PhD Thesis 2019

Universidade Vigo

PLATINUM AND OTHER TECHNOLOGY-CRITICAL ELEMENTS:

BIOACCUMULATION AND BEHAVIOUR IN COASTAL SYSTEMS

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TESE DE DOUTORAMENTO

Platinum and other Technology-Critical Elements: Bioaccumulation and Behaviour in Coastal Systems

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Ano:

2018

"Mención Internacional"

Juan Santos Echeandía e Antonio Cobelo García

FAN CONSTAR que a presente tese doutoral tradicional con artígos, titulada "Platinum and other Technology–Critical Elements: Bioaccumulation and Behaviour in Coastal Systems", que presenta Patricia Neira del Río, foi elaborado baixo a súa dirección no programa de doutoramento "Ciencias mariñas, tecnoloxía e xestión (Campus do Mar)" interuniversitario das Universidades UVigo, UdC, USC, Aveiro, Tras os Montes Alto Douro e Minho.

Vigo 5 de decembro 2018.

Os Directores da tese de doutoramento

Juan Santos Echeandía   Antonio Cobelo García

Ao meu pai

Gustaríame comezar agradecendo a tódalas persoas que, dun xeito ou doutro, fixeron posible esta tese, tanto pola súa contribución académica e profesional como polo seu apoio moral.

Primeiro agradecer aos meus directores de tese. Grazas ao Dr. Juan Santos Echeandía, por dirixirme a pesares da distancia, por estar sempre a miña disposición e polo seu consello sen o cal a elaboración desta tese tería sido moito máis difícil. Grazas ao Dr. Antonio Cobelo García, pola súa sabedoría, experiencia e apoio que foron fonte de inspiración para este traballo. Tamén agradecer ao resto de membros do departamento de Bioxeoquímica Mariña, Dr. Ricardo Prego e a Susana Calvo, por axudarme en todo canto puideron e máis.

Agradecer ao Campus do Mar polo programa de doutoramento e por permitirme formar parte do mesmo. Especialmente á miña Comisión de Seguimento, formada polo Dr. Óscar Nieto Palmeiro e o Dr. Armando Costa Duarte, que seguiron este proceso de cerca e contribuíron a el coa súa visión e palabras de alento.

Durante o desenvolvemento desta tese tamén puiden gozar de estancias de investigación que gardo na memoria con agarimo. *Merci beaucoup* ao Dr. Jörg Schäfer por recibirme na Universidade de Bordeaux e por brindarme a oportunidade de aprender ó seu carón. Agradezo a tódalas persoas que contribuíron a facer da miña estancia en Francia unha grata experiencia. *Muito obrigada* ao Dr. Miguel Caetano do IPMA de Lisboa, así como a todo o seu equipo, por acollerme no seu laboratorio e axudarme neste camiño. Foi un pracer poder contar co voso impulso e colaboración, espero que nos podamos volver a encontrar de novo.

Tamén agradecer ó Instituto Español de Oceanografía, especialmente á Dr. Victoria Besada e o Dr. Juan Bellas, pola súa contribución ó desenvolvemento desta tese. Grazas a todos os meus compañeiros e compañeiras do Instituto de Investigacións Mariñas e da Universidade de Vigo polo seu apoio, colaboración, palabras de estímulo e momentos de relax.

E por último, pero non menos importante, agradecementos para a miña familia e amizades. Á miña nai polo seu apoio incansable e perseveranza que son un exemplo para min. Grazas aos que se toparon comigo algunha vez polo camiño e dalgunha maneira axudaron a alimentar a miña curiosidade. Grazas polas mostras de preocupación pola evolución desta tese, polos ánimos e por axudarme a facelo todo máis sinxelo.

Con agarimo, moitas grazas.

Patricia Neira del Río

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RESUMO

Esta tese pretende mellorar a comprensión do ciclo bioxeoquímico dun conxunto de elementos considerados críticos e esenciais para o desenvolvemento de novas tecnoloxías, especialmente os coñecidos como elementos do grupo platino (PGE, siglas en inglés) e do propio platino máis concretamente. O obxectivo é describir o impacto que teñen as actividades humanas sobre os niveis e a distribución destes elementos traza no medio ambiente mariño.

Os ecosistemas están actualmente suxeitos a procesos de cambio global, e no presente traballo centrámonos nas perturbacións das condicións naturais nos ciclos bioxeoquímicos debido ao impacto das actividades humanas enfocándoo na zona costeira. Esperamos que as conclusións acadadas nesta tese de doutoramento contribúan a coñecer como o uso destes metais nas novas tecnoloxías pode ter un impacto nas súas concentracións ambientais.

O obxectivo principal desta tese doutoral é, polo tanto, a avaliación dos factores que controlan os cambios nas concentracións ambientais de elementos denominados críticos para as novas tecnoloxías (TCEs, siglas en inglés) como as terras raras (REEs, siglas en inglés), o talio (Tl) ou o niobio (Nb); con especial atención ao platino (Pt) e a outros elementos de importancia tecnolóxica como uranio (U), antimonio (Sb), torio (Th), volframio/tungsteno (W), prata (Ag) ou ouro (Au) que foron pouco estudados ata o de agora, dende o punto de vista da bioacumulación en organismos mariños.

Centrámonos nestes elementos porque, en xeral, e con algunhas excepcións específicas, atópanse excluídos dos programas de seguimento ambiental a nivel mundial debido ás súas baixas concentracións naturais, xeralmente por debaixo dos límites de detección da maioría dos procedementos analíticos utilizados. e a ausencia dun papel industrial significativo no pasado, sen aparentes implicacións ambientais que poidan facelos perigosos para os ecosistemas. Non obstante, esta situación está a mudar actualmente, xa que moitos destes compostos químicos "menos estudados" son agora compoñentes esenciais para o desenvolvemento das novas tecnoloxías. O impacto ambiental e sobre os ciclos bioxeoquímicos, provocados polo crecente uso antropoxénico destes elementos "pouco estudados" necesita, polo tanto, ser avaliado con máis detalle.

Temos partido a tese en dous grandes bloques:

(i) A acumulación de platino – como contaminante emerxente – no medio mariño tanto en sedimentos como en organismos.

O estudo destes diferentes compartimentos ambientais pódenos dar unha idea da súa taxa de acumulación e a súa biodispoñibilidade para os organismos mariños. Para isto, realizouse a análise das concentracións en sedimentos superficiais (cores de 35–60 cm de profundidade) e unha serie temporal de mexillóns para o estudo do impacto do platino como un contaminante emerxente no medio mariño.

Centrámonos no platino como un contaminante emerxente porque se observou que certas actividades antropoxénicas baseadas no uso deste metal, principalmente os convertedores catalíticos dos automóbiles, causaron un aumento nas concentracións ambientais de platino. Dende a introdución a mediados da década dos 80s destes convertedores catalíticos nos automóbiles, houbo un aumento nas concentracións de platino no medio ambiente, provocando un crecente interese por coñecer os perigos potenciais e o ciclo bioxeoquímico deste metal Os convertedores catalíticos utilizan o platino como compoñente activo, este platino é erosionado da superficie do catalizador e posteriormente emitido a través do tubo de escape. O platino tamén pode entrar nos ecosistemas por outras vías de emisión como a elaboración de xoias ou procesos industriais, como en industrias electrónicas, químicas, de refinación de petróleo ou de fabricación de vidro, e tamén a través de augas residuais en instalacións médicas, posto que o platino é usado en ligas para odontoloxía e en medicamentos para o tratamento do cancro.

O coñecemento sobre o ciclo do platino é limitado, debido primeiro á dificultade que existe para a súa determinación, xa que se atopa en concentracións ultra–traza (por baixo de 1 ng/g) na natureza, e segundo porque non foi ata recentemente que comezou a ser utilizado e emitido en cantidades significativas para o medio ambiente e, polo tanto, espertou o interese por parte da sociedade. A determinación do platino nas mostras ambientais é un desafío dende o punto de vista analítico, xa que require métodos de detección moi sensibles e técnicas de mostraxe e análise ultra–limpas para evitar a súa contaminación. Outro problema engadido á hora de analizar platino é a falta de materiais de referencia axeitados para a análise de mostras reais, xa que as que existen claramente superan os niveis que podemos atopar na natureza. Debido a esta gran complexidade hai poucos estudos sobre platino en mostras naturais coas correspondentes respostas naturais nos ecosistemas costeiros.

Este bloque está dividido en tres partes:

1. Avaliación da contaminación de platino nos ambientes de deposición mariños e estuarinos, con testemuñas de sedimento recollidas na desembocadura do río Texo e o seu pro–delta (en Lisboa (Portugal), ao oeste da

Península Ibérica). O obxectivo é poder estudar a evolución temporal do platino depositado en ambientes mariños e estuáricos.

Observamos que a concentración de platino no sedimento superficial do estuario aumenta a medida que nos achegamos a áreas onde o tráfico de vehículos é elevado en comparación cos niveis naturais da litosfera, e diminúe na parte inferior das testemuñas de sedimento, indicando a ausencia de contaminación significativa antes da introdución dos convertedores catalíticos nos automóbiles. Os niveis máis altos das primeiras seccións das testemuñas de sedimento demostran que a existencia de contaminación nos sedimentos é debido á actividade antropoxénica na zona.

Mentres tanto, as mostras no pro–delta mostran outro resultado, non se observa un máximo en superficie, xa que por ser unha zona sen presión antropoxénica está sometida aos patróns de circulación oceánica. A concentración máxima de platino, no entanto, atópase ao final da capa de mestura e un segundo máximo ao final da capa re–mestura do material. O motivo é que, dado que se trata dun medio mariño non influído antropoxénicamente, existen outros factores que controlan a distribución do platino, como o potencial redox, o que suxire a existencia de mobilidade post–deposicional do platino que pode esvaecer a contaminación que se concentra na zona superficial característica dos ecosistemas costeiros suxeitos á influencia das actividades humanas.

2. Revisión bibliográfica sobre a acumulación dos elementos do grupo de platino (platino, paladio, rodio, osmio, rutenio e iridio) en organismos mariños e terrestres salvaxes. Ademais, realizouse unha revisión crítica das obras existentes, destacando as limitacións e as dificultades atopadas.

Todos os elementos do grupo de platino (PGEs) teñen características físicas e químicas similares que os fan necesarios para moitas tecnoloxías emerxentes, como a súa resistencia á corrosión sobre un amplo rango de temperaturas, alto punto de fusión, elevada resistencia mecánica, boa ductilidade e excelentes propiedades catalíticas. Os máis utilizados e de maior importancia económica son platino, paladio e rodio, polo que a maioría dos estudos se centran neles.

Esta revisión bibliográfica enfocámola sobre estudos dos elementos do grupo de platino en organismos vivos, tanto vexetais como animais, e en ambientes tanto mariños coma terrestres. Ademais, compiláronse estudos sobre as súas fontes de emisión, as transformacións fisicoquímicas que sofren tras a súa difusión ao medio ambiente e as limitacións no estudo destes metais, debido á necesidade de técnicas analíticas moi sensibles para a detección de trazas e a falta de materiais de referencia aptos para a análise de mostras biolóxicas.

A vexetación é o primeiro elo da cadea alimentaria, polo que a acumulación de contaminantes nestes organismos será o primeiro paso para a súa transferencia a través da cadea alimentaria. Atopamos altas concentracións de PGEs nas plantas atopadas na beira das estradas e autoestradas, especialmente paladio, que é o máis biodispoñible para as plantas, seguido de rodio e platino. En termos de vexetación acuática, a exposición a PGEs prodúcese principalmente pola escorrenta do po das estradas, e pode afectar diferentes especies en función das condicións do medio acuático (pH, materia orgánica, etc.). Hai poucos estudos sobre PGEs na fauna salvaxe, a maior parte dos traballos describen experimentos executados no laboratorio. Os que existen mostran que os PGEs poden ser asimilados pola fauna e acumulados nos tecidos. Do mesmo xeito que nas plantas, os organismos adoitan acumular principalmente paladio, seguido de rodio e platino.

Ao levar a cabo esta revisión bibliográfica decatámonos de que hai poucos traballos sobre os efectos ambientais e o destino dos PGEs na natureza e poucos datos sobre as concentracións naturais en ambientes non perturbados polo home. En futuros estudos débese prestar máis atención ás concentracións e transformacións na natureza para saber cando estes elementos poden ser biodispoñibles para os organismos. O noso coñecemento sobre as transformacións, especiación e biodispoñibilidade destes metais é limitado. Aínda que estes elementos atópanse principalmente na natureza en forma inerte, non podemos ignorar o feito de que actualmente as cantidades emitidas están a aumentar e que unha fracción destas emisións é absorbida e acumulada por plantas e animais.

3. Estudo da transferencia e acumulación de platino nos organismos mariños a través da análise dunha serie temporal (1991–2011) de mexillóns recollidos na praia urbana de Samil (Vigo (España) ao noroeste da Península Ibérica) e a súa comparación con organismos procedentes dunha zona libre de contaminación. O obxectivo é determinar a variación temporal na adquisición biolóxica do platino durante as últimas dúas décadas e definir a posible relación entre esta variación temporal na acumulación de platino polos mexillóns e o uso antropoxénico deste elemento durante ese período de tempo.

As emisións antropoxénicas de platino ao medio ambiente aumentaron significativamente durante as últimas décadas, especialmente despois da incorporación dos convertedores catalíticos nos automóbiles. Para comprobar se isto afecta aos niveis deste metal en organismos vivos, analizamos o tecido muscular dunha serie de 20 anos de mexillóns recollidos nunha praia urbana na cidade de Vigo. Os mexillóns son organismos ideais para o seu uso como bioindicadores xa que ó ser organismos filtrantes adoitan acumular as sustancias presentes na auga. Os mexillóns, ademais, son abundantes na área de estudo e son fonte principal de alimento para peixes e outros depredadores, permitindo a entrada de platino na cadea alimentaria.

A acumulación de platino na área urbana de mostraxe (Samil, Vigo) excede o valor obtido a partir da análise do tecido de mexillóns da mesma especie recollidos nun punto de control distante de actividades humanas importantes e vai acompañado dunha diminución da concentración de chumbo, metal historicamente asociado á contaminación causada polos vehículos a motor. Ademais, a acumulación de platino nas mostras segue unha tendencia temporal significativa e correlacionada coa demanda europea de platino para os catalizadores de automóbiles, e de forma máis significativa coa venda de autos na Península Ibérica, principal fonte de emisión de platino antropoxénico. Isto demostra que o platino se está a acumular en organismos debido á actividade humana.

(ii) Estudo dos elementos denominados "críticos para tecnoloxías", TCEs.

Dentro deste grupo inclúense os elementos coñecidos como terras raras (lantano, cerio, praseodimio, neodimio, samario, europio, gadolinio, terbio, disprosio, holmio, erbio, tulio, iterbio e lutecio), así como niobio, talio, tántalo e galio, xermanio, indio e telurio (Cobelo-García et al., 2015). Omitimos os elementos do grupo de platino porque xa nos referimos a eles na primeira parte da tese.

Dous factores determinan cando un elemento pode considerarse tecnolóxicamente crítico: que sexa necesario e esencial para o desenvolvemento de certas tecnoloxías de gran importancia, como a tecnoloxía da información, as telecomunicacións ou as enerxías renovables, e que sexa escaso na codia terrestre, difícil de acadar ou que o seu abastecemento estea suxeito a cambios xeopolíticos. O impacto debido á crecente extracción destes elementos aínda non foi avaliado e/ou non ten unha lexislación adecuada en relación aos niveis perigosos ou nocivos no ambiente, xa que non foi ata hai pouco que comezou a súa explotación masiva, a súa comercialización e o seu uso en diferentes tecnoloxías emerxentes.

Coa notable extracción que se está a levar a cabo na actualidade, e a súa conseguinte remobilización no medio ambiente, os ciclos bioxeoquímicos destes elementos "menos estudados" están sendo alterados. Como no caso do platino, a análise dos elementos considerados críticos para as novas tecnoloxías supón unha serie de problemas debido ás concentracións ultra–traza ás que podemos atopar estes elementos na natureza, para o cal é necesario un método analítico moi sensible que fai a súa análise máis complicada, lenta e con requerimentos técnicos de mostraxe e análise ultra–limpos co fin de evitar a contaminación das mostras. Actualmente existe a urxente necesidade de estudar o impacto das actividades humanas sobre os ciclos bioxeoquímicos dos TCEs, a fin de comparar as concentracións ambientais suxeitas a presións antropoxénicas con aqueles que reflicten os valores naturais en áreas prístinas, e crear unha base de datos que poida ser utilizada en futuros estudos, xa que se espera que esta extracción continúe a aumentar en todo o mundo e, polo tanto, os niveis destes TCEs no medio ambiente.

Temos abordado esta segunda parte da tese en dúas partes:

1. Revisión bibliográfica da información existente nos definidos anteriormente como elementos críticos para as novas tecnoloxías, con especial atención ás concentracións en augas e organismos mariños en ecosistemas naturais.

É conveniente lembrar que estes elementos xeralmente están excluídos dos programas oficiais de seguimento ambiental ou de biomonitoreo, como a Directiva Europea Marco sobre a Auga (2000/60/CE) ou a Directiva Marco de Estratexias Mariñas (2008/56/CE). Pero actualmente, co desenvolvemento industrial, o uso destes elementos "menos estudados" está a intensificarse, xa que son compoñentes clave das novas tecnoloxías, como as pantallas de cristal líquido, os sistemas de telecomunicacións ou as enerxías renovables (solar, eólica, etc.). Polo tanto, o impacto ambiental do crecente uso antropoxénico dos TCEs debe ser avaliado en profundidade.

Hai unha gran falta de datos sobre a bioxeoquímica, a bioacumulación e a toxicidade destes elementos. É necesario determinar as concentracións naturais de TCEs en augas e organismos antes de que os ecosistemas se vexan contaminados. Para concluír se permanecen inertes ou son adquiridos polos seres vivos, debemos coñecer o seu fraccionamento no medio acuático, xa que non todas as especies se comportan da mesma forma ou teñen o mesmo grado de toxicidade.

Xeralmente, nas augas oceánicas, a concentración aumenta coa profundidade, pero nas augas costeiras podemos observar un máximo superficial que diminúe ata alcanzar un valor máis ou menos estable en augas máis profundas. Hai poucos estudos que reflicten as concentracións naturais dos TCEs nos organismos mariños, polo que é difícil sacar conclusións. De xeito xeral, as especies de fitoplancto, zooplancto e algas acuáticas mostran maiores concentracións que especies de crustáceos, moluscos ou peixes.

2. Estudo da acumulación de TCEs nunha serie temporal (1991–2014) de mexillóns recollidos na praia urbana de Samil (Vigo (España) ao noroeste da Península Ibérica), para estudar como a influencia antropoxénica e os cambios nas condicións hidrográficas afectan a absorción destes "contaminantes emerxentes" por parte de organismos.

Non atopamos diferenzas estatísticamente significativas entre o punto de estudo e a zona de control nas concentracións de terras raras, niobio, antimonio, volframio/tungsteno, talio, bismuto, torio ou uranio; polo que non hai evidencia de impacto antropoxénico na zona para estes elementos.

Só dous elementos amosan unha clara caída temporal nas súas concentracións: a prata e o ouro. No caso da prata, hai documentación sobre contaminación de prata nos ecosistemas acuáticos no pasado debido ao uso deste metal en películas fotográficas, actualmente dado o desenvolvemento da fotografía dixital a demanda de prata caeu e, polo tanto, a súa presenza no medio ambiente e, consecuentemente, nos organismos. En canto ao comportamento do ouro, presentamos dúas explicacións: influencia da actividade mineira no pasado na zona ou debido tamén ao seu uso no proceso fotográfico.

Aínda que non temos ningunha evidencia do impacto da actividade humana sobre os elementos coñecidos como Terras Raras, atopamos un comportamento deste grupo que vale a pena destacar. Ao normalizar as terras raras coa auga do Atlántico Norte observamos unha tendencia temporal de partición dos elementos, con un maior enriquecemento en terras raras lixeiras (lantano, cerio, praseodimio e neodimio) en mexillóns sobre pesadas (terbio, disprosio, holmio, erbio, tulio, iterbio e lutecio). Por estudos previos sabemos que as especies acuáticas tenden a asimilar mellor as terras raras cando están na súa forma libre e cando están a formar complexos con outras especies. Usando un modelo de equilibrio químico reparamos en que baixo calquera circunstancia de cambio natural do pH ou concentración de carbonatos dentro da ría, sempre hai unha maior proporción de terras raras lixeiras libres, mentres as pesadas adoitan formar compostos coas especies disolvas na auga do mar Debido a esta fracción máis elevada de lixeiras libres con respecto a pesadas libres, e sendo este o xeito máis favorablemente asimilado polos organismos, os mexillóns tenderán a estar enriquecidos en terras raras lixeiras no canto de a terras raras pesadas.

Do mesmo xeito a nosa serie tempo mostra que non só os mexillóns están a acumular máis terras raras lixeiras que pesados, senón que esta proporción está aumentando significativamente ao longo do tempo. Hai determinadas variables que poden influír na especiación química das terras raras na auga do mar como a salinidade ou o pH. Entre as diversas variables químicas do medio, nos centrámonos na concentración de carbonatos. A Ría de Vigo é unha área suxeita a eventos *upwelling*, nos que entra auga do océano que trae consigo altas concentracións de carbonatos, aumentando así a proporción de terras raras lixeiras libres respectando a pesadas libres. Se empregamos a cantidade de auga oceánica que está a entrar na ría como un indicador indirecto da concentración de carbonatos que entra no sistema, obtemos unha correlación significativa co cociente de terras raras lixeiras e pesadas acumulado nos organismos estudados. Con isto podemos concluír que a distribución de terras raras nos tecidos do mexillón reflicte os cambios hidrográficos, como o aumento que se está a producir de entrada de auga do océano na ría ao longo dos últimos anos.

Esta tese desenvolve un pouco máis o coñecemento que temos sobre o ciclo bioxeoquímico de elementos non estudados comunmente ou non incluídos nas estratexias de contaminación ambiental, e como a influencia humana e os cambios nas condicións oceanográficas inflúen nestes ciclos. O ecosistema costeiro é especialmente vulnerable ás alteracións no medio natural debido aos efectos do cambio global, e neste traballo centrámonos principalmente nos cambios que se produciron nas últimas dúas décadas en organismos e sedimentos mariños. Espérase que as conclusións obtidas teñan un impacto no progreso da xestión ambiental e na comprensión do ciclo bioxeoquímico destes elementos críticos para as novas tecnoloxías.

OVERVIEW

The main objective of this doctoral thesis is the evaluation of the factors controlling the changes in the environmental concentration of the **Technology Critical Elements (TCEs)** with especial attention to **platinum (Pt)** from different points of view:

(i) Platinum is accumulated – as an emerging metallic contaminant - in marine environment in both sediments and organisms. The study of those environmental compartments can give us an idea of its rates of accumulation and bioavailability for marine organisms. Through the analysis of its concentration in recent sediments and time series of marine organisms we study the impact of platinum as an emerging contaminant. We have three parts for this section:

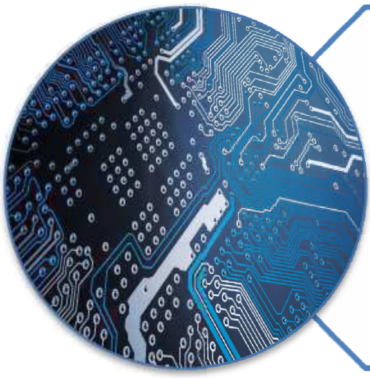
1. Bibliographic review of platinum bioaccumulation in marine organisms.
2. Evaluation of the contamination of Pt in coastal depositional environments, sediments from cores collected at the mouth of the Tagus River and its pro-delta (W Iberian Peninsula), to understand how the changes on Pt concentration may be influencing these environments.
3. Study on how Pt can be transferred and accumulated in marine organisms, with analysis of a time series (1991-2011) of mussels in the urban beach of Samil (Vigo, NW Iberian Peninsula) and its comparison with mussels collected from a pristine area.

(ii) The study of Technology Critical Elements (TCEs) group, we have considered as TCEs: Rare Earth Elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), niobium (Nb), thallium (Tl), tantalum (Ta), gallium (Ga), germanium (Ge), indium (In) and tellurium (Te), and omitted de Platinum Group Elements (PGEs) as we have referred to them in the first part of the thesis. Two factors determine when an element can be referred as technology-critical: they are necessary and indispensable for certain emerging technologies of great importance (information technology, telecommunications or green energy technologies) and they are scarce in the Earth's crust or hard to obtain. The impact of the increasing extraction of these elements has not been yet evaluated nor have an appropriate legislation on what levels can be dangerous or harmful, since it has not been until now when they have started to be massively extracted, traded and utilized in the so–called new emerging technologies. We have addressed this issue in two parts:

1. Bibliographic review of TCEs in the marine environment, special attention to concentrations in water and organisms in natural systems.
2. Study on the accumulation of TCEs on a time series (1991-2014) of mussels from an urban beach in Vigo (NW Iberian Peninsula), to study the anthropogenic influence and the changing hydrographical conditions on the accumulation trend of these less-studied trace elements.

PART I Introduction
Chapter 1. Comprehensive Introduction

PART II Platinum bioaccumulation and behaviour in coastal systems
Chapter 2. Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal)
Chapter 3. A critical review on Platinum Group Elements levels and dynamics in natural living organisms
Chapter 4. Evidence of increased anthropogenic emissions of platinum: Time-series analysis of mussels (1991-2011) of an urban beach



PART III Technology-Critical Elements bioaccumulatin and behaviour in coastal systems
Chapter 5. A critical review on Technology Critical Elements behaviour and concentrations in oceans and marine organisms
Chapter 6. Temporal trends of the accumulation of less-studied trace elements (including TCEs) in mussels from an urban beach coastal area (1991-2014): Anthropogenic incluence vs. changing hydrographical conditions

PART IV Conclusions
Chapter 7. General Conclusions

AIMS AND SCOPE

The thesis aim is to answer the following questions:

- Is there evidence of increased Pt in the environment?
- Is it accumulated and assimilated by organisms?
- What about TCEs on marine systems?

We try to respond to the behaviour of the platinum in natural ecosystems and to evaluate its sources of emission, especially from human origin, through the following specific objectives:

- The determination of concentrations of Pt in biological matrices, including the background level without anthropogenic pressure.
- The improvement of the knowledge of their sedimentary behaviour and the postdepositional processes in an estuary.
- The analysis of some TCEs in organisms and comparison between two different areas.

This thesis attempts to improve the understanding of the biogeochemical cycle of Pt and TCEs and to describe the impact of human activities on these trace elements. The ecosystems are currently changing due to global change, especially in coastal regions. We hope that the conclusions reached in this thesis can contribute to a better management of the risks that elevated concentrations of these elements may have for human health and the environment.

PART I

INTRODUCTION

Chapter 1 – Comprehensive Introduction

1.1. Brief introduction to marine biogeochemistry

1.2. Platinum Group Elements

1.3. Platinum

1.3.1. Sources and anthropogenic uses of platinum
1.3.2. The cycle of platinum and post–depositional processes
1.3.3. Determination of platinum: strengths and weaknesses
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REFERENCES

1. Comprehensive Introduction

1.1. Brief introduction to marine biogeochemistry

Biogeochemistry studies the physical, biological, geological and chemical processes and reactions of every chemical component found on the Earth's crust and living organisms (Bashkin, 2002). In particular, it is the study of the cycles of chemical elements and compounds, including their spatial distribution, sources and sinks, and their interaction and incorporation into biota (Butcher et al., 1992). The study of this discipline is necessary to understand the functioning of all living organisms, from the level of cellular organization to ecosystems, and to understand many of the current problems such as global change or environmental pollution (Bashkin, 2002). Marine biogeochemistry focuses, therefore, on the cycling of the chemical elements and their compounds in the oceans and the impact that human activities may have disrupting the natural conditions.

The biogeochemical cycles of major elements such as carbon, nitrogen, sulphur or phosphorus and also several trace elements (e.g. Fe, Cu, Zn, Cd) are at present well understood; however, for other trace elements (including most of the PGEs and TCEs) due to their extremely low concentrations and no previous anthropogenic use, have not gained especial attention so far. However, this situation is now changing due to the increase on its use in a variety of technologies. Therefore, their environmental aspects such as their sources, sinks, internal cycling and chemical speciation now deserve more studies to be conducted (Cobelo-García et al., 2015). This doctoral thesis, tries to investigate further on the factors that controls the Biochemistry of platinum in the marine environment.

1.2. Platinum Group Elements

Platinum Group Elements (PGEs) (Figure 1.1) include platinum (Pt), palladium (Pd), rhodium (Rh), osmium (Os), iridium (Ir), and ruthenium (Ru). These elements are among the least abundant in the Earth's crust (average abundance <1 ng/g) (Rudnick and Gao, 2003); average concentrations in the upper continental crust is shown on Table 1.1.

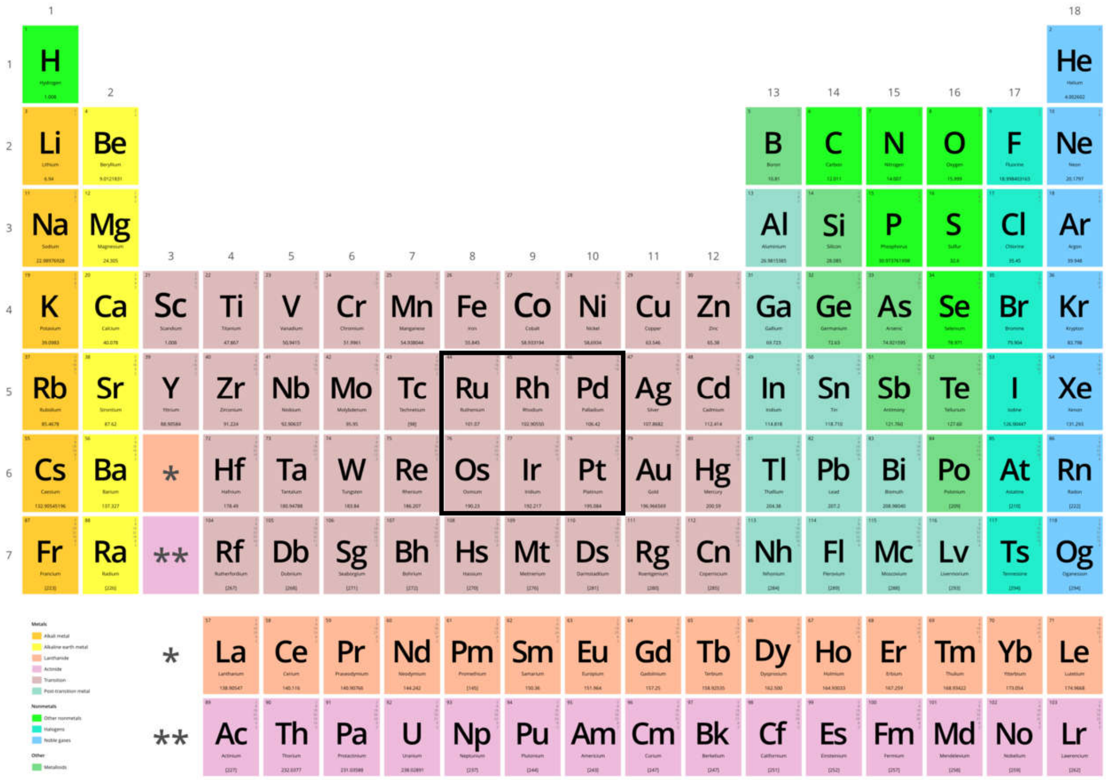

Figure 1.1. Periodic table of elements where the Platinum Group Elements are highlighted

These elements tend to occur together in the same ore deposits and are difficult to separate from each other (Harris and Cabri, 1988). They also have similar physical and chemical properties like high mechanical strength, good ductility, resistance to chemical corrosion and oxidations, and also have important catalytic properties (Sobrova et al., 2012). These properties joined with their low abundance make PGEs critical to emerging technologies. The uses are diverse, including e.g. catalytic converters for exhaust control of greenhouse gases in vehicles, catalyst for chemical process facilities like oil refineries, electronic components, jewellery and medical uses.

Table1.1. Relative abundances (ng/g) of Platinum Group Elements in the upper continental crust.

Element	Concentration	Reference
Pt	0,51	Peucker-Ehrenbrink and Jahn 2001
Pd	0,52	Peucker-Ehrenbrink and Jahn 2001
Rh	0,06	Wedepohl, 1995
Os	0,03	Peucker-Ehrenbrink and Jahn 2001
Ru	0,21	Peucker-Ehrenbrink and Jahn 2001
Ir	0,02	Peucker-Ehrenbrink and Jahn 2001

1.3. Platinum

In this doctoral thesis we focused on platinum because it has been observed that certain anthropogenic activities that use Pt, with special relevance in catalytic converters for automobiles, are causing an increase in Pt concentrations in the environment. Several studies have shown that environmental Pt concentrations are subject to significant anthropogenic disturbance, including sediment samples from an urban lake (Rauch et al., 2004), roadside grass (Lesniewska et al., 2004; Hooda et al., 2007; Akrivi et al., 2012), tree bark (Becker et al., 2000; Ma et al., 2001), plants (Djingova et al., 2003), feathers of birds (Jensen et al., 2002) and freshwater species (Moldovan et al., 2001; Haus et al., 2007). Pt levels have been studied on risk population such as nursing staff (Nygren and Lundgren, 1997), traffic police officers (Iavicoli et al., 2004) or tram drivers (Iavicoli et al., 2007) due to its toxicity and possible interference with metabolic processes (Rauch and Morrison, 1999). According to (Sen and Peucker-Ehrenbrink, 2012) the flux of Pt at the Earth's surface is among the most disturbed by anthropogenic activities with respect to its natural flux (Figure 1.2).

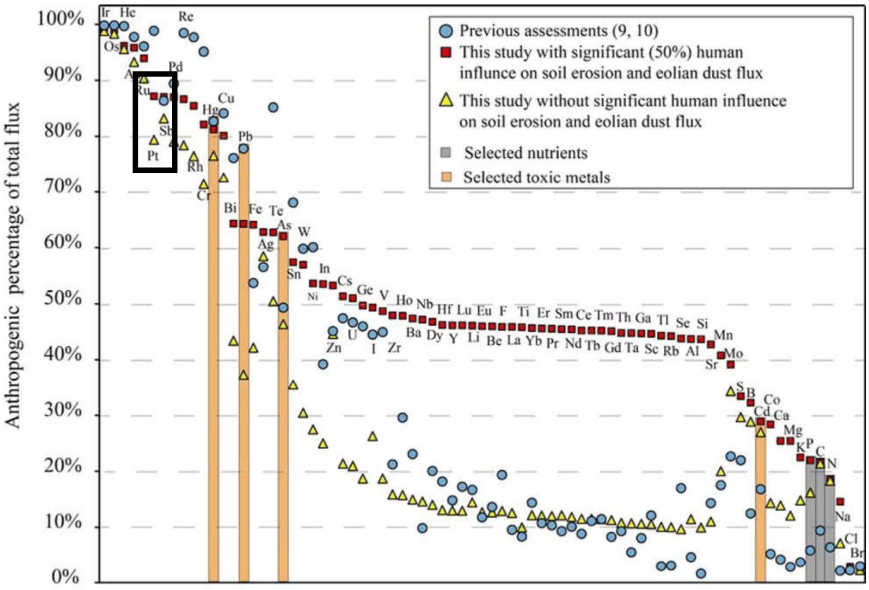

Figure 1.2. Natural versus anthropogenic element fluxes (Sen and Peucker-Ehrenbrink, 2012). Platinum anthropogenic flux is greater (≈80%) than the respective natural flux.

1.3.1. Sources and anthropogenic uses of platinum

There are different and diverse sources of platinum from natural inputs (Soyol-Erdene et al. 2011; Sen and Peucker-Ehrenbrink, 2012) such as: (i) contributions from extraterrestrial dust, which has led Pt to be considered as a proxy of extraterrestrial matter (Gabrielli et al., 2004); and (ii) volcanic activity due to the highly siderophile nature of the PGEs. Accordingly, it has been estimated that most of the Earth's Pt resides at the core, with a concentration of 5.5 µg/g (Lorand et al., 2008). It is through these intrusions of magma, e.g. volcanic eruptions, hydrothermal plumes or partial melting of the mantle, that Pt deposits are generated. There are not many economically viable Pt deposits, the largest being found in South Africa (Bushveld Igneous Complex, the most important being about 75% of world Pt (Cawthorn, 2010)), Russia (Noril'sk), US (Stillwater Complex) and Zimbabwe (Great Dyke) (Holwell and Mcdonald, 2010).

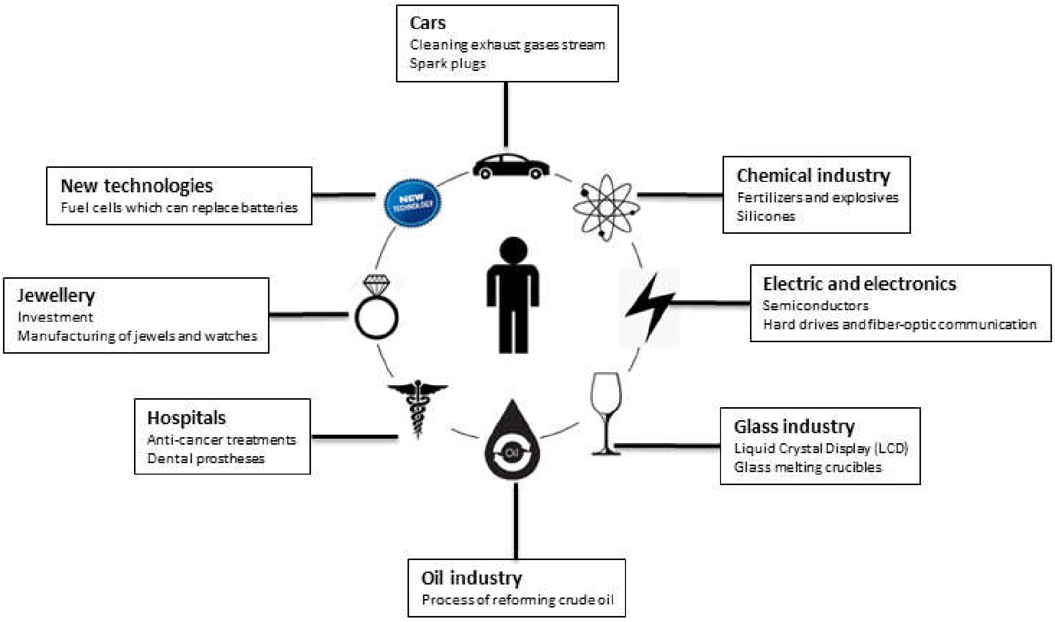

Figure 1.3. Pathways by which anthropogenic platinum is released into the environment.

There are several uses for Pt in different industries and day-to-day equipments which have led the introduction of platinum in the environment (Figure 1.3). For example, platinum is highly valued in jewellery due to its beauty and chemical resistance. The global demand for platinum can be seen in Figure 1.4, where only about 23% of the total demand of Pt is recycled and reutilised (Johnson Matthey, 2010).

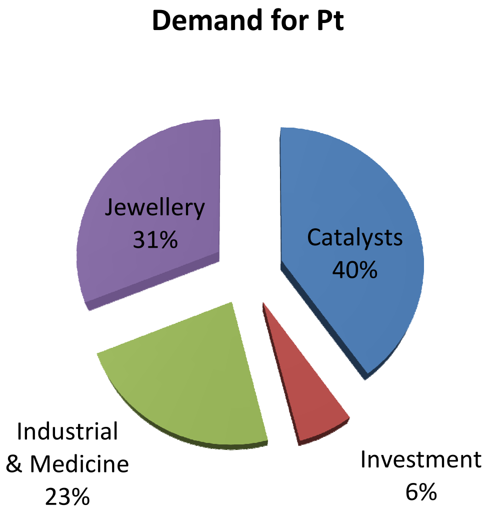

Figure 1.4. Demand for Pt (%) according to Johnson-Matthey's PGM Market Report (November 2016).

Together with Pd and Rh, Pt is used in catalysts for vehicles for cleaning exhaust gases. The automobile catalyst were developed with the aim of reducing emissions of hydrocarbons, carbon monoxide and nitrogen oxides, these three harmful gases are reduced to less toxic forms, i.e. carbon dioxide, molecular nitrogen and water vapour (Barefoot, 1999; Farrauto and Heck, 1999; Palacios et al., 2000). The amount and rate of Pt emissions are affected by different factors such as the type of fuel additives, diesel catalyst release more Pt than gasoline catalyst (Moldovan et al., 2002); age, catalyst show a tendency towards lower emission, by an order of magnitude, of Pt with increasing age of the catalyst (Moldovan et al., 2002); the amount of Pt release for the catalyst also depend on the speed of the automobile (Artelt et al., 1999). Since its introduction in 1975 in USA, one year later in Japan and in 1986 in Europe (Balcerzak, 2011), the results of different studies have confirmed that the emission from catalytic converters is the main source of Pt in the environment (Helmers, 1996; Cicchella et al., 2003; Leśniewska et al., 2004; Rauch et al., 2004).

Platinum emitted from catalytic converters is released into the environment in the form of nanoparticles (Gómez et al., 2000; Moldovan et al., 2002) in small amounts (ng/km range) and mainly in elemental or oxide forms, considered as virtually biologically inert, attached to µm-sized Al oxide particles (Merget and Rosner, 2001). The amounts of Pt released from catalytic converters are supposed to be non-toxic, but even when the inhalation of Pt from the exhaust does not seem to pose a direct health risk to general population at present (Caroli et al. 2001; Merget and Rosner 2001; Gómez et al. 2002; Bocca et al. 2004);

the levels of Pt in the air are increasing especially in areas with a high traffic density, where it can be higher by two orders of magnitude (Bocca et al., 2004; Iavicoli et al., 2004) compared to the background levels. Now we know that not all the released Pt is inert, although this soluble salts include a small fraction, about 10% of the total amount released (Moldovan et al., 2002).

Platinum is also used in electrical and electronic industries for the manufacture of hard disks, optical fibre wires or infrared detectors; in chemistry for the conversion of NH_3 to HNO_3 in fertilizers and explosives or as a catalyst; or in the glass and oil industries. From this industrial sources of anthropogenic Pt is important to know the chemical form in which Pt is released because it determines its chemical form and potential reactivity and toxicity (Tuit et al., 2000).

A last major use of Pt is in medicine as anti-cancer drugs and implants, higher values of Pt have been found in the urine of people with dental platinum alloys (Begerow et al., 1999; Schierl, 2000). Since the introduction in 1978 of cisplatin into chemotherapies as an anticancer agent (Arnesano and Natile 2009; Balcerzak, 2011) it has been worldwide expanded as a drug in cancer chemotherapies and as catalyst for the synthesis of pharmaceuticals (Lásztity et al., 2002). It has been estimated that hospital emissions are lower than those emitted by cars, but Pt is released into the water bodies of municipal and hospital effluents through urinary excretion of these pharmaceutical compounds by the patients (Kümmerer and Helmers 1997; Kümmerer et al. 1999; Hann et al. 2003; Lenz et al. 2005) and can pose a risk to aquatic organisms due to the high reactivity of cisplatin (Hann et al. 2003; Fonseca et al. 2017) which can cause nausea, neurotoxicity, nephrotoxicity or ototoxicity. The nurses who care for these patients also show high values of Pt (Nygren and Lundgren, 1997) so it is important to continue monitoring this source.

1.3.2. The cycle of platinum and post–depositional processes

The knowledge of the Pt cycle has been limited due to the difficulty of determining the ultra-trace concentrations in which Pt is found in nature; and also because historically there has not been, until recent years, an anthropogenic activity that significantly releases this element to the environment. However, due to the introduction of catalytic converters (1975–1986) there has been an increase in Pt concentrations in the environment causing a growing interest in the biogeochemical study of this metal. Catalytic converters from cars use Pt as active component; the Pt is eroded from the surface of the catalyst and then emitted through the car exhaust. Most of this Pt is emitted in metallic form (Ek et al. 2004), inert for biological reactions, but a small proportion is released in form of soluble species (Hees et al., 1998; Moldovan et al., 2002), that can form compounds that are potent sensitizers, causing allergic reaction in tissues, with different toxic potentials for human health representing an environmental risk due to its bioavailability and accumulation in the environment (Figure 1.5).

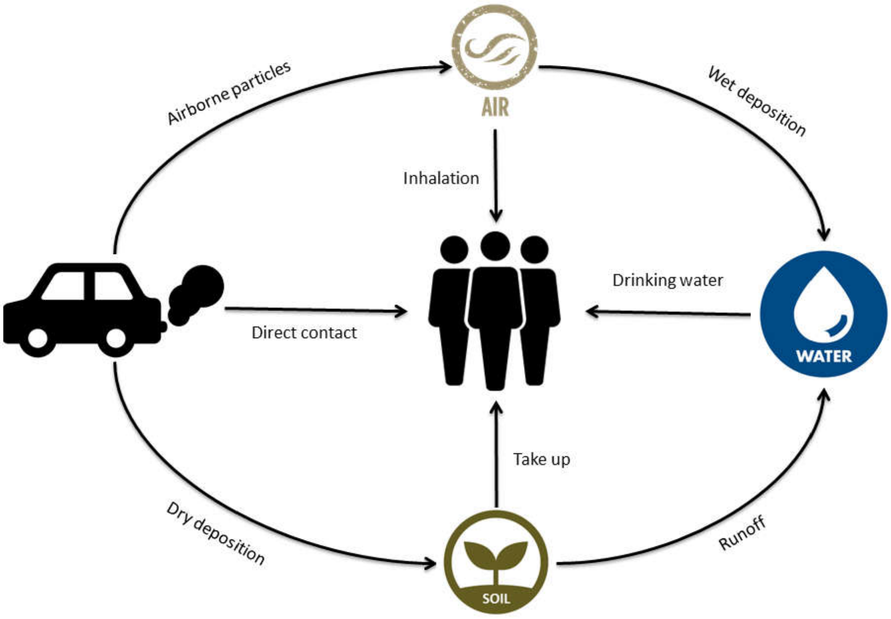

Figure 1.5. Platinum environmental pathways coming from vehicle catalysts in the environment to reach food web and therefore, humans.

Platinum can also enter the environmental compartments from other sources like metal production and mining or medical facilities wastewaters. Elevated concentrations of Pt were found in soil and grass in mining areas and near smelters (Rauch and Fatoki, 2013). Hospitals and other medical facilities are other source of Pt due to their application in dental alloys and by urinary excretion of patient treated with cisplatin, an anticancer drug (Kümmerer et al., 1999; Lenz et al., 2005). Pt can reach sewage system throughout the industrialized world (Tuit et al., 2000) through industries, mining, hospitals or steam exhaust from cars.

However, the most important anthropogenic source is Pt emitted from automobile catalysts (Ravindra et al., 2004), especially in roads and highways (Petrucci et al., 2000), high concentration of Pt has been found in soil and plants

(Schäfer and Puchelt, 1998; Leśniewska et al., 2004; Sutherland et al., 2007; Akrivi et al., 2012) compared with the natural geochemical background. It has been found a decreasing concentration with the increasing distance from the road suggesting a dependency of traffic intensity and a significant anthropogenic source. Pt emitted by cars can enter the environment through the air by two ways: regional transport using rainwater as a medium of transportation (wet deposition) or long-range transportation by gravitational falling (dry deposition). Emissions of Pt are not restricted to urban or important industrial areas but also in rural environments (Sen et al., 2013) and areas far away from human activities (Zereini et al., 2001). Evidence from global Pt disturbance and long-range transport has been seen in Greenland (Barbante et al. 2001; Rauch et al. 2005) and Antarctic snow (Soyol-Erdene et al., 2011), Alps snow (Rauch et al. 2005), and lichens from Patagonia (Pino et al., 2010) representing an important component in the environmental cycle of emitted Pt.

Metallic Pt emitted from car catalysts may undergo several transformation processes (Vaughan and Florence, 1992; Moldovan et al., 2001) when deposited as road dust to soluble forms providing compounds ready to migrate into environmental compartments. The transformation of Pt into mobile forms is a long-term process and can include different steps like chemical oxidation (Lustig et al., 1996), dissolution by natural complexing agents (Lustig et al., 1998) or just rainwater leaching can be enough (Fliegel et al. 2004; Rauch et al. 2005) to mobilized the emitted Pt into bioavailable species. In marine sediments, Pt is associated with organic matter and can be transformed into soluble Pt by the natural process of oxidation of the organic matter, Pt in harbour sediments was found to be 5 times higher than the natural background (Tuit et al., 2000). Also some microorganisms can transform metallic Pt into labile species (Lustig et al., 1997) that can be taken up by the organisms (Tuit et al., 2000), like plants (Ely et al., 2001) and then enters the food web. Pt shows a high–affinity for Fe-chelating compounds secreted by some microorganisms found in soils which have the potential of increase its bioavailability (Dahlheimer et al., 2006).

There are several possible processes of physical, chemical and biological transformation of Pt after deposition, with a great number of products, complexes and equilibrium reactions that can be taken up by the organisms. The mechanism of Pt uptake by organisms depends on the form Pt is present, being Pt (IV) more likely taken up than Pt (II) (Rauch and Morrison 1999). Pt is also more likely to be taken up when dissolved in acidic medium (Godlewska-Zylkiewicz, 2003). The accumulation of Pt in the organisms is dependent with time (Moldovan et al. 2001; Mulholland and Turner 2011). Pt in aquatic systems is mostly found in sediments (Rauch and Morrison, 1999) between the fine sediments and associated with the organic matter (Wei and Morrison, 1994), which provide a food source for animals; e.g. Pt can be taken up by *Asellus aquaticus* (Haus et al., 2007) with a rate comparable to some essential metals. As platinum accumulates in the tissues of prey species will be accumulated further in the tissues of predatory species that feed on these organisms. Pt can be accumulated by humans through different routes: inhalation, direct contact with the particles, through the diet or contaminated water (Figure 1.3).

1.3.3. Determination of platinum: strengths and weaknesses

The ultratrace concentrations of this element in solid matrices (i.e. sediment, rocks or soils), waters and biological matrices, make the determination of Pt a significant challenge from the analytical point of view, requiring highly sensitive methods to carry out the determination of Pt in natural samples. The analytical techniques used for the analysis of Pt concentrations in environmental samples are limited to fundamentally ICP-MS and voltammetry.

We must perform separation and preconcentration processes before the analysis. Each step can lead to problems such as loss of analyte or contamination of the sample (Pearson and Woodland 2000). Firstly, sampling techniques must be clean and careful. During the preparation process of the sample and due to the complexity of natural environmental samples, all the organic matter and effects that can interfere in the quantification of the metal must be eliminated. The analysis itself must be carried out using clean techniques inside a laboratory where we can control all environmental parameters. Accuracy is very important for the determination of Pt traces. The accurate determination of Pt in environmental samples is a difficult step. We need sensitive and selective specific analytical techniques due to its low concentration levels (Mesquita da Silva et al., 2001) and complex environmental matrices where Pt is found (Balcerzak, 1997).

1.3.3.1. Analytical techniques

The analysis of the Pt requires extremely sensitive and selective methods and with a very high limit of detection for determination of traces (Mesquita da Silva et al., 2001), especially in complex biological materials. Pt concentrations in these matrixes are very low and there are numerous interfering effects from matrix (e.g. organic matter) that requires preparation steps such as transformation of the metals into soluble species, separation from interfering elements, and preconcentration up to a level detectable by the technique used (Balcerzak, 2011).

Determinations of Pt can be achieved with different techniques. One of the most widely used techniques because of its speed and high precision is Inductively Coupled plasma-Mass Spectrometry (ICP-MS) (Begerow et al., 1996; Becker et al., 2000; Moldovan et al., 2001; Ek et al., 2004; Iavicoli et al., 2004, 2007; Hooda et al., 2007). Adsorptive Cathodic Stripping Voltammetry (ACSV) is also widely used (Nygren and Lundgren, 1997; Schierl, 2000; Zimmermann et al., 2002; Haus et al., 2007) due to its high sensibility especially when the second derivative is used (Cobelo-García et al., 2014; Almécija et al., 2015). Neutron Activation Analysis (NAA) (Hoffman et al., 1978) or Electrothermal Atomic Absorption Spectrometry (ET-AAS) are also valid techniques for the determination of PGEs. All these techniques are summarized in Table 1.2.

Table 1.2. The most commonly used techniques for PGEs analysis with their main advantages and limitations.

Analytical Technique	Vantages	Disadvantages
Electrothermal Atomic Absorption Spectrometry (ET-AAS)	Can often be directly applied. Excellent sensitivity	Interfering matrix effects. Small linear concentration ranges. Low productivity.
Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)	Robust technique. High sensitivity. Simultaneous multi-element determination. Rapid. Low detection limits.	Interfering matrix effects. Need of an appropriate sample introduction method.
Adsorptive Cathodic Stripping Voltammetry (ACSV)	Very sensitive technique. Low detection limits.	Overlap of peak potential signals. Time-consuming.
Neutron Activation Analysis (NAA)	High sensitivity. Practical lack of blanks.	Access to a radiation source. Need of a safety procedure.

1.3.3.2. Certificate reference materials

One of the major problems on the analysis of Pt and PGEs is the lack of an appropriate reference material for environmental samples (Bettner et al., 1996; Balcerzak, 1997). A Certificate Reference Material (CRM) is used to check the accuracy of the analytical procedure. There is no suitable CRM for biological samples; and Pt concentration in other reference materials, i.e. road dust (BCR-723) and river sediment (JSd-2), clearly exceeds the concentrations that we found in nature (Barefoot, 1997). There is a necessity to create adequate reference material containing Pt in a concentration of interest for the analysis of natural samples.

1.3.3.3. Importance of real models

Due to the great complexity of the analysis of real samples and the different processes that exist in nature, it has been tried to recreate natural processes in the laboratory through exposure studies. In these experiments the concentrations used often far exceed that than we found in nature, to be able to see a response in a short period of time.

This doctoral thesis is based only in real samples and the natural responses of aquatic sediments and biota after the accumulation period. We compare zones with different conditions and anthropogenic pressures, to show the different uses of platinum as a tracer of contamination and oceanographic conditions now and in the past. Although the Pt concentrations that we found in nature are relatively low, the Pt uptake can be relatively high, in the same order of some essential metals, and higher than the results obtained in exposure studies previously.

1.4. Technology–Critical Elements

Technology critical elements (TCEs) are termed like that because they represent critical concentration levels due to their low reserve in the Earth's crust; they are trace elements with concentrations below 1 ng/g, with respect to their high demand for being key elements to many new technologies, e.g. green energy technologies, computing devices, mobile, etc (Cobelo-García et al., 2015).

Most of the chemical elements are present in the crust, with different proportions and heterogeneous distribution (Yaroshevsky, 2006). The upper crust is the most accessible part of the solid earth and where biogeochemical processes take place (Rudnick and Gao, 2003). This crust is composed mainly of silicates, carbonates and oxides (Yaroshevsky, 2006), although it is also composed of other elements that are in less abundance, the trace elements. Within these trace elements we consider technologically critical to those elements that are necessary for the operation of innovative scientific and technical applications (Cobelo-García et al., 2015).

According to the COST action TD1407: network on technology–critical elements (NOTICE) from environmental processes to human health threats (Cobelo-

García et al., 2015), the list of these elements is composed of gallium (Ga), germanium (Ge), Indium (In), tellurium (Te), niobium (Nb), tantalum (Ta), thallium (Tl), yttrium (Y), Platinum Group Elements (Pt, Pd, Rh, Os, Ir, Ru) and the Rare Earth Elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu).

Today a remarkable extraction of these elements is taking place with its consequent remobilization in the environment. The applications of these elements in the new technologies are many, e.g. green energy, energy efficiency, telecommunications, mobile devices, aerospace industry, electronics, semiconductors, etc. The TCEs are in very little natural concentration in the environment; their biogeochemical cycles are being altered by the increase in the mining of these elements and their use in emerging technologies.

The analysis and evaluation of TCEs involves a series of problems such as its ultra-trace concentrations and the need for highly sensitive analytical methods that make its determination more complicated and time–consuming; the lack of knowledge of their biogeochemical cycle due to the absence of their presence and use in the past; and possible adverse effects due to the increased concentrations nowadays.

There is a current need to study the impact of human activities on the biogeochemical cycle of TCEs, to compare concentrations in environments subject to anthropogenic pressures with natural values, to create a database for future studies since it is expected that their extraction and use continue to increase worldwide. We would continue to discuss about TCEs on the Part III of this thesis work.

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PART II

PLATINUM BIOACCUMULATION AND BEHAVIOUR IN COASTAL SYSTEMS

Chapter 2 – Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal)

ABSTRACT

2.1. Introduction

2.2. Materials and Methods

2.3. Results and Discussion

2.4. Conclusion

REFERENCES

We start with the evaluation of platinum as an emerging contaminant with the assessment of the concentration of this metal in estuarine and coastal sediments of the river-mouth of the Tagus (estuarine sediments) and its prodelta (coastal sediments).

This chapter is based on the article (Appendix 12):

Cobelo-García, A., Neira, P., Mil-Homens, M., & Caetano, M.D. (2011). Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal). *Marine Pollution Bulletin,* 62, 646–650.

Marine Pollution Bulletin 62 (2011) 646–650

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal)

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2. Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal)

ABSTRACT

Platinum contamination in estuarine and coastal sediments has been evaluated in three cores collected from the Tagus Estuary and Prodelta shelf sediments. Elevated concentrations, up to 25-fold enrichment compared to background values, were found in the upper layers of the estuarine sediments. The degree of Pt enrichment in the estuarine sediments varied depending on the proximity to vehicular traffic sources, with a maximum concentration of 9.5 ng g^{-1}. A considerable decrease of Pt concentrations with depth indicated the absence of significant contamination before the introduction of catalytic converters in automobiles. Platinum distribution in the Tagus Prodelta shelf sediment core showed no surface enrichment; instead a sub-surface maximum at the base of the mixed layer suggested the possibility of post-depositional mobility, thereby blurring the traffic-borne contamination signature in coastal sediments.

2.1. Introduction

The platinum group elements (PGE), namely ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), are amongst the least abundant elements in the Earth's crust, with average concentrations typically less than 1 ng g^{-1} (Rudnick and Gao, 2003). There are a number of factors, however, which may lead to elevated concentrations of these elements in the environment. In marine sediments these include: siderophile sources (Gabrielli et al., 2008), hydrothermal vents (Cave et al., 2003), formation of ferromanganese crusts (Halbach et al., 1989), accumulation at redox boundaries (Colodner et al., 1992) and anthropogenic emissions (Tuit et al., 2000).

Current interest in the environmental concentrations and geochemical behavior of Pt (together with Pd and Rh) is based on significant increases in their anthropogenic emissions over the past 3 decades. Apart from their traditional use in jewellery, dentistry, chemicals, or electronics, their demand sharply increased in the 1980s in North America and in the 1990s in Europe. This was due to their use in catalytic converters for automobiles in order to reduce emissions of pollutant exhaust gases. Currently, their incorporation into catalytic converters accounts for 32% of Pt, 52% of Pd and 86% of Rh of the total World demand (Johnson Matthey, 2013). During abrasion and ageing of the washcoat layer of a catalyst, metallic and oxide forms of PGE are emitted as particles (normally in the size range of 10–30 lm) at rates per vehicle up to several hundred ng km^{-1} (Ravindra et al., 2004). Once in the environment, particulate PGE are subject to mobilization through interaction/complexation with naturally occurring inorganic/organic ligands and bacterial action (e. g. Dahlheimer et al., 2007; Wei and Morrison, 1994). Accordingly, PGE concentrations well above background values have been reported in areas subject to vehicular traffic (Ravindra et al., 2004). Also, evidence for their long range atmospheric transport has been shown by the contamination of Greenland snows with PGE (Barbante et al., 2001).

While most the studies have focused on Pt concentrations in sediments of lakes and urban rivers (e. g. Haus et al., 2007; Rauch and Hemond, 2003), little is known about its geochemical behaviour and current contamination in anthropogenically-impacted estuarine and coastal systems.

2.2. Materials and methods

The Tagus Estuary is one of the largest European estuaries with an area of approximately 320 km^2 formed by several channels and islands (Figure 2.1). The intense urban sprawl and industrial growth of Lisbon (approximately 2.5 million inhabitants) has been responsible for the inputs of anthropogenic metals and persistent organic pollutants to the Tagus Estuary (e. g. Canário et al., 2005; Figueres et al., 1985; Nogueira et al., 2003; Vale et al., 2008). In common with many large rivers, the Tagus Prodelta patch (Figure 1.1) accumulates riverine, estuarine and marine-borne fine-grained materials (Jouanneau et al., 1998). These prodeltaic deposits have been used to reconstruct the historical increase of metal concentrations in the Tagus adjacent to the catchment's area (Mil-Homens et al., 2009).

Three sediment cores were collected in the Tagus Estuary and its Prodelta (Figure 2.1). Two sediment cores were collected in the estuary close to a motorway bridge (Vasco da Gama bridge opened to traffic in 1998; Site 1) and nearby old chemical and pyrite roasting plants closed during the 1990s (Site 2). Sediments were characterized by reducing conditions (Sundby et al., 2003), with typical oxic layer depths of less than 2 mm. Since the sediments were composed of 99% fine-grained material with a grain size <63 µm, no sieving was carried out. Cores were sectioned, dried at 40 °C and ground using an agate mortar. Additionally, three sediments from the bridge gullypots were collected. A sediment core in the Tagus Prodelta (Site 3, PO287–26–1B) was collected during the PALEO1 cruise in 2002 onboard R/V Poseidon. The core was sectioned, the coarser fraction (>2 mm) removed by wet sieving and then dried and ground as indicated above. Sediments were analyzed for Al, Pb and Hg using well–established procedures (Costley et al., 2000; Mil-Homens et al., 2009).

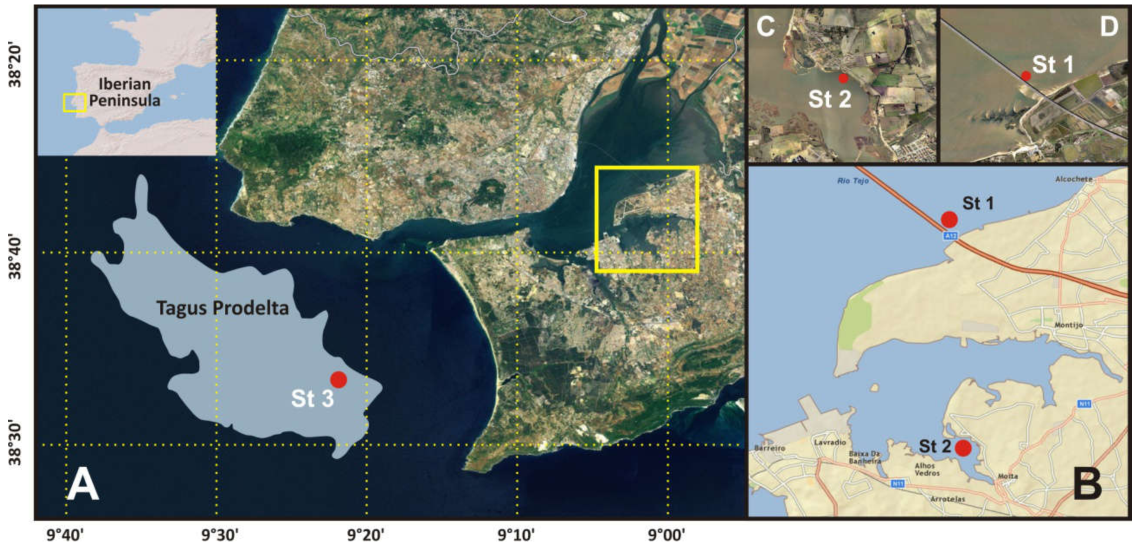

Figure 2.1. Map showing the location of the sediment cores in the Tagus Estuary at Site 1 (St 1), Site 2 (St 2) and Prodelta at Site 3 (St 3).

The determination of Pt in the sediments was undertaken by means of catalytic adsorptive cathodic stripping voltammetry (catalytic AdCSV) after appropriate digestion. Before digestion, and in order to remove organic material that interferes with the voltammetric determination, approximately 0.15 g of the ground sediment was ashed in quartz crucibles up to 800°C following the heating scheme given in Nygren et al., 1990. Ashed sediments were then transferred to 30 mL Teflon® PFA vessels with screw caps (Savillex) for digestion with 5 mL of concentrated HCl and 3 mL of concentrated HNO_3 at 210°C for 4 h. Following the digestion, the vessel caps were removed and the acids evaporated at 210°C to near dryness. The residue was re-dissolved with 1 mL of concentrated HCl and 1 mL of concentrated H_2SO_4, evaporated at 210°C until no fumes were observed and a near constant volume, comprising mostly sulphuric acid, 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 pore size filters) and made up to 25 mL in polypropylene volumetric flasks. The detection limit (defined as three times the standard deviation of the blank) for a typical mass of 0.15 g of sediment was 0.05 ng g^{-1}. The accuracy was checked using river sediment certified reference material (JSd–2; Geological Survey of Japan) and good agreement was obtained with the certified concentrations (Table 2.1).

Table 2.1. Platinum concentrations, ng g^{-1}, obtained for the river sediment certified reference material JSd–2 in this study and by other authors.

Imai et a. (1999)[1]	Hall and Oates (2003)[2]	Djingova et al. (2003)[3]	Tsogas et al. (2008)[4]	This study[5] (n=3)
16.7 ± 2.8	14.5 ± 2.8	15 ± 2	15.9 ± 1.1	14.6 ± 0.8

[1]Indicative value given by the Geological Survey of Japan.
Decomposition/separation procedure: [1]$HCl/HNO_3/HF$ digestion, MIBK extraction; [2]Pb fire assay; NiS fire assay; HCl/HNO_3 digestion (ashed and non-ashed sample). [3]$HNO_3/HCl/HF$ microwave-assisted digestion. [4]HNO_3/HF microwave-assisted digestion. [5]HCl/HNO_3 digestion of ashed sediment.
Determination: [1]flameless AAS; [2]ICP-MS. [3]ICP-MS. [4]GF-AAS. [5]Stripping Voltammetry.

2.3. Results and discussion

The down–core Pt distribution at Site 1 shows a clear indication of recent input of this element into the Tagus Estuary. Elevated Pt values at the top of the core, up to 9.5ng g^{-1}, are observed, which decrease sharply with depth below 5 cm to background values in the range of 0.3–0.4 ng g^{-1} (Figure 2.2). The elevated Pt concentrations at the sediment surface are in accordance with the Pt concentrations in three independent gullypot sediments from the bridge: 7.5, 21 and 157 ng g^{-1}, which are typical of other urban gullypot sediments (Fliegel et al., 2004; Jackson et al., 2007; Wei and Morrison, 1994). At Site 2, a similar depth profile was found, although the degree of Pt enrichment in the uppermost layer is much lower, with a maximum value of 0.9 ng g^{-1}. This area is one of the most contaminated in the Tagus Estuary due the historical impact of a chemical plant (Vale et al., 2008) and significant contamination from industrial metals is also evident (e.g. Pb in Figure 2.2). Furthermore, a lower radiogenic Pb isotopic signature in upper sediment layers at Site 2 is indicative of increase fraction of anthropogenic Pb (Caetano et al., 2007). Conversely, reduced pressure from traffic in this part of the estuary may explain the lower Pt concentrations. The abrupt decrease of Pt with depth to background values in Sites 1 and 2 indicates the absence of previous significant contamination due to other sources signifying the catalytic converters as the major input for the recent enrichment.

Results for Site 3 (Figure 2.3), collected at the Tagus Prodelta (see Mil-Homens et al., (2009) for a complete characterization of other metals and 210Pb–dating for this core), has a different Pt profile with no maximum concentrations at the top of the core. Instead, Pt values increase with depth from 0.65 ng g^{-1} at surface to 0.89 ng g^{-1} at the base of the mixed layer which is located at approximately 7 cm depth. This is followed by a sharp decrease to 0.51 ng g^{-1} at 13 cm corresponding to reworked material (Mil-Homens et al., 2009). The Pt profile (Fig. 3b) mimics the depth variation of other metals such as Hg and Pb, which are significantly correlated ($P < 0.01$ and <0.05, respectively, for 2–tailed testing).

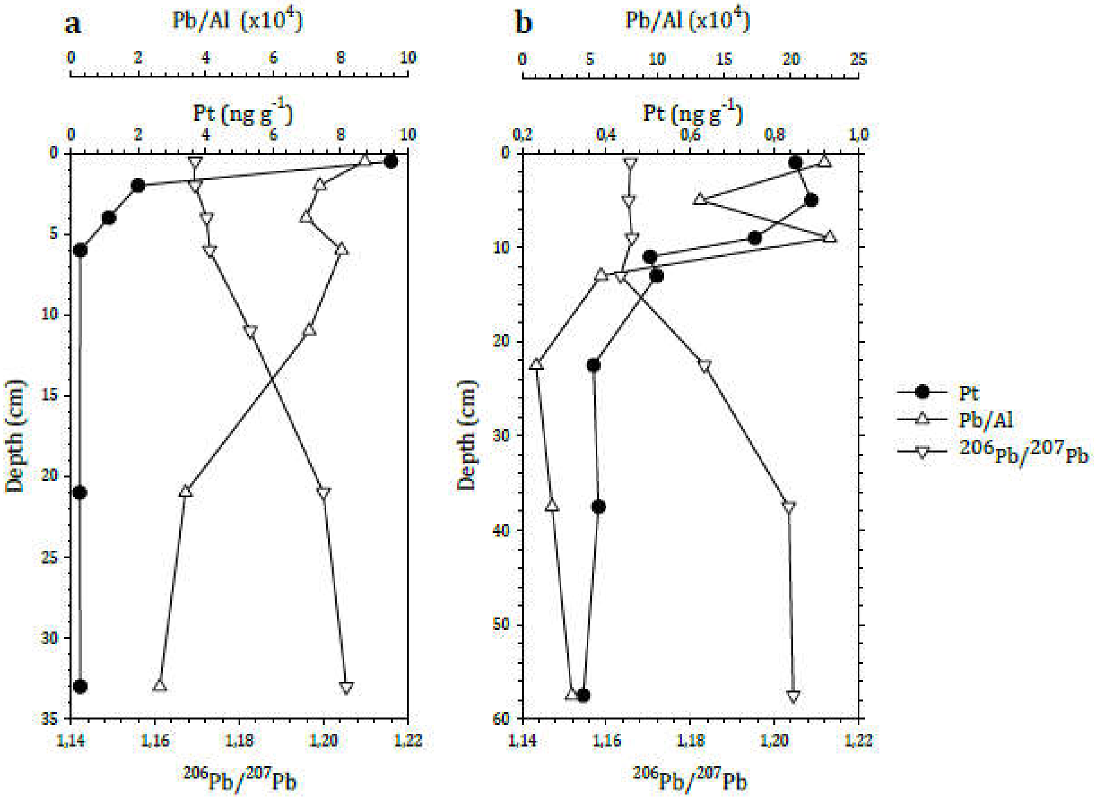

Figure 2.2. Depth profiles of Pt, Pb and 206Pb/207Pb ratios in cores from Sites 1 (a) and 2 (b).

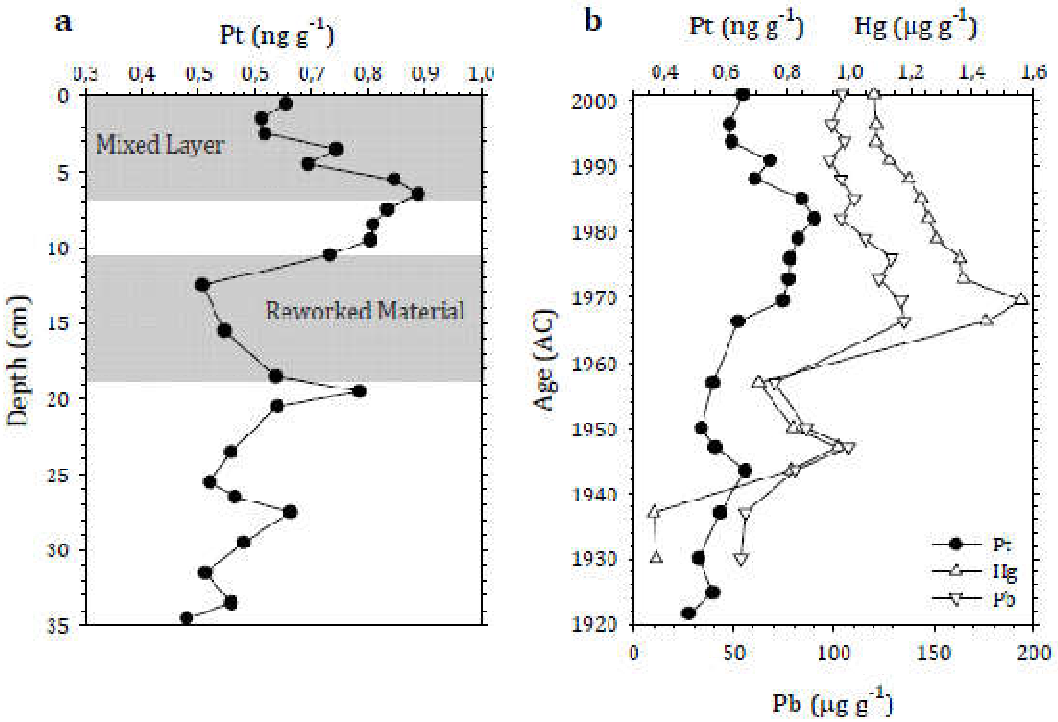

Figure 2.3. Depth profile of Pt at Site 3 (Tagus Prodelta). (a) Variation of Pt, Hg and Pb concentrations vs sediment age. (b) See Mil-Homens et al. (2009) for a complete description.

The time profile (Figure 2.3b) suggests an elevated input of Pt from the early 1970s to the mid 1980s compared to recent years. However, (i) catalytic converters in automobiles were not introduced in Europe until sometime in the late 1980s or early 1990s and (ii) no Pt enrichment was observed in the deep layers of the two cores collected in the Tagus Estuary which would indicate alternative Pt sources in the past. Therefore, sub-surface Pt enrichment in the Tagus Prodelta may not reflect actual anthropogenic inputs but post-depositional mobility. Here we suggest that the Pt maximum found at the base of the surface mixed layer is probably driven by the scavenging of Pt at the oxic/anoxic boundary. This behavior has also been observed by Tuit et al., (2000) in sediment cores collected in the Boston Harbour. Colodner et al., (1992) and Wei and Morrison, (1994) reported that a significant fraction of Pt in marine and road sediments is labile, being associated with Fe-Mn oxyhydroxides and organic-rich particles. This chemical association contributes to Pt mobilization and diffusion being fixed at the redox boundary, which may explain Pt behaviour at Site 3. In Cores 1 and 2 the absence of a higher Pt depth resolution does not allow an observation of the presence of such behaviour.

Studies of Pt geochemical behaviour and contamination in estuaries and coastal systems are scarce in the literature. A comparison of available data is given in Table 2.2. Background values for the Tagus Estuary and its shelf are 0.32 ± 0.05 ng g^{-1} and 0.56 ± 0.06 ng g^{-1}, respectively. These values agree well with the average Pt crustal abundance of 0.5 ± 0.5 ng g^{-1} (Rudnick and Gao, 2003) and also with the background concentration reported for Massachusetts Bay of 0.6 ± 0.3 ng g^{-1} (Tuit et al., 2000). Concentrations of Pt reported herein for the surface mixed layers are in the range of those found in the Boston Harbour (USA) and the Venetian Lagoon (Italy), but lower than in the Humber Estuary (UK) or Avondale Creek (Australia).

Table 2.2. Platinum concentrations (means ± 1 σ) in the Tagus Estuary and Prodelta obtained in this study compared to other estuarine systems. Values in brackets represent concentration ranges.

	Platinum concentration, ng g^{-1}	**References**
Estuarine and coastal sediments		
Avondale Creek (Australia)	21 ± 6; n=2 (17–25)	(Pratt and Lottermoser, 2007)
Huber Estuary (UK)	7 ± 1; n=4 (6–8)	(Prichard et al., 2008)
Venetian Lagoon (Italy)	0.9 (0.02–10.0)	(De Boni et al., 2007)
Boston Harbour (USA)	4 ± 3; n=14 (0.8–12.5)	(Tuit et al., 2000)
Tagus Estuary (Portugal)	2 ± 3; n=8 (0.5–9.5)	This study
Portuguese Shelf (Tagus Prodelta)	0.74 ± 0.10; n=9 (0.6–0.9)	This study
Background values		
Massachusetts Bay (USA)	0.6 ± 0.3 (n=5)	(Tuit et al., 2000)
Tagus Estuary (Portugal)	0.32 ± 0.05 (n=6)	This study
Portuguese Shelf (Tagus Prodelta)	0.56 ± 0.06 (n=9)	This study
Crustal abundance	0.5 ± 0.5	(Rudnick and Gao, 2003)

2.4. Conclusion

At present it is not possible to estimate, accurately, the rate and extent of increase of Pt concentrations in the environment. The total World demand of Pt for use in the catalytic converters has increased in the past 3 decades (21.2 tonnes in 1980 to 128.9 tonnes in 2007); however, the demand fell by 45% from 2007 to 2009 (Johnson Matthey, 2013) due to the global economic crisis which also affected the automotive industry. Also, the amount of Pt (together with Pd and Rh) loaded into catalytic converters is being continually modified by the manufacturers as more efficient formulations are developed. In gasoline vehicles, for example, most of the manufacturers are substituting Pt–based catalysts with Pd (Johnson Matthey, 2013), which would lead to lower emissions of Pt. Only future studies will test this hypothesis.

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Chapter 3 – A critical review on Platinum Group Elements levels and dynamics in natural living organisms

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3. A critical review on Platinum Group Elements levels and dynamics in natural living organisms

3.1. Introduction

The platinum group elements (PGEs), sometimes referred as the platinum group metals (PGMs), include the rare metals such as platinum (Pt), palladium (Pd), rhodium (Rh), osmium (Os), ruthenium (Ru) and iridium (Ir). Although most studies as well as this literature review focus on the top three, Pt, Pd and Rh for being the most frequently used and of major economic importance. Platinum group elements can be naturally found only at very low concentration in the Earth crust, average crustal abundance of 0.5 ng g^{-1} (Rudnick and Gao, 2003). They have similar physical and chemical properties which make them critical to many emerging technologies, resistance to chemical corrosion over a wide temperature range, high melting point, high mechanical strength, good ductility and outstanding catalytic properties, and they tend to occur together in the same mineral deposits.

The purpose of this review is to focus on studies of the Platinum Group Elements in living organisms, both plants and animals, marine and terrestrial in natural environments. Special attention is also given to emission sources and limitations for the study of these elements.

3.1.1. Sources of PGEs in the environment

Natural biogeochemical cycles are dominated by erosion of the continental crust, volcanic eruptions and accretion of extraterrestrial matter (Sen and Peucker-Ehrenbrink, 2012). Although natural environmental concentrations of platinum group elements are extremely low, levels of PGEs are increasing in the environment largely due its use in several anthropogenic activities and mainly because of their use in the catalytic converter of motor vehicles (Zereini et al., 2007). Autocatalysts were initially installed in cars produced in USA in 1975, and in 1986 in Europe (Wiseman and Zereini, 2009), they have been mandatory in the European Union since 1993 (Moldovan, 2007).

The automobile catalysts converters use noble metals as active components, and were developed with the aim of reducing emissions of hydrocarbons, carbon monoxide and nitrogen oxides, about 90% of these emissions are transformed to harmless products by autocatalysts (Barefoot, 1999). The hot exhaust gases flowing through the converter cause abrasion/ablation of these elements, leading amounts of PGEs released into the environment (Bencs et al., 2003) through exhaust fumes during vehicle operation. The amount and rate of PGEs emission are affected by the speed of the automobile, the type of the engine, the type and age of the catalyst and the type of fuel additives (Artelt et al., 1999) with a tendency towards lower emission values with increasing age of the catalyst.

What was supposed to be mitigation in greenhouse gas emissions has resulted in increased levels of PGEs in the environment (Ely et al., 2001; Fritsche and Meisel, 2004; Lesniewska et al., 2004; Schäfer et al., 1999; Zereini et al., 2001). Emitted PGEs are dispersed from the places near to the emission points, such as roads and other traffic routes, subsequently PGEs can be transported to aquatic systems through runoff and they are introduced and accumulated in living organisms through diverse pathways. These novel anthropogenic metals have an increasing impact on the environment due to the actual growing number of cars equipped with catalytic converters (Ravindra et al., 2004).

The automobile industry is the major consumer of PGEs but may not be the single most important source (Figure 3.1), contributions from other sources including the manufacture of jewellery (Rakhtasaum, 2013; Wright, 2002), as catalysts in the chemical, electrical, glass and petroleum industries (Saurat and Bringezu, 2008), mining (Singh et al., 2014), or in medicine (Kümmerer et al., 1999; Lenz et al., 2005) as dentistry alloys and cancer treatment drugs can be important. Electrical applications, chemical industries, jewellery and dental applications are unlikely sources of PGEs due its high recycling rates. Emissions from mining, production activities, industrial emissions and emissions from medical centres as excreted PGEs after treatments are along with automobile catalyst the most important sources in the environment. A secondary PGEs source can be the urban sewage and waste (Laschka and Nachtewey, 1997) during treatment, reuse and disposal and can result in the release of these elements into the aquatic environment.

Also evidence for a long range transport and global platinum environmental perturbation has been given (Soyol-Erdene et al., 2011) founding atmospheric deposition rates of PGEs in Antarctic snow. These PGE polluted places located far away from the emission points indicates a large-scale contamination impact of the vehicle catalysts (Barbante et al., 2001), and supports contributions are from different sources which can contribute significantly to the global PGEs budget.

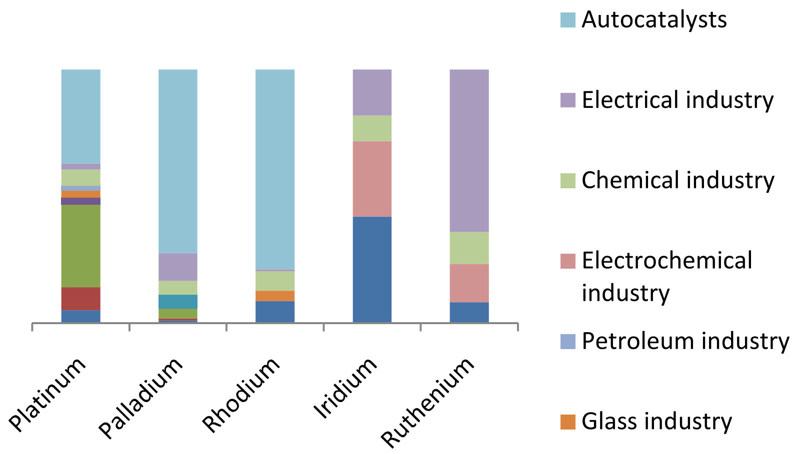

Figure 3.1. Estimated demand rates of Pt, Pd, Rh, Ir and Ru (no data found for Os) for different areas of use (Johnson-Matthey, 2013).

3.1.2. Physical and chemical transformations after deposition

The PGEs of automobile catalytic converters are eroded by mechanical abrasion or also catalyst deterioration from the surface of the catalyst and then emitted mainly in metallic form or as oxides, there is evidence that at least part of this particles is soluble (Ravindra et al., 2004) constituting a serious threat to plants and animals. It has been demonstrated that autocatalys–emitted PGEs can be transformed into soluble species in soil or water (Moldovan, 2007), becoming bioavailable for living organisms, and they may pose a threat to humans.

The PGEs are subject to various physical and chemical transformations after deposition and under field conditions providing compounds ready to migrate into environmental compartments (Moldovan et al., 2001; Vaughan and Florence, 1992). Rainwater usually provides a significant medium for the transportation of PGE particles (Ravindra et al., 2004). Emitted PGEs may be easily mobilised and solubilised by various compounds commonly present in the environment, thereby enhancing their bioavailability.

The degree of toxicity depends on its form; the most soluble ones are the most toxic. The metallic form of these elements is generally considered to be inert as regards to biological reactions and non–toxic and non-allergenic, however PGEs emitted from cars are at least partly soluble, about 2.5–6.9% of total PGE present in traffic–related dust was soluble (Alt et al., 1993), this suggest that PGEs may not be released in a metallic form or at least they can be rapidly altered once deposited (Jarvis et al., 2001).

Biological availability is one of the most decisive issues so that PGEs can be absorbed by organisms and be a possible threat to ecosystems. The speciation is a decisive factor affecting biological availability, and it is influenced by the water chemistry e.g. the existence of humic substances (Zimmermann et al., 2005; Zimmermann and Sures, 2004).

The processes of transformation of these elements in the environment must be elucidated, so that PGEs can be absorbed by organisms (i.e. metal binding and granules, Rauch and Morrison, 1999) and search for the environmental conditions that make these elements biologically available. Their speciation and determination in various environmental compartments appears to be a challenging task. Basic knowledge of PGEs levels in plants and organisms is essential to assessing the potential risk to human health.

3.2. Limitation for PGEs studies in living organisms

Despite his growing interest as emerging contaminants in recent decades, the knowledge about their levels in different environmental matrixes and their mechanisms of mobility is limited. Limitation in studies of PGEs in the different environmental matrices is mainly due to two causes: 1) need for analytical techniques with a high sensitivity, the low natural background levels facilitate the detection of even small anthropogenic emissions but also make the samples susceptible to contamination during and after sampling; and 2) the lack of certified reference materials for the analysis of PGEs in biological samples.

3.2.1. Analytical techniques

The analysis of the platinum group elements requires extremely sensitive and selective methods and with a very high limit of detection for determine traces (Alsenz et al., 2011; Mesquita da Silva et al., 2001), especially in complex biological materials. PGEs concentrations in these matrixes are very low, and numerous interfering effects from matrix elements require preparation steps like transformation of the metals into soluble species, separation from interfering elements, and pre-concentration up to the level detectable by the technique used (Balcerzak, 2011).

Determinations of PGEs can be achieved with different techniques (Table 3.1).One of the most widely used techniques because of its speed, high precision and low cost is Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) (Becker et al., 2000; Begerow et al., 1996; Ek et al., 2004; Hooda et al., 2007; I. Iavicoli et al., 2004; 2007; Moldovan et al., 2001), Adsorptive Cathodic Stripping Voltammetry (ACSV) is also widely used (Haus et al., 2007; Nygren and Lundgren, 1997; Schierl, 2000; Zimmermann et al., 2002) due to its high sensibility especially when the second derivative is used (Almécija et al., 2015; Cobelo-García et al., 2014; Neira et al., 2015), Neutron Activation Analysis (NAA) or Electrothermal Atomic Absorption Spectrometry (ET–AAS) are also valid techniques for the determination of trace of PGEs.

3.1.1. Certified reference materials

Certified Reference Materials (CRMs) are vital in analytical work; they offer means of checking the accuracy of an analytical method. A certified reference material is a material which one or more of whose properties has been certified by a technically valid procedure.

There are some CRMs for the PGEs (Appendix 1); unfortunately most of them are geological samples (Fragnière et al., 2005), these consist of rocks, sediments, ores, and tailings. Even so there has been a need for other CRM with very low concentrations of PGEs in biological samples. A fundamental problem to be resolved is the lack of suitable reference materials in biological matrixes containing platinum group elements at concentration levels of interest.

PGEs concentrations in geological standards are much larger than those encountered in environmental materials. BCR-723 (road dust) is the only environmental CRM, with certified mean concentrations and 95% confidence intervals for Pt, Pd and Rh.

Table 3.1. The most commonly used techniques for PGEs determination with their main advantages and limitations.

Analytical Technique	Procedure	Vantages	Disadvantages
Electrothermal Atomic Absorption Spectrometry (ET-ASS)	Spectroanalytical procedure using the absorption of optical radiation by free atoms in the gaseous state. A small volume of the sample is heated in a graphite tube and the absorption of the produced atoms is measured against the standards.	Can often be directly applied. Excellent sensitivity.	Interfering matrix effects. Small linear concentration ranges. Lower productivity.
Inductively Coupled Plasma-Mass Spectrometry **(ICP–MS)**	Type of mass spectrometry by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions.	Robust technique. High sensitivity. Simultaneous multi-element capability. Rapid determination at trace/ultratrace levels. Low detection limit.	Interfering matrix effects. Need of an appropriate choice of sample introduction method.
Adsorptive Voltammetry (AV)	Formation and adsorptive accumulation of PGE complex on the surface of a hanging mercury drop electrode.	Very sensitive technique. Adequate detection limits for the determination of traces.	Overlap of peak potential signals.
Neutron Activation Analysis **(NAA)**	Production and detection of specific radionuclides of particular elements. When the sample is bombarded with neutrons the stable isotopes become activated.	High sensitivity. Practical lack of blanks.	Access to a radiation source. Safety of clinical procedure.

3.2. Platinum Group Elements in living organisms along the food chain

The food chain describes transfer process of the nutritional substances through the different species of a biological community. As a "chain" each link or trophic level gets the energy needed of the immediately preceding level.The energy is obtained through the photosynthesis process whereby primary producers transform luminous energy into chemical energy thanks to the Sun, the water, and the mineral salts.

PGEs entry into the food chain is caused by plants or algae (primary producers), to go up trophic levels when it is consumed by the different organisms (herbivores and carnivores) up to human being levels. If it is proven that these PGEs bioaccumulate and biomagnify along the food chain it would represent a new hazard to humans.

3.2.1. Vegetation

The PGE (especially palladium) can be taken up by plants, enter the food chain and thus contribute to the exposure of the population (Ravindra et al., 2004). Plants constitute the first link in the food chain. Several studies demonstrated that PGE are biologically available to plants, and plants are able to take up and accumulate these elements. The concentrations of PGEs in various terrestrial and aquatic plants are shown in Appendix 2.

3.2.1.1. Terrestrial flora

Roadside grass and vegetation samples near roads and highways are often examined for the assessment of the bioavailability of automotive–emitted PGEs. In all cases studied the spatial distribution of PGEs is the same, contents higher near of motorways were concentration of PGE far exceeds the natural background levels, and higher in the plant samples than in the soil samples were the concentration rapidly decreased with increasing distance from the motorway (Djingova et al., 2003; Hooda et al., 2008; Zechmeister et al., 2006). Roadside grass concentrations in PGEs are strongly related to their respective concentrations in road dust and adequately reflecting seasonal changes and spatial characteristics (Akrivi et al., 2012).

Regarding the distribution within the vegetation, the highest metal levels are detected in the roots, followed by the shoots and leaves (Klueppel et al., 1998;

Verstraete et al., 1998).When the metals are translocated to the aboveground tissues they are associated with toxic symptoms (Ravindra et al., 2004).It is important to notice that plants also exhibited a higher content in the vegetative part than in the regenerative part (Fragnière et al., 2005).

Other plant samples have also been proved to be useful bioindicators. Platinum content of uncontamined tree barks were below 0.01 ng/g (Becker et al., 2000; Ma et al., 2001) (Appendix 2) while contaminated samples revealed values up to several ng g^{-1}. Pine needles (Dongarra et al., 2003) showed Pt and Pd levels two orders of magnitude higher (Appendix 2) than the crustal abundance (0.5 ng g^{-1}).Mosses (Zechmeister et al., 2006) showed the same pattern than grass samples, as higher concentrations were found in areas close to the road with decreasing values with the distance. There have been further studies on bioindicator plants as dandelion, plantain, moss, mushrooms or annual ryegrass. These studies have demonstrated that PGEs do not enter the plant only as a result of direct interaction with the dust (Djingova et al., 2003) but also by means of their roots. Thus more studies to evaluate the transfer of PGEs between soil and vegetation should be conducted.

Palladium presents the highest bioavailability for plants followed by rhodium and platinum (Hees et al., 1998; Rojas et al., 2006; Schäfer et al., 1998). Several studies show that PGEs, mainly palladium, are absorbed by the roots from contaminated soils and then incorporated into the plant biomass in the presence of complexing agents and transported by means of their binding to low mass molecules (Hees, Wenclawiak, Lustig, Schramel, Schwarzer, Schuster, et al., 1998; Rojas et al., 2006). As an example, a study carried out with grass treated with an aqueous solution containing Pt, 90% of the Pt found was bound to low molecular mass species (about 1 kDa) (Messerschmidt and Alt, 1994). Plants not only assimilate metals from the soil and water by roots, but also by contact after sedimentation in their surface. In several works it is observed that the concentration in plants decreased about 2–3 times after washing (Ely et al., 2001; Hooda et al., 2008; Zimmermann and Sures, 2004).

Regarding their transfer coefficient, defined as the ratio between the concentration in the plant and the concentration in the soil, PGEs transfer coefficients tend to be situated between poorly and medium available metals for plants. Pt and Rh have a similar mobility close to the one shown by Cu and Ni, whereas Pd has a higher mobility close to Zn (Almécija et al., 2016; Schäfer and Puchelt, 1998; Zimmermann and Sures, 2004).

3.2.1.2. Aquatic flora

In addition, to the increased concentrations of PGE in terrestrial ecosystem, these metals are also introduced into aquatic habitats, e.g. by road run–off (Ravindra et al., 2004) from places near the emission points. Seaweed was also used as sentinel organisms for the PGEs due to its ecological importance, wide distribution and bioaccumulating activities. Pd and Pt concentrations were determined for 20 species of seaweed from the California coast, U.S.A. (Yang, 1989), the contents varied from 0.09 to 0.61 ng g^{-1} and 0.25 to 1.75 ng g^{-1} respectively (Appendix 2).

The equilibrium behaviour of Pd and Pt may be in many aspects similar but their kinetics are quite different. Removal of Pt (Pt (II) and Pt (IV)) is slower than removal of Pd (Pd (II)) by an order of magnitude by the green alga *Ulva lactuca* (Cosden et al., 2003) and both strongly influenced by system hydrodynamics (i.e. faster removal under turbulent conditions). Recent exposure studies with the marine microalga *Chlorella stigmatophora* (Shams et al., 2014) demonstrated accumulation of PGEs in short–term exposures suggesting that the accumulation is determined by the reactivity of the alga surface, the abundance of PGEs and the nature of the alga, in the order Rh >Pd>> Pt. By the other hand long–term exposures with the same microalga confirm that the differences in the equilibrium chemistries of PGEs depend of the different kinetics revealing competition between the different metals. Rh is removed to the greatest extent involved in biological transport processes; Pd is also involved in transport mechanisms and possesses a rapid biological reactivity; while Pt exhibits a continuous increase in internalisation during long–term exposure experiments.

The uptake of PGEs may be affected by the pH of the water (Godlewska-Zylkiewicz, 2003; Turner et al., 2007). In submerged and terrestrial plants grown in nutrient solutions containing PGEs at pH 8 and with the addition of humic acid the concentration was the doubled than the control. With increasing pH in seawater uptake of Rh increases, but Pt show only a small increase while Pd do not show a clear dependence on pH (Turner et al., 2007).

For better understanding of the PGEs toxicity, and in order to recreate a real field situation, the effects not only with single species but also on natural communities need to be measured. The periphyton communities are a complex mixture of algae, cyanobacterias, microbes and detritus attached to submerged surfaces which can absorb contaminants removing them from the water. After an exposure to Pt in these communities (Rauch et al., 2004) an increased uptake of Pt for a short-term exposure was observed. In addition, this study suggests that the active ligands that made Pt more bioavailable for these communities were humic acids.

3.2.2. Animals

Although there is a major increase of PGE concentrations in the environment since implementation of the automobile catalyst, only little information about PGEs in the biosphere, especially in fauna, is known. There are few data on the toxicity of PGEs to animals under natural conditions since most of the works are addressing to describe research performed in the laboratory. Despite this, the limited number of studies carried out, show us the real accumulation of these metals in the environment, due to their relatively high bioavailability, their adverse effects and their wide distribution. Thus, field studies should be increased in order to monitor distributions and transfer in the trophic chain to prevent chronic effects on the biosphere. Natural concentrations on organisms are shown in Appendix 3.

3.2.2.1. Terrestrial fauna

The bioavailability of PGEs has been investigated using laboratory animals. After inhalation, intratracheal and intravenous exposure of rats, demonstrate that the routes follow this order from more important to least: inhalation>oral>intravenous (Moore et al., 1975a; 1975b). The accumulation of Pt derived from automobile exhaust catalyst was studied in a 90–day study with rats; Pt was found in the blood, urine and faeces and all important organs like liver, spleen, kidneys or stomach (Artelt & Levsen, 1999), demonstrating bioavailability of fine dispersed Pt as emitted from cars constituted over 30% of the total dose deposited in the lungs. Pd distribution and elimination following oral exposure was determined (Iavicoli et al., 2009) concluding that concentrations in organs was kidney>liver>spleen>lung>adrenal>>blood, and the main excretion route was faeces, two orders of magnitude higher than urinary elimination, with a significant linear correlation (0.99–0.95) with exposed dose.

PGE concentrations were determined in the feathers of three raptor species and two prey species. PGEs contamination was revealed to be predominantly external and, only Pd can penetrate deep into the feathers, in the form of nanometer–sized particles externally attached to the feather. This analysis has revealed a clear important increase of their PGE (Pd>Rh>>Pt) contents from 1917 to 1999 (Jensen et al., 2002) (Appendix 3). Evidence for an increasing temporal trend was observed, reflecting implementation of automobile catalysts converters. Raptors are useful for investigate the impact of metals because they are found in both urban and rural environments and they are at the top of the food chain. PGEs concentrations were studied in raptor eggs, faeces, blood, liver and kidney (Ek et al., 2004). These studies demonstrated that, levels of Pt, Pd and Rh were higher in blood, while Pd and Rh were rapidly transferred to eggs, liver and kidney. Finally, Pd was also found to be sequestered into feathers (Appendix 3).

3.2.2.2. Aquatic fauna

Aquatic organisms have also proved that are capable of assimilating PGEs from environmental samples. Bioavailability of Pt for the freshwater isopod *Asellus aquaticus* has been demonstrated by the analysis on the body tissues and on the exoskeleton (Rauch and Morrison, 1999). Exposure studies with this species over various exposure periods demonstrated a time–dependence for PGEs uptake. This uptake also depends on water chemical compounds (Moldovan et al., 2001) being the elements more accessible: Pd>Pt>Rh. The macroinvertebrate *Asellus aquaticus* exhibits a strong linear relationship between body content of PGEs and mortality rates (Palacios et al., 2000).

Several studies have investigated PGEs accumulation in two different mussels' species. The first one is *Dreissena polymorpha* (zebra mussel). After exposure of this species to road dust, it has been demonstrated that Pd concentration factor was 5 times higher than Pb and 6 times lower than Cu (Sures et al., 2002). Other studies with this species were carried out with ground material from unused automobile catalytic converters (Sonja Zimmermann et al., 2005) or water containing PGEs salts (Sures and Zimmermann, 2007). These studies demonstrated that Pt, Pd and Rh, in that order, were taken up and accumulated by the bivalves. Humic substances can increase the solubility of PGEs (Wood, 1996; Zimmermann et al., 2002; Zimmermann and Sures, 2004). The results of an experiment comparing bioavailability of this metals with zebra mussels in non–chlorinated tap water and humic water of a bog lake (Sonja Zimmermann et al., 2002) demonstrated humic substances can enhance the metal uptake in mussels of PGEs.

Recent studies of Pt on time–series of wild mussels (*Mytulus galliprovincialis*) showed a statistically significant temporal increase correlated with the demand of this element for autocatalyst and the car sales (Neira et al., 2015). The bioaccumulation factor (BF) for Pt calculated in this study (5.10^3) is greater than previously reported BFs (Sures and Zimmermann, 2007). This fact was associated to several factors that differ between lab and field experiments. This is just enhancing the importance of the field experiments that are limited at this moment and should be conducted in the future.

The influence of traffic related heavy metals on aquatic ecosystems was studied in macroinvertebrates and amphipods used as bioindicators. Platinum was found to be widespread even in moderately polluted water bodies. Bioavailability of Pt was demonstrated in amphipods (Haus et al., 2007) with relatively high bioconcentration factors (0.11–0.16). Platinum was also found to be accumulated in Zebra fish (*Danio rerio*) and Ramshorn snail (*Marisa cornuarietis*) in exposure studies with Pt chloride (Osterauer et al., 2009). Pt was shown to alter the heart rate, and at a higher concentration decelerated the hatching rate of the embryos of both species, and also was observed retard of the general development and a loss of weight due to Pt exposure.

The Pd emitted by automobile catalyst is also bioavailable for aquatic organisms, as it has been demonstrated in experimental studies with European eels (*Angilla angilla*), PGEs are uptaken and found in the liver of eels (Sures et al., 2001) one of the most important organs which accumulate heavy metals, followed by gills (where Pt and Rh absorption takes place), intestines, bile duct and kidneys. Due to their accumulation capacity eels are suitable as bioindicators of Pd pollution in aquatic habitats. European eels also accumulated Pt and Rh (Zimmermann et al., 2004), but in smaller amounts. Due to their accumulation capacities fish parasites can be applied as accumulation indicators to assess the degree of environmental PGE pollution in the aquatic fauna (Zimmermann and Sures, 2004). The parasite of European eels, *Paratenuisentis ambiguus*, take up and accumulate 50 times higher Pt and 1600 times higher Rh concentration compared to the water, while no metal uptake was found in examined host tissues (Sures et al., 2003) in exposed studies to ground catalytic converter material. The gills of the barbel (*Barbus barbus*) accumulate the highest levels of PGEs; however, its intestinal parasite *Pomphorhynchus laevis* had concentration factors three times higher (Sures et al., 2005).

The first study carried out on the accumulation of PGEs in marine mammals showed major PGEs levels in dolphin liver (Essumang, 2008).This study demonstrated that PGE pollution is very significant even in the open ocean. This fact is associated with the bio-magnification factor. If PGE have been accumulated in tissues of prey species then PGE will accumulate further in the tissues of predators that feed on these organisms, so PGE accumulation may also occur in humans as they occupy the top of the trophic chain.

3.3. Conclusions, risks and perspectives

There are few studies on the environmental effects and destination of these elements and little is known of the baseline levels of PGEs in the biosphere or background levels of this metals. It is important to know when the PGEs are biologically available to evaluate the possible threat of these noble metals to ecosystems. In the future, special attention should be paid to speciation studies of PGEs in environmental matrices in order to assess more reliably their transformations in the nature. Our knowledge regarding the transformation behaviour, speciation and bioavailability of the platinum group elements in the physical environment and organisms once they are taken up is limited. In the last 15 years, PGEs levels in air have increased by two orders of magnitude, especially in heavy traffic areas (Bocca et al., 2004).

There are a real need for sensitive and selective analytical methods for their determination at very low levels, and reference materials for the PGEs in different matrices. Improvements in analytical methods, like pre–concentration methods, are of great interest. Inter laboratory experiments should be done to ensure the good quality of the results for what international cooperation is desirable to improve the work in toxicology and long term bioavailability studies on organisms and monitoring studies along roadsides are necessary to control the impact of PGEs emissions (Hees et al., 1998).

Concentration of PGEs has been increased much in the environment. PGEs from exhaust catalysts are deposit on roadsides and can be transported to water bodies; other sources like hospitals and industry discard these metals directly into the sewage system. It is important to study how these metals may become chemically/biochemically active and mobile for interactions with various environmental matrices under the changing climatic conditions, to give a prediction on the possible hazards of PGEs for human health.

Accordingly, the occurrence and distribution of the traffic–related precious metals should be monitored carefully to prevent adverse effects of these metals for the biosphere (Haus et al., 2007). More information about exposure to PGEs and the health effects are urgently required (Fragnière et al., 2005).

Because of their inertness PGEs have been considered harmless for a long time. Now it is known that they are present at higher levels in the environment, taken up by plants, and can possibly enter the food chain (Rao and Reddi, 2000). Plants and animals can uptake and accumulate soluble species of PGEs, especially palladium, in plants deposition occurs in the roots by binding to low molecular weight cells, while animals accumulate PGEs mainly in liver and kidney. Although environmental levels of PGEs are still relatively low, recent reports of a progressive increase in these concentrations makes further research essential. Manufacturing solution to minimize the release of these metals from catalytic converters should be done.

The environment and health risks of exposures to these metals are greater than once thought (Wiseman and Zereini, 2009), the levels of PGEs in human samples are higher than might be expected from the crustal abundance (Vaughan and Florence, 1992), recent studies on PGEs toxicity, environmental bioavailability and concentration in biological matrix indicate that environmental exposures to these metals may pose a health risk. Due their dispersion in the environment, mainly on roads and highways, it is necessary to track the possible pathways of these contaminants (Mesquita da Silva et al., 2001). The problem of environmental dispersion of PGEs should be carefully followed.

Platinum has received most attention, but works about other elements, like palladium and rhodium also used in automotive catalytic converters, are necessary to be improved in environmental studies. Palladium has increasingly being used in catalytic converters and its emission rate seems to be superior to platinum, and it has been reported its higher mobility (Moldovan, 2007), and it seems to be more bioavailable in plants and water–living organisms (Bocca et al., 2004). Moreover, iridium has recently been introduced in Japan catalysts to reduce the emission of nitrogen oxides in lean-burn engines (Merget and Rosner, 2001). Iridium emissions should be assessed due to its high volatility.

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Chapter 4 – Evidence of increased anthropogenic emissions of platinum: Time–series analysis of mussels (1991–2011) of an urban beach

ABSTRACT

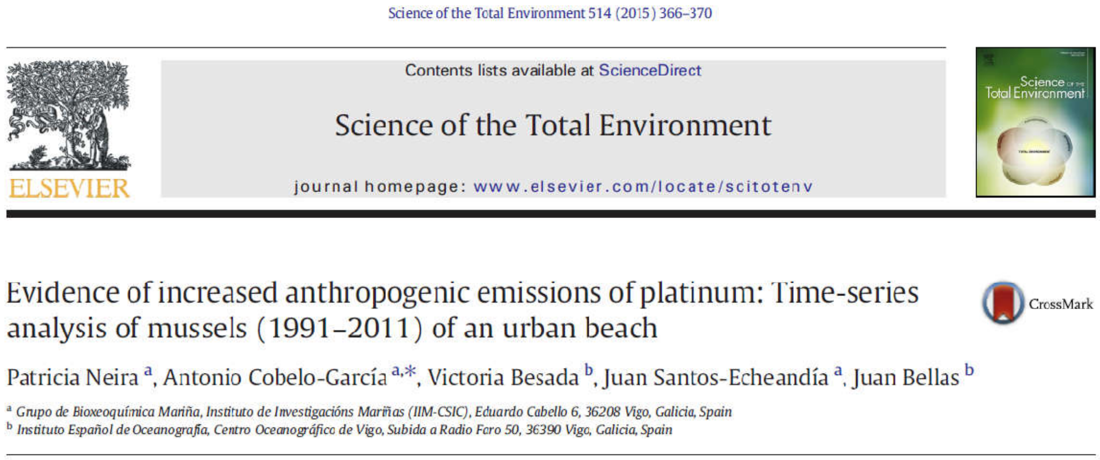
- 4.1. Introduction
- 4.2. Materials and Methods
  - 4.2.1. Sampling area
  - 4.2.2. Pretreatment
  - 4.2.3. Pt analysis
- 4.3. Results and Discussion
  - 4.3.1. Temporal trend of Pt accumulation in mussels
  - 4.3.2. Link between Pt accumulation and traffic–borne contamination
  - 4.3.3. Extent of bioaccumulation of Pt in *M. galloprovincialis*
- 4.4. Conclusion

REFERENCES

We evaluate the role of platinum as an emerging contaminant by the analysis of Pt concentration in a time-series of 20 years of wild mussels; with this we try to explain the accumulation of Pt in the marine environment plus the bioavailability of this metal to the organisms and its potential entry into the food chain.

This chapter is based on the article (Appendix 13):

Neira, P., Cobelo-García, A., Besada, V., Santos-Echeandía, J., & Bellas, J. (2015). Evidence of increased anthropogenic emissions of platinum: time–series analysis of mussels (1991-2011) of an urban beach. *The Science of the Total Environment*, 514, 366–70.



Science of the Total Environment 514 (2015) 366–370

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Evidence of increased anthropogenic emissions of platinum: Time-series analysis of mussels (1991–2011) of an urban beach

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4. Evidence of increased anthropogenic emissions of platinum: Time–series analysis of mussels (1991–2011) of an urban beach

ABSTRACT

The anthropogenic emissions of Pt to the environment have increased significantly over the past decades, especially after the introduction of the catalytic converters in motor vehicles. In order to check whether this is affecting the levels of this trace metal on living organisms, time-series analysis of freeze-dried soft tissue material of wild mussels (*Mytilus galloprovincialis*) covering the period from 1991 to 2001 and collected at an urban beach in the city of Vigo (NW Iberian Peninsula) was conducted. Concentrations ranged from 0.30 to 0.68 ng g^{-1} with an average concentration of 0.47±0.10 ng g^{-1} (n=21); these concentrations were higher than those obtained for samples collected at a control location away from anthropogenic pressure (0.31 ± 0.10 ng g^{-1}; n = 5). Platinum concentrations followed a statistically significant temporal trend (at the 0.020 level), and the excess of Pt in mussels over the 1991–2011 period compared to the control location were correlated with the European Pt autocatalyst demand (p=0.0006) and, especially, the car sales in Spain (p=0.0001). A bioaccumulation factor of $\approx 5 \cdot 10^3$ was derived, which is greater than those previously calculated for Pt from exposure experiments, but 1–2 orders of magnitude lower than other trace elements (e.g. Zn, Cu, Pb, Cd).

4.1. Introduction

The natural environmental concentrations of platinum in the biosphere are extremely low, with average crustal abundance of 0.5 ng g^{-1} (Rudnick and Gao, 2003). However, Pt concentrations are currently increasing in the environment due to its use in a variety of anthropogenic activities, the most important including the use of this element in automobile catalytic converters and the manufacture of jewellery, representing 43% and 31%, respectively, of the total Pt demanded during the last decade (Johnson Matthey, 2013). The anthropogenic disturbance of the cycle of Pt at the Earth's surface is such that it has been estimated that more than 80% of the Pt flux is derived from anthropogenic activities (Sen and Peucker-Ehrenbrink, 2012).

As a result of the Pt emissions from catalytic converters in motor vehicles, this element currently represents a new category of traffic related trace metal contaminant in the environment (Haus et al., 2007). Accordingly, elevated Pt concentrations have been reported in areas and environmental compartments subject to vehicular traffic pressure such as road dust, roadside soils, sewage sludge and sediments of urban rivers and harbour basins (Ely et al., 2001; Fritsche and Meisel, 2004; Leśniewska et al., 2004; Schäfer et al., 1999; Zimmermann and Sures, 2004); also, evidence for a long range transport and global platinum environmental perturbation has been given (Soyol-Erdene et al., 2011).

The bioavailability and uptake of Pt emitted from catalytic converters and from soluble Pt species were demonstrated in exposure studies using different aquatic organisms, including freshwater isopods (Moldovan et al., 2001), European eels (Zimmermann et al., 2004), zebra mussels (Sures and Zimmermann, 2007), or common periwinkles (Mulholland and Turner, 2011). However, to date only few studies have been carried out reporting ambient concentrations of Pt in biological matrices. Among these, (i) Jensen et al., (2002) analysed the contamination of feathers from raptor species showing an increased temporal trend of Pt concentrations reflecting the introduction of automobile catalytic converters; also, (ii) Haus et al., (2007) demonstrated the bioavailability of traffic–borne Pt in field samples of freshwater crustaceans from the Ruhr district (Germany) showing bioaccumulation factors in the range of other traffic related metals.

In this study we report Pt concentrations in time-series samples (1991–2011) of wild mussels (*Mytilus galloprovincialis*) collected in an urban beach of the Vigo Ria (NW Iberian Peninsula (Fig. 1). Mussels are ideal organisms for use as bio-indicators because as filtering organisms they tend to accumulate dissolved substances in the environment (e.g. Bellas et al., 2014; Goldberg, 1986; Soto et al., 1997) and have been widely used in the study area for biomonitoring of metal contamination (Besada et al., 2002; 2011). The main aim of this study is therefore to determine the temporal variation of Pt biological uptake in an urban beach during the past two decades and results will be discussed in terms of the potential link between the temporal variation of Pt accumulation in mussels and the anthropogenic use of this element from the early 1990's.

4.2. Materials and Methods

4.2.1. Sampling area

Wild mussels (*M. galloprovincialis*) were collected manually and during low tides, in the period of September–November, which corresponds to the second pre–spawning period in this area (Cáceres-Martínez and Figueras, 1998) in order to minimize variations caused by differences in the mussel physiology and therefore minimize seasonal environmental variations. Sampling strategies during this two decade long program are described elsewhere (Besada et al., 2014).

Mussels were collected at Samil beach in the Vigo Ria, an urban beach located in the city of Vigo (Figure 4.1) which holds a population of approx. 300,000 inhabitants; an urban stream (Lagares, mean annual flow of aprox. $4m^3\ s^{-2}$; Perez-Arlucea et al., 2005) discharges at the western part of the beach. For comparison purposes, mussel samples from a control point (Oia, Figure 4.1) located around 40 km southward and far from any significant contamination influence were analysed for selected years (1991, 1995, 2000, 2005, 2010). The excess Pt fraction in the Samil beach samples was calculated subtracting the concentrations obtained from the control point.

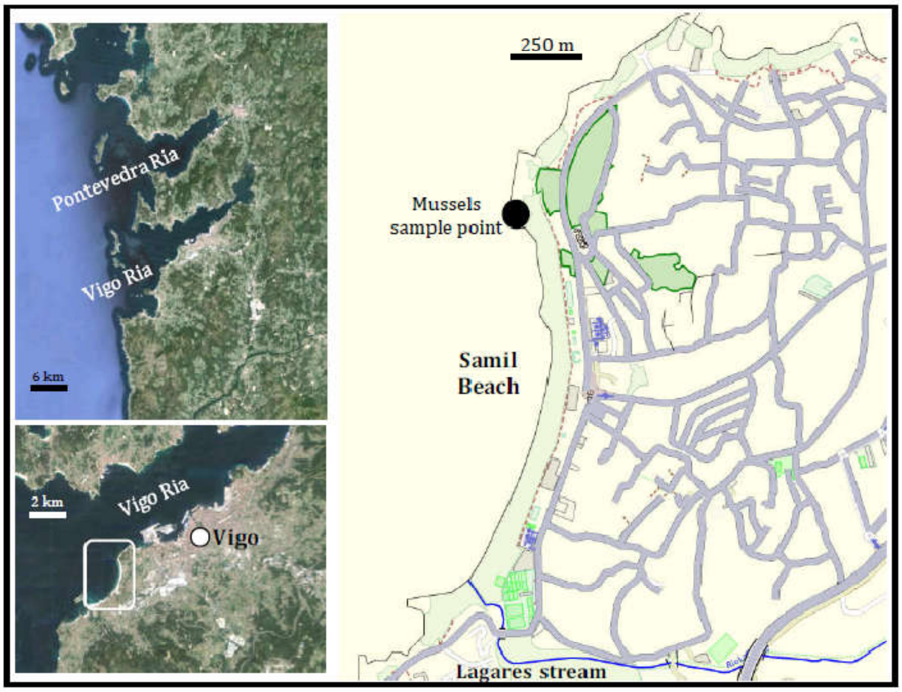

Figure 4.1. Sampling location of mussels in the Samil beach (42°13.177 N, 08°46.604 W) of the Vigo Ria (NW Iberian Peninsula).

4.2.2. Pretreatment

Each sample of mussels was prepared from 50 or more individuals representing the available size range (35–60 mm) existing in the sampling location. Soft tissues were separated from the shells, triturated with Ultraturrax and freeze-dried. An aliquot of the liophilized sample was withdrawn to calculate its water percentage (drying at 105 °C for 24 h, until constant weight). After a freeze-drying process, samples were homogenised again with a mixer mill and stored in acid-washed glass vials at room temperature until analysis.

4.2.3. Pt analysis

Platinum analysis was performed by means of catalytic adsorptive cathodic stripping voltammetry after appropriate digestion (Cobelo-García et al., 2014); briefly, around 100 mg of sample was ashed up to 800 °C in quartz crucibles in order to eliminate refractory organic material that may interfere during the voltammetric determination. Once cooled, a mixture of 3 mL of HCl and 1 mL of HNO_3 was added to the crucible and allowed to rest for at least 1 h. Then, the acid mixture was transferred to uncapped 30 mL PFA vials (Savillex) and placed on a Teflon-coated hot plate at 195 °C and allowed to evaporate until near dryness. After cooling down, 1 mL of H_2SO_4 was added to the vials and placed again on the hot plate until no fumes were observed (only sulphuric acid was present). After cooling, samples were diluted with 0.1 M HCl and transferred to 25 mL polypropylene volumetric flasks pending analysis. Typically, 3 independent digestions were performed for each sample and the relative standard deviation (RSD%) was generally below 15%.

In order to avoid contamination of samples, sample pretreatment and manipulation were performed in a laminar flow bench (ISO–5) housed inside and ISO–7 lab. Voltammetric determinations were carried out using a µAutolab Type III potentiostat (Metrohm Autolab B.V.) connected to a polarographic stand (Metrohm model 663VA). Details of the voltammetric procedure for the Pt determination are given in Cobelo-García et al. (2014). The detection limit was determined as three times the standard deviation of the blanks (n=15) and was found to be 0.04 ng g^{-1}. Concentrations are expressed as in ng g^{-1} dry weight. Since at present there are no certified reference materials (CRMs) for platinum in biological matrices, the accuracy of the analytical procedure was checked using BCR–723 (road dust; Institute for Reference Materials and

Measurements, Belgium) and JSd–2 (river sediment; Geological Survey of Japan), obtaining recoveries greater than 95% (BCR–723) and 80% (JSd–2).

4.3. Results and discussion

4.3.1. Temporal trend of Pt accumulation in mussels

The results obtained for the time series (1991–2011) of mussels collected in the Samil urban beach ranged from 0.30 to 0.68 ng g^{-1} (Figure 4.2), with an average concentration of 0.47 ± 0.10 ng g^{-1} (average ± 1SD; n = 21). Lower concentrations were obtained for the samples collected at the control location (Oia, Fig. 4.1): 0.31 ± 0.10 ng g^{-1} (n = 5), indicating the higher anthropogenic pressure at the urban beach. These concentrations are in the range of those given for other aquatic organisms previously reported in the literature (with the exception of the elevated concentrations given for the freshwater crustacean *Asellus aquaticus* in two Swedish rivers subject to traffic pressure; Appendix 4) which indicates that Pt is typically present at the nanogram or sub-nanogram per gram level in aquatic biota. These values are also similar to the crustal abundance of Pt (0.5 ng g^{-1}; Rudnick and Gao, 2003) or its concentrations in uncontaminated coastal sediments (0.3–0.6 ng g^{-1}; Cobelo-García et al., 2011).

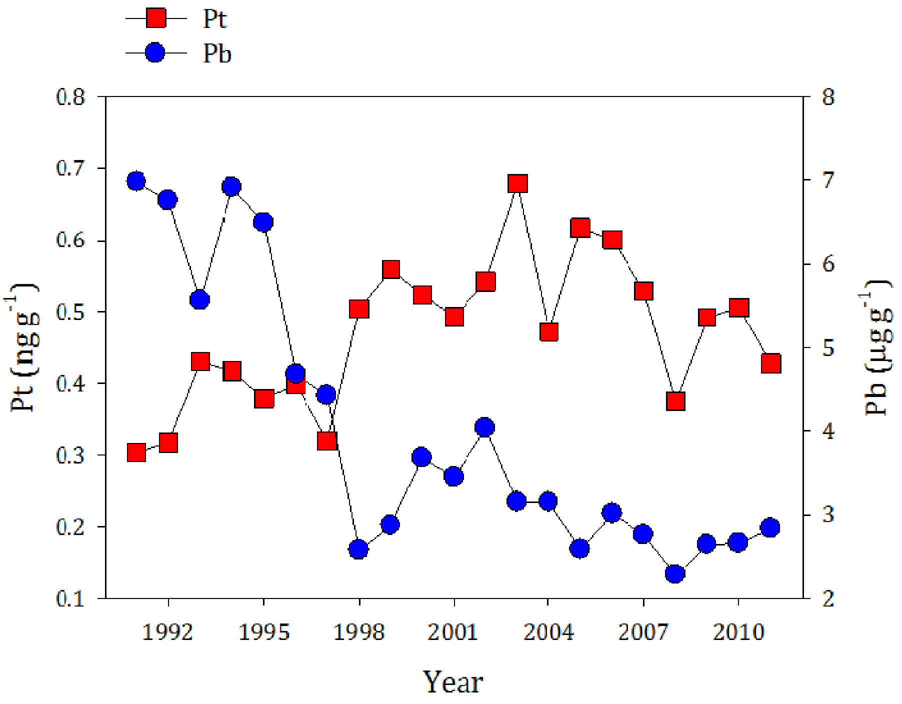

Figure 4.2. Pt (ng g^{-1}) and Pb (µg g^{-1}; Victoria Besada et al., (2014) concentrations in mussels at Samil beach (see Fig. 4.1). Sample pre-treatment and the analytical procedure are given in Section 4.2.

In order to check whether the Pt concentrations followed a statistically significant temporal trend, the Kendall's Tau–b correlation coefficients were calculated as described earlier (Besada et al., 2002; 2014). A Kendall Tau–b coefficient of 0.324 was obtained, which represents a significance level of 0.020. This significant increase in Pt concentrations is accompanied by a decrease in Pb (Figure 4.2; Kendall Tau–b = 0.663, significance level 0.000), a metal historically linked to traffic–borne pollution due to the use of leaded gasoline in the past. The phasing-out of leaded gasoline during the mid to late 1990's was simultaneous with the introduction of catalytic converters (containing precious metals — Pt, Pd, and Rh) and thus explains their opposite temporal trend observed (Fig. 2).

4.3.2. Link between Pt accumulation and traffic–borne contamination

Since the most important anthropogenic input of Pt to the environment is currently its use in vehicle catalytic converters (e.g. Cobelo-García et al., 2011), the excess (or anthropogenic) fraction of Pt in mussels from the urban beach — calculated as indicated in Section 4.2.1 — were compared to the autocatalyst platinum demand in Europe and the car sales in Spain and Portugal (due to the proximity of Vigo to Portugal, i.e. ≈30 km) — owing that the Pt release rate from new cars is significantly greater than for old cars; (Palacios et al., 2000) — for the studied period (Figure 4.3). Inspection of Figure 4.3 shows that the increase of the excess fraction of Pt starts in the late 1990's, well before the sharp increase in the Pt autocatalyst demand during the 2000's but coincident with the rise of car sales for those years. A decrease in the excess Pt in the last years in agreement with the drop in Pt demand and car sales provoked by the recent economic crisis is also evident. A significant correlation was obtained between the excess Pt and the autocatalyst demand (two–tailed $p < 0.0001$) and the car sales in Spain and Portugal ($p < 0.01$), which provides a strong evidence of the traffic-borne contamination as the source of the increased Pt concentrations in the mussel samples in the past two decades at this urban beach.

4.3.3. Extent of bioaccumulation of Pt in *M. galloprovincialis*

The bioaccumulation factor (BF) of platinum, defined as:

$$BF = [Pt_m] / [Pt_w]$$

where $[Pt_m]$ is the Pt concentration in the mussels (expressed as nanograms of Pt per kilogram of mussel in a dry weight basis) and $[Pt_w]$ is the dissolved Pt concentration in the

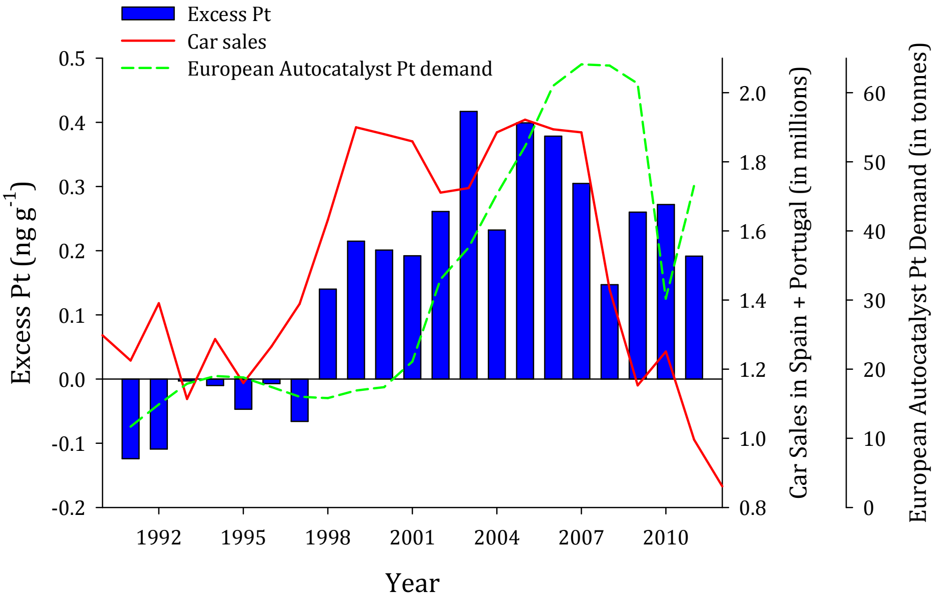

Figure 4.3. Excess of Pt in mussels from Samil beach with respect to the background levels and compared to car sales in Spain and Portugal (data from www.anfac.com and www.autoinforma.pt; internet access: January 2015) and European autocatalyst Pt demand (data from www.platinum.matthey.com; internet access: January 2015).

water column (expressed as nanograms of Pt per kilogram of water), was calculated using the average concentrations in the mussels (470 ng kg^{-1}; Appendix 4) and a typical dissolved Pt concentration in the Vigo Ria of 0.5 pM, i.e. 0.1 ng kg^{-1} (Cobelo-García et al., 2013), resulting in a BF of $\approx 5 \cdot 10^3$. This indicates that Pt is effectively bioaccumulated by aquatic organisms, as already observed in previous exposure studies (e.g. (Sures and Zimmermann, 2007; Zimmermann et al., 2005); however, bioaccumulation factors derived by the latter yielded systematically lower values. For example, Sures and Zimmermann (2007) reported BFs ranging from 40 to 100 for the freshwater zebra mussel (*Dreissena polymorpha*) exposed to dissolved Pt added in the form of $PtCl_4$; similarly, Veltz et al. (1996) obtained a BF of 96 for the worm

Lumbriculus variegatus exposed to $PtCl_6^{2-}$. For seawater organisms, Mulholland and Turner (2011) derived a BF of 300 for themacroalgae *Ulva lactuca* and 20–30 for the marine gastropod *Littorina littorea* exposed to Pt in the form of $PtCl_6^{2-}$/$PtCl^{5-}$.

The higher accumulation factor obtained in this study compared to exposure experiments may be explained by (i) the low incubation periods — generally from few days to one month — used in exposure studies which may underestimate the bioaccumulation due to non-equilibrium conditions (Veltz et al., 1996), and (ii) the uptake of suspended particles containing elevated Pt concentrations in real ambient conditions; accordingly, in coastal areas subject to urban pressure, whereas dissolved Pt may be similar or only slightly higher than uncontaminated waters, Pt concentrations in suspended matter may greatly exceed typical background values due to the input of strongly–bound Pt–rich particles from catalytic converters (Cobelo-García et al., 2013).

Compared to other trace metals, the BF obtained in this study for Pt ($\approx 5 \cdot 10^3$) is significantly lower. For example, using the metal concentrations in the same mussels samples from the Vigo Ria reported earlier (Besada et al., 2014) and the typical dissolved metal concentrations in this basin (Santos-Echeandía et al., 2009), BFs around 1–2 orders of magnitude higher are obtained for Zn (BF $\approx 5 \cdot 10^5$), Cu (BF $\approx 2 \cdot 10^4$), Pb (BF $\approx 9 \cdot 10^4$) or Cd (BF $\approx 1 \cdot 10^5$).

4.4. Conclusion

The present study reports, for the first time, the temporal variation of Pt concentrations in aquatic organisms and shows evidence of the link of the observed increased levels in the recent years with the use of this metal in anthropogenic activities (i.e. catalytic converters in motor vehicles). This is especially relevant since the potential health risk from exposures to Pt is greater than once thought (Wiseman and Zereini, 2009) and, therefore, increasing Pt concentrations may lead in the future to toxic effects on living organisms. These results point the need for more field studies on the accumulation of Pt in organisms subject to traffic–borne contamination, as well as including other elements also used in automobile catalytic converters, i.e., Rh and, especially, Pd since it has shown a higher degree of mobilization from particles emitted by catalytic converters than Pt or Rh (Dahlheimer et al., 2007).

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PART III

TECHNOLOGY–CRITICAL ELEMENTS BIOACCUMULATION AND BEHAVIOUR IN COASTAL SYSTEMS

Chapter 5 – A critical review on Technology Critical Elements behaviour and concentrations in oceans and marine organisms

5.1. Introduction

5.2. The Lanthanide Series or Rare Earth Elements (REEs)

5.3. Group 5 – Niobium and Tantalum

5.4. Group 13 – Gallium, Indium and Thallium

5.5. Group 14 – Germanium

5.6. Group 16 – Tellurium

5.7. Outlook and Conclusions

REFERENCES

5. A critical review on Technology Critical Elements behaviour and concentrations in oceans and marine organisms

5.1. Introduction

The Earth's crust is composed of a great variety of igneous, metamorphic and sedimentary rocks, mainly composed of a few elements (e.g. Si, Al, Fe, Ca, Na, K, Mg) and their oxides (Rudnick and Gao, 2003). The majority of these "abundant" elements are regulated by protocols and directives (i.e. EU Water Framework Directive 2000/60/CE and 2008/56/CE) that determine their appropriate environmental concentrations. These elements (e.g. Cd, Pb, Hg, Ni) are periodically measured. This official biomonitoring is because of their proved adverse environmental effects at elevated concentrations.

A significant number of trace elements are, however, excluded in these studies. This is due to: i) their low ambient concentrations, generally below the detection limits of the analytical procedures employed, and ii) the absence of any significant industrial role in the past, thus having no apparent environmental implications (Cobelo-García et al., 2015). This situation is currently changing, since several of these non–regulated trace elements are now key components in the development of new technologies, including electronic displays, semiconductors, energy–related technologies or telecommunications technology. They are defined as Technology Critical Elements (TCEs) (Figure 5.1), and include tellurium (Te), germanium (Ge), gallium (Ga), indium (In), thallium (Tl), niobium (Nb), tantalum (Ta), the platinum group elements (PGEs: Pt, Pd, Rh, Os, Ir, Ru and the rare earth elements (REEs: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu). The extent of the environmental impact of the increasing anthropogenic use of these technology–critical elements needs therefore to be further assessed.

These TCEs usually appear at lower concentrations in seawater with respect to those of the continental crust. This is due to the biogeochemical cycle of metals in the oceans where they tend to be adsorbed onto surfaces and deposited in the sediments (Orians and Boyle, 1993), usually those metals are not in the oceans long enough to be entirely incorporated into the ocean cycle. The ecotoxicological effects of TCES on organisms and hazardous adverse consequences for the environment depend on various factors such as chemical form of the compounds (if it is bioavailable) or anthropogenic concentration with respect to the natural background levels. To accurately measure trace levels of metals in seawater and organisms we need very precise and sensitive analytical instrumentation, usually after preconcentration processes and removal of ions and dissolved organic matter that may interfere with the signal. It is also important to proceed with clean trace metal sampling strategies to avoid sample contamination.

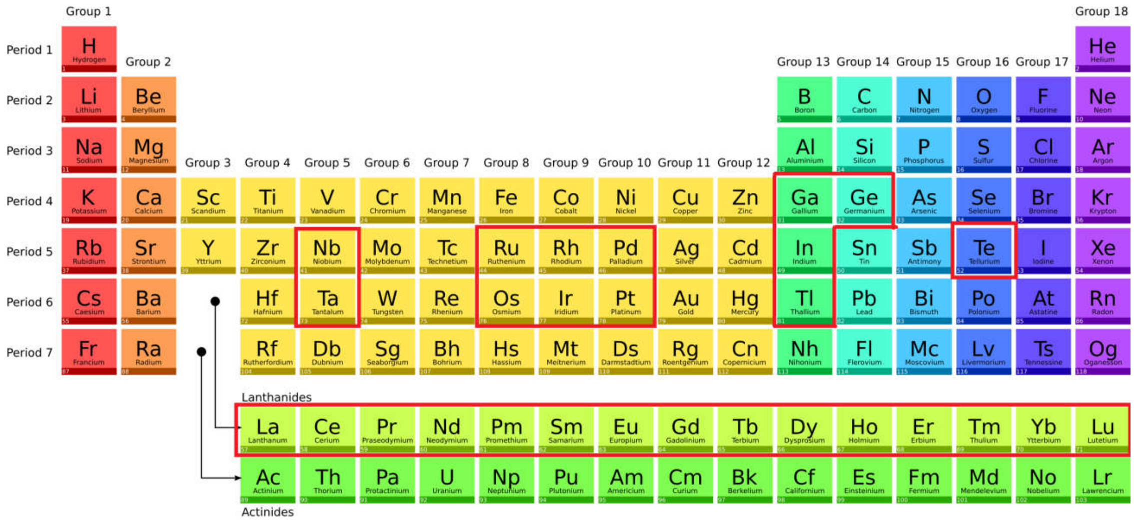

Figure 5.1. Technology-Critical Elements highlighted in the Periodic Table.

The possible hazardous of TCEs are subject to economic and geopolitical aspects (Gwenzi et al., 2018) and more chronic and acute toxicity data is necessary to develop appropriate water concentration standards, elaborate guidelines and mitigation strategies to deal with the possible toxicity of TCEs for the organisms and the environment. Actually inputs of TCEs to the biosphere are growing with the consequent impact on the biogeochemical cycles and increasing the exposure of living organisms to yet unknown effects. This chapter approach a review of TCEs (except PGEs already discussed in Chapter 3) in the marine environment with special attention to marine organisms. This review will critically examine the existing information looking for strengths and weaknesses of this new area of research.

5.2. The Lanthanide Series or Rare Earth Elements (REEs)

There are 15 elements classified as the Rare Earth Elements (REEs): lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm; synthetic, made in the laboratory), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). These elements are also subdivided into three categories depending on their atomic number; the light REEs (LREE) are those with the lowest atomic number: La, Ce, Pr and Nd, while heavy REEs (HREE) have the highest atomic number: Tb, Dy, Ho, Er, Tm, Yb and Lu. There is also another category called the medium REE (MREE): Sm, Eu and Gd. Scandium (Sc) and yttrium (Y) can also be considered as REEs for their similar physico–chemical properties and economic importance.

The REEs are characterized for having similar physical and chemical properties, which vary small but systematically along the series (Elderfield and Greaves, 1982), and for usually being found together in nature in the same ore deposits (Chua, 1998). The term "rare" is not due to their low abundance, but because to the difficulty of separate the different elements and the lack of economically exploitable ore deposits, supplied mainly by China (97%), (Massari and Ruberti, 2013). In aqueous solution REEs predominantly exist in the trivalent oxidation state (3+) (Elderfield and Greaves, 1982), the only exceptions are Ce (4+) and Eu (2+) (Olías et al., 2005), although Eu can be reduced (2+) or oxidized (4+) depending on the media conditions (Hatje et al., 2014).

REEs are used in modern industry for the manufacture of important products, in agriculture for pesticides and are key components for the modern life as part of basic technologies and green technologies (Wen et al., 2006; U.S. GAO, 2010). Some of the most important technological applications of REEs are summarized in Table 1 as a proof of their classification as Technology Critical Elements (TCEs), being the most commonly used the LREE (La, Ce, Pr and Nd) (European Commision, 2011; Massari and Ruberti, 2013).

Table 5.1. Examples of the most common applications of the Rare Earth Elements.

Application	Examples	Rare-earth elements
MAGNETICS	- Automotive parts - Computer hard drives - Magnetic Resonance Imaging (MRI) - Green-energy power generation	**Pr, Nd, Sm, Tb, Dy**
PHOSPHORS	- Fibre optic - Lasers and LED lighting - Medical imaging - Screen displays	**Pr, Nd, Eu, Gd, Tb, Er, Tm, Yb**
METAL ALLOYS	- Al/Mg alloys - Fuel cells - NimH batteries - Steel	**La, Ce, Pr, Nd**
CATALYSTS	- Air pollution controls - Chemical processing - Petroleum refining - Water treatment	**La, Ce, Pr, Nd**
CERAMICS	- Capacitors - Colorants - Refractories - Sensors	**La, Ce, Pr, Nd, Gd, Ho, Er, Lu**
GLASS	- Coatings - Pigments - Polishing - UV resistant glass	**La, Ce, Pr, Nd, Gd, Ho, Er, Yb**

DEFENSE	- Aircraft structures - Guidance systems - Satellite communication - Smart missiles	**La, Pr, Nd, Sm, Eu, Tb, Dy, Lu**

Besides, REEs in fertilizers, bactericides and animal food for animal husbandry and aquaculture are widely used in China since early 70s (Fang et al., 2007; Sun et al., 1994) with extraordinary short–term results for plant and animal growing, constituting an important route of entry of anthropogenic REEs into the environment (Gwenzi et al., 2018). The difficult access to REEs ore deposits and the lack appropriate toxicological studies and rigorous data treatment make their use in Europe not legal (d'Aquino et al., 2009).

Other important use of the REEs is in geology as tracers of geochemical process (Bau and Dulski, 1996). Due to their coherent behaviour as a group, the geochemical processes affect the REEs series depending on their atomic number (Elderfield et al., 1990), which lead REEs to show a fractionation depending on the chemical circumstances (Akagi et al., 2004), by the analysis of REEs series we can infer the past conditions and rebuild past biogeochemical cycles, organisms bioaccumulation, water masses origin, etc.

With this expanding use of REEs the presence of these elements in the environment is increasing, and will continue for the next decades (Volokh et al., 1990) reaching all environmental compartments, from soils to water bodies and finally into the food chain (Miao et al.; 2011). REEs in aquatic systems can come from erosion and runoff from soils, terrestrial landfills or mine wastes, also from discharge or runoff from industrial effluents of wastewater systems (Gwenzi et al., 2018). Once there, REEs can be uptaken by algae or fish and finally impact the human health through the consumption of contaminated food or water.

REEs dissolved in oceans come from continental weathering transported through rivers, the pattern for the majority of rivers span a wide range depending on the shale concentrations, with an enrichment in HREE in the dissolved phase (Elderfield et al., 1990; Goldstein and Jacobsen, 1988; Nozaki et al., 2000). This fractionation of REEs compared with the continental crust reflects the geochemical processes occurred. But most important for establish the REEs composition in rivers is the physico–chemical parameters (Elderfield et al., 1990; Goldstein and Jacobsen, 1988). Concentration of REEs in rivers is pH–dependent, with higher pH we found lower concentration and more fractionation of the elements with a major abundance of HREE (Sholkovitz, 1995). As the REEs are transported to the oceans via estuaries, the coastal waters will exhibit concentrations between river and ocean waters (Elderfield et al., 1990), reflecting river and ocean influences, REE fractionation and pH dependence.

The natural concentrations of REEs in seawater are very low (pmol/kg) (Appendix 5), this added to the fact that REEs tend to fraction depending on the chemical conditions make the determination of REEs in natural waters a laborious task compared with continental studies where the concentrations are higher (Hatje et al., 2014). For the determination of REEs in aquatic systems we need to be able to multi–element quantification, with high precision and sensitivity, over a wide concentration range (Hatje et al., 2014). Despite this, detectable levels of REEs have been reported worldwide in rivers, lakes, groundwater, coastal seawater and tap water (Akagi et al., 2004; Kulaksiz and Bau, 2007; Merschel et al., 2015; Tepe et al., 2014).

The distribution of REEs in aquatic systems is very complex and dependent on various factors such as salinity, ionic strength and especially pH (Cantrell and Byrne, 1987; Elderfield et al., 1990). Sediment operates as a contaminant reservoir while water transports this elements to the organisms (Drabaek et al., 1987; Weltje et al., 2002; Yang et al., 1999). During this transport REEs tend to form complexes mainly with carbonates, but also sulphate, chloride and fluoride complexes (Cantrell and Byrne, 1987). Column distribution of REEs in seawater follows an increase pattern with depth, with a maximum concentration of HREEs at around 3.000 m while the LREEs maximum can be found even deeper (Piepgras and Jacobsen, 1992), due to moderation by scavenging processes in the upper ocean (Bertram and Elderfield, 1993). The distribution of REE in seawater is generally dependent on the oceanographic parameters of the area (Cantrell and Byrne, 1987; Piepgras and Jacobsen, 1992) and due to mixing processes in estuaries (Lawrence and Kamber, 2006). The cycle and flux of REEs in seawater is also controlled by the concentration of REEs within the upper sediments which act as a source of REEs to the water column (Abbott et al., 2015).

Within the limitation of existing studies on REEs in seawater, the highest values for each element have been found for Ce (778 pmol/kg), followed by Gd (181 pmol/kg), La (180 pmol/kg) and Nd (118 pmol/kg) (Akagi and Edanami, 2017) in a study of REEs concentration in three port areas of Japan. On the contrary, the lowest levels, within the maximums found for each element, are those of Tm (5.24 pmol/kg), Tb (5.43 pmol/kg), and Ho (9.22 pmol/kg) (Akagi and

Edanami, 2017). Here again, with no exception, the maximum values are registered in the port areas of Japan.

We also discover high concentration values for REEs in surface samples taken near the coast, as the case of the Weser Estuary (Kulaksiz and Bau, 2011a), the Coral Sea in Australia (Lawrence and Kamber, 2006) and the San Francisco Bay Plume (Hatje et al., 2014a). In addition, we can also detect high concentration values in deep water oceanic samples, bottom waters from the Eastern North Pacific Ocean display the high oceanic concentration found (Piepgras and Jacobsen, 1992) for all REEs except Ce which maximum oceanic value was encountered in deep waters from the North Atlantic Ocean (Elderfield and Greaves, 1982).

Regarding the lowest values found to date among the few studies conducted on REEs in seawater, they tend to appear in surface oceanic water samples. Especially low are values of the North Pacific Ocean (Hatje et al., 2014a; Piepgras and Jacobsen, 1992). Only Ce, show its lowest value at depths around 1000–3000m in samples taken in the Indian Ocean (Bertram and Elderfield, 1993).

As a general rule, it seems that the values of REEs are higher near the coast and in deep oceanic waters. This is due to the continental origin of REEs which main sources of entry to the marine environment are rivers, runoff from soils, terrestrial landfills or mine waster, discharge or runoff from industrial effluents or wastewater systems (Gwenzi et al., 2018). Therefore highest REEs levels are usually found in semi–enclosed coastal or port areas (estuaries), decreasing as we move to the open ocean. Finally note that within ocean waters, the levels are generally higher in deeper waters (Piepgras and Jacobsen, 1992), probably due to remineralization processes or sedimentary inputs where the REEs have been accumulated after passing through the water column.

The possible risk of REEs to the environment resides in their bioavailability. In order to estimate the bioavailability it is necessary to measure the concentration of REEs at which organisms have a response (Fang et al., 2007) keeping in mind that REEs tend to fractionate depending on the chemical conditions (Shan et al., 2003; Wang et al., 2004). In seawater, HREE tend to remain in solution while LREE tend to be assimilated by organisms or adsorbed onto surfaces (Byrne and Kim, 1990; Elderfield et al., 1990; Goldstein and Jacobsen, 1988; Nozaki et al., 2000; Sholkovitz, 1992). This is due to the HREEs small ionic radii which allows HREEs to remain stable in solution through the formation of strong complexes (Piepgras and Jacobsen, 1992; Sholkovitz, 1995). The free form of REEs is the preferably assimilated by the organisms (Strady et al., 2015). In solution there is a small fraction of free REEs, mostly free LREE, able to be incorporated into the food chain (Li et al., 2016; Squadrone et al., 2017; Strady et al., 2015; Yang et al., 2016), thus having LREE a major biological impact. REEs abundance in marine organisms (Appendix 6) is related with sediment or suspended particles composition, not with the amount of REEs dissolved in seawater unless filtering organisms (Akagi and Edanami, 2017). Colloidal phase is also important in REEs fractionation in aquatic systems, as they contribute to the adsorption of LREE leaving HREE remain in the solution phase (Sholkovitz, 1992).

REEs are not considered as contaminants today in aquatic systems at the levels they appear in aquatic flora and fauna (Appendix 6), but the increasing use of these elements could change this situation in the future. Detectable concentrations of anthropogenic REEs were already found in the shells of mussels in rivers in Europe and North America (Merschel and Bau, 2015), proving their bioavailability and their entry into the food chain.

Highest values on REEs accumulation in nature were found in a study on seaweed from the northwest Mediterranean Sea (Squadrone et al., 2017). Maximum values for all REEs were discovered in algae species collected in the Marine Protected Area of the Ligurian Sea, which despite being a preserved area is heavy influenced by the proximity of an industrial and commercial harbour with high shipping traffic. Besides seaweed species that display the highest values for all REEs series, some bivalve species are also characterized for high REEs accumulation, especially when tissue is analyzed. Bivalves as filtering organisms tend to accumulate substances dissolved in the surrounding water (Goldberg, 1986).

The lowest REEs values were found in wild coral and fish species. Exceptionally low are REEs concentrations in marine fish species collected from local markets and supermarkets ready for human consumption in the Shandong province of China, located in the Yellow Sea (Yang et al., 2016). Also low were values discovered in coral species collected in the overseas regions of Bermuda North Rock, and particularly, in the Tarawa atoll, Kiribati (Sholkovitz and Shen, 1995).

We can conclude that REEs accumulation depends on the trophic level and no biomagnifications seems to occur. Vegetable organisms and herbivores show the highest levels, because they feed on the material present in the aquatic environment. As we go through the food chain, REEs concentration decreases, crustacean and sellfish organisms have concentrations two orders of magnitude lower than algae species. Finally some fish and coral varieties accumulate REEs even up to six orders of magnitude less than the vegetable genus.

Particularly studied has been the evidence of anthropogenic Gd in natural waters (Bau et al., 2006; Elbaz-Poulichet et al., 2002; Hatje et al., 2014; Kulaksiz and Bau, 2007, 2011a; 2013; Lawrence, 2010; Merschel et al., 2015; Nozaki et al., 2000; Tepe et al., 2014) highly correlated with the use of this metal in contrasting agents for magnetic resonance imaging (MRI), especially in densely populated areas with developed medical and healthcare systems (Bau and Dulski, 1996; Bau et al., 2006; Kulaksiz and Bau, 2007, 2011a; Nozaki et al., 2000). The increasing of anthropogenic Gd can be concerning due to its influence on calcium chemistry in cellular processes but is generally not reactive (Tepe et al., 2014). Positive anthropogenic Gd anomalies can be used as a pseudo–natural tracer of water discharge from waste–water treatment plants with emerging microcontaminants, since Gd cannot be removed by common sewage treatment technology (Bau et al., 2006; Kulaksiz and Bau, 2007; Lawrence, 2010; Lawrence et al., 2009; Tepe et al., 2014). Similar contamination for anthropogenic positive La anomalies was found in the Rhine River (Kulaksiz and Bau, 2011b) due to the use of this metal in catalytic cracking catalysis production. In addition to Gd other anthropogenic REEs, La and Sm, are also being found in industrial wastewater from catalysts production for petroleum refining (Kulaksız and Bau, 2013).

Mitigation strategies for REEs pollution are needed. It has been recently found that the macroalgae *Gracilaria gracilis* was able to effective remove and recover REEs from low concentration wastewaters (Jacinto et al., 2018). Andrès et al., (2003) also found promising results in REEs removal with the use of microbial biomass.

5.3. Group 5 – Niobium and Tantalum

Niobium (Nb) and tantalum (Ta) are metals belonging to the Group 5 of the Periodic Table of Elements. Nb and Ta are closely related as they have similar ionic radii and atomic diameters, and they are usually found together in nature forming complexes (Schroeder and Balassa, 1965). The most commonly known ore of Nb–Ta is called "coltan" and it is widely known for its extraordinary properties. Both Nb and Ta belong to the TCEs category mainly because of the coltan mineral which is used in several novel technologies (e. g. mobile phones) and because its extraction is produced in warfare regions of Africa (e. g.

Democratic Republic of Congo) which limited its extraction due to rebel movements and illegal mining (Mancheri et al., 2018).

The main uses of Nb comprise a wide range, just to mention some: electrolytic capacitors (as an alternative for Ta), photo–chromic devices, memristors and solar cells (Nico et al., 2016). The properties of Ta are not less, and Ta is used for automotive industries, aerospace, chemical processing, electronics and metallurgy among others (Nassar, 2017).

As well as REEs are used as tracers of past oceanographic conditions, the ratio Nb/Ta is also used to characterize oceanic water masses (Firdaus et al., 2011) but their analysis tend to be more difficult. The ratio is useful to trace water masses as this number tends to dismiss from the continental crust to open oceans (Firdaus et al., 2008).

There is no environmental sign of pollution due to anthropogenic activities or adverse effects after industrial exposure yet. But as their technological uses increases, the possibility of Nb and Ta exposure to the environment is escalating. Nowadays their determination in routine water analysis is not mandatory in the official directives due to the recent use of these metals and the difficulty of an accurate analysis because of their low concentrations in seawater and complexity.

They have an average crustal abundance of 130 µmol/kg for Nb and 5 µmol/kg for Ta (Rudnick and Gao, 2003), being the terrigenous source the most important for these elements to the oceans (Firdaus et al., 2011). Nb is known to be ubiquitous in water and living organisms (Schroeder and Balassa, 1965). The concentrations of Nb and Ta in seawater (Appendix 7) are much lower about 20 and 6 pmol/kg respectively (Li, 1991) than in the continental crust.

There are some studies on Nb and Ta concentrations in seawater but to the date little is known about the biogeochemistry of these metals. Generally, Nb shows a depletion in surface water increasing near the bottom; and Ta, which appears mainly in its particulate form (Filella, 2017) also shows a profile characterized for an increase of concentrations with depth (Firdaus et al., 2008). Only data for environmental seawater from the Pacific Ocean is available. Na and Ta concentrations in the North Pacific Ocean are lower (2.6–3.8 and 0.06–0.29 pmol/kg respectively) (Firdaus et al., 2007; Sohrin et al., 1998) than those found in Central Pacific Ocean (15.1–30.1 and 4.97–7.18 pmol/kg respectively) (Sun and Li, 2015).

There is no known biological role for Nb (Schroeder and Balassa, 1965) or Ta (Filella, 2017). Likewise there is not much information regarding biological concentrations of Nb and Ta in aquatic organisms. Some simple marine organisms as sea squirts (ascidians) are known to be able to absorb trace elements including Nb (Rayner-Canham, 1984) but this communication shows no concentration data.

5.4. Group 13 – Gallium, Indium and Thallium

Gallium (Ga), Indium (In) and Thallium (Tl) are in the same column of the periodic table as Aluminium (Al), so it could be expected they share similar physicochemical behaviour. Aluminium is one of the most abundant elements on the Earth's crust (Al_2O_3: 150 µmol/kg) (Rudnick and Gao, 2003) and in this theory of similar geochemical behaviour are based most studies on those elements. Among the TCEs included in the group 13 of the Periodic Table, the most abundant in the upper continental crust is Ga (250 µmol/kg) followed by Tl (4.4 µmol/kg) and In (0.5 µmol/kg) (Rudnick and Gao, 2003).

Already in the 80's some authors pointed to anthropogenic inputs of Ga into the rivers (Shiller and Boyle, 1987) probably due to coal burning (Bertine and Goldberg, 1971). Nowadays, gallium arsenide (GaAs) and indium arsenide (InAs) are frequently used in photovoltaic devices and electronics (e.g. light emitting diodes (LEDs), laser diodes, liquid crystal displays (LCDs), biosensors, microcircuits, semiconductors, photovoltaic devices, etc.). One of the biggest issues is that there are no current regulatory limits for the discharge of Ga and In to streams (Zeng et al., 2017) unlike the case of Tl (Peter and Viraraghavan, 2005). Dissolved Ga has also potential to be used as a tracer of marine processes (Orians and Boyle, 1993) because its variability due to the geographic location and depth, large residence times, 50 years, but not as large as to show regional characteristics.

Dissolved concentrations of Ga and Al are correlated through different marine environments suggesting same origin, probably through the wind (Shiller, 1988). Despite these similarities Ga shows important geochemical differences with Al (Benezeth et al., 1997). For example, the Ga/Al ratio was found to be higher by an order of magnitude in seawater ($0.8 \cdot 10^{-3}$ – $2.3 \cdot 10^{-3}$) than crustal rocks ($0.1 \cdot 10^{-3}$) (Shiller, 1988). The reason of this different behaviour could be the preferred dissolution of Ga embraced in solid phases and preferential removal of dissolved Al. The easily mobilization of Ga is due to the greater radius of Ga^{+3} respect to Al^{+3} (Benezeth et al., 1997). This removal Al also may implicate different processes as precipitation of solids, complexation processes, adsorption onto surfaces and/or organic matter.

Open sea concentrations of Ga are in the range of 2 to 60 pmol/kg (Orians and Boyle, 1993) while the crustal abundance is of 200 µmol/kg (Rudnick & Gao, 2003). Appendix 7 shows concentrations of Ga from the limited studies carried out in seawater samples. Lower concentrations of Ga were found in the cold deep water of the oceanic platform from the Sargasso Sea (11 pmol/kg) (Shiller, 1988), where higher values of 46 pmol/kg were found in superficial oceanic waters of the Atlantic Ocean compared with superficial samples taken near the coast in the Pacific Ocean (9–11 pmol/kg). The profile of dissolved Ga in the Arctic Ocean shows a smooth gradient from low concentrations similar to the Pacific Ocean (4–6 pmol/kg) to higher concentrations with deepth similar to those of the Atlantic Ocean waters (25–28 pmol/kg), showing the mixture of waters that takes place through the termocline in the Arctic Ocean (McAlister and Orians, 2015).

Recently biotoxicity test were developed in order to assess the possible toxicity of Ga released from alumina refinery, electronic industries or corrosion of electronic and photovoltaic devices to reach the marine environment. No detectable toxicity was found for tropical marine microalga *Isochrysis galbana* in a 72h exposure test with concentrations up to 90 µmol/kg of Ga (Trenfield et al., 2015). Notice that these levels are much higher than the maximum concentration measured in real seawater samples (46 pmol/kg (Shiller, 1988)). Minimal toxicity effects were found in the tropical marine snail *Nassarius dorsatus* when exposed during 96h to concentrations up to 100 µmol/kg of Ga**.** No discernible effects of Ga (van Dam et al., 2016) were found on the barnacle *Amphibalanus amphitrite* even at higher concentrations than discharged by the target alumina refinery studied. Limited toxic effects to vertebrate species were found at concentrations up to 15 and 10 nmol/kg of Ga (III) and In (III) respectively in toxicity assays (Olivares et al., 2016). No inhibitory effects were also found in different bioassays at high concentrations of 300 and 200 nmol/kg of Ga (III) and In (III) respectively, with the marine bacterium *Aliivibrio fischeri* and the crustacean *Daphnia magna* (Zeng et al., 2017) suggesting that Ga and In cannot be considered as a threat nowadays.

Despite this experimental data suggesting the low toxicity of Ga in marine systems, the information on chronic toxicity for marine organisms is still scarce. Suitable guidelines on water quality for Ga to achieve an appropriate environmental protection on this every day more used element are also needed.

On the other hand, indium is very similar to Ga in aqueous solution in terms of chemistry, it forms insoluble In^{3+} hydroxides but it also can form In salts which are soluble (Ladenberger et al., 2015; Wood and Samson, 2006). Like gallium, In also appears to have a similar geochemistry to aluminium.

Indium is a scarce element with several industrial applications which are increasing with the new technologies (White and Hemond, 2012) which fits this element into the classification as technology–critical metal. One important use of In is in copper–indium–gallium–selenide (CIGS) cells for thin–film photovoltaic technology. This cells have the advantage of being more durable and efficient than the more environmental friendly organic–photovoltaic (OPV) cells, with the detriment of the release of toxic materials (García-Valverde et al., 2010). When the CIGS cells are exposed to UV light and weather conditions the release of $Ga(OH)_4^-$ and particulate In to seawater may occur (Brun et al., 2016). Also, the indium–nitrate compound is widely used for chemical and medical applications and, its discharge trough waste streams into surface waters may represent a major source of anthropogenic pollution (Zurita et al., 2007).

The most important source of In to oceans, both natural and anthropogenic, is atmospheric deposition of mineral dust (Obata et al., 2007; White and Hemond, 2012) and also riverine inputs must be considered to a lesser extent (Alibo et al., 1998; Obata et al., 2004). Inputs from volcanism (White and Hemond, 2012) could also be important, and of course industrial inputs. And as for gallium, In/Al ratio in seawater is higher than in continental crust indicating processes of scavenging or weathering in estuaries and coastal systems between this two elements (Obata et al., 2004).

Open sea concentrations of In (Appendix 7) are in the range of 0.1–2.0 pmol/kg (Orians and Boyle, 1993) much smaller than its crustal abundance of 0.5 µmol/kg (Rudnick and Gao, 2003). There are important differences in In concentrations among different oceans, concentration in the Pacific ocean is clearly lower (0.09–0.15 pmol/kg) than in the Atlantic Ocean (0.6–1.5 pmol/kg) (Alibo et al., 1998; 1999) due to important processes of scavenging. Both vertical profiles, Pacific and Atlantic Oceans, have similarities with a surface maximum that decreases with depth to a minimum value found around 300–500m, from this point the concentrations increase again with depth to bottom waters. Concentrations of In the Mediterranean Sea are much higher, in the range of 6.5–10.7 pmol/kg (Alibo et al., 1999), with the maximum concentration located at 200m. Waters near the coast of Japan present a different behaviour, the surface maximum (0.58 pmol/kg) dramatically decreases with depth until stability in bottom waters (Obata et al., 2007).

Toxicological investigations on In are very limited and generally have been carried out under conditions that do not represent those in nature. Generally there is not a clear risk to aquatic biota. Inhibition of the bacterium *Vibrio fischeri* bioluminescence, decline on the proliferation of the alga *Chlorella vulgaris* and diminution of the crustacean *Daphnia magna* mobility were found in a study with concentrations as high as 3000 µg/L of indium nitrate (Zurita et al., 2007). An exposure study with In determined the LD_{50} at the range of 24–51 mg/L for the saltwater rotifer *Brachionus plicatilis* (Onikura et al., 2008).

Indium has not been labelled as a hazardous metal, but due to the lack of knowledge on its geochemical behaviour and environmental effects, In impact on ecosystems may be underestimated. Many studies suggest that the In form that reaches the ocean is not soluble but biodisponible compounds of In are extremely toxic (White and Hemond, 2012). Concentrations of In in nature are very low, but depending on the chemical form of In and the environmental conditions different toxic effects could appear. It is important to continue to study both chronic and acute toxicity of In compounds in the environment to assess potential risk of indium in natural waters due to the increasing use of this metal for industrial applications.

As for Ga and In there is another element from the group 13 of the Periodic Table that also fits into the category of technology–critical element, thallium (Tl). Tl in nature is found in two oxidation states: Tl (I) thermodynamically stable and Tl (III) highly volatile, more reactive and toxic (Lan and Lin, 2005; Turner et al., 2010). The same manner Ga and In geochemistry can be compared to that of Al, Tl geochemistry and behaviour is often compared with potassium (K) due to the similar ionic radius of Tl^+ and K^+ (Belzile and Chen, 2017; Rehkämper and Nielsen, 2004),.Thallium cation is the predominant form in aquatic systems and is less reactive and more stable (Ospina-Álvarez et al., 2015) than other forms. The cycle of Tl in oceans appears to be similar to K (Flegal et al., 1986) but more reactive (tendency to form Fe–Mn deposits) and with a shorter residence time, aprox. 20kyr, compared to that of potassium (4.5 My) (Baker et al., 2009; Rehkämper and Nielsen, 2004). Monovalent Tl cation participates and interferes with K^+ processes imitating the behaviour of monovalent K with a clear inability by cell membranes to distinguish between ions (Peter and Viraraghavan, 2005). Meanwhile Tl^{3+} posses a biogeochemistry more similar to that of Al, Ga and In (Del Valls et al., 1999) and is the most toxic and reactive form of Tl in aquatic environments (Ospina-Álvarez et al., 2015).

Tl has many industrial applications (e. g. electronics industry, catalyst in organic reaction, formation of alloys, pharmaceutical applications) (Onikura et al., 2008; Turner et al., 2010) enabling the entry of significant levels of Tl into the environment. Thallium concentrations are increasing in the environment due to human activities and technological development. Once there and due to several physico–chemical transformations Tl is redistributed throughout the water column and can end up being part of the food chain.

Natural sources of Tl to the environment are rivers, hydrothermal fluids, mineral aerosols and atmospheric loads form volcanic emissions (Baker et al., 2009). Anthropogenic Tl can enter the environment via coal combustion, cement production and metal mining, smelting and processing (Ralph and Twiss, 2002; Turner et al., 2010), especially via atmospheric transportation and deposition in the oceans (Duan et al., 2012). Conventional wastewater treatment plants and factory control of emissions have little effect on Tl removal due to the formation of high volatile compounds of Tl at elevated temperatures (Peter and Viraraghavan, 2005).

Concentrations of Tl in open oceans (Appendix 7) are often in the range of 50–70 pmol/kg (Flegal and Patterson, 1985) and rarely exceeds 100 pmol/kg (Belzile and Chen, 2017). In the oceans Tl geochemistry is determined by the adsorption and removal of this metal on ferro–manganese (Fe–Mn) minerals under reducing conditions and posterior incorporation into the lattice of clay minerals (Matthews and Riley, 1970). Concentration in the North Atlantic seawater was determined in the range of 40–50 pmol/kg in the water column (Matthews and Riley, 1970). Concentrations in the Northeast Pacific showed a notable vertical gradient (Flegal et al., 1989) that diminished offshore and is regulated by scavenging, inorganic processes and also highly correlated with particulate organic carbon and the upwelling event. While in the North Sea seasonal variations and tide changes regulated Tl distribution in the dissolved phase, also with removal cause by scavenging and incorporation into Mn minerals (Böning et al., 2018). Vertical profiles of Tl showed a conservative distribution (mean value of 46 pmol/kg) in the unpolluted area of the Ross Sea, Southern Ocean, (Turetta et al., 2010). Concentrations of Tl in the macrotidal Tamar estuary (England) previously mined for sulphidic ore extraction were about 30 pmol/kg with a non–conservative behaviour but non bioaccumulation or biomobilization was found for organisms through ingesta (Anagboso et al., 2013).

As many others TCEs, Tl has different behaviour depending on whether we study oceanic or coastal waters. Atlantic oceanic water show an increasing concentration with depth (Matthews and Riley, 1970; Schedlbauer and Heumann, 1999) while coastal waters from the Pacific Ocean have a surface maximum and stability with depth (Flegal et al., 1989).

Recently, it has been discovered that under certain conditions Tl^{+} in sediments can be oxidized to Tl^{3+} by planktonic bacteria (He et al., 2015) in freshwater. This remobilization of Tl should be taken into account as it supposes another hazard for aquatic organisms. Unlike Ga and In, Tl is known to be highly toxic to organisms, more than mercury or cadmium, and it is included in some directives for its biomonitoring (Peter and Viraraghavan, 2005). Despite its well known toxicity, there are few studies regarding Tl toxicity and environmental behaviour and distribution, mainly due to its low industrial applications and economic value until recently and the extreme difficulty to measure trace levels of Tl in natural samples (Belzile and Chen, 2017; Peter and Viraraghavan, 2005).

Due to the toxic characteristics of Tl its determination in the environment should be monitored. Tl does not suppose a threat nowadays, only locally, but its increasing use may result in problems in the near future. For that reason we need more information regarding bioavailabily of Tl and its speciation and behaviour once in the environment. Tl can be transferred into the food chain and accumulated by plankton or molluscs (Flegal et al., 1986; Zitko and Carson, 1975) in low degree (Appendix 8). Tl concentrations in phytoplankton of the Pacific Ocean were in the range of 20–800 µg/kg and 30–500 µg/kg for zooplankton in the same area (Flegal et al., 1986) denoting the constant distribution of Tl in seawater, similar behaviour with the alkali metals which Tl is compared to. A study conducted in a estuary from Spain after a mining spill showed higher Tl concentrations in fish and crab compared to filtering organisms like bivalves or oysters, in any case the concentration found had any adverse effect on the organisms (Del Valls et al., 1999).

The toxicity of Tl was found to be higher than that of other heavy metals for marine organisms. In a study of exposure to high concentrations of Tl, the lethal dose (LD_{50}) was 15 and 50 µmol/kg for the crustaceans *Americamysis bahia* and *Artemia salina* respectively (Onikura et al., 2008). The same study concluded that as other heavy metals, the toxicity of Tl increases when the salinity diminishes but other studies suggest the opposite (Belzile and Chen, 2017). A toxic response for the macroalga *Ulva lactuca* was found at exposure concentrations of 50 nmol/kg Tl in coastal and estuarine waters (Turner and Furniss, 2012) and determined a linear relationship between the aqueous concentration of Tl and its accumulation into the aquatic organisms. When exposure to contaminated food, the marine gastropod *Littorina littorea* was found to be able to accumulate Tl, at a cellular level by binding with molecules (probably due to mimic of K–dependent biological reactions) not only from seawater but also from the food source (Turner and Pilsbury, 2013).

These exposure studies use concentrations that far exceed those found in nature and more similar to contaminated areas, concentrations in heavy polluted groundwater from mine regions in China were found to be up to 300 nmol/L (Xiao et al., 2004). And as for field studies, concentration of Tl in the wild marine turtle *Caretta caretta* from Casey Key (Florida) was found to be so low in whole blood and keratin (<0.1 µg/g) that could not cause any negative impact for the nesting turtles (Perrault et al., 2017).

5.5. Group 14 – Germanium

Germanium (Ge) share electronic configuration with silicon (Si) and both have similar ionic radii (Lewis et al., 1988). The geochemical behaviour of Ge in natural waters shows a tendency to replace Si. Dissolved Ge in aqueous solution is uptaken by diatoms, with some kind of discrimination (Ellwood et al., 2006), instead of Si to form structures (Mortlock and Froelich, 1996). Ge is removed from seawater mainly by two routes: 1) incorporation into the biogenic opal of diatoms, radiolarians and sponges and following burial at the seafloor; 2) trapped into F^- (or U^-), showing a different behaviour non–analogue of Ge respect to Si (Murnane et al., 1989; Pokrovsky et al., 2006; Tribovillard et al., 2011). Unlike Si, Ge speciation is affected by the presence or dissolved organic matter with which dissolved Ge can form organic complexes (Pokrovski et al., 2000).

Ge is widely used for different applications in electronics (e.g. infrared lenses or alloys to increase strength and hardness), computer engineering (e.g. semiconductors), and medicine (Lee et al., 1990). Since it has not an essential function for organisms (Höll et al., 2007), biogeochemical cycle of Ge is mostly not known despite it can be accumulated, even at an intracellular level, for aquatic organisms.

Both Ge and Si enter the oceans from mineral weathering via riverine, hydrothermal fluids or as the result of coal combustion (Lewis et al., 1988). Once in estuaries and oceans Ge has a nutrient–like behaviour similar to that of Si, making the determination of Ge a potential tracer for the biogenic silica cycle in oceans, as Ge is incorporated and released replacing Si (Mortlock and Froelich, 1996a). Ge/Si ratio is used as a tracer of aquatic processes and fractionation in oceans (Murnane et al., 1989), as this ratio can reflect drainage mineralogy of pristine versus industrialized areas where this ratio is higher, giving us a glimpse of the biogeochemical cycles of Ge and Si in past and present oceans.

Average concentration of Ge in whole rocks and minerals is about 20 µmol/kg (Rudnick and Gao, 2003), while concentrations in open ocean (Appendix 7) are in the range of 2–30 pmol/kg in surface waters and 100–180 pmol/kg in bottom waters (Lewis et al., 1988; Mortlock and Froelich, 1996). One must take into account that >70% of Ge present in the oceans is in non–reactive forms discriminated from the Si cycle (Murnane et al., 1989). In natural waters Ge can also appear in the form of inorganic Ge which tends to replace Si in silicate minerals; and additionally can be present as two non–reactive species: monomethylgermanium and dimethylgermanium which do not imitate the behaviour of Si (Lewis et al., 1988).

According to the analogous behaviour of Ge and Si, concentration of Ge will increase with depth, as the biogenic opal of diatoms sediments and dissolves, as is shown in Ge concentrations from both Atlantic and Pacific Oceans (Lewis et al., 1988; Mortlock and Froelich, 1996) increasing up to one order of magnitude more in bottom waters. Also, surface South Pacific Ocean (30 pmol/kg) water concentrations are significantly higher than those found in the superficial waters of the Sargasso Sea in the Atlantic Ocean (2.0 pmol/kg).

The studies of Ge toxicity are mainly focused in exposure studies of diatoms, radiolarians and sponges, as Ge is taken up and released in the same manner as Si. Germanium is a non–essential metal but it can be accumulated by organisms. This accumulation was found to be, in the case of the microbial *Nitzschia alba*, energy–dependent and incorporated into the cell wall (Lee et al., 1990). As the use of Ge for different technologies continues to grow the necessity to understand the mechanisms that regulates Ge behaviour in the environment and its toxicity for organisms also increases.

5.6. Group 16 – Tellurium

The last element included in the TCEs category is tellurium (Te) belonging to the group 16 of the Periodic Table (chalcogens), which also includes oxygen (O), sulphur (S), selenium (Se), and polonium (Po), all of them of biologic interest. But unlike its neighbouring elements, Te has not a known biological role (Belzile and Chen, 2015; Nolan et al., 1991), the reason behind the lack of studies regarding Te. However, Te and their compounds are known to be part of a natural cycle from soil to plant (Diksic and Cole, 1977; Schroeder et al., 1967) and highly toxic to humans after industrial exposure although contact and poisoning with Te and its compounds is very rare (Ba et al., 2010). The biogeochemical behaviour of Te is similar to S and Se, all of them tend to occur in nature forming compounds rather than in isolation or in the elemental state (Schroeder et al., 1967), but Te biogeochemistry also displays notable differences with S and Se such as different oxidation stability and redox behaviour (Ba et al., 2010). Te can be in several different oxidation states: telluride (Te (II): Te^{2-}), elemental Te (Te (0): Te^0), tellurite (Te (IV): TeO_3^{2-} (oxyanion); the most soluble and toxic species) and tellurate (Te (VI): TeO_4^{2-}) (Arenas et al., 2014; Turner et al., 2012).

Te is widely used in new technologies to improve the thermal, optical and electrical properties of alloys in industrial steels and solar panels (Turner et al., 2012). Cadmium–tellurite (CdTe) is used in semiconductor materials for its optical and electrical properties especially in the production of solar cells (Ramos-Ruiz et al., 2016). Due to this application soluble species of Te can be released to the environment (e. g. landfills).

The main sources of Te to the oceans are direct discharges, riverine input and through biological activities (Duan et al., 2014). In seawater Te behaviour is supposed to be determined for scavenging from solution to sediments, specially for the most toxic form, the tellurite (Te (IV)) (Lee and Edmond, 1985) which is also the dominant species in surface water (Andreae, 1984; Nolan et al., 1991) after tellurate (Te (VI)), both with similar biogeochemical behaviour to Se (Belzile and Chen, 2015).

The presence of Te in natural waters worldwide supports the possibility that Te may be mobile and actually available to marine organisms (Belzile and Chen, 2015). Its abundance in seawater (Appendix 7) was predicted to be too low (less than 10–15 pmol/kg (Belzile and Chen, 2015)) to be bioavailable to the marine organisms (Schroeder et al., 1967) making it challenging to determine trace levels of Te in organisms and marine samples. While no reliable data was found on Te abundance on the upper continental crust. In a study of Te concentrations in waters from the Gulf of Mexico, values were between 2.2–6.2 pmol/kg (Andreae, 1984), showing a maximum in surface that diminishes until 200m to increase again in the bottom, displaying similar behaviour than some profiles of Nb and In.

One of the first hints of Te toxicity and long–distance transport was determined when samples containing Te radionuclides were found as far as Monaco from Chernobyl after the Chernobyl catastrophic nuclear accident (1986) in samples of the wild mussel *Mytilus galloprovincialis*, water and air (Whitehead et al., 1988a; 1988b). However this study only show radioactive activity (Bq/kg and Bq/l) not the total concentration. High values of Te were also found in marine sediments of the East China Sea in the western Pacific due to biological and anthropogenic activities (Duan et al., 2014).

In an exposure experiment to toxic species of Te it was found that the bioluminescence of the marine bacterium *Aliivrio fischeri* was affected from concentrations of tellurite and tellurate up to 8.6 and 10.2 mg/L respectively (Ramos-Ruiz et al., 2016) which can be defined as moderate and mild toxic effects. There are several studies regarding bacterial mechanisms that can lead to the reduction of more toxic forms of Te, tellurite, to stable forms that can be accumulated in the sediments (bioremediation or phytoremediation). The theory is that those microorganisms can grow under the presence of Te compounds and transform this metal in the aquatic environment reducing it to the insoluble form which then sink in pellets to the bottom (Turner et al., 2012) where marine ferromanganese oxides are extremely enriched with Te due to the incorporation of tellurite through coprecipitation (Kashiwabara et al., 2014). Under laboratory experiments it was found that tellurite is transformed to tellurate and elemental Te by marine phytoplankton *Dunaliella tertiolecta* and *Thalassiosira pseudonana* (Nolan et al., 1991). Tellurite–resistant bacteria form the extreme Antarctic environment also reduces Te (IV) to a less toxic form as is the elemental Te (Te^0) favouring the accumulation of Te in the sediments, the most important deposit of Te in the aquatic environment (Arenas et al., 2014).

It is not possible to mimic the natural conditions in laboratory experiments, and once again we found the same problem regarding toxicological studies on TCEs. Also the low concentrations at what Te is found in environmental samples oblige the use of sophisticated, accurate and precise analytical techniques. It is important to continue to monitoring Te in the environment not just only for its present use but because of its possible future uses as biological markers or antibiotics (Ba et al., 2010).

5.7. Outlook and Conclusions

In waters, generally the concentration for all REEs is increasing with depth. In Germany, Kulaksiz and Bau (2007) found higher concentration values for REEs in waters of the estuary of Weser than in the North Sea; also higher values of REEs in water were found in the San Francisco Bay plume compared with the Pacific Ocean (Hatje et al., 2014b). This confirms the tendency to display higher values near the coast compared with ocean waters, due to the continental origin of TCEs, confirmed with the discovery of anomalously high REEs values detected in the Coral Seal near Brisbane, Australia, (Lawrence and Kamber, 2006). For the other TCEs the distribution in waters is similar, the concentration increases with depth in ocean waters and for coastal waters we find higher concentrations with a surface maximum that decreases with depth until certain stability.

As for marine organisms, Tl is the only element studied with natural values found in the environment. Phytoplankton and zooplankton show high values (Flegal et al., 1986), molluscs have lower values (Del Valls et al., 1999), and values of Tl increasing again in organisms like crustaceans and fishes (Del Valls et al., 1999). Most of REEs show a similar behaviour, the organisms with higher concentration of REEs are bivalves and algae species; and lower values correspond with some fish and coral species.

There are still numerous gaps regarding technology–critical elements concentrations, biogeochemistry, bioaccumulation and toxicity in the complex aquatic system. It remains unclear the estuarine geochemistry of these emerging contaminants and the fate and pathways of the anthropogenic input of TCEs. One of the main issues when analyzing TCEs are their low concentrations, rarely exceed 100 pmol/kg in seawater samples and only some algae and bivalve species present concentrations in the ng/kg range, which make their quantification extremely difficult demanding highly sensitive methods of analysis and meticulous sample collection and preparation processes to avoid possible contamination.

The increasing consumption of high–technology products and the rapid development on new technologies usually translates into increased releasing of these TCEs to the environment. It is important to determine the natural background concentrations, before ecosystems become contaminated, and the natural biogeochemical behaviour and distribution of these elements to be alert in case their cycle changes due to the anthropogenic input. It is essential to know the fractionation of those elements in the aquatic environment in order to determine their pathways and behaviour, if they will remain inert or could be taken up by the organisms. This is a difficult task due to the extremely low concentration of TCEs in real samples and the necessity of sensitive and accurate measurement procedures under clean techniques to avoid samples contamination.

Some of the TCEs (e.g. Tl and Te) have a known potential toxicity but the effects of most of the TCEs remain uncertain. It is important to determine the bioavailability, uptake ratio and mechanisms of incorporation of the TCEs to be able to define long–term effects for organisms exposed to those chemicals. Most of the toxicity experiments on organisms were developed under laboratory parameters far from the environmental conditions (e. g. pH and temperature) and also with exposure concentrations that far exceed those found in nature (by several orders of magnitude). There is a need for experiments under more realistic concentrations and monitoring of environmental samples. Using higher concentrations than those that we find in nature help us to reduce time exposure and to observe more pronounced effects, but it may be obscuring other responses like interaction or competition with other trace elements, especially considering that some of the TCEs imitate the behaviour of other essential elements in seawater.

The majority of the TCEs are not included in official biomonitoring programs and they have not defined any mitigation strategies. As we will continue to extract TCEs in the future in order to satisfy the growing demand we need to develop a sustainable ore extraction technology and develop some environmental remediation strategies. There is a necessity to create a plan for its industrial use and sustainability to assess about the amount of TCEs that can migrate in potentially mobile forms to the estuaries and oceans. The current removal from waters and wastewaters system has proved to be inefficient for some labile forms of TCEs.

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Chapter 6 –Temporal trends of the accumulation of less–studied trace elements (including TCEs) in mussels from an urban coastal area (1991–2014): Anthropogenic influence vs. changing hydrographical conditions

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6. Temporal trends of the accumulation of less–studied trace elements (including TCEs) in mussels from an urban coastal area (1991–2014): Anthropogenic influence vs. changing hydrographical conditions

6.1. Introduction

Several trace elements and their compounds are included in the European Directive of priority substances in the field of water policy under the Water Framework Directive, specifically Cd, Pb, Hg, Ni and Sn (as tributyltin) (European Union, 2008). Accordingly, official (bio)monitoring programs are generally focused on these priority trace elements as well as other well–studied metals and metalloids (e.g. Cu, Zn, As: Besada et al., 2014; Green et al., 2008) due to their potential to cause adverse environmental effects at elevated concentrations.

A significant number of trace elements (e.g. platinum group elements, rare earth elements, etc.) are, however, excluded in these studies due to (i) their low ambient concentrations, generally below the detection limits of the analytical procedures employed, and (ii) the absence of any significant industrial role in the past, thus having no apparent environmental implications. This situation is currently changing, since several of these less–studied trace elements are now key components in the development of new technologies, including information and telecommunications technology, semiconductors, electronic displays, optic/photonic or energy-related technologies, and are defined as 'technology–critical elements' (TCEs; Cobelo-García et al., 2015). The extent of the environmental impact of the increasing anthropogenic use of these less–studied elements needs therefore to be further assessed.

The aim of the present work is to study the temporal trends during the past two decades in the accumulation of several of these less–studied trace elements (Rare Earth Elements, Nb, Ag, Au, Sb, W,Th, U, Tl, and Bi) in wild mussels (*Mytilus galloprovincialis*) from an urban beach in the Vigo Ria (NW Iberian

Peninsula), in order to (i) ascertain whether a change in their anthropogenic impact is observed and, due to the ever changing anthropogenic activities and contaminant inputs, (ii) generate a database for future studies. Mussels are ideal organisms for use as bio–indicators because as filtering organisms they tend to accumulate dissolved substances in the environment (e.g. Bellas et al., 2014; Goldberg, 1986; Soto et al., 1997) and have been widely used in the study area for biomonitoring of metal contamination (Besada et al., 2002; 2011).

6.2. Materials and Methods

6.2.1. Sampling area

Wild mussels (*M. galloprovincialis*) were collected manually and during low tides, in the period of September–November, which corresponds to the second pre–spawning period in this area (Cáceres-Martínez and Figueras, 1998) in order to minimize variations caused by differences in the mussel physiology that could lead to seasonal environmental variations. Sampling strategies during this two decade long program are described elsewhere (Besada et al., 2014). Mussels were collected at Samil beach in the Vigo Ria, an urban beach located in the city of Vigo (Figure 6.1) which holds a population of approx. 300,000 inhabitants; an urban stream (Lagares, mean annual flow of ~4 m^3s^{-1}; Perez-Arlucea et al., 2005) discharges at the western part of the beach. For comparison purposes, mussel samples from a control point (Oia) located around 40 km southward and far from any significant contamination influence were analyzed for selected years (1991, 1995, 2000, 2005, 2010).

6.2.2. Sample treatment

Each sample of mussels was prepared from 50 or more individuals representing the available size range (35–60 mm) existing in the sampling location. Soft tissues were separated from the shells, triturated with Ultraturrax and freeze-dried. An aliquot of the lyophilized sample was withdrawn to calculate its water percentage (drying at 105 °C for 24 h, until constant weight). After a freeze-drying process, samples were homogenized again with a mixer mill and stored in acid–washed glass vials at room temperature until analysis.

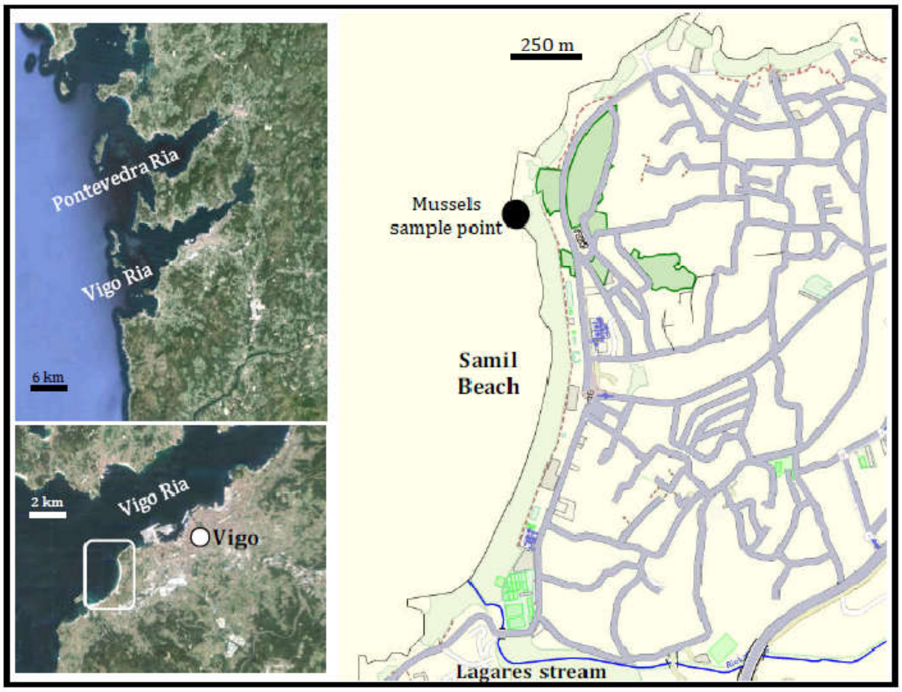


Figure 6.1. Sampling location of mussels in the Samil beach (42°13.177 N, 08°46.604 W) of the Vigo Ria (NW Iberian Peninsula).

6.2.3. Sample digestion and analysis

Approximately 100 mg of freeze–dried sample was placed in a Teflon microwave digestion bomb and 9mL HNO3 (65%, Merck Suprapur) and 3mL H2O2 (≥30%, Sigma Aldrich) were added and allowed to react overnight at room temperature. Then, full digestion was achieved using a microwave oven (MarsXpressCem) and heated at 179 °C for 5 min after 15 min ramp-up time. After digestion samples were transferred to 50 mL polypropylene volumetric flasks and diluted to the mark with Milli–Q water. Analysis of target trace elements was carried out by means of ICP–MS (X7 Series II, THERMO). In order to avoid contamination, manipulation and analysis of samples were performed inside an ISO–7 laboratory. Accuracy and precision were controlled during each analytical session, and all results were blank-corrected. The accuracy of the analytical procedure was checked using DORM–2 (fish tissue, NRC Canada) as certified reference materials, obtaining good agreement with the certified concentrations and literature values (Appendix 9).

6.2.4. Speciation calculations

A model was used to calculate the speciation of the Rare Earth Elements (REEs) depending on the variation in carbonate concentration and pH. The modelling was performed using Visual MINTEQ 3.1 and with the stability constants included in the software. Parameters were selected (Table 6.1) to mimic conditions of the area.

Table 6.1. Parameters used for Visual MINTEQ 3.1 model speciation.

Ionic strength	**T^a^**	**REEs conc.**	**F^-**	**Cl^-**	**SO_4^{2-}**	**CO_3^{2-} (range)**	**pH (range)**
0.7	25°C	$1 \cdot 10^{-12}$	$5.8 \cdot 10^{-5}$	0.56	$9.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$– $3.5 \cdot 10^{-3}$	7.5–8.5

6.3. Results and Discussion

6.3.1. Concentrations and Temporal Trends in the 'less-studied' trace elements in wild mussels (*Mytilus galloprovincialis*)

The mean (±1 sd) and median concentrations of trace elements for both the study site and the control station are compiled in Table 6.2. Also, the values reported by Costas-Rodríguez et al., (2010) in mussels from cultivated rafts (Table 6.2) are included for comparison.

Table 6.2. Mean (± 1sd) and median concentrations (ng/g) of trace elements in *Mytilus galloprovincialis* from the Samil beach (Vigo Ria) for the period 1991–2014 (n=24). Also included for comparison the values for the control station (Fig. 6.1) in samples taken in selected years (n=5).

* Concentrations are statistically different ($p<0.05$) to the control point (two–tailed test assuming unequal variances).

[1] For comparison, values obtained in cultivated rafts from the Vigo Ria (taken in 2005–2006) are given (Costas-Rodríguez et al., 2010).

Element	**Samil Beach (Vigo Ria)**		**Control Station (Oia)**		**Cultivated Rafts[1]**
	Mean ± 1sd	**Median**	**Mean ± 1sd**	**Median**	**Median, Mean (Range)**
Nb (ng/g)	44 ± 14	41	32 ± 14	29	<6, 20 (<6–161)
Ag (ng/g)*	172 ± 157	141	43 ± 22	33	25, 27 (12–53)
Sb (ng/g)	26 ± 8	25	36 ± 12	30	13, 14 (7–35)
W (ng/g)	55 ± 11	52	69 ± 13	66	–
Au (ng/g)*	7.8 ± 4.3	6.0	3.5 ± 0.6	3.7	–
Tl (ng/g)	12 ± 4	12	16 ± 7	11	5.5, 6.2 (<0.6–19)
Bi (ng/g)	41 ± 8	42	65 ± 29	50	–
Th (ng/g)	160 ± 70	130	290 ± 170	210	38, 46 (7–207)
U (ng/g)	260 ± 80	260	300 ± 130	250	141, 141 (75–207)
(REEs)					
La (ng/g)	225 ± 95	205	270 ± 150	205	122, 142 (30–469)
Ce (ng/g)	400 ± 180	375	555 ± 310	420	238, 267 (50–915)
Pr (ng/g)	53 ± 21	49	70 ± 38	54	27, 31 (6–110)
Nd (ng/g)	210 ± 80	200	280 ± 150	215	107, 122 (25–420)
Sm (ng/g)	45 ± 15	44	67 ± 39	50	24, 27 (6–92)
Eu (ng/g)	7.3 ± 2.0	7.2	10.1 ± 5.3	7.7	4.9, 6.1 (1.6–18.8)
Gd (ng/g)	26 ± 8	26	36 ± 22	26	24, 27 (6–92)
Tb (ng/g)	5.7 ± 1.6	5.7	7.7 ± 5.1	5.2	–
Dy (ng/g)	34 ± 10	33	43 ± 29	28	16, 19 (4–68)
Ho (ng/g)	5.2 ± 1.3	5.3	6.0 ± 3.8	3.8	2.9, 3.3 (0.7–12.3)
Er (ng/g)	12.8 ± 3.3	13.4	14.2 ± 8.8	8.8	8.3, 9.6 (1.9–34)
Tm (ng/g)	1.6 ± 0.4	1.6	1.8 ± 1.1	1.1	1.4, 1.4 (<0.7–4.2)
Yb (ng/g)	12.0 ± 3.5	11.8	13.2 ± 8.8	7.9	5.9, 7.3 (1.4–26)
Lu (ng/g)	1.4 ± 0.4	1.4	1.6 ± 1.1	0.9	2.0, 2.4 (<0.6–6.8)
ΣREEs (ng/g)	1040 ± 410	980	1370 ± 770	1040	–
LREEs/HREEs*	33 ± 9	32	42 ± 6	42	–

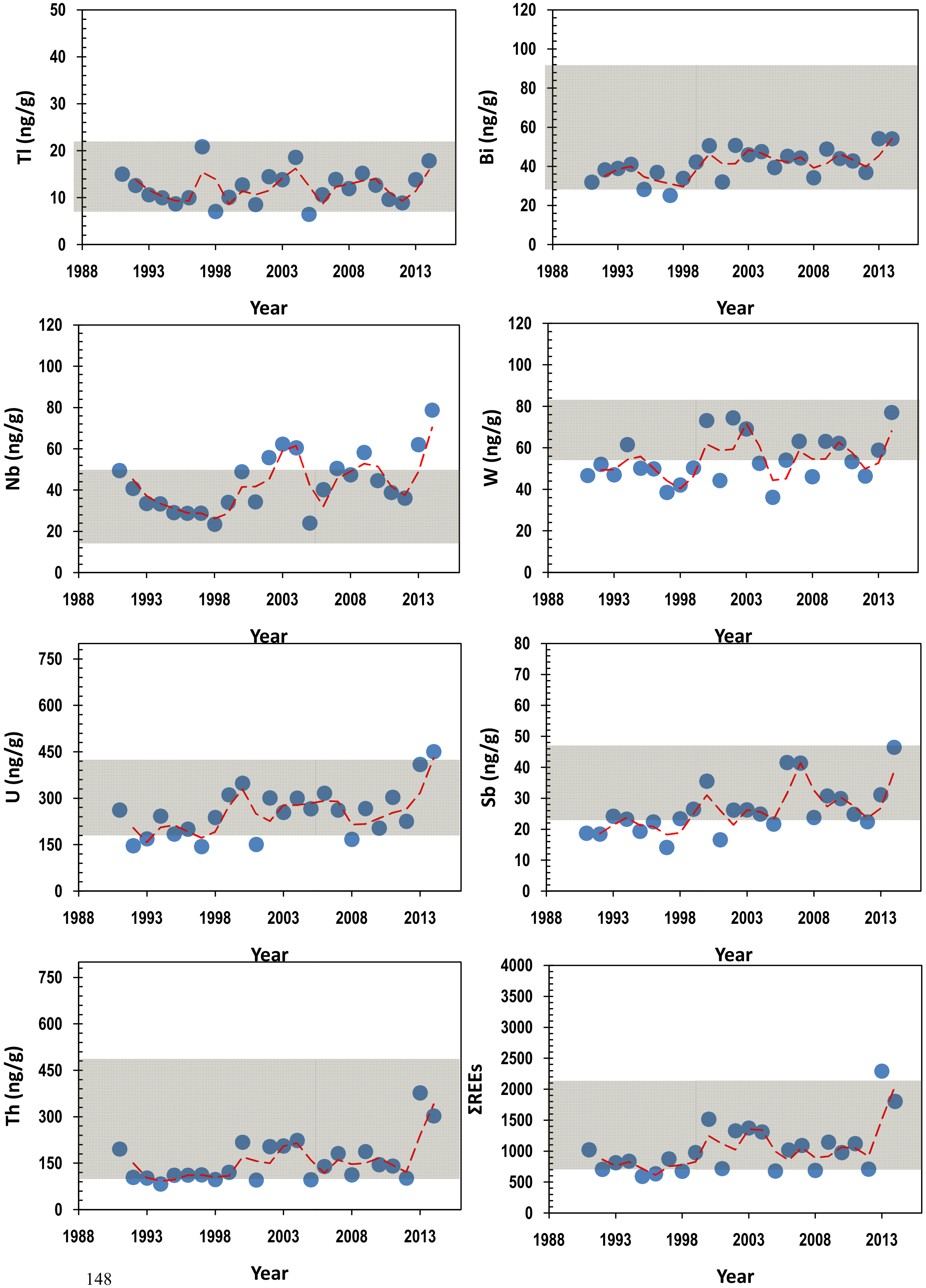


Figure 6.2. Temporal trends of several less-studied trace elements. The shaded area corresponds to the concentration range observed in the control point.

6.3.1.1. REEs, Nb, Sb, W, Tl, Bi, Th and U

No statistically–significant differences were observed for the concentrations of these elements in the study site with respect to the control point (Table 6.2), indicating no evident anthropogenic impact on their accumulation in mussels of the Vigo Ria; this is further supported by the strong correlation observed for most of these elements (Appendix 10). In fact, for several of these elements (e.g. REEs, Sb, W, Tl, Bi, Th, and U) the average concentrations at the control station were higher than at the study site, indicating that the different characteristics of the ambient water at both stations is playing a major role on their accumulation by the mussels. This can also explain the differences in concentrations of this study when compared to those reported for mussels from cultivated rafts (Table 6.2). Accordingly, concentrations of Nb, Sb, Tl, and Th are generally within the range of those reported by Costas-Rodríguez et al., 2010) although our average values are clearly higher.

Time series analysis using the Mann–Kendall test provided a significant ($p<0.05$) positive temporal trend for Th ($p=0.039$), U ($p=0.018$), Sb ($p=0.004$), Bi ($p=0.011$), REEs ($p=0.034$), and Nb ($p=0.039$). However, upon visual inspection of Figure 6.2, it appears that these significant trends may be driven by the elevated concentrations obtained for several elements in the last two monitored years (2013 and 2014); accordingly, removing those two data points results in a non-significant temporal trend ($p>0.05$) for these elements with the exception of Sb ($p=0.036$). A highly significant temporal trend was found for the ratios LREEs/HREEs ($p<0.001$) and MREEs/HREEs ($p=0.005$), and were still significant at the $p<0.05$ level if the two last data points are removed: $p=0.0003$ for LREEs/HREEs and $p=0.042$ for MREEs/HREEs. On the other hand, the LREEs/HREEs ratios at the study site were statistically different ($p<0.05$) to the control site (Table 6.2). Possible mechanisms explaining the temporal changes in the REEs composition and among different areas are discussed in detail in Section 6.3.2.

6.3.1.2. Ag and Au

Silver and gold were the only two elements showing a clear temporal decrease in their concentrations (Figure 6.3), down to values in the recent years comparable to those obtained for the control point. Maximum concentrations of ~ 600 and 15 ng g^{-1} for Ag and Au, respectively, were obtained during the 90's which represent an upper–limit contamination factor in that period of about 26

(Ag) and 4 (Au) if compared to the values recorded in the recent years: 23 ± 5 ng g^{-1}(Ag) and 4± 1 ng^{-1} (Au) for the period 2008–2014.

A global past Ag contamination in coastal systems as observed from its concentrations in marine biota and sediments is well documented (e.g. Flegal et al., 2007; Lanceleur et al., 2011). In their study, Lanceleur et al., (2011) ascribed the elevated Ag concentrations in oysters from the Gironde Estuary during the mid–1990's and early 2000's to the silver use in photographic films; the development of the digital photography led to a drastic drop in the Ag demand for this industry by mid–2000's, which would explain the drop in the oysters Ag concentrations they observed by 2005. The drop in Ag concentrations to in Ag concentrations to natural, background values in our study is dated around 2004 (Figure 3), similar to that of Lanceleur et al., (2011), which suggests that the same major anthropogenic source was responsible for the past Ag contamination. No increase in Ag concentrations was found in our study for the recent years, indicating that new emerging sources of Ag contamination (e.g. Ag nanoparticles; Markus et al., 2013) are not of concern in this area. For Au, to the knowledge of the authors, no such past contamination has been reported in the literature. Recently, Cobelo-García et al., (2017) reported a similar temporal trend in Au contamination in the neighbouring Ulla River from archived salmon scale analysis, and this was related to a past mining activity in the watershed of this river. However, this river discharges into a different ria (Arousa Ria; 100km to the north) making it unlikely that this could be the cause of the Au behaviour in our study site. Alternatively, the presence of significant amounts of Au in the photographic process, as it has been used for stabilizing and protecting the silver image (Ware, 2006), could explain the similar decrease in their concentrations.

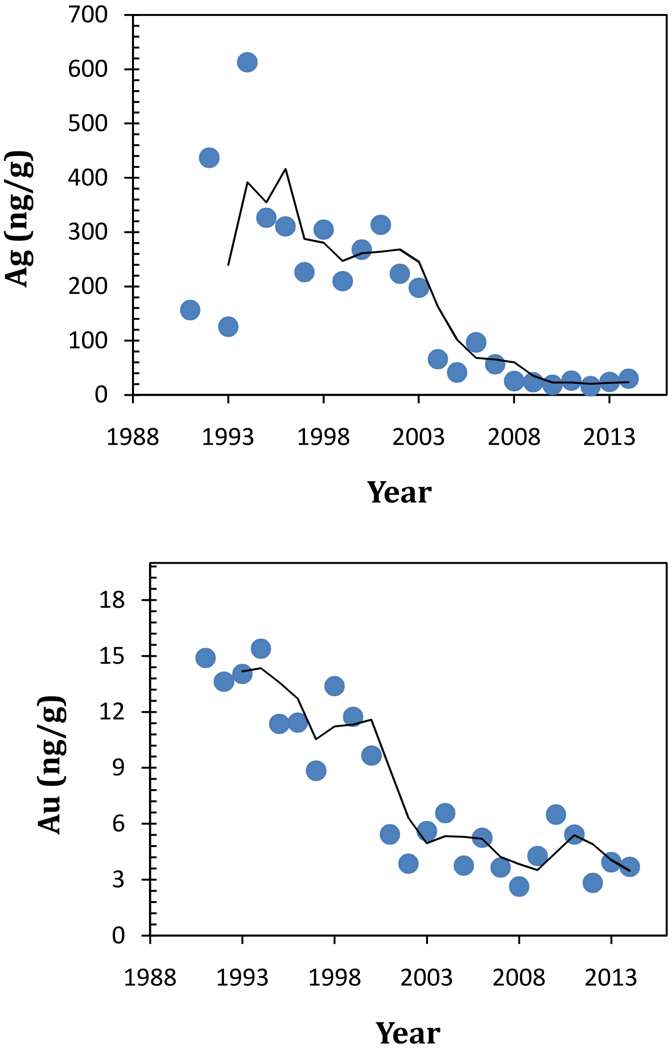


Figure 6.3. Temporal trends of silver and gold.

6.3.2. Is the temporal variation of the distribution of the REEs in mussels a response to changing hydrographical conditions in the Vigo Ria?

6.3.2.1. REEs pattern in mussels from the Vigo Ria

Rare earth elements comprise a group of 14 elements from La (atomic mass 57) to Lu (atomic mass 71) that are similar in atomic structure and chemical properties, therefore displaying coherent behaviour in the natural environment. Based on their chemical/physical separability and ion radius, they are often divided into light REEs (LREEs: La, Ce, Pr, Nd), medium REEs (MREEs: Sm, Eu, Gd) and heavy REEs (HREEs: Tb, Dy, Ho, Er, Tm, Yb, Lu). The distinct patterns observed for different (bio)geological materials make this group of elements useful for identification of sources in sedimentary environments (Gwenzi et al., 2018; Macedo et al, 2018; Merschel and Bau, 2015). In waters, the REEs speciation is greatly dominated by the pH/carbonate system (Appendix 11), which poses a major impact in their accumulation in biogenic material such as corals (Wyndham et al., 2004) or mussel shells (Ponnurangam et al., 2016), or their uptake by phytoplankton (Strady et al., 2015).

6.3.2.2. Effect of the input of oceanic water into the Vigo Ria on the REEs speciation and bioavailability

The uptake of REEs by marine plankton is greatly control by their speciation; accordingly, Strady et al., (2015) observed a good correlation between the dissolved free REEs fraction (REE^{3+}) and their concentrations in plankton from the Mediterranean Sea, but not with their total dissolved concentrations. The control of pH and/or carbonate concentrations on the dissolved REEs speciation will have a significant impact on their bioavailability (Appendix 11) for a primary food source for mussels such as plankton.

The Vigo Ria is a coastal upwelling system which experiences upwelling–favourable northerly winds from April–May to September–October (Gago et al., 2003). The upwelled Eastern North Atlantic Central Waters (ENACW) transport nutrients into the ria which are consumed at high rates. An important factor of the input of ENACW is that this water mass transports elevated carbonate concentrations into the ria (Gago et al., 2003). In general, the fraction of REEs bound to carbonates increases when moving from the LREEs to HREEs (Appendix 11) which is in agreement with the higher mussel REE concentrations observed in our samples relative to seawater for the LREEs (Figure 6.4). An increase of carbonate in the system will lead to a lower free (REE^{3+}) fraction for all the REEs; however, this decrease in the REE^{3+} is more intense as we move from the LREEs to the REEs, resulting in an increase of the free LREEs/HREEs as the carbonate concentrations increases. It is therefore expected that the fractionation of the REEs caused by an increase in the carbonate concentrations – and the implications this have for their bioavailability – will be reflected in their fractionation in the biota.

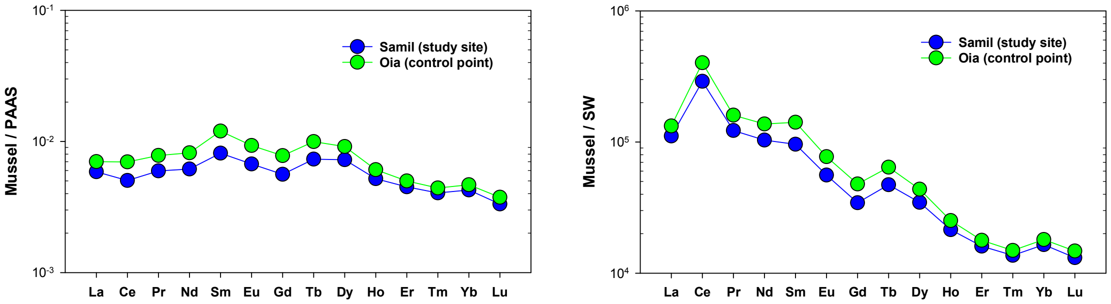


Figure 6.4. Speciation of REEs normalized with PAAS and North Atlantic seawater (SW)

6.3.2.3. Relationship between the input of oceanic water into the Vigo Ria and the REEs distribution in mussels

Given that the input of upwelled water results in an increase in carbonate concentrations in the implications this has on the changes in the intra-bioavailability of the REEs series, the LREEs/HREEs and MREEs/HREEs ratios were compared to the 5–year averaged seawater input to the Vigo Ria (Figure 6.5). It can be observed that the 'anomalous' high LREEs/HREEs agrees well with also a maximum in the seawater input. Moreover, when the REEs ratios in the mussels are plotted against the seawater input, a significant correlation is obtained (Figure 6.6), indicating that the intra–REEs variations in the mussels appear to be reflecting the changes in the hydrographic conditions of the system.

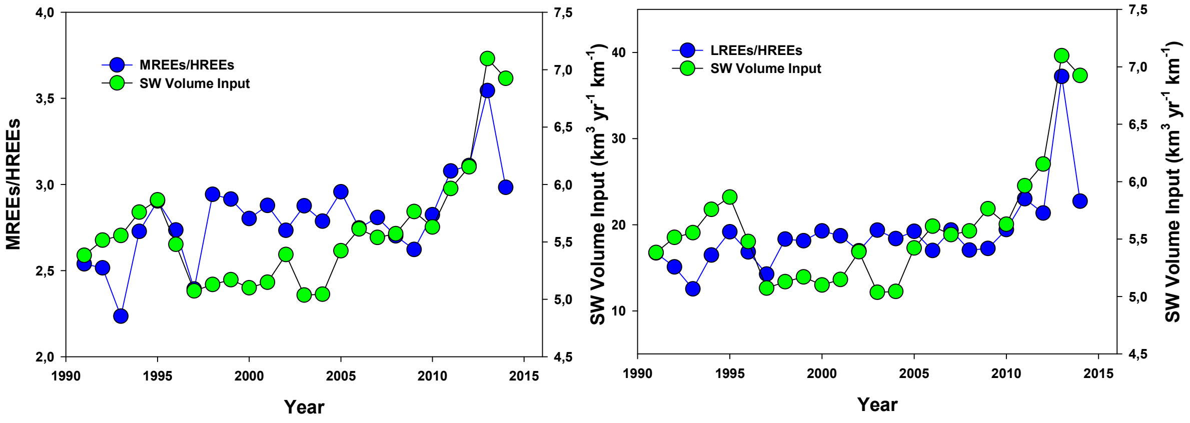
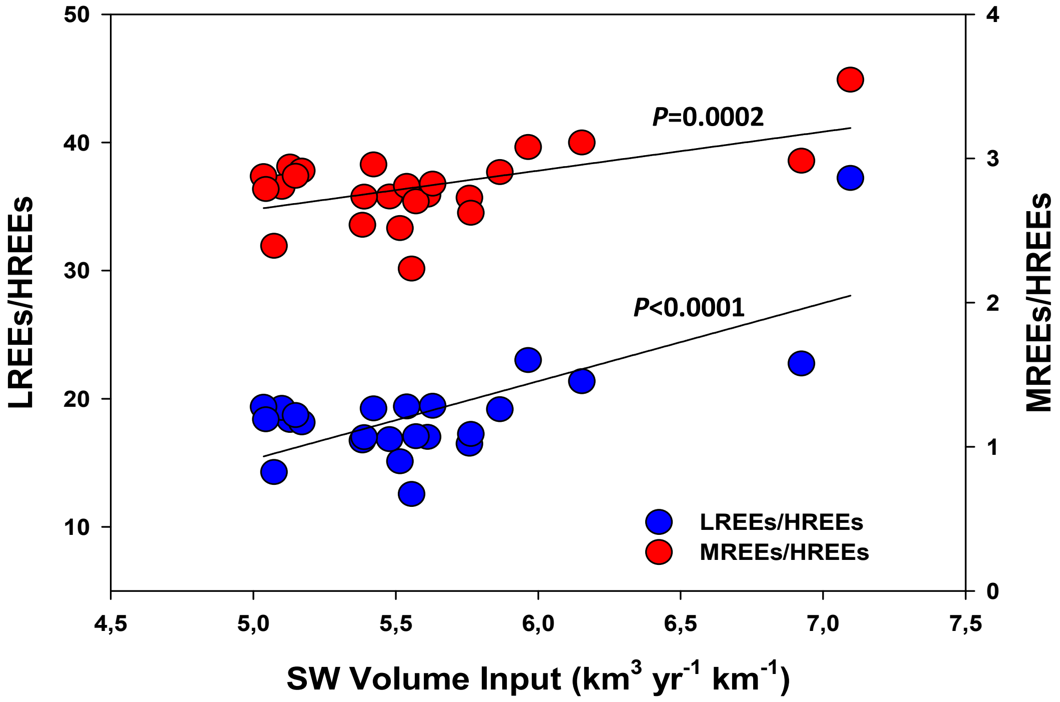


Figure 6.5. Comparison between the ratios MREEs/HRREs and LREEs/HREEs and 5–years average seawater input to the Vigo Ria.



6.4. Conclusions

This study did not find statistically-significant differences between the sample and control points for REEs, Nb, Sb, W, Tl, Bi, Th and U, with also a strong correlation between those elements. Only the ratio LREEs/HREEs is statistically different to the control point but we cannot conclude that there is evidence of anthropogenic influence on the accumulation of *M. galloprovincialis* for the metals referred. In the case of REEs, Sb, W, Tl, Bi, Th and U concentrations in mussels at the control point were higher than at the study point. This reveals that the accumulation of those metals in the organisms is due to hydrographic characteristics and not anthropogenic impact.

We found a significant increasing temporal trend on the accumulation of REEs, Sb, Bi, Th and U, but after a closer inspection this result may be owing to the fact that during the last two years monitored (2013 and 2014) the concentration found was significantly higher than in previous years. When we removed the data for those years, only Sb continued with a significant positive temporal trend. On the other hand, the ratios LREEs/HREEs and MREEs/HREEs exhibit a highly significant positive temporal trend which is still significant after removal of the two last data points.

Silver and gold displayed similar behaviour with a clear decreasing temporal trend down to background values. For silver there is documentation of a global past contamination in coastal systems due to the use of this metal in photographic films that ended with the development of digital photography in the early 00's. However, no evidence of such past contamination for gold was found. There are two possible explanations: (i) similar temporal trend was found in a close river related to past mining activity although this possibility is remote due to the existing distance between the two rias, and (ii) the use of gold also in the photographic process.

For REEs we tried to establish if the change in their concentrations was due to anthropogenic impact or changing hydrographical conditions in the study site. The Vigo Ria is an area subject to upwelling events and the speciation of REEs in water systems is controlled by the pH/carbonate system. When inputs of highly carbonate concentrated water enter the ria twice a year affects the speciation of REEs. Those carbonates are going to react with the free REEs in solution which is preferentially assimilated form for the organims, primarily with HREEs resulting in an increase of free LREEs/free HREEs ratio. We used the oceanic water that enters the ria as a proxy for the concentration of carbonates that enters the system and observed that the values agreed with the LREE/HREE and MREE/HREE ratios included the anomalous maximum points for the last two years. Also, the LREE/HREE and MREE/HREE ratios are significantly correlated with the seawater input. This reveals that variations of REEs reflect the changing hydrographical conditions.

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PART IV

CONCLUSIONS

Chapter 7 – General Conclusions

7.1. Platinum accumulation on marine sedimentary environment

7.2. Platinum Group Elements in the biosphere

7.3. Platinum accumulation on marine organisms

7.4. Technology Critical Elements in the aquatic environment

7.5. Less–studied elements, including TCEs, in marine organisms

7. General Conclusions

7.1. Platinum accumulation on marine sedimentary environment

In the first part we evaluated the platinum as an emerging contaminant in estuarine and marine sediments of the river mouth of the Tagus and its prodelta from three cores: one close to a motorway located under of the Vasco da Gama bridge, the second also inside the estuary and located near to an industrial area closed during the 1990s, and the last one in the Tagus Prodelta located in a marine environment.

The Pt concentration obtained from the first two cores analysed show elevated values in the upper layers of the estuarine sediments when compared with the background values for the area, values up to 9.5 and 0.9 ng g^{-1} under the bridge and in the industrial area respectively, when the background crustal abundance is about 0.3–0.4 ng g^{-1}. This enrichment on Pt concentrations resulted to be related with road traffic as the values were higher on the proximity to vehicular traffic sources like the Vasco da Gama Bridge. When we analysed Pt concentration in the lower layers of the core we observed a decrease on the concentration which indicate the lack of past Pt contamination in the area concordant with the theory of traffic–borne contamination of Pt in the area due to erosion of the catalytic converters.

A different outcome we obtained when analysed the samples of the Tagus Prodelta, here the concentration showed no surface enrichment as the other sample points. We could observe two sub–surface maximums, one at the base of the mixer layer located 7 cm depth (0.89 ng g^{-1}) and other behind the reworked material layer at 13 cm depth (0.51 ng g^{-1}). This result suggests the possibility of post–depositional mobility of Pt which might be able to conceal the surface traffic–borne contamination that we observed earlier. The mobility of Pt after deposition in the sediments may be due to differences in the redox potential which can contribute to Pt mobilization and diffusion at the oxic/anoxic boundary.

This chapter agrees with previous studies about the increasing rate of Pt concentrations in the environment. This rate is expected to increase in the future owing to the use of catalytic converters in motor vehicles. The concern is not just about the platinum, similar metals as palladium, also belonging to the platinum group elements, is starting to be used in catalytic converters because of its lower price.

7.2. Platinum Group Elements in the biosphere

As for the second part of the evaluation of the platinum as an emerging contaminant we discuss about its bioavailability for organisms after deposition in the environment.

We started with a critical review, in which we included all metals correspondent to the Platinum Group Elements (PGEs), and deal with the levels and dynamics in natural living organisms. We have included all the elements because they tend to appear in the same ore deposits, behave similar and also have similar physic–chemical properties what make us think that they can follow similar patterns in nature.

We have different sources for the appearance of PGEs in the environment including natural sources as erosion of rocks, volcanic eruptions or the impact of meteorites. The natural environmental concentrations of PGEs place them among the scarcest elements on Earth, generally below 1 ng g^{-1}. For this reason, we have focused our review on anthropogenic sources. The main anthropogenic source of PGEs to the environment is because the use of these metals in catalytic converters of automobiles. But this is not the only non–natural source, we should also have into account jewellery manufacture, its use in several industrial applications (e. g. chemical, electrical, glass or petroleum industries), dentistry alloys and as part of treatment drugs. On account of all these several sources of anthropogenic emission of PGEs, we can find traces of these metals globally even far away from the pollution sources.

Once in the environment the real thread of PGEs lie in its bioavailability for living organisms, in the possibility for the amounts of PGEs emitted to be transformed into soluble species. Different physical and chemical transformations are responsible for the PGEs bioavailability. First they need a medium for transportation and that could be wind or rainwater. But the most important fact regarding PGEs toxicity is its speciation, the most soluble forms are the most toxic. While the metallic form of PGEs are generally inert and therefore non–toxic, now we know that a small part of the PGEs emitted to the environment are in soluble forms or can transform into soluble forms after deposition, due to the water chemistry or the presence of humic substances. We need more information about the transformation processes that take place after the deposition and the environmental conditions that make PGEs biologically available to assess their potential risk.

The assessment of PGEs in environmental matrices has two main limitations that make their study complex and arduous. The first main issue that we stall with when we attempt to study the environmental levels of PGEs is the need of specific analytical techniques. These elements are found in nature at very low concentrations so its analysis requires of extremely sensitive and selective techniques with high detection limits. Moreover, the complexity of environmental matrices requires preparation processes for the samples in order to avoid interfering signals and level up the concentration. We emphasise on four analytical techniques for the achievement of realistic concentrations that we can use depending on our requirements: Neutron Activation Analysis (NAA), Electro–thermal Atomic Absorption Spectrometry (ET–AAS), Adsorptive Voltammetry (AV) and Inductively Coupled Plasma–Mass Spectrometry (ICP–MS). The second issue regarding the study of PGEs in the environment is the lack of suitable Certified Reference Materials (CRMs), first most of them are geological samples inappropriate when analysing biological samples, and secondly the concentrations in these CRMs often exceed those we find in nature.

Despite these problems in PGEs analysis there are several studies on natural concentrations for these elements. We have divided our review depending on the type of organisms studied if vegetal or animal, terrestrial or aquatic.

Flora usually constitutes the entry of metals in the food chain. In the case of PGEs this is evident for roadside grass and vegetation which are located in the vicinity of roads; they tend to show higher concentrations near the motorways which decrease as they are separated from the road. Not only plants near the motorways can be used as PGEs bioindicators, also tree bark, pine needles or mosses are used to study the entry and transfer of PGEs. The entry of PGEs in terrestrial vegetation can take place in the roots from contamination of soil or water or for sedimentation in the surface of the plant. The transfer of metals through the plants depends on its bioavailability being palladium the most rapidly assimilated followed by rhodium and platinum. Not only terrestrial plants are being affected for the increasing emission of PGEs, seaweed has also been used as sentinel organisms for PGEs contamination. The availability of these metals for seaweed follows a similar pattern than for terrestrial vegetation being rhodium the most easily accumulated but also the fastest being removed for biological transport, palladium also possess a rapid bioavailability and its removal depends on the hydrodynamic conditions (e.g. turbulence), similar behaviour has platinum although exhibits a higher internalisation on long–term exposure. The uptake of PGEs for aquatic plants is highly dependent on water characteristics, the presence of humic substances and higher pH can increase the concentration of PGEs on plants.

There are little information regarding natural responses of increasing concentrations of PGEs for fauna, most studies are based on laboratory experiments. It is important to monitor wild animals to determine the distribution and transfer of PGEs throughout the food chain. Increasing concentrations of PGEs due to the implementation of catalytic converters were determined in feathers, internal organisms and eggs of raptor species. There is more information regarding organisms from aquatic environments. Bioavailability of PGEs has been proved in several aquatic species depending on the time of exposure and chemical composition of the water. Mussels have been found to be ideal organisms to assess water contamination accumulating PGEs dissolved in water or directly for contact with the ground metal of the catalytic converter. Platinum is the metal preferentially assimilated by those organisms, followed by palladium and rhodium. The same as seaweed, the presence of humic substances can enhance the solubility of PGEs and therefore its availability. Mussels also show correlation with the use of platinum in catalytic converters as its increasing concentration is correlated with the platinum demand and the sale of cars. Palladium contained in catalytic converters can also be found in the internal organs and parasites of eels and barbels or goat fishes. We need to continue with the study of PGEs bioavailability as their levels will continue to increase in the future, especially in heavy traffic areas.

7.3. Platinum accumulation on marine organisms

The last section regarding platinum contamination presents a study on platinum concentration in a time–series of 20 years of wild mussels, where we show the accumulation and bioavailability of platinum in an urban area, related to the increasing anthropogenic emissions of this metal in catalytic converters over the past decades.

The average platinum concentrations in mussels from an urban beach (0.47±0.10 ng g^{-1}) were higher than those of mussel from a pristine area (0.31±0.10 ng g^{-1}) located away from anthropogenic emissions, showing a higher anthropogenic pressure at the sampling point but yet similar values to the background levels (0.3–0.6 ng g^{-1}).

More importantly, platinum concentration in mussel showed an increasing rate over the years compared with the control point which remain more or less steady. This increasing temporal trend is accompanied by a decreasing temporal trend in lead concentrations, metal linked to traffic pollution before the implementation of catalytic converters. This excess of Pt concentration in the urban area was correlated with the European demand for Pt in catalytic converters and the car sales in the Iberian Peninsula. This Pt excess began to be noticeable in the late 1990's but had its acute increase during the 2000's coinciding with the increase in the sale of vehicles. We could observe a decrease in the last years of the study caused by the global economic crisis with the corresponding decrease on car sales. This study shows evidence of the link between the use of platinum in the catalytic converters from automobiles and the increasing platinum levels in the environment in recent years.

7.4. Technology Critical Elements in the aquatic environment

Technology Critical Elements (TCEs) are a group of elements from the Periodic Table which are indispensable for the development of important nowadays technologies, such as telecommunication or green energy. TCEs are in addition scarce or difficult to obtain due to complications to isolate the metals, also often TCEs are found in conflictive areas of the world. The main problem of the TCEs is their unknown effect for the organisms and the environment. TCEs have not been mined or traded until recently and their background concentrations are low respect to other elements more studied and included in biomonitoring programs.

TCEs have different behaviour in coastal and oceanic waters. Coastal waters have a maximum surface concentration which tends to stabilize with depth. Concentrations of TCEs near the coast are slightly higher than those in the open ocean, due to the continental origin of TCEs. The TCEs are transported to the marine environment through rivers, runoff, landfills or wastewater disposal, and TCEs concentrations are decreasing as we move to the open ocean. In the ocean, however, the concentration of TCEs tends to increase with depth, acting the sediment as a contaminant reservoir often involved in remineralization processes. In some cases, there is a higher concentration in surface waters which decreases to a minimum to increase again until a maximum in deep waters. The concentrations are, in any case, significantly lower than those we found in the continental crust.

Organisms also show a different accumulation rate depending on the trophic level and the metal studied. Thallium (Tl) and Rare Earth Elements (REEs) tend to be more concentrated in organisms like phytoplankton, zooplankton and algae species. The organisms with the Tl lowest concentration are molluscs, while for REEs are some coral and fish species. This highlights the many gaps existing concerning bioaccumulation and toxicity for TCEs in biota.

The demand for TCEs is continuously growing and yet we do not know the effects it can cause. On account of laboratory experiments we know that some TCEs species are highly toxic for the organism but there is little information regarding natural response or long–term effects. We need more studies on anthropogenic impact and their natural biogeochemical cycle and concentrations to be capable of ascertain biomonitoring strategies and a sustainability program to continue developing technology without endanger ecosystems.

7.5. Less–studied elements, including TCEs, in marine organisms

This last part of the thesis was about some "poor studied" elements which included several TCEs. The area of study is an urban beach in the northwest Iberian Peninsula from which we used a time–series of wild mussels from the last two decades (1991–2014). This study contributes to the biogeochemical knowledge of some elements usually not incorporated in biomonitoring programs.

We did not found statistically–significant differences for the majority of the elements studied when compared with a control point located away from anthropogenic influence. The elements show a strong correlation between them which supports the theory of non–anthropogenic impact in the area. Even more, concentrations at the control point where significantly higher than in the study site in some cases, which suggest that the oceanographic conditions may have a strong influence in the bioaccumulation factor.

Only two elements show a different behaviour, gold and silver. Both show a pronounced temporal decrease down to levels similar to those of the control point. Silver decrease may be explained for the drop demand for this metal in the photographic films, due to the breakthrough of digital photography, main source of aquatic silver contamination. There is no such recognizable interpretation for gold past contamination, it could be due to a past mining activity in the area or the use of gold to protect the photographic film, hence the coincidence of silver and gold temporal decrease.

The case of Rare Earth Elements (REEs) deserves to be underscored as it demonstrates that the role of the ambient water on the bioaccumulation should not be undervalued. REEs are often divided in light REEs (LREEs) and heavy REEs (HREEs), also medium REEs (MREEs), depending on their atomic number. When normalized REEs with the surrounding water we found that mussels are enriched in LREEs respect to HREEs. Knowing that the free form of REEs is preferentially assimilated for organisms we performed a chemical equilibrium model. The results obtained show a constant higher proportion of free LREEs under changing conditions of pH and carbonate concentration. Due to this greater fraction of free LREEs respect to HREEs in the water and being this the most favourably assimilated form, mussels will be enriched in LREEs versus HREEs, as our samples show.

Not only mussels accumulate more LREEs than HREEs, this ratio LREE/HREEs is also significantly increasing with time in our organisms. There are several variables that can influence of the speciation of REEs in seawater such as salinity or pH, but we have focused on the carbonate concentration. When we used the amount of oceanic water that enters the system, due to upwelling events, as a proxy for the carbonate concentration we achieve a significant correlation with the increasing LREE/HREE ratio. We can conclude that the distribution of REEs reflects the hydrographic changes, such as an increasing entry of ocean water into the estuary over the years.

This thesis work addresses a profound study on the bioaccumulation and behaviour of Technology Critical Elements (TCEs), with special emphasis on the Platinum Group Elements (PGEs), and primarily platinum. We have focused this work on the marine environment, with studies on sediments and biota. Besides, we have developed an intensive bibliographic work with the aim of compile previous work on the accumulation of these metals on natural environmental compartments.

This thesis develops a little more the knowledge we have about the biogeochemical cycle of elements not commonly studied or not included in environmental pollution strategies, and how human influence and changes in oceanographic conditions are influencing these cycles. The coastal ecosystem is especially vulnerable to alterations in the natural environment due to the effects of global change, and this work is based mainly on the changes that have occurred in the last two decades in organisms and a sedimentary core dating back to 120,000 years. The conclusions obtained here hope to have an impact on the progress of environmental management and on the understanding of the biogeochemical cycle of these critical elements for new technologies.

APPENDIX

Appendix 1. Values for PGEs in certified reference materials. Please note that some of the values are (*) only provisional values or (**) information values.

Name	Type	Pt (ng/g)	Pd (ng/g)	Rh (ng/g)	Ru (ng/g)	Ir (ng/g)	Os (ng/g)	Organization
SARM–1	Felsphaticpyroxenite	0.24	0.76	0.05	–	0.031	–	Council for Mineral Technology (South Africa)
CHR–Bkg	Chromitite	50*	70*	9*	67*	28*	27*	Centre Eecherches Petrographiques et Geochimiques (France)
BCR–723	Road dust	81.3	6	12.8	0.85	–	–	Community Bureau of Reference (Belgium)
Po724–T	Pyrrhotite	38700	48900	35800	31000	34000	36500	Memorial University (Canada)
Po727–T1	Pyrrhotite	36100	47800	41600	36800	45500	45000	Memorial University (Canada)
SRM 2556	Used auto catalyst (pellets)	697400	326000	51200	–	–	–	National Institute of Standards and Technology (USA)
SRM 2557	Used auto catalyst (monolith)	1131000	233200	135100	–	–	–	National Institute of Standards and Technology (USA)
TDB–1	Diabase rock	5.8	22.4	0.7*	0.3**	0.15*	–	Natural Resources (Canada)
UMT–1	Ultramafic ore tailing	129	106	9.5	10.9	8.8	8.0*	Natural Resources (Canada)
WGB–1	Gabbro rock	6.1	13.9	–	–	–	–	Natural Resources (Canada)
WMG–1	Mineralized gabbro	731	382	26.3	34.7	46.4	24.1*	Natural Resources (Canada)
WMS–1a	Ore sulphide	1910	1450	222	145*	322*	150**	Natural Resources (Canada)
WPR–1	Altered peridotite	285	235	13.4	21.6	13.5	13.3*	Natural Resources (Canada)
PTC–1a	Copper–nickelsulphide	2720	4480	330	210*	110*	–	Natural Resources (Canada)
SU–1a	Nickel–copper–cobalt ore	491	791	–	–	–	–	Natural Resources (Canada)
8b	Syntetic pyrrhotite	63200	68500	57900	58800	56900	68500	University of Münster (Germany)

Appendix 2. Literature data on Pt, Pd and Rh content in terrestrial and marine vegetation.

Species	Location	Technique	Certified Reference Material (CRM)	Values (ng g^{-1})			Reference
				Pt	Pd	Rh	
Terrestrial							
Grass (*Poa trivialis*)	Bialystok (Poland)	HR–ICP–MS	BCR–723 (roaddust)	8.98 ± 0.39	3.20 ± 0.23	0.68 ± 0.18	Lesniewska et al., 2004
Grass	Oxfordshire and London (UK)	ICP–MS	Control protocols	5.52 – 12.04	7.13 -–14.28	0.90 – 2.34	Hooda et al., 2007
Grass (family *Graminae*)	Ioannina (Greece)	EAAS	Fortifying uncontaminated samples with known amounts of PGEs.	3.4 – 5.2	1.3 – 1.9	2.6 – 3.0	Akrivi et al., 2012
Moss	Austria	ICP–MS	WGB–1 (rock material)	0.4 – 51	0.1 – 25	0.1 – 12	Zechmeister et al., 2006
Tree bark (sycamore, beech, poplar and horse chestnut)	Sheffield and London (UK)	DF–ICP–MS	CTA–OTL–1 (oriental tobaccoleaves)	0.1 – 5.4	1.6 – 3.2	<0.05 – 1.8	Becker et al., 2000
Bark samples (beech, cedar, oak, plane, pine and poplar)	Sheffield (UK)	ICP–MS	SRM–613 (glass) NIES No8 (vehichle exhaust particulates)	3.94 ± 1.92			Ma et al., 2001
	London (UK)			5.56 ± 1.62			
	Madrid (Spain)			5.21 ± 2.60			
	Tenerife (Spain)			5.59 ± 1.25			
	Tokyo (Japan)			12.8 ± 9.6			
	Yakushima (Japan)			5.58 ± 1.81			
	San Francisco (USA)			13.0 ± 11.7			
	Hawaii (USA)			5.40 ± 2.52			

Appendix 2. (Continued).

Species	Location	Technique	Certified Reference Material (CRM)	Values (ng g^{-1})			Reference
				Pt	Pd	Rh	
Pine needles (*Pinuspinea* L.)	Palermo (Italy)	ICP–MS	V–7 (vegetationstandard)	1 – 102	1 – 45	–	Dongarrá et al., 2003
Dandelion (*Taraxacumofficinale*)	Highways and streets in Germany	ICP–MS and ICP–AES	SARM–7 (platinum ore) JSd–2 (river sediment)	5.4 – 30	0.83 – 1.5	2.0 – 7.0	Djingova et al., 2003
Plantain (*Plantagolanceolata*)				3.6 – 10.1	0.45 – 2.1	1.1 – 3.4	
Mushrooms (*Vascellum pratense*)				5.9 ± 0.6	0.2 ± 0.1	0.5 ± 0.1	
Moss (*Rhytidialdelphussquarrosus*)				30 ± 2	2.4 ± 0.3	5.4 ±0.5	
Ryegrass (*Loliummultiflorum*)				4.6 – 5.8	0.10 ± 0.3	2.1 – 2.2	

Appendix 2. (Continued).

Species	Location	Technique	Certified Reference Material (CRM)	Values (ng g^{-1}) Pt	Pd	Rh	Reference
Marine							
Red algae (*Prionitesaustrais*)	California (USA)	AAS	PCC–1 (peridodite) DTS–1 (dunite)	0.19			Hodge et al., 1986
Red algae (*Opuntiellacalifornica*)				0.08			
Brown algae (*Macrocystispyrifera*)				0.22			
Brown algae (*Pterygophoracalifornica*)				0.32			
Brown algae	California (USA)	AAS	USGS DTS–1 PCC–1	0.28 – 0.67	0.08 – 0.14		Yang, 1989
Non-calcareous red algae				0.98 – 1.50	0.34 – 0.59		
Calcareous red algae				0.42 – 0.71	0.14 – 0.19		
Green algae				0.39 – 1.75	0.11 – 0.61		
Salt–marshplant (*Sarcocornia fruticosa*)	Lisbon (Portugal)	AV	Jsd–2	0.9±0.6 (Roots) 0.029±0.039 (Stems) 0.043±0.061 (Leaves)			Almécija et al., 2016

Appendix 3. Literature data on Pt, Pd and Rh content in terrestrial and marine organisms.

Species	**Location**	**Technique**	**Certificate Reference Material (CRM)**	Values (ng g^{-1})			**Reference**
				Pt	**Pd**	**Rh**	
Terrestrial							
Peregrine falcon (*Falco peregrinus*)	Sweden	ICP–MS	Laboratory reference material (falcon feathers)	0.25 – 1.1	0.9 – 2.1	0.3 – 0.45	Jensen et al., 2002
Housesparrow (*Passer domesticus*)			Laboratory reference material (house sparrow feathers)	1.46 ± 0.18	3.89 ± 0.56	0.54 ± 0.06	
Sparrowhawk (*Accipiter nisus*)				0.8 – 1.8	0.9 – 2.1	0.3 – 0.6	
Gyrfalcon (*Falco rusticolus*)				0.65	0.6	0.3	
Willowgrouse (*Lagopus lagopus*)				0.65	0.9 - 1.0	0.3	
Falcon (*Falcon peregrinus*)	Göteborg (Sweden)	ICP–MS	Laboratory reference material (4 hen eggs)	0.5	1.4	0.3	Ek et al., 2004
Marine							
Isopod (*Asellus aquaticus*)	Göteborg (Sweden)	ICP–MS	CW7 (tunneldust)	5.1 – 118.8	76.9 – 284.2	3.6 – 48.2	Moldovan et al., 2001
Amphipod (*Gammarus pulex*)	Ruhrdistrict (Germany)	ACSV	SL–1 (lake sediment) BCR–723 (road dust)	0.58 ± 0.02			Haus et al., 2007
Amphipod (*Dikerogammarus villosus*)			DORM–2 (dogfish muscle)	0.81 – 0.94			
Isopod (*Asellus aquaticus*)				0.54 ± 0.032			

Appendix 3. (Continued)

Species	Location	Technique	Certificate Reference Material (CRM)	Values (ng g-1)			Reference
				Pt	**Pd**	**Rh**	
Mussel (*Dreissena polymorpha*)	Lake Mondsee (Austria)	CSV	DORM–2 (dogfish muscle)	0.1 – 0.5	1.0		Zimmermann et al., 2002
Mussel (*Mytilus galloprovincialis*)			DORM–2 (dogfish muscle)	0.30 – 0.68			Neira et al., 2015

Appendix 4. Range of platinum concentrations (ng/g) in several aquatic organisms.
[a] Adsorptive cathodic stripping voltammetry [b] Quadrupole inductively coupled plasma mass spectrometry [c] Atomic absorption spectrometry

Species	Pt (ng/g)	Location	Technique	Reference
Freshwater species				
Fish liver	0.23 – 0.33	German river	?	(Hees et al., 1998)
Freshwater crustacean (*Asellus aquaticus*)	330 – 1100 5 – 119 (38±35) <0.36 – 0.54	Swedish river (Kvillebäcken) Swedish river close to car traffic (Mölndal) Aquatic habitats close to car traffic in the Ruhr district (Germany)	ACSV[a] Q-ICP-MS[b] ACSV[a]	(Rauch and Morrison, 1999) (Moldovan et al., 2001) (Haus et al., 2007)
Freshwater crustaceans (*Gammarus pulex* and *Dikerogammarus villosus*)	<0.36 – 1.3	Aquatic habitats close to car traffic in the Ruhr district (Germany)	ACSV[a]	(Haus et al., 2007)
Seawater species				
Seaweed (various species)	0.25 – 1.75 (0.74±0.40) 0.08 – 0.32	California coast (USA) California coast (USA)	AAS[c] AAS[c]	(Yang, 1989) (Hodge et al., 1986)
Oysters (*Crassostea gigas*)	0.16 – 0.53 (0.35±0.08)	Gironde Estuary (France)	ACSV[a]	(Abdou et al., 2016)
Mussels (*Mytillus galloprovincialis*)	0.30 – 0.68 (0.47±0.10)	Vigo Ria (Spain)	ACSV[a]	This work

Appendix 5. Concentrations (pmol/kg) of REEs in natural seawater samples

Location	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
North Atlantic	≈0m	36.7	66.3	–	34.3	6.01	0.620	5.59	Mass spectrometer	Elderfield and Greaves, 1982
North Atlantic	100m	13.0	16.8	–	12.8	2.67	0.644	3.41		
North Atlantic	1500m	22.8	9.71	–	19.0	3.72	0.954	5.31		
North Atlantic	>4000m	54.4	55.1	–	45.8	8.25	1.22	8.27		
Seychelles Bank (South Indian)	100m	15.2	8.01	–	10.9	2.14	0.600	3.47	Mass spectrometer	Bertram and Elderfield, 1993
Seychelles Bank (South Indian)	1000m	24.0	4.75	–	14.9	2.93	0.830	4.77		
Seychelles Bank (South Indian)	2000m	29.0	6.97	–	20.9	3.95	1.07	6.70		
Seychelles Bank (South Indian)	>4000m	–	–	–	27.5	5.05	1.50	7.50		
Mascarene Islands (South Indian)	≈0m	8.57	6.11	–	7.68	1.65	0.453	2.15		
Mascarene Islands (South Indian)	100m	9.84	5.11	–	8.16	1.65	0.494	2.75		
Mascarene Islands (South Indian)	1000m	23.7	3.28	–	13.2	2.49	0.785	4.60		
Mascarene Islands (South Indian)	2000m	33.1	4.78	–	20.8	3.86	1.05	5.90		
Mascarene Islands (South Indian)	3000m	41.6	5.99	–	25.9	4.73	1.28	6.79		

Appendix 5. (Continued).

Location	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Mascarene Islands (South Indian)	>4000m	40.9	5.88	–	28.8	5.62	1.21	7.21	Mass spectrometer	Bertram and Elderfield, 1993
Madagascar Basin (South Indian)	≈0m	9.84	7.42	–	7.95	1.63	0.470	2.54		
Madagascar Basin (South Indian)	100m	9.73	7.96	–	7.83	1.59	0.463	2.51		
Madagascar Basin (South Indian)	1000m	15.9	2.24	–	10.1	1.90	0.530	3.37		
Madagascar Basin (South Indian)	2000m	30.0	4.36	–	16.5	3.01	0.834	4.89		
Madagascar Basin (South Indian)	3000m	–	–	–	23.2	4.28	1.14	6.60		
Madagascar Basin (South Indian)	>4000m	42.7	6.46	–	24.5	4.83	1.22	7.19		
Somali Basin (South Indian)	≈0m	8.21	4.96	–	6.90	1.40	0.412	2.28		
Somali Basin (South Indian)	100m	13.2	3.14	–	9.16	1.88	0.578	3.02		
Somali Basin (South Indian)	1000m	23.9	3.80	–	15.8	2.93	0.839	5.73		
Somali Basin (South Indian)	2000m	32.1	4.62	–	19.5	3.62	1.01	6.23		
Somali Basin (South Indian)	3000m	43.0	4.49	–	25.2	4.59	1.23	7.35		
Somali Basin (South Indian)	>4000m	43.2	5.54	–	28.4	5.15	1.32	7.29		

Appendix 5. (Continued).

Location	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Arabian Sea (North Indian)	≈0m	11.7	13.9	–	11.4	2.38	0.653	3.41	Mass spectrometer	Bertram and Elderfield, 1993
Arabian Sea (North Indian)	100m	12.3	9.80	–	11.3	2.40	0.644	3.66		
Arabian Sea (North Indian)	1000m	–	5.30	–	14.4	3.77	0.742	4.22		
Arabian Sea (North Indian)	2000m	–	4.90	–	17.5	3.37	0.942	5.03		
Arabian Sea (North Indian)	3000m	–	5.70	–	22.6	4.16	1.34	6.30		
Arabian Sea (North Indian)	>4000m	–	6.70	–	24.6	4.44	1.25	6.71		
Gulf of Oman (North Indian)	≈0m	12.5	11.3	–	11.7	2.54	0.694	3.32		
Gulf of Oman (North Indian)	100m	13.9	5.55	–	10.2	2.14	0.596	3.38		
Gulf of Oman (North Indian)	1000m	19.9	3.95	–	12.4	2.44	0.675	3.89		
Gulf of Oman (North Indian)	2000m	23.4	2.70	–	15.2	2.91	–	4.72		
Northwest Pacific Basin	≈0m	22.6	8.03	–	15.9	2.88	0.750	4.01	Mass spectrometer	Piepgras and Jacobsen, 1992
Northwest Pacific Basin	100m	36.3	6.44	–	22.2	4.09	1.06	5.84		
Northwest Pacific Basin	500m	42.0	7.67	–	24.4	4.52	1.17	6.62		

Appendix 5. (Continued).

Location	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Northwest Pacific Basin	>4000m	61.6	8.44	–	44.4	8.60	2.20	11.7	Mass spectrometer	Piepgras and Jacobsen, 1992
Western North Pacific	≈0m	5.82	4.98	–	5.41	1.14	0.320	1.75		
Western North Pacific	100m	7.83	4.88	–	6.75	1.43	0.403	2.21		
Western North Pacific	1000m	35.5	4.05	–	20.0	3.65	0.992	5.77		
Western North Pacific	2000m	46.9	3.95	–	28.2	5.13	1.40	7.75		
Western North Pacific	3000m	53.7	4.67	–	34.9	6.36	1.72	9.32		
Western North Pacific	>4000m	52.7	5.68	–	35.0	6.54	1.71	9.21		
Eastern North Pacific	>4000m	79.5	13.0	–	62.8	12.6	3.21	15.8		
Coral Sea (Australia)	≈0m	78.9	85.5	15.1	79.0	22.0	–	17.9	ICP–MS	Lawrence and Kamber, 2006
Weser Estuary (Germany)	≈0m	42.0–68.2	42.3–106	8.3–16.6	38.9–75.0	9.3–19.0	2.5–4.8	45.1–94.8	ICP–MS	Kulaksiz and Bau, 2007
North Sea (Germany)	≈0m	20.6–26.8	16.6–33.2	4.4–6.0	20.2–25.8	5.0–6.5	1.3–1.9	11.2–14.1		
San Francisco Bay Plume (USA)	≈0m	31.4–41.0	26.6–34.6	6.39–7.65	31.6–36.6	7.29–9.13	2.04–2.42	10.7–14.8	HR–ICP–MS	Hatje et al., 2014
North Pacific	≈0m	10.9	6.18	1.64	8.53	2.36	0.430	2.18		

Appendix 5. (Continued).

Location	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Ogishima Port (Japan)	Non–detailed	180.0	777.9	39.5	58.5	10.2	2.63	72.5	ICP–MS	Akagi and Edanami, 2017
Kanazawa-hakkei Station (Japan)	Non–detailed	91.4	534	32.6	117.8	22.7	6.91	56.5		
Daiba Island (Japan)	Non–detailed	21.0	99.9	13.2	52.9	12.2	4.01	180.6		

Location	Depth	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
North Atlantic	≈0m	–	5.00	–	3.63	–	3.15	–	Mass spectrometer	Elderfield and Greaves, 1982
North Atlantic	100m	–	4.78	–	4.07	–	3.55	–		
North Atlantic	1500m	–	6.03	–	5.30	–	4.99	–		
North Atlantic	>4000m	–	6.83	–	5.34	–	5.16	–		
Seychelles Bank (South Indian)	100m	–	4.09	–	3.73	–	3.55	0.600	Mass spectrometer	Bertram and Elderfield, 1993
Seychelles Bank (South Indian)	1000m	–	5.61	–	5.26	–	5.42	0.960		
Seychelles Bank (South Indian)	2000m	–	7.12	–	6.85	–	7.37	1.27		
Seychelles Bank (South Indian)	>4000m	–	8.56	–	7.87	–	8.46	1.31		

Appendix 5. (Continued).

Location	Depth	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Mascarene Islands (South Indian)	≈0m	–	2.94	–	2.52	–	2.14	0.300	Mass spectrometer	Bertram and Elderfield, 1993
Mascarene Islands (South Indian)	100m	–	3.44	–	2.80	–	2.61	0.420		
Mascarene Islands (South Indian)	1000m	–	5.21	–	5.33	–	5.42	0.935		
Mascarene Islands (South Indian)	2000m	–	7.08	–	6.79	–	7.23	1.30		
Mascarene Islands (South Indian)	3000m	–	8.10	–	7.54	–	8.10	1.49		
Mascarene Islands (South Indian)	>4000m	–	8.10	–	7.34	–	7.66	1.18		
Madagascar Basin (South Indian)	≈0m	–	3.17	–	2.74	–	2.07	0.320		
Madagascar Basin (South Indian)	100m	–	3.15	–	2.82	–	2.13	0.325		
Madagascar Basin (South Indian)	1000m	–	3.96	–	4.12	–	4.12	0.750		
Madagascar Basin (South Indian)	2000m	–	5.98	–	6.05	–	6.16	1.14		
Madagascar Basin (South Indian)	3000m	–	7.67	–	7.10	–	7.53	1.41		
Madagascar Basin (South Indian)	>4000m	–	8.40	–	8.38	–	7.27	1.89		
Somali Basin (South Indian)	≈0m	–	3.00	–	2.49	–	1.81	0.340		

Appendix 5. (Continued).

Location	Depth	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Somali Basin (South Indian)	100m	–	3.74	–	3.44	–	3.20	0.620	Mass spectrometer	Bertram and Elderfield, 1993
Somali Basin (South Indian)	1000m	–	5.74	–	5.48	–	5.38	1.03		
Somali Basin (South Indian)	2000m	–	6.86	–	6.57	–	6.95	1.28		
Somali Basin (South Indian)	3000m	–	7.95	–	7.50	–	8.08	1.55		
Somali Basin (South Indian)	>4000m	–	8.26	–	7.22	–	7.14	1.65		
Arabian Sea (North Indian)	≈0m	–	3.94	–	3.09	–	2.49	0.655		
Arabian Sea (North Indian)	100m	–	3.41	–	3.39	–	2.64	0.451		
Arabian Sea (North Indian)	1000m	–	4.54	–	–	–	4.84	0.863		
Arabian Sea (North Indian)	2000m	–	6.60	–	6.14	–	6.78	1.30		
Arabian Sea (North Indian)	3000m	–	7.28	–	7.20	–	7.79	1.40		
Arabian Sea (North Indian)	>4000m	–	–	–	7.52	–	8.08	1.46		
Gulf of Oman (North Indian)	≈0m	–	3.95	–	2.91	–	1.77	0.506		
Gulf of Oman (North Indian)	100m	–	3.74	–	3.20	–	2.99	0.508		

Appendix 5. (Continued).

Location	Depth	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Gulf of Oman (North Indian)	1000m	–	4.41	–	4.27	–	4.38	0.778	Mass spectrometer	Bertram and Elderfield, 1993
Gulf of Oman (North Indian)	2000m	–	6.02	–	6.51	–	7.30	1.16		
Northwest Pacific Basin	≈0m	–	4.65	–	4.22	–	3.52	0.605	Mass spectrometer	Piepgras and Jacobsen, 1992
Northwest Pacific Basin	100m	–	6.72	–	6.13	–	6.00	1.07		
Northwest Pacific Basin	500m	–	7.89	–	7.57	–	7.84	1.42		
Northwest Pacific Basin	>4000m	–	12.4	–	10.5	–	11.1	1.97		
Western North Pacific	≈0m	–	2.10	–	1.78	–	1.34	0.213		
Western North Pacific	100m	–	2.70	–	2.32	–	1.92	0.312		
Western North Pacific	1000m	–	6.78	–	6.66	–	6.88	–		
Western North Pacific	2000m	–	9.41	–	9.21	–	9.97	1.84		
Western North Pacific	3000m	–	10.8	–	9.97	–	10.7	1.93		
Western North Pacific	>4000m	–	10.1	–	9.19	–	9.80	1.81		
Eastern North Pacific	>4000m	–	16.8	–	13.5	–	14.0	2.44		

Appendix 5. (Continued).

Location	Depth	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Coral Sea (Australia)	≈0m	3.76	23.2	6.64	16.4	3.14	11.3	1.76	ICP–MS	Lawrence and Kamber, 2006
Weser Estuary (Germany)	≈0m	2.1–3.7	14.9–26.5	3.9–6.7	13.7–23.3	–	15.3–24.0	2.7–4.1	ICP–MS	Kulaksiz and Bau, 2007
North Sea (Germany)	≈0m	1.3–1.6	8.80–10.5	2.3–2.5	7.4–9.0	–	7.5–9.0	1.3–1.5		
San Francisco Bay Plume (USA)	≈0m	1.6–2.0	11.3–14.4	2.86–3.77	9.2–12.5	1.34–1.82	8.5–12.0	1.3–1.9	HR–ICP–MS	Hatje et al., 2014
North Pacific	≈0m	0.340	2.34	0.600	1.88	0.240	1.30	0.19		
Ogishima Port (Japan)	Non–detailed	2.54	16.2	4.63	19.7	3.49	25.9	5.54	ICP–MS	Akagi and Edanami, 2017
Kanazawa-hakkei Station (Japan)	Non–detailed	5.43	35.7	9.22	34.1	4.97	33.8	6.34		
Daiba Island (Japan)	Non–detailed	3.51	24.2	7.15	29.8	5.24	46.6	10.2		

Appendix 6. Concentrations (μg/kg) of REEs in wild marine species.

Species	Location	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Coral (*Montastrea annularis*)	Tarawa atoll, Kiribati	0.007–0.012	0.018–0.024	–	0.014–0.007	0.004–0.007	–	0.006–0.098	ID–TIMS	Sholkovitz and Shen, 1995
Coral (*Diploria labyrinthiformis*)	Bermuda	0.019	0.061	–	0.031	0.010	0.002	0.013		
Coral (*Diploria strigosa*)	Bermuda	0.013–0.017	0.021–0.028	–	0.019–0.023	0.005–0.007	0.001	0.008–0.010		
Coral (*Porites astreoides*)	Bermuda	0.026	0.043	–	0.033	0.010	0.002	–		
Coral (*Montastrea annularis*)	Bermuda	0.013	0.017	–	0.018	0.006	0.001	–		
Mussel (*Cyprina islandica*)	Denmark	1950–2690	1710–3190	–	–	150–290	40.0–60.0	–	INAA	Drabaek et al., 1987
Mussel (*Mytilus edulis*)	Denmark	300–1360	210–3250	–	370–570	4.0–160	6.0–27	–		
Coral (*Goniastrea pectinata*)	Sesoko-jima Island (Japan)	2.10–5.54	5.53–11.9	0.593–1.41	2.58–5.78	0.607–1.30	0.173–0.337	0.917–1.67	ICP–MS	Akagi et al., 2004
Coral (*Goniastrea pectinata*)	Sioya-wan Bay (Japan)	15.4–65.6	30.9–140	3.86–14.2	15.6–51.3	3.28–9.07	0.856–2.14	4.63–9.62		
Coral (*Oulastrea crispata*)	Sesoko-jima Island (Japan)	3.28–5.81	9.44–17.7	0.714–1.23	2.98–5.23	0.650–1.14	0.173–0.296	0.918–1.52		
Coral (*Oulastrea crispata*)	Sioya-wan Bay (Japan)	22.6–35.8	45.4–94.4	5.09–8.22	21.3–34.0	4.30–6.86	0.992–1.58	4.64–7.34		

Appendix 6. (Continued).

Species	Location	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Coral (*Porites lutea*)	Sesoko-jima Island (Japan)	1.81–13.0	4.33–15.8	0.388–2.97	1.59–12.2	0.356–2.50	0.103–0.652	0.538–3.18	ICP–MS	Akagi et al., 2004
Coral (*Porites lutea*)	Sioya-wan Bay (Japan)	24.8–70.8	24.8–132	3.28–14.8	12.8–55.5	2.59–10.6	0.650–2.43	3.37–10.9		
Coral (*Stylophora pistillata*)	Sesoko-jima Island (Japan)	1.11–1.42	5.95–9.70	0.234–0.318	0.933–1.21	0.211–0.254	0.061–0.074	0.335–0.387		
Coral (*Stylophora pistillata*)	Sioya-wan Bay (Japan)	7.67–9.33	16.5–22.1	1.41–1.72	5.52–6.84	1.28–1.47	0.352–0.406	1.90–2.15		
Fish (*Ostracion Meleagris*)	South China Sea	1.62	2.29	0.311	1.05	0.183	0.061	0.430	ICP–MS	Li et al., 2016
Fish (*Cephalopholis argus*)	South China Sea	1.02	1.60	0.242	0.951	0.302	0.147	0.221		
Fish (*Balistapus undulatus*)	South China Sea	1.30	2.09	0.286	0.876	0.145	0.088	0.371		
Fish (*Cephalopholis urodelus*)	South China Sea	2.60	1.90	0.305	0.881	0.479	0.339	0.240		
Fish (*Gymnothorax moringa*)	South China Sea	2.97	5.92	0.678	2.20	0.557	0.258	0.551		
Fish (*Kyphosus lembus*)	South China Sea	1.32	2.28	0.336	1.14	0.280	0.137	0.804		
Fish (*Parupeneus multifasciatus*)	South China Sea	1.82	1.86	0.325	1.59	0.583	0.257	0.414		
Fish (*Parupeneus pleurostigma*)	South China Sea	2.34	3.59	0.413	2.15	0.445	0.198	0.740		
Fish (*Melichthys vidua*)	South China Sea	2.78	4.81	0.549	2.64	0.598	0.285	0.869		

Appendix 6. (Continued).

Species	Location	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Fish (*Pervagor melanocephalus*)	South China Sea	8.87	9.09	1.47	7.01	1.53	0.592	1.89	ICP–MS	Li et al., 2016
Fish (*Cheilinus fasciatus*)	South China Sea	2.66	4.80	0.651	2.77	0.792	0.347	0.970		
Fish (*Cheilinus rhodochrous*)	South China Sea	2.45	3.41	0.600	2.06	0.795	0.207	0.840		
Fish (*Cephalopholis sonnerati*)	South China Sea	3.70	5.55	0.600	2.88	0.693	0.249	0.778		
Fish (*Odonus niger)*	South China Sea	1.50	2.26	0.286	1.16	0.281	0.121	0.395		
Fish (*Cypselurus katoptron*)	South China Sea	2.25	4.74	0.577	2.19	0.559	0.186	0.452		
Fish (*Heteropriacanthus cruentatus*)	South China Sea	1.03	1.41	0.220	1.23	0.247	0.120	0.321		
Fish (*Gnathodentex aureolineatus*)	South China Sea	3.00	2.96	0.495	2.06	0.357	0.286	0.544		
Fish (*Paraluteres prionurus*)	South China Sea	7.11	10.1	1.24	5.46	0.889	1.90	1.48		
Fish (*Myripristis kuntee*)	South China Sea	2.55	3.04	0.487	2.00	0.504	0.418	0.711		
Fish (*Epinephelus hexagonatus*)	South China Sea	8.20	3.00	0.439	2.02	0.555	6.44	0.706		
Fish (*Coris gaimard*)	South China Sea	1.01	1.79	0.194	0.905	0.193	0.146	0.289		
Fish (*Scarus forsteri*)	South China Sea	3.46	2.84	0.649	2.76	0.810	0.288	1.20		

Appendix 6. (Continued).

Species	Location	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Fish (*Diodon hystrix*)	South China Sea	5.64	7.48	0.863	3.58	0.432	0.160	0.690	ICP–MS	Li et al., 2016
Fish (*Parupeneus trifasciatus*)	South China Sea	1.34	2.37	0.315	1.12	0.351	0.146	0.472		
Fish (*Epinephelus* fam.)	South China Sea	2.34	4.56	0.575	2.58	0.353	0.109	0.822		
Fish (*Lutjanus kasmira*)	South China Sea	1.52	2.43	0.406	1.47	0.628	0.216	0.680		
Fish (*Cephalopholis urodelus*)	South China Sea	7.14	12.7	1.27	5.09	1.25	0.402	1.09		
Fish (*Pterophyllum scalare*)	South China Sea	1.12	2.40	0.278	1.39	0.114	0.11	0.170		
Fish (*Ctenochaetus striatus*)	South China Sea	6.26	5.28	1.22	5.22	0.974	0.413	1.45		
Fish (*Thalassoma quinquevittatum*)	South China Sea	3.48	3.14	0.575	2.32	0.530	0.449	0.867		
Shellfish (*Lobatus gigas*)	South China Sea	21.2	15.4	3.36	15.8	4.53	1.15	7.16		
Shellfish (*Trochus niloticus*)	South China Sea	20.4	27.7	4.42	18.9	4.20	1.15	4.89		
Shellfish (*Linnaeus*)	South China Sea	9.92	7.18	1.29	5.59	1.22	0.406	1.47		
Shellfish (*Harpago chiragra*)	South China Sea	807	296	67.0	245	25.5	4.17	17.2		
Shellfish (*Tridacna squamosa*)	South China Sea	18.5	12.4	3.18	15.1	3.91	0.983	4.72		

Appendix 6. (Continued).

Species	Location	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Crustacean (*Dromia dehaani*)	South China Sea	85.4	71.7	15.8	71.5	17.4	4.88	24.2	ICP–MS	Li et al., 2016
Crustacean (*Paguridae* fam.)	South China Sea	182	186	41.7	180	47.9	10.8	59.7		
Crustacean (*Podophthalmus vigil*)	South China Sea	24.9	19.5	4.84	20.9	5.48	1.63	6.59		
Crustacean (*Carpilius convexus*)	South China Sea	46.0	31.2	7.20	31.7	8.81	2.46	12.0		
Algae (*Codium bursa*)	Bergeggi (Ligurian Sea)	3500	6300	810	3100	650	170	680	ICP–MS	Squadrone et al., 2017
Algae (*Flabellia petiolata*)	Bergeggi (Ligurian Sea)	4300	8800	1000	4000	850	160	830		
Algae (*Padina pavonica*)	Bergeggi (Ligurian Sea)	3900	7200	910	3600	770	160	780		
Algae (*Halopteris filicina*)	Bergeggi (Ligurian Sea)	4300	8800	1100	4100	870	170	870		
Algae (*Ganonema farinosum*)	Bergeggi (Ligurian Sea)	2500	4800	550	2200	460	100	470		
Algae (*Codium bursa*)	Elba Island (Ligurian Sea)	1500	2800	340	1400	280	72.0	290		
Algae (*Flabellia petiolata*)	Elba Island (Ligurian Sea)	2200	3500	470	1900	400	100	450		
Algae (*Caulerpa racemosa*)	Elba Island (Ligurian Sea)	1100	1800	240	1000	220	50.0	240		
Algae (*Padina pavonica*)	Elba Island (Ligurian Sea)	1600	2000	330	1400	290	75.0	330		

Appendix 6. (Continued).

Species	Location	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Algae (*Halopteris filicina*)	Elba Island (Ligurian Sea)	290	640	70.0	310	70.0	10.0	70.0	ICP–MS	Squadrone et al., 2017
Algae (*Dictyota dichotoma*)	Elba Island (Ligurian Sea)	1800	3300	410	1600	340	90.0	360		
Algae (*Peyssonnelia squamaria*)	Elba Island (Ligurian Sea)	1600	2600	320	1300	250	70.0	260		
Algae (*Laurencia obtusa*)	Elba Island (Ligurian Sea)	1300	2300	280	1200	250	60.0	270		
Algae (*Codium bursa*)	Capraia Island (Ligurian Sea)	760	1600	180	730	130	22.0	120		
Algae (*Flabellia petiolata*)	Capraia Island (Ligurian Sea)	610	1300	140	590	110	21.0	120		
Algae (*Halimeda tuna*)	Capraia Island (Ligurian Sea)	1510	3000	370	1400	260	40.0	250		
Algae (*Padina pavonica*)	Capraia Island (Ligurian Sea)	1900	3200	440	1800	340	60.0	350		
Algae (*Halopteris filicina*)	Capraia Island (Ligurian Sea)	2730	6200	650	2700	510	100	510		
Algae (*Cystoseira* spp.)	Capraia Island (Ligurian Sea)	1000	1500	230	990	220	50.0	250		
Algae (*Peyssonnelia squamaria*)	Capraia Island (Ligurian Sea)	1520	2900	350	1400	260	50.0	260		
Algae (*Dudresnaya verticillata*)	Capraia Island (Ligurian Sea)	520	800	90.0	350	60.0	10.0	70.0		

Appendix 6. (Continued).

Species	Location	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Fish (*Pylodictis olivaris*)	Shandong Province (China)	0.013	0.006	$6.5\cdot10^{-4}$	0.002	$4.6\cdot10^{-4}$	$1.3\cdot10^{-4}$	$5.5\cdot10^{-4}$	ICP–MS	Yang et al., 2016
Fish (*Scophthalmus maximus*)	Shandong Province (China)	0.002	0.005	$5.0\cdot10^{-4}$	0.002	$7.8\cdot10^{-4}$	$1.4\cdot10^{-4}$	$6.0\cdot10^{-4}$		
Fish (*Trichiurus lepturus*)	Shandong Province (China)	0.005	0.004	$4.5\cdot10^{-4}$	0.002	$4.2\cdot10^{-4}$	$9.0\cdot10^{-4}$	$4.5\cdot10^{-4}$		
Fish (*Lateolabrax japonicus*)	Shandong Province (China)	0.005	0.004	$3.9\cdot10^{-4}$	0.002	$6.9\cdot10^{-4}$	$1.3\cdot10^{-4}$	$4.5\cdot10^{-4}$		
Fish (*Sphyraenus* spp.)	Shandong Province (China)	0.015	0.011	0.001	0.005	0.001	$2.7\cdot10^{-4}$	0.001		
Fish (*Larimichthys polyactis*)	Shandong Province (China)	0.011	0.007	$7.1\cdot10^{-4}$	0.003	$6.8\cdot10^{-4}$	$1.8\cdot10^{-4}$	$6.9\cdot10^{-4}$		
Clam shell (*Ruditapes philippinarum*)	Ogishima Port (Japan)	35.1±1.3	70.7±1.9	7.61±0.26	27.2±1.3	5.70±0.3	1.35±0.1	6.48±0.3	ICP–MS	Akagi et al., 2017
Mussel shell (*Mytilus galloprovincialis*)	Ogishima Port (Japan)	19.6±2.5	27.7±4.2	2.07±0.42	6.5±1.4	0.75±0.08	0.14±0.01	0.970±0.1		
Clam shell (*Ruditapes philippinarum*)	Kanazawa-hakkei Station (Japan)	32.0±4.5	63±10	7.14±1.0	30.3±3.9	6.40±0.8	1.57±0.2	8.0±1.0		
Clam tissue (*Ruditapes philippinarum*)	Kanazawa-hakkei Station (Japan)	317±19	471±32	74.1±1.7	367±5.7	101±2.2	25.1±0.4	134±2.6		
Clam shell (*Phacosoma japonicum*)	Kanazawa-hakkei Station (Japan)	103±33	209±36	27.2±3.7	121±17	27.0±3.6	6.35±0.8	31.5±3.7		
Clam tissue (*Phacosoma japonicum*)	Kanazawa-hakkei Station (Japan)	522±86	1156±15	169±1.6	654±9.4	138±1.1	35.1±0.1	168±1.4		
Clam shell (*Mactra veneriformis*)	Kanazawa-hakkei Station (Japan)	24.1±5.4	48.6±2.0	5.23±0.8	21.6±3.8	4.93±0.8	1.39±0.2	6.5±0.7		

Appendix 6. (Continued).

Species	Location	La	Ce	Pr	Nd	Sm	Eu	Gd	Analytical Method	Reference
Clam tissue (*Mactra veneriformis*)	Kanazawa-hakkei Station (Japan)	532±14	1100±160	177±2.5	855±6.4	203±1.6	52.0±1.3	230±7.3	ICP–MS	Akagi et al., 2017
Clam shell (*Ruditapes philippinarum*)	Daiba Island (Japan)	104±10	186±13	24.0±1.7	89.6±6.6	18.4±1.6	4.62±0.3	21.5±1.3		
Clam tissue (*Ruditapes philippinarum*)	Daiba Island (Japan)	643±47	1161±34	99.4±3.2	411±20	89.0±4.8	23.4±1.0	113±5.7		
Clam shell (*Mercenaria stimpsoni*)	Daiba Island (Japan)	96.0±4.4	180±15	22.6±0.2	97.6±3.5	19.3±0.02	4.60±0.01	21.4±0.1		
Clam tissue (*Mercenaria stimpsoni*)	Daiba Island (Japan)	353±17	337±75	52.8±2.0	223±5.8	45.1±0.4	11.53±0.4	58.5±1.7		

Appendix 6. (Continued).

Species	Location	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Coral (*Montastrea annularis*)	Tarawa atoll, Kiribati	–	0.005–0.006	–	0.004–0.006	–	0.002–0.003	0.003–0.004	ID–TIMS	Sholkovitz and Shen, 1995
Coral (*Diploria labyrinthiformis*)	Bermuda	–	0.011	–	0.009	–	0.008	0.001		
Coral (*Diploria strigosa*)	Bermuda	–	0.008	–	0.006–0.007	–	0.006–0.007	0.001		
Coral (*Porites astreoides*)	Bermuda	–	0.010	–	0.008	–	0.006	0.001		
Coral (*Montastrea annularis*)	Bermuda	–	0.010	–	0.009	–	0.007	0.001		
Mussel (*Cyprina islandica*)	Denmark	–	–	–	–	–	–	–	INAA	Drabaek et al., 1987
Mussel (*Mytilus edulis*)	Denmark	–	–	–	–	–	0.190–0.370	–		
Coral (*Goniastrea pectinata*)	Sesoko-jima Island (Japan)	0.149–0.264	1.06–1.85	0.257–0.435	0.766–1.38	0.087–0.162	0.422–0.838	0.061–0.128	ICP–MS	Akagi et al., 2004
Coral (*Goniastrea pectinata*)	Sioya-wan Bay (Japan)	0.618–1.34	3.98–8.21	0.851–1.71	2.29–4.97	0.204–0.578	0.685–3.10	0.087–0.422		
Coral (*Oulastrea crispata*)	Sesoko-jima Island (Japan)	0.140–0.226	0.986–1.49	0.247–0.356	0.875–1.14	0.132–0.149	0.893–1.04	0.150–0.183		
Coral (*Oulastrea crispata*)	Sioya-wan Bay (Japan)	0.648–1.03	4.05–6.35	0.858–1.33	2.49–3.80	0.341–0.475	2.23–2.58	0.353–0.381		
Coral (*Porites lutea*)	Sesoko-jima Island (Japan)	0.092–0.377	0.681–2.06	0.183–0.440	0.627–1.30	0.095–0.160	0.446–0.865	0.072–0.149		
Coral (*Porites lutea*)	Sioya-wan Bay (Japan)	0.496–1.47	3.36–8.81	0.788–1.80	2.63–5.54	0.367–0.710	2.42–4.34	0.367–0.614		

Appendix 6. (Continued).

Species	Location	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Coral (*Stylophora pistillata*)	Sesoko-jima Island (Japan)	0.057–0.067	0.400–0.452	0.105–0.122	0.358–0.396	0.054–0.061	0.328–0.384	0.063–0.079	ICP–MS	Akagi et al., 2004
Coral (*Stylophora pistillata*)	Sioya-wan Bay (Japan)	0.308–0.358	2.10–2.42	0.500–0.597	1.60–1.92	0.209–0.240	1.11–1.36	0.154–0.192		
Fish (*Ostracion Meleagris*)	South China Sea	0.048	0.130	0.037	0.044	0.001	0.125	0.009	ICP–MS	Li et al., 2016
Fish (*Cephalopholis argus*)	South China Sea	0.047	0.109	0.030	0.108	0.044	0.174	0.017		
Fish (*Balistapus undulatus*)	South China Sea	0.069	0.109	0.025	0.064	0.009	0.123	0.017		
Fish (*Cephalopholis urodelus*)	South China Sea	0.059	0.229	0.080	0.129	0.023	0.133	0.055		
Fish (*Gymnothorax moringa*)	South China Sea	0.062	0.399	0.106	0.204	0.074	0.167	0.044		
Fish (*Kyphosus lembus*)	South China Sea	0.067	0.413	0.039	0.219	0.041	0.283	0.056		
Fish (*Parupeneus multifasciatus*)	South China Sea	0.071	0.647	0.064	0.375	0.057	0.225	0.054		
Fish (*Parupeneus pleurostigma*)	South China Sea	0.085	0.492	0.149	0.244	0.019	0.263	0.047		
Fish (*Melichthys vidua*)	South China Sea	0.112	0.742	0.110	0.282	0.079	0.424	0.039		
Fish (*Pervagor melanocephalus*)	South China Sea	0.260	1.55	0.418	0.922	0.196	0.871	0.102		
Fish (*Cheilinus fasciatus*)	South China Sea	0.103	0.619	0.130	0.320	0.045	0.357	0.059		

Appendix 6. (Continued).

Species	Location	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Fish (*Cheilinus rhodochrous*)	South China Sea	0.089	0.412	0.042	0.217	0.045	0.328	0.047	ICP–MS	Li et al., 2016
Fish (*Cephalopholis sonnerati*)	South China Sea	0.155	0.548	0.103	0.366	0.075	0.523	0.069		
Fish (*Odonus niger)*	South China Sea	0.119	0.201	0.341	0.189	0.131	0.293	0.029		
Fish (*Cypselurus katoptron*)	South China Sea	0.094	0.241	0.064	0.109	0.035	0.216	0.063		
Fish (*Heteropriacanthus cruentatus*)	South China Sea	0.064	0.184	0.027	0.058	0.006	0.254	0.002		
Fish (*Gnathodentex aureolineatus*)	South China Sea	0.116	0.402	0.051	0.277	0.015	0.228	0.018		
Fish (*Paraluteres prionurus*)	South China Sea	0.300	0.755	0.159	0.325	0.086	0.360	0.070		
Fish (*Myripristis kuntee*)	South China Sea	0.108	0.653	0.126	0.445	0.081	0.411	0.036		
Fish (*Epinephelus hexagonatus*)	South China Sea	0.183	0.406	0.082	0.287	0.087	0.283	0.061		
Fish (*Coris gaimard*)	South China Sea	0.113	0.117	0.028	0.129	0.019	0.141	0.009		
Fish (*Scarus forsteri*)	South China Sea	0.184	0.704	0.132	0.443	0.093	0.404	0.108		
Fish (*Diodon hystrix*)	South China Sea	0.138	0.460	0.337	0.297	0.108	0.419	0.042		
Fish (*Parupeneus trifasciatus*)	South China Sea	0.033	0.222	0.132	0.048	0.061	0.179	0.016		

Appendix 6. (Continued).

Species	Location	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Fish (*Epinephelus* fam.)	South China Sea	0.746	0.627	0.109	0.276	0.050	0.226	0.030	ICP–MS	Li et al., 2016
Fish (*Lutjanus kasmira*)	South China Sea	0.099	0.438	0.063	0.266	0.023	0.360	0.064		
Fish (*Cephalopholis urodelus*)	South China Sea	0.170	0.878	0.295	0.407	0.109	0.513	0.071		
Fish (*Pterophyllum scalare*)	South China Sea	0.115	0.201	0.019	0.100	0.010	0.067	0.012		
Fish (*Ctenochaetus striatus*)	South China Sea	0.237	1.32	0.281	0.825	0.119	0.692	0.090		
Fish (*Thalassoma quinquevittatum*)	South China Sea	0.214	0.516	0.099	0.379	0.053	0.211	0.053		
Shellfish (*Lobatus gigas*)	South China Sea	0.981	6.09	1.82	3.26	0.598	2.13	0.298		
Shellfish (*Trochus niloticus*)	South China Sea	0.620	3.28	0.722	1.92	0.332	1.92	0.303		
Shellfish (*Linnaeus*)	South China Sea	0.378	1.18	0.221	0.735	0.119	0.596	0.102		
Shellfish (*Harpago chiragra*)	South China Sea	1.70	8.17	1.75	4.69	0.636	2.35	0.428		
Shellfish (*Tridacna squamosa*)	South China Sea	0.707	4.78	0.935	2.68	0.431	2.50	0.430		
Crustacean (*Dromia dehaani*)	South China Sea	3.62	22.9	4.95	13.9	2.05	12.4	1.88		
Crustacean (*Paguridae* fam.)	South China Sea	9.55	60.2	12.4	35.5	5.02	29.1	4.49		

Appendix 6. (Continued).

Species	Location	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Crustacean (*Podophthalmus vigil*)	South China Sea	1.12	6.98	1.58	4.45	0.637	3084	0.618	ICP–MS	Li et al., 2016
Crustacean (*Carpilius convexus*)	South China Sea	1.83	11.0	2.55	7.61	1.09	6.95	1.12		
Algae (*Codium bursa*)	Bergeggi (Ligurian Sea)	140	510	150	260	50.0	200	43.0	ICP–MS	Squadrone et al., 2017
Algae (*Flabellia petiolata*)	Bergeggi (Ligurian Sea)	160	600	160	300	60.0	250	51.0		
Algae (*Padina pavonica*)	Bergeggi (Ligurian Sea)	130	580	140	300	50.0	240	41.0		
Algae (*Halopteris filicina*)	Bergeggi (Ligurian Sea)	220	640	220	320	80.0	270	78.0		
Algae (*Ganonema farinosum*)	Bergeggi (Ligurian Sea)	80.0	350	80.0	190	30.0	150	30.0		
Algae (*Codium bursa*)	Elba Island (Ligurian Sea)	65.0	220	68.0	110	20.0	90.0	20.0		
Algae (*Flabellia petiolata*)	Elba Island (Ligurian Sea)	91.0	340	100	180	40.0	150	33.0		
Algae (*Caulerpa racemosa*)	Elba Island (Ligurian Sea)	40.0	200	50.0	110	20.0	80.0	20.0		
Algae (*Padina pavonica*)	Elba Island (Ligurian Sea)	52.0	260	60.0	140	20.0	110	17.0		
Algae (*Halopteris filicina*)	Elba Island (Ligurian Sea)	10.0	50.0	10.0	30.0	31.0	20.0	3.00		
Algae (*Dictyota dichotoma*)	Elba Island (Ligurian Sea)	60.0	270	70.0	150	20.0	110	20.0		

Appendix 6. (Continued).

Species	Location	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Algae (*Peyssonnelia squamaria*)	Elba Island (Ligurian Sea)	50.0	180	50.0	90.0	20.0	70.0	10.0	ICP–MS	Squadrone et al., 2017
Algae (*Laurencia obtusa*)	Elba Island (Ligurian Sea)	50.0	210	50.0	110	20.0	80.0	20.0		
Algae (*Codium bursa*)	Capraia Island (Ligurian Sea)	17.0	85.0	18.0	46.0	7.00	37.0	6.00		
Algae (*Flabellia petiolata*)	Capraia Island (Ligurian Sea)	16.0	86.0	18.0	47.0	7.00	48.0	8.90		
Algae (*Halimeda tuna*)	Capraia Island (Ligurian Sea)	30.0	170	30.0	90.0	12.0	71.0	9.00		
Algae (*Padina pavonica*)	Capraia Island (Ligurian Sea)	46.0	250	50.0	140	18.0	110	16.0		
Algae (*Halopteris filicina*)	Capraia Island (Ligurian Sea)	70.0	340	73.0	170	25.0	130	22.0		
Algae (*Cystoseira* spp.)	Capraia Island (Ligurian Sea)	40.0	200	40.0	120	16.0	96.0	15.0		
Algae (*Peyssonnelia squamaria*)	Capraia Island (Ligurian Sea)	40.0	180	40.0	90.0	13.0	70.0	11.0		
Algae (*Dudresnaya verticillata*)	Capraia Island (Ligurian Sea)	10.0	40.0	10.0	20.0	2.00	13.0	2.00		
Fish (*Pylodictis olivaris*)	Shandong Province (China)	$6.0\cdot10^{-5}$	$3.2\cdot10^{-4}$	$5.0\cdot10^{-5}$	$1.7\cdot10^{-4}$	$1.0\cdot10^{-5}$	$1.3\cdot10^{-4}$	$1.0\cdot10^{-5}$	ICP–MS	Yang et al., 2016
Fish (*Scophthalmus maximus*)	Shandong Province (China)	$9.0\cdot10^{-5}$	$5.6\cdot10^{-4}$	$1.2\cdot10^{-4}$	$3.5\cdot10^{-4}$	$4.0\cdot10^{-5}$	$2.6\cdot10^{-4}$	$3.0\cdot10^{-5}$		

Appendix 6. (Continued).

Species	Location	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Fish (*Trichiurus lepturus*)	Shandong Province (China)	$5.0\cdot10^{-5}$	$3.2\cdot10^{-4}$	$6.0\cdot10^{-5}$	$1.9\cdot10^{-4}$	$5.0\cdot10^{-5}$	$1.5\cdot10^{-4}$	$2.0\cdot10^{-5}$	ICP–MS	Yang et al., 2016
Fish (*Lateolabrax japonicus*)	Shandong Province (China)	$6.0\cdot10^{-5}$	$3.7\cdot10^{-4}$	$7.0\cdot10^{-5}$	$2.2\cdot10^{-4}$	$2.0\cdot10^{-5}$	$1.7\cdot10^{-4}$	$2.0\cdot10^{-5}$		
Fish (*Sphyraenus* spp.)	Shandong Province (China)	$1.06\cdot10^{-4}$	$8.9\cdot10^{-4}$	$1.7\cdot10^{-4}$	$4.9\cdot10^{-4}$	$5.0\cdot10^{-5}$	$3.7\cdot10^{-4}$	$5.0\cdot10^{-5}$		
Fish (*Larimichthys polyactis*)	Shandong Province (China)	$1.0\cdot10^{-4}$	$5.4\cdot10^{-4}$	$1.1\cdot10^{-4}$	$3.2\cdot10^{-4}$	$3.0\cdot10^{-5}$	$2.4\cdot10^{-4}$	$3.0\cdot10^{-5}$		
Clam shell (*Ruditapes philippinarum*)	Ogishima Port (Japan)	0.91±0.05	5.41±0.3	1.12±0.04	3.40±0.2	0.40±0.05	2.65±0.3	0.42±0.06	ICP–MS	Akagi et al., 2017
Mussel shell (*Mytilus galloprovincialis*)	Ogishima Port (Japan)	0.11±0.01	0.79±0.07	0.19±0.02	0.69±0.03	0.11±0.01	0.54±0.04	0.10±0.01		
Clam shell (*Ruditapes philippinarum*)	Kanazawa-hakkei Station (Japan)	1.13±0.1	6.99±0.9	1.48±0.2	4.63±0.6	0.59±0.08	3.74±0.4	0.62±0.09		
Clam tissue (*Ruditapes philippinarum*)	Kanazawa-hakkei Station (Japan)	15.6±0.3	99.8±1.5	19.7±0.4	54.5±0.6	6.63±0.1	45.5±0.3	8.86±0.3		
Clam shell (*Phacosoma japonicum*)	Kanazawa-hakkei Station (Japan)	4.44±0.5	28.0±3.8	6.03±0.8	18.1±2.1	2.20±0.2	12.7±1.5	1.83±0.2		
Clam tissue (*Phacosoma japonicum*)	Kanazawa-hakkei Station (Japan)	22.5±0.4	130±1.0	26.2±0.1	77.5±3.2	9.84±0.3	59.5±1.0	10.2±0.4		
Clam shell (*Mactra veneriformis*)	Kanazawa-hakkei Station (Japan)	0.91±0.1	5.58±0.6	1.18±0.1	3.53±0.3	0.44±0.05	2.73±0.27	0.39±0.04		
Clam tissue (*Mactra veneriformis*)	Kanazawa-hakkei Station (Japan)	27.6±0.7	144±1.5	27.3±0.4	70.8±0.7	7.85±0.08	44.5±0.4	6.43±0.2		

Appendix 6. (Continued).

Species	Location	Tb	Dy	Ho	Er	Tm	Yb	Lu	Analytical Method	Reference
Clam shell (*Ruditapes philippinarum*)	Daiba Island (Japan)	3.00±0.2	17.7±1.3	3.76±0.3	12.3±1.1	1.48±0.1	9.54±0.8	1.35±0.1	ICP–MS	Akagi et al., 2017
Clam tissue (*Ruditapes philippinarum*)	Daiba Island (Japan)	13.6±0.6	74.7±2.8	14.5±0.3	38.7±1.0	4.48±0.2	24.6±1.5			
Clam shell (*Mercenaria stimpsoni*)	Daiba Island (Japan)	3.09±0.01	18.2±0.04	3.96±0.01	11.8±0.05	1.48±0.01	9.28±0.02			
Clam tissue (*Mercenaria stimpsoni*)	Daiba Island (Japan)	6.59±0.2	32.7±1.3	6.12±0.2	15.6±0.2	1.62±0.05	9.26±0.4			

Appendix 7. Concentrations (pmol/kg) of TCEs in natural seawater samples.

Element	Location	Depth	Concentration	Analytical Method	Reference
Nb	North Pacific	≈0m	2.7	ICP–MS	Sohrin et al., 1998
	North Pacific	100m	2.6		
	North Pacific	400m	3.7		
	North Pacific	1500m	3.5		
	North Pacific	>4000m	3.8		
Nb	North Pacific (Japan)	650m	3.7±0.3	ICP–MS	Firdaus et al., 2007
Nb	Central Pacific	5m	15.1	Q–ICP–MS	Sun and Li, 2015
	Central Pacific	100m	18.3		
	Central Pacific	>4000m	30.1		
Ta	North Pacific	≈0m	0.09	ICP–MS	Sohrin et al., 1998
	North Pacific	100m	0.12		
	North Pacific	400m	0.06		
	North Pacific	1500m	0.12		
	North Pacific	>4000m	0.29		
Ta	North Pacific (Japan)	650m	0.05±0.01	ICP–MS	Firdaus et al., 2007
Ta	Central Pacific	5m	7.18	Q–ICP–MS	Sun and Li, 2015
	CentralPacific	100m	6.08		
	Central Pacific	>4000m	4.97		
Ga	Sargasso Sea (Northwest Atlantic)	≈0m	11–46	Mass Spectrometer	Shiller, 1988
	California Current (Northeast Pacific)	≈0m	9±1		
	Point Arena (California, USA)	≈0m	11		
Ga	Arctic Ocean	<150m	4–6	ICP–MS	McAlister and Orians, 2015
	Arctic Ocean	>350m	25–28		
In	Northwest Pacific	≈0m	0.14	ICP–MS	Alibo et al., 1998
	Northwest Pacific	500m	0.09		

Appendix 7. (Continued).

Element	Location	Depth	Concentration	Analytical Method	Reference
In	Northwest Pacific	1500m	0.14	ICP–MS	Alibo et al., 1998
	Mediterranean Sea	20m	7.64±0.14		
	Mediterranean Sea	200m	10.71±0.16		
	Mediterranean Sea	500m	7.08±0.14		
	Mediterranean Sea	1000m	6.58±0.41		
	Cape Verde (North Atlantic)	10m	0.64±0.08		
	Cape Verde (North Atlantic)	200m	0.59±0.02		
	Cape Verde (North Atlantic)	600m	0.72±0.07		
	Cape Verde (North Atlantic)	1000m	0.82±0.01		
	Cape Verde (North Atlantic)	2000m	1.49±0.11		
In	Sea of Okhotsk (Japan)	≈0m	0.58	ICP–MS	Obata et al., 2007
	Sea of Okhotsk (Japan)	100m	0.17		
	Sea of Okhotsk (Japan)	1000m	0.10		
	Sea of Okhotsk (Japan)	2000m	0.15		
	Sea of Okhotsk (Japan)	3000m	0.15		
Tl	North Atlantic	≈0m	46.0	NAA	Matthews and Riley, 1970
	North Atlantic	1000m	48.9		
	North Atlantic	2500m	53.3		
Tl	Point Sur (California, USA)	100m	34.2	AAS	Flegal et al., 1989
	Point Sur (California, USA)	1000m	4.31		
	Point Sur (California, USA)	2000m	3.96		
	California Current (Northeast Pacific)	100m	10.3		
	California Current (Northeast Pacific)	1000m	3.72		
	California Current (Northeast Pacific)	2000m	8.32		

Appendix 7. (Continued).

Element	Location	Depth	Concentration	Analytical Method	Reference
Tl	Subtropical Gyre (Northeast Pacific)	100m	24.5	AAS	Flegal et al., 1989
	Subtropical Gyre (Northeast Pacific)	1000m	48.4		
	Subtropical Gyre (Northeast Pacific)	2000m	132.1		
Tl	Atlantic Ocean	4000m	54.3–71.0	PTI–IDMS	Schedlbauer and Heumann, 1999
Ge	South Pacific	≈0m	29.8	ID–HG–ICP–MS	Mortlock and Froelich, 1996
	South Pacific	400m	58.2		
	South Pacific	2000m	85.4		
	South Pacific	>4000m	107.7		
	Sargasso Sea (Northwest Atlantic)	≈0m	2.0		
	Sargasso Sea (Northwest Atlantic)	400m	3.3		
	Sargasso Sea (Northwest Atlantic)	2000m	16.1		
	Sargasso Sea (Northwest Atlantic)	>4000m	29.6		
Ge	Sargasso Sea (Northwest Atlantic)	≈0m	5.0	AAS	Lewis et al., 1988
	Sargasso Sea (Northwest Atlantic)	>4000m	100–180		
Te	Florida Strait (Gulf of Mexico)	≈0m	4.1±0.8	GF–AAS	Andreae, 1984
	Florida Strait (Gulf of Mexico)	100m	2.2±0.6		
	Florida Strait (Gulf of Mexico)	400m	6.2±0.8		
	Gulf of Mexico	≈0m	3.0±0.5		

Appendix 8. Concentrations (µg/kg) of Tl in wild marine species.

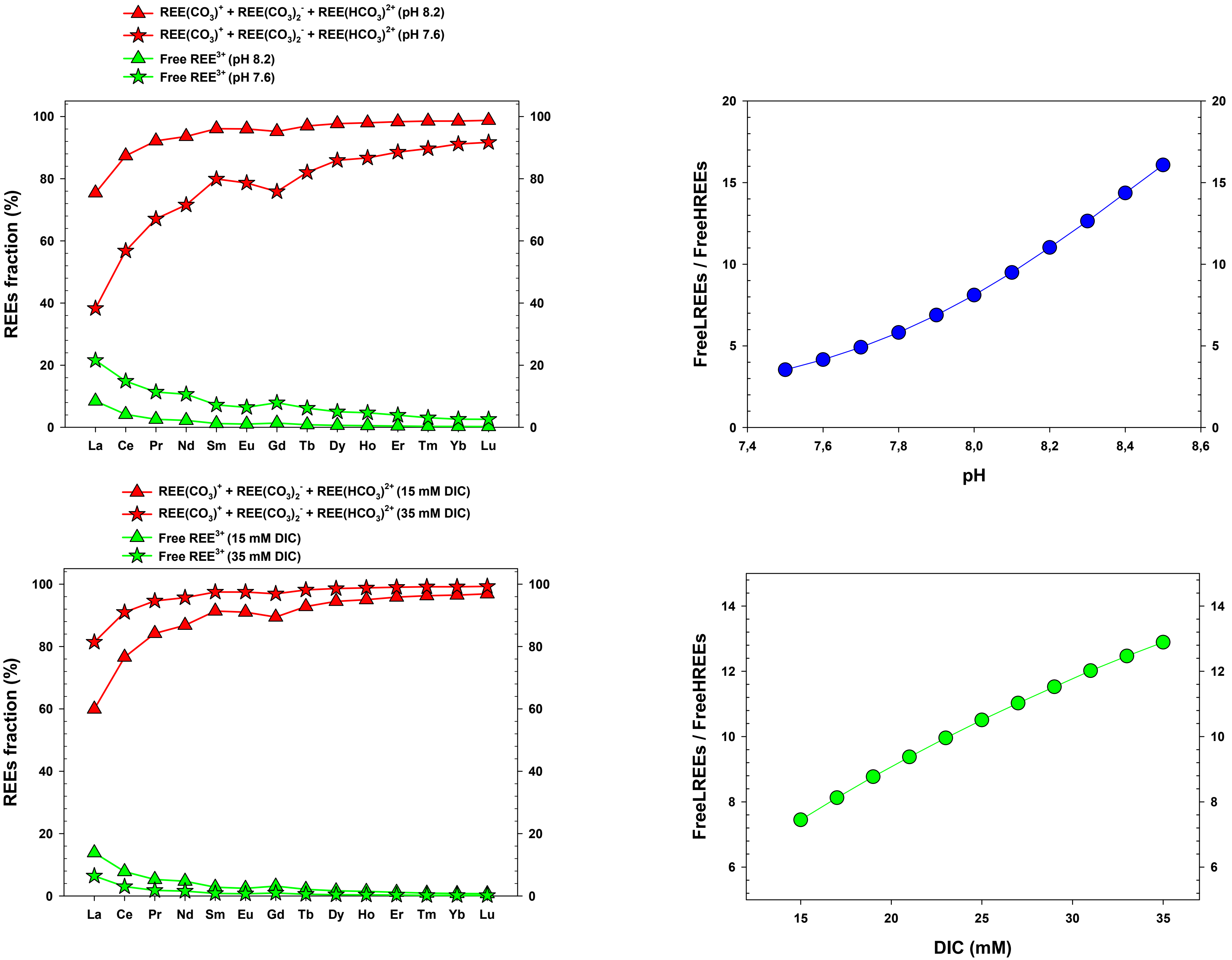
Species	Location	Concentration	Analytical Method	Reference
Phytoplankton	Central Pacific	20–800	NAA	Flegal et al., 1986
Zooplankton	Central Pacific	30–500		
Bivalve (*Scrobicularia plana*)	Guadalquivir Estuary (Spain)	40–90	GFAAS	Del Valls et al., 1999
Fish (*Liza ramada*)	Guadalquivir Estuary (Spain)	80–210		
Oyster (*Crassostea angulata*)	Guadalquivir Estuary (Spain)	15–98		
Crab (*Uca tangeri*)	Guadalquivir Estuary (Spain)	75–125		

Appendix 9. DORM–2 (dogfish muscle certified reference material for trace metals) concentrations found in this study and compared with informative reference values (Sturgeon, 1999, NRC–CNRC) and literature data (Engström et al., 2004).

Element	This study	Certified values	Literature values
U	0.80 ± 0.16	–	0.76 ± 0.03
Sb	20.5 ± 0.60	–	22.0 ± 2.0
Th	0.69 ± 0.20	–	0.59 ± 0.14
W	10.7 ± 1.10	–	8.00 ± 1.1
Ag	26.3 ± 0.30	41.0 ± 13.0	35.0 ± 3.0
Au	0.34 ± 0.10	–	0.23 ± 0.04
Nb	1.84 ± 0.10	–	2.8 ± 0.30
Tl	3.98 ± 0.41	4.00	3.70 ± 0.10
La	1.59 ± 0.42	–	1.40 ± 0.10
Ce	2.85 ± 0.73	–	2.20 ± 0.10
Pr	0.36 ± 0.09	–	0.19 ± 0.02
Nd	1.14 ± 0.27	–	1.10 ± 0.10
Sm	0.18 ± 0.04	–	–
Eu	0.12 ± 0.04	–	–
Gd	0.11 ± 0.05	–	–
Tb	0.014 ± 0.004	–	–
Dy	0.15 ± 0.03	–	–
Ho	0.027 ± 0.007	–	–
Er	0.10 ± 0.04	–	–
Tm	0.013 ± 0.005	–	–
Yb	0.12 ± 0.02	–	–
Lu	0.015 ± 0.006	–	–

Appendix 10. Correlations between the elements studied ($p<0.05$ (95%)).

	REEs	**LREE/HREE**	**MREE/HREE**	**Th**	**U**	**Ag**	**Sb**	**W**	**Tl**	**Bi**	**Nb**	**Au**
REEs	0	0.0001	0.0184	<0.0001	<0.0001	0.0903	0.0027	0.0004	0.0087	<0.0001	<0.0001	0.0805
LREE/HREE	0.0001	0	<0.0001	0.0001	0.0012	0.0739	0.1402	0.2741	0.9935	0.0189	0.0560	0.0338
MREE/HREE	0.0184	< 0.0001	0	0.0227	0.0035	0.1817	0.2085	0.4470	0.2108	0.0613	0.3258	0.0216
Th	<0.0001	0.0001	0.0227	0	<0.0001	0.0444	0.0045	0.0013	0.0042	<0.0001	<0.0001	0.0692
U	<0.0001	0.0012	0.0035	<0.0001	0	0.0822	<0.0001	0.0023	0.2662	<0.0001	0.0008	0.1185
Ag	0.0903	0.0739	0.1817	0.0444	0.0822	0	0.0438	0.8762	0.2900	0.1015	0.0435	<0.0001
Sb	0.0027	0.1402	0.2085	0.0045	<0.0001	0.0438	0	0.0002	0.3245	<0.0001	0.0020	0.0461
W	0.0004	0.2741	0.4470	0.0013	0.0023	0.8762	0.0002	0	0.0692	<0.0001	<0.0001	0.2518
Tl	0.0087	0.9935	0.2108	0.0042	0.2662	0.2900	0.3245	0.0692	0	0.2039	0.0005	0.4306
Bi	<0.0001	0.0189	0.0613	<0.0001	<0.0001	0.1015	0.0001	<0.0001	0.2039	0	<0.0001	0.0425
Nb	<0.0001	0.0560	0.3258	<0.0001	0.0008	0.0435	0.0020	<0.0001	0.0005	<0.0001	0	0.0243
Au	0.0805	0.0338	0.0216	0.0692	0.1185	<0.0001	0.0461	0.2518	0.4306	0.0425	0.0243	0



Appendix 11. Modeling of REEs using Visual MINTEQ 3.1 with the parameters specified in Table 6.1.

Marine Pollution Bulletin 62 (2011) 646–650

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal)

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ARTICLE INFO

Keywords:
Platinum
Contamination
Coastal sediments
Catalytic converters
Tagus Estuary

ABSTRACT

Platinum contamination in estuarine and coastal sediments has been evaluated in three cores collected from the Tagus Estuary and Prodelta shelf sediments. Elevated concentrations, up to 25-fold enrichment compared to background values, were found in the upper layers of the estuarine sediments. The degree of Pt enrichment in the estuarine sediments varied depending on the proximity to vehicular traffic sources, with a maximum concentration of 9.5 ng g^{-1}. A considerable decrease of Pt concentrations with depth indicated the absence of significant contamination before the introduction of catalytic converters in automobiles. Platinum distribution in the Tagus Prodelta shelf sediment core showed no surface enrichment; instead a sub-surface maximum at the base of the mixed layer suggested the possibility of post-depositional mobility, thereby blurring the traffic-borne contamination signature in coastal sediments.

The platinum group elements (PGE), namely ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), are amongst the least abundant elements in the Earth's crust, with average concentrations typically less than 1 ng g^{-1} (Rudnick and Gao, 2003). There are a number of factors, however, which may lead to elevated concentrations of these elements in the environment. In marine sediments these include: siderophile sources (Gabrielli et al., 2008), hydrothermal vents (Cave et al., 2003), formation of ferromanganese crusts (Halbach et al., 1989), accumulation at redox boundaries (Colodner et al., 1992) and anthropogenic emissions (Tuit et al., 2000).

Current interest in the environmental concentrations and geochemical behavior of Pt (together with Pd and Rh) is based on significant increases in their anthropogenic emissions over the past 3 decades. Apart from their traditional use in jewellery, dentistry, chemicals, or electronics, their demand sharply increased in the 1980s in North America and in the 1990s in Europe. This was due to their use in catalytic converters for automobiles in order to reduce emissions of pollutant exhaust gases. Currently, their incorporation into catalytic converters accounts for 32% of Pt, 52% of Pd and 86% of Rh of the total World demand (Johnson Matthey, 2010). During abrasion and ageing of the washcoat layer of a catalyst, metallic and oxide forms of PGE are emitted as particles (normally in the size range of 10–30 μm) at rates per vehicle up to several hundred ng km^{-1} (Ravindra et al., 2004). Once in the environment, particulate PGE are subject to mobilization through interaction/complexation with naturally occurring inorganic/organic ligands and bacterial action (e.g. Wei and Morrison, 1994; Dahlheimer et al., 2007). Accordingly, PGE concentrations well above background values have been reported in areas subject to vehicular traffic (Ravindra et al., 2004). Also, evidence for their long range atmospheric transport has been shown by the contamination of Greenland snows with PGE (Barbante et al., 2001).

While most the studies have focused on Pt concentrations in sediments of lakes and urban rivers (e.g. Rauch and Hemond, 2003; Haus et al., 2007), little is known about its geochemical behavior and current contamination in anthropogenically-impacted estuarine and coastal systems.

The Tagus Estuary is one of the largest European estuaries with an area of approximately 320 km^2 formed by several channels and islands (Fig. 1). The intense urban sprawl and industrial growth of Lisbon (approximately 2.5 million inhabitants) has been responsible for the inputs of anthropogenic metals and persistent organic pollutants to the Tagus Estuary (e.g. Figuères et al., 1985; Nogueira et al., 2003; Canário et al., 2005; Vale et al., 2008). In common with many large rivers, the Tagus Prodelta patch (Fig. 1) accumulates riverine, estuarine and marine-borne fine-grained materials (Jouanneau et al., 1998). These prodeltaic deposits have been used to reconstruct the historical increase of metal concentrations in the Tagus adjacent to the catchment's area (Mil-Homens et al., 2009).

Three sediment cores were collected in the Tagus Estuary and its Prodelta (Fig. 1). Two sediment cores were collected in the estuary close to a motorway bridge (Vasco da Gama bridge opened to

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0025-326X/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2010.12.018

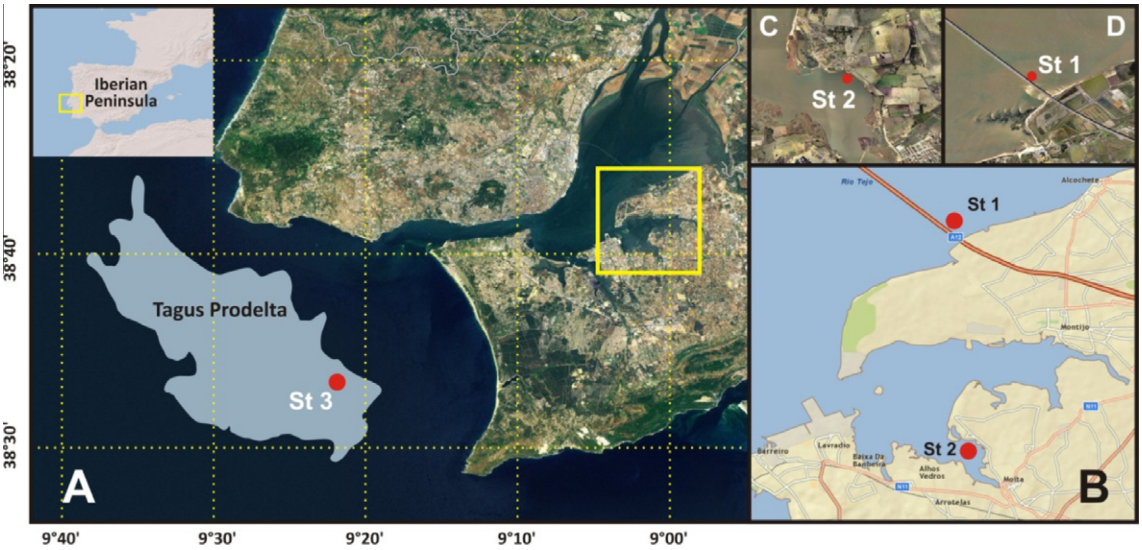

Fig. 1. Map showing the location of the sediment cores in the Tagus Estuary at Site 1 (St 1), Site 2 (St 2) and Prodelta at Site 3 (St 3).

traffic in 1998; Site 1) and nearby old chemical and pyrite roasting plants closed during the 1990s (Site 2). Sediments were characterized by reducing conditions (Sundby et al., 2003), with typical oxic layer depths of less than 2 mm. Since the sediments were composed of 99% fine-grained material with a grain size <63 μm, no sieving was carried out. Cores were sectioned, dried at 40 °C and ground using an agate mortar. Additionally, three sediments from the bridge gullypots were collected. A sediment core in the Tagus Prodelta (Site 3, PO287-26-1B) was collected during the PALEO1 cruise in 2002 onboard R/V Poseidon. The core was sectioned, the coarser fraction (>2 mm) removed by wet sieving and then dried and ground as indicated above. Sediments were analyzed for Al, Pb and Hg using well-established procedures (Mil-Homens et al., 2009; Costley et al., 2000).

The determination of Pt in the sediments was undertaken by means of catalytic adsorptive cathodic stripping voltammetry (catalytic AdCSV) after appropriate digestion. Before digestion, and in order to remove organic material that interferes with the voltammetric determination, approximately 0.15 g of the ground sediment was ashed in quartz crucibles up to 800 °C following the heating scheme given in Nygren et al. (1990). Ashed sediments were then transferred to 30 mL Teflon® PFA vessels with screw caps (Savillex) for digestion with 5 mL of concentrated HCl and 3 mL of concentrated HNO_3 at 210 °C for 4 h. Following the digestion, the vessel caps were removed and the acids evaporated at 210 °C to near dryness. The residue was re-dissolved with 1 mL of concentrated HCl and 1 mL of concentrated H_2SO_4, evaporated at 210 °C until no fumes were observed and a near constant volume, comprising mostly sulphuric acid, 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 pore size filters) and made up to 25 mL in polypropylene volumetric flasks. The detection limit (defined as three times the standard deviation of the blank) for a typical mass of 0.15 g of sediment was 0.05 ng g^{-1}. The accuracy was checked using river sediment certified reference material (JSd-2; Geological Survey of Japan) and good agreement was obtained with the certified concentrations (Table 1).

The down-core Pt distribution at Site 1 shows a clear indication of recent input of this element into the Tagus Estuary. Elevated Pt values at the top of the core, up to 9.5 ng g^{-1}, are observed, which decrease sharply with depth below 5 cm to background values in the range of 0.3–0.4 ng g^{-1} (Fig. 2). The elevated Pt concentrations at the sediment surface are in accordance with the Pt concentrations in three independent gullypot sediments from the bridge: 7.5, 21 and 157 ng g^{-1}, which are typical of other urban gullypot sediments (Wei and Morrison, 1994; Fliegel et al., 2004; Jackson et al., 2007). At Site 2, a similar depth profile was found, although the degree of Pt enrichment in the uppermost layer is much lower, with a maximum value of 0.9 ng g^{-1}. This area is one of the most contaminated in the Tagus Estuary due the historical impact of a chemical plant (Vale et al., 2008) and significant contamination from industrial metals is also evident (e.g. Pb in Fig. 2). Furthermore, a lower radiogenic Pb isotopic signature in upper sediment layers at Site 2 is indicative of increase fraction of anthropogenic Pb (Caetano et al., 2007). Conversely, reduced pressure from traffic in this part of the estuary may explain the lower Pt concentrations. The abrupt decrease of Pt with depth to background values in Sites 1 and 2 indicates the absence of previous significant contamination due to other sources signifying the catalytic converters as the major input for the recent enrichment.

Results for Site 3 (Fig. 3), collected at the Tagus Prodelta (see Mil-Homens et al., 2009 for a complete characterization of other metals and ^{210}Pb-dating for this core), has a different Pt profile

Table 1
Platinum concentrations, ng g^{-1} obtained for the river sediment certified reference material JSd-2 in this study and by other authors.

Imai et al. (1996)[1]	Hall and Oates (2003)[2]	Djingova et al. (2003)[3]	Tsogas et al. (2008)[4]	This study[5] ($n = 3$)
16.7 ± 2.8	14.5 ± 2.8	15 ± 2	15.9 ± 1.1	14.6 ± 0.8

[1]Indicative value given by the Geological Survey of Japan.

Decomposition/separation procedure: [1]$HCl/HNO_3/HF$ digestion, MIBK extraction; [2]Pb fire assay; NiS fire assay; HCl/HNO_3 digestion (ashed and non-ashed sample). [3]$HNO_3/HCl/HF$ microwave-assisted digestion. [4]HNO_3/HF microwave-assisted digestion. [5]HCl/HNO_3 digestion of ashed sediment.

Determination: [1]flameless AAS; [2]ICP-MS. [3]ICP-MS. [4]GF-AAS. [5]Stripping Voltammetry.

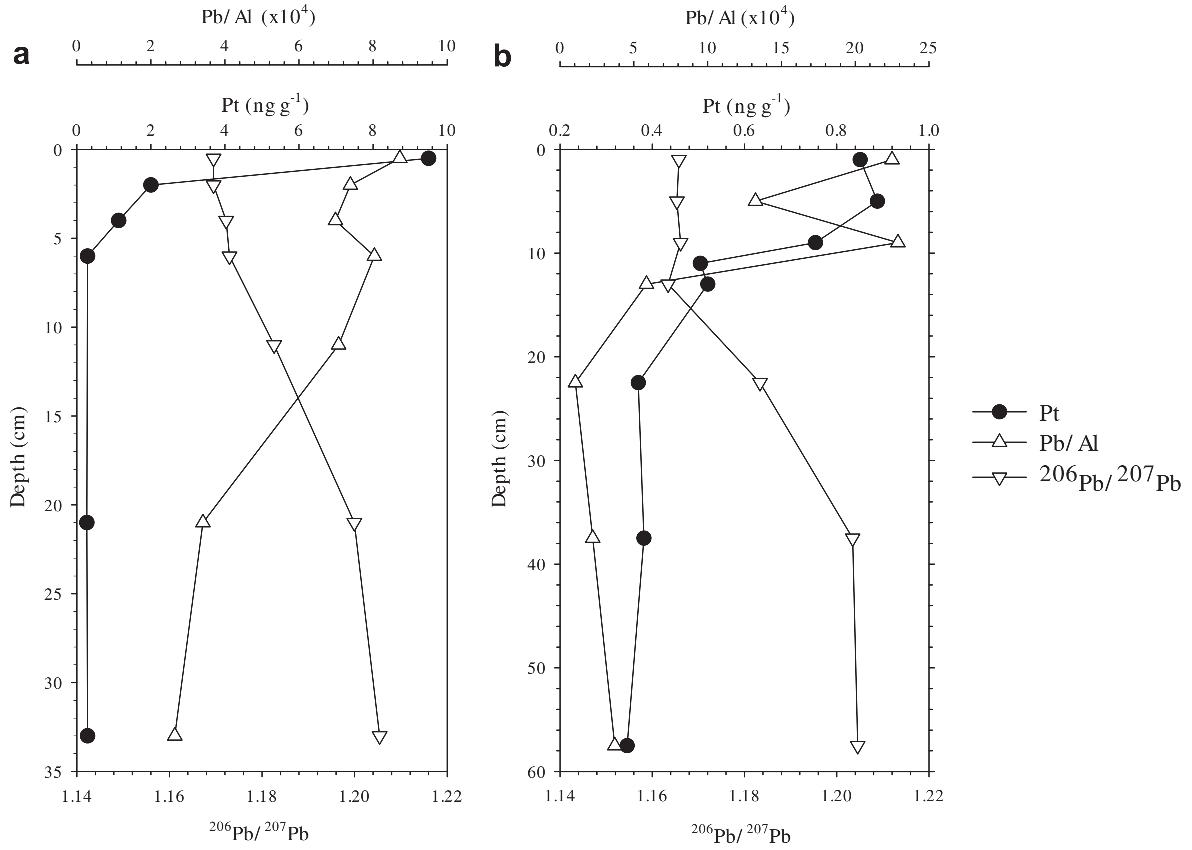

Fig. 2. Depth profiles of Pt, Pb and ^{206}Pb/^{207}Pb ratios in cores from Sites 1 (a) and 2 (b).

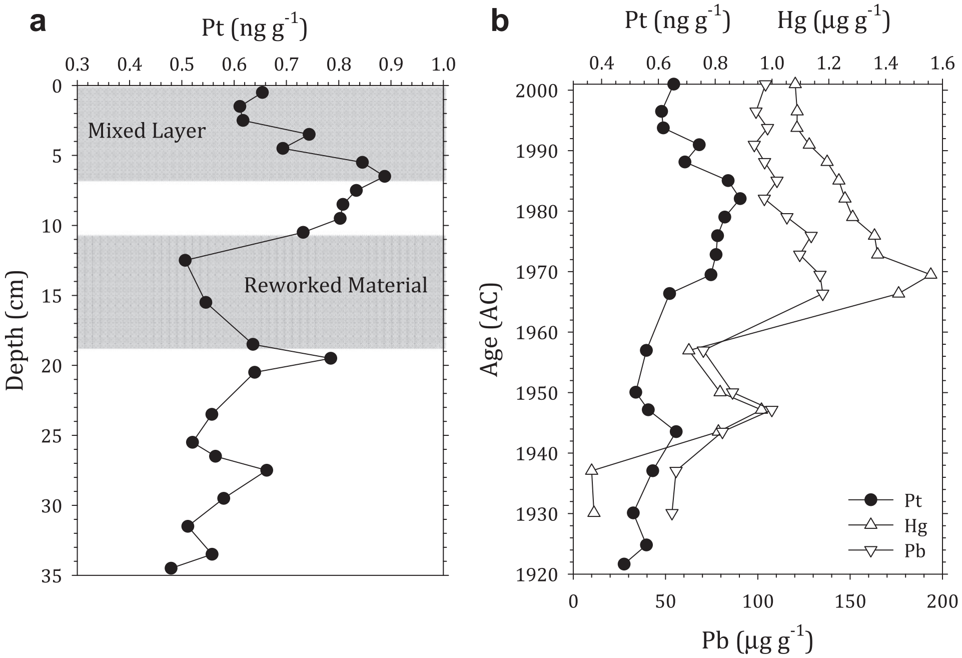

Fig. 3. Depth profile of Pt at Site 3 (Tagus Prodelta). (a) Variation of Pt, Hg and Pb concentrations vs sediment age. (b) See Mil-Homens et al. (2009) for a complete description of the core characteristics and sediment dating.

with no maximum concentrations at the top of the core. Instead, Pt values increase with depth from 0.65 ng g^{-1} at surface to 0.89 ng g^{-1} at the base of the mixed layer which is located at approximately 7 cm depth. This is followed by a sharp decrease to 0.51 ng g^{-1} at 13 cm corresponding to reworked material (Mil-Homens et al., 2009). The Pt profile (Fig. 3b) mimics the depth variation of other metals such as Hg and Pb, which are significantly correlated ($P < 0.01$ and <0.05, respectively, for 2-tailed testing).

Table 2
Platinum concentrations (means ± 1σ) in the Tagus Estuary and Prodelta obtained in this study compared to other estuarine systems. Values in brackets represent concentration ranges.

	Platinum concentration, ng g-1	References
Estuarine and coastal sediments		
Avondale Creek (Australia)	21 ± 6; *n* = 2 (17–25)	Pratt and Lottermoser (2007)
Humber Estuary (UK)	7 ± 1; *n* = 4 (6–8)	Prichard et al. (2008)
Venetian Lagoon (Italy)	0.9 (0.02–10.0)	De Boni et al. (2007)
Boston Harbour (USA)	4 ± 3; *n* = 14 (0.8–12.5)	Tuit et al. (2000)
Tagus Estuary (Portugal)	2 ± 3; *n* = 8 (0.5–9.5)	This study
Portuguese Shelf (Tagus Prodelta)	0.74 ± 0.10; *n* = 9 (0.6–0.9)	This study
Background values		
Massachusetts Bay (USA)	0.6 ± 0.3 (*n* = 5)	Tuit et al. (2000)
Tagus Estuary (Portugal)	0.32 ± 0.05 (*n* = 6)	This study
Portuguese Shelf (Tagus Prodelta)	0.56 ± 0.06 (*n* = 9)	This study
Crustal abundance	0.5 ± 0.5	Rudnick and Gao (2003)

The time profile (Fig. 3b) suggests an elevated input of Pt from the early 1970s to the mid 1980s compared to recent years. However, (i) catalytic converters in automobiles were not introduced in Europe until sometime in the late 1980s or early 1990s and (ii) no Pt enrichment was observed in the deep layers of the two cores collected in the Tagus Estuary which would indicate alternative Pt sources in the past. Therefore, sub-surface Pt enrichment in the Tagus Prodelta may not reflect actual anthropogenic inputs but post-depositional mobility. Here we suggest that the Pt maximum found at the base of the surface mixed layer is probably driven by the scavenging of Pt at the oxic/anoxic boundary. This behavior has also been observed by Tuit et al. (2000) in sediment cores collected in the Boston Harbour. Colodner et al. (1992) and Wei and Morrison (1994) reported that a significant fraction of Pt in marine and road sediments is labile, being associated with Fe–Mn oxyhydroxides and organic-rich particles. This chemical association contributes to Pt mobilization and diffusion being fixed at the redox boundary, which may explain Pt behavior at Site 3. In Cores 1 and 2 the absence of a higher Pt depth resolution does not allow an observation of the presence of such behavior.

Studies of Pt geochemical behavior and contamination in estuaries and coastal systems are scarce in the literature. A comparison of available data is given in Table 2. Background values for the Tagus Estuary and its shelf are 0.32 ± 0.05 ng g^{-1} and 0.56 ± 0.06 ng g^{-1}, respectively. These values agree well with the average Pt crustal abundance of 0.5 ± 0.5 ng g^{-1} (Rudnick and Gao, 2003) and also with the background concentration reported for Massachusetts Bay of 0.6 ± 0.3 ng g^{-1} (Tuit et al., 2000). Concentrations of Pt reported herein for the surface mixed layers are in the range of those found in the Boston Harbour (USA) and the Venetian Lagoon (Italy), but lower than in the Humber Estuary (UK) or Avondale Creek (Australia).

At present it is not possible to estimate, accurately, the rate and extent of increase of Pt concentrations in the environment. The total World demand of Pt for use in the catalytic converters has increased in the past 3 decades (21.2 tonnes in 1980 to 128.9 tonnes in 2007); however, the demand fell by 45% from 2007 to 2009 (Johnson Matthey, 2010) due to the global economic crisis which also affected the automotive industry. Also, the amount of Pt (together with Pd and Rh) loaded into catalytic converters is being continually modified by the manufacturers as more efficient formulations are developed. In gasoline vehicles, for example, most of the manufacturers are substituting Pt-based catalysts with Pd (Johnson Matthey, 2010), which would lead to lower emissions of Pt. Only future studies will test this hypothesis.

Acknowledgements

This work was partially supported by a P.I. project (ref. 200830I150) granted to A.C.G. from the Spanish Ministry of Science and Innovation. INGMAR project funded the PALEO1 cruise where Prodelta sediment core was collected and FCT project TAGUSED (POCTI/2001/CTA/41411) financed the analytical work on this core. The authors wish to thank J. Raimundo and R. Cesario from IPIMAR for field work and technical assistance, and Prof. Geoff Millward (University of Plymouth) for valuable comments on the paper.

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Science of the Total Environment 514 (2015) 366–370

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Evidence of increased anthropogenic emissions of platinum: Time-series analysis of mussels (1991–2011) of an urban beach

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HIGHLIGHTS

- Platinum (0.30 to 0.68 ng g^{-1}) was determined in time-series (1991–2011) samples of wild mussels from an urban beach
- Platinum concentrations followed a statistically significant temporal trend
- The excess of Pt in mussels over the 1991–2011 period was correlated with the Pt autocatalyst demand and car sales
- A bioaccumulation factor of ~ 5 10^{3} was derived, greater than those previously calculated for Pt from exposure experiments

ARTICLE INFO

Article history:
Received 16 December 2014
Received in revised form 3 February 2015
Accepted 5 February 2015
Available online xxxx

Editor: Thomas Kevin V

Keywords:
Bioaccumulation
Mytilus galloprovincialis
Urban contamination
Field study

ABSTRACT

The anthropogenic emissions of Pt to the environment have increased significantly over the past decades, especially after the introduction of the catalytic converters in motor vehicles. In order to check whether this is affecting the levels of this trace metal on living organisms, time-series analysis of freeze-dried soft tissue material of wild mussels (*Mytilus galloprovincialis*) covering the period from 1991 to 2001 and collected at an urban beach in the city of Vigo (NW Iberian Peninsula) was conducted. Concentrations ranged from 0.30 to 0.68 ng g^{-1} with an average concentration of 0.47 ± 0.10 ng g^{-1} ($n = 21$); these concentrations were higher than those obtained for samples collected at a control location away from anthropogenic pressure (0.31 ± 0.10 ng g^{-1}; $n = 5$). Platinum concentrations followed a statistically significant temporal trend (at the 0.020 level), and the excess of Pt in mussels over the 1991–2011 period compared to the control location were correlated with the European Pt autocatalyst demand ($p = 0.0006$) and, especially, the car sales in Spain ($p = 0.0001$). A bioaccumulation factor of ~$5 \cdot 10^3$ was derived, which is greater than those previously calculated for Pt from exposure experiments, but 1–2 orders of magnitude lower than other trace elements (e.g. Zn, Cu, Pb, Cd).

1. Introduction

The natural environmental concentrations of platinum in the biosphere are extremely low, with average crustal abundance of 0.5 ng g^{-1} (Rudnick and Gao, 2003). However, Pt concentrations are currently increasing in the environment due to its use in a variety of anthropogenic activities, the most important including the use of this element in automobile catalytic converters and the manufacture of jewellery, representing 43% and 31%, respectively, of the total Pt demanded during the last decade (Johnson Matthey, 2013). The anthropogenic disturbance of the cycle of Pt at the Earth's surface is such that it has been estimated that more than 80% of the Pt flux is derived from anthropogenic activities (Sen and Peucker-Ehrenbrink, 2012).

As a result of the Pt emissions from catalytic converters in motor vehicles, this element currently represents a new category of traffic related trace metal contaminant in the environment (Haus et al., 2007). Accordingly, elevated Pt concentrations have been reported in areas and environmental compartments subject to vehicular traffic pressure such as road dust, roadside soils, sewage sludge and sediments of urban rivers and harbour basins (Schäfer et al., 1999; Ely et al., 2001; Fritsche and Meisel, 2004; Lésniewska et al., 2004; Zimmermann and Sures, 2004); also, evidence for a long range transport and global platinum environmental perturbation has been given (Soyol-Erdene et al., 2011).

The bioavailability and uptake of Pt emitted from catalytic converters and from soluble Pt species were demonstrated in exposure studies using different aquatic organisms, including freshwater isopods (Moldovan et al., 2001), European eels (Zimmermann et al., 2004), zebra mussels (Sures and Zimmermann, 2007), or common periwinkles (Mulholland and Turner, 2011). However, to date only few studies have been carried out reporting ambient concentrations of Pt in biological matrices. Among these, (i) Jensen et al. (2002) analysed the contamination of feathers from raptor species showing an increased temporal

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http://dx.doi.org/10.1016/j.scitotenv.2015.02.016

trend of Pt concentrations reflecting the introduction of automobile catalytic converters; also, (ii) Haus et al. (2007) demonstrated the bioavailability of traffic-borne Pt in field samples of freshwater crustaceans from the Ruhr district (Germany) showing bioaccumulation factors in the range of other traffic related metals.

In this study we report Pt concentrations in time-series samples (1991–2011) of wild mussels (*Mytilus galloprovincialis*) collected in an urban beach of the Vigo Ria (NW Iberian Peninsula; Fig. 1). Mussels are ideal organisms for use as bio-indicators because as filtering organisms they tend to accumulate dissolved substances in the environment (e.g. Goldberg, 1986; Soto et al., 1997; Bellas et al, 2014) and have been widely used in the study area for biomonitoring of metal contamination (Besada et al., 2002, 2011). The main aim of this study is therefore to determine the temporal variation of Pt biological uptake in an urban beach during the past two decades and results will be discussed in terms of the potential link between the temporal variation of Pt accumulation in mussels and the anthropogenic use of this element from the early 1990's.

2. Material and methods

2.1. Sampling area

Wild mussels (*M. galloprovincialis*) were collected manually and during low tides, in the period of September–November, which corresponds to the second prespawning period in this area (Caceres-Martinez and Figueras, 1998) in order to minimize variations caused by differences in the mussel physiology and therefore minimize seasonal environmental variations. Sampling strategies during this two decade long program are described elsewhere (Besada et al., 2014).

Mussels were collected at Samil beach in the Vigo Ria, an urban beach located in the city of Vigo (Fig. 1) which holds a population of approx. 300,000 inhabitants; an urban stream (Lagares, mean annual flow of ~4 $m^3 s^{-2}$; Perez-Arlucea et al., 2005) discharges at the western part of the beach. For comparison purposes, mussel samples from a control point (Oia, Fig. 1) located around 40 km southward and far from any significant contamination influence were analysed for selected years (1991, 1995, 2000, 2005, 2010). The excess Pt fraction in the Samil beach samples was calculated subtracting the concentrations obtained from the control point.

2.2. Pretreatment

Each sample of mussels was prepared from 50 or more individuals representing the available size range (35–60 mm) existing in the sampling location. Soft tissues were separated from the shells, triturated with Ultraturrax and freeze-dried. An aliquot of the liophilized sample was withdrawn to calculate its water percentage (drying at 105 °C for 24 h, until constant weight). After a freeze-drying process, samples were homogenised again with a mixer mill and stored in acid-washed glass vials at room temperature until analysis.

2.3. Pt analysis

Platinum analysis was performed by means of catalytic adsorptive cathodic stripping voltammetry after appropriate digestion (Cobelo-García et al., 2014); briefly, around 100 mg of sample was ashed up to 800 °C in quartz crucibles in order to eliminate refractory organic material that may interfere during the voltammetric determination. Once cooled, a mixture of 3 mL of HCl and 1 mL of HNO_3 was added to the crucible and allowed to rest for at least 1 h. Then, the acid mixture was transferred to uncapped 30 mL PFA vials (Savillex) and placed on a Teflon-coated hot plate at 195 °C and allowed to evaporate until near dryness. After cooling down, 1 mL of H_2SO_4 was added to the vials and placed again on the hot plate until no fumes were observed (only sulphuric acid was present). After cooling, samples were diluted with 0.1 M HCl and transferred to 25 mL polypropylene volumetric flasks pending analysis. Typically, 3 independent digestions were performed for each sample and the relative standard deviation (RSD%) was generally below 15%.

In order to avoid contamination of samples, sample pretreatment and manipulation were performed in a laminar flow bench (ISO-5) housed inside and ISO-7 lab. Voltammetric determinations were carried out using a μAutolab Type III potentiostat (Metrohm Autolab B.V.) connected to a polarographic stand (Metrohm model 663VA). Details of the voltammetric procedure for the Pt determination are given in

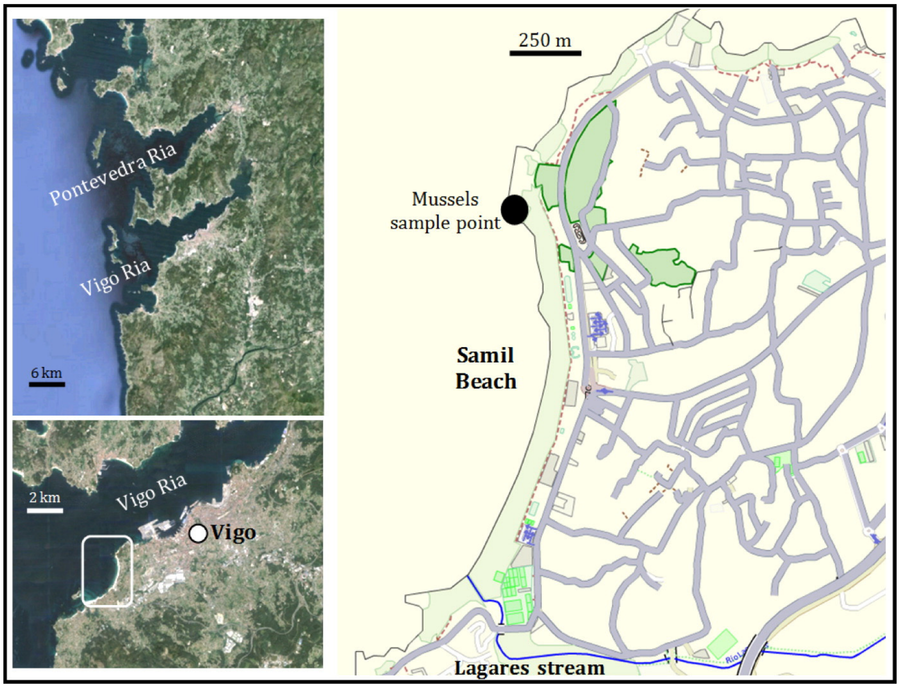


Fig. 1. Sampling location of mussels in the Samil beach (42°13.177 N, 08°46.604 W) of the Vigo Ria (NW Iberian Peninsula).

Cobelo-García et al. (2014). The detection limit was determined as three times the standard deviation of the blanks ($n = 15$) and was found to be 0.04 ng g^{-1}. Concentrations are expressed as in ng g^{-1} dry weight. Since at present there are no certified reference materials (CRMs) for platinum in biological matrices, the accuracy of the analytical procedure was checked using BCR-723 (road dust; Institute for Reference Materials and Measurements, Belgium) and JSd-2 (river sediment; Geological Survey of Japan), obtaining recoveries greater than 95% (BCR-723) and 80% (JSd-2).

3. Results and discussion

3.1. Temporal trend of Pt accumulation in mussels

The results obtained for the time series (1991–2011) of mussels collected in the Samil urban beach ranged from 0.30 to 0.68 ng g^{-1} (Fig. 2), with an average concentration of 0.47 ± 0.10 ng g^{-1} (average ± 1SD; $n = 21$). Lower concentrations were obtained for the samples collected at the control location (Oia, Fig. 1): 0.31 ± 0.10 ng g^{-1} ($n = 5$), indicating the higher anthropogenic pressure at the urban beach. These concentrations are in the range of those given for other aquatic organisms previously reported in the literature (with the exception of the elevated concentrations given for the freshwater crustacean *Asellus aquaticus* in two Swedish rivers subject to traffic pressure; Table 1) which indicates that Pt is typically present at the nanogram or sub-nanogram per gram level in aquatic biota. These values are also similar to the crustal abundance of Pt (0.5 ng g^{-1}; Rudnick and Gao, 2003) or its concentrations in uncontaminated coastal sediments (0.3–0.6 ng g^{-1}; Cobelo-García et al., 2011).

In order to check whether the Pt concentrations followed a statistically significant temporal trend, the Kendall's Tau-b correlation coefficients were calculated as described earlier (Besada et al., 2002, 2014). A Kendall Tau-b coefficient of 0.324 was obtained, which represents a significance level of 0.020. This significant increase in Pt concentrations is accompanied by a decrease in Pb (Fig. 2; Kendall Tau-b −0.663, significance level 0.000), a metal historically linked to traffic-borne pollution due to the use of leaded gasoline in the past. The phasing-out of leaded gasoline during the mid to late 1990's was simultaneous with the introduction of catalytic converters (containing precious metals — Pt, Pd, and Rh) and thus explains their opposite temporal trend observed (Fig. 2)

3.2. Link between Pt accumulation and traffic-borne contamination

Since the most important anthropogenic input of Pt to the environment is currently its use in vehicle catalytic converters (e.g. Cobelo-García et al., 2011), the excess (or anthropogenic) fraction of Pt in mussels from the urban beach — calculated as indicated in Section 2.1 — were compared to the autocatalyst platinum demand in Europe and the car sales in Spain and Portugal (due to the proximity of Vigo to Portugal, i.e. ~30 km) — owing that the Pt release rate from new cars is significantly greater than for old cars; (Palacios et al., 2000) — for the studied period (Fig. 3). Inspection of Fig. 3 shows that the increase of the excess fraction of Pt starts in the late 1990's, well before the sharp increase in the Pt autocatalyst demand during the 2000's but coincident with the rise of car sales for those years. A decrease in the excess Pt in the last years in agreement with the drop in Pt demand and car sales provoked by the recent economic crisis is also evident. A significant correlation was obtained between the excess Pt and the autocatalyst demand (two-tailed $p < 0.0001$) and the car sales in Spain and Portugal ($p < 0.01$), which provides a strong evidence of the traffic-borne contamination as the source of the increased Pt concentrations in the mussel samples in the past two decades at this urban beach.

3.3. Extent of bioaccumulation of Pt in M. galloprovincialis

The bioaccumulation factor (BF) of platinum, defined as:

$$BF = [Pt_m]/[Pt_w]$$

where $[Pt_m]$ is the Pt concentration in the mussels (expressed as nanograms of Pt per kilogram of mussel in a dry weight basis) and $[Pt_w]$ is the dissolved Pt concentration in the water column (expressed as nanograms of Pt per kilogram of water), was calculated using the average concentrations in the mussels (470 ng kg^{-1}; Table 1) and a typical dissolved Pt concentration in the Vigo Ria of 0.5 pM, i.e. 0.1 ng kg^{-1} (Cobelo-García et al., 2013), resulting in a BF of $\sim 5 \cdot 10^3$. This indicates that Pt is effectively bioaccumulated by aquatic organisms, as already

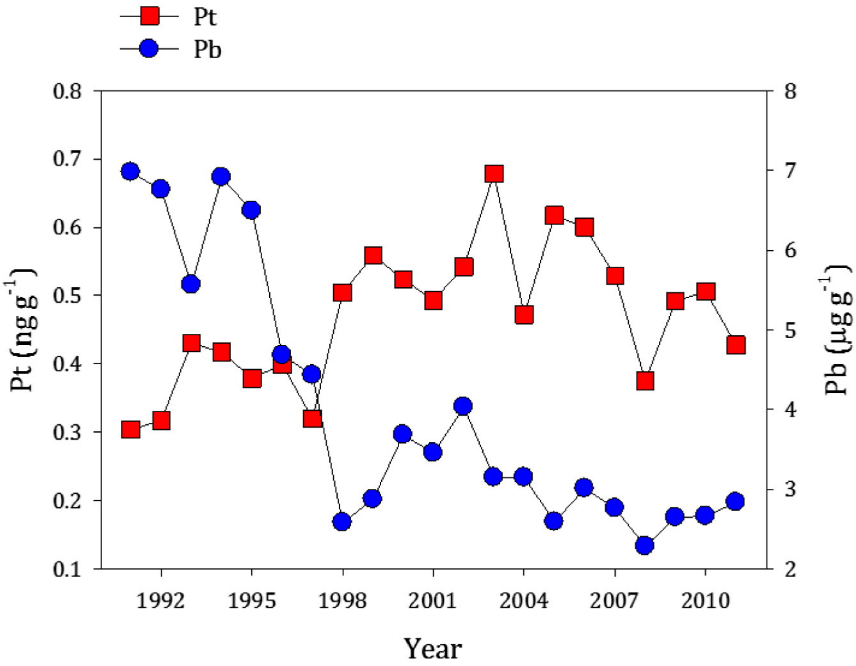


Fig. 2. Pt (ng g^{-1}) and Pb (µg g^{-1}; Besada et al., 2014) concentrations in mussels at Samil beach (see Fig. 1). Sample pre-treatment and the analytical procedure are given in Section 2.

Table 1
Summary of Pt concentrations reported in the literature for aquatic organisms in field studies. Concentrations refer to dry weight except for the data of Haus et al. (2007) which are expressed with respect to wet weight.

Species	Pt (ng/g)	Location	Technique	Reference
Freshwater species				
Fish liver	0.23–0.33	German river	?	Hees et al. (1998)
Freshwater crustacean (*Asellus aquaticus*)	330–1100	Swedish urban river (Kvillebäcken)	ACSV[a]	Rauch and Morrison (1999)
	5–119 (38 ± 35)	Swedish river close to car traffic (Mölndal)	Q-ICP-MS[b]	Moldovan et al. (2001)
	<0.36–0.54	Aquatic habitats close to car traffic in the Ruhr district (Germany)	ACSV[a]	Haus et al. (2007)
Freshwater crustaceans (*Gammarus pulex* and *Dikerogammarus villosus*)	<0.36–1.3	Aquatic habitats close to car traffic in the Ruhr district (Germany)	ACSV[a]	Haus et al. (2007)
Seawater species				
Seaweed (various species)	0.25–1.75 (0.74 ± 0.40)	California coast (USA)	AAS[c]	Yang (1989)
	0.08–032	California coast (USA)	AAS[c]	Hodge et al. (1986)
Oysters (*Crassostea gigas*)	0.16–0.53 (0.35 ± 0.08)	Gironde Estuary (France)	ACSV[a]	Abdou (2014)
Mussels (*Mytilus galloprovincialis*)	0.30–0.68 (0.47 ± 0.10)	Vigo Ria (Spain)	ACSV[a]	This work

[a] Adsorptive cathodic stripping voltammetry.
[b] Quadrupole inductively coupled plasma mass spectrometry.
[c] Atomic absorption spectrometry.

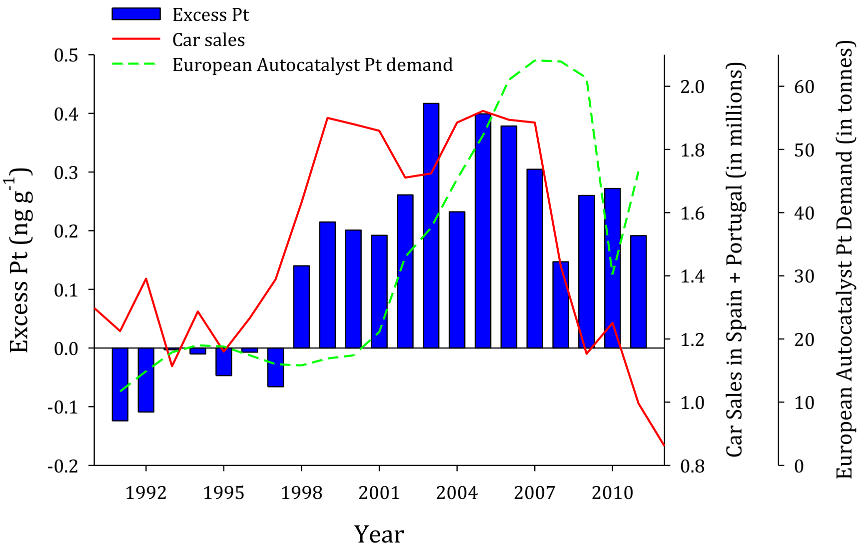
observed in previous exposure studies (e.g. Zimmermann et al., 2005; Sures and Zimmermann, 2007); however, bioaccumulation factors derived by the latter yielded systematically lower values. For example, Sures and Zimmermann (2007) reported BFs ranging from 40 to 100 for the freshwater zebra mussel (*Dreissena polymorpha*) exposed to dissolved Pt added in the form of $PtCl_4$; similarly, Veltz et al. (1996) obtained a BF of 96 for the worm *Lumbriculus variegatus* exposed to $PtCl_6^{2-}$. For seawater organisms, Mulholland and Turner (2011) derived a BF of 300 for the macroalgae *Ulva lactuca* and 20–30 for the marine gastropod *Littorina littorea* exposed to Pt in the form of $PtCl_6^{2-}/PtCl_5^{-}$.

The higher accumulation factor obtained in this study compared to exposure experiments may be explained by (i) the low incubation periods — generally from few days to one month — used in exposure studies which may underestimate the bioaccumulation due to non-equilibrium conditions (Veltz et al., 1996), and (ii) the uptake of suspended particles containing elevated Pt concentrations in real ambient conditions; accordingly, in coastal areas subject to urban pressure, whereas dissolved Pt may be similar or only slightly higher than uncontaminated waters, Pt concentrations in suspended matter may greatly exceed typical background values due to the input of strongly-bound Pt-rich particles from catalytic converters (Cobelo-García et al., 2013).

Compared to other trace metals, the BF obtained in this study for Pt ($\sim 5 \cdot 10^3$) is significantly lower. For example, using the metal concentrations in the same mussels samples from the Vigo Ria reported earlier (Besada et al., 2014) and the typical dissolved metal concentrations in this basin (Santos-Echeandía et al., 2009), BFs around 1–2 orders of magnitude higher are obtained for Zn ($BF \sim 5 \cdot 10^5$), Cu ($BF \sim 2 \cdot 10^4$), Pb ($BF \sim 9 \cdot 10^4$) or Cd ($BF \sim 1 \cdot 10^5$)

4. Conclusions

The present study reports, for the first time, the temporal variation of Pt concentrations in aquatic organisms and shows evidence of the link of the observed increased levels in the recent years with the use of this metal in anthropogenic activities (i.e. catalytic converters in motor vehicles). This is especially relevant since the potential health risk from exposures to Pt is greater than once thought (Wiseman and Zereini, 2009) and, therefore, increasing Pt concentrations may lead in the future to toxic effects on living organisms. These results point the need for more field studies on the accumulation of Pt in organisms subject to traffic-borne contamination, as well as including other elements also used in automobile catalytic converters, i.e., Rh and, especially, Pd since it has shown a higher degree of mobilization from



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particles emitted by catalytic converters than Pt or Rh (Dahlheimer et al., 2007).

Acknowledgements

The authors would like to thank the technical staff of the Chemical Pollution Laboratory of the Centro Oceanográfico de Vigo (Instituto Español de Oceanografía), for their cooperation during sampling and sample preparation in particular to Fernando Schultze for participating in the analytical work, as well as Susana Calvo (IIM-CSIC) for technical assistance during analysis. The C.S.I.C., under the program JAE-Doc (*Junta para la Ampliación de Estudios*) co-funded by the *Fondo Social Europeo* (FSE), is greatly acknowledged for the post-doctoral contract to J. Santos-Echeandía.

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