pt and Os in interstitial waters, 0.1-0.7 ng L^{-1} for Pt and 0.03-0.10 ng L^{-1} for Os, were higher than typical values for uncontaminated waters. Based on the obtained results two sources of Pt and Os into the Tagus Estuary salt marshes were identified: a regional input linked with industrial activities affected by fossil oils combustions and regional traffic, and a local source associated with the nearby traffic density. Estimations of Os and Pt released by catalytic converters support this two-source model. Besides the different

sources, ability of dispersion (Pt is released as particles and Os as gaseous OsO_4) and different dissolution/mobility processes reinforce the decoupled behavior between Pt and Os; these findings question the use of Os isotopes as a proxy of platinum group elements sources to the environment.

4.1 Introduction

Platinum group elements (PGEs: ruthenium, rhodium, palladium, osmium, iridium and platinum) are amongst the least abundant elements in the upper continental crust, where their typical concentrations range from 0.02 ng g^{-1} (Ir) to 0.5 ng g^{-1} (Pt, Pd) (Peucker-Ehrenbrink and Jahn, 2001). 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 (Naldrett et al., 2008) and Noril'sk (Malitch and Latypov, 2011). The use of PGEs in several human activities is increasing their environmental concentrations (Rauch and Morrison, 2008; Sen et al., 2013); accordingly, it has been estimated that 86-98% of PGE total flux at Earth's surface derives from anthropogenic activities (Sen and Peucker-Ehrenbrink, 2012). One of the main application of PGEs (especially Pt, Pd and Rh) is due to their use in automobile catalytic converters, to reduce the emissions of CO, NO_x and hydrocarbons (Farrauto and Heck, 1999). This industrial application has been greatly responsible for an exponential increase of the PGE demand over the past 40 years (Johnson Matthey, 2013). A catalytic converter emits during its lifetime microparticles of 1 - 63 μm (Artelt et al., 1999) covered by tiny fragments <0.3 μm (Prichard and Fisher, 2012), down to the nanoparticle size, of Pt, Pd, and Rh –active components in catalytic converters (Palacios et al., 2000)–, and include smaller amounts of Os, Ir, and Ru –as impurities (Fritsche and Meisel, 2004)–. As a result, elevated PGE concentrations are generally found in areas close to high traffic density within ~2 m near the road (Tuit et al., 2000; Whiteley and Murray, 2005; Sutherland et al., 2007; Cobelo-García et al., 2011). Evidence for a global scale PGE contamination has also been observed in ice from Greenland and Antarctica (Barbante et al., 2001; Soyol-Erdene et al., 2011).

Several studies have characterized the anthropogenic contribution of PGEs in the environment using the Os isotope signature $^{187}Os/^{188}Os$ (Esser and Turekian, 1993; Ravizza and Bothner, 1996; Rauch et al., 2004a, 2004b, 2005, 2010) taking advantage of the $^{187}Os/^{188}Os$ ratio as a tracer of a variety of anthropogenic and natural sources (Esser and Turekian, 1993; Peucker-

Ehrenbrink and Jahn, 2001; Rauch et al., 2010, 2006; Sharma, 2011). For example, the typical $^{187}Os/^{188}Os$ ratios of the PGE ores associated with mantle-derived rocks, like the Bushveld complex (Naldrett et al., 2008), are 0.10-0.20 (Schoenberg et al., 1999) while ratios from the upper continental crust are 1.05±0.23 (Peucker-Ehrenbrink and Jahn, 2001), allowing the estimation of the Os anthropogenic fraction in environmental samples (Rauch et al., 2004b, 2006, 2010; Sharma, 2011). Assuming that Os and other PGEs derive from the same anthropogenic sources, the Os isotopic composition has been used to estimate the anthropogenic fraction of Pt, Pd, and Rh, mainly in urban environments (Esser and Turekian, 1993; Ravizza and Bothner, 1996; Rauch et al., 2004a, 2005). It has been argued, however, that the anthropogenic Os source(s) to the environment may be decoupled with the sources that affect to other PGEs. Therefore, the of Pt, Pd, and Rh estimation of anthropogenic contribution may not be based on Os isotope signature (Sharma, 2011).

In order to shed light on the contamination sources and geochemical behavior of PGEs in the environment, we studied salt marsh sediments under different degrees of traffic influence (Cobelo-García et al., 2011), (Tagus Estuary, SW Europe). This area has been characterized for the behavior of other trace elements (Caetano et al., 2008; Santos-Echeandía et al., 2010, Caetano et al., 2008). The main aims of this research are: (1) to better understand the geochemical behavior of PGEs and Os in salt marshes; (2) quantify the anthropogenic source of Pt and Os in sediments and interstitial waters in salt marshes affected by different traffic impact; and (3) assess the coupling/decoupling processes in the Pt and Os anthropogenic sources and geochemical behavior.

4.2 Material and methods

4.2.1 Study area

The Tagus Estuary in Lisbon, Portugal (SW Europe; Figure 4.1) is one of the largest estuaries in Europe, with an extension of 320 km^2 and a volume of 1900 Hm^3. 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 under significant human pressure with around 3 million inhabitants in the area (Valentim et al., 2013).

Cores were collected from two stations in the intertidal salt marshes at the southern bank of

Tagus Estuary, with different traffic pressure (Figure 4.1). High Traffic Station –*Samouco* salt marsh (Figure 4.1A)– 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 (Instituto de Intraestructuras Rodoviárias IP (Portugal), 2013). Past anthropogenic activities in the area were negligible. Low Traffic Station –*Rosario* salt marsh (Figure 4.1B)– had important human activities in the past; the Barreiro Chemical Complex, the first heavy industry in the Tagus Estuary, was established nearby the Low Traffic Station around 1900 and its contaminating effects in this area have been previously reported (Caetano et al., 2007; Mil-Homens et al., 2013). The most intense activity in this complex was from 1940's to 1970's, while in the 1980's the introduction of waste treatment and a more efficient industrialization resulted in a reduction of pollution on the surrounding environment (Mil-Homens et al., 2013). In the last period a pyrite roasting plant operated in the complex (until 1980, Mil-Homens et al., 2013), that tried to implement an industrial method to extract Pt, Au and Ag from pyrite but the industrial processes gave no results. Thus in the last three decades no activity related with pyrite roasting operated in the chemical complex of the Tagus estuary. Furthermore, the traffic pressure nearby this local area is very low.

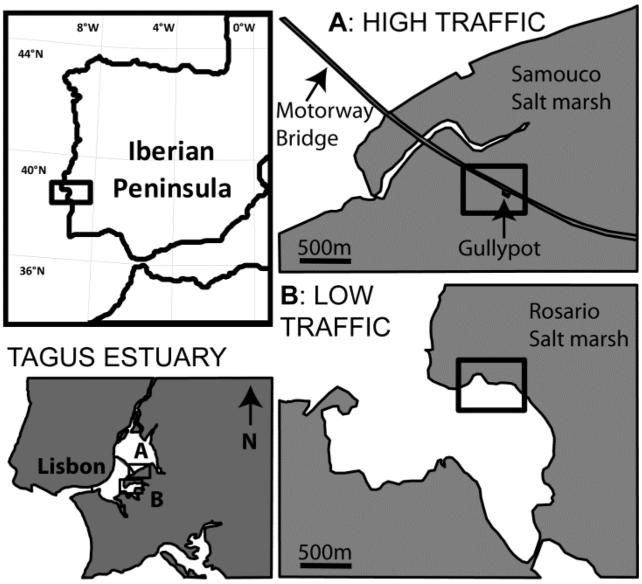


Figure 4.1: Map of study area location in the south bank of the Tagus Estuary (A: High Traffic Station, B: Low Traffic Station).

4.2.2 Sampling

Several 20 cm long cores were sampled in the intertidal area of both salt marshes in March 2011 (Low Traffic Station) and September 2011 (High Traffic Station). Porewater and sediment were collected every 2 cm in the first 10 cm and every 3 cm between 10 and 20 cm depth. Each core was sampled *in situ* and stored in acid-clean high-density polyethylene bottles avoiding the air presence inside to minimize sediment oxidation. Bridge-gullypot sediment was also sampled at the High Traffic Station (Figure 4.1). Interstitial waters were extracted by centrifugation at 8000 rpm for 30 minutes at +4°C, filtered through 0.45 µm polycarbonate membranes, stored in acid-clean low-density polyethylene bottles and acidified using Suprapur©(Merck) HCl (pH ~1). A refractometer (Atago S/Millα 0-100‰) was used to measure salinity in porewater. Sediment samples were oven-dried (<60 °C) until constant weight and ground in an agate mortar. All materials were acid-cleaned prior to use and samples were manipulated inside laminar flow hoods. Procedural blanks were prepared using Milli-Q© (Millipore) water.

Table 4.1: Blanks, detection limits (3xSD) and reference materials for the study: BCR-723 road dust reference material (Institute of Reference Materials and Measurements, 2013), PACS-2 marine sediment reference material (National Researcher council Canada, 2013). (mean ± SD; n= number of replicates)

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 ± 0.00011
DL	13	0.21	-	0.00025
BCR-723 (road dust)	81500 ± 6300 (*n=7*)	457(1)	0.53(1)	-
		635(2)	0.43(2)	-
	(cert. 81300 ± 2500)	(cert. 460 ± 20)*		
PACS-2 (sediment)	-	-	-	6.78 ± 0.75 (*n=4*) (cert. 6.63 ± 0.32)

Sediment blanks for typical sediment mass of 200 and 500 mg for Pt and Os respectively.

*No certified value of Os in IRMM, value from Meisel et al. (2003).

(1)replicate 1 and (2)replicate 2 of BCR-723 reference material (road dust).

Porewater sample	Pt (pg L^{-1})	Os (pg L^{-1})	^{187}Os/^{188}Os	
Blank	3 ± 3 (*n=13*)	1.3 ± 0.6 (*n*=2)	0.368 ± 0.044(*n=2*)	-
DL (porewater)	10	1.8	-	-

Interstitial water blanks for 2 and 40 mL of sample for Pt and Os respectively.

4.2.3 Analytical methods

Platinum was determined in sediments and interstitial waters by means of catalytic adsorptive cathodic stripping voltammetry (catalytic AdCSV) (van den Berg and Jacinto, 1988; Cobelo-García et al., 2011, 2013). For interstitial waters (Figure 4.2), and in order to remove organic matter that may severely interfere during the voltammetric determination of Pt, diluted (1:11) samples were UV-digested for 4 h as described earlier by Cobelo-García et al. (2013) in the presence of 22 mM H_2O_2 (TraceSelect© Ultra, Fluka). For interstitial waters, we obtained blanks of 3±3 pg L^{-1} ($\bar{x} \pm SD$; *n=13*) and detection limit ($3 \times SD_{blank}$) of 10 pg L^{-1} (Table 4.1).

For sediments (Figure 4.2), the removal of organic matter was achieved by ashing the sediments (around 200 mg) at 800 °C in quartz crucibles (Cobelo-García et al., 2011). 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. The detection limit ($3 \times SD_{blank}$) for a typical mass of 200 mg of sediment was 13 pg g^{-1} (Table 4.1); average blank value is 24±4 pg g^{-1} (n=10). The accuracy was checked using road dust certified reference material BCR-723 (Institute of Reference Materials and Measurements, 2013) and good agreement was obtained with the certified concentrations (yield for Pt of 100%, Table 4.1).

Osmium concentration and isotopic composition in sediments and interstitial water were quantified with negative thermal ionization mass spectrometry (N-TIMS). For interstitial waters the procedure described by Chen and Sharma (2009) was followed (Figure 4.3). About 30-50 mL of ^{190}Os spiked sample were frozen into quartz carious tubes at –20 °C. After at least 48 h, 500 µL of Jones Reagent (dissolution of $Cr^{VI}O_3$ in H_2SO_4 6 M, distilled ACS grade Fisher Scientific) were added, the tubes closed carefully and placed into a High Pressure Asher for the oxidation-equilibration reaction under 128 bars and 300 °C during 16 h. In this step all the Os will be as OsO_4 (sample freezing avoids reaction starts before being under the ideal conditions of pressure and temperature). Osmium extraction was carried out by double-distillation: Os is

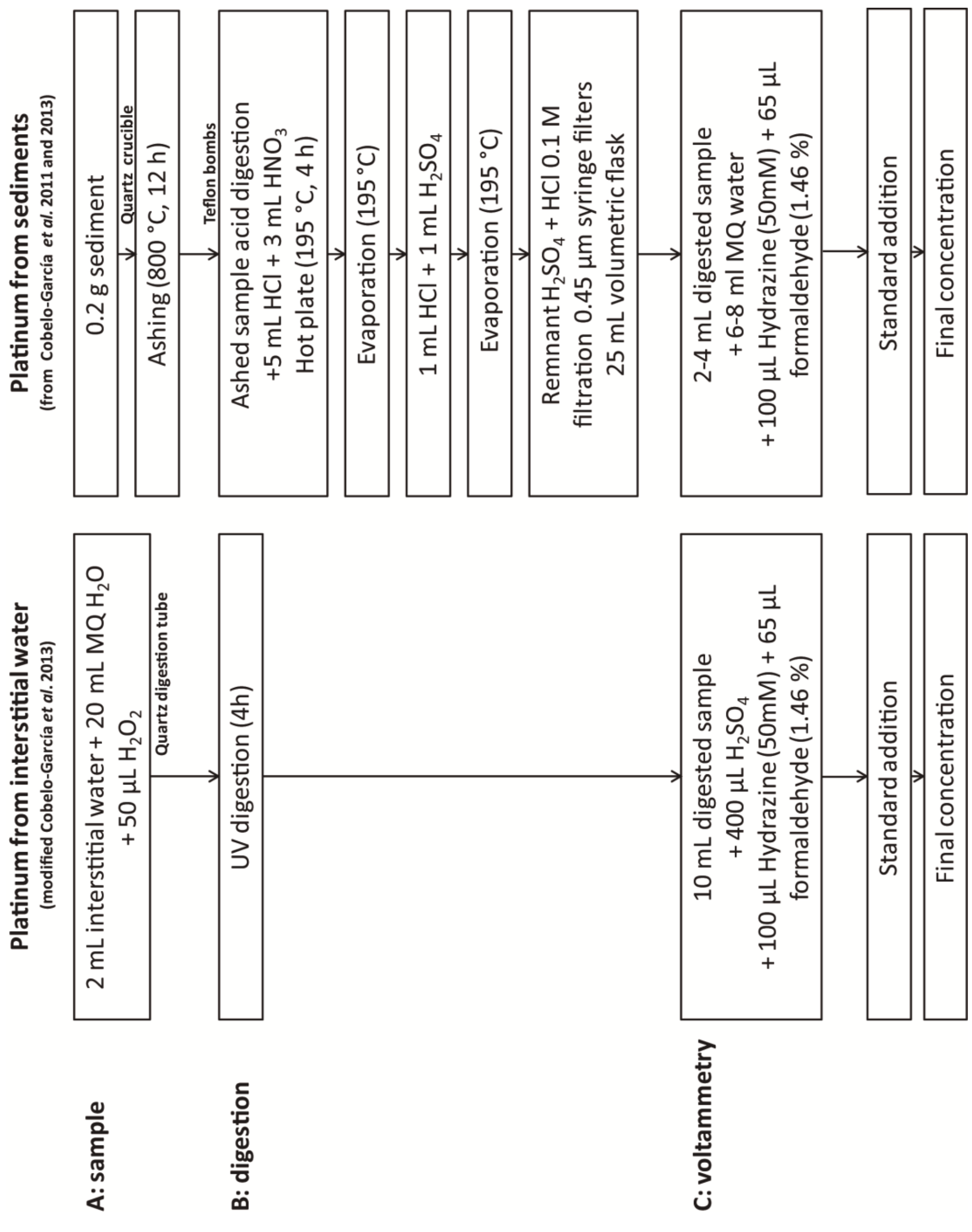


Figure 4.2: Detailed process of Pt analysis in interstitial waters and sediments (Cobelo-García et al., 2011, 2013).

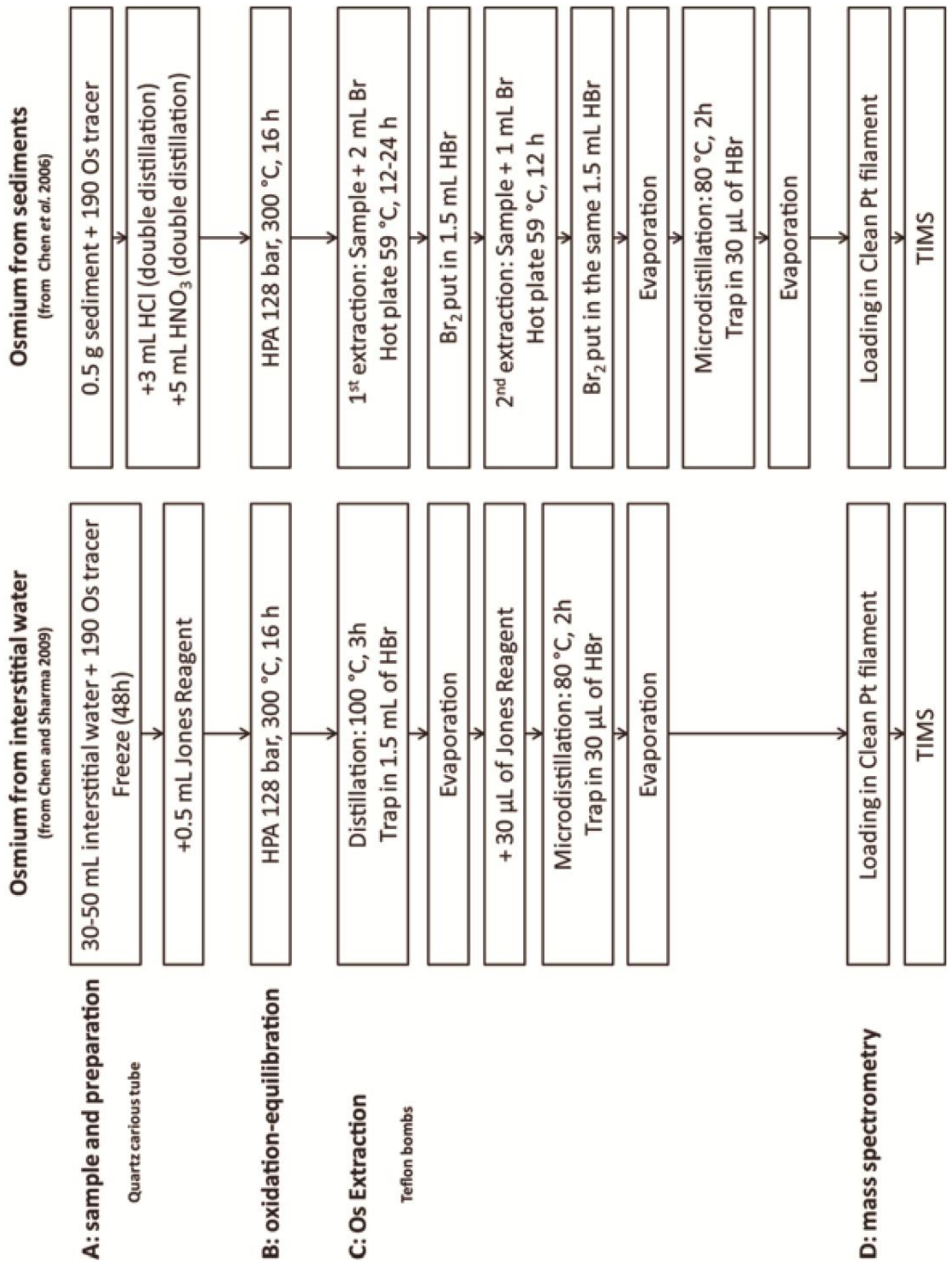


Figure 4.3: Detailed process of Os concentration and isotopic composition analysis in interstitial waters (Chen and Sharma, 2009) and sediments (Chen et al., 2006).

trapped in 1.5 mL of cold HBr (double distilled, Seastar) at 100 °C during 3 h and, after drying, 30 µL of Jones Reagent was added and microdistillated at 80 °C into a 5 mL conical-interior Teflon® vial (Savillex) during 2 h, trapping Os in 30 µL of HBr. The sample is loaded on Pt-filament (HF and HBr preclean) to run the mass spectrometry; some $Ba(OH)_2$ is added to provide a better ion emission. Procedural blanks (using Milli-Q water), of 1.3±0.6 pg L^{-1} ($\overline{x} \pm SD$; *n*=2) for Os concentration and 0.368±0.044 for $^{187}Os/^{188}Os$ were obtained and detection limit ($3 \times SD_{blank}$) was 1.8 pg L^{-1} (Table 4.1). For sediments (Figure 4.3), following the method described by Chen et al. (2006), 0.5 g of ^{190}Os spiked dry samples were acid digested (chilled 3 mL HCl and 5 mL HNO_3, double distilled Fisher) into a High Pressure Asher (300 °C, 128 bars, 16 h) to transform all the Os to OsO_4. Double-extraction of Os by liquid bromine was carried out: the sample with 2 mL of liquid bromine is located on a hot plate (59 °C, 12 h); bromine is transferred to 1.5 mL HBr (doubled distilled, Seastar) to extract Os; the same process is performed for the second extraction using 1 mL liquid bromine. Around 65% of the Os is recovered by this procedure (Chen et al., 2006). After this Os extraction the analytical process is the same used for interstitial samples: a microdistillation in conic vials to purify and sample-loading on the filament to be analyzed (more information in Figure 4.3). Blank for a typical mass of 500 mg shows values of 0.19±0.07 pg g^{-1} (*n*=2) with a detection limit of 0.21 pg g^{-1} and 0.288±0.003 (*n*=2) for $^{187}Os/^{188}Os$ ratios (Table 4.1). All the materials were HCl, HNO_3 and HBr pre-cleaned before their use. Table 4.1 provides some values of Os concentration and $^{187}Os/^{188}Os$ ratios for road dust reference materials (Institute of Reference Materials and Measurements, 2013) and compares our values with other authors´ results (Meisel et al., 2003) 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 (Lamble and Hill, 1998). Table 4.1 gives information about blanks, detection limit and reference materials for Al analysis (National Researcher council Canada, 2013).

4.2.4 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 4.2) were calculated using the following equation:

$$EF_{Pt\ or\ Os} = \frac{([Pt\ or\ Os]/[Al])_{sample}}{([Pt\ or\ Os]/[Al])_{local\ background}} \qquad \text{[Eq. 4.1]}$$

The anthropogenic fraction of Pt (AFPt, %) was calculated normalizing by Pt/Al instead of using Pt/Os ratios (Rauch et al., 2006) to avoid the influence of coupled/decoupled behavior of Os and Pt by means of:

$$AF_{Pt}(\%) = \left(1 - \frac{([Pt]/[Al])_{local\,background}}{([Pt]/[Al])_{sample}}\right) x100 = \left(1 - \frac{1}{EF_{Pt}}\right) x100 \qquad \text{[Eq. 4.2]}$$

The equation proposed by Rauch *et al*. (2004b, 2006) were used to calculate the anthropogenic fraction of Os (EF_{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 (Peucker-Ehrenbrink and Jahn, 2001) (Table 4.2).

$$AF_{Os}\,(\%) = \frac{\left(\frac{^{187}Os}{^{188}Os}\right)_{local\,background} - \left(\frac{^{187}Os}{^{188}Os}\right)_{sample}}{\left(\frac{^{187}Os}{^{188}Os}\right)_{local\,background} - \left(\frac{^{187}Os}{^{188}Os}\right)_{anthropogenic}} \times 100 \qquad \text{[Eq. 4.3]}$$

Natural and anthropogenic concentrations of Os and Pt are calculated applying this AF (%) to the total concentrations (Rauch et al., 2006).

4.3. Results

4.3.1 Concentrations of Pt and Os in sediments

Platinum concentrations in sediments cores from both stations showed a surface peak, being the value at High Traffic Station (40100 pg g^{-1}) much higher than at Low Traffic Station (2750 pg g^{-1}; Figure 4.4, Table 4.2, for the complete dataset see Table 4.3). Concentrations decreased with depth, reaching similar average background values below 5 cm (Figure 4.4, Table 4.2): 670±89 pg g^{-1} (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 4.4, Table 4.2): 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 background layers (>5 cm depth) were 36±6.8 (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 (Wei and Morrison, 1994), contained 157000 pg g^{-1} of Pt and 114 pg g^{-1} of Os (Table 4.2).

Table 4.2: 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 (McLennan, 2001; Peucker-Ehrenbrink and Jahn, 2001), range of oceanic waters (Bruland and Lohan, 2006) and water from North Atlantic (Chen et al., 2009; Chen and Sharma, 2009; Cobelo-García et al., 2013).Anthropogenic fractions for Os (AF_{Os}) are calculated by Rauch et al. (2004b, 2006) 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 et al., 2004b, 2006) 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

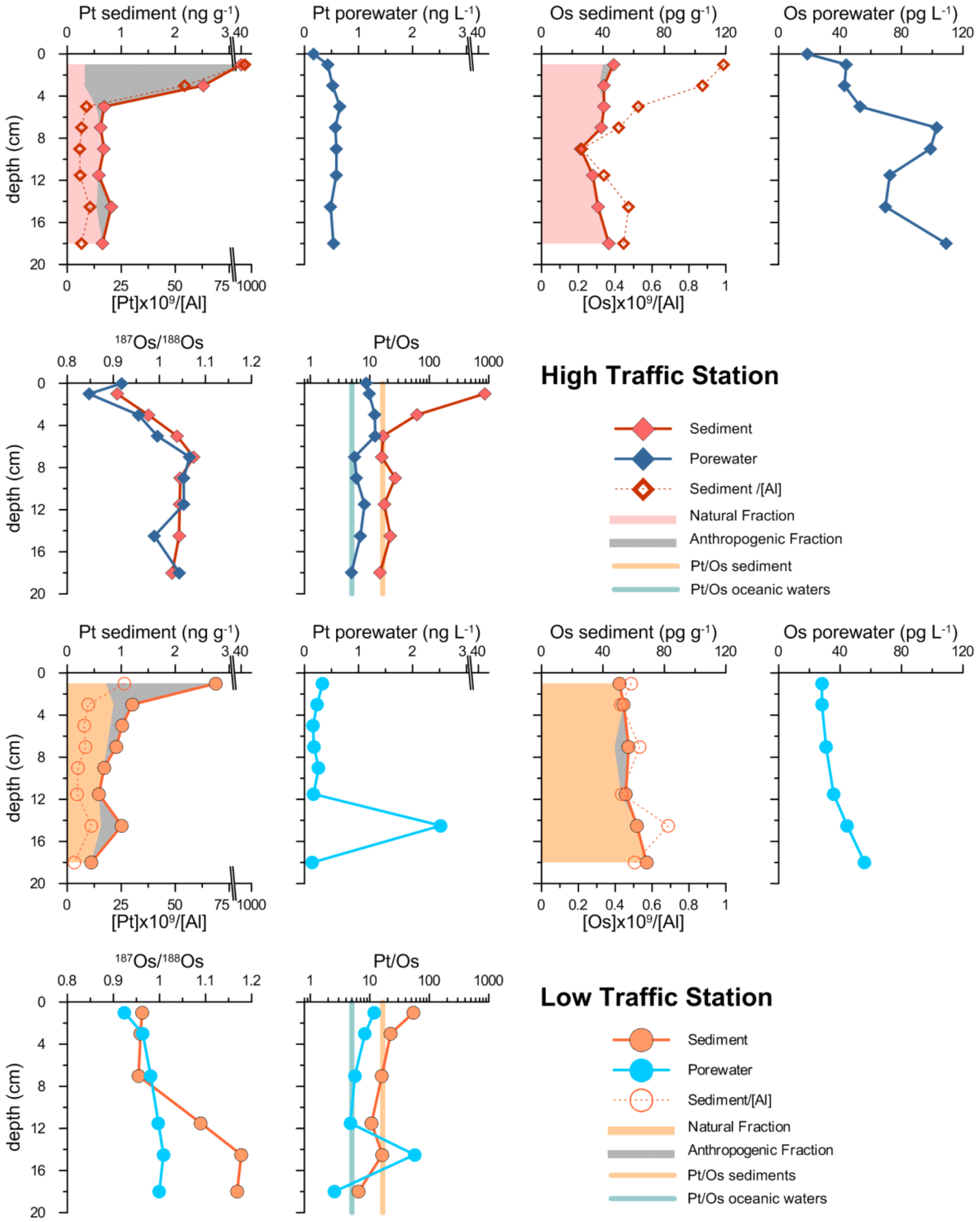


Figure 4.4: Pt concentration in sediment (ng g^{-1}) and porewater (ng L^{-1}) –normalized by Al in dashed lines–, Os concentration in sediment (pg g^{-1}) and porewater (pg L^{-1}), ^{187}Os/^{188}Os and Pt/Os ratios. Natural (coloured area) and anthropogenic (grey area) fractions for Pt and Os in sediments are shown in the total concentration. Mean Pt/Os ratios in oceanic waters (blue, North Atlantic; Chen and Sharma, 2009; Cobelo-García et al., 2013) and sediment (orange, Peucker-Ehrenbrink and Jahn, 2001) are vertical lines in Pt/Os.

Table 4.3: Pt concentration (pg g^{-1}); Os concentration (fg g^{-1}) and $^{187}Os/^{188}Os$ for samples of interstitial and overlying water and sediment from High Traffic Station (summer) and Low Traffic Station (spring).

			Interstitial water			sediment		
sample	season	Depth (cm)	[Pt] ng L^{-1}	[Os] ng L^{-1}	$^{187}Os/^{188}Os$	[Pt] pg g^{-1}	[Os] pg g^{-1}	$^{187}Os/^{188}Os$
High Traffic overlying	Summer	0	0.164	0.0188	0.918	-	-	-
High Traffic 0-2		0-2	0.429	0.0440	0.847	40100	46.9	0.908
High Traffic 2-4		2-4	0.520	0.0428	0.955	2520	40.6	0.976
High Traffic 4-6		4-6	0.656	0.0530	0.996	683	40.8	1.038
High Traffic 6-8		6-8	0.571	0.103	1.066	619	39.0	1.074
High Traffic 8-10		8-10	0.592	0.0988	1.053	682	25.5	1.045
High Traffic 10-13		10-13	0.589	0.0724	1.053	584	33.4	1.044
High Traffic 13-16		13-16	0.484	0.0695	0.989	816	36.8	1.043
High Traffic 16-20		16-20	0.535	0.109	1.044	653	43.8	1.028
Low Traffic 0-2	Spring	0-2	0.334	0.0281	0.924	2750	50.7	0.962
Low Traffic 2-4		2-4	0.234	0.0282	0.964	1200	53.5	0.959
Low Traffic 4-6		4-6	0.156	-	-	1020	-	-
Low Traffic 6-8		6-8	0.173	0.0308	0.906	906	56.7	0.954
Low Traffic 8-10		8-10	0.262	-	-	684	-	-
Low Traffic 10-13		10-13	0.169	0.0357	0.998	588	54.9	1.090
Low Traffic 13-16		13-16	2.52	0.0446	1.008	1.01	62.1	1.178
Low Traffic 16-20		16-20	0.143	0.0559	1.000	0.444	68.4	1.168

Table 4.4: Bibliographic Pt and Os concentration and ^{187}Os/^{188}Os ratios in sediment: contaminated and background values.

Sediment		Pt (pg g^{-1})		Os (pg g^{-1})		^{187}Os/^{188}Os	
		contam.	background	contam.	background	contam.	background
Loess	Peucker-Ehrenbrink&Jahn 2001	-	510	-	31		1.05
Harbour	Esser&Turekian, 1993	-	-	64 - 770	40	0.22 - 0.60	1.06
Peat bog (US)	Rauch *et al.*, 2004b	3500 - 290000	-	6.9 - 24	-	0.36 - 0.77	
Peat bog (NW Iberia)	Rauch *et al.*, 2010		-	-	-	0.50 - 1.1	0.54 - 0.86
Turbiditic	Colodner *et al.*, 1992	800 - 2800	-	-	-	-	-
Pelagic	Colodner *et al.*, 1992	1200 - 5200	-	-	-	-	-
Urban lake	Rauch *et al.*, 2004a	11000 - 30000	1000 - 1700	150	56 - 71	0.65	1.9
Urban watersheds	Sutherland *et al.*, 2007	57000 - 70000	-	-	-	-	-
Urban stream sediments	Prichard *et al.*, 2008	410000	3000-64000	-	-	-	-
Gullypot	Wei & Morrison, 1994	8900	3000	-	-	-	-
Gullypot	Fliegel *et al.*, 2004	150000	-	-	-	-	-
Tunnel dust	Helmers & Mergel 1998	Up to 730000	-	-	-	-	-
Road side grass	Helmers & Mergel 1998	30-10000	< 30	-	-	-	-
Tunnel dust	Fliegel *et al.*, 2004	98000 - 300000	-	-	-	-	-
Urban Infiltration basin	Whiteley & Murray, 2005	11000 - 100000	990	-	-	-	-
Road side	Zereini *et al.*, 2001	2000-390000	600-1600	-	-	-	-
Road side	Fritsche & Meisel, 2004	9100 - 130000	400	40 - 250	50	-	-
Road dust	Schäfer and Puchelt, 1998	12000 - 1100000	-	-	-	-	-
Road side soil	Schäfer and Puchelt, 1998	20000-200000	1000-10000	-	-	-	-
Iberian Pyrite Belt	Mathur *et al.*, 1999	-	-	-	50-700	-	0.4-29
High traffic salt marsh	This study	40000	670	-	36	0.91	1.04
Bridge-Gullypot	This study	160000	-	110	-	1.4	-

4.3.2 Concentrations of Pt and Os in overlying and interstitial waters

This study reports the first data of dissolved Pt and Os in interstitial waters. The values obtained ranged from 0.14 to 0.66 ng L^{-1} (with the exception of a 2.5 ng L^{-1} peak at Low Traffic Station) for Pt and between 0.028 and 0.11 ng L^{-1} for Os (Figure 4.4, Table 4.3). Dissolved concentrations of Pt (0.21±0.07 ng L^{-1}) and Os (0.037±0.011 ng L^{-1}) at the Low Traffic Station were, in general, lower than at High Traffic Station (0.55±0.07 ng L^{-1} for Pt and 0.074±0.027 ng L^{-1} for Os). In overlying water levels of Pt and Os were of 0.164 ng L^{-1} and 0.019 ng L^{-1}, respectively. These Os concentrations were lower than values found in interstitial waters.

4.3.3 $^{187}Os/^{188}Os$ ratios in sediments and interstitial waters

The $^{187}Os/^{188}Os$ ratios in the sediment ranged from 0.908 to 1.178, while in interstitial waters values varied between 0.847 and 1.066 and in the overlying water the ratio was 0.918 (Figure 4.4, Table 4.2, complete dataset in Table 4.3). Gullypot sediment exhibits the highest ratio, 1.257. Profiles in interstitial waters and sediments had a similar trend at High Traffic Station, with lower $^{187}Os/^{188}Os$ ratios in surface increasing with depth. In sediments and interstitial waters of Low Traffic Station ratios were similar in the upper 8 cm, but values increased markedly towards the bottom in the sediments while in interstitial waters the increase was slighter.

4.4 Discussion

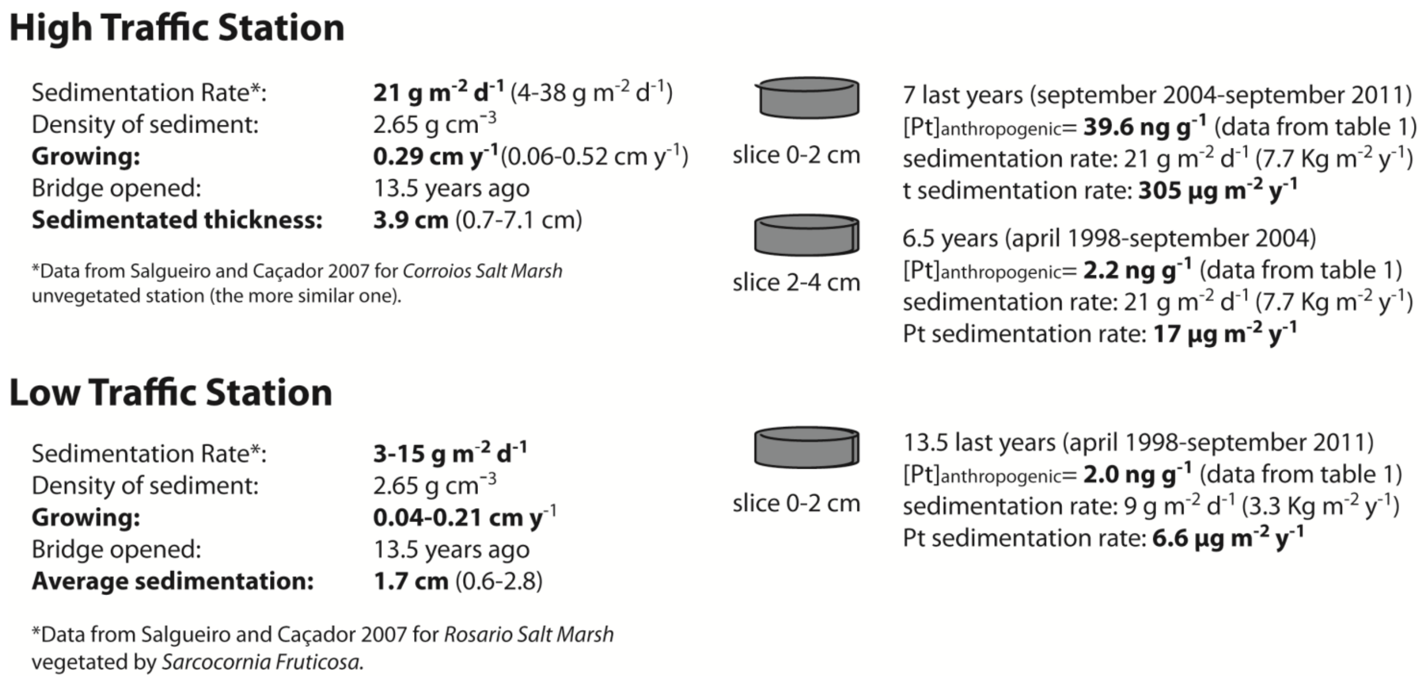
4.4.1 The anthropogenic impact on Pt and Os

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 4.4 (Colodner et al., 1992; Esser and Turekian, 1993; Wei and Morrison, 1994; Helmers and Mergel, 1998; Schäfer and Puchelt, 1998; Mathur et al., 1999; Zereini et al., 2001; Fliegel et al., 2004; Fritsche and Meisel, 2004; Rauch et al., 2004a, 2004b; Whiteley and Murray, 2005; Sutherland et al., 2007; Prichard et al., 2008; Rauch et al., 2010). 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 4.2). Based on Eq. 4.1, the enrichment factor for Pt (EF_{Pt}) was 119 in the upper sediments (<2 cm) from High Traffic Station, but decreased sharply to 8 at 2-4 cm depth. In the Low Traffic Station, the enrichment was lower at surface (<2 cm) with EF_{Pt}= 4 decreasing to half at 2-4 cm depth (Table 4.2).

Noteworthy, the EF_{Os} in sediments from both High and Low Traffic Stations suggest minor to null anthropogenic enrichment. At Low Traffic Station a EF_{Os}= 1 (i.e. no enrichment) was obtained despite the higher Os concentrations compared to High Traffic Station. The calculated anthropogenic fractions (*AF*; Eq. 4.2 and 4.3) 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 ng g^{-1}) corresponds to this source. 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 surface sediments. It should be noted that 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 4.2) was higher than 50% (0-2 cm and 2-4 cm at High Traffic Station and 0-2 cm at Low Traffic Station), using the sedimentation rates reported earlier (Salgueiro and Caçador, 2007) for both stations (see Figure 4.5 for a detailed explanation of the calculations). The average estimated deposition rates were 6.6 µg Pt m^{-2} y^{-1} at Low Traffic Station (0-2 cm) and 310 µg Pt m^{-2} y^{-1} (0-2 cm) and 17 µg Pt m^{-2} y^{-1} (2-4 cm) at High Traffic Station. The low deposition rates found in the Low Traffic Station were comparable to deposition rate up to 8.4 µg Pt m^{-2} y^{-1} estimated by Schäfer *et al.* (1999) in urban environments of Germany, whereas Rauch *et al.* (2004a) estimated accumulation rates of 9±5 µg Pt m^{-2} y^{-1} for the period 1992-2002 in an urban lake (Upper Mystic Lake, USA). However; it is evident the elevated Pt accumulation in sediments from the High Traffic Station.

Since the car traffic over the motorway bridge is the most important human activity at High Traffic Station, calculations were undertaken to evaluate whether this source explains all Pt contamination and deposition rates. 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 (Instituto de Intraestructuras Rodoviárias IP (Portugal), 2013); (ii) an estimation of 37% of vehicles with gasoline engine and 63% with diesel (*"Instituto Nacional de estadística"*); (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 experimental studies (Palacios et al., 2000); (iv) a release of 100 ng Pt Km^{-1} and 6-8 ng Pt Km^{-1} for new and old gasoline vehicles, respectively, from experimental studies (Palacios et al., 2000); (v) a release of 270 ng Pt Km^{-1} for every car, as an alternative based on real environmental data (Schäfer et al., 1999; Zereini et al., 2001); (vi) the bridge is 17.2 Km long; (vii) 4928 days have passed since the bridge started to operate (April 1998) until the sampling (September 2011). Based on these, catalytic converters released



High Traffic Station

Sedimentation Rate*:	**21 g m^{-2} d^{-1}** (4-38 g m^{-2} d^{-1})
Density of sediment:	2.65 g cm^{-3}
Growing:	**0.29 cm y^{-1}**(0.06-0.52 cm y^{-1})
Bridge opened:	13.5 years ago
Sedimentated thickness:	**3.9 cm** (0.7-7.1 cm)

*Data from Salgueiro and Caçador 2007 for *Corroios Salt Marsh* unvegetated station (the more similar one).

7 last years (september 2004-september 2011)
$[Pt]_{anthropogenic}$= **39.6 ng g^{-1}** (data from table 1)
sedimentation rate: 21 g m^{-2} d^{-1} (7.7 Kg m^{-2} y^{-1})
t sedimentation rate: **305 µg m^{-2} y^{-1}**

6.5 years (april 1998-september 2004)
$[Pt]_{anthropogenic}$= **2.2 ng g^{-1}** (data from table 1)
sedimentation rate: 21 g m^{-2} d^{-1} (7.7 Kg m^{-2} y^{-1})
Pt sedimentation rate: **17 µg m^{-2} y^{-1}**

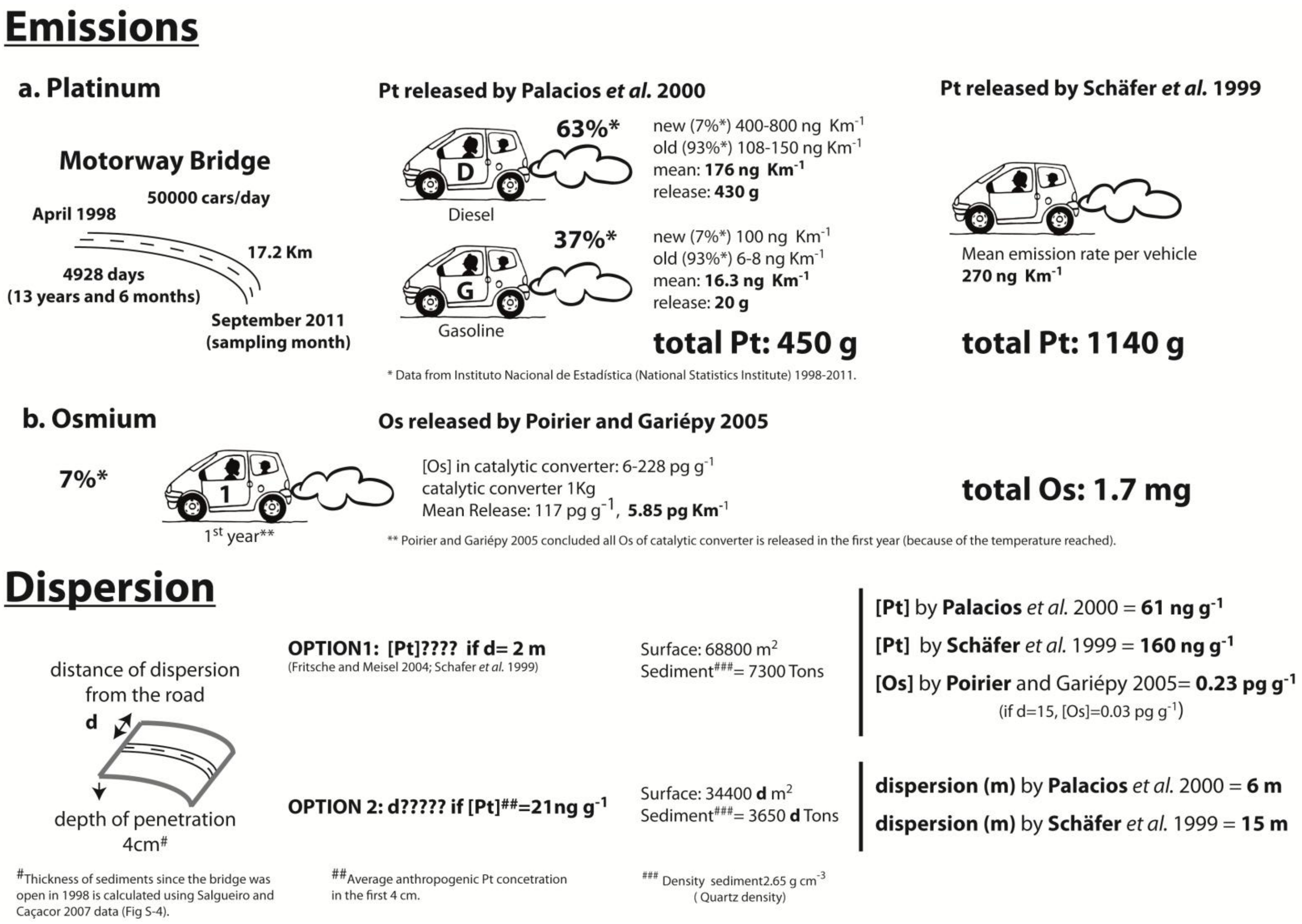
Low Traffic Station

Sedimentation Rate*:	**3-15 g m^{-2} d^{-1}**
Density of sediment:	2.65 g cm^{-3}
Growing:	**0.04-0.21 cm y^{-1}**
Bridge opened:	13.5 years ago
Average sedimentation:	**1.7 cm** (0.6-2.8)

*Data from Salgueiro and Caçador 2007 for *Rosario Salt Marsh* vegetated by *Sarcocornia Fruticosa.*

13.5 last years (april 1998-september 2011)
$[Pt]_{anthropogenic}$= **2.0 ng g^{-1}** (data from table 1)
sedimentation rate: 9 g m^{-2} d^{-1} (3.3 Kg m^{-2} y^{-1})
Pt sedimentation rate: **6.6 µg m^{-2} y^{-1}**

Figure 4.5: Estimation of deposited thickness since the motorway bridge was open (April 1998) and estimation of Pt sedimentation rate (using data from Salgueiro and Caçador, 2007).



Emissions

a. Platinum

Motorway Bridge

50000 cars/day

April 1998

17.2 Km

4928 days
(13 years and 6 months)

September 2011
(sampling month)

Pt released by Palacios *et al.* 2000

63%*

Diesel

new (7%*) 400-800 ng Km^{-1}
old (93%*) 108-150 ng Km^{-1}
mean: **176 ng Km^{-1}**
release: **430 g**

37%*

Gasoline

new (7%*) 100 ng Km^{-1}
old (93%*) 6-8 ng Km^{-1}
mean: **16.3 ng Km^{-1}**
release: **20 g**

total Pt: 450 g

Pt released by Schäfer *et al.* 1999

Mean emission rate per vehicle
270 ng Km^{-1}

total Pt: 1140 g

* Data from Instituto Nacional de Estadística (National Statistics Institute) 1998-2011.

b. Osmium

7%*

1st year**

Os released by Poirier and Gariépy 2005

[Os] in catalytic converter: 6-228 pg g^{-1}
catalytic converter 1Kg
Mean Release: 117 pg g^{-1}, **5.85 pg Km^{-1}**

total Os: 1.7 mg

** Poirier and Gariépy 2005 concluded all Os of catalytic converter is released in the first year (because of the temperature reached).

Dispersion

distance of dispersion from the road

d

depth of penetration 4cm#

OPTION1: [Pt]???? if d= 2 m
(Fritsche and Meisel 2004; Schafer *et al.* 1999)

Surface: 68800 m^2
Sediment###= 7300 Tons

OPTION 2: d????? if [Pt]##=21ng g^{-1}

Surface: 34400 **d** m^2
Sediment###= 3650 **d** Tons

[Pt] by **Palacios** *et al.* 2000 = **61 ng g^{-1}**

[Pt] by **Schäfer** *et al.* 1999 = **160 ng g^{-1}**

[Os] by **Poirier** and Gariépy 2005= **0.23 pg g^{-1}**
(if d=15, [Os]=0.03 pg g^{-1})

dispersion (m) by **Palacios** *et al.* 2000 = **6 m**

dispersion (m) by **Schäfer** *et al.* 1999 = **15 m**

#Thickness of sediments since the bridge was open in 1998 is calculated using Salgueiro and Caçacor 2007 data (Fig S-4).

##Average anthropogenic Pt concetration in the first 4 cm.

Density sediment2.65 g cm^{-3}
(Quartz density)

to the environment 450 or 1140 g of Pt –following experimental data (Palacios et al., 2000) or real environmental rates (Schäfer et al., 1999; Zereini et al., 2001)– (see Figure 4.6 for further information on this estimation).

Given that, almost all the Pt contamination is in the top 4-cm sediment layer based on the AF_{Pt} obtained for the top 4 cm (Table 4.2). Accordingly, we calculated a deposition of 3.9 cm since the bridge was open in 1998 (Figure 4.5) using the sedimentation rates reported previously (Salgueiro and Caçador, 2007). Thus, estimated Pt enrichment in the vicinity of the motorway bridge may be calculated provided the dispersion range of the emitted particles from catalytic converters. If a 2-m dispersion is taken into consideration based on studies in roadside soil (Helmers and Mergel, 1998; Schäfer and Puchelt, 1998; Fritsche and Meisel, 2004), an enrichment of 61-160 ng g^{-1} of Pt would be expected in the vicinity of the road bridge (depending on the model of emissions: Schäfer et al., 1999; Palacios et al., 2000; Zereini et al., 2001). However, this estimated range of enrichment is higher than the concentration found in the sediments from the High Traffic Station (40 ng g^{-1}). The difference may be due to higher dispersion of particles from the bridge than from a regular road. Moreover, it should be accounted that a fraction of the emitted particles is collected in the gullypot sediments. Accordingly, and using the estimation above of Pt emitted, a particle dispersion of 16 m would be needed to explain the enrichment found at High Traffic Station. (or 6 m following experimental studies (Palacios et al., 2000); more information in Figure 4.6).

The concentration of Os at the High Traffic Station was estimated following the previous assumptions (number of vehicles, length of bridge, etc) and coupled with (i) the release 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 (Poirier and Gariépy, 2005); and (ii) catalytic converters contain 6-228 pg g^{-1} of Os (Poirier and Gariépy, 2005). On this basis, an estimation of 1.7 mg input of Os to the roadside was found. 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

Figure 4.6 (see pag 146): Calculations for Pt and Os release and dispersion at High Traffic Station (data from different studies: Helmers and Mergel, 1998; Schäfer et al., 1999; Palacios et al., 2000; Fritsche and Meisel, 2004; Poirier and Gariépy, 2005; Salgueiro and Caçador, 2007; Instituto Nacional de estadística).

dispersion). These calculations show that the Os supply from catalytic converters is negligible compared to natural background concentrations or other processes that introduce Os to the sedimentary environment (e.g. regional atmospheric deposition) masking this source. Rauch *et al.* (2010) 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 will be expected in the top 4-cm sediment layer, i.e., which is 16-160 times higher than the Os that catalytic converters could supply.

The surface sediments have low $^{187}Os/^{188}Os$ ratios compared to the background values. The presence of a less radiogenic source in the surface is consistent with the surface anthropogenic Os contribution at both stations (Table 4.2). The isotopic composition of each anthropogenic endmember can be achieved from the representation of $^{187}Os/^{188}Os$ ratios against the inverse of

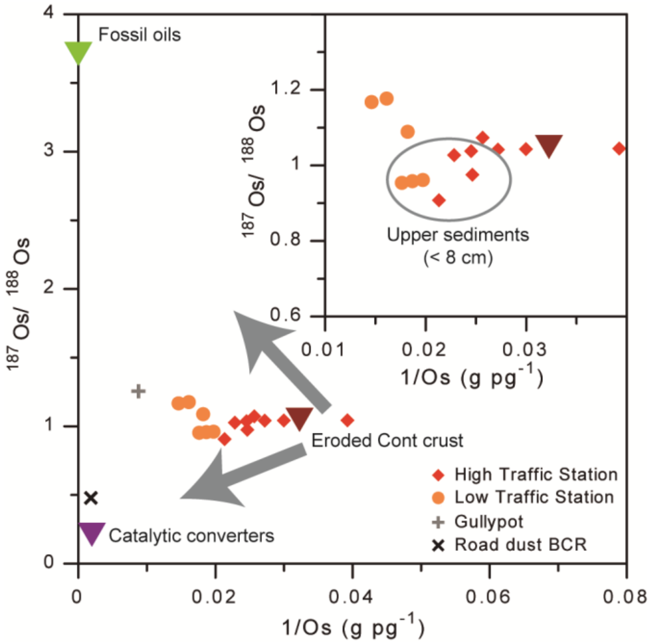


Figure 4.7: $^{187}Os/^{188}Os$ vs. $1/[Os]_{total}$ (g pg^{-1}) in High Traffic Station and Low traffic Station sediments, bridge gullypot and road dust reference material for this study. Fossil fuels (Rodushkin et al., 2007; Selby et al., 2007), catalytic converters (Poirier and Gariépy, 2005; Rodushkin et al., 2007) and eroded continental crust (Peucker-Ehrenbrink and Jahn, 2001) define the endmembers. The plot shows two tendencies of anthropogenic impact (grey arrows).

Os concentration (Figure 4.7). Three endmembers –fossil oils (radiogenic, Os= 204000 pg g^{-1}, ^{187}Os/^{188}Os= 3.7; Rodushkin et al., 2007; Selby et al., 2007); catalytic converters (unradiogenic, Os= 501 pg g^{-1}, ^{187}Os/^{188}Os= 0.21; Poirier and Gariépy, 2005; Rodushkin et al., 2007) and eroded continental crust (Os= 31 pg g^{-1}, ^{187}Os/^{188}Os= 1.05; Peucker-Ehrenbrink and Jahn, 2001)– have been identified (triangles, Figure 4.7) to explain the Os isotope compositions. Samples from High Traffic Station (diamonds, Figure 4.7) fall close to the eroded continental crust endmember, but catalytic converters influence surface samples (closer to the surface, more influenced) overlapping on the line defined by these two endmembers. Interestingly, the interpretation of ^{187}Os/^{188}Os ratios in sediments from Low Traffic Station (dots, Figure 4.7) is more complex. Surface sediments show an isotopic composition similar to High Traffic Station, pointing a link to the catalytic converters source. However, deeper sediments show a higher influence of the third endmember, fossil oils. The higher industrial activity that Barreiro Chemical Complex had until 1970´s, where a pyrite roasting plant (that processed pyrite from Iberian Pyritic Belt, whose average ^{187}Os/^{188}Os is 9; Mathur et al., 1999) and a smelter were located, all of them using fossil combustibles to perform their activity, may explain fossil oils influence. Also the gullypot sediment sample shows an important contribution of this more radiogenic endmember. Thus, two anthropogenic endmembers (fossil oils and catalytic converters) influence the deeper sediment isotopic values. Rauch *et al.* (2010) defined similar endmembers to explain the isotopic composition of a peat bog in the NW Iberian Península where the effect of three similar endmembers was detected for the last 50 years, included the Iberian Pyritic Belt mining activities.

Concentrations of Pt and Os in interstitial waters (Pt: 0.14-0.66 ng L^{-1}, Os: 0.028-0.11 ng L^{-1}) were higher than typical values for oceanic waters (0.04-0.3 and 0.008 ng L^{-1} for Pt and Os, respectively; Bruland and Lohan, 2006), and for estuarine waters (S= 30; 0.08-0.11 ng L^{-1} for Pt, Cobelo-García et al., 2013; and 0.01 ng L^{-1} for Os, Turekian et al., 2007). By using North Atlantic waters (Chen and Sharma, 2009; Cobelo-García et al., 2013) 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 redissolved in the interstitial water and eventually transported to the estuarine waters. The Os isotopic composition in interstitial waters and sediments suggest the existence of quasi-equilibrium conditions between both phases. Osmium is mobilized from the sediments to the interstitial water. The lower Os concentration in overlying water leads to an upward flux towards the water column. Surprisingly, the isotopic composition of overlying water shows almost the same ratios than open oceanic waters (0.95

for the North Atlantic; Chen et al., 2009) suggesting the role of salt marshes as a source of Os to the ocean. Nevertheless, the export of Os would deplete the pool in sediments if not balanced by equivalent inputs. Conservation of mass requires an import to the sediment by settling of suspended particles, advection of atmospheric deposition.

4.4.2 Os-Pt decoupling in the environment

The Pt/Os ratios of sediments show a wide range of values (Figure 4.4, Table 4.2Table 4.2). Ratios of Pt/Os for background sediments at High (19±5) and Low Traffic Stations (11±5) were comparable to average eroded continental crust (16.5; Peucker-Ehrenbrink and Jahn, 2001). However, ratios in surface sediments near the bridge (High Traffic Station) are ~45 times higher than background levels and 5 times the background at the Low Traffic Station. The highest Pt/Os ratio was found in the gullypot sediment, which was twice the value in surface sediments at High Traffic Station. In addition, if the Pt and Os derived only from anthropogenic sources are considered Pt/Os ratios were 5600 and 220 in High and Low Traffic Station, respectively (ratios are calculated using the amount of Pt and Os and applying them the AF_{Pt} and AF_{Os}). Thus, the regional common source indentified in the Low Traffic Station (Pt sedimentation rate 6.6 µg m^{-2} y^{-1}), has a Pt/Os ratio of 220. The other local source (Pt sedimentation rate 300 µg m^{-2} y^{-1}) that is related to vehicular traffic emissions (High Traffic Station) had Pt/Os ratio ∼5400, which is in agreement with the elevated values for the particles emitted from catalytic converters ($4x10^{6}$-$2x10^{8}$; Palacios et al., 2000; Fritsche and Meisel, 2004; Poirier and Gariépy, 2005). The different impact of the catalytic converters on the levels of Pt and Os may be explained by the limited dispersion of Pt as particles, whereas Os is emitted in gaseous form that have a wider dispersion.

In interstitial waters Pt/Os ratios are lower and within a narrow range of 5-12 in all the profiles (Figure 4.4), which are close to ratios for North Atlantic waters (Pt/Os= 5, Figure 4.4, light blue straight line; Table 4.2), except for ratio from Pt peak at Low Traffic Station (Pt/Os= 57; 14.5 cm). The absence of a surface peak in Pt/Os suggests that Pt is, in general, less soluble and mobile than Os. The results obtained suggest different post-depositional processes of anthropogenic Pt and Os: while most of Pt cycled inside the sediment, Os appears to cycle between the sediment and the water column and eventually exported to the estuary.

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

-regional source, whose Pt/Os is ~220 linked to human activities around Lisbon area including a large scale traffic (Schäfer et al., 1999; Rauch et al., 2004a) and industrial effects with emphasis to fossil oils as a relevant endmember.

-local source, linked just to traffic emissions. The height of the road (bridge) determines the dispersion of these emissions.

This gives support to a decoupled behavior of Pt and Os in the environment relative to both their sources and mechanisms of release and dispersion, as well as their different reactivity and mobility, i.e., Pt is released as solid and non-reactive particulates whereas, Os is emitted as gaseous OsO_4 and when deposited displays a higher mobility. This should be taken into consideration when using the Os isotope ratios for the reconstruction of the sources and contamination of platinum group elements in environmental matrices.

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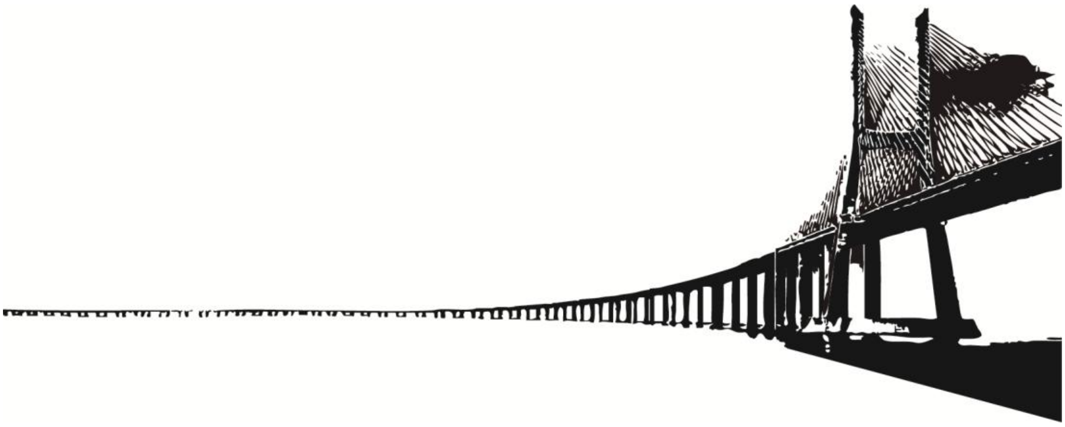
Chapter 5

Osmium and platinum diffusive fluxes in salt marsh sediments (Tagus Estuary, SW Europe)

Based on the work to be submitted to *Chemosphere* by

C. Almécija, A. Cobelo-García, J. Santos-Echeanadía, M. Caetano and M. Sharma



Osmium and latinum diffusive fluxes in salt marsh sediments (Tagus Estuary, SW Europe)

Abstract

Fluxes quantification in coastal environments is one of the most important issues for the characterization of the biogeochemical cycles of human-impacted elements. Platinum group elements are part of the so called emerging contaminants due to their use mainly in the catalytic converters that release particles to the environment. Thus, the aim of this study is estimating the diffusive fluxes of osmium (Os) and platinum (Pt) in salt marsh sediments to assess if salt marshes are working as sinks or sources of these elements to estuarine waters.

Two sediment cores with their corresponding overlying water were taken in the salt marshes of Tagus estuary in March and September 2011 and interstitial water was extracted by centrifugation, filtered and stored (pH ~1). Platinum concentration was analyzed by catalytic adsorptive stripping voltammetry (catalytic AdCSV) after UV-digestion and Os concentration and isotopic composition was determined by negative thermal ionization mass spectrometry (N-TIMS) after double distillation with HBr. Procedural blanks were analyzed to correct values. Diffusive fluxes were calculated applying the Fick´s first law for porous sediments, ruled by the gradient of concentrations of these elements between interstitial and overlying waters. Besides, the diffusion coefficients (298 ºK) of Os and Pt in their typical chemical species in salty water

were theoretically estimated due to the lack of literature values.

Platinum exhibits a different behavior in spring and summer: salt marshes hold Pt during spring (–370 ng m^{-2} y^{-1}) and export a small amount of Pt in summer (+49 ng m^{-2} y^{-1}) working as a net sink of Pt in the yearly cycle. The release/retention of Pt (1.6 g and 12 g respectively) is negligible compared to the input of Pt linked to the traffic. Nevertheless, salt marshes behave as a source of Os to the estuary and ocean during the whole year (spring 0.71-1.4 ng m^{-2} y^{-1}, summer 1000-1900 ng m^{-2} y^{-1}, depending on the speciation) releasing 32-61 g of Os to the estuary only in summer, the 19-32% of the Os that arrives to Tagus Estuary in one year. So, world salt marshes are described as a key compartment in Os cycle, releasing 25-40 % of the total amount of Os in the oceans. We consider these results, that point to a decoupled behaviors between Os and Pt, outstanding enough to be taken in account, despite several efforts and deepenings should be done in order to improve the knowledge on the biogeochemical cycle of these elements.

5.1 Introduction

In order to improve the knowledge on the biogeochemical cycles of trace elements, especially the emerging contaminants derived from recent anthropogenic activities, there are some areas of special interest due to their complexity and unique characteristics like coastal systems including estuaries and salt marshes. Accordingly, the GEOTRACES program (An international study of Marine Biogeochemical cycles of Trace Elements in their isotopes, www.geotraces.org) highlights the importance of describing and quantifying fluxes at the land-sea interface to better constrain the marine biogeochemical cycle of trace elements. Also, their particular susceptibility to global change enhances the importance to assess the transport, reactivity and fate of trace elements (Blasco et al., 2000; Caetano et al., 2012).

Physical, chemical and microbial processes condition the biogeochemistry of salt marsh sediments (Taillefert et al., 2007). Previous work has been focused on fluxes in salt marsh sediments (Caetano et al., 1997; Falcão and Vale, 1998; Cabrita et al., 1999; Taillefert et al., 2007; Deborde et al., 2008; Santos-Echeandía et al., 2010; Caetano et al., 2012), including diffusive fluxes –caused by the differences in the concentration of any element between the interstitial and the overlying water (Berner, 1980; Breier et al., 2009)– and advective fluxes in which flooding water breaks the water-sediment equilibrium and forces mechanisms for element exportation (Falcão and Vale, 1998; Cabrita et al., 1999; Caetano et al., 2007). Particular attention has been paid for elements whose geochemical cycle is being affected by anthropogenic activities because of the importance of their post-deposition mobility (Sundby, 2006; Santos-Echeandía et al., 2012).

An important group of human-impacted elements is the platinum group elements (PGEs) – platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh) and ruthenium (Ru)– mainly used in catalytic converters in automobiles. Actually, almost 70% of the European Pt demand is for the manufacture of autocatalysts (Johnson Matthey, 2013). Their generalized use since the '70s in United States (Rauch et al., 2004a) and '80s-'90s in Europe (Fritsche and Meisel, 2004) has caused a surface enrichment of PGEs, which has been reported in several studies in human-influenced environments (Tuit et al., 2000; Fritsche and Meisel, 2004; Rauch et al., 2004a; Whiteley and Murray, 2005; Sutherland et al., 2007) but evidence for a long-range transport affecting remote areas was given (Rauch et al., 2004b, 2010; Soyol-Erdene et al., 2011).

The objective of this short communications is to report the first data on Pt and Os diffusive fluxes in salt marsh sediments (Tagus Estuary, Lisbon, Portugal) as well as theoretical values of their diffusive coefficients, currently unavailable in the literature for environmental temperatures. Also, an estimation and significance of the Os export from salt marshes to oceans and its residence time will be given.

5.2 Material and methods

5.2.1 Study area and sampling strategy

The salt marshes of Tagus Estuary (W Iberian Peninsula; ~128 Km^2) are one of the largest in Europe and one of the highest human-impacted due to the 3 millions habitants that live in Lisbon and surrounding areas (Valentim et al., 2013). Sediment cores were collected in spring (March 2011) and summer (September 2011), in salt marshes at a station under a motorway bridge (High Traffic Station), where daily average traffic is around 50,000 vehicles (Instituto de Intraestructuras Rodoviárias IP (Portugal), 2013). However, human activities before the bridge was opened in 1998 were almost inexistent.

From these 20-cm-length cores, sediments were sampled every 2 cm in the first 10 cm and every 3 cm between 10 and 20 cm and stored in high-density polyethylene bottles without air space to minimize oxidation. Overlying waters were also sampled. Once in the lab, porewater extraction was carried out by centrifugation (8000 rpm, 30 minutes, +4 °C). This water was filtered through 0.45 µm polycarbonate membranes, stored in low-density polyethylene bottles and acidified using Suprapur$^{©}$(Merck) HCl (pH ~1). A refractometer (Atago S/Millα 0-100‰) was used to measure salinity. All materials were acid-cleaned prior to use and samples were manipulated inside laminar flow hoods. Procedural blanks were prepared using Milli-Q$^{©}$ (Millipore) water.

5.2.2 Analytical methods

Platinum was determined by catalytic adsorptive stripping voltammetry (catalytic AdCSV) using an adaptation of the method developed by van den Berg and Jacinto, (1988) and described in Cobelo-García *et al.* (2013) for oceanic and estuarine waters. Briefly, 2 mL of porewater were diluted with 20 mL of Milli-Q water (1:11 dilution), and 50 µL of H_2O_2 (TraceSelect$^{©}$ Ultra, Fluka) were added. The dissolution was UV-digested for 4h to remove organic material prior to analysis (Figure 5.1).

Osmium concentrations and isotopic composition were determined by means of negative thermal ionization mass spectrometry (N-TIMS;Figure 5.1); here, 30-50 mL of interstitial water, previously spiked with ^{190}Os, was analyzed following the procedure described by (Chen and Sharma, 2009). The oxidation and equilibration of Os in the sample was carried out adding Jones Reagent to the frozen sample (to avoid prompt reactions) and putting the sample in a high pressure asher at 128 bar, 300 ºC during 16 hours. Then the Os extraction was made by double-distillation, trapping Os in HBr. At this point, the sample is ready to be charged on the acid-precleaned filament to run the mass spectrometry. Procedural blanks were analyzed for both elements, giving values of 3±3 pg L^{-1} (*n=13*) for Pt and 1.3±0.6 pg L^{-1} (*n*=2) for Os. The detection limits of Pt and Os determination, calculated as 3 times the standard deviation of blanks, were 10 and 1.8 pg L^{-1} for Pt and Os respectively.

5.2.3 Estimation of diffusive coefficients and fluxes

Exchange of elements between interstitial and overlying water was quantified by diffusive flux, which is governed by the gradient of concentrations of these elements in porewaters and given by Fick´s first law for porous sediments (Berner, 1980):

$$J_i = \phi D_s^i \left(\frac{dC_i}{dx}\right) \qquad \text{[Eq 5.1]}$$

where J_i is trace element flux (pmol m^{-2} y^{-1}) –positive towards the overlying water, negative towards the interstitial water–, ϕ is the porosity of the sediment (Santos-Echeandía et al., 2010), D_s^i is the diffusion coefficient for each metal (m^2 s^{-1}), C_i is the concentration of metal (fM) and x the distance of diffusion (m). Diffusion coefficient is a function of porosity and the

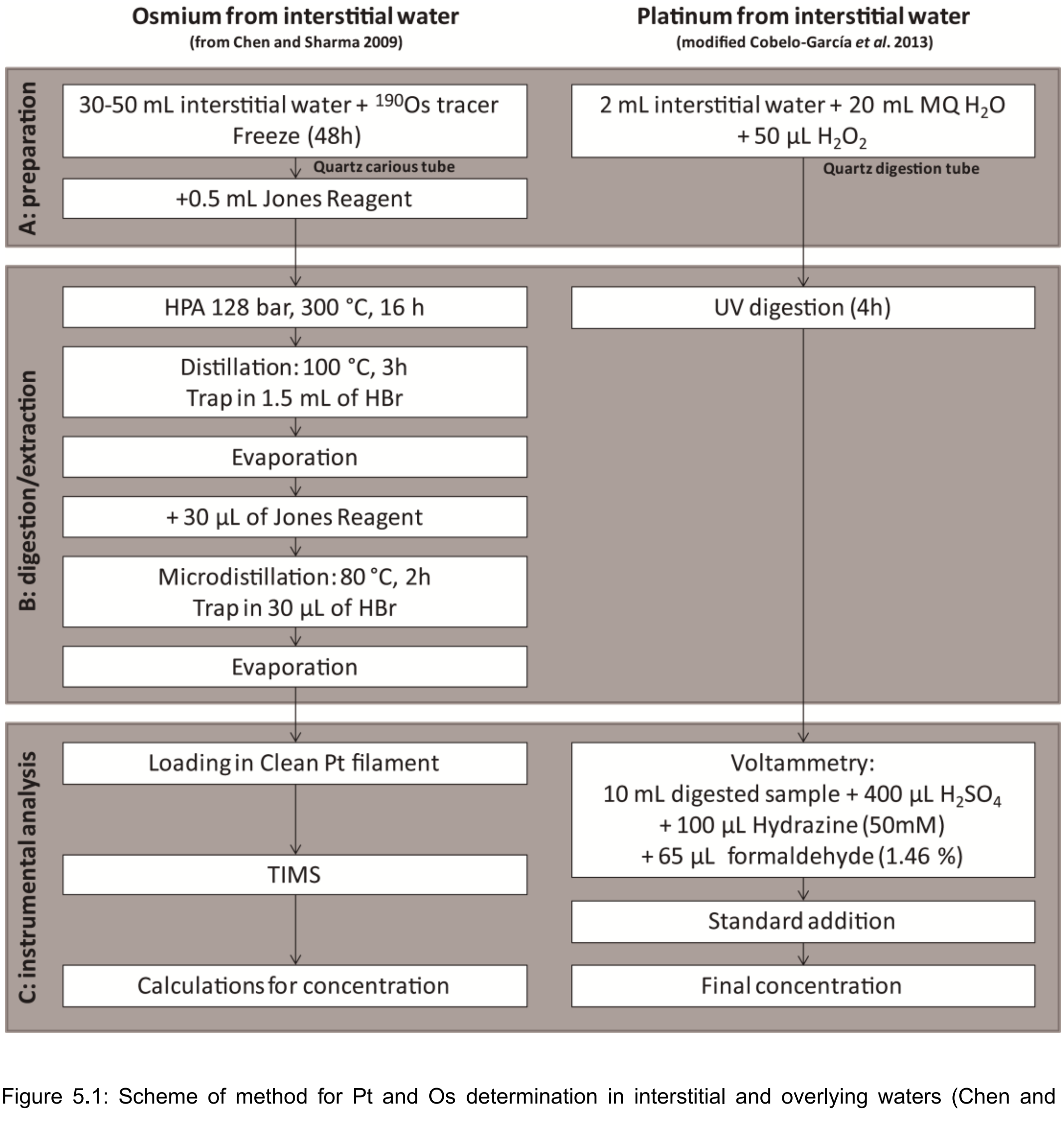


Figure 5.1: Scheme of method for Pt and Os determination in interstitial and overlying waters (Chen and Sharma, 2009; Cobelo-García et al., 2013).

diffusion coefficient of a metal at a given temperature and in a particular solute (D_o^i):

$$D_s^i = \phi^2 D_o^i \qquad \text{[Eq 5.2]}$$

For some elements, these values of D_o^i in water at environmental temperatures are given in the literature (Yuan-Hui and Gregory, 1974) but not in the case of Os and Pt. Therefore, a numerical approximation using the Equation of Stokes-Einstein is necessary.

$$D_o^i = \frac{k \cdot T}{6\pi\eta a} \qquad \text{[Eq 5.3]}$$

where k is the constant of Boltzman (J K^{-1}), T is the absolute temperature (K), η is the viscosity (kg m^{-1} s^{-1}) calculated for a given temperature (298 °K) and known salinity –using the method described by El-Dessouky and Ettouney, (2002)–, and a the radius of the chemical species (m) assuming spherical shape. Value of a is calculated as the summation of ionic radium of the elements that compound the species: in seawater (or waters with high salinity) the most common chemical species of Pt and Os are $PtCl_5(OH)^{2-}$ (Cobelo-García et al., 2013) and OsO_4 (Byrne, 2002) or $H_3OsO_6^-$ (Palmer et al., 1988), respectively. Here we note that Os and Pt could be bound by organic matter (Koide et al., 1991) but this was not considered. Table 5.1 summarizes the calculated diffusion coefficients for Pt and Os in waters at environmentally-relevant temperatures. We find that the calculated D values are of the same order of magnitude as those for other elements (10^{-10} m^2 s^{-1}; Santos-Echeandía et al., 2010).

Table 5.1: Ionic radium of main chemical species of Pt and Os in seawater (calculated by adding up the radium of elements according with the geometry of the species), measured salinity, viscosity (calculated by El-Dessouky and Ettouney, 2002) and diffusion coefficient of a element (298 ºK).

species	radium (Å)	S‰	η (Kg/m·s)*	D_0 (m^2 s^{-1})*
$PtCl_5(OH)^{2-}$ a	6.37	19	9.255 x10-4	3.703 x10-10
		35	9.58 x10-4	3.577 x10-10
H_3OsO^{6-} b	6.41	19	9.255 x10-4	3.680 x10-10
		35	9.58 x10-4	3.555 x10-10
OsO_4 c	3.33	19	9.255 x10-4	7.084 x10-10
		35	9.58 x10-4	6.843 x10-10

*Viscosity and diffusion coefficient calculated at 298°K.

a: $PtCl_5(OH)^{2-} = rPt^{4+} + 2rO^{2-} + 2rH^{+}$ ($2rO^{2-} + 2rH^{+} > 2rCl^{-}$); *b*: $H_3OsO_6^{-} = rOs^{8+} + 2rO^{2-} + 2rH^{+}$; *c*: $OsO_4 = rOs^{8+} + 2rO^{2-}$ (Pt^{4+}: 0.65Å, Cl^{-}: 1.81Å, O^{2-}: 1.32Å, Os^{8+}: 0.69Å, H^{+}: 1.54Å; from Haynes *et al.* (2012).

5.3 Results and discussion

5.3.1 Osmium and platinum concentrations and diffusive fluxes

Dissolved Pt in the entire core exhibits an average concentration of 330±50 pg L^{-1} ($\bar{x} \pm SD$, *n=8*, spring) and 550±70 pg L^{-1} ($\bar{x} \pm SD$, *n=8*, summer) for interstitial waters and 1600 and 160 pg L^{-1} for overlying water (spring and summer); while Os concentration was 40±9 pg L^{-1} ($\bar{x} \pm SD$, *n=5*, spring) and 74±27 pg L^{-1} ($\bar{x} \pm SD$, *n=8*, summer) for interstitial waters and 36 and 19 pg L^{-1} (spring and summer) for overlying waters (Figure 5.2, Table 5.2). The ^{187}Os/^{188}Os ratios ranged from 0.989 to 1.040 (spring) and from 0.847 to 1.066 (summer) in interstitial waters and 0.946 (spring) and 0.918 (summer) in overlying waters. These Pt and Os concentrations found for interstitial waters are higher than typical values for oceanic or estuarine waters (Table 5.2).

For Pt in porewater, there is a clear inverse trend during both samplings: spring presented the highest concentration in overlying water and the lowest in porewater and, contrary, summer presented a higher concentration in porewater than in overlying water (Figure 5.2). The calculated fluxes (ng m^{-2} y^{-1} or nmol m^{-2} y^{-1}) Pt indicates a –370 ng m^{-2} y^{-1} flux in spring and +49 ng m^{-2} y^{-1} in summer (Table 5.3). Negative values indicate fluxes towards interstitial water while positive values indicate fluxes towards overlying waters. The net flux between both seasons is negative, suggesting salt marshes as a sink of Pt in the environment. Previous studies have

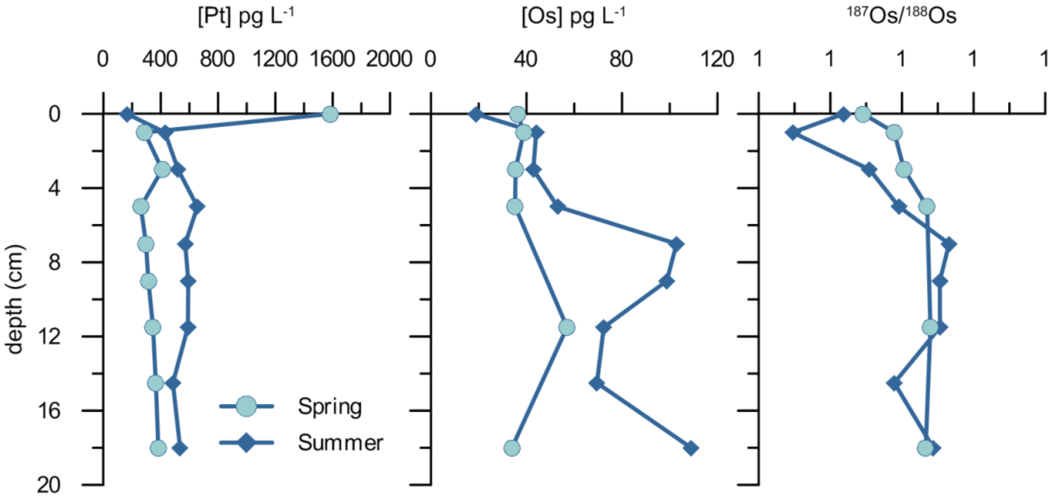


Figure 5.2: Profiles of Pt, Os and ^{187}Os/^{188}Os in spring (dots) and summer (diamonds) in overlying (depth= 0 cm) and interstitial waters.

Table 5.2: Pt and Os concentrations and ^{187}Os/^{188}Os for interstitial and overlying waters from High Traffic Station (spring and summer). Values from oceanic, North Atlantic and estuarine waters have been obtained from the existing bibliography (Bruland and Lohan, 2006; Turekian et al., 2007; Chen and Sharma, 2009; Cobelo-García et al., 2013).

sample	season	Depth (cm)	[Pt] pg L^{-1}	[Os] pg L^{-1}	^{187}Os/^{188}Os
High Traffic overlying	Spring	0	1580	36.3	0.946
High Traffic 0-2		0-2	286	38.8	0.989
High Traffic 2-4		2-4	410	35.4	1.003
High Traffic 4-6		4-6	260	35.2	1.035
High Traffic 6-8		6-8	297	-	-
High Traffic 8-10		8-10	313	-	-
High Traffic 10-13		10-13	346	57.0	1.040
High Traffic 13-16		13-16	366	-	-
High Traffic 16-20		16-20	383	33.8	1.033
High Traffic average		-	333 ± 52	40.0 ± 9.66	-
High Traffic overlying	Summer	0	164	18.8	0.918
High Traffic 0-2		0-2	429	44.0	0.847
High Traffic 2-4		2-4	520	42.8	0.955
High Traffic 4-6		4-6	656	53.0	0.996
High Traffic 6-8		6-8	571	103	1.066
High Traffic 8-10		8-10	592	98.8	1.053
High Traffic 10-13		10-13	589	72.4	1.053
High Traffic 13-16		13-16	484	69.5	0.989
High Traffic 16-20		16-20	535	109	1.044
High Traffic average		-	547 ± 71	74.1 ± 26.8	-
Oceanic waters		-	39 - 380	2.9 - 11.7	-
North Atlantic		-	51	9	0.95
Estuarine Waters (S=30)		-	78-107	10	-

estimated the atmospheric deposition of Pt linked to traffic in urban-influenced areas around 8400 ng m^{-2} y^{-1} (Schäfer et al., 1999; Zereini et al., 2001) and 6000-7000 ng m^{-2} y^{-1} in the Tagus estuary (Almécija et al., in revision a). Although diffusive fluxes of dissolved Pt are negligible compared to atmospheric total deposition fluxes, both are consistent indicating the

Table 5.3: Fluxes of Pt and Os (nmol m^{-2} y^{-1}; ng m^{-2} y^{-1}) and total amount released or removed (g) in each season (positive values for release, negative values for removal). For calculations each season has been considered as 0.25 years, and the extension of the salt marsh in Tagus estuary is 2000000 m^2 (Valentim et al., 2013). Two values for Os are given depending on which Os species exists (b= $H_3OsO_6^-$, c= C, OsO_4).

	Flux (ng m^{-2} y^{-1})			Flux (nmol m^{-2} y^{-1})			Released (g)		
	Pt	Os[b]	Os[c]	Pt	Os[b]	Os[c]	Pt	Os[b]	Os[c]
Spring	–370	+0.71	+1.4	–1.9	+0.0037	+0.0072	–12	+0.02	+0.04
Summer	+49	+1000	+1900	+0.25	+5.3	+10	+1.6	+32	+61

role of salt marshes as a sink for this element.

For Os, both of the calculated fluxes (depending on Os chemical specie, section 2.3) present positive values (from +0.71 to +1900 ng m^{-2} y^{-1}, Table 5.3) indicating that salt marshes, especially in summer, are a net source of Os to the estuary. Besides, although Os inputs to this area have been quantified, e.g. an autocatalyst-derived Os of 0.24-1.8 ng m^{-2} y^{-1} (Almécija et al., in revision a) and a regional atmospheric deposition of 30 ng m^{-2} y^{-1} (Rauch et al., 2010), these inputs are lower than the Os released by diffusion from the sediments.

5.3.2 The Os source in interstitial waters

The Os isotope signature in porewater is closely correlated with that in sediments (Figure 5.3a, sediment data only in summer, from Almécija *et al.* in revision a). However, a deviation from a 1:1 relationship is observed especially at surface, low $^{187}Os/^{188}Os$ values; here, porewater shows lower $^{187}Os/^{188}Os$ than those expected from the sediments, suggesting other sources in the dissolved phase lowering the isotope signature. When the $^{187}Os/^{188}Os$ ratios are plotted versus 1/Os in porewaters, an inverse correlation is observed (Figure 5.3b), with isotopic ratios tending to local background sediment values with increasing porewater Os concentrations. It appears that a natural source of Os in porewaters, leading to higher concentrations in the deeper layers than in surface, is driving the diffusive fluxes of this element from the salt marsh.

5.3.3 Mass balance

Despite of the fact that previous studies in the area have reported that there is an intense input of particulate Pt linked to the traffic pressure (Cobelo-García et al., 2011; Almécija et al., in revision a), Pt has been characterized as low-mobile element (Chapter 3 and Almécija et al., in revision a). Accordingly, although up to 99% of the surface sediment Pt is derived from anthropogenic source (Almécija et al., in revision a), no Pt enrichment in porewaters was observed in the upper layers. Applying this assumption to the whole Tagus Estuary (known the extension: 128 Km^2; Valentim et al., 2013), it results in a release from the sediments of 1.6 g of dissolved Pt during the summer (what means 0.25 years) but a sink of 12 g during the spring period (Table 5.3).

Based on several considerations from our previous studies in the area (Almécija et al., in revision a) (1) Os is not affected by traffic borne contamination (the influence of traffic in Os pool is almost insignificant by comparison with atmospheric input), (2) the anthropogenic fraction of Os in sediments is no greater than 15% and (3) isotopic composition indicates a clear relation between sediments and porewater, being the Os in sediments (natural) the source of Os to the interstitial water. Assuming that this applies to the entire salt marsh, it results in a 0.2 g (or 0.4 g, depending on the Os speciation chose, Table 5.3) of dissolved Os released by the salt marsh to the Tagus estuary in spring and 32 g (or 61 g) in summer (0.25 years). This yearly Os output

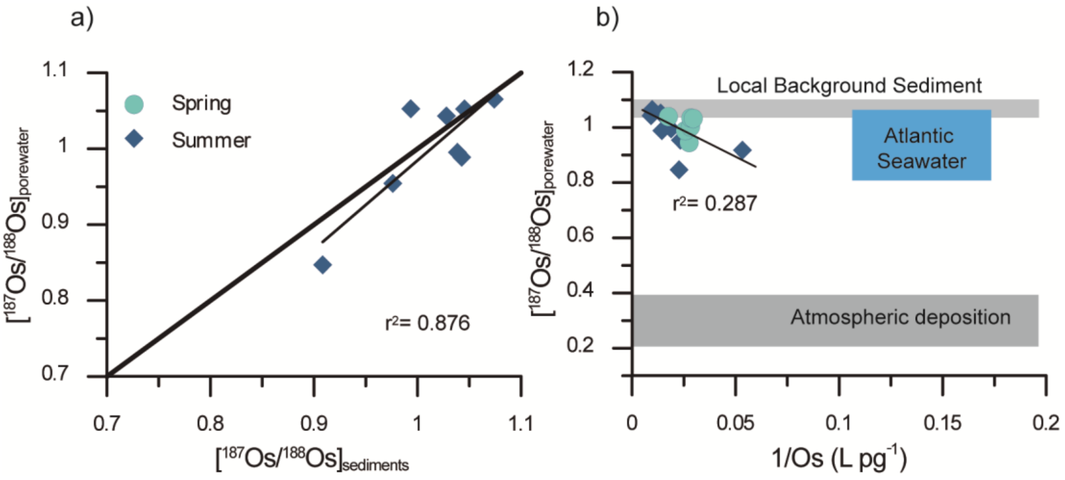


Figure 5.3: (a) Relationship between the Os isotope ratio in sediments (Almécija et al., in revision a) and porewater for the summer core (no Os sediment data for the spring core). The solid line represents the 1:1 mixing line; (b) Plot of the porewater Os isotope ratio vs 1/Os for the summer (blue dots) and spring (green dots) cores. For comparison, the isotope ratios for the local background sediment (Almécija et al., in revision a) and precipitation (Chen et al., 2009) are given; also indicated the typical Os isotope ratios and 1/Os for Atlantic waters (Chen et al., 2009; Chen and Sharma, 2009).

is, accordingly, significant if compared to other Os inputs in the estuary (an estimation of a yearly release of 0.13 mg of Os from catalytic converters since the bridge was open has been previously done, (Poirier and Gariépy, 2005; Almécija et al., in revision a).

Therefore, Tagus salt marshes release 32-61 g of Os to the estuary only in summer, leading to an increase in the concentration of estuarine waters of 17-33 ng L^{-1} over a typical concentration of ~10 ng L^{-1} at salinity= 30 (Turekian et al., 2007). By assuming just the transport throughout diffusion, estuaries may represent a significant Os source to the ocean. Annual quantity of Os in an estuary depends on the balance between inputs and outputs. We can estimate the Os released by the river and salt marshes in the estuary to the coastal zone per year (Eq. 5.4) and the residence time of this Os (Eq. 5.5):

$$I_{Os}^{e} = I_{Os}^{r} + I_{Os}^{m} = (1 - f_{Os}^{e})Q^{r}C_{Os}^{r} + J_{Os}^{m}S^{m}t \qquad \text{[Eq. 5.4]}$$

$$\bar{\tau}_{Os}^{e} = \frac{N_{Os}^{e}}{I_{Os}^{e}} \qquad \text{[Eq. 5.5]}$$

where $I_{Os}^{r} + I_{Os}^{m}$ are river and salt marshes contributions respectively; f_{Os}^{e} is the fraction of Os from rivers trapped in estuaries, Q^{r} is the annual water discharge from the river, C_{Os}^{r} is the Os concentration of Os in the river, J_{Os}^{m} is the diffusive flux from salt marshes (Table 5.3), S^{m} the surface of the salt marshes, t is the season time and N_{Os}^{e} is the total amount of Os in the Tagus estuary. Thus, assuming that (i) estuaries trap 15% of Os (Turekian et al., 2007), (ii) average Tagus river water discharge of 400 m^{3} s^{-1} (Valentim et al., 2013), (iii) average Tagus river Os concentration of 13 pg L^{-1} (Turekian et al., 2007), (iv) the Os released by the salt marshes is not affected by estuarine trap (15%), (v) Os diffusive flux in salt marsh sediment is 1-2 µg m^{-2} y^{-1} during 0.25 y, (vi) salt marsh extension is 128 km^{2} (Valentim et al., 2013), (vii) the averaged Os concentration in the estuary is 10 pg L^{-1} at salinity 30 (Turekian et al., 2007) and (viii) the volume of the Tagus Estuary is 1900x10^{6} m^{3} (Valentim et al., 2013), Tagus Estuary releases 171-203 g to the coastal zone every year due only to the summer fluxes of Os, of which 19 (or 32%) were from salt marshes. Besides, the residence time of Os in the estuary, taking in account only the summer release is estimated around 34-41 days.

Previous studies have indicated that continents supply annually 81% of Os to the ocean, which 270 kg come from rivers (Sharma, 2011) and 14 kg from desert dust (Sharma, 2011). We estimate, using diffusive fluxes, that 95-190 kg of Os are annually released from salt marshes all around the world (world marshes surface is 3.8x10^{5} km^{2}; Jickells and Rae, 2005). So, using this new input of Os to the ocean, between 25% and 40% of the total amount of oceanic Os may be derived from marshes. Besides, we can rewrite the equation of the residence time of Os in the oceans where $\bar{\tau}_{Os}^{sw}$ described by Sharma, (2011), adding a new member referred to salt marsh contribution $J_{Os}^{m}S^{m}$:

$$\bar{\tau}_{Os}^{sw} = \frac{N_{Os}^{sw}}{(1-f_{Os}^{e})\left(\frac{QC_{Os}^{c}}{f_{Os}^{c}}\right)(J_{Os}^{m}S^{wm})} \qquad \text{[Eq. 5.6]}$$

where N_{Os}^{sw} is the total amount of Os in the oceans (66x10^{6} mol), Q is the annual volume of water discharged from all the rivers to the ocean (3.74x10^{16} Kg y^{-1}), C_{Os}^{c} is the average concentration of Os in continental waters (45x10^{15} mol Kg^{-1}), f_{Os}^{c} is the fraction of river supplies (recalculated as 0.57-0.71 considering the salt marshes contribution), and S^{wm} the total surface of salt marshes around the world. Thus, the recalculated residence time changes from 37,000±14,000 years to 24,000-31,000 years but it is still much longer that ocean mixing time, i.e. 1,500 years (Sharma, 2011).

5.3.4. Limitations and considerations

Although the preliminary results of this study add new and significant information on the geochemistry of Os and Pt, we understand that these interpretations are only an initial study to check the behavior of Pt and Os in salt marshes. Estimations are given as a semiquantitative approximation. We lack enough data to resolve the complete role of salt marshes in Pt and Os geochemical behavior but results point to salt marshes as a remarkable compartment worthy to take in account for future investigations. Besides, the special vulnerability of these coastal environments to global change reinforces the necessity of further studies. Other interesting matters related to a future research that could improve our current knowledge on PGE biogeochemical cycles are the study of advective fluxes in a tidal affected area, the assessment of the role of vegetation, the chemical speciation of Os in natural environments, the quantification of how much Os or Pt are bound to organic matter (therefore affecting their reactivity) or the study of a whole year cycle of fluxes.

5.4 Conclusions

In salt marshes, both interstitial water profiles and diffusive fluxes indicate an opposite behavior for Os and Pt showing an inert behavior of Pt that is trapped in salt marshes, and a higher mobility of Os, exported to estuarine and oceanic waters. Therefore, world salt marshes could behave as an important source of Os to the oceanic, supplying between 25-40% to the ocean. Besides, this fact supports the idea already introduced in previous studies (Sharma, 2011; Almécija et al., in revision a) about the absence of a coupled behavior between Os and other PGEs, at least Pt (Almécija et al., in revision a) and Rh (Almécija et al., in revision b), questioning the use of Os isotopes as a source-proxy for the other PGEs.

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Chapter 6

Platinum group elements in stream sediments of mining zones: the Hex River (Bushveld Igneous Complex, South Africa)

Based on the work submitted to *Journal of Geochemical Exploration* by

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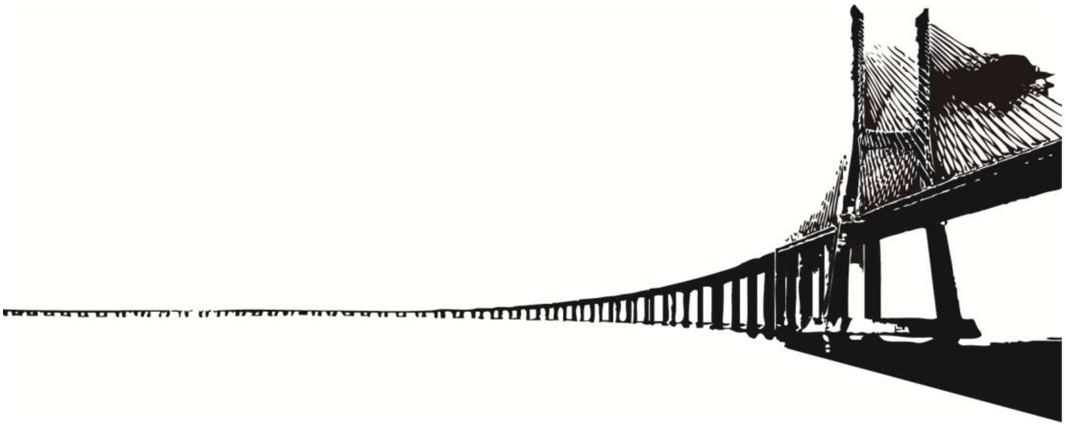


Platinum group elements in stream sediments of mining zones: the Hex River (Bushveld Igneous Complex, South Africa)

Abstract

Assessment of the environmental impact of platinum group elements (PGEs) and other trace elements from mining activities is essential to prevent potential risks for populations. This study evaluates the concentrations of PGEs in stream sediments of the Hex River, which drains the mining area of the Bushveld Igneous Complex (South Africa), at four sampling points. Major and trace elements (Fe, Ca, Al, Mg, Mn, V, Cr, Zn, Cu, As, Co, Ni, Cd and Pb) were analyzed by FAAS and ETAAS in suspended particulate matter and different sediment fractions (<63, 63-500 and 500-2000 µm), and Pt, Pd, Rh, and Ir were measured by ICP-MS after removal of interfering elements (cation exchange resin 50W-DOWEX-X8). Procedures were blank-corrected and accuracy checked using reference materials. Nickel, Cr, Pt, Pd, Rh and Ir show concentrations 3-, 13- 18-, 28-, 48- and 44- fold the typical upper continental crust levels, respectively, although lower than concentrations reported for the parent rocks. Highest concentrations were observed closer to the mining area, decreasing with distance and in the <63 µm fraction, probably derived from atmospheric deposition and surface runoff of PGE-rich particles released from mining activities.

Thus, anthropogenic activities like mining are causing some disturbance of the surface PGE

geochemical cycle, increasing the presence of PGEs in the fine fraction of river sediments. We propose indicators such as airborne particulate matter, and soil and river sediment quality, be added to the protocols that evaluate the sustainability of mining activities.

6.1 Introduction

Platinum group elements (Ru, Rh, Pd, Os, Ir, and Pt; PGEs) are highly siderophile elements and, as such, the bulk of Earth's PGE budget is thought to reside in the core, estimated to be more than 99.8% (Lorand et al., 2008), as evidenced by the relative depletion of PGEs in Earth's upper mantle relative to chondrite meteorites. This siderophile character explains the ultra-trace concentrations of PGEs in the Earth’s crust, being amongst the rarest elements in the environment with average crustal concentrations ranging between 0.02 ng g^{-1} (Ir) and 0.5 ng g^{-1} (Pt and Pd, Rudnick and Gao, 2003). Typical Pt and Pd concentrations in mantle rocks are around 1-100 ng g^{-1} as compared with 1-10 mg g^{-1} in chondrites, iron meteorites and, presumably, the Earth's core (Lorand et al., 2008).

The development of mantle partial melts and their intrusion into the crust, followed by particular mechanisms that serve to concentrate the PGEs (Naldrett et al., 2008), leads to the formation of economically viable PGE-rich deposits. An example of this is the Bushveld Igneous Complex (South Africa; Figure 6.1), which contains about 75%, 52%, and 82% of the world resources of Pt, Pd, and Rh, respectively; its reserves are large enough to meet the world demand for decades (Cawthorn, 2010).

Several studies have been focused on the geochemistry and mineralogy of river sediments and soils of the Bushveld Complex mining area to trace PGE-rich layers or to gain an understanding of weathering processes and sedimentological characteristics affecting PGEs (Wilhelm et al., 1997; Cawthorn, 2001; Oberthür et al., 2004). From an environmental perspective, Gzik et al. (2003) studied soils contaminated by trace elements associated with Bushveld Complex mining activities and how contamination affects the biological communities, whereas Kaonga and Kgabi (2011) investigated the source of atmospheric particulate matter in the Marikana mining area and concluded that, effectively, the mining activities are the source of these airborne particles (airborne trace metals). Subsequently, Rauch and Fatoki (2013) studied the occurrence of platinum in soils and vegetation (grass) in the vicinity of mines in the Bushveld Complex; although elevated concentrations in this area may be the result of natural occurrence, they found evidence of anthropogenic platinum enrichment linked to platinum mining activities due to atmospheric transport of PGE-rich particles from smelters. Also, in the same study Rauch and Fatoki (2013) concluded that atmospheric deposition is the main source of platinum in grass, while uptake of bioavailable Pt in soils has a lower impact on platinum levels in grass.

In order to provide additional information, the objective of this study was to assess the impact of mining activities in the Bushveld Igneous Complex on the surrounding environmental compartments. To this aim, a suite of platinum group elements (Rh, Pd, Ir and Pt) and a range of other trace elements (Cu, Zn, Cr, V, Pb, Cd, Ni, Co and As) were analyzed in the stream sediments of a river (Hex River) draining the Bushveld Complex mining area, and the results are discussed in terms of the anthropogenic impact on the PGE concentrations.

6.2 Materials and methods

6.2.1 Sampling

The Hex River flows in a northerly direction past the city of Rustenburg (North West Province, South Africa) and drains one of the most important mining areas in the western limb of the Bushveld Igneous Complex (Figure 6.1) where the PGE-rich Merensky Reef and the UG-2 chromitite layer are mined. Water and surface sediment were sampled at four points (A: upstream; B: urban; C: intermediate; and D: downstream) along the Hex River (Figure 6.1) during high-flow conditions in March 2006. Firstly, water samples were collected using a telescopic pole with a bottle holder in acid-cleaned 1 L high-density polyethylene bottles that were subsequently kept in zip-lock bags and placed in a cooler box for transportation. For sediments, in order to ensure representivity of the samples, composite samples were obtained at each sampling point by mixing equal volumes of discrete grab samples of surface sediments collected in an area of 15 m^2 covering both river banks. The surface sediments were collected using a plastic spatula and stored in zip-lock plastic bags. Samples were collected at least 10 m away from roads to avoid including the impact of PGE emissions from automobile exhaust catalysts (e.g. catalytic converters) on PGE concentrations (Schäfer et al., 1999).

Physicochemical variables, i.e. temperature, pH, conductivity and dissolved oxygen (DO) were measured in situ using a calibrated WTW 340i sensor package (Nova Analytics). In the laboratory at the University of Johannesburg, 100 mL aliquots of water samples were vacuum-

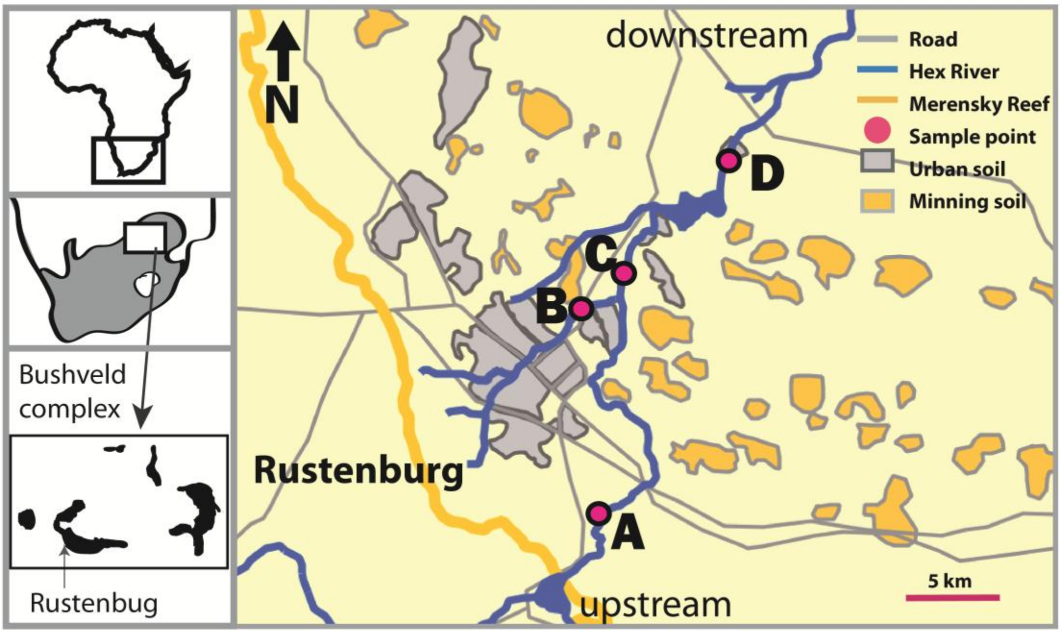


Figure 6.1: Geographic location of sampling points in a river that drains mining areas (Hex River, Rustenburg, in Bushveld Complex, South Africa). Two main land uses are urban and mining activities (including mines, smelters, processing plants and shafts).

filtered using an acid-cleaned Nalgene-type filtration unit fitted with acid-cleaned and pre-weighed 0.45 µm pore size polycarbonate filters (Pall Corporation). Filters with the retained suspended particulate matter (SPM) were stored frozen in plastic Petri dishes pending their analysis for major and trace elements. For the analysis of dissolved organic carbon (DOC), separate 100 mL aliquots of water samples were vacuum-filtered through pre-combusted GF/F filters (Whatman) in a Millipore glass filtration unit. Filters were stored frozen in Petri dishes, and filtrates were collected in pre-combusted glass vials, acidified with HCl (analytical reagent grade, Merck) to pH ~2, and frozen until analysis.

Sediments were dried (<60 °C) and sieved into three size fractions following the Wentworth Grain Size Class (Wentworth, 1922), i.e. silt and clay (<63 µm), fine-medium sand (63-500 µm) and coarse sand (500-2000 µm). After sieving, sediment samples were ground using an agate mortar and pestle, in order to homogenize the sample.

Table 6.1: Comparison between certified reference materials and analysis under different ashing temperatures (not ashed, 450 °C, 800 °C). Non-ashed samples overestimated Ir concentrations due to the presence of isobaric interferences; ashing at 800 °C samples lose Pd (Meisel et al. 2003).

		Pt (ng g^{-1})	Pd (ng g^{-1})	Rh (ng g^{-1})	Ir (ng g^{-1})
BCR-723	certified value	81.3±2.5	6.1±1.9	12.8±2.5	0.26±0.09*
	not ashed	82.4±6.4	3.9±1.5	13.3±0.6	0.85±0.05
	450° C	79.9±7.8	3.6±1.6	13.4±0.4	0.34±0.10
	800° C	78.7±2.7	2.6±1.0	11.7±0.5	0.27±0.03
JSd-2	certified value	16.7	21.2	-	-
	not ashed	14.2±0.2	18.5±8.8	2.1±0.1	0.24±0.02
	450° C	14.3±1.4	17.4±1.2	2.6±0.2	0.24±0.02
	800° C	14.1±0.4	14.7±2.2	2.6±0.1	0.25±0.02

Values: mean value (n=3) ± error (confidence interval 95%) *from Meisel et al. (2003)

6.2.2 Analysis of dissolved and particulate organic carbon, and major and trace elements

Dissolved organic carbon (DOC) was measured in the thawed samples by high-temperature catalytic oxidation using a total organic carbon analyzer (Shimadzu Carbon-5000), and air-dried GF/F filters were analyzed for total carbon and nitrogen using a CHN analyzer (Carlo Erba EA1110). Major and trace elements (Fe, Ca, Al, Mg, Mn, V, Cr, Zn, Cu, As, Co, Ni, Cd and Pb) in suspended particulate matter and sediments were determined by the microwave-assisted sample digestion technique in a Teflon® bomb (MarsXpress, CEM) using a 3:1 mixture of HNO_3 (Hiperpur© 69% Panreac) and HF (Suprapur© 40% Merck). Analysis of major elements in the digests was conducted by means of a flame atomic absorption spectrophotometer (Varian SpectrAA 220FS), whereas trace elements were determined using an electrothermal atomic absorption spectrophotometer (Varian SpectrAA 220). One blank was run every ten samples and results were therefore blank-corrected. The accuracy of the analytical methodology was checked using PACS-2 marine sediment reference material (NRC, Canada) and LGC6137 (LGC Standards) sediment reference material; and results obtained were within the certified concentration range (Table 6.1).

6.2.3 Analysis of platinum group elements in sediments

A Thermo X series II ICP-MS, using external standard calibration, was used for all inductively coupled plasma-mass spectrometer analyses to determine the concentrations of the following platinum group elements, namely platinum (Pt), palladium (Pd), rhodium (Rh) and iridium (Ir). A modified version of the procedure given by Sutherland et al. (2007) was employed for sample digestion and removal of spectral interferences (Figure 6.2); accordingly, about 100 mg of sediment was ashed in quartz crucibles for 5 hours at 450 °C in order to remove organic matter. The optimization of the ashing step (Table 6.1) was achieved using two certified reference materials: river sediment JSd-2 (Geological Survey of Japan) and road dust BCR-723 (European Institute of Reference Materials and Measurements). Ashed sediment samples were

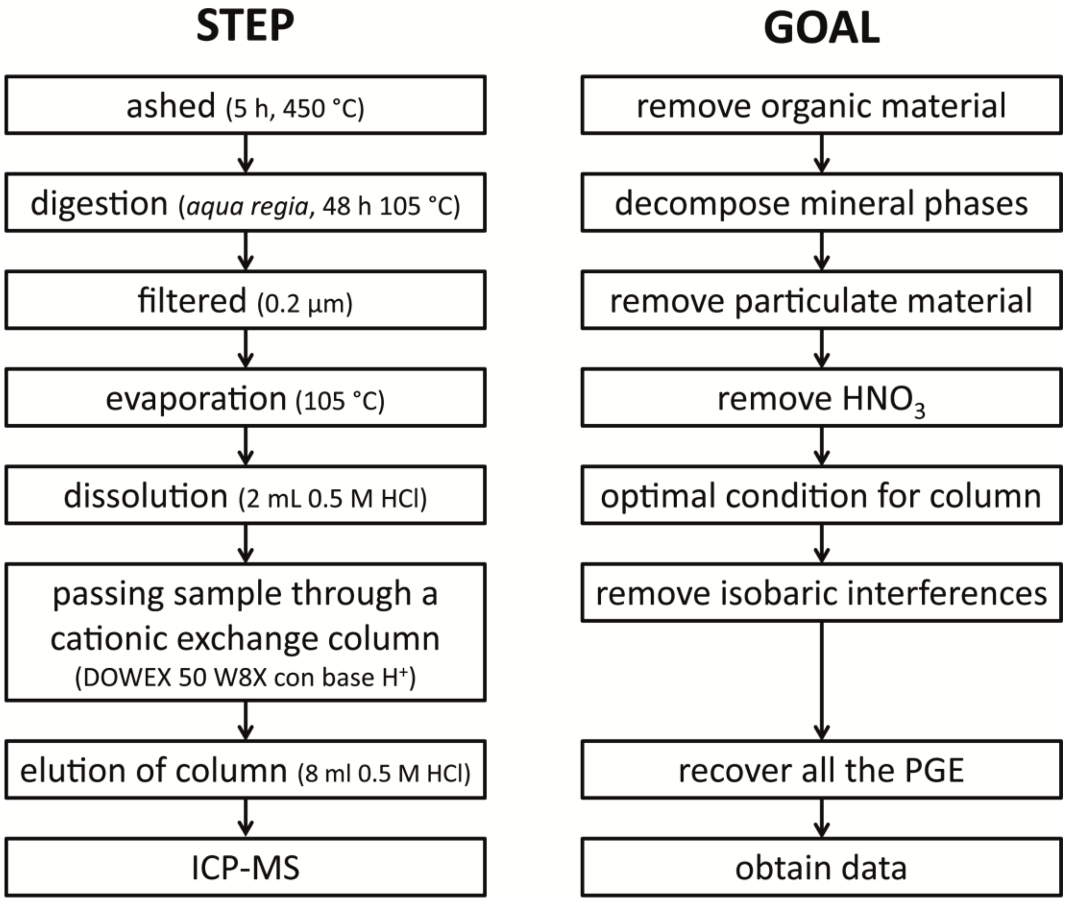


Figure 6.2: Diagram of sample processing methods with associated objectives of each step.

Table 6.2: Parameters of Hex River water at the four sample points (SPM: suspended particulate matter; DO: dissolved oxygen; Sat DO: % saturation of oxygen; DOC: dissolved organic carbon; POC: particulate organic carbon; PON: particulate organic nitrogen). Sand River data from Seanego and Moyo, 2013.

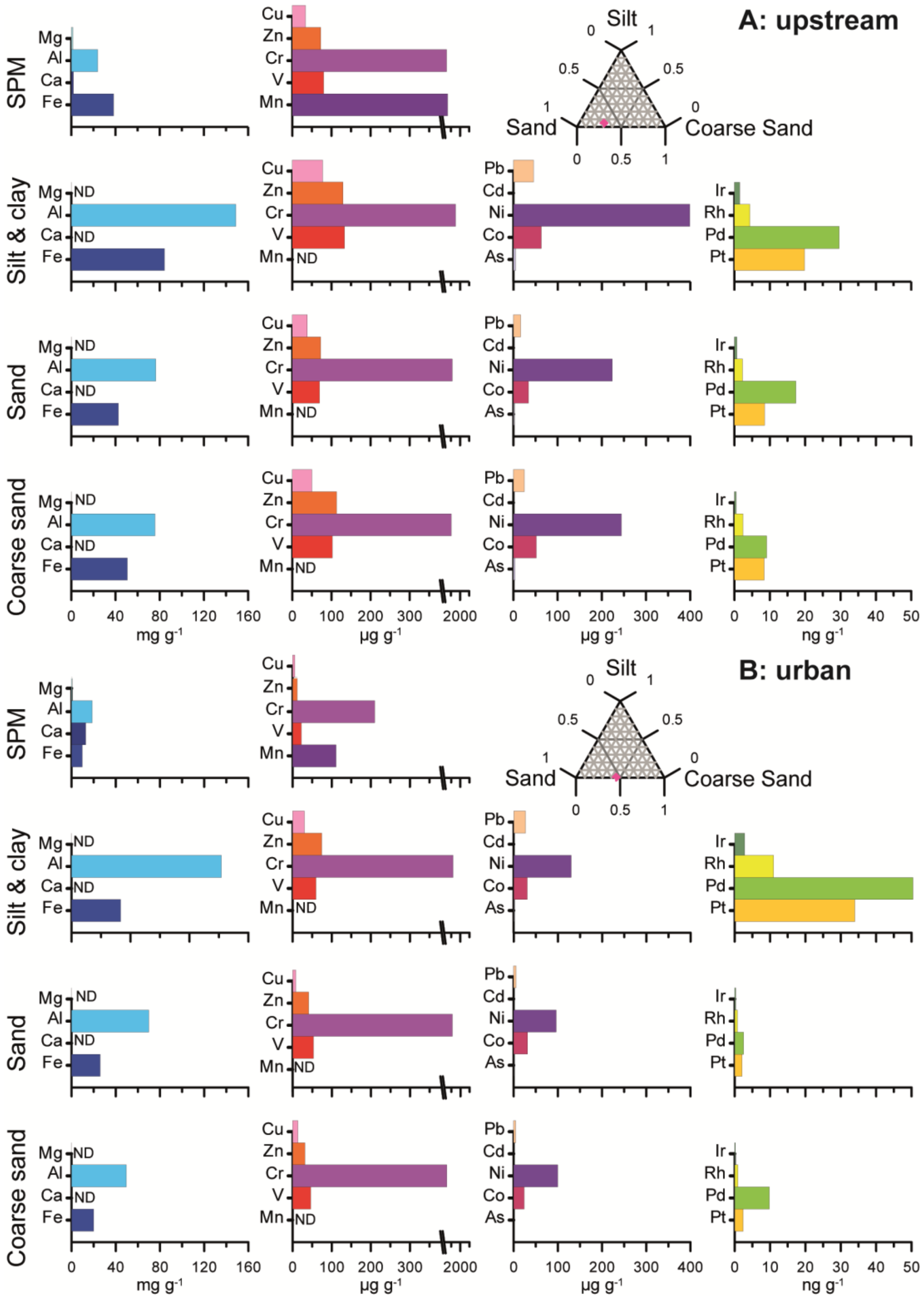
Sample point	pH	SPM (mg L^{-1})	Conduct (µS cm^{-1})	Temp (°C)	DO (mg L^{-1})	Sat DO (%)	DOC (mg L^{-1})	POC (%)	PON (%)	C:N
A upstream	7.35	30.0	501	19.8	8.92	98	1.3	5.7	0.3	22
B urban	7.30	31.9	443	23.0	8.65	104	1.5	11.2	1.3	10
C intermediate	7.39	28.6	1015	21.5	8.98	102	2.2	11.0	1.4	9
D downstream	8.59	6.1	817	26.2	8.05	106	2.2	33.3	1.7	23
Sand River	7.30	60±7	1100	-	-	-	-	-	-	-

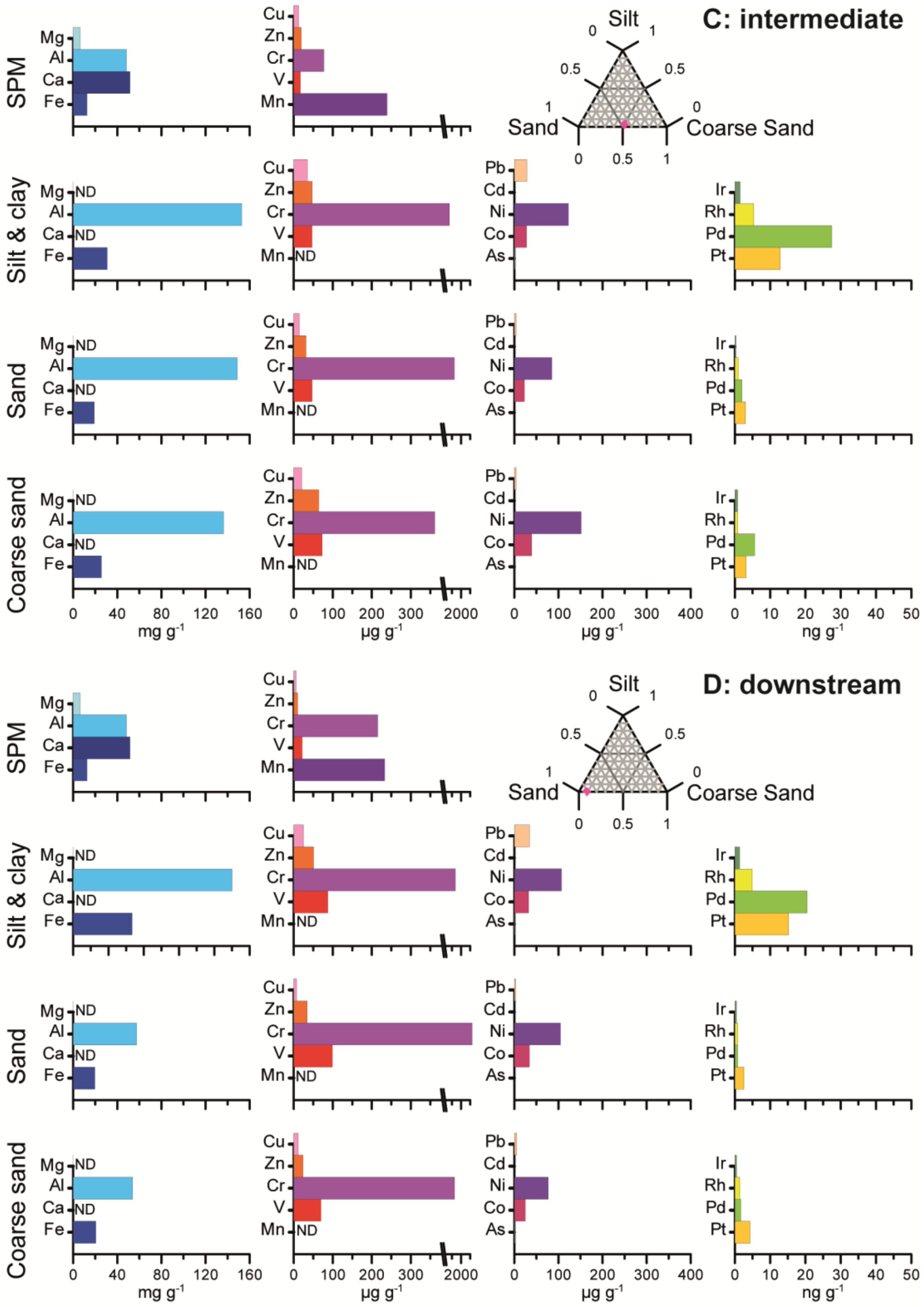
digested in aqua regia (HNO_3 65% and HCl 30%, Suprapur© Merck) for 48 h at 105 °C and then allowed to cool down and syringe-filtered through 0.2 µm Supor™ hydrophilic polyethersulfone membranes (Pall©). The filtered digest was then evaporated until near dryness and diluted in 2 mL of 0.5 M HCl; in order to remove isobaric interferences, solutions were passed through a 2 cm^3 (0.4 cm diameter x 16 cm length) Teflon® column of cation exchange resin (50W-DOWEX-X8, hydrogen form, 100-200 mesh), that was previously acid-cleaned and conditioned with 10 mL of HCl 6 M and 10 mL of HCl 0.5 M. Samples were stored in Teflon® vials pending analysis. The presence of potential isobaric interferences was checked during analysis. Results for the reference materials (JSd-2: river sediment and BCR-723, road dust, Table 6.1) indicated a good recovery (>80%) except for Pd in BCR-723 where a recovery of 59% was obtained.

6.3 Results and discussion

6.3.1 Ancillary parameters

The pH (7.30-7.39), SPM (28.6-31.9 mg L^{-1}), temperature (19.8-23.0 °C) and DO (8.65-8.98 mg L^{-1}, 98-106% of saturation) values obtained at sampling points A, B, and C indicated similar conditions and were in the range of other rivers draining the Bushveld Complex (Seanego and Moyo, 2013) (Table 6.2). However, the presence of a dam upstream of sampling point D reduced flow capacity and competence, producing a decrease in SPM levels of 80% and a


A: upstream
B: urban
SPM
Silt & clay
Sand
Coarse sand
Silt
Sand
Coarse Sand
0
0.5
1
Mg
Al
Ca
Fe
Cu
Zn
Cr
V
Mn
Pb
Cd
Ni
Co
As
Ir
Rh
Pd
Pt
ND
0 40 80 120 160
mg g-1
0 100 200 300 2000
µg g-1
0 100 200 300 400
µg g-1
0 10 20 30 40 50
ng g-1


C: intermediate
D: downstream
Silt
Sand
Coarse Sand
0
0.5
1
SPM
Silt & clay
Sand
Coarse sand
Mg
Al
Ca
Fe
Cu
Zn
Cr
V
Mn
Pb
Cd
Ni
Co
As
Ir
Rh
Pd
Pt
ND
0
40
80
120
160
mg g^{-1}
0
100
200
300
2000
µg g^{-1}
0
100
200
300
400
µg g^{-1}
0
10
20
30
40
50
ng g^{-1}

slight increase in pH as a result of biological activity. As the Hex River flows past Rustenburg, the amount of organic material in water due to urban and domestic inputs, here measured as DOC, POC, and PON, increased from sampling points A to B. Dissolved oxygen concentrations, saturated at all stations, showed that the system still had self-purification capacity (Seanego and Moyo, 2013).

6.3.2 Major and trace elements

Remarkable elevated concentrations of Ni and Cr were observed in all sampling points and fractions, compared with other trace elements (Figure 6.3 and Figure 6.4; Table 6.3). The concentration of Ni was found to be 3-fold higher and the Cr concentration was 13-fold higher than typical upper continental crust values (Table 6.3). These values agree with the concentrations of several trace elements in Bushveld Complex rocks near Rustenburg (known as Rustenburg Layered Suite), which are highly enriched compared to mean upper continental crust values, i.e. 22-fold for Cr and Ni, 12-fold for Cu and 5-fold for Co (Barnes and Maier, 2002).

In general, higher concentrations of trace elements both in sediments and SPM were observed at sampling point A compared to the other stations. This may be explained by its location just downstream of the Merensky Reef, (Figure 6.1) and therefore containing a significant fraction of eroded metal-rich particles. Lower trace metal concentrations were recorded in the SPM fraction than in the sediments at all the sampling stations, due to a higher proportion of non-detrital material (e.g. organic matter) as observed by the lower concentrations of Al and Fe in the SPM fraction (Figure 6.3 and Figure 6.4).

Figure 6.3 (see pag. 188): Major, minor and trace elements in each fraction of river sediments at sampling points A and B (A: upstream sampling point, away from mining areas; river has eroded Merensky Reef; and B: urban sampling point, the closest to mining area; river has crossed Rustenburg). Triangular diagram shows the grain-size distribution of each sample. [SPM= suspended particulate matter, ND= no data]

Figure 6.4 (see pag. 189): Major, minor and trace elements in each fraction of river sediments at sampling points C and D (C: intermediate sampling point; river near urban and mining area; and D: downstream sampling point; river has crossed urban and mining areas). Triangular diagram shows the grain size distribution of each sample. [SPM= suspended particulate matter, ND= no data]

Table 6.3: Concentrations of major, minor and trace elements in suspended particulate matter (SPM> 0.45 µm) and different size fractions (Silt & Clay <63 µm; fine-medium sand 63-500 µm; coarse sand 500-2000 µm) of river sediments at the Hex River sample points given in Figure 1. Average values for the upper continental crust and drill core near Rustenburg from Rudnick and Gao (2003) and Barnes and Maier (2002) respectively (data from PGE-rich layer are not included in the average).

Sample point	Fraction	FeO (%)	Al_2O_3 (%)	CaO (mg g^{-1})	MgO (mg g^{-1})	MnO (µg g^{-1})	V (µg g^{-1})	Cr (µg g^{-1})
A upstream	SPM	5.0	9.0	1.8	1.5	642	80	525
	silt & clay	10.9	28.1	-	-	-	134	1520
	fine-medium sand	5.5	14.4	-	-	-	69	1140
	coarse sand	6.5	14.3	-	-	-	102	1040
B urban	SPM	1.3	7.1	12.7	0.6	111	22	210
	silt & clay	4.3	19.2	-	-	-	60	1220
	fine-medium sand	3.3	13.2	-	-	-	53	1120
	coarse sand	2.6	9.4	-	-	-	46	519
C intermediate	SPM	1.6	18.2	51.5	6.2	238±83	17	77
	silt & clay	4.0	28.9	-	-	-	47	732
	fine-medium sand	2.5	28.1	-	-	-	47	1250
	coarse sand	3.3	25.8	-	-	-	73	361
D downstream	SPM	0.9	4.4	8.4	1.1	233	21	215
	silt & clay	4.3	17.0	-	-	-	87	1370
	fine-medium sand	2.5	10.8	-	-	-	99	3220
	coarse sand	2.6	10.2	-	-	-	70	1290
Upper Continental Crust		5.0±0.5	15.4±0.8	3.59±0.2	2.48±0.35	775±77	97±11	92±17
Rustenburg Layered Suite (*n=14-24*)		8.3±2.0	13.3±3.5	7.14±1.5	16.5±3.1	1140±160	92±15	2010±308
LGC6137	Values obtained	3.9	3.6	52.2	13.4	642	51.4	51.0
	Certified values	3.9±0.2	3.6±0.7	51.1±2.6	11.1±0.8	665±27	-	47±7
PACS-2	Values obtained	5.3±0.1	25.0±1.2	-	-	-	131±4	84.5±6.1
	Certified values	5.3±0.2	22.5±0.5	-	-	-	133±5	90.7±4.6

Values: mean value ± error (confidence interval 95%)

In agreement with these elevated concentrations of trace elements found in sediments and SPM of the Hex River, especially for Cr and Ni, Gzik *et al.* (2003) also observed Cr and Ni enrichment in agricultural and grassland soils in this area (on a farm 10 km east of Rustenburg);however, these high concentrations did not have an inhibitory influence on micro-organisms or the enzyme activity of soils, and no obvious influence on the health of animals was observed (Gzik et al., 2003).

Table 6.3 (cont): Concentrations of major, minor and trace elements in suspended particulate matter (SPM> 0.45 µm) and different size fractions (Silt & Clay <63 µm; fine-medium sand 63-500 µm; coarse sand 500-2000 µm) of river sediments at the Hex River sample points given in Figure 1. Average values for the upper continental crust and drill core near Rustenburg from Rudnick and Gao (2003) and Barnes and Maier (2002) respectively (data from PGE-rich layer are not included in the average).

Sample point	Fraction	Zn (µg g^{-1})	Cu (µg g^{-1})	As (µg g^{-1})	Co (µg g^{-1})	Ni (µg g^{-1})	Cd (µg g^{-1})	Pb (µg g^{-1})
A upstream	SPM	72.7	33.5	-	-	-	-	-
	silt & clay	130	77.3	4.9	62.9	399	0.1	45.1
	fine-medium sand	72.4	38.3	1.8	34.3	224	0.1	16.2
	coarse sand	113	49.9	3.8	51.9	244	0.1	24.5
B urban	SPM	11.5	5.8	-	-	-	-	-
	silt & clay	74.6	30.1	0.9	30.5	130	0.1	26.6
	fine-medium sand	40.4	7.7	0.6	31.5	96.2	0.0	5.4
	coarse sand	31.5	13.5	0.1	23.8	99.6	0.0	4.7
C intermediate	SPM	19	12.1	-	-	-	-	-
	silt & clay	47.3	34.7	1.6	27.6	123	0.1	28.0
	fine-medium sand	31.3	14.3	0.2	23.1	85.0	0.0	4.5
	coarse sand	63.9	20.2	0.6	39.3	151	0.1	4.3
D downstream	SPM	9.8	5.9	-	-	-	-	-
	silt & clay	50.5	25.0	1.0	32.4	107	0.0	34.1
	fine-medium sand	34.3	7.1	0.3	34.0	105	0.0	3.4
	coarse sand	23.8	11.0	1.5	24.7	77	0.0	5.3
Upper Continental Crust		5.0±0.5	67±6	28±4	4.8±0.5	17±1	47±11	0.09±0.01
Rustenburg Layered Suite (*n=14-24*)		8.3±2.0	-	328±123	< 0.5	79±15	1030±340	-
LGC6137	Values obtained	253.0	31.5	-	-	-	-	-
	Certified values	231±16	31.6±1.6	-	-	-	-	-
PACS-2	Values obtained	374±14	291±21	30.8±3.6	11.4±0.6	41.2±4.2	1.9±0.5	182±10
	Certified values	364±23	310±12	26.2±1.5	11.5±0.3	39.5±2.3	2.1±0.2	183±8

Values: mean value ± error (confidence interval 95%)

6.3.3 PGE concentrations

Sediment samples from the Hex River showed the weighted average PGE concentration of 14±10 ng g^{-1} being the individual concentrations of Pt 4.8±2.9 ng g-1, Pd 7.3±6.2 ng g^{-1}, Rh 1.4±0.7 ng g^{-1} and Ir 0.54±0.13 ng g^{-1} (Table 6.4, Figure 6.3 and Figure 6.4). In terms of the spatial distribution of the respective platinum group elements, sampling point A showed, in general, the highest weighted average for each element (9.0±0.6, 15.7±1.1, 2.4±0.0 and

0.68±0.01 ng g^{-1} for Pt, Pd, Rh and Ir, respectively) followed by sampling point B~C~D (Table 6.4). Concentrations of PGEs in silt and clay at each sampling point (A: 55.2±5.7, B: 98.1±35.7, C: 47.1 and D: 42.0±2.9 ng g^{-1}, Table 6.4) were always higher than the average values (14±10 ng g^{-1}). These values indicate a PGE enrichment with respect to the upper continental crust concentrations of 10, 15, 23 and 29 times for Pt, Pd, Rh and Ir, respectively (Wedepohl, 1995; Peucker-Ehrenbrink and Ravizza, 2000), but are lower than the concentrations reported by Barnes and Maier (2002) for a drill-core sample of the rocks near Rustenburg, without considering the PGE ore layers (Table 6.4).

PGE-rich layers in the Bushveld Igneous Complex are associated with chromitite, e.g. Cr-rich (and Cu-Ni-rich) rocks. In fact, PGE extraction and purification includes Ni by-products in many cases (Glaister and Mudd, 2010). Typical Cr-PGE correlation coefficients range between 0.829 (for Pt) and 0.946 (for Ir), except for Pd whose coefficient is 0.224 (Barnes and Maier, 2002). The PGE/Cr ratios reported in this study are consistent with those reported for other stream sediments (Wilhelm et al., 1997) and drill cores of the parent rock (Barnes and Maier, 2002) in the area (Figure 6.5). The highest PGE concentrations (Pt 35 ng g^{-1}) in river sediments reported in the Wilhelm et al. (1997) study are in line with elevated concentrations of Cu (77 µg g^{-1}), Ni (150 µg g^{-1}) and, especially, Cr (1 600 µg g^{-1}), but also of V (134 µg g^{-1}) and Co (54 µg g^{-1}). The recent study of Rauch and Fatoki (2013) also reported elevated values of Pt (12-698 ng g^{-1}), Cu (22-136 µg g^{-1}) and Cr (43-340 µg g^{-1}) in soils affected by the mining activities in the Bushveld Complex.

6.3.4 Impact of mining activities on PGE concentrations

As explained in the previous section, the soils and sediments of the Bushveld Complex are naturally enriched in PGEs and other elements (e.g. Cr, Ni) due to the presence of a mafic-ultramafic intrusion which contains about 75%, 52%, and 82% of the world's known resources of Pt, Pd, and Rh, respectively (Cawthorn, 2010). The presence of intensive mining and associated activities (e.g. processing plants, smelters) in the Bushveld Complex may lead to an anthropogenic increase in PGE concentrations over the –already– elevated background levels. Rauch and Fatoki (2013) demonstrated such anthropogenic enrichment for Pt in soils from the Bushveld Complex; accordingly, they found the highest concentrations of Pt in soils at a smelter (698±178 ng g^{-1}), while lower concentrations were recorded for processing plants, shafts and nearby towns. It was suggested that such contamination was derived from the emission of fine

Table 6.4: PGE concentrations in grain size fractions (silt & clay <63 µm; fine-medium sand 63-500 µm; coarse sand 500-2000 µm) of river sediments at the Hex River sample points given in Figure 1. Average values for the upper continental crust and drill core near Rustenburg (data from PGE-rich layer are not included in the average) (Wedepohl 1995; Peucker-Ehrenbrink and Jahn 2001; Barnes and Maier 2002).

Sample point	Fraction	PGE (ng g^{-1})	Pt (ng g^{-1})	Pd (ng g^{-1})	Rh (ng g^{-1})	Ir (ng g^{-1})
A upstream	silt & clay (*n=2)*	55.2±5.7	19.8±1.3	29.6±7.0	4.4±0.2	1.48±0.16
	fine-medium sand*	28.9	8.5	17.4	2.3	0.70
	coarse sand (*n=2)*	20.4±4.4	8.4±1.8	9.1±2.6	2.4±0.1	0.47±0.02
	Weighted average	-	*9.0±0.6*	*15.7±1.1*	*2.4±0.0*	*0.68±0.01*
B urban	silt & clay (*n=2)*	98.1±35.7	34±11.6	50.4±24.1	11.0±0.0	2.80±0.04
	fine-medium sand (*n=2)*	5.7±4.5	2.1±0.7	2.5±3.4	0.8±0.2	0.29±0.19
	coarse sand (*n=2)*	13.3±3.4	2.4±0.1	9.8±3.2	0.9±0.1	0.22±0.02
	Weighted average	-	*3.2±0.7*	*7.9±4.5*	*1.2±0.2*	*0.36±0.15*
C intermediate	silt & clay	47.1	12.8	27.4	5.4	1.46
	fine-medium sand (*n=2)*	6.4±0.1	3.0±0.1	2.0±0.0	1.0±0.0	0.28±0.03
	coarse sand (*n=2)*	10.2±6.0	3.2±0.5	5.6±5.4	0.8±0.2	0.75±0.83
	Weighted average	-	*3.4±0.3*	*4.5±2.7*	*1.0±0.1*	*0.54±0.42*
D downstream	silt & clay (*n=2)*	42.0±2.9	15.2±2.1	20.5±5.1	4.9±0.1	1.37±0.02
	fine-medium sand (*n=2)*	4.6±1.7	2.6±0.9	0.8±0.4	0.8±0.1	0.45±0.27
	coarse sand (*n=2)*	7.9±0.4	4.3±0.7	1.7±1.0	1.4±0.0	0.49±0.1
	Weighted average	-	*3.5±1.1*	*1.2±0.6*	*1.1±0.1*	*0.58±0.32*
Average values		14.1±9.5	4.8±2.9	7.3±6.2	1.4±0.7	0.54±0.13
Upper continental crust		-	0.51	0.52	0.06	0.02
Core from Rustenburg (*n=14-24*)		-	81±28	42±16	4.8±1.7	2.4±0.8

Values: mean value ± standard deviation

* one of the replicates presented interference problems and was rejected for the study.

Pt-rich particles from the smelters in the Bushveld Complex and, importantly, this atmospheric deposition was the main source of Pt in the local vegetation (Rauch and Fatoki, 2013).

The highest PGE concentration was observed to be in the silt and clay fraction at the sampling point closest to the mining areas (B: urban) with a Pt concentration similar to that reported in previous studies (34 ng g^{-1}, Wilhelm et al. 1997). Thus, although PGE minerals tend to occur naturally in the silt and clay fraction, most PGE minerals in the PGE-rich layers occur in grain sizes of less than 50 μm (Oberthür et al., 2004), atmospheric deposition of mining emissions also increases the Pt accumulation; Rauch and Fatoki (2013) reported that the Pt-rich particles in soils near mine activities are <125 μm. In addition, the PGE concentration decreases with increasing distance to the mining area.

In order to assess whether the atmospheric deposition of fine PGE-rich particles derived from the mining activities had an impact on the sediments of the Hex River, the ratios of the PGE concentrations in the silt and clay fraction (<63 μm) to the total, weighed-averaged concentrations (Table 6.4) were calculated (Figure 6.6). Since higher concentrations in the fine sediments compared to coarser fractions may be the result of a natural process (e.g. the smaller the particle, the larger the relative surface area and therefore increased adsorptive capacity), these ratios were also calculated for comparison with other relevant elements in this area (Cr, Ni, Cu). As observed in Figure 6.6, the PGE enrichment in the silt and clay fractions was clearly higher than for the other elements suggesting a source of PGE-rich fine particles in this area. The highest PGE enrichment was observed at sampling points B, C and D (Figure 6.6), which are situated close to or downstream of the mining activities and therefore are subject

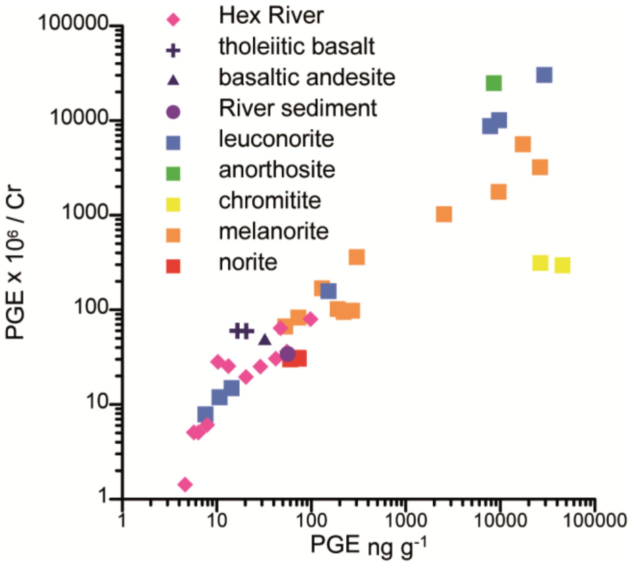


Figure 6.5: PGE/Cr vs. PGE ratios in Hex River (this study), river sediment (Wilhelm et al. 1997) and Impala Mine core (Barnes and Maier 2002).

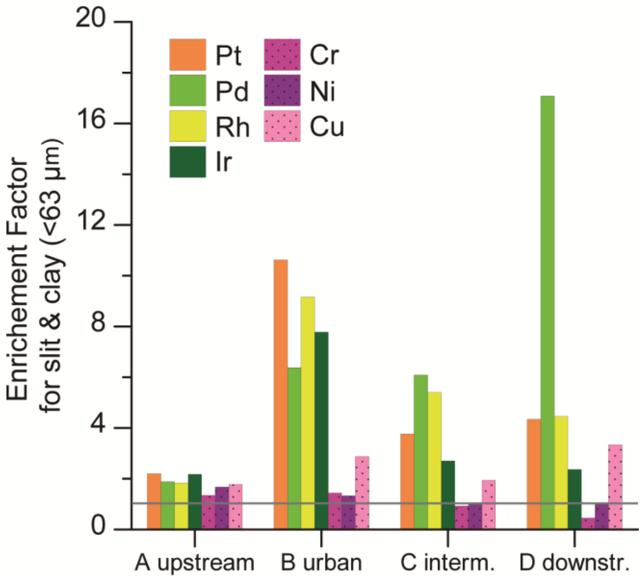


Figure 6.6: Enrichment factors for the silt and clay fraction, defined as the ratio of the element concentrations in the < 63 µm fraction to the weighted-average total fraction.

to a significant input of particles from direct deposition and surface runoff. In contrast, the location of sampling point A upstream of the mining activities and just after the river traverses the Merensky Reef could explain the lower enrichment in the fine fraction found, being less affected by surface runoff, and the higher PGE concentration in the sand and coarse sand fractions, due to the direct erosion of the PGE-rich layer.

6.4 Conclusions

The elevated concentrations of PGEs and other trace elements (Cr-Ni-Cu) found in sediments of the Hex River (South Africa) which traverses the Bushveld Igneous Complex, correspond mainly to natural levels in the parent rock. However, mining activities in the Bushveld Complex cause some disturbance of the surface PGE geochemical cycle. Accordingly, increased concentrations of PGEs in the silt and clay fraction (<63 µm) were observed, probably derived from atmospheric deposition and surface runoff of PGE-rich particles released from mining activities. This is especially relevant since this atmospheric deposition of PGE-rich particles in the Bushveld Complex is impacting the concentrations of PGEs in the local vegetation of this area

(Rauch and Fatoki, 2013), and therefore anincreased exposure of the local population to platinum group elements (Wiseman and Zereini, 2009; Rauch and Fatoki, 2013).

Based on the results reported in this and previous studies (Kaonga and Kgabi, 2011; Rauch and Fatoki, 2013) we propose that indicators such as airborne particulate matter, and soil and river sediments should be considered in protocols that evaluate the sustainability of mining activities in order to enhance the environmental quality and protect the local population.

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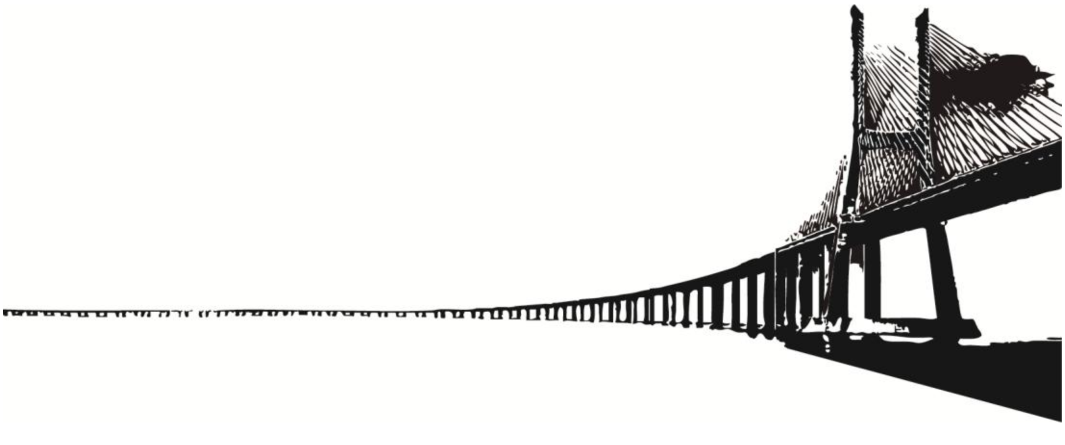
Chapter 7

Synthesis and general conclusions



Synthesis and general conclusions

This thesis reports an extensive study on the sedimentary behavior of Platinum Group Elements (PGEs) in anthropogenically-impacted sediments as well as their sources. Platinum group elements are amongst the rarest elements in the Earth crust –due to their siderophile characteristics–, although their concentrations in surface sediments are being increased because of their use in several human activities, especially catalytic converters.

Two different areas have been chosen to carry out the study:

a) The Hex River, that drains the largest mining area of PGEs, in the Bushveld Igneous Complex (South Africa),

b) The salt marshes of Tagus Estuary (W Iberian Peninsula), under different traffic pressures.

Hence, several objectives were proposed: (i) to improve the analytical methods for PGE determination, (ii) to ascertain the sedimentary behavior of PGEs and the processes that control their geochemistry, especially the presence of vegetation and the possible incorporation of PGEs to the biological tissues, (iii) to evaluate the anthropogenic contribution and the coupled PGE behavior after their emission, (iv) to describe the influence of salt marshes on the PGE geochemical cycle and (v) to assess the impact of mining activities on the surrounding areas. To achieve all these aims *trace-clean* techniques have been employed and the accuracy of the analytical procedures has been checked through all the work with certified reference materials.

7.1 Analytical improvements

This thesis constitutes an important progress in the analytical determination of different PGEs by the use of different methods. Consequently, natural and human-contaminated concentrations of PGEs have been reported using diverse methodologies.

Adsorptive cathodic stripping voltammetry was used for the measurement of platinum in different matrices applying the method developed by van den Berg and Jacinto (1988) and modified by Cobelo-García *et al.* (2011). A specific protocol of sample preparation and appropriated analysis conditions was established for interstitial waters and biological tissues. Besides, a new method to analyze rhodium by adsorptive cathodic stripping voltammetry was proposed, applying the second derivative transformation previously described by Cobelo-García *et al.* (2014). Also, negative thermal ionization mass spectrometry was used to analyze Os concentration and isotopic composition. In addition inductive coupled plasma mass spectrometry was applied for the analysis of sediment samples, after the use of a cation exchange column to remove interferences, in order to determine a pool of PGEs simultaneously. The optimization of the sample preparation (ashing temperature) was also performed.

Platinum and Os concentrations in interstitial waters were reported for the first time in the literature, making this thesis (and the resulting articles) a scientific reference for future studies on the geochemical cycle of PGEs. Moreover, some non-certified data of the most common reference material of PGEs, road dust BCR-723 and JSd-2, are also reported (e.g. Rh in JSd-2 by different methods).

7.2 The sedimentary behavior of platinum group elements from catalytic converters in the salt marshes

The behavior of different PGEs (especially Pt and Os) was studied in the salt marshes of Tagus Estuary (W Iberian Peninsula) under different traffic pressures. There, the role of vegetation is essential in the sedimentary behavior of Pt, because roots of halophytic plants control the geochemistry in the surrounding sediments (redox conditions, presence of O_2, organic matter degradation) that determine the chemical species in solid and dissolved phases. A clear relationship between dissolved Pt and Mn has been found in the interstitial waters of salt marshes, similar to the Pt-Mn relation found in Fe-Mn curst and nodules, that pinpoints to a co-precipitation/adsorbing/scavenging processes in the Mn-oxides formation. The Pt concentration in roots, that reflect the Pt concentration in interstitial waters at every moment, and the low translocation of Pt to the aerial tissues, indicate the lack of a real Pt-bioaccumulation and the Pt incorporation to the food chain.

Two different anthropogenic sources of PGEs exist in the Tagus Estuary salt marshes:

> -a regional PGEs source linked to human activities around Lisbon area including industrial activities or large scale traffic, affecting all the area and leading to a small, but significant, enrichment in PGEs respect to background concentrations (Pt/Os ~200)
>
> -a local PGEs source linked to traffic emissions, that causes a surface enrichment of Pt (also Rh) which affects only nearby the road/motorway (Pt/Os >> 200)

Thus, a decoupled behavior of the different PGEs in the environment is observed, specially of Os respect to the other PGEs, relative to both their sources and mechanisms of release and dispersion, as well as their different reactivity and mobility. Platinum remains associated to the sediments –its inertness does not favor the dissolution to the interstitial water–, defining sediments as an effective sink of anthropogenic Pt; while Os, that is emitted as gaseous OsO_4, exhibits a higher mobility, being exported to estuarine and oceanic waters. In fact, at least 20% of the Os that arrives to the Tagus estuary every year comes directly from salt marsh sediments. Besides, the Os released by salt marshes all around the world could reach the 40% of the oceanic Os input, making salt marshes a primary compartment in the cycle of Os. Consequently, this Pt-Os decoupling should be taken into consideration when using the Os isotope ratios for the reconstruction of the sources and contamination of platinum group elements in environmental matrices.

7.3 The influence of PGE mining activities in the surrounding aquatic environments

Although the elevated concentrations of PGEs (and other trace elements) in the sediments of mining rivers correspond mainly to the natural lithology of the area, the mining activities cause disturbances of the surface geochemical cycle of PGEs, like the increased concentrations in the silt and clay fraction (<63 µm) derived from atmospheric deposition and surface runoff. Thus, this atmospheric deposition could affect the local vegetation and crops and increase exposure of the local population to platinum group elements.

We propose that indicators such as airborne particulate matter, and soil and river sediments should be considered in protocols that evaluate the sustainability of mining activities in order to enhance the environmental quality and protect the local population.

As general conclusion, this thesis sheds light on the understanding of the biogeochemical cycles of PGEs and the disturbance that human development is causing on them. The prompt variation of natural conditions that ecosystems are suffering in the last decades has an important relevance in the coastal regions where environments are especially vulnerable to the global change. Therefore, we hope that all the conclusions drawn from this thesis could contribute to progress in the geochemical knowledge of the PGEs, as well as, to the improvement of the environmental management.

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