



SIQUIMAR

XIX SEMINARIO IBÉRICO DE QUÍMICA MARINA

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VI INTERNATIONAL SYMPOSIUM ON MARINE SCIENCES 2018

Universidade de Vigo



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**DYNAMICS OF PARTICLE FLUXES OFF NORTHWESTERN
AFRICA:
INFLUENCE OF ATMOSPHERIC DUST AND EFFECT OF
LATERAL TRANSPORT**

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Abstract

Eastern Boundary Upwelling Ecosystems (EBUEs) cover only about 1% of the total ocean area but contribute with about 15% of the total marine primary production (Carr, 2002). Roughly, 20% of the marine global fish catch is provided by the four major EBUEs: the Canary, the Benguela, the Californian and the Humboldt Current Systems (Freon et al., 2009). EBUEs may be responsible for >40% of the carbon sequestration in the ocean (Muller-Karger et al., 2005) and are thus relevant for the global carbon cycle. The Canary EBUE along the Northwestern African margin extends approximately between 12° and 35°N and is affected by diverse factors (trade winds, chlorophyll filament, nutrient availability, lateral advection). These factors influence the productivity in surface waters in different ways, depending on the intensity of each factor and each particular area along margin.

This conference will address the seasonal and multiannual variability of particles fluxes dynamics, with particular focus on the Mauritanian upwelling. In this coastal area, the University of Bremen maintains a continuous monitoring program of particle dynamics using moorings since 1988. Our observations reveal strong interannual fluctuations, superimposed on a decadal fluctuation pattern. Distinct dust outbreaks and deposition in winter enhances particle sedimentation and carbon export on short timescales via the ballasting effect. Episodic perturbations of the marine carbon cycle by dust outbreaks might have weakened the relationships between fluxes and large-scale climatic oscillations. A significant amount of diatoms, biogenic silica (opal) and organic carbon produced in waters overlying the Mauritanian shelf is effectively transported in intermediate waters at the outer slope. The impact of the intermediate and bottom-near nepheloid layers-driven transport in the transfer of valves and bulk particulates and its potential contribution to the export of biogenic materials from the shelf and uppermost slope might play a significant role in hemipelagial fluxes off Mauritania.

Key words: coastal upwelling, diatoms, nepheloid layers, NW Africa, particle fluxes.

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CONFERENCIA PLENARIA

MONITORING COASTAL WATER QUALITY

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Abstract: Coastal environments are vulnerable ecosystems providing a variety of unique services. However, coastal water bodies, including transition waters and the coastal ocean, also face increasing pressure due to worldwide demographic trends and industrial development. Nutrient and contaminant inputs from continental sources may undergo rapid changes and their superposition with other environmental stressors (e.g. temperature, pH, parasites, etc.) may cause adverse effects on coastal ecosystem health and productivity. Water quality monitoring is part of the ecological status assessment of transition waters and the coastal ocean, supported by regulations such as the European Water Framework Directive and the Marine Strategy Framework Directive. Monitoring efficiency, related understanding of biogeochemical cycles and risk assessment depends on various factors, such as analytical limitations, observation strategies, regulation, etc., leaving room for improvement and challenging perspectives, not only for emerging contaminants. Perspectives of using examples of traditional monitoring tools and such recently under development, as well their combination with different approaches, including exposure experiments, are addressed.

CONFERENCIA PLENARIA

OCEAN REANALYSIS FOR THE STUDY OF THE EVOLUTION OF THE STATE OF THE OCEAN OVER THE LAST DECADES

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Abstract: Assessing the role of the ocean and sea ice on climate variability is critical for understanding global climate change. The oceans have the largest heat capacity in the climate system, and ocean circulation redistributes this heat. Moreover, variability in ocean circulation determines seasonal to decadal variability in climate. Ocean synthesis products are extensively used for this purpose. Ocean syntheses are comprehensive estimations of the ocean state over the last decades (mainly temperature, salinity, sea level and currents) calculated by merging hydrodynamic ocean models and all available observations using data assimilation. Ocean syntheses are used as initial conditions for operational estimations of the ocean state, for short-term predictions aiming at studying specific processes, for seasonal and decadal predictions, and for climate-related activities. They can be also used to estimate the interaction between the ocean and the atmosphere, needed to assess the role of the ocean in the heat balance of the Earth and its influence in the global water cycle. Ocean syntheses are necessary to compute transports across ocean basins and key straits, in order to understand how heat is transported across the ocean.

The COST Action “Evaluation of Ocean Syntheses” (EOS) is an initiative aiming at promoting the use of ocean syntheses and reanalyses among the scientific community, by raising awareness of these products and promoting their use. A series of networks have been created to inter-compare several ocean syntheses in different regions, with the aim of providing a well-documented quality assessment on the various products that will allow the end user to choose the ocean synthesis that is more appropriate for their intended use. After an introduction to ocean syntheses, the main advancements achieved through the COST Action EOS and the main conclusions reached will be presented to the audience.

CONFERENCIA PLENARIA

**"THE SECRET LIFE OF DIATOMS: FASCINATING QUESTIONS
FROM UNICELLULAR MICROALGAE"**

Marina Montresor

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Abstract: Diatoms, as many unicellular eukaryotes, have life histories that include different phases: a growth phase in which they divide and increase their numbers, a resting phase in which they can withstand adverse environmental conditions, a sexual phase in which genetic recombination occurs. Diatom cells progressively decrease in size following cell division and large cells are produced during the sexual cycle, thus counteracting the miniaturization process.

I will illustrate examples of research on diatom life histories including observations at the Long Term Ecological Research site in the Gulf of Naples, experimental investigations carried out in the laboratory and molecular studies aimed at detecting the molecular mechanisms regulating diatom sexual phase. I will outline the implications that different aspects of life histories have for population dynamics and micro-evolution of this group of microalgae.

CONFERENCIA PLENARIA

**RIA DE VIGO: WHEN THE ATLANTIC KNOCKS ON YOUR
DOOR**

Ricardo Torres

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Abstract: The Ria de Vigo is one of the four semi-enclosed and elongated bays of the Rias Baixas system situated at the northern limit of the Iberian-Canary Current Eastern Boundary Upwelling Ecosystem. The Ria de Vigo has one of the most important mariculture industries in Europe and a rich history of oceanographic research spanning the last seven decades. In this talk I will review how our understanding of the circulation of the Ria de Vigo has evolved, from the pioneering work in the 50s through to the 80s from such scientists like Fernando Fraga and Ramon Margalef to the subsequent substantial contributions of Ricardo Prego, Francisco Figueiras, Xose Alvarez-Salgado, Fiz Perez and today's efforts led by Gabriel Roson, Miguel Gilcoto and Eric Desmond Barton and of course many others. The talk will trace the evolution over the years of our understanding of how Atlantic wind patterns and the circulation on the adjacent shelf (namely upwelling and downwelling events) shape the circulation inside the Ria.

CONFERENCIA PLENARIA

LA ISLA DE COCO Y LA IMPORTANCIA DE SER PATRIMONIO NATURAL DE LA HUMANIDAD

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Abstract: La Isla del Coco, Costa Rica, está ubicada a 500 km de la costa en el Pacífico Tropical Oriental (PTO). Es una isla oceánica con un alto endemismo terrestre (~35%) y una alta diversidad marina (más de 1700 especies). Se diferencia de otras islas oceánicas del PTO por ser muy húmeda y estar cubierta de vegetación, es por eso que ha sido visitada y estudiada desde el Siglo XVI. A finales del Siglo XIX un gran número de expediciones empiezan a desarrollar investigaciones en el Isla y se ha generado gran cantidad de información, sin embargo, se continúa descubriendo nuevas especies. Geopolíticamente es muy importante para Costa Rica ya que le genera más del 50% de su mar patrimonial. La Isla del Coco fue declarada Parque Nacional en 1978, Patrimonio Natural de la Humanidad de la UNESCO en 1997 y Humedal de Importancia Internacional Ramsar en 1998. La Isla del Coco se ha llamado la Isla del Tesoro, porque hay leyendas de varios tesoros enterrados allí, siendo el más grande el Tesoro de Lima. El Parque Nacional Isla del Coco (PNIC) es de los sitios mejor protegidos, sin embargo, sufre el embate de la pesca ilegal y anteriormente el de la búsqueda de tesoros. Con la declaratoria del PNIC como Patrimonio de la Humanidad se detuvo totalmente todo intento de búsqueda del tesoro. Esta declaratoria también ha servido internacionalmente para resaltar la importancia del PNIC en el PTO y a nivel mundial como uno de los últimos refugios de grandes pelágicos (tiburones, atunes, picudos, entre otros). Además, la destaca como un sitio especial, principalmente para el turismo de buceo. Localmente, la declaratoria de Patrimonio de la Humanidad, ha servido para aumentar la conciencia sobre la importancia de ambientes naturales bien protegidos y ha generado interés nacional por su conservación, principalmente marina.

Key words: Isla de Coco, Patrimonio Natural, UNESCO



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DYNAMIC OF GREENHOUSE GASES (CO₂, CH₄, AND N₂O) ALONG THREE ESTUARIES OF THE SOUTHERN IBERIAN ATLANTIC BASIN

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Abstract: Estuaries are highly dynamic and complex coastal ecosystems, which usually act as a source of greenhouse gases to the atmosphere. In order to have a better knowledge of these systems, the partial pressure of CO₂ (pCO₂) and the concentration of dissolved CH₄ and N₂O have been studied along the salinity gradient and in relation with the tides in three estuaries of the southern Iberian Atlantic basin: Guadalquivir, Tinto-Odiel and Guadiana. Samples were taken in July 2017 on board the B/O UCADIZ.

In general, in the three systems there is an increase in the concentration of gases toward the inner part of the river, which highlights the importance of the fluvial entry of greenhouse gases into the estuary, as occurs in many other estuarine systems (Harley et al., 2015, Teodoru et al., 2015, Burgos et al., 2017). The pCO₂, and the dissolved CH₄ and N₂O show the highest values and intervals of variation in the Guadalquivir (pCO₂: 504-2940 µatm, CH₄: 4.9-441.9 nM, N₂O: 7.2-101.6 nM) followed by Guadiana (pCO₂: 485-1401 µatm, CH₄: 9.3-287.9 nM, N₂O: 6.5-9.1 nM) and Tinto and Odiel (pCO₂: 513-1144 µatm, CH₄: 8.0-194.3 nM, N₂O: 6.0-7.3 nM). The three systems are oversaturated with CO₂, CH₄ and N₂O, as a consequence they act as a source of these greenhouse gases to the atmosphere, reaching the maximum saturation percentages of CH₄ and N₂O in the Guadalquivir, 18493% and 1376% respectively and ΔpCO₂ (pCO_{2water} – pCO_{2atmosphere}) show a maximum value of 2531 µatm in the same estuary.

pCO₂ and the concentrations of CH₄ and N₂O showed daily variations coupled to the tidal cycles in the three systems, being more evident in the Guadalquivir estuary. The highest concentrations were measured during ebb, which suggest that the systems export CO₂, CH₄ and N₂O to the Gulf of Cádiz.

Key words: greenhouse gases, estuaries, Southern Iberian Atlantic basin, pCO₂, CH₄, N₂O.

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GLOBAL ASSESMENT OF SEAWATER CO₂ DATA WITH EMPHASIS ON PH

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Abstract: Ocean acidification (OA) is one of the side effects derived from the global experiment accomplished by humankind since the industrial revolution, and associated with the service provided by the oceans, the uptake and storage of anthropogenic carbon from the atmosphere, which contributes to mitigate global warming. OA is equivalent to an alteration of seawater CO₂ equilibriums: Total Alkalinity (TA) remains constant while Dissolved Inorganic Carbon (DIC) increases, ion carbonate decreases and bicarbonate increases as does the protons concentration (pH decrease). Quantifying those changes is supposed to be easy-piece, solved with long-term sustained time series for CO₂ variables in sensitive areas in the open and coastal ocean. This is far from being true. Methodological challenges (mainly related to spectrophotometric pH) and gaps in our knowledge of the seawater CO₂ system are still hampering an efficient and referenced global network on OA observations based on commonly assessed and agreed methodologies. A selection of double checked cruises from the best to our knowledge global data product for water column CO₂ data and ancillary variables GLODAPv2 (Group 1) is selected to perform an internal consistency analysis. More recent GO-SHIP repeat hydrographic cruises (Group 2) are also included in this analysis. The main difference between both groups of data affects pH: Group 1 contains manual methods for spectrophotometric pH using unpurified m-cresol and Group 2 automated methods using purified m-cresol. In addition to the internal consistency analysis we quantified uncertainties in derived CO₂ variables from different input pairs plus K1 & K2 constants. We detect non-random biases in the residuals (measured minus calculated) variables which point to unresolved issues in the methods and consistency of CO₂ calculations in seawater.

Key words: seawater CO₂ variables, internal consistency, pH methods.

Acknowledgments: MEDSHIP18 structural IEO project

BAND NEW WATER COLUMN MEASUREMENTS OF CO₂ IN THE MEDITERRANEAN SEA, MSM72, MARCH 2018

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Abstract: The Mediterranean Sea (MedSea) is considered a laboratory basin where open ocean processes occur on spatial and temporal scales much shorter, and therefore are supposed to be easily monitored, detected and quantified. In this sense the MedSea is supposed to be already affected by anthropogenic carbon uptake and associated ocean acidification, it is prone to absorb anthropogenic carbon from the atmosphere and store it at depth (low Revelle factor and relevant overturning circulation). Despite this, basin-wide water column CO₂ measurements are scarce (CIESM, 2012) and consequently the oceanographic community on border countries around the MedSea committed to design and sustain a program, MedSHIP, to monitor hydrographic, biogeochemical and transient tracers conditions at shorter spatial and temporal scales, in order to observe and quantify long-term changes in this mini-ocean (Schroeder et al., 2015). The first hydrographic sampling for MedSHIP was done on board RV Meteor in April 2011 (Álvarez et al., 2014). Seven years after we present the repetition of this hydrographic cruise. The INOrganic Chemical oceanography (INOCEN) group was responsible for the water column CO₂ measurements on board RV Maria S Merian (IP Dagmar Hainbucher, Univ. Hamburg), cruise MSM72, March 2018 (Heraklion-Cádiz). We present brand new pH, Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA) and ion carbonate (CO₃²⁻) data from this cruise. An effort has been done to improve the intercomparability of pH with purified and unpurified m-cresol purple. We will check the internal consistency among CO₂ variables and as a first attempt, compare our 2018 data with the 2011 cruise.

Key words: Mediterranean Sea, CO₂ variables, temporal change, internal consistency.

Acknowledgments: MEDSHIP18 structural IEO project

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EFFECT OF GLOBAL CHANGE ON THE ACCUMULATION OF TRACE ELEMENTS IN MARINE MUSSELS

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Abstract: In the current context of global change, the proposed future oceanic scenarios include acidification, warming, and changes in oxygen content, salinity and T°. The CO₂ concentration, which contributes to all these changes, is expected to rise above 1100 ppm by the end of this century (IPCC, 2013), which means an increase of 300% of the current content. This climate-related increase would largely modify the vulnerability of human and natural systems, including their ability to adapt. Metal bioavailability greatly depends on its speciation, which is related to multiple factors such as water pH, carbonate concentration or temperature, and therefore is sensitive to the global change scenario. In this context, studies concerning how climate factors may affect metal bioavailability and thus toxicity to organisms are gaining more interest (Stahl et al., 2013), and is essential for the future risk assessment of metal-pollution. Mussels are extensively used as a particular good target group for monitoring environmental conditions in coastal ecosystems (Sureda et al., 2018). Additionally, recent studies have revealed that bivalves may also be negatively affected by high expositions of CO₂ (Babarro et al., 2018). In the present study, aggregations of *M. galloprovincialis* (18 individuals) were exposed in mesocosm tanks with 3 different levels of CO₂: 400, 800 and 1200 ppm under controlled conditions and constant water removal during 3-weeks period. After exposure, mussel soft tissue, foot and byssus, were sampled and metal content were determined by ICP-MS. Results will try to identify if metal accumulation will be affected by the increase of CO₂ content in water.

Key words: bioaccumulation, metal availability, global change, coastal systems

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HIGH RESOLUTION CO₂ MEASUREMENTS OVER COLD WATER CORALS FOLLOWING THE MEDITERRANEAN SEA WATER PATH IN THE NORTH ATLANTIC

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Abstract: Cold Water Corals (CWC) are supposed to be conditioned by biogeochemical conditions in the water column just above them, especially with regard to CO₂ chemistry. The EU ATLAS project was designed to address the interconnectivity between CWC in the Mediterranean Sea and those communities found in the adjacent Eastern North Atlantic (ENA) Ocean. In this sense, the MEDWAVES cruise on board RV Sarmiento de Gamboa in September 2016, particularly sampled CWC found over seamounts inside the Mediterranean Sea and outside in the ENA, following the Mediterranean Sea Water signal. High resolution biogeochemical data with emphasis on CO₂ variables was sampled in the near bottom. We compare this data set with available high quality GLODAPv2 data to check if particular conditions are found over those areas conditioning the CWC distribution. The sensitivity of those areas will be assessed using buffer factors discerning the effect on CO₂ chemical conditions (pH, ion carbonate concentration and aragonite and calcite saturation) due to changes in inorganic carbon at constant alkalinity, this is, the uptake of anthropogenic carbon, causing ocean acidification.

Key words: Mediterranean Sea Water, CO₂ variables, high resolution, cold water corals.

Acknowledgments: ATLAS UE project, MEDWAVES physics team, Captain and crew BO Sarmiento de Gamboa.

SERIES TEMPORALES DE PH EN LAS RÍAS DE VIGO Y AROUSA: LA INTELIGENCIA ARTIFICIAL EN LA GENERACIÓN DE NUEVOS DATOS

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Abstract: Las Rías Gallegas son un ecosistema de gran variabilidad fisicoquímica. La contribución a la economía local de las pesquerías localizadas en ellas hace necesario enfrentarse a esta variabilidad para desentrañar las condiciones a las que se ven sometidas. El pH del agua de mar es una variable influyente en los organismos del ecosistema y por ende en la estabilidad de éste. Este trabajo pretende mostrar y evaluar el ciclo estacional del pH. Para ello, se diseñó una red neuronal que fue entrenada con datos oceanográficos de las Rías Baixas adquiridos entre 1976 y 2018. El error de la red fue de ~0.025 unidades de pH. La relación obtenida a través de ésta entre los predictores utilizados (posición, variables hidrográficas, biogeoquímicas y temporales) y el pH se utilizó para generar nuevos datos sobre la red de muestreos de INTECMAR. El set seleccionado de esta base de datos abarca medidas semanales de los predictores utilizados en la red desde 2006 hasta 2017 en las rías de Vigo y Arousa. De esta forma se han obtenido series temporales de pH localizadas en 17 estaciones con tres profundidades (2.5m, 7.5m y 12.5m). El ciclo estacional se evidencia de forma clara en todas ellas. El rango anual medio se sitúa entre 0.2 y 0.3 unidades de pH. Estos valores muestran la gran variabilidad a la que se someten los organismos costeros respecto a los oceánicos (~0.05 unidades; Bates et al., 2014). La disponibilidad de estas series temporales pretende contribuir a mejorar los estudios relacionados con la variabilidad natural del pH. La futura extensión temporal de las mediciones de INTECMAR y la potencialidad de las redes neuronales podría dar lugar a la extracción de la tendencia antropogénica del pH en este sistema de gran variabilidad natural y ser utilizada en evaluaciones relacionadas con el cambio climático.

Key words: Variabilidad del pH, Series Temporales, Rías Baixas, Redes Neuronales

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THE MARINE STRATEGY FRAMEWORK DIRECTIVE: UNATTAINABLE GOAL FOR TRACE METALS

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Abstract: Trace metals are relatively enriched in the Earth's crust, however their concentrations are very low in the sea, mainly because of their low solubility and effective biological and chemical removal from the water column. Nowadays, it is scientifically recognized that any study in the marine environment that involves the analysis of metals requires water sampled under strict clean protocols. Thus, with appropriated sampling devices (e.g. towed sampling devices or metal-free sampling rosettes) we can obtain a representative sample of the water compartment ensuring precise and accurate results even with the most low-level trace elements. In 2008, the EU established the Marine Strategy Framework Directive (MSFD; Directive 2008/56/EC) with the objective to protect more effectively the marine environment across Europe and to achieve Good Environmental Status of marine waters by 2020 (1). This directive introduces the obligation to the Members States of develop marine strategies, including monitoring programmes, to maintain biodiversity and preserving diversity and dynamism of oceans and seas. Through the Directives 2008/105/EC and 2013/39/EU the EU establish the environmental quality standards (EQS) of chemical substances with potential significant risk to the environment or to human health in surface coastal waters, and includes as priority elements the metals Cd, Pb, Hg, Ni. However, this Directive miss specifications regarding sampling techniques, which are essential to guarantee reliable result of metals in marine system and is producing that the data generated by different regions to be inaccurate and unhelpful.

Key words: Marine Strategy Framework Directive, Trace metals, Clean techniques

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RARE EARTH ELEMENTS IN THE MIRA RIVER-ESTUARY SEDIMENTS

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Abstract: The Mira River-estuary system located in southwestern of Portugal features an urbanized and agricultural catchment with no industrial influences. The river basin crosses the Iberian Pyrite Belt, a massive sulphide deposits, and is one of the few Portuguese rivers that flows in the Southeast-Northwest direction. The objective of this study was to evaluate the distribution of rare earth elements (REE) in the river-estuary sediments. Twenty-five surface sediment samples and a sediment core were collected from the estuary mouth to the upstream dam and analyzed for REE (Y and La to Lu) and major elements (Al, Fe and Mn). Yttrium and total REE concentrations (Σ REE) in sediments ranged between 1.8–17 mg kg⁻¹ and 9.9–182 mg kg⁻¹ being lower in the estuary mouth compared with upstream stations. The ratio of Light REEs (LREE) to Heavy REEs (HREE) was 12±2.2, where LREE represented about 92% of Σ REE. The PAAS (Post-Archean Australian Shale) normalized YREE content revealed two distinct fractionation patterns along the Mira River-estuary. An almost flat PAAS (Post-Archean Australian Shale) normalized profile with a positive Eu anomaly was found in medium to coarse-grained material from coastal origin. This Eu anomaly derived from the natural enrichment related to the drainage of mineralized areas composed mostly by feldspar minerals. Conversely, fine-grained sediments from the upstream of the river showed an enrichment of LREE over HREE, with $(La/Yb)_{PASS}=1.58\pm 0.44$. This profile shape was also found in the sediment core collected at the estuary mouth, with no statistical differences ($p>0.05$) in depth. Results indicate that REE can be used as a powerful tool for the study of the coupling mechanism between riverine, estuarine and coastal areas, either as a provenance tracer or as a signal of environmental change.

YTTRIUM AND RARE EARTH ELEMENTS FRACTIONATION IN SALT MARSH HALOPHYTE PLANTS FROM TAGUS ESTUARY (PORTUGAL)

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Abstract: The yttrium and rare earth elements (YREE) increased use has resulted in a large widespread in the aquatic environment, and particularly, in estuaries, where salt marshes act as natural deposits of different contaminants from industrial and urban wastes (Brito et al., 2018).

Halophyte plants, such as *Sarcocornia fruticosa* and *Spartina maritima*, known to sequester some metals in the rhizo-sediments, can accumulate at levels that may exceed those of surrounding environment (Caetano et al., 2008; Pedro et al., 2015). To the best of our knowledge, no data exist regard the YREE accumulation, distribution and fractionation in halophyte plants.

Yttrium and REE have been characterised neither as essential elements for life nor as strongly toxic elements in the environment (e.g. Hu et al., 2006; Tyler, 2004). Previous studies found no correlation between YREE contents in plants and rhizo-sediment, but data on its fractionation mechanisms in plant organs is still scarce (Liang et al., 2008; Wytttenbach et al., 1998).

The aim of this work was to study the YREE accumulation, fractionation and transference from sediments to *S. fruticosa* and *S. maritima*, the translocation from roots to the aboveground plant organs and its fractionation in the plant organs. The study was carried out at the Rosário salt marsh, in the Tagus Estuary (SW Europe), using the ICP-MS analytical technique to quantify YREE contents.

Results showed slight REE enrichment in both colonised sediments, suggesting an influence in sediment REE availability promoted by roots activities, but no significant differences in Y contents were found. Different roots YREE fractionation patterns were observed compared to the sediments but no significant accumulation of YREE was measured in the

belowground organs. Contents of YREE in the aboveground organs were significantly lower compared to the roots, suggesting low YREE translocation to aboveground plant organs.

Key words: yttrium, rare earth elements, fractionation, salt marshes, halophytes

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HISTORICAL RECORD OF PLATINUM-GROUP ELEMENTS IN INDUSTRIALISED SEDIMENTS FROM TAGUS ESTUARY

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Abstract: The presence of platinum-group elements (PGE) in the environment has been attributed to anthropogenic emissions over the past decades, mainly deriving from automotive catalytic converters (ACC). However, other sources may contribute significantly to the increase of PGE in aquatic systems, such as industrial activities, medicinal uses and jewellery. With the known historical record of industrial activities in Tagus estuary, described for other contaminants (e.g. Hg), we hypothesised that sediments could contain the PGE signature imprinted. In this work, we used three sediment cores collected in 2010 in industrial areas of the Tagus: BRR, a dismantled area with an historical industrial variety of activities; CN, where presently operates a chemical-complex unit; and one core distant from the other areas, located in the Natural Reserve. In addition, different samples from industrial residues in the southern bank of the Tagus estuary were also analysed. Samples were acid-digested and analysed by AdCSV and ICP-MS.

The highest PGE concentrations were found in the deeper sediments. These results evidence the clear signature from the historical industrial activities that occurred previously to the implementation of ACC in the early 1990s. Relatively high PGE concentrations were also found in the industrial residue samples, supporting the same industrial source. This work significantly contributes the current and limited knowledge of PGE resulting from industrial sources.

Key words: PGE, industrial activities, historical contamination

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EVOLUTION OF METAL CONCENTRATIONS IN THE GULF OF CÁDIZ IN THE LAST YEARS: IMPACT OF MINING ACTIVITIES

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The Estuary of Huelva is strongly affected by acid mine drainage (AMD) caused by historical mining in the Iberian Pyrite Belt (IPB). The Tinto and Odiel rivers drain the IPB, collecting numerous mine effluents, thus, both rivers transport a huge amount of metals to the estuary (e.g. around 7900 t/yr of Fe, 5800 t/yr of Al, 3500 t/yr of Zn, 1700 t/yr of Cu and 1600 t/yr of Mn [1]). Although these metals are strongly removed from solution during estuarine mixing processes and retained in sediments, a fraction of the most mobile elements crosses the estuary, reaching the Gulf of Cádiz and even the Strait of Gibraltar [2]. This study reviews and compares the results obtained by different historical and recent samplings performed in this area to trace the fate of the metals and their content along the Gulf of Cádiz. The flood events associated with rainy periods play a key role in the metal transport in semiarid and mineralized catchments as the Tinto and Odiel watersheds due to the washout of evaporitic sulfate salts. Thus, the more intense and frequent floods induced by climate change could be changing the metal transport patterns and leading to an increase of metal concentrations in oceanic waters. Furthermore, potential accidental mine spills may also lead to the occurrence of acute metal contamination episodes, giving rise to short-term increasing levels of metals in the Gulf of Cádiz.

Key words: Acid Mine Drainage (AMD), Estuary, Toxic elements, chronic pollution.

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CONTAMINACIÓN POR ELEMENTOS TRAZA EN LA RÍA GALLEGA DE MUROS. INFLUENCIA DE LA MINERÍA DE W-Sn

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Resumen: La ría de Muros es la más septentrional de las Rías Bajas gallegas situadas en el noroeste de la península Ibérica. Esta ría, sistema frontera tierra-océano con una superficie de 125 km², se halla bajo la influencia del afloramiento costero estacional de Galicia y el caudaloso río Tambre (54 m³·s⁻¹). En la cabecera de la ría se encuentra el Complejo geológico de Noia, que es rico en minerales como casiterita, volframita, pirita, calcopirita y arsenopirita (IGME, 1982). En esa zona, a 11 km del mar, está situada la mina de San Fins que extrajo Cu, Sn y W en diferentes períodos de explotación hasta su cierre en la década de los 80 del pasado siglo. En el entorno abandonado de la mina se detectaron niveles fitotóxicos de Cu y Zn (Alvarez et al., 2003). Durante el siglo XX el conocimiento sobre metales en el sedimento de esa ría era muy escaso (Prego y Cobelo, 2003). Posteriormente, dos testigos de sedimento señalaron altos contenidos de Cu, Pb y Zn desde el medioevo que asociaron a actividades portuarias en la villa de Muros (Andrade et al., 2014), algo común actualmente (García et al., 2013). Sn y W son considerados materiales estratégicos para la U.E., que insta a sus países miembros través del horizonte 2020 para que aumenten la producción de sus minas, que se localizan en España, Portugal y Austria. Es conveniente conocer la presencia de elementos traza en la ría a fin de conocer su contaminación y disponer de referencias cara a eventos posteriores.

Al, As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sn, W and Zn (por AAS y ICP-MS). PIC, POC, PON, PS (por Análisis Elemental)

the abstract should be 300 words at most in one page. It should succinctly summarize the purpose of the paper, the methods used, the major results, and conclusions

Palabras clave: Contaminación, Sedimento, Mina, Ría

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MEDIDA DE LA REGENERACIÓN BENTÓNICA DE NUTRIENTES EN SISTEMAS COSTEROS SOMETIDOS A LA ACCIÓN DE LAS MAREAS: USO DE CÁMARAS BENTÓNICAS VS INCUBACIÓN DE CORES

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Abstract: la cuantificación de la regeneración bentónica de nutrientes ocupa desde hace tiempo un lugar relevante en el estudio de los sistemas costeros debido, sobre todo, a la importancia que tiene su contribución al mantenimiento de la productividad primaria de esas zonas. A lo largo de las últimas décadas se han desarrollado diferentes procedimientos y se han mejorado las técnicas para la cuantificación de la velocidad del proceso de transferencia de materia entre el sedimento y la columna de agua basadas, principalmente, en la medida directa de sus efectos: el aumento de la concentración de nutrientes en la lámina de agua sobrenadante al sedimento.

De toda ellas, dos son las que han alcanzado una mayor aceptación por los investigadores que estudian este tema: el uso de cámaras bentónicas y la incubación en el laboratorio de testigos de sedimento. En ambos casos, se admite que la medida de la regeneración de nutrientes afecta al propio proceso de transferencia de materia a través de la interfase agua-sedimento y, por ello, se han elaborado modelos que permiten el cálculo de la regeneración en el único instante en el que aún no se ha alterado el proceso que se desea medir; esto es, justo en el instante en el que se inicia la medida del flujo bentónico y por tanto todavía no se ha producido una perturbación en el sistema en estudio por el uso de los sistemas de medida). Los dos procedimientos indicados presentan ventajas e inconvenientes y aunque es una opinión generalizada que el primero de ellos es el que ofrece mejores resultados, esto no es necesariamente siempre así.

En este trabajo se presenta una comparación general de ambos métodos y se analizan las posibilidades y las limitaciones que presentan ambos cuando se estudian sistemas costeros sujetos a la acción de las mareas y, con ello, sometidos a fuertes variaciones en los valores de la concentración de nutrientes en sus aguas. Esta discusión es ampliable a todos los procesos que impliquen una transferencia de materia a través de la interfase agua-sedimento.

Key words: regeneración bentónica, nutrientes, sedimentos, zona costeras, mareas

SEDIMENT BIOGEOCHEMISTRY AND VARIABILITY OF CH₄ IN MUD VOLCANOES OF THE GULF OF CADIZ

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Abstract:

Samplings of sediment cores were realised with a gravity core in three mud volcanoes (Anastasya, Pipoca and San Petersburgo) of the Gulf of Cadiz, during two cruises in June and December 2016 on board the R/V's Angeles Alvariño and Ramon Margalef. In the sediment has been determined the vertical variation of porosity and content of C, N, S and CH₄ and, on the other hand, in the pore water, CID, COD, nutrients and majority elements concentrations have been defined to different depths. The observed variations in the vertical profiles of the species analysed in the sediment and pore water have been associated with the own existence of diagenetic processes of the organic matter (Emerson et al., 1980, Morel and Hering, 1993). In turn, diffusive fluxes were determined in the surface area of the sediments, although changes in the concentration gradients at intermediate depths have been observed, which suggest variations in the transport mechanisms of the volcanic flow and/or the irrigation of the benthic macrofauna associated to the mud volcanoes (e.g. Mau et al., 2006). The CH₄ concentrations analysed in the sediment for Anastasya (0.5 - 115.3 μM) and San Petersburgo (0.03 - 126.1 μM) were much higher than for Pipoca (0.03 - 0.8 nM), what it could be associated with a certain volcanic activity in these volcanoes. In addition, the CH₄ concentration in the water column above the volcanoes has studied also; it showed a behaviour practically constant, except for Anastasya with concentrations of 120 nM in the bottom water. Finally, it has estimated that this area acts as a source of CH₄ to the atmosphere, with fluxes contain between 15.2 and 33.8 μmol m⁻² d⁻¹, similar to other zones affected by submarine volcanism (Jayakumar et al., 2001; Amouroux et al., 2002).

Key words: Gulf of Cadiz, mud volcano, sediment, pore water, methane

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MOLECULAR FINGERPRINTING OF DISSOLVED ORGANIC MATTER USING PYROLYSIS-GC-MS

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Abstract: The amount of organic carbon dissolved in the oceans represents one of the largest reservoirs of organic carbon in the biosphere (Perdue and Benner 2009). Furthermore, the diversity of molecules, estimated in tens to hundred thousands (Dittmar 2015), leads to individual compound concentrations in the picomolar range. The difficulty of isolating sufficient sample material from these low individual concentrations in a matrix with 34-38 g L⁻¹ of salts and the current methodological limitations makes disentangling the molecular composition of marine dissolved organic matter (DOM) particularly challenging (Repeta 2015). Pyrolytic degradation of ultrafiltered DOM (UDOM; >1000 Da) into gas chromatography amenable fragments (Py-GC-MS) constitutes an alternative approach to decipher DOM molecular fingerprint, and in particular the high molecular weight (>2000 Da) fraction, which is, nowadays, not among the analytical tools considered for characterization of marine DOM. Aiming to understand the major sources of DOM from the Iberian margin we focus on the NW coast, creating a unique sample set including DOM from seawater (depth range of 40-5000 m), rainwater, sediment porewater and riverine water. Py-GC-MS data suggest that the marine DOM has a large proportion of N-containing structures, which has been argued (based on presence of propionamide) to originate predominantly from peptidoglycan in bacterial cell walls, which is in concert with the very low C/N ratio (well below 15) of the UDOM. Black carbon (BC) also appears to be a large source of the DOM and increases with increasing depth of the water masses analyzed. In rivers BC is abundant, probably a product of charcoal from wild fires. Phenols' relatively large abundance in the fluvial samples may indicate that they originate predominantly from lignin or proteinaceous DOM. These samples also display a strong signature of algae, possibly from accumulation of aquatic primary biomass in upstream reservoirs, and minor terrestrial plant signature.

Key words: marine DOM, molecular fingerprinting, pyrolysis-GC-MS, peptidoglycan, black carbon.

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SEASONAL DISTRIBUTION OF DISSOLVED ORGANIC MATTER IN THE GULF OF CADIZ

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Abstract: The Gulf of Cádiz (GC) is a semi-enclosed basin that connects the North Atlantic Ocean and the Mediterranean Sea playing a key role in the exchange of organic matter between the two basins through the Strait of Gibraltar. Moreover, four rivers, with different organic matter quality, flow into this basin discharging large amounts of freshwater to the Atlantic Ocean (González-Ortegón et al. 2018). On the other hand, chlorophyll levels followed a seasonal pattern with highest concentrations at coastal zone during spring (González-García et al. 2018). In the GC, vertical and seasonal dynamics of dissolved organic matter (DOM) were assessed using optical properties during four oceanographic cruises. Fluorescence DOM (FDOM) was analyzed combining emission-excitation matrixes and multivariate parallel factor analysis (PARAFAC, Murphy et al. 2013, 2014). Five widely distributed PARAFAC components/fluorophores were identified; a marine humic-like, two terrestrial humic-like and two protein-like that resembles the amino acids tryptophan and tyrosine. Seasonal differences were observed in FDOM components indicating changes in the DOM quality and source. During summer, the fluorophore tryptophan-like accounted for almost 80% of the total FDOM pool. On the other hand, humic-like compounds dominated the FDOM pool in autumn and winter. Marine humic-like substances made 30-40% of total fluorescence and terrestrial humic-like compounds accounted for ~50%. Source and sinks of FDOM giving rise to the observed seasonal distribution will be discussed.

Key words: FDOM, PARAFAC, Gulf of Cadiz, seasonal patterns.

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NEODYMIUM ISOTOPES IN SEAWATER: THE GEOTRACES ERA

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Abstract: Neodymium ($^{143}\text{Nd}/^{144}\text{Nd}$) isotopes measured in seawater are increasingly recognized as an ocean circulation and paleocirculation tracer [1]. The international program GEOTRACES has played a central role by providing the opportunity to measure basin-scale hydrographic sections of this oceanographic tracer with unprecedented detail [2]. GEOTRACES also allows us to address more specific questions about the global Nd cycling in the ocean such as the impacts of “boundary exchange” near continental margins, water-particle interactions and hydrothermal vents, etc. [3]. We will present findings obtained by the LDEO group over the last 5 years about these issues.

For example, our results confirm first order “quasi-conservative” behavior of ϵNd along two north and south Atlantic GEOTRACES hydrographic sections in intermediate and deep waters. Local impacts on the seawater ϵNd are minor and confined to surface waters above the thermocline, and close to continental margins. Local inputs cause near surface deviations from conservative behavior, but they do not propagate to the intermediate or deep waters. Thus, our results confirm that Nd isotopes can be used with confidence as a tracer for deep water mass mixing and advection studies.

Key words: Neodymium, isotopes, tracer, GEOTRACES

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IRON COMPLEXATION BY PHENOLIC LIGANDS IN SEAWATER

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Abstract: Iron is an essential micronutrient for phytoplankton and can limit the primary production in the ocean. Fe chemistry is highly controlled by the interaction with organic complexes (> 99%). It is still unknown which organic compounds produced by cells have the ability to bind iron. Within the pool of organic ligands, polyphenols are known to be exudated by marine diatoms and, in this study, the role of three of them ((±) – catechin, sinapic acid and gallic acid) was studied in terms of dissolved Fe complexation via kinetic and titration approaches, and also as a source of Fe(II) in seawater. The results demonstrated that these three polyphenols are weak L₄-type Fe-binding ligands according to the conditional stability constant, computed by using the kinetic approach ($\log K'_{FeL} = 8.86 - 9.2$), where the formation rate constant (k_f) was $3.14 \cdot 10^5 - 4.17 \cdot 10^5 \text{ M}^{-1}\text{s}^{-1}$ and the dissociation rate constant (k_d) was $2.43 \cdot 10^{-4} - 4.4 \cdot 10^{-4} \text{ s}^{-1}$, with a 1:1 stoichiometry between Fe and the studied ligands. These studied ligands also regenerate Fe(II) in seawater from 0.05% to 11.92%. The results obtained in this study suggest that polyphenols increase the persistence of dissolved Fe and should be considered as key Fe-binding ligands in seawater to better understand the global biogeochemical cycles.

Key words: Fe-binding ligands, complexation, polyphenols, Fe(III), Fe(II)

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INTERACCIONES REDOX ENTRE EL HIERRO Y EL COBRE EN AGUA DE MAR: PROPUESTA DE UN MODELO CINÉTICO

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Abstract: En este trabajo se estudió la oxidación del Cu en presencia de Fe(II) o Fe(III) ($[Cu(I)]_0=100$ nM; $[Fe]_0=0-200$ nM). Con los resultados experimentales obtenidos en este trabajo relativos a la interacción Cu(I)-Fe(II) y Cu(I)-Fe(III) y los previamente publicados por González et al. 2016, relativos a la interacción entre el Cu(II) y el Fe(II) ($[Cu(II)]_0=100$ nM, $[Fe(II)]_0=0-200$ nM) bajo diferentes condiciones de concentración de oxígeno y H₂O₂, se ha elaborado un modelo cinético que describe simultáneamente la química redox del Fe y del Cu en agua de mar. De esta forma, el modelo cinético se puede comparar con una base sólida de datos experimentales que tiene en cuenta todas las posibles interacciones entre Fe y Cu en sus distintos estados de oxidación y proporciona un amplio campo de variables y resultados experimentales a los que da respuesta el modelo que proponemos. Los resultados experimentales mostraron que la oxidación de Cu(I) en condiciones de saturación de oxígeno depende linealmente de la concentración de Fe. Dicha dependencia consiste en una disminución de la velocidad de oxidación en presencia de Fe(II) y un aumento en presencia de Fe(III). El efecto del Fe(II) en la velocidad de oxidación del Cu(I) es mayor que el del Fe(III), con una pendiente que es un orden de magnitud superior. El modelo muestra que la descripción real de los procesos redox de ambos metales en agua de mar tiene que tener en cuenta tres aspectos fundamentales: a) competitividad de ambos metales por los intermedios de reacción; b) Reacciones redox directas entre el Fe y el Cu y c) Dado que las velocidades de oxidación del Cu(I) y del Fe(II) son diferentes a la velocidad de oxidación de cada uno de estos metales en ausencia del otro, en presencia de ambos metales se forman especies Fe-Cu que intervienen de forma directa en la oxidación de ambos metales.

Key words: Copper, Fe(II), Oxidation, Seawater

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THE REMOTE ORIGIN OF DISSOLVED LEAD IN THE WATER COLUMN OF THE GULF OF MEXICO

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Abstract: The surface waters of the North Atlantic Ocean have been the main sink for anthropogenic lead (Pb) emitted into the atmosphere during the last century and have, therefore, been subjected to intense monitoring^{1,2}. However, many oceanic regions and marginal seas, like the Gulf of Mexico (GoM), remain unexplored and little is known about their Pb concentrations and vertical distributions³. Results of dissolved Pb concentrations in the upper 1000 m of the GoM showed significant vertical gradients and scavenged-type profiles that decreased from 18.8 ± 4.3 pmol kg⁻¹ (10 m depth) to 8.2 ± 2.5 pmol kg⁻¹ (1000 m depth). These average concentrations are lower than those recently reported for the same depth range in the North Atlantic Ocean. Our analysis suggests that the surface maximum is due to direct atmospheric Pb depositions, mainly from North Africa dust plume, combined with the strong circulation prevalent in the ocean surface layer. However, intermediate and deep waters masses are barely influenced by these atmospheric depositions; and the magnitude of the dissolved Pb concentrations below 150 m depth is determined by the concentrations of the source water masses in their sites of origin and the scavenging along the flow path toward the GoM.

Key words: lead, lead isotopes, atmospheric depositions, Gulf of Mexico

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AN INTEGRATIVE STUDY ON THE EFFECTS OF RICE CROP WATER DYNAMICS OVER THE COMERCIAL BIVALVES COMMUNITY OF THE ALFACS BAY (NW MEDITERRANEAN)

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Abstract: Bivalves are worldwide sentinels of anthropogenic pollution. Mussel, *Mytilus galloprovincialis*, cockle, *Cerastoderma edule* and razor shell, *Solen marginatus* are species of high economic interest in the Iberian Peninsula and in the Ebro delta bays. In this area of high ecological importance, agriculture, fisheries and touristic activities coexist. Some of these anthropogenic activities (e.g. pesticide application for pest control) can negatively affect marine fauna, including shellfish production. Therefore, the goal of this work was to perform an integrative study identifying the main contaminants accumulated in these three species and their biological responses by using biomarkers of exposure to anthropogenic chemicals and any possible pathological incidences.

Bivalves from Alfacs bay were sampled in April, May, June and July 2017. Environmental and biological data including water temperature, salinity, oxygen and chlorophyll a were recorded. The sampling campaigns took place, two before the discharge of residual water from the rice fields into the bay and two after the discharge of water from the fields into the bay, right after pesticide application. In addition to pesticides, other sources of contamination can be identified such as urban treated and untreated waste water discharges. Consequently, an analytical method taking into account a mixture of pollutants was used. Biomarkers of pesticide exposure such as esterases and oxidative stress parameters, histological analyses of bivalve's tissue, and bioaccumulation of chemicals were combined and related to environmental water variables using a multidimensional scale approach. The integration of the multi parametrical responses indicated an influence of the water discharges from the crop fields on bivalves. Mussels proved to be the most sensitive bivalve species reflecting water properties and carboxylesterases a sensitive biomarker of pesticide exposure.

Key words: anthropogenic water discharges, bivalves, pesticides, carboxylesterases.

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MITIGATING THE IMPACT OF AQUACULTURE BY THEIRSELF: ACCUMULATION OF MUSSEL DEBRIS AND EFFECT ON BIOCHEMICAL PROCESS

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Abstract: Organic pollution is widespread in coastal areas and can have profound impacts on the seabed. Coastal sediments play an important role at a global scale in the recycling of organic matter, and this process is influenced by the habitat complexity of the sediments, among other factors. Mollusc shells constitute a waste product from a range of anthropogenic activities and can cause a problem in aquaculture systems. The shells of molluscs in various states of decomposition are important elements of the habitat structure that promote its complexity, by modifying grain size and augmenting the surface for sessile organism attachment. As a preliminary step to an adequate management for this waste is necessary to know its effects on marine sediments which have a major role in the mineralization of organic matter and are a habitat for ecosystems with species of commercial interest. Thus, in previously studies we demonstrate the capacity of mollusc shell to change the biogeochemical fluxes in organic polluted sediments mitigating their negative ecological consequences. To increase the knowledge of this potential tool to ameliorate the organic pollution in sediments, we have made two additional experiments: 1) mesocosm experiment to test the effect of mollusc shells on sediment biogeochemical processes along a gradient of organic pollution; 2) a manipulative experiment to test the changes in the macrofauna communities related with mollusc shells and organic pollution. The preliminary results highlight the possibilities to use this tool to buffer the negative biogeochemical consequences of organic pollution and increase the habitat complexity to promote macrofauna community and thus, improve the ecological status of sediment. Although organic pollution is widespread in marine sediments, mitigation measures are rarely implemented. The possibility of this tool can enhance aquaculture sustainability by promoting circular economy.

Key words: Biogeochemical fluxes, macrofauna, mussel shell, organic pollution, sediment

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THREE PATHS TO CHECK AN AREA OF GREAT ECONOMIC AND ECOLOGICAL IMPORTANCE: TEMPORAL, SPATIAL AND FOCUS ASSESSMENT

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Abstract: The focus area for this research is Ría de Arousa, located in North West Spain between 42°25' - 42°42'N and 8°40' - 9°07'W with an area of 230 km² and a maximum water depth of 69 m. Ria de Arousa is where over 70% of all installed rafts for mussel culture are located in Galicia with an important economical impact in the area. Besides, this ria has an significant environmental richness with worldwide admired beaches, spectacular islets, a nature reserve (Punta Carreirón) and even part of a National Park (NP of Atlantic islands)

The three approaches used in this research allow a combined environmental evaluation. As a first approach we develop a temporal study which offer a deep description of the past and present situation of the Ría (temporal distribution), the second one implies a comprehensive assessment of the general nowadays situation (spatial distribution) and finally we perform a focus evaluation of the specific impacts in the area.

As the first step the sampling cruise was configured to obtain an extensive number of samples that cover the ambitious study, comprising 37 superficial samples to cover the whole geographical area and will allow the distribution evaluation, 5 core samples to know the temporal changes in the area and a number of superficial sediments specifically influenced by rafts.

The sediments were extracted by ASE (Accelerated Solvent Extraction) procedure and the quantification of PAHs was performed using gas chromatography coupled to mass spectrometry (GC-MS). Organic carbon and particle size analysis were also done to complete the sediments characterization and facilitate data interpretation.

The study includes a robust statistical analysis and also an ecotoxicological sediment assessment.

The three ways have to be used unquestionably together and constitute an interest tool to perform a complete environmental evaluation.

Key words: Temporal evaluation, spatial distribution, PAHs, marine sediments.

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ORGANOCHLORINE COMPOUNDS IN EGGS OF YELLOW LEGGED GULLS FROM CIES ISLANDS

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Abstract: Levels of fourteen PCBs congeners and ten organochlorine pesticides were measured in eggs of yellow-legged gulls (*Larus michahellis*) from the Cies Islands. These islands are part of the Maritime-Terrestrial National Park of the Atlantic Islands of Galicia. Most of these pollutants have been banned in the Western European countries since the 1970s-90s but are still present in the environment.

The Σ CB7 (sum of 7 individual PCB congeners) was in the range of 100-600 ng/g w.w., lower than those reported in the Ebro delta National Park (Morales et al., 2012), but well above the Ecological quality Objective (EcoQO) proposed by OSPAR for seabird eggs in the North Sea. DDE was prominently dominant among the DDT metabolites measured, suggesting a degradation process and not a recent use in the area.

Persistent chemicals such as organochlorine compounds may affect the reproduction of seabirds by eggshell thinning, which in turn makes eggs more vulnerable.

Key words: organochlorine compounds, seabird eggs, yellow-legged gull.

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BIOCONCENTRATION AND DEPURATION OF SELECTED PERSONAL CARE PRODUCTS IN *RUDITAPES PHILIPPINARUM*

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Abstract: There has been a growing interest over the last decade in the study of the occurrence, distribution and effects of emerging organic contaminants (EOCs) in aquatic systems. Among the different classes of EOCs, personal care products (PCPs) are frequently detected in wastewater treatment plant effluents and the receiving waters. In the present study, we have measured the bioconcentration factors in the marine clam *Ruditapes philippinarum* for four hydrophobic PCPs ($\log K_{ow} > 3.5$) of wide use that were previously detected in coastal environments (Pintado-Herrera, 2017): an antimicrobial (triclosan, TCS), a fragrance (OTNE) and two UV filters, benzophenone-3 (BP-3) and octocrylene (OC).

The four chemicals were tested individually in 40 L tanks ($n = 4$) filled with 50 organisms per tank, whereas blank and solvent controls were also performed in parallel. A nominal concentration of $10 \mu\text{g L}^{-1}$ was used, and the clams were subjected to exposure for 26 days. This phase was followed by a depuration period of 7 days. The extraction of the contaminants from the clams was achieved by pressurized liquid extraction (PLE) with in-cell clean-up using silica. Progressive uptake by the clam was observed for the target analytes, and the maximum concentrations in tissues were reached at the end of the exposure phase (day 26), up to levels of $0.62 \mu\text{g g}^{-1}$, $23.9 \mu\text{g g}^{-1}$, $0.78 \mu\text{g g}^{-1}$ and $17.5 \mu\text{g g}^{-1}$ for OTNE, BP-3, OC and TCS, respectively. During the depuration phase the removal percentages were higher than 50% after 7 days. BP-3 was the most highly accumulated chemical in the organisms, although it was eliminated from the clam easily compared to the rest of contaminants. The logarithm of the bioconcentration factor, static and kinetic (ratio between the uptake and depuration rates) ranged between 1.5 and 3.5. The half-life of these compounds was short compared to others organic pollutants, indicating a quick removal or degradation.

Key words: Personal care products, bioconcentration, clams, depuration, pressurized liquid extraction.

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IDENTIFICATION OF PRIORITY MIXTURES OF CONTAMINANTS IN MUSSELS FROM EBRO DELTA

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Abstract: The Ebro delta is a wetland area of international importance for waterbird conservation and one of the most important sites for shellfish aquaculture in the Spanish Mediterranean. This area supports a well-developed rice farming activity with the consequent input of agricultural waste into Alfacs and Fangar bays. Besides, there are urban and industrial waste water discharges and recreational activities, all this delivers a “cocktail” of contaminants of potential concern. These xenobiotics interact with aquatic organisms and may be bioaccumulated. They can have negative implications from an environmental point of view but also they may be of concern from a human health perspective, when they are accumulated in highly consumed organisms like mussels. Therefore, the goal of this study was to identify priority mixtures of contaminants of potential concern accumulated in mussels destined for human consumption.

A field experiment was carried out in Alfacs and Fangar bays in June 2017. Mussels from a shellfish farm allocated outside of Alfacs Bay and considered as “clean site” were transplanted into several sampling points in Alfacs and Fangar bays. They were cohabiting with others bivalves for aquaculture production during 1 month. After this period the mussels were collected and transported to the laboratory for their analysis. A fast analytical method previously developed by our research group was used. It consisted on QuEChERS extraction followed by dispersive Solid Phase Extraction. For the identification and quantification of contaminants the samples were injected in Orbitrap-Q-Exactive. Preliminary results show bioaccumulation of pesticides, plasticizers, stimulants and antibacterials but the levels found in mussels are not of health concern for regular consumers of this type of seafood.

Key words: mussel, mixture, contaminants, levels, seafood.

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EFFECTS OF PLASTIC AND ORGANIC POLLUTION IN SEABED BIOGEOCHEMISTRY

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Abstract: In the last 70 years, the proliferation of plastic products has been excessive. Nearly 300 million tons of plastic are produced each year, of which more than 8 million tons end up in the oceans. Plastics are designed to be long lasting, which is why they remain in the environment and release pollutants. In the manufacturing process plastics are treated with additives which can be destructive to the surrounding environment. This study offers a pioneer analysis on the effect of plastics and organic pollution on the biogeochemical flows of marine sediment. Two types of conventional plastic and two types of biodegradable plastic, all with known compositions, were selected in order to study their degradation under a sediment mesocosms. Measures of O₂ and TCO₂ were taken to estimate sediment metabolism. The results showed the highest TCO₂ production and O₂ consumption in organic polluted cores. TCO₂ production was notably higher in cores with biodegradable plastic than in control ones. O₂ consumption showed higher values in cores with plastics than in control ones. In organic polluted sediment, both types of plastic may increase aerobic metabolism of the sediment. The results of this study are important in a changing world with increasing plastic pollution.

Key words: biogeochemical fluxes, marine sediments, plastic, organic pollution

EFFECT OF MICROPLASTICS ON THE TOXICITY OF CHLORPYRIFOS TO THE MICROALGAE *ISOCHRYSIS GALBANA*, CLONE T-ISO

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Abstract: The objectives of this study were i) to assess the toxicity of MPs and the pesticide chlorpyrifos (CPF) to the microalgae, *Isochrysis galbana*, clone t-ISO and ii) to ascertain if the presence of MPs influences the toxicity of CPF. The endpoint was the microalgae growth rate. As a microplastic model, a commercial virgin PE micronized powder was selected, with a mean size ranged from 2 to 6 microns, assayed until 25 mg l⁻¹. CPF was tested at concentrations ranged from 0 to 3 mg l⁻¹. A constant concentration of MPs (5 mg l⁻¹) was loaded with increasing doses of CPF (0-3 mg l⁻¹) with an incubation time of 2 h. Bioassays were carried out at 20 °C, in glass tubes of 50 ml, with air and constant light. The exposure time was 72 hours. Cell counts were performed using a Coulter Counter Multisizer III. HPLC was used to quantify the partition of this pollutant among MP and water. Microalgae growth was not affected by the MP. On the contrary, growth was clearly affected by the exposure to CPF from 2 mg l⁻¹ onwards, with a total growth inhibition at concentrations upwards of 3 mg l⁻¹. After incubation, 80% of CPF was sorbed onto MP surfaces. CPF bioassays showed two different dose-response curves depending on the presence of MP, with lower percentages of inhibition when CPF is offered through to MP. Thus, the adsorption of CPF onto MP surfaces reduced its toxicity to microalgae.

Key words: microalgae, microplastic, chlorpyrifos, toxicity, growth

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DISSOLVED ORGANIC CARBON LEACHING FROM PLASTICS STIMULATES MICROBIAL ACTIVITY IN THE OCEAN

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Abstract: More than 5.25 trillion of plastic pieces have been estimated to be floating at the sea surface (Eriksen et al., 2014). Plastic marine debris on beaches and floating in seawater is exposed to solar UV radiation undergoing weathering degradation (Andrady, 2011). It can develop surface cracks and fragment into progressively smaller particles reaching microscopic sizes (< 5 mm, microplastics). Detrimental effects of plastics on marine organisms at different trophic levels have been widely reported, making plastic pollution a global environmental concern. However, the impacts of plastic debris on the lowest trophic levels, such as the microbial food web, remain enigmatic. Plastic is known to leach organic compounds to the aquatic media (Suhrhoff et al., 2016). The smaller the piece, the higher its surface to volume ratio and its potential for leaching. However, the contribution of plastic leaching to the dissolved organic carbon (DOC) pool in the ocean and its impact on the lowest trophic levels, such as the microbial food web, is still unknown. In this work we present experimental evidence that plastics release dissolved organic carbon (DOC) into the ambient seawater stimulating the activity of heterotrophic microbes. About 60% of the DOC leached from plastics is available to microbial utilization in less than 5 days. It is predicted that plastic waste entering the ocean will increase by 10-fold over the next decade (Jambeck et al., 2015), resulting in an increase in plastic-derived DOC that could have unaccounted consequences for the activity of marine microbes and for the ecosystem.

Key words: plastics, microplastics, leaching, DOC, microbial uptake

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MERCURY CONTENT IN BEACHED AND VIRGIN PLASTICS: ENVIRONMENTAL AND ECOTOXICOLOGICAL IMPLICATIONS

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Abstract: During the last decades much attention has been paid to marine litter pollution, mainly due to plastics and microplastics. The problem of these plastics is not only physical, but also associated to the pollutants contained in this material during its production or adsorbed once the plastics are released to the marine environment. Most of the research about pollutants associated to plastics has been focused in the organic contaminants due to their hydrophobicity, but recent studies have demonstrated that once in the environment, plastics are able to adsorb metals and concentrate them (Ashton et al., 2010; Holmes et al., 2012). This fact can have several environmental and ecotoxicological implications as the adsorption-desorption kinetics of metals and plastics under different environmental conditions (i.e. pH, salinity or temperature) will release these metals from plastics to the water column or, in contrast, will act as metal carriers (Brennecke et al., 2016) to the trophic chain, entering through the filter-feeder animals for example.

The study aims to quantify and compare the content of mercury (Hg) and other metals in plastics collected in two beaches, i) impacted (Portman, Spain), ii) not impacted (Los Urrutias, Spain) and iii) "Virgin" commercial plastic. Samples were collected randomly. Once in the lab, they were classified by colour. The Hg content was measured with a Leco AMA254 Mercury Analyzer. The results revealed the presence of Hg, in order of ng/g in all the analyzed materials. Differences in the content of Hg based on origin and colour of material were observed. On average, the highest Hg content was quantified in plastics of Portman, followed by Los Urrutias and "Virgin" plastic. These results can be attributed to adsorption processes, such is the case of Portman where mineral residues from an old mine are present in the beach and surrounding environments.

Key words: Plastic, metals, pollution, marine environment.

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CHARACTERIZATION OF THE RIA FORMOSA WATER BODIES IN SPRING 2017

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Abstract: The susceptibility of coastal systems to climate change and anthropogenic pressures is an important issue for the management of ecosystem values and services. In this context, UBEST project aims to improve the global understanding of the biogeochemical buffering capacity of coastal systems, regarding their responses to futures global changes. Ria Formosa lagoon is one of the most valuable ecosystems in the south coast of Portugal and one of our goals was to characterize the seasonal variability of its water bodies, defined by Ferreira *et al.* (2005) under the Water Framework Directive. Here we present data for Spring, from seven places covering globally the Ria Formosa water bodies. *In situ* measurements (temperature, salinity, pH, dissolved oxygen), and water samples for nutrients, chlorophyll *a* and suspended solids quantification were taken every two hours during a semidiurnal tidal cycle. The results, while typical for this season, clearly describe a spatial variability pattern. The lowest variability occurred at the boundary station – the main inlet, in opposition to the stations located at the edges of the lagoon. Globally, temperature, chlorophyll *a*, phosphate and silicate were highest at the eastern station where the water column was the shallowest, accompanied by an extreme variation of dissolved oxygen. The only site influenced by freshwater input showed a maximum of nitrate and ammonium concentrations. Despite that, nutrients as well chlorophyll *a* concentrations were relatively low for Spring. However, it is known that this ecosystem responds rapidly to the oceanographic processes occurring on the coast, such as upwelling, able to supply nutrients and fertilize the Ria Formosa. These data, together with others gathered under different seasonal conditions, will contribute to better understand the global functioning of this system and further to validate the numerical hydrodynamic-biogeochemical models used to simulate and anticipate the susceptibility of Ria Formosa to future scenarios.

Key words: Coastal lagoon, Ria Formosa, nutrients, chlorophyll *a*, dissolved oxygen.

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GLOBAL VALIDATION OF PALEOPRODUCTIVITY PROXIES AND THE ROLE OF DEPOSITIONAL CONDITIONS

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Abstract: Ocean primary productivity is a key element of the marine carbon cycle. However, its quantitative reconstruction in the past relies on the use of biogeochemical models as the available proxy approaches are qualitative at best. Here, we present an approach that evaluates the uncertainties and constraints in the use of phytoplanktonic biomarkers (i.e. chlorins and alkenones) as quantitative proxies to reconstruct past changes in marine productivity. We also study organic matter fluxes and depositional conditions as another source of variability in sedimentary chlorins content.

We use remote sensing to infer chlorophyll-*a* concentration on the ocean surface, which is used in models for estimating primary productivity, and laboratory analysis to quantify sedimentary biomarkers. The satellite data used in this study have been merged from different sensors: SeaWiFS (1997-2010), MERIS (2002-2012), MODIS (2002-2017), VIIRS (2012-2017). In this way, we estimate sea-surface chlorophyll-*a* concentration in a global scale over the last 20 years, and compare it with biomarkers concentration, which we measured in a global suite of core-top sediments. We also compare chlorins content with *in situ* biogeochemical data: bottom oxygen concentration, water depth and sedimentation rate. Our findings show that both sedimentary chlorins and alkenones can be used to quantitatively track total sea-surface chlorophyll-*a* abundance as an indicator for past primary productivity. Estimates from chlorins records have lower uncertainty than from alkenones. However, alkenones concentration correlate linearly with sea surface chlorophyll-*a* for the whole range, meanwhile degradation processes restrict the application of chlorin proxy to concentrations below a threshold value (1 µg/g). Depositional conditions

considered in this study have not a predominant role in controlling chlorins content. In conclusion, as long as specific constraints are taken into account, our study evaluates the use of chlorins and alkenones as reliable quantitative proxies of past primary productivity.

Key words: paleoproductivity, remote sensing, chlorins, alkenones

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DISSOLVED ORGANIC NITROGEN DOMINATES NITROGEN EXPORT IN THE SUBPOLAR NORTH ATLANTIC

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Abstract:

Dissolved organic nitrogen (DON) is produced and accumulated in the surface ocean and is transported horizontally and vertically by ocean currents, overturning and turbulent mixing. Remineralization of this material occurs downstream of the source region in time-scales of months-to-years, fueling heterotrophic processes. In the subpolar North Atlantic (SPNA), the subtropical mode waters (STMW) transported northwards by the North Atlantic Current are transformed into subpolar mode waters (SPMW) that sink and return southwards as part of the Meridional Overturning Circulation (MOC). Here, we have calculated DON and nitrate fluxes and net budgets in a box in the eastern SPNA, delimited by the Greenland-Portugal OVIDE 2002 section to the south and the Greenland-Iceland-Scotland (GIS) sills to the north. At the OVIDE 2002 section, the net transports of nitrate and DON were southwards at rates of $-1.1 \pm 8.6 \text{ kmol s}^{-1}$ and $-11.5 \pm 2.7 \text{ kmol s}^{-1}$. The transport through the GIS sills was southwards for nitrate ($-17.8 \pm 12.0 \text{ kmol s}^{-1}$) and northwards for DON ($4.3 \pm 5.3 \text{ kmol s}^{-1}$). Hence, the net transport was of $19.3 \pm 14.8 \text{ kmol s}^{-1}$ into the box for nitrate and $-14.3 \pm 6.0 \text{ kmol s}^{-1}$ out of the box for DON. Assuming steady-state conditions inside the box implies a net production of DON that represents 75% of the nitrate supply to the eastern SPNA. The DON produced locally, together with the DON transported by the STMW, was retained in the SPMW that sank and was exported towards the Labrador Sea with the East Greenland Current, in the lower limb of the MOC. These results thus suggest that the subduction of DON-rich SPMW represented a major pathway for DON export to the deep ocean.

Key words: Dissolved organic nitrogen, Subpolar North Atlantic, Cyclonic Subpolar Gyre Circulation, Meridional Overturning Circulation

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ORIGIN OF METHANE IN THE GULF OF CADIZ

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Abstract: The concentration of CH₄ were measured in five transects in the Gulf of Cadiz (Trafalgar, Sancti Petri, Guadalquivir, Tinto y Odiel and Guadiana) in four cruises during Spring, Summer, Autumn and Winter of 2016. Moreover, we sampled in three mud volcanoes (San Petersburgo, Anastasya and Pipoca) situated in the Gulf of Cadiz during two cruises. The concentration of CH₄ was obtained by using a gas chromatograph. In addition, the stable carbon isotopic compositions ($\delta^{13}\text{C}$) were measured to try to establish the origin of methane in the study area. The mean CH₄ value for this area was 9.49 ± 2.4 nM, with large spatial and temporal variations. The highest values were found in June 2016 and the lowest in Spring 2016. In most of the sampling area the highest concentration of CH₄ was found in subsurface waters at depths close to the thermocline, and in the bottom waters near the coast. Moreover, the decreased of the gas concentration in the farthest stations indicated a coastal input. The stable carbon isotopic compositions ranged between -29.2 and -50.7 ‰. The less negative values were associated with the highest CH₄ concentrations in the mud volcanoes samples, showing a thermogenic origin of methane (Kim et al., 1984; Brooks et al., 1987; Schoell, 1988) in the gulf of Cadiz. The seawater-air flux of CH₄ ranged between 12.4 and 37.7 $\mu\text{mol m}^{-2} \text{d}^{-1}$, showing that the study area acts as a source of CH₄ to the atmosphere. The CH₄ fluxes increased with proximity to the coast, with the highest values in summer 2016.

Key words: Methane, Isotope signature, Continental shelf, Mud volcanoes, Gulf of Cadiz

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SUBMARINE GROUNDWATER DISCHARGE IN RIA DE VIGO

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Abstract: Submarine Groundwater Discharge (SGD), i.e. any flow across the sediment-water interface (Burnett et al. 2003), is now recognized as the major source of continental water to the global ocean, thus exerting a major control over coastal water composition (Kwon et al. 2014). State-of-the-art methods are being used to evaluate, for the first time, the occurrence and magnitude of SGD in Ría de Vigo. Landsat Enhanced Thematic Mapper (ETM+) thermal infrared (TIR) imagery is used to obtain medium-to-high resolution sea surface temperature maps of the ria (Wilson and Rocha 2012). These are used to identify warm groundwater plumes within the system. Thermal imagery is complemented with basin-scale surveys where surface water samples are collected for the determination of the activity of ²²²Rn and ²²⁶Ra. Surveys cover the entire shoreline of the ría, with special focus on the areas potentially affected by fresh SGD as inferred from thermal imagery. Additionally, the activity of ²²²Rn and ²²⁶Ra is also determined in the aquifer systems surrounding the ría, beach porewaters, sediment incubations, atmosphere and the adjacent coastal sea. The system revealed as naturally enriched in ²²²Rn due to the widespread presence of granitic basement rocks in the region. Although variable, high ²²²Rn activities (up to 10⁵ Bq m⁻³) are detected in boreholes surrounding the ría. Concomitantly, high ²²²Rn activity (>400 Bq m⁻³) is measured in certain areas of the ría. Closer to the shore, ²²²Rn time series in surface waters of selected beaches showed activities higher than 4000 Bq m⁻³ mainly restricted to low tide, suggesting high local SGD rates there. The information gathered (mass balance for excess ²²²Rn, i.e. that not supported by internal ²²⁶Ra decay, thermal imagery) is used to perform a first volumetric estimation of total SGD in Ría de Vigo.

Keywords: SGD, thermal imagery, ²²²Rn, ²²⁶Ra, Ría de Vigo

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POSIDONIA OCEANICA AS A SOURCE OF CHROMOPHORIC DISSOLVED ORGANIC MATTER FOR THE OLIGOTROPHIC NW MEDITERRANEAN COAST

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Abstract: Seagrass meadows of *Posidonia oceanica* in the Mediterranean coast provide important ecosystem services and play plentiful roles in biogeochemical cycles. Despite their importance as a source of dissolved organic matter (DOM) derived from exudation and leaching of seagrass leaves has been already recognized, very little is known about the impact of *P. oceanica* on the coloured fraction of DOM (CDOM). In this study, we monitored for two years the optical properties of CDOM in two adjacent but contrasting sites of Mallorca coast. The first site was a rocky shore free of seagrass meadows, and the second site was characterized by the accumulation of non-living seagrass material in form of banquettes on the beach shore. On average, the integrated colour over the 250-600 nm range was almost 6-fold higher in the beach compared with the rocky shore. Furthermore, the shapes of the CDOM spectra in the two sites were also different. A short incubation experiment demonstrated that the spectral differences were due to leaching from *P. oceanica* leaf decomposition. Moreover, occasionally the spectra of *P. oceanica* was distorted by a marked absorption increase at wavelength < 265 nm, presumably related the release of H₂S associated to the anaerobic decomposition of seagrass leaves in the banquettes. Our results provide the first evidence that *P. oceanica* is a source of CDOM. Future research is necessary to confirm our hypothesis about H₂S, to better quantify and characterize the chemical nature of the colour released by *P. oceanica* and to deeper understand the dynamics of the banquettes and its relevance for biogeochemical cycles.

Key words: Coastal Mediterranean Sea, *Posidonia oceanica*, seagrass-derived organic matter, banquettes, CDOM.

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COMPARISON OF UV/H₂O₂ AND UV/PERSULFATE SYSTEMS FOR WATER DISINFECTION

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Abstract: Seawater treatment is increasingly required in order to avoid microbiological pollution related to aquaculture or ballast water management (Penru et al., 2012). Advanced Oxidation Processes (AOPs) for water disinfection appears as an efficient alternative for these purposes. In this sense, two different photochemical processes have been evaluated based on the generation of hydroxyl (HR-AOPs) or sulfate (SR-AOPs) free radicals (Rodríguez-Chueca et al., 2018). The main goal is to evaluate the disinfection efficiency of both H₂O₂ and persulfate (PS) activated with UV-light against *E. faecalis* in bench-scale. After testing a range of PS (0–10 mM), H₂O₂ concentrations (0-5 mM) and exposure times (0-5 min), we determined concentrations up to 0.5 mM (PS) and 0.15 mM (H₂O₂) as an optimum dosage. Disinfection efficiency was determined by kinetic modelling; it was enhanced by 44.94% for SR-AOP and 33.85% for HR-AOP in comparison with UV irradiation. The results suggest photochemical processes as an attractive alternative to other biocides currently in use for seawater treatments and merits further testing at a larger scale. Specially, UV/PS system seems consistent with the chemistry of typical seawaters: the activation of PS, and the resulting addition of SO₄²⁻ to the water would be inconsequential compared with background levels in seawater (Ahn et al., 2013).

Key words: Seawater disinfection, *E. faecalis*, photochemistry, persulfate, UV/H₂O₂

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TRANSPORT AND MOBILITY OF TOXIC ELEMENTS ALONG AN AMD-AFFECTED ESTUARY (RIA OF HUELVA, SW SPAIN) AFTER AN ACCIDENTAL MINE SPILL

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The Estuary of Huelva is formed by the confluence of two rivers extremely affected by acid mine drainage (AMD), the Odiel and Tinto rivers, which suffer a chronic metal exposure due to intense mining activities developed since ancient times [1]. The existence of numerous derelict mines, with total absence of control measures, increases the vulnerability of this area to acid mine water spills. In this sense, an accidental spill from La Zarza mine in May 2017 led to the release of around 270.000 m³ of highly polluted acidic waters, of which 80% reached rapidly to the Odiel river, causing a drastic increase in metal and metalloids concentrations. A detailed sampling along the Odiel river-estuary system was carried out to investigate the transport and mobility of these toxic elements and to quantify the amount of elements reaching the estuary, and through it to the Atlantic Ocean. Results evidence a strong removal of most metals (i.e. Cu, Zn, Mn, Pb, Co, Ni, and Fe) to the sediments as a consequence of pH and salinity increases along the estuary. However, some elements such as As, Mo, Sb, V or U exhibited a different behavior; increasing their concentration with pH and salinity, reaching even to higher values than those reported in the river reach. This fact, that can be attributed to desorption processes from particulate material, seems also affecting Fe. Despite the strong removal mechanism during estuarine mixing processes, a fraction of the metals delivered by the river after the spill, reached the oceanic coast. This study highlights that potential accidental spills, as well as intense flood events after dry period constitute, at least seasonally, acute contaminant episodes of environmental concern, which not only affect to the estuary but also the coast of the Gulf of Cádiz [2].

Key words: Acid Mine Drainage (AMD), Estuary, Toxic elements, chronic pollution.

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HIGH-FREQUENCY MEASUREMENTS OF METAL CONTAMINATION IN A SPANISH ESTUARY: STEPS TOWARDS THE ACCEPTANCE OF PASSIVE SAMPLERS FOR REGULATORY MONITORING

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Abstract: The main driver of this study is to respond to European Directive demands for the assessment of the chemical status of transitional and coastal waters. *Diffusive Gradient in Thin Films* (DGT) and passive samplers (PS), in general, are already widely used in investigative monitoring and there is an increasing interest in their use for the environmental assessment of water bodies, within European policies requirements. The main barrier hindering the regulatory acceptance of PS for compliance checking is the lack of appropriate Environmental Quality Standards (EQSs). EQSs for metals are defined in the dissolved fraction, preventing the use of DGT-labile concentrations for the establishment of the chemical status of water bodies. Thus, adaptation of already existing EQSs for DGTs would allow their use for regulatory monitoring. The specific objectives of this study are: (1) to investigate the relationship between dissolved metal concentrations from spot sampling with DGT-labile metal concentrations, (2) to evaluate the reliability of the techniques used for the measurement of metal concentrations in estuaries and (3) to provide recommendations for the use of DGTs to develop environmental guidelines. Hence, one station was selected at the mouth of the Oiartzun estuary, which has been classified as highly impacted. At this station, 12 DGTs were deployed simultaneously and triplicates were retrieved after 3, 6, 9 and 12 days. Concurrently, spot water samples were collected every day, at the same depth than DGTs, at low and high tide during the DGT deployment period. Water samples were filtered on site by syringe filters for the posterior analysis of metals, dissolved organic carbon and the quantification of SPM. The metals under study were Cd, Cu, Ni, Pb and Zn. Hydrographic parameters were measured at each sampling time. The relationships between dissolved and labile metal concentrations and the environmental factors influencing such correlations were analysed. First results show that dissolved Ni and Cd appear mostly labile and available for uptake by DGTs, while most of the dissolved Cu, Pb and Zn are forming

organic complexes no detected by DGTs. Based on the information obtained, an approach to define quality objectives for DGT-labile metal concentrations is being developed in the MONITOOL project.

Key words: Passive samplers, DGT, Environmental Quality Standards, metals, marine waters

Acknowledgments: This research was supported by the INTERREG Atlantic Area Programme (MONITOOL project, grant agreement no. EAPA_565/2016).

***PERSISTISTROMBUS LATUS* (GMELIN, 1791) AS A SENTINEL ORGANISM FOR THE COASTAL ENVIRONMENT CONTROL OF METALS (Cr, Cu, Zn, Ni, As, Cd AND Pb) IN THE CAPE VERDEAN REGIONS, WEST AFRICA**

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Abstract: Considered as a coastal entity, the coastal areas of Cabo Verde play an important role in the sustainable economic growth. Therefore, the coastal areas are impacted by an overexploitation of resources, discharges of untreated effluents, uncontrolled discharges of solid wastes, and the use of organic compounds in the agricultural activity. In order to implement an environmental monitoring program in Cabo Verde, the determination of Cr, Ni, Cu, Zn, As, Cd and Pb in biota and sediments have been carried out. As an alternative to the lack of bivalves to be collected in Cabo Verde (Lopes, 2012) the current study proposes the use of the mollusk *Persististrombus latus* as an indicator organism of contamination, due to its wide spread and low mobility. The sample of *P.latus* and sediments were collected through diving in seven sites in Cabo Verde, on the islands of Santo Antão, São Vicente, São Nicolau, Sal, Santiago and Fogo. The metal concentrations were determined in the digestive gland and muscle of *P.latus* by ICP-MS, and by ICP-OES for the determination of these metals in sediments. Highest average concentrations of Cr, Ni, Cu and Zn in the digestive gland of *P.latus* were observed in the island of Fogo. Likewise, the highest concentrations of Pb were estimated in *P.latus* digestive gland collected in São Vicente. Relationships between concentrations of metals in sediment and *P.latus* samples were established in order to assess the suitability of *P.latus* as sentinel organisms. For that purpose Bioaccumulation factors were calculated and results were compared with reference values, for sediments or another marine organisms such as ERL-ERM (Long et. Al 1995) or TEL-PEL (Macdonald et. Al. 1996) values, among others. According to the present study, *P.latus* can be used as a contamination indicator by metals in the coastal system of Cabo Verde and West Africa because of its wide spread and the ability to concentrate metals in its tissues with greater accumulation in the tissues of the digestive gland.

Key words: *Persististrombus latus*, Sediments, Metals, Coastal pollution, Cabo Verde.

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UNRAVELING NEW ORGANIC CONTAMINANTS IN THE OCEAN BY NON-TARGET SCREENING

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Abstract: Nowadays, there are around 140,000 chemicals produced or imported to the EU according to the REACH legislation. As regulatory monitoring in the environment is still restricted to only a small number of well-known contaminants, assessing the fate of new substances in the environment is a major time- and resource-intensive challenge. This is of special interest in the ocean, the ultimate sink of most of these contaminants. A novel approach to help solve this problem is non-target screening (NTS) using high resolution mass spectrometry (HRMS) (Hollender et al., 2017). In this work, we used this strategy for the first time to identify a wide range of chemicals in coastal and oceanic water samples from the Gulf of Cadiz (SW Spain) that were also present in effluents from wastewater treatment plants (WWTPs) in that area. Solid phase extraction followed by liquid-chromatography HRMS were used in combination with statistical tools (e.g., principal component and cluster analyses), specific vendor and open-access software, and online library searches (mzCloud) to tentatively identify more than 300 sewage features persistent enough to be detected in oceanic waters. These compounds included different classes of surfactants (e.g., linear alkylbenzene sulfonates) and their byproducts (e.g., DATS) and metabolites (e.g., NPEC), polymers (PEG, PPG and many ethoxylated derivatives), pharmaceuticals (e.g., valsartan, diclofenac, carbamazepine, etc.), personal care products (UV stabilizers) and food additives (e.g., sucralose), some of them (e.g., sulfurol) identified in the environment for the first time. The list of compounds reflected here not only shows many of the substances that can potentially escape from wastewater treatment but also constitutes a first step towards a more detailed characterization of the chemical exposome in the marine environment.

Key words: contaminants, seawater, wastewater, mass spectrometry

Acknowledgments: we acknowledge project HORACIO (CTM2015-70731-R) from MINECO for funding this research.

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EVOLUCION INTRA-ANNUAL DEL MÁXIMO DE REMINERALIZACIÓN COSTERO FRENTE A LA RIA DE VIGO. RESULTADOS PRELIMINARES

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Resumen: Cada región de afloramiento costero tiene sus propias características pero, en todas ellas, un efecto de la alta producción primaria es la presencia de una marcada zona subsuperficial de remineralización, normalmente dentro de la plataforma continental. En el afloramiento costero estacional de Galicia (Fraga, 1981) uno de los sitios donde se ha observado este proceso se encuentra frente a la ría de Vigo (Prego & Bao, 1997; Álvarez-Salgado et al., 2006; Castro et al., 2006). En el continuo río-ría-plataforma los afloramientos son el principal evento en el aporte de sales nutrientes y en la formación de un máximo costero de remineralización, el cual presenta un mínimo de saturación de oxígeno disuelto junto con un máximo de concentración de nitrato en torno a la isóbata de 120 m (Prego et al., 1999); no obstante, las contribuciones continentales también podrían influir en el mantenimiento del citado máximo durante otras épocas del año. Esta hipótesis es analizada en base a los datos hidrográficos, sales nutrientes, oxígeno disuelto y materia orgánica obtenidos en la columna de agua de la isóbata de 125 m durante las diez primeras campañas realizadas de junio a noviembre de 2017 en el B/O Mytilus. A la espera de disponer de los datos correspondientes a las campañas de diciembre 2017 a junio 2018, los resultados preliminares sugieren que el máximo de remineralización se mantuvo, con mayor o menor intensidad, durante todo ese periodo de verano-otoño.

Palabras clave: afloramiento, remineralización, plataforma continental, Galicia

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OXIDATION KINETICS OF Fe(II) IN THE NORTH ATLANTIC

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Abstract: The Fe(II) oxidation rate was studied in different water masses present in the Subarctic North Atlantic along the 59.5°N trasatlantic section. The combined effect of temperature, pH, salinity and total organic carbon under different conditions were considered in order to understand the variables that control the Fe(II) oxidation kinetic in the ocean. The study shows that the master variable which controls 75% of the pseudo-first order kinetic rate, k' , in natural conditions, is temperature. This value rises to 90% when pH_F and salinity are also considered. At fixed temperature, 72% of k' is controlled by pH and at both fixed temperature and pH, salinity controls 62% of the Fe(II) oxidation rate. Sources and characteristics of TOC are important factors influencing the oxidation of Fe(II) depending on its marine and terrestrial origin and location, including oceanic, coastal and bottom waters. The energy of activation for Fe(II) oxidation was calculated for surface and bottom waters. An empirical equation considering the natural conditions of temperature, pH_F , salinity and TOC for the area allows calculation of Fe(II) oxidation rate constants in the region. This equation could be incorporated in global Fe models.

Key words : Fe(II), Oxidation, Atlantic Subarctic

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THE ROLE OF PENGUINS RECYCLING METALS IN THE SOUTHERN OCEAN

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Abstract: Numerous biogeochemical studies in the Southern Ocean have focused on the importance of trace metals in controlling primary production (e.g. Fe, Co) or as potentially toxic to the ecosystem (e.g. Ag, Cd). However, the reasons why Fe limitation is prevalent in the Southern Ocean or the concentrations of non-biogenic elements in surface waters are higher than those reported in other oceans are not fully understood. As the Southern Ocean is not influenced by direct anthropogenic inputs and trace metal additions do not occur

naturally, special attention is being allocated to the recycling processes that control trace metal cycling in the ecosystem. Yet, the importance of penguins, one of the most abundant animal in the Southern Ocean, in trace metals cycling has not been addressed. Here, we have characterized the trace metal composition of guano samples from the two of most abundant penguin's species living in Antarctica (the Chinstrap: *Pygoscelis antarctica* and Papua: *Pygoscelis papua*) as well the composition of krill (*Euphausia superba*) as the main prey of penguins and phytoplankton as the lowest link in the trophic Antarctic chain. The high metal concentrations measured in material defecated by *P. papua* and *P. antarcticus* (e.g. 759 ± 285 and 930 ± 75 $\mu\text{g/g}$ of Fe, respectively) suggest that penguins can be playing a fundamental role in the biological recycling in Antarctic waters and influencing their environmental concentrations and ecological functioning.

Key words: Penguins, trace metals, Antarctic, Biogeochemical cycles

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THE ESTUARINE AND MARINE BEHAVIOUR OF PLATINUM

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Abstract: Platinum is one the most economically important metal in the industrial sector. It is widely used in jewellery, biomedical devices, high temperature engineering (glass fibre, turbine engines), catalyst chemical process (ammonia oxidation), sensors (oxygen sensors engine), petrochemistry, automobile exhaust catalysts, hard disks, silicone manufacture and anticancer drugs (Johnson Matthey 2017). Hospital emissions (anticancer drugs) and automobile exhaust catalysts are considered the principal sources of platinum inside the aquatic environments. Here we report the analysis of samples from the Pontevedra Ria during two different periods, during 2008 and also during 2011. We found values ranging between 0.02-0.62 pM ($n=15$) with a detection limit of 0.02 pM obtaining $96\pm 4\%$ of recovery percent (Cobelo-García et al., 2013). We also analysed samples from the Gironde estuary (France) observing values of 0.35 ± 0.14 pM ($n=15$) during 2012 and 0.50 ± 0.06 pM ($n=11$) during 2013, working with a 0.02 pM of detection limit and obtaining a 80-95% of recovery percent (Cobelo-García et al., 2014). We found that platinum behaviour in both estuaries is non conservative. Besides we analysed samples ($n=59$) from the West Atlantic Ocean in three different profiles. Samples were collected during the Dutch GAO2 GEOTRACES cruise on board the R/V Pelagia in 2011 (-39.399°W , 47.801°N ; -40.8835°W , 7.7664°N ; -39.4425°W , $-35.00835^{\circ}\text{S}$). Values ranged from 0.11 to 0.37 pM, with an average value of 0.26 ± 0.06 pM. We found important contribution of the water mass system over our profiles, the water masses involved are North Atlantic Depth Water (NADW), the Antarctic Intermediate Water (AAIW), upper Circumpolar Deep Water (uCDW) and the Antarctic Bottom Water (AABW). Depth profiles showed a non-conservative behavior, in contrast with the only previous studies in the Atlantic waters which were reported more than two decades ago. Possible causes for these discrepancies are discussed (López-Sánchez et al., 2017).

Key words: estuaries, platinum behavior, no conservative, water mass

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COLOURED DISSOLVED ORGANIC MATTER IN THE CAPE VERDE FRONTAL ZONE (NW AFRICA)

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Abstract: The Cape Verde frontal zone (NW Africa) separates North and South Atlantic central waters. Furthermore, the interaction between the Mauritanian coastal upwelling system and the Cape Verde front produces the giant filament of Cap Blanc. This filament plays a key role in the export of biogenic organic matter from the coast to open ocean. During the FLUXES I cruise (12 July – 11 August, 2017) hydrographic and chemical data were recorded along a box embracing the Cap Blanc filament and the Cape Verde front. Here, we focus on the impact of the intricate hydrography of the area on the optical properties of dissolved organic matter (DOM). Water samples for DOM absorption spectra (CDOM) and fluorescence excitation-emission matrix (FDOM) determination were collected through the water column. Central waters at stations located south of the Cape Verde front presented lower salinity, 35.92 ± 0.10 , and dissolved oxygen, $54 \pm 2 \mu\text{M O}_2$, than at stations located north of the front (salinity, 35.42 ± 0.02 ; dissolved oxygen, $142 \pm 10 \mu\text{M O}_2$). These differences are due to the fact that stations south of the Cape Verde front are occupied by the hypoxic South Atlantic Central waters, compared to the stations north of the front, where the oxygenated North Atlantic Central waters prevail. These contrasting hydrographic characteristics produce an impact on the optical properties of DOM. Samples south of the Cape Verde front showed 44% more absorption at 340 nm, which is a proxy to aromaticity, and 17% more fluorescence intensity of the aromatic compounds that absorb at 340 nm, indicating that the quantum yield of fluorescence is less efficient in hypoxic waters. Our observations demonstrate that water masses drive the distribution of chromophoric and fluorescent organic matter in the Cape Verde frontal zone.

Key words: Cape Vert front, CDOM, FDOM, quantum yield

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EVOLUCIÓN DEL OXÍGENO DISUELTO EN LA ZONA DEL MÍNIMO DE OXÍGENO (OMZ) EN EL MEDITERRÁNEO OCCIDENTAL DURANTE LA ÚLTIMA DÉCADA

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Abstract: En el proyecto RADMED hemos medido el oxígeno disuelto ($\mu\text{mol/kg}$) en toda columna de agua, 4 veces al año, desde el año 2007 hasta el año 2016, en aproximadamente 80 estaciones de muestreo en el Mediterráneo Occidental. La zona del mínimo de oxígeno (OMZ) se encuentra alrededor de los 400 metros de profundidad identificada por su valor de oxígeno disuelto menor de $186 \mu\text{mol/kg}$. En esta zona se ha buscado el valor mínimo de oxígeno disuelto. Para este trabajo se ha utilizado la base de datos regionales IBAMar en donde hemos seleccionado 11 estaciones de muestreo que incluyen 101 perfiles. Estas estaciones tienen más de 300 metros de profundidad, y además del oxígeno disuelto, salinidad y temperatura, se ha analizado la estructura de la comunidad de fitoplancton en la zona fótica. La evolución a lo largo de estos últimos 10 años nos indica que el oxígeno disuelto en la OMZ ha aumentado desde el año 2007 ($\sim 158 \mu\text{mol/kg}$) hasta el año 2012 ($\sim 178 \mu\text{mol/kg}$) para estabilizarse a hasta el año 2016. Las causas de esta evolución se analizarán los datos disponibles.

Key words: Oxígeno disuelto, Zona del Mínimo de Oxígeno, Mar Mediterráneo

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TRANSPORT OF NUTRIENTS, CHLOROPHYLL AND SUSPENDED SOLIDS CONTENT AT THE ARADE LOW ESTUARY UNDER DRY WINTER CONDITIONS

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Abstract: The Arade Estuary is the second most important in southern Portugal, but little is known about its hydrodynamics, including the exchanges of matter content with the adjacent ocean. In this study, results from a tidal cycle survey performed on 10 January 2018 under dry winter conditions and intermediate tidal range (1.41 m) are reported. Current velocities were measured quasi-continuously with a shipborne ADCP along a (~270 m-long) fixed cross-channel transect at the lower estuary, together with hourly near bed and surface sampling of temperature, salinity, pH, O₂, suspended solids, nutrients and chlorophyll *a* at 3 stations along this cross-section (middle of the channel and margins). The surveyed area consists of a deep channel (~6 m) at east and a shallow area at west where current measurements at low tide were not possible. Results indicate that the water was vertically well-mixed through the tidal cycle, with a small contribution of freshwater to the salinity variability at the cross-section that was maximum around low water (ca. 15%). A global antiphase pattern of nutrients concentration with tidal height was observed, with a general decrease (increase) during the flood (ebb), except for an increase of ammonium and phosphate concentrations around high water. Additionally, spatial variability was observed for currents and suspended solids, chlorophyll *a* and nutrients. While the currents were stronger at the deeper channel the highest nutrients concentration were recorded in the opposite margin. This fact may reflect the impact of discharges from the sewage treatment plant upstream of the section. Flow residuals were seaward at the deep channel (due to larger ebb than flood velocities), and even during dry winter conditions still contribute to fertilize the coast. Moreover, this circulation seems to be counter-balanced by landward residuals at the western shallow area, providing a mean for efficient estuary/ocean exchanges.

Keywords: Arade estuary, transport, nutrients, suspended solids, chlorophyll *a*

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INORGANIC CHEMICAL OCEANOGRAPHY CAPABILITIES AND TIMES SERIES AT IEO A CORUÑA

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Abstract: times series to detect, quantify and explain any alteration on ocean biogeochemistry rely on sustained and quality controlled data. Slow science is dependent on sustained funding to build on three main pillars: equipment, consumables and manpower. Here we present the current capabilities for INOrganic Chemical oCEaNography in the IEO-A Coruña (INOCEN lab), showing the lab commitments associated with the environmental monitoring programs lead by IEO in Northern Spain (<http://www.seriestemporales-ieo.com/>), and both the strengths and weaknesses. The service for chemical oceanography in IEO A Coruña (SEROQUIÑA) ascribed to INOCEN lab is responsible for the inorganic nutrient analysis of RADIALES, also serving analysis for dissolved oxygen, salinity and CO₂ variables in some of them; and as advisor for any other IEO introducing those techniques. We present our current analytical capabilities along with the quality control procedures for each technique. Our responsibilities related to IEO time series (RADIALES Vigo, A Coruña, Cantábrico, RADPROF) and the strengths (sustained small budget, boss obstinacy, group support) and weaknesses (sampling and conservation logistics, lack of qualified technicians, administrative collapse) of our lab.

Key words: IEO time series, biogeochemistry, capability, weaknesses and strengths

Acknowledgments: RADIALES-20 structural IEO project and all the scientific and technical personnel involved.

CHARACTERIZATION OF ZOOXANTHELLAE LIVING IN SYMBIOSIS WITH THE JELLYFISH *COTYLORHIZA* *TUBERCULATA*

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Abstract: The symbiotic association between the zooxanthellae *Symbiodinium* sp. and its host jellyfish, the rhizostome scyphozoan *Cotylorhiza tuberculata* collected from the Mar Menor coastal lagoon, was investigated. Measurements were carried out in two different sections of the medusa body: oral arms and umbrella. Medusae carbon and nitrogen composition was higher in the oral arms section than the umbrella (4.5 and 3.7 respectively). No significant differences were found in the chlorophyll *a* content amongst the two sections, however, zooxanthellae density was higher in oral arms than umbrella tissue. A total of 13 different pigments were revealed by the High Performance Liquid Chromatography (HPLC) method, the most representative pigments were chlorophyll *a*, chlorophyll *c*₂ and peridinin, typical pigments of dinoflagellates. Cell diameter was significantly higher for zooxanthellae freshly isolated from the host (8.71 μm) than those maintained in culture (6.78 μm). The growth rate value for zooxanthellae in culture was 0.52 d⁻¹. Maximal photosynthetic rate was reached at 5.22 10⁻² mgC (mg chl-*a*)⁻¹h⁻¹. The absorption spectra of three tissue sections of the medusae umbrella were studied to know the spectral composition of the light field surrounding the symbiont, two absorption peaks of 270 and 330 nm were observed suggesting that medusae tissue protects the zooxanthellae from the negative effect of the high energetic ultraviolet radiation. The presence of a dense zooxanthellae population and the protection to UVR provided by medusae tissue maintaining zooxanthellae in optimal light conditions to photosynthesis may be a reason added to explain the population success of *Cotylorhiza tuberculata*.

Key words: jellyfish, zooxanthellae, symbiosis, pigments, absorbance.

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FEDDING BEHAVIOUR OF MUSSEL EXPOSED TO MICROPLASTICS

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Abstract: Filter feeding invertebrates, such as mussel, are especially susceptible target species to microplastic (MP) ingestion. Field and laboratory studies have reported that MP are ingested and retained by mussels. However, there exist a gap of knowledge on the feeding behavior of MPs by mussel. In this context, a laboratory experiment was conducted to investigate and track the uptake, egestion and accumulation of MP particles within tissues (digestive gland, gills and mantle) of the mussel, *Mytilus galloprovincialis*. To this end, individual mussels were exposed into 1-liter glass beakers to a single dose ($2 \text{ mm}^3 \text{ l}^{-1}$) of a heterogeneous mixture of non-uniform MP particles of oxidized high-density polyethylene (HDPE, Micro Powders Inc.). We investigated the uptake kinetic (0-60 minutes, ~acceptability) and the size-dependent ingestion of the MP particles and compare it with that of microalgae (*Isochrysis galbana*, clone t-ISO). The results showed that MP particles were effectively cleared (accepted) and taken up by mussels. We investigated the elimination (egestion) of MP particles by quantifying the volume (mm^3) and the size (μm) of the MP particles egested throughout faecal casts along an 11 days period. The results showed that the highest volume of MP particles was egested in the faeces produced in the first 24 hours after the exposure. We observed a size-dependent pattern distribution along time of the MP particles contained in faeces. Larger MP particles were eliminated in the first hours after the exposure, which may be related to the pre-ingestive and post-ingestive particle size selection mechanisms by mussel. We monitored the accumulation of MP particles in the digestive gland and gills. The evolution on the particle size distribution of the MP accumulated in faeces and digestive gland from the beginning to the end of the experiment allowed us to work out the feeding behavior of MP by mussel.

Key words: microplastic, mussel, feeding, accumulation, marine environment

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MICROPLASTICS IN MARINE SEDIMENTS FROM THE RÍAS BAIXAS (NW SPAIN).

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Abstract: The first time that plastics were reported in oceans was in the 1970s (Carpenter and Smith, 1972). Today plastic litter is ubiquitous in all marine environment around the world from the Arctic to the Antarctic (Browne et al., 2011). Microplastics (MPs) are synthetic polymers measuring less than 5 mm (Arthur et al., 2009). MPs have been recognized recently as an emerging pollutant in the marine environment (Law and Thompson, 2014). A recent estimation suggested there could be between 7000 and 35000 tons of plastic floating in the open ocean (Cózar et al., 2014).

The consequences of microplastics for marine biota and the environment are not clear yet, although the number of studies focusing on plastic litter in marine environment has been increasing during the last years (Gago et al., 2018). Some studies show that MPs can be ingested by marine organisms and therefore they enter the food chain. This causes bioaccumulation at higher trophic levels and could affect human health

Sediment samples were collected during SECON 16 cruise, using a box corer dredge in several points exposed to different anthropogenic activities pressures (fishing port, industrial port, UWWTP...). The studied area is the Rías Baixas, that are located to the NW of the Iberian Peninsula. The main aim of our study is to describe, analyse and quantify microplastic pollution in sediments of Rías Baixas. The methodology used to extract MPs is the density separation (Masura et al., 2015) with a hypersaline solution of NaCl (d~1.2g/L) and ZnCl₂ (d~1.7g/L). The supernatant is filtered with a vacuum pump and the filter is examined under a stereomicroscope, to identify microplastics based on shape, colour and size.

Keywords: marine debris, microplastics, sediments, pollution, NW Spain.

Acknowledgments: This study was done in the framework of BASEMAN and ESMAROS17 projects.

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SORPTION AND DESORPTION KINETICS OF MERCURY ONTO MICROALGAE AND MICROPLASTICS

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Abstract: The research about the sorption of metallic contaminants by microplastics (MPs) in the marine environment is limited. This is related to the fact that MPs are generally regarded to be relatively inert towards aqueous metals ions, contrarily to what occurs with organic contaminants. In this context, this work was aimed to investigate the kinetic of sorption and desorption of mercury (Hg) onto microalgae (MA) and MPs. The MP used was polyethylene (PE), which has been frequently found in the marine environment. Specifically, we used a virgin oxidized synthetic polymer powder of high density PE composed by a heterogeneous mixture of non-uniform particles (0-30 μm ; mean 10-15 μm). Mercury was selected as a model metal due to its high toxicity and potential to biomagnify through all the trophic levels of aquatic ecosystems. The MA *Isochrysis galbana* was used as a representative species of marine algae. The sorption experiments were carried out by incubating MA for 24 hours and MP for 7 days with Hg solutions (HgCl_2) in a ratio $1.5 \mu\text{g Hg}/1 \cdot 10^9 \mu\text{m}^3$ for MA, and $10 \mu\text{g Hg}/1 \cdot 10^9 \mu\text{m}^3$ ($\approx 1 \text{ mg}$) for MP. Then, the Hg was quantified in the supernatants after centrifuging at 3500 rpm for 5 minutes for MA, and in the MP powder, after filtering and drying it for MP. The results showed that Hg sorption rate was higher for MA than for MP. The maximum sorption of Hg onto MA ($1 \mu\text{g Hg}/1 \cdot 10^9 \mu\text{m}^3$) and onto MP particles ($0.6 \mu\text{g}/\text{mg}$) occurred after 24 hours and 7 days of incubation, respectively. The desorption of Hg from MA and from MP to seawater was investigated after re-suspending both types of Hg-loaded particles into clean seawater. Similarly to sorption, the desorption rate of Hg to seawater was higher for Hg-loaded particles of MA than for Hg-loaded particles of MP.

Key words: microplastic, heavy metals, marine environment, sorption, *Isochrysis galbana*

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EFFECTS OF TRICLOSAN AND ITS MIXED WITH MICROPLASTICS ON ACETYLCHOLINESTERASE PRESENT ON HEAD OF *SOLEA SENEGALENSIS*.

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Abstract:

In the last decades, different components from personal care products that contain plastic microbeads have arrived at aquatic ecosystems because these products are not biodegraded or removed in wastewater treatment plants. Thus, the aquatic organisms are exposed to complex mixtures of environmental contaminants as biocides and microplastics.

The goal of this work is the study of the effects of microplastics interaction with triclosan, a biocide, on juveniles of *Solea senegalensis*.

Creams commonly used and available in supermarkets of our area were used by these assays. The microspheres available in these samples were separated and characterized. The particles were identified by Fourier transform-infrared (FT-IR) spectroscopy using a PerkinElmer Spectrum 100. These microplastics were used in toxicity test.

The toxicity studies were carried out during 96 hours with continuous ventilation and water renewal every 24 hours, at a temperature of 19-20°C and under 12h light/12h dark exposure. The juveniles of *Solea senegalensis* (weight 3.39 ±0.56 g) were exposed to five nominal concentrations of triclosan (0.1—0.5 mg/l), three concentrations on this compound mixed with microplastics (triclosan: 0.1-0.2-0.3 mg/l; microplastics: 0.150 mg/l), microplastics alone (0.150 mg/l), plus an untreated control and a solvent control (acetone). In these assays, not mortality was observed on juveniles with both compounds and their mixtures.

Cholinesterases (ChE) have been used as specific biomarkers to diagnose exposure of natural populations to organophosphates pesticides. In general, there are two type of ChE presented in fish, acetylcholinesterase (AChE) and butyrylcholinesterase (BChE). The AChE was analyzed on the head homogenate of juveniles, after this crude was inhibited with

iso-OMPA, which is a specific inhibitor of BChE. The results showed that there was not inhibition activity in the head of *Solea senegalensis* in presence of triclosan and its mixture with microplastics.

Key words: Microplastics, Toxicity, Triclosan, Acetylcholinesterase, *Solea Senegalensis*

Acknowledgements: Authors are grateful to the Laboratory of Marine Culture at University of Cádiz for providing the experimental fish used in this study. This work was supported by University of Cadiz (Pr2017-008) and in part by the Andalusian Plan for Research, Development and Innovation (PAIDI group: RNM-345 and TEP-181).

CHARACTERIZATION AND BEHAVIOUR OF NANOPLASTICS IN FRESHWATER, SEAWATER AND HEMOLYMPH SERUM AND THEIR RELATION WITH IMMUNE RESPONSES IN THE MUSSEL MYTILUS SP.

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Abstract: Plastics are present in a wide number of objects: toys, cosmetics, good sports, textiles, etc. Their occurrence has been reported in the marine environment (e.g. coastal areas, open sea, rivers, sediment and marine organisms). The degradation of these materials leads to plastics nanoscale level; they are lower to 1µm and imperceptible to the human eye even with optical microscope. Due to small size of nanoplastics, they can be accumulated by marine organisms and they can trigger effects to cellular and molecular levels; however few data are available about its behaviour in aquatic environment and biological fluids as well as the impact on marine organisms. The bivalve *Mytilus sp* has been proven as a suitable model invertebrate for assessing the potential effect of nanoparticles (NPs) in the marine environment. Furthermore, the immune system of mussels is a sensitive system for different NPs types. Due to growing concern about nanoplastics, the goal of this work was to study i) the behaviour over time of nanoplastics of polystyrene the range of size: (0.05 - 1 µm) in different media; (ultrapure water, artificial marine water and haemolymph serum); ii) to establish the relation of nanoplastic size with effects in immune cells and iii) bioaccumulation in haemocytes of *Mytilus sp*. The results of this work have shown that size distribution and zeta potential of nanoplastics depending on environment characteristics, showing lower aggregation in serum haemolymph respect to ultrapure water and artificial marine water. This behaviour of nanoplastics is related to its interaction with cells and can modulate their toxicity and stress responses of haemocyte cells.

Key words: haemocytes, nanoplastic, mussel, toxicity

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ESTIMATION OF MICROPLASTIC PARTICLES DISCHARGED INTO THE MARINE ENVIRONMENT BY WASTEWATER TREATMENT PLANT (WWTP) IN SOUTHERN SPAIN

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Abstract:

Microplastics (MPs) are particles less than five millimetres in size that deteriorate from larger plastic pieces that have entered the oceans. The issue with them has recently come into light due to the use of plastic microbeads in personal care products such as exfoliating shower gel, toothpaste, and makeup, which all wash down the drain and coming mainly from urban wastewater. Most of wastewater treatment plants (WWTPs) receive a significant amount of MPs, which are partly transferred and retained in the sewage sludge and the other fraction flows downstream WWTPs without any structural modification. This fact leads us to consider WWTPs as a common pathway of microplastics to the oceans (Talvitie *et al.*, 2015).

In this work, an estimate of the number of MPs discharged by the coastal municipalities of the province of Cádiz is made taking into account the annual volume of discharge (m³), the % of remove of the treatment plants (according to official data from the Regional Government of Andalusia) and bibliographic data (Dyachenko, *et al.*, 2017; Murphy *et al.*, 2016; Magnusson & Noren, 2014; Carr *et al.*, 2016; Dris *et al.*, 2015).

Also an extraction method was adapted from the National oceanic and Atmospheric Administration's (NOAA) protocol based on Catalytic Wet Peroxidation Oxidation (CWPO), and the particles were identified by Fourier transform-infrared (FT-IR) spectroscopy using a PerkinElmer Spectrum 100. For this purpose, influent and effluent samples from a representative wastewater treatment Plant (WWTP) from Cadiz province are collected over a stack of four 20 cm diameter stainless steel sieves (VWR) of various mesh

sizes: 5 mm, 1 mm, 0.355 mm and 0.100 mm. The results are described according to the size, color and type of microparticles that spectrum provide.

Preliminary studies revealed a discharge of approximately $2.4 \cdot 10^{11}$ MPs currently reaching the marine environment by 14 coastal cities (province of Cádiz) with an annual discharge of about 65 million cubic meters and the composition was mainly polyethylene and butyl stearate.

Key words: Microplastic identification, Treated waste water, FT-IR spectroscopy, marine litter

Acknowledgements: This work has been supported by University of Cadiz (Preparación Proyecto Puente- Pr2017-008) and in part by the Andalusian Plan for Research, Development and Innovation (PAIDI group: RNM-345 and TEP-181).

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POTENTIAL TRANSFER OF ORGANIC POLLUTANTS FROM LITTORAL PLASTICS DEBRIS TO THE MARINE ENVIRONMENT

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Abstract: Plastic polymers act as passive samplers in air system and concentrate hydrophobic organic contaminants by sorption or specific interactions, which can be transported to other systems such as the marine environment. In this study plastic debris was sampled in the surrounding area of a Mediterranean lagoon in order to determine the concentration of persistent and emerging organic contaminants. More specifically, desorption of 91 regulated and emerging organic contaminants (polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorinated pesticides, current-use pesticides, personal care products, other pesticides and plastic additives) was characterized for the first 24 h from different polymers to seawater and the remaining content of these contaminants was also extracted by ultrasonic extraction with methanol. All samples were analyzed by Stir Bar Sorptive Extraction coupled to GC/MS. A significant fraction of sorbed contaminants in polymers was desorbed in the first 24 h, particularly for triazines and organophosphorus pesticides due to their lower hydrophobicity than other considered analytes. The remaining contaminants contained in plastics can be also transferred to seawater, sediments or biota. Considering 24 h desorbed fraction plus the remaining methanol extracted fraction, the highest transfer levels corresponded to personal care products, plastic additives, current-use pesticides and PAHs. This is the first study to show the relevance of the transport of organic contaminants on plastic debris from littoral areas to the marine environment.

Key words: Regulated and emerging contaminants; desorption; seawater; littoral plastics; potential transfer; marine environment

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EXTRACTION AND PRECONCENTRATION OF PERSISTENT ORGANIC POLLUTION (POPS) FROM MARINE SEDIMENTS WITH SOLID PHASE EXTRACTION (SPE)

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Abstract: Due to anthropogenic activities and its ubiquity, persistent organic pollutants (POPs) are present at marine environment and especially at marine sediments (Jones and de Voogt, 1999; Lara-Martin *et al.*, 2005; Neves *et al.*, 2018). There are different optimized extraction methods of POPs determination on sediments (Björklund *et al.*, 2000; Basheer, Obbard and Lee, 2005), but in many cases it is necessary to combine them with a preconcentration phase to be able to determinate contaminants at real samples at trace concentrations. In this study we have optimized POPs extraction from sediment and its preconcentration using solid phase extraction (SPE), with a subsequent analysis by gas chromatography with mass detection (GC-MS).

The optimization of the methodology gave as optimal conditions, the use 15 mL of methanol as extractant for 10 grams of sediments with the help of an ultrasound bath. This extract is diluted in a proportion 1/10 in Mill-Q water and passed through a SPE ENVI-18 cartridge (Supelco®). Desorption was made with n-hexane for the determination by gas chromatography with mass detection (GC-MS).

The method was applied to samples collected at different beaches at Gran Canaria island (Canary Islands, Spain).

Key words: Marine sediments, Solid Phase Extraction (SPE), Persistent organic pollutants (POPs), preconcentration.

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ASSESSMENT OF ORGANIC POLLUTANTS IN *PERSISTISTROMBUS LATUS* (GMELIN, 1791) AND MARINE SEDIMENTS FROM THE COASTAL ENVIRONMENTAL AREAS OF CAPE VERDE, WEST AFRICA

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Abstract: The coastal areas of Cape Verde are impacted by an increasing human activity, playing an important role in the sustainable economic growth. Hence, there is a necessity of implementing an environmental monitoring program in Cabo Verde in order to control the pollution of persistent organic contaminants such as organochlorine pesticides, polychlorinated biphenyls (PCB's) and polycyclic aromatic hydrocarbons (PAH). Because of the absence of bivalves used in the monitoring programs of the north Atlantic coast, It is proposed the use of the mollusk *Persististrombus latus* as an indicator organism of contamination, due to its wide spread and low mobility. The samples of *P.latus* and sediments were collected through diving in seven sites in Cabo Verde, on the islands of Santo Antão, São Vicente, São Nicolau, Sal, Santiago and Fogo. The digestive gland and the muscle tissue were separated in *P. latus* for analysis and all organic pollutants were determined by using gas chromatography coupled to a mass spectrometry detector. High concentrations of heptachlor, superior of 185.8 ng/g, were observed on the digestive gland of *P. latus* from Santo Antão, São Vicente and Sal islands. Concentration superior of 61.9 ng/g of dieldrin were observed on the digestive gland of *P. latus* from São Vicente and Sal Island. High concentrations of low molecular weight PAH were observed in sediments of the marina area of São Vicente Island. Relationships between concentrations of metals in sediment and *P.latus* samples were established in order to assess the suitability of *P.latus* as sentinel organisms. For that purpose bioaccumulation factors were calculated and results were compared with reference values, for sediments or another marine organisms, such as those reported by Long *et. al* (1995) and Macdonald *et. al.* (1996). According to the present study, *P.latus* can be used as a contamination indicator by organic pollutants in the coastal system of Cabo Verde and West Africa because of its wide spread and the ability to concentrate metals in its tissues with greater accumulation in the tissues of the digestive gland. Results of this study show a local contamination source due to marine activities in the Marina area and a source due to the agricultural activities.

Key words: *Persististrombus latus*, Organochlorine pesticides, PCBs, PAHs, Cabo Verde

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POLLUTANTS IN SANTANDER BAY SEDIMENTS

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Abstract: Surface sediment samples were taken in Santander Bay by means of a box-core. The samples were distributed along a transect covering from the most inner part of the Bay to the platform area nearby. A whole core of pollutants were analysed in the sediments: metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs). Besides, both grain size and TOC (total organic carbon) were determined to define the sediment type. The methods used for analyses are described elsewhere (Gonzalez-Quijano and Fumega, 1996; Quelle et al., 2011; Viñas Diéguez et al., 2002) and they are under a QA/QC system that guarantees the quality of the results. A gradient is clearly observed with higher values for most of the pollutants in the inner part of the bay that quickly decreases as we move outwards to the open sea. The values were compared with those environmental assessment criteria available, some of the sampling sites in the inner part of the bay exceed the ERL but the middle and outer area are near or below the BAC.

Keywords: sediment, metals, organic pollutants, environmental assessment.

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OCCURRENCE AND DISTRIBUTION OF PHARMACEUTICALS, PERSONAL CARE PRODUCTS AND CURRENT-USE PESTICIDES IN VIGO ESTUARY AND MAR MENOR LAGOON

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Abstract: The spatial and seasonal distribution of pharmaceuticals and personal care products (PPCPs) and current-use pesticides (CUPs) were characterized in surface seawater and sediments from the Vigo estuary and the Mar Menor lagoon during spring and autumn 2015. PPCPs and CUPs were found in seawater and sediments from both Spanish coastal areas. Fragrances were found in all seawater samples showing their amply distribution in both coastal areas. Triazines (prometryn and terbuthylazine) and insect repellents (icaridin) were detected in all Mar Menor seawater samples. In the case of sediments, 9 triazines, 5 acidic herbicides, 8 organophosphorus pesticides, 7 additional pesticides, 2 UV-filters, 7 pharmaceuticals, 4 synthetic musks, 2 insect repellents, the antimicrobial agent triclosan and one of its biodegradation intermediates triclosan-methyl were detected in some of the studied areas. The highest mean concentrations in sediments were found for PPCPs in spring in both areas of study, with a maximum concentration close to 60 ng g⁻¹ d.w., being the main contributor the pharmaceutical ketoprofen. Attending to the results of this study four different sources of contaminants were identified the first source related to urban and tourism, the second one associated with agriculture and gardening activities, the third related to human and veterinary pharmaceuticals applications and the last one to the specific use of acidic herbicides.

Key words: Pharmaceuticals, synthetic musks, UV-filters, fragrances, current-use pesticides, seawater and sediment, distribution, coastal areas

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BIOACCUMULATION OF PHARMACEUTICAL COMPOUNDS IN CLAMS (*RUDITAPES DECUSSATUS*) TRANSPOSED TO AN AREA INFLUENCED BY TREATED URBAN WASTEWATER DISCHARGES, IN THE RIA FORMOSA LAGOON

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Abstract: Pharmaceutical compounds (PhCs) are emerging contaminants of environmental-health concern that, if not controlled in Wastewater Treatment Plants (WWTPs), could adversely affect the aquatic environment and surrounding biota. Among other objectives, LIFE Impetus project - Improving current barriers for controlling pharmaceutical compounds in urban wastewater treatment plants - includes studies of PhC bioaccumulation in clams. This communication presents the preliminary data of PhC bioaccumulation in clams *Ruditapes decussatus* exposed to realistic conditions in an area influenced by discharges from a nearby WWTP, in the Ria Formosa Lagoon. This lagoon accounts for *ca.* 90% of the clams' national production. Clams taken from a relatively clean site (control) were exposed, at four different sites, along a spatial gradient of dilution of the discharged effluents (down to 1.5 km), during 1 summer month (June-July 2016). This corresponds to a period of increased anthropogenic touristic pressure in Ria Formosa and also to an enlarged clam consumption. After depuration (*ca.* 24 h), clam extracts ($n \geq 8$), along with water from the sites where clams were collected, were analysed in duplicate, by QuEChERS-LC-MS/MS, for 24 target PhCs. Preliminary results show the difficulty in finding pristine places regarding PhCs since residues of some of these compounds were found in the control. Even so, concentrations of PhC compounds in the clams can be considered low (in the ng/g range). The most abundant PhC in clams was caffeine, increased relatively to the control, depicting a relatively similar pattern in the water from the collection sites. However, in the water the most abundant PhC was diclofenac. Spatially, there was a general decrease of caffeine along the dilution gradient of the effluents, although this was not so evident at the farthest sampling site. This can be associated with external sources of this PhC, due to the closeness of that site to Faro city, the most populated in the region.

Key words: pharmaceuticals, WWTP, clams, Ria Formosa

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EXPERIMENTAL SETUP SYSTEM FOR ASSESSING SINGLE AND MIXTURES OF POLLUTANTS IN MARINE ENVIRONMENT

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Abstract: The risk of pollutants is carried out in systems with single species, frequently. In order to get more environmental relevance, we have proposed a complex system, with several organisms representing different levels of the food web. The objective is to improve the knowledge of the effect of pollutant as single or mixture of pollutants in more real scenarios and to avoid the use of mesocosms, because they are affected by high uncertainty and logistic difficulties which make very complicated, in many cases, their implementation and the interpretation of results. The experiment setup is composed for methacrylate tanks (40 L) with natural seawater and sediment in a ratio 3:1, subjected at photoperiod 12:12, with aeration and temperature (20°C) under control, for 7 days. The system includes: marine microalgae species (*Phaeodactylum tricorutum* and *Nannochloropsis gaditana*), brine shrimp (*Artemia franciscana*) and clams (*Scrobicularia plana*). Samples for microbiome analysis are collected from sediment and water compartments. The selected concentrations were 5 and 50 $\mu\text{g}\cdot\text{L}^{-1}$. Samples were collected at different times (0, 2 and 7 days) to know the behaviour of metals and stress responses of microalgae. Endpoints such as growth, intracellular reactive oxygen, effective quantum yield of photosystem II and membrane permeability in microalgae and antioxidant enzyme activities in the clams were measured. Also samples of microbiome of water and sediment were collected at the end of the experiment. The experimental setup have shown to be reliable and useful for testing single and mixture of pollutants. This approach allow to improve the understanding of interactions between pollutants and species at different food web levels.

Key words: complex systems, pollutants, mixture, endpoints toxicity

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ARE Pb SEDIMENT CONTENTS IN THE RIA OF VIGO DOCUMENTING THE CERAMIC'S FACTORY CLOSURE AND THE UNLEADED FUEL USE?

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Abstract: The contents of Pb and Al were determined in fifty-one surface sediments collected in three sectors of the Ria of Vigo using a Van-Veen grab during two monitoring surveys in 1999 and 2005. After an acid decomposition of c.a. 100mg of sediment with HF and Aqua Regia, the total content of Pb and Al were measured by ICP-MS and FAAS, respectively. The main objective is to assess spatial distributions and temporal trends of contents of Pb and Al. Both sampling years have a similar spatial distribution for Pb and Al, with the low contents found in the outer area. The highest median contents of Al were obtained in the intermediate area, while the inner area is characterized by the highest total and median contents of Pb found in the vicinities of the inactive ceramic factory since 2001. The contents of Al in the outer area was statistically significantly lower than in the intermediate and inner areas, while there was no statistically significant difference between the inner and intermediate areas. Meanwhile, the contents of Pb in each sampling year were statistically significant different among the three areas.

The temporal trend of the median content of Pb for the outer area does not reveal variation. Meanwhile, the contents of Pb between the two sampling years in the two most inner areas are not statistically significantly different, despite the decrease of median contents. A possible explanation is associated with local hydrodynamic, responsible for the resuspension of deposited contaminated sediments. As a result, the contents of Pb are kept relatively constant or showing a slight reduction although the past and dominant Pb anthropogenic sources (e.g., ceramic factory, leaded gasoline, coal combustion) stopped or decreased. This may reflect the legacy of the historical contamination in the environment and its maintenance for many years.

Key words: Ria of Vigo, sediments, Pb contamination

SPATIAL DISTRIBUTION OF PLATINUM AND RHODIUM IN SUPERFICIAL SEDIMENTS FROM TAGUS ESTUARY

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Abstract: Platinum-group elements (PGE), in which (Pt) and rhodium (Rh) are included, are widely used in a variety of technology-based industries. Thus, PGE are emergent contaminants in the environment, potentially bioavailable and posing hazardous impacts. Despite being well characterised in urban environments, Pt and Rh remain poorly understood in aquatic systems. In this study, Pt and Rh concentrations quantified in 72 superficial sediment samples from Tagus estuary were spatially resolved to assess their sources and pathways within the estuary. Both elements were simultaneously quantified by Adsorptive Cathodic Stripping Voltammetry. Master environmental parameters were also determined to better understand metal variability. Concentrations of Pt and Rh ranged 0.18 – 5.1 ng Pt g⁻¹ and 0.019 – 1.5 ng Rh g⁻¹. According to the spatial distribution of both elements, four distinct PGE areas are discussed: industrialised, motorway bridges, waste- (WWTP) and pluvial discharges and ‘PGE-clean’ areas. Two main origins of Pt and Rh to the Tagus estuary were addressed: historical and present day industrial activities and automotive catalytic converters (ACC). Significant correlations were found for Pt with Al, Fe, Mg and LOI contents, while for Rh no relationships were found. This dissimilar behaviour suggests a differentiate reactivity of both elements. Besides a large dilution effect in the estuary, hydrodynamics (mesotidal) coupled with other physical mechanisms may be the dominant factors driving the transport of Pt and Rh in Tagus estuary.

Key words: platinum and rhodium, sediments, spatial distribution, Tagus estuary

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TRACE METAL BIOACCUMULATION IN THE GUADALQUIVIR ESTUARY FOOD WEB

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Abstract: Trace metal bioaccumulation and biotransfer from lower (zooplankton and suprabenthos) to upper trophic levels (nekton) in an estuarine food web have been studied in the Guadalquivir estuary. Trace metal (Fe, Al, Sr, Zn, Cu, Mn, Ba, Ga, B, As, Ni, Pb, Cr, V, Zr, Co, Cd, Mo, Ag, Bi and Ti) concentrations were measured in tissues from fish *Pomatoschistus* spp. (estuarine) and *Engraulis encrasicolus* (marine), decapods *Palaemon longirostris* (estuarine) and *Crangon crangon* (marine), mysids (500- μ m size fraction) and copepods (200- μ m size fraction) caught at two sampling stations, located at 8 (oligohaline) and 32 (polyhaline) km from the river mouth. High trace metal concentrations were found in estuarine species, particularly in lower trophic levels. Nevertheless, no biomagnification from preys (copepods and mysids) to predators (fish and decapods) were observed except for Ag and As. In fact, lower trophic levels showed concentrations around 20 times higher for Al, Fe, Ni, Pb and Cr than found in marine and estuarine species of fish and decapods. Trace metal concentrations showed significant differences among species ($R = 0.90$; $P < 0.001$) and functional groups ($R = 0.71$; $P < 0.001$). However, there were no spatial differences between the upper and the downer stations ($R = 0.01$; $P > 0.05$). In summary, trace metal bioaccumulation seems to be specific for each taxonomic group and/or trophic level. However, higher bioaccumulation seems to occur at lower trophic levels, which does not appear to biomagnify at the following trophic levels.

Key words: biogeochemical cycles, estuaries, nekton, suprabenthos, zooplankton

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HIGH RESOLUTION XRF ANALYSIS IN THE CACTI OF THE UNIVERSITY OF VIGO

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Abstract: The Scientific and Technological Research Assistance Centre (CACTI) of the University of Vigo has a facility dedicated to high resolution X-ray fluorescence (XRF) analysis of marine and estuarine samples, mainly split-cores, since 2012. Samples are analysed in an ITRAX core scanner, which allows obtaining high-resolution compositional data by EDXRF analysis (both qualitative and semi-quantitative), and, in addition, high resolution digital and radiographic images (Croudace et al., 2006). The analysis of Magnetic Susceptibility (MS) is also available since 2013. Since the opening of this service in the University, it has been analysed more than 250 m of sedimentary record from the Iberian coast, from estuarine areas to the continental shelf. It allows studying environmental changes, either natural or anthropogenic, at different time-scales (Plaza-Morlote et al., 2017; Álvarez-Iglesias et al., 2016). Sampling resolution can be down to 0.2 mm, although the stepsize of 2.0-5.0 mm is usually selected for XRF analysis. Counting times, depending on the elements of interest, have been usually 10-20 seconds, related to the capabilities of the XRF SiDD detector of the equipment (maximum counts in this case: 35,000). Two different anodes can be selected for XRF analysis, the Molybdenum tube and the Chromium tube, the Cr tube being selected for improving the detection of light elements. Elements present in the sample at trace quantities, such as REE or harmful elements, can be quantified selecting appropriate counting times. When using appropriate reference materials data are also validated. The potential of this equipment is illustrated by different examples considering different working conditions. Tests performed for improving element quantification by using different certified reference materials and discrete samples are also presented.

Key words: high-resolution analyses, EDXRF, marine sediments

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