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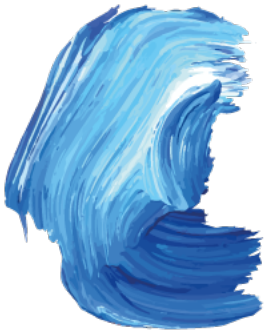

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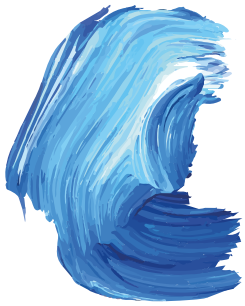

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INNOVATIVE MODULAR SENSING SYSTEMS FOR AUTONOMOUS IN SITU MONITORING OF TRACE METALS, NUTRIENTS, SPECIES RELEVANT TO THE CARBON CYCLE, AND POTENTIALLY HARMFUL ALGAE

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Abstract: The oceans have a huge impact on our daily lives. They play an integral role in the Earth's climate and weather. The marine ecosystems are also vital to the livelihood and food security of billions of people around the world, and to the economic prosperity of most countries. Marine environments, including organisms, are vulnerable and influenced by a wide diversity of anthropogenic and natural substances that may have adverse effects on the ecosystem equilibrium, living resources and, ultimately human health. Identification of relevant types of hazards at the appropriate temporal and spatial scale is thus crucial to detect their sources, to understand the processes governing their magnitude and distribution, and ultimately to evaluate and manage their risks and consequences to maintain marine biodiversity and prevent economic losses.

Nowadays, monitoring approaches involve the use of submersible sensing devices providing capability for in situ, long-term and frequent analysis. However, the commercial availability of field deployable sensors and sensing devices is still limited, and most of these tools tend to be too large, expensive, and power-hungry, thus preventing their widespread use.

Current research and developments focus on more robust, easily usable, cost effective multifunctional autonomous sensing tools that provide reliable in-situ measurements of key parameters. In order to reach these objectives, involved institutions have to tackle technical and analytical challenges. This will be illustrated by the presentation of compact, low power consumption, multichannel submersible probes recently developed for autonomous in situ monitoring of trace metals, nutrients, species relevant to the carbon cycle, and harmful algae. Potential of these devices will be demonstrated by examples of in situ measurements performed in marine coastal area characterized by contrasting conditions.

Key words: In situ sensing probes; Autonomous monitoring; Trace metals; Carbonate; pH; CO_2; (Harmful) algae.

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References: www.schema-ocean.eu

ESTUARIES AND THE RIVERINE INPUT OF GEOGENIC RARE EARTH ELEMENTS AND ANTHROPOGENIC GADOLINIUM INTO SEAWATER

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Abstract: Over the past two decades, the REE have turned from a group of "exotic" trace elements used as geochemical proxies to "critical" and "strategic" resources, and became the darlings of journalists, politicians and investors. Besides the complexity and scale of REE deposists, secure REE supply is a challenge, because world production is strongly dominated by China as the single producer. Individual REE have very specific applications and have become essential for many high-technology processes and products, ranging from wind turbines and electromobility to petroleum refining and medical imaging. Along with increased usage, however, came an increasing release of REE into the environment. Thus, the current REE inventory of Earth's surface environment is often composed of a mix of geogenic REE and anthropogenically introduced REE. While (micro)contamination with an individual REE can easily be recognized by positive anomalies in normalized REE distribution patterns, this is often difficult if the (micro)contaminant is a natural substance. In this case, however, additional Nd isotope data can be useful, as anthropogenic REE are usually derived from the Bayan Obo REE deposit in China, which is characterized by a specific Nd isotope signature.
Depending on the composition of the nanoparticulate and colloidal load of river waters, the transfer of riverine REE into seawater may be significantly different, which will be discussed showing results from experiments with tropical and arctic rivers aiming at simulating estuarine mixing. The observation of widespread (micro)contamination of river waters by anthropogenic REE and the presence of anthropogenic REE in coastal seawater suggest that, in marked contrast to the geogenic REE, at least a certain fraction of anthropogenic REY is not particle-reactive and not trapped in estuaries by removal during freshwater-saltwater mixing. This will be exemplified by the behaviour of anthropogenic Gd relative to geogenic REE during estuarine mixing.

METALS IN MICROPLASTICS AND THEIR POTENTIAL IMPACTS ON ESTUARINE AND COASTAL BIOGEOCHEMICAL CYCLES

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Abstract: Manufactured plastics are often impregnated with metallic additives or contain traces of metallic residues. Historically, many of these additives contained restricted and harmful metals and metalloids, like mercury, cadmium, antimony, chromium (VI) and lead, and although these metals have since been banned or phased out, the recycling of goods has ensured that they remain dispersed in contemporary plastic goods. Measurements of marine and coastal microplastics collected from various beaches in southwest England reveal high concentrations of metals in many samples; specifically, concentrations of Cd and Pb of up to 5,000 μg g^{-1} and 50,000 μg g^{-1}, respectively, are encountered in brightly coloured fragments and concentrations of Sb of up to 20,000 μg $g^{-1}$are found in many neutrally coloured plastics. The occurrence of Cd and Pb is attributed to the historical use of lead chromate and cadmium sulphide pigments, and the presence of antimony is attributed to its pervasive use as a flame retardant synergist in electronic plastics. Given that corresponding natural background concentrations in sediment are orders of magnitude lower, small quantities of microplastic are able to readily contaminate sediment with hazardous metals. Samples of microplastic subjected to simulated digestive conditions encountered in seabirds and invertebrates reveal bioaccessibilities in some cases that exceed 10% of the total metal content, suggesting that plastic additives and residues may be highly mobile under specific but realistic conditions. With these observations, the potential role of microplastics in metal biogeochemical cycles in estuarine and coastal environments is discussed.

Key words: microplastics, biogeochemistry, cadmium, lead, antimony

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LONG-TERM SUBSURFACE DISSOLVED OXYGEN TREND IN THE NW IBERIAN COASTAL UPWELLING SYSTEM (NE ATLANTIC ITLE OF THE COMMUNICATION

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Abstract: This study aims to analyze long-term dissolved O2 (DO) trend in the NW Iberian coastal upwelling system in order to better understand physical and biological processes affecting biogeochemical characteristics of the subsurface Eastern North Atlantic Central Waters (ENACW). A high-quality 43 yr (1970-2013) data set collected at the 27.1 isopycnal level (representative of ENACW) from an area between 41º-43ºN and 9º-11ºW was analyzed.
Since the seventies, subsurface DO levels declined with a rate of 0.39 µmol O2 Kg-1 yr-1 despite no sustained decrease trend through time was registered for temperature and salinity. DO tendency to drop ran in parallel with significant increments of both sea surface temperature (SST) and subsurface apparent oxygen utilization (AOU) annual means, pointing to the increase in the subsurface waters residence time as responsible for the deoxygenation processes registered in the study area. Moreover, natural decadal variability of both thermohaline properties and DO annual mean concentrations at the ENACW isopycnal level agreed with changes in the North Atlantic Oscillation (NAO) index. In this regard, we can state that overprinted to the last 40-yr DO decreasing trend observed in the NW Iberian coastal upwelling system, natural subsurface waters oxygenation may have occurred when high positive NAO phases promote the strengthening and eastward expansion of the subpolar gyre, bringing cooler and more oxygenated conditions to the study area.

Key words: deoxygenation, Eastern North Atlantic Central Water, Coastal upwelling, NE Atlantic

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DISSOLVED OXYGEN DYNAMICS IN RIA FORMOSA LAGOON - AN *IN SITU* HIGH RESOLUTION MONITORING APPROACH

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Abstract: Coastal lagoons are tightly interlinked ecosystem between the land-ocean interfaces where complex interactions of physical-chemical-biological-geological parameters occur over a variety of scales. This highlights the need of conducting observations at appropriate or relevant spatial and temporal resolution, ranging from short to large scales. In this context, the deployment of *in situ* sensors for measurements of biogeochemical parameters is helping a lot the knowledge and understanding of the functioning of coastal systems. This is the case of Ria Formosa lagoon, the most important coastal system in the south coast of Portugal and a productive ecosystem highly valuable in terms of ecological and socio-economical viewpoint, representing the most important national center of bivalves. Within the scope of UBEST project (PTDC/AAG-MAA/6899/2014) an EXO-2 multiparameter sonde (YSI) was deployed on a real-time monitoring station, as part of an observatory, installed in an inner area representative of a water body (WB2). This sonde is acquiring temperature, salinity, pH, dissolved oxygen, chlorophyll-*a* and turbidity data continuously for almost 2 years since May 2017. Sensors have been checked and calibrated every month with specific standard solutions. The acquired data and particularly those of dissolved oxygen, represent a benefit, allowing to look at complex issues and questions, traditionally difficult to address, since conventional campaigns cannot cover such a high sampling frequency and long period. This is a key water quality parameter showing how this ecosystem behave in terms of photosynthesis *vs*. respiration, its metabolism along different temporal scales: semidiurnal and fortnightly tides, daily, seasonally, interanually and in response to oceanographic/meterorological mesoscale conditions. This study aims to demonstrate how dissolved oxygen, in this inner area of Ria Formosa, is highly variable in time (*ca.* 30- 125%). It reflects short to long term time scales, highlighting the relevance of conducting high temporal *in situ*/online observations to better understand its functioning.

Key words: Ria Formosa, online data acquisition, deployment of *in situ* sensors, coastal lagoons

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METHANE DISTRIBUTION IN THE ELBE ESTUARY WITH HIGH SPATIAL RESOLUTION

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Abstract: Rivers are suspected to be a main source of greenhouse gases (methane and carbon dioxide) for coastal seas, while the role of the interjacent tidal flats is still ambiguous. In this study we investigated the role of the river Elbe and the Elbe estuary as source of methane to the North Sea. With high spatial resolution by an underway degassing system and subsequent analysis by cavity ring down spectroscopy a high resolution picture of the methane distribution in surface waters and hydrographic parameters was obtained in autumn to spring 2018/19. For most areas, riverine methane was simply diluted by seawater, overlain by a strong tidal influence. However at several occasions unexpected high methane concentrations were observed. By further detailed analysis we will elucidate the role of riverine versus tidal impact on the methane flux from the coastal North Sea.

Key words: methane, surface water, River Elbe, North Sea, tidal impact

EMISSIONS OF CO_2, CH_4, AND N_2O IN THREE ESTUARIES OF THE SOUTHERN IBERIAN ATLANTIC BASIN

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Abstract: The partial pressure of CO_2 (pCO_2) and the concentration of dissolved CH_4 and N_2O have been studied in three estuaries of the southern Iberian Atlantic basin: Guadalquivir, Tinto - Odiel and Guadiana during July 2017. Moreover, a second sampling has been made in March - April 2018 in Guadalquivir estuary in extreme rainy conditions. Two different types of sampling were carried out for each estuary: a longitudinal sampling across the river and a tidal cycle sampling of 24 h in the mouth of the estuary. In general, in the three systems there is an increase in the concentration of gases toward the inner part of the river, behaviour observed in other estuaries (Harley et al., 2015; Sturm et al., 2016; Burgos et al., 2018). Also, daily variations coupled to the tidal cycles in the three systems were observed. The highest concentrations were measured during ebb, which suggest that the estuaries export CO_2, CH_4 and N_2O to the Gulf of Cádiz. The three gases show the highest values and ranges of variation in the Guadalquivir (pCO_2: 381.7 – 6059.2 µatm, CH_4: 4.9 - 441.9 nM, N_2O: 7.2 - 101.6 nM) followed by Guadiana (pCO_2: 379.9 – 1413.8 µatm, CH_4: 9.3 - 287.9 nM, N_2O: 6.5 - 9.1 nM) and Tinto and Odiel (pCO_2: 349.5 – 1232.5 µatm, CH_4: 8.0 - 194.3 nM, N_2O: 6.0 - 7.3 nM). In addition, seasonal variations were observed in the Guadalquivir estuary between July 2017 (pCO_2: 917.5 ± 485.8 µatm, CH_4: 54.1 ± 74.5 nM, N_2O: 14.1 ± 16.1 nM) and March and April 2018 (pCO_2: 835.3 ± 250.0 µatm, CH_4: 17.9 ± 20.2 nM, N_2O: 22.2 ± 12.3 nM). The water - atmosphere fluxes of the pCO_2, CH_4 and N_2O are positive, showing that the study area acts as a source of these gases to the atmosphere.

Key words: Greenhouse gases, water - atmosphere fluxes, estuaries, Southern Iberian Atlantic basin.

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COLORED DISSOLVED ORGANIC MATTER (CDOM) DYNAMICS IN THE PRISTINE KRKA RIVER ESTUARY (CROATIA)

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Abstract: The Krka River is located in the karstic region without significant anthropogenic influence, thus showing low input of nutrients and terrigenous material in the estuary (Legović et al., 1994). The 23 km long estuary is permanently vertically stratified. These features makes it an interesting and unconventional system for DOM dynamics study. In this work we present first DOM study in the Krka river estuary using UV/Vis and fluorescence spectrometry. Samples were collected at 16 locations during two contrasting periods of the year (summer and winter). Dissolved organic carbon (DOC) is exceptionally low for both seasons (35-145 μM), particulary in winter when it is lower in the river than at the open coastal location. DOC and absorbance (a_{254}) showed nonconservative behaviour in the salinity gradient (increase in the mixing area) for both sampling periods. Regarding this and overall results DOM in the estuary can be divided into three sections with different optical characteristics; (1) riverine DOM (2) DOM in the mixing area and (3) DOM introduced by seawater. Results also showed evident differences in DOM composition between contrasting seasons. Lower SUVA (chromophoric content) and higher spectral slope S_{275} (lower molecular weight and aromaticity) in summer point to the higher degree of photodegradation or/and *in-situ* production. PARAFAC analysis of EEMs of winter samples provided three distinct components. Microbial (C1) and terrestrial (C2) humic-like components showed conservative behaviour indicating terrestrial origin. Conversely, protein-like component (C3) showed increased intensities in the mixing area and at the halocline, clearly indicating *in-situ* production.

Key words: CDOM, DOC, Estuaries, UV/Vis spectroscopy, Fluorescence

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CHARACTERIZATION OF RIVERINE DOM USING THERMAL SLICING PYROLYSIS GC-MS: IMPLICATIONS FOR ANTHROPOGENIC INFLUENCE AND ORGANIC MATTER LABILITY

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Abstract: Dissolved organic matter (DOM) is one of the largest pools of reduced carbon on the planet. This massive carbon reservoir is dynamic and cycled actively through different biogeochemical reactions. Riverine DOM is one of the key substrates for microbial metabolism supplied from land to ocean, yet only a small fraction of it has been characterized at the molecular level. Here we reported molecular structures of DOM (>1 kDa) isolated by ultrafiltration from nine North American rivers as characterized using thermal slicing pyrolysis gas chromatography–mass spectrometry (Py-GC–MS). We also characterized stable isotopic and elemental composition as well as total hydrolyzable amino acids (THAA) of the DOM samples. A degradation index derived from the THAA data revealed a range of degradation and bio-lability between the rivers, while the more enriched δ^{15}N signatures from several more developed watersheds pointed to anthropogenic influence on the DOM. The thermal slicing Py-GC-MS results provided insights into the molecular characteristics of different DOM pools with different bio-labilities based on a consistent progression of molecules with each successive thermal range in the pyrolyzer. Degradation indices of the riverine DOM were significantly correlated to molecular diversity and total normalized peak areas from Py-GC–MS. This relationship suggests that DOM from different river basins had undergone different degradation processes; also, the major driver in differences between the molecular composition of riverine DOM was degradative processes. The data also showed that relatively thermally stable DOM lacked molecular diversity compared to the more thermally labile DOM matrices, indicating that less diverse matrices may be more degraded or environmentally refractory. Overall, the thermal slicing Py-GC–MS shows great potential in deciphering molecular structures of riverine DOM, particularly when in combination with specific compound or isotope analyses.

Key words: Pyrolysis-GC-MS, DOM characterization, nitrogen isotope, ultrafiltration, North American Rivers

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GROUNDWATER-DERIVED TERRIGENOUS DISSOLVED ORGANIC MATTER FLUXES TO COASTAL OCEAN

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Abstract: An increasing number of studies show the importance of integrating the contribution of submarine groundwater discharge (SGD) to coastal carbon budgets. During its transit from the aquifer to the coastal zone, groundwater flows through soils and organic horizons that release terrigenous dissolved organic matter (tDOM). The behaviour of this tDOM in the coastal ocean remains poorly understood. Furthermore, within the context of climate change and the inevitable sea-level rise, the impact of buried soil horizons on carbon fluxes needs to be investigated in order to assess the consequences of the landward migration of coastlines on the biogeochemistry of coastal oceans. The main objective of this project is to quantify SGD-derived tDOM fluxes to the coastal ocean. Here, we propose to combine hydrogeological and geochemical approaches to investigate the hydrogeochemical behavior of tDOM at the land-sea interface.

The studied beach (St-Siméon, Canada) has accumulated over peaty soils (~2000 ^{14}C yr BP) buried below a few decimeters of marine sand. Piezometers equipped with pressure sensors were inserted into the beach, allowing the continuous measurement of the water table levels and the determination of hydraulic gradients. Furthermore, direct measurements of groundwater seeps were combined to measurements of ^{222}Rn activity in the pore waters to quantify SGD fluxes. Results show a clear relation between SGD fluxes and tide levels. Indeed, Darcy flows, seepage meters and ^{222}Rn activity suggest that the maximum SGD flow occurs at low tide. These results reveal the key role of tidal pumping on SGD fluxes and, therefore, on tDOM fluxes.

Key words: Submarine groundwater discharge, Fluxes, Dissolved organic matter.

SOURCES AND DIAGENETIC STATE OF ORGANIC MATTER IN AN ENGINEERED PROGRADING DELTA: A MULTI-PROXY APPROACH

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Abstract: River deltas account for approximately 41% of the organic carbon that gets buried along continental margins (Smith et al., 2015). However, river engineering, along with sea level rise, has put many of the worlds deltas at risk of being lost (Giosan et al. 2014, Syvitski et al., 2009). The Mississippi River Delta lost approximately 4,833 km^2 of land area from 1932 to 2016 (Couvillion et al., 2017). One mechanism to combat this loss is through engineered river diversions, in which subdeltas may develop. Wax Lake Delta is an example of a prograding delta that resulted from an artificial river diversion in the Mississippi River Delta. Previous work by our group found that this delta has stored carbon at an average rate of 250 g m^{-2} yr^{-1} (Shields et al., 2017), which is similar to or greater than marsh, mangrove, and seagrass ecosystems (McCleod et al., 2011). Here we investigate the sources and diagenetic state of the sedimentary organic matter using bulk stable carbon isotopes, total hydrolyzable amino acids and lignin oxidation products. The changes in both OM source and quality are correlated to changes in the delta's elevation. In addition to the changes observed for OM source and quality, the OC loadings (OC/SA; mg C m^{-2}) also increase as the delta aggrades; transitioning from sediments similar to other delta topsets and mobile mud banks (OC/SA < 0.4) to typical riverine sediments (0.5 < OC/SA < 1) and eventually to those found in highly productive regions (OC/SA > 1). Linking this multiproxy approach with environmental variables such as elevation provides a path for incorporating OM dynamics into geomorphic models.

Key words: Biomarkers, Organic Matter, Coastal Delta

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SEASONAL MAGNITUDE OF SUBMARINE GROUNDWATER DISCHARGE IN RÍA 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 recognized as a major source of continental water to the global ocean, thus exerting a major control over coastal water composition (Kwon et al. 2014). Radioisotopes are used to evaluate, for the first time, the seasonal occurrence and magnitude of SGD in Ría de Vigo, a large embayment affected by seasonal, wind-driven upwelling. The activities of ^{222}Rn and ^{226}Ra are determined in surface and deep waters of Ría de Vigo during five seasonal basin-scale surveys. Additionally, the activities of ^{222}Rn and ^{226}Ra are also seasonally determined in the aquifer systems surrounding the ría, beach porewaters, sediment incubations, atmosphere and the adjacent coastal sea. The system reveals as naturally enriched in ^{222}Rn due to the widespread presence of granitic basement rocks in the region. High ^{222}Rn activities (up to 10^5 Bq m^{-3}) are detected in boreholes surrounding the ría, with a general strong seasonal variation in the ^{222}Rn content. Concomitantly, high ^{222}Rn activity (>400 Bq m^{-3}) is measured in certain areas of the ría showing also strong seasonality. Box model, mass balance techniques are used to account for the different circulation patterns found in the embayment and thus, to perform a volumetric estimation of total and freshwater SGD in Ría de Vigo. The contribution of fresh groundwater revealed a relevant component of solute transport to the ría, equivalent to ~10% of the volume discharged through surface freshwaters to the system. On the other hand, the large magnitude of seawater recirculating through permeable sediments, determined by the circulation pattern inside the embayment and enhanced during storm events, shows the potential for being a large source of regenerated solutes to the ría.

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

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RARE EARTH ELEMENTS FRACTIONATION IN SALT MARSH HALOPHYTE PLANT *HALIMIONE PORTULACOIDES* FROM TAGUS ESTUARY (PORTUGAL)

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Abstract: The rare earth elements (REE) increased use has resulted in a large widespread in the aquatic environment. In estuaries, where salt marshes act as a natural sink of different contaminants from industrial and urban wastes (Brito et al., 2018b) the REE use may be fingerprinted.
Halophyte plants, such as *Halimione portulacoides*, known to sequester some metals in the rhizo-sediments, may accumulate at levels exceeding those of surrounding non-vegetated sediments (Caetano et al., 2008; Pedro et al., 2015). Brito et al. (2018a) in a study with other salt marsh halophyte species reported a REE enrichment in colonised sediments, suggesting an influence in biogeochemistry promoted by roots activities. The authors observed different REE fractionation patterns in roots when compared to the surrounding sediments, but no significant metal accumulation was found in the plants, suggesting low roots uptake and minor translocation to aboveground plant organs.
The aim of this work was to study the REE accumulation, fractionation and mobilization from sediments to *H. portulacoides*. The REE translocation from roots to the aboveground plant organs and its fractionation in the different plant organs was also investigated. The study was carried out at the Rosário salt marsh, in the Tagus Estuary (SW Europe), using the ICP-MS analytical technique to quantify REE contents. The results suggest that the accumulation of REE in the salt marsh halophytes is species-dependent and may vary throughout the year, depending on plant metabolism. On the other hand, the REE retained in the plants also suggest that accumulation is related to the sedimentary REE fraction that regulates their bioavailability.

Key words: rare earth elements, fractionation, salt marshes, halophyte plants

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BIOGEOCHEMICAL BEHAVIOUR OF TELLURIUM IN A MAJOR EUROPEAN FLUVIAL-ESTUARINE SYSTEM (GIRONDE, FRANCE)

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Abstract: The biogeochemical behaviour of tellurium (Te) in continent-ocean transition systems and its role as an environmental emerging contaminant are widely unknown, especially in aquatic systems (Belzile and Chen 2015, Filella et al. 2019). This is due to lack of environmental studies and to analytical challenges limiting the determination of Te naturally low (ultra-trace) levels (Belzile and Chen 2015, Filella et al. 2019). A comprehensive study of Te was performed in the Lot-Garonne-Gironde fluvial-estuarine system including (i) long-term records (2014-2017) of dissolved (Te_d) and particulate (Te_p) Te concentrations and fluxes in fluvial and estuarine reaches, (ii) records of past industrial Te_p concentrations from an upstream watershed sediment core, and (iii) historical Te bioaccumulation in wild oysters at the Gironde Estuary mouth (RNO/ROCCH, 1984-2017). All samples were analyzed with the new generation ICP-MS-MS (Thermo® iCAP TQ). Fluvial concentrations at all studied sites averaged ~1 ng L^{-1} and ~50 µg kg^{-1} with temporal patterns following parallel seasonal variations for both Te_d and Te_p, not reported until now. These synchronous patterns result in constant solid/liquid partitioning along the year (log_{10} Kd ~4.75 L kg^{-1}). Estuarine reactivity in contrasting hydrological conditions (from flood to drought) suggests non-conservative behavior of Te along the salinity and turbidity gradients, potentially dominated by mineralization and re-adsorption processes. Historical bioaccumulation of Te in wild oysters showed no clear long-term trend (average 2.08 µg kg^{-1} dry weight) despite evidences of river sediment contamination in the upstream watershed due to former ore-processing activities. This study provides rare knowledge on Te environmental biogeochemistry mainly related to its geological origin, showing a high particle affinity, apparent low recent anthropogenic influence and non-negligible bioavailability to marine organisms.

Key words: Technology Critical Element, distribution coefficient, temporal series, bioconcentration factor

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PLATINUM – AN EMERGING CONTAMINANT IN ESTUARINE/COASTAL SYSTEMS

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Abstract: Continuously increasing mining, use and release of Technology Critical Elements (TCE) pose growing concerns regarding their environmental dispersion, fate, and ecotoxicology. Among them, platinum (Pt) still is an emerging contaminant applied in various relatively recent applications, including car catalytic converters (vehicle emission control) as well as anti-cancer drugs. Environmental Pt levels, its behaviour and reactivity in aquatic systems remain widely unknown, especially in estuarine/coastal environments that are under high anthropogenic pressure. Analytical challenges in terms of sensitivity and interference control required for Pt ultra-trace detection in marine matrices may explain such general lack of information. The inexistence of Certified Reference Materials is an additional problem. The present work presents Inter-comparison and validation of optimised Adsorptive Cathodic Stripping Voltammetry (Ad-CSV) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) methods for Pt measurements in marine bivalves. Field monitoring studies on Pt biogeochemistry have been performed in key estuarine/coastal European systems, including Pt distribution between seawater, particles, and living organisms. Historical Pt contamination in a major fluvial-estuarine system and a highly urbanized harbour reflects past contamination and currently increasing Pt levels. Spatial biomonitoring in marine bivalves from contrasting areas along urbanized coastlines suggests a relation between the degree of "urban exposure" and Pt concentrations in soft tissues. While wild bivalves prove to be good biomonitors of Pt contamination, Pt in coastal water may have the potential to serve as a tracer of modern urban (medical, traffic) sources. Field observations suggest that biogeochemical processes leading to changes in Pt partitioning and carrier phases at short temporal scale may enhance its bioavailability, including in phytoplankton, and ultimately induce toxic effects on marine organisms.

Key words: Platinum, Distribution, Contamination, Estuarine/Coastal Systems, Biomonitoring

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EVALUATION OF PLATINUM AND RHODIUM IN URBAN ROAD DUST: INERT OR SOLUBLE IN AN ESTUARY?

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Abstract: The behaviour and physicochemical characteristics of Pt and Rh remain poorly understood despite their increase in the environment. There is a generalized idea of inertness of the metallic species emitted from catalytic converters, being their potential solubility often disregarded. In this work, Pt and Rh dissolution from road dust under relevant environmental conditions was evaluated. A composite sample (<0.063 mm), collected on a high-traffic road, was thoroughly characterized. Batch experiments were performed by exposing road dust aliquots in synthetic rainwater and seawater adjusted to pH 4.0 and 8.2, respectively, and incubated at different times. Leachates were retrieved after filtration (0.45 µm), acidified and analysed for Pt and Rh by AdCSV, after UV irradiation, and ICP-MS. Rhodium measured by AdCSV was higher than Pt irrespective of the medium used. In the leachates, ICP-MS data evidenced larger concentrations of both metals than those obtained by AdCSV. The differences are due to the presence of metallic nanoparticles, not detected during the voltammetric determination. Leachates were also analysed by NTA and SEM, confirming the existence of nanoparticles. In average, truly dissolved metals measured by AdCSV represented 4–10 % of total Pt present in the leachates, while for Rh the average is higher than Pt, corresponding to 31–41%. Moreover, concentrations of Pt and Rh in the leachates presented temporal variations, in particular after 24h of incubation. Pt concentration increased in seawater while in rainwater decreased. Those variations are most likely related to the nanoparticles chemistry since truly dissolved concentrations remained similar over time.

The relevance of Pt and Rh soluble species over nanoparticles in terms of their potential availability and toxicity in the environment is still not well understood. Our results highlight that Pt and Rh speciation in aquatic systems can be obtained by a combination of suitable techniques.

Key words: Platinum-group elements, road dust, solubility, metallic nanoparticles

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'ANTHROPOCENE' IMPRINT OF SHIPBUILDING INDUSTRY. BLOSSOM, DECAY AND REACTIVATION

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Abstract: The globalization of the industrialization is being pointed out as the synchronous and global event that potentially marks the starting point of a current-proposed stratigraphic epoch: the 'Anthropocene'. Its study makes necessary high-resolution (yearly) works on recent stratigraphic records such as estuarine sediments. Concerning industrialization, the Ria of Ferrol represents a paradigmatic example in the NW of the Iberian Peninsula. This area is under the impact of military shipyards since 1730. Their maximum activity happened after 1947, consequence of the industry restructuring and the implementation of civil shipbuilding (including oil super-tankers). The present study focused on a sediment core of 50 cm long that holds record since the beginning of the 20th century, according to Pb-210 dating. Trace metal contents were evaluated to identify the human imprint. Background levels established in nearby areas with similar mineralogical characteristics were considered. Three main periods can be distinguished based on the trace-element to Al ratios: (i) from the beginning of the 20th century until about 1970, when ratios increase usually about 1.5 to 2.4 times, (ii) between around 1970 to 1990, when these ratios decrease usually about 1.4 to 2.3 times, and (iii) from 1990 to 2010, when ratios maintained. The studied sediments reflect the human-environment relationship in the area during the 20th century: the metal to Al ratios, sediment accumulation rates, total metal fluxes and enrichment factors show a first period of increasing industrialization without environmental concern, followed by an industrial collapse and a subsequent reactivation while implementing environmental friendly processes and policies.

Key words: shipyards, trace metals, Pb-210 dating, estuarine sediments, Ria of Ferrol.

Acknowledgments: This study from the project “Coastal contributions of trace elements during different oceanographic periods” (CTM2011-28792-C02-02), funded by MINECO.

WHAT CONTROLS WATER COLUMN METHYLMERCURY CONCENTRATIONS IN ESTUARINE ECOSYSTEMS? INSIGHTS FROM MEASUREMENTS AND MODELING

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Abstract: Anthropogenic activity has increased mercury (Hg) in the biosphere which has led to elevated levels of methylmercury (MeHg) in coastal biota, a health concern for fish consuming humans and wildlife. Research suggests that the dominant MeHg uptake pathway into coastal biota is from the water column, but it is difficult to constrain the dynamic sources and sinks of water column MeHg using standard sampling techniques. We used a statistical approach combined with targeted studies to better understand the sources and fate of MeHg in estuarine water columns, and the primary ecosystem properties linked to water column MeHg levels. To do this, data were combined from several ecosystems from Maine to Maryland, USA, varying in historic Hg contamination and current land use. Sites also varied in size, water residence time, mean summer temperature and chlorophyll concentrations. Samples were collected between 2013 and 2016 over a salinity range of 0-32 ppt and sediment Hg levels of <0.01-36 µg/g. The statistical analyses used included linear regressions to determine major relationships, principal component analysis to identify relationships between these explanatory variables, and partial least squares regression to reduce the variables to those most important for explaining MeHg and HgT levels across the ecosystems. The targeted studies examined the role of sediment resuspension, water column Hg methylation, and water column speciation in controlling MeHg concentration and bioavailability. Overall, the results suggest that sediments are a minor source of MeHg to estuarine waters except for sites with significant historic Hg contamination. Instead, MeHg levels are generally controlled by partitioning, total Hg and C indices, which are related to watershed HgT/C loading and *in situ* biological production. The presentation will go into further detail on these results, provide a conceptual model of the findings, as well as discuss how sources may impact bioaccumulation into coastal food chains.

Key words: methylmercury, estuary, water column, mercury

MIXING BEHAVIOUR OF TRACE ELEMENTS AT THE MOUTH OF THE ISONZO/SOČA RIVER (GULF OF TRIESTE, NORTHERN ADRIATIC SEA)

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Abstract: Estuaries represent a crucial link between land and sea where river fluxes of trace elements are subjected to a variety of physical and biogeochemical processes. The boundary conditions are extremely variable in the estuarine mixing zone affecting trace element speciation and their partitioning among different phases.
The Isonzo/Soča River represents the main source of Hg in the Gulf of Trieste due to past mining activity at the Idrija mercury mine (Slovenia). The aim of this work is to evaluate trace element occurrence, size partitioning and mixing behaviour at the mouth of the Isonzo/Soča River. For this purpose, large volume water samples were collected from surface, mixing and bottom layers under various seasonal conditions. Size fractionation was performed using vacuum filtration and cross-flow ultrafiltration to isolate the suspended particulate matter (SPM) and the colloidal retentate solution, respectively, from the truly dissolved. Trace elements appear to be mainly associated with the SPM and dilution effects between riverine and marine particles are responsible for the decrease in their concentration along the water column. As expected, Hg was notably present during winter in the surface freshwater, in particular under conditions of elevated river discharge. On the contrary, Mn was found to be higher at the bottom, particularly during summer, as a consequence of oxidation processes followed by the precipitation of Mn oxy-hydroxides promoted by high water temperature. The strong physico-chemical gradients, especially in terms of salinity, are often responsible for the non-conservative behaviour of several trace elements. Iron, Mn and Cu displayed a non-conservative behaviour during mixing and simultaneously showed the highest content of colloidal material. On the contrary, conservative behaviour was found for As and Cs which are often present under ionic dissolved forms in natural water systems.

Key words: trace elements, salinity, size partitioning, estuaries

BEHAVIOR OF NUTRIENTS AND TRACE METALS AT THE HEAD OF ESTUARIES BEFORE MIXING OF RIVER AND SEAWATERS

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Abstract: The distribution across the horizontal salinity gradient is a key characteristic of the chemical substances behavior in estuaries. The processes taking place at the head of estuary before mixing of river and seawaters attract less attention. We studied the distribution of nutrients, dissolved and suspended forms of some trace metals (Fe, Mn, Zn, Cu) in the upper parts of three microtidal estuaries within northwestern coast of the Sea of Japan: Tumen, Razdolnaya and Amur rivers, which are very different by runoff, and anthropogenic load. Thermohaline structure, content of suspended solids, dissolved organic carbon (DOC), humic substances, and chlorophyll "a" were registered as well. Salinity shown uniform "river" values in these upper parts of estuaries within surveys. Nutrients and DOC also had minor variability within surveys, though difference between rivers were significant. At the same time dissolved (<0.45 mkm) Fe, Mn, and at less extent Zn revealed notable 1.7-6 times decrease downstream within 10-15 km area before the beginning of mixing zone in all three estuaries. The high enough initial concentration of dissolved metals in river waters (more than 500 nM Fe and 50 nM Mn) seems a prerequisite of such decrease. Contrariwise, dissolved Cu shown rather constant concentration in this area in accordance with unchanging salinity. Unified linear relationship between dissolved Fe and Mn observed for the estuaries studied allow to suggest formation of colloidal/suspended hydroxides as a mechanism of decline of dissolved Fe and Mn in the river oxygenated waters. The appearance of this effect at the head of estuaries before beginning of mixing with seawaters could be explained by the slowdown of river current in this area due to tides.

Key words: Estuary, dissolved trace metals, nutrients, Sea of Japan

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IMPACT OF OCEAN ACIDIFICATION ON THE AVAILABILITY AND UPTAKE OF TRACE ELEMENTS BY MUSSELS

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Abstract: Global environmental changes have been reported over the last years and their impact on organisms' behaviour has been studied. Recent studies already demonstrated that in marine systems the release of contaminants in association with predicted environmental changes (increase in CO_2 and decrease in pH) may play a key role not only in the organisms' behavior but also on contaminants toxicity. Therefore, the aim of the present study is to assess the impact of oceanic acidification on the bioavailability of well-study metals (Cd, Cu, Pb, Ag) and emerging contaminants (Ce and Pt) and to understand if this environmental change will increase the adverse effects in aquatic environments, using mussels (*M. galloprovincialis*) as bioindicators. Metal treatments were done by a mixture of isotopically-labelled metals at realistic concentrations: ^{111}Cd (80 ng/L), ^{65}Cu (2 µg/L), ^{207}Pb (200 ng/L), ^{109}Ag (20 ng/L), ^{142}Ce (20 ng/L) and ^{194}Pt (2 ng/L). Two different seawater CO_2 concentrations were selected: 400 ppm (current value) and 1200 ppm (estimated content for 2100) (IPCC, 2014). Mussels were exposed for 21 days at spiked-seawater constant flow (9 ml/min), under control conditions (16ºC, 12:12 photoperiod) and with constant food addition (1:1, *Rhodomonas:T-Iso*) (1 mg/L). During the exposure period samples of seawater and phytoplankton were taken to determine metal content and isotopic composition. During the experimental period biological responses were measured by analyzing weekly filtration rates (PAMAS laser particle counter), and at the end of this period by measuring byssus strength. Biochemical responses were assessed by measuring mussel metabolic capacity, energy-related biomarkers, oxidative stress and neurotoxic status. Chemical analyses were done in mussel byssus, gills, feet, glands and soft bodies as well as in water samples. Expected results will help us to understand the influence of seawater acidification on the impacts of pollutants and sensitivity of mussels towards these pollutants, identifying possible synergistic effects.

Key words: Global change, metal pollution, biomarker, *Mytilus galloprovincialis.*

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AN EXTREME EUTROPHICATION EVENT IN A SPANISH COASTAL LAGOON (MAR MENOR, SE SPAIN): THE ROLE OF BENTHIC FLUXES

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Abstract: Coastal lagoons are areas subjected to high anthropogenic pressures due to human settlements, agricultural activities and local industry. As a consequence, levels of contaminants and nutrients can rapidly increase causing ecosystem degradation. One of the most dangerous events for these areas are eutrophication events, usually as a result of high nutrients availability that provoke great blooms of phytoplanktonic species with negative consequences as light attenuation and dissolved oxygen depletion. The Mar Menor (SE Spain) is one of the biggest lagoons in the Mediterranean basin. The main pressures over this area are the intensive agriculture of the adjacent Campo de Cartagena, the seasonal tourism and the historical exploitation of the mines in the southern margin. In 2016, lagoon waters turned green as a consequence of extreme phytoplanktonic blooms and chlorophyll a increased values one to two orders of magnitude over historical baseline ones. As a consequence, almost 85% of the bottom vegetation disappeared and levels of organic matter increased in the waters. In the beginning, the increased levels of nutrients that could have unchained this event were supposed to come from the historically contaminated quaternary aquifer through submarine groundwater discharges, but benthic fluxes of these nutrients may be playing a relevant role. Nutrient concentrations in porewaters were about ten to hundred times higher than levels in the overlying waters. This would imply potential benthic fluxes of nutrients to the Mar Menor water column. In addition, as a result of the changing conditions of the physicochemical variables (i.e. redox conditions) of the sediment-water interface due to the eutrophication process, the historic trace metal reservoir of the sediments could be also activated and transfer dissolved metals to the water column. Thus, bottom sediments of the Mar Menor may be acting as a nutrient and metal source with negative consequences to the quality of this coastal lagoon waters.

Key words: eutrophicaton, lagoon, nutrients, metals

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SYNTHESIS AND ASSIMILATION OF B VITAMINS BY BACTERIOPLANKTON DURING A PHYTOPLANKTON BLOOM

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Abstract: Recent evidence indicates heterotrophic marine bacteria are important providers of B vitamins needed for growth by some auxotrophic phytoplankton. The aim of this work was to establish how bacterial vitamin metabolism influences phytoplankton blooms in the NW of the Iberian Peninsula. In order to do this, the prokaryote's metatranscriptomic profile was studied in mesocosm experiments simulating an upwelling situation over a week. The B vitamin synthesis genes expressed by bacterioplankton were more abundant than those related with vitamin assimilation throughout the experiment. Our analysis showed that bacterial B vitamin metabolism could have a profound impact on the phytoplankton proliferation as the expression of genes related to the vitamins' synthesis, especially the vitamins B1 and B12, was significantly higher before the maximum of phytoplankton biomass was reached. Bacteria seemed to mostly assimilate vitamin B1, which is consistent with the idea of widespread auxotrophy for this vitamin among bacteria. Conversely, vitamin B7 was similarly synthesized and assimilated by the prokaryotic community, suggesting that it could be mostly transferred among bacteria. Collectively, these findings suggest that bacteria play a key role both as producers and as consumers of B vitamins in this productive ecosystem.

Key words: B vitamins, gene expression, auxotrophy, phytoplanktonic bloom, bacterioplankton.

THE IMPACT OF SALMON FARMING ON BIOGEOCHEMICAL CYCLING IN THE MACRO-ESTUARINE SYSTEM OF CHILEAN PATAGONIA

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Abstract: The Chilean Patagonian fjords, channels and island archipelagos form an extensive shelf-scale estuarine system and host the 2nd largest salmon farming industry in the world (after Norway). Dissolved and particulate waste from fish farms is difficult to observe *in situ* due to rapid uptake and transformation by the local ecosystem, dispersal by tides and currents and patchy deposition on the seabed, however chronic broad-scale impacts on water quality have been described in other regions of intensive aquaculture. We use a fine-scale (600m spatial resolution, 1 hour time-step), 3D biogeochemical model to quantify the transformation and fate of Chilean fish farm waste and its impact on the cycling of nitrogen, phosphorous, carbon and dissolved oxygen through phytoplankton, zooplankton, detritus and dissolved organic and inorganic pools in the water column and surface sediments. Model results are validated against observations including new fine-scale nutrient and optical data obtained from field deployments of an autonomous glider and an underway wet chemistry nutrient analyser. Results show broad-scale estuarine circulation across the northern Chilean Patagonian shelf with strong east-west gradients in surface phosphorous and nitrogen. In regions of freshwater influence, the reduced supply of phosphorous and limited light availability restricts the growth of phytoplankton, even in zones with intense fish farming activity. These results are significant for the management of fish farming impacts on water quality in phosphorous depleted estuarine waters.

Key words: Atlantic salmon, nitrogen, phosphorous, autonomous systems, biogeochemical model

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MONTHLY INORGANIC BIOGEOCHEMISTRY TIME SERIES IN THE NE SPAIN GULF OF ARTABRO, 2014-2018

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Abstract: the Ria de A Coruña is located in the Gulf of Artabro in the North Western corner of Spain, this estuary is marginally affected by coastal upwelling, and receives high river inputs from a highly populated area. We present monthly time series along three hydrographic stations geographically covering the estuary: CTD continuous data along with discrete inorganic biogeochemistry variables, dissolved oxygen, inorganic nutrients, pH and alkalinity were taken from 2014 to 2018. This high resolution data set allows discerning the main drivers of the biogeochemical variability in the area: marginal influence of the upwelling of central North Atlantic waters, river input and benthic activity.

Key words: Gulf of Artabro, monthly sampling, CTD, inorganic biogeochemistry, CO2, benthic activity, river input.

DISSOLVED INORGANIC NITROGEN UPTAKE KINETICS OF DOMINANTS MACROPHYTES IN A COASTAL LAGOON UNDER ANTROPHIC PRESSURE

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Abstract: In shallow coastal ecosystems, as for example coastal lagoons, macrophytes account for high biomasses and productivity (Sand-Jensen 1975, Viaroli *et al*. 1996) being able to play a major role in the biogeochemical cycles of nutrients (Romero et al. 2006, Touchette and Burkholder 2000). When strong inputs of nutrients occur, due to natural and/or anthropogenic causes, these communities can function as natural biofilters, buffering the effect of these nutrient increases through their assimilation and therefore determining resilience capacity of the ecosystem against this type of pressure (Sandoval-gil et al. 2015). The objective of this study was to evaluate dissolved inorganic nitrogen (DIN) incorporation capacities of the two dominant macrophytes (the marine angiosperm *Cymodocea nodosa* and the macroalga *Caulerpa prolifera*) in the Mar Menor coastal lagoon (Spain), where eutrophication phenomenon has recently been documented (Belando et al. 2017). To this end, shoots and stolons from meadows of both species with different degrees of exposure to nutrient inputs were incubated with N^{15}-labeled tracers ($^{15}NH_4^+$ and $^{15}NO_3^-$) under laboratory controlled conditions and DIN uptake kinetics in leaves and fronds were assessed. Intraspecific and interspecific differences in uptake kinetics strategies (*maximum uptake rate*, *Vmax*, and/or *affinity coefficient*, α) were observed. While both macrophytes were efficient in exploiting a valuable source of NH_4^+, especially in areas with a high load of anthropogenic nutrients, only *C. prolifera* showed a high uptake capacity of NO_3^- from the water column. Our results showed that macrophyte meadows could have a high capacity to control nutrient cycles in the Mar Menor coastal lagoon, acting as a buffer mechanism to the massive entry of these pollutants.

Key words: *Cymodocea nodosa*, *Caulerpa prolifera*, DIN, Mar Menor lagoon, Mediterranean sea

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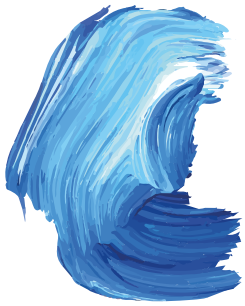

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REVISITING THE CONTENTS OF MERCURY IN THE SURFACE SEDIMENTS OF THE TAGUS ESTUARY

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Abstract: The contents of total mercury (Hg) were determined in sixty-eight surface sediments of the Tagus estuary collected in 2016-17 to represent the spatial distribution of mercury in recent sediments. Total Hg ranged from 0.03 to 26.3 mg kg^{-1} with a median value of 0.31 mg kg^{-1}. The highest total contents were observed in the proximities of the past anthropogenic source (Complexo Quimigal, main activity pyrite roasting) located in the southern margin (Figuères et al., 1985). Considering the highest value, this is c.a. 40% lower than those obtained by Figuères et al. (1985) and Canário et al. (2005). Despite the decrease of contents of Hg probably associated with the improvement of treatment of industrial effluents the and/or modification of the manufacturing processes of some industrial sources, the maintenance of the relatively high contents of Hg can be associated with the hydrodynamic conditions of the estuary responsible for the resuspension and redeposition of historically contaminated sediments. This, together with the mixture with recent uncontaminated sediments and/or with particles derived from other industrial sources not Hg enriched may also contribute to the decrease of contents of Hg observed. The obtained results suggest the legacy of the historical Hg contamination is still present in sediments.

Key words: Tagus estuary, sediments, mercury contents

Acknowledgments: This study was co-financed by the MAR2020 program.

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ANTHROPOCENE HUMAN FOOTPRINT IN THE NALÓN ESTUARINE SEDIMENTS (NORTHERN SPAIN)

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Abstract: Sediment cores of four boreholes (length from 9 to 27 m), retrieved in the Nalón estuary (Asturias, north of Spain), were investigated to assess the historical human footprint on the sedimentary sequence. Analytical measurements of grain-size, geochemical composition (major and trace elements) and stable Pb isotopic ratios were performed. Two different phases were identified throughout the sedimentary sequence by means of the Pb isotopic ratios. The upper sediment layer of the cores (variable depths between 3 to 9 m) showed a decrease of the $^{208}Pb/^{206}Pb$ ratios and an increase of the $^{206}Pb/^{207}Pb$ ratios whereas in the deep layers these ratios remained constant. These variations reflected additional no-natural inputs of Pb to the estuarine sediments which were identified from mining activities when the Pb composition of the different phases were compared to potential anthropogenic sources. A similar insight occurred with the variation of trace element concentration with depth. The enrichment factors of As, Hg, Pb, Sb and Zn related to the background values allowed to distinguish the impact of the intense human activity, mainly linked to the different mining activities developed in the region. Despite the decrease and closure of mining exploitations during the second half of the 20th century, results showed ongoing input of As, Hg, Pb, Sb and Zn to the coastal sediments. Thus, the legacy of contamination by these elements, mainly from leaching of slags and tailings dams, is still recorded in the estuarine sediments.

Key words: Estuarine sediments, Anthropocene, Trace elements, Pb isotopes

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PLATINUM-GROUP ELEMENTS DOWN-CORE DISTRIBUTION IN SEDIMENTS AT INDUSTRIAL SITES OF TAGUS ESTUARY

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Abstract: Anthropogenic emissions of platinum-group elements (PGE) has led to an increase in their environmental concentrations over the past decades. Their main source has been attributed to automotive catalytic converters. However, the contribution of other sources may increase PGE in aquatic systems, such as industrial activities and medical uses. The Tagus estuary is well known for its historical record of industrial activities described for other metals (e.g. As, Pb, Hg). We hypothesized that sediments could also have a PGE signature imprinted previously to the introduction of catalytic converters. To this aim, three sediment cores collected at industrial areas of the Tagus were used: BRR, a dismantled industrial area with a historical diversity of activities; CN, where a chemical-complex unit continuous operating; and one core distant from the industrial areas, located in the Natural Reserve. Samples were acid-digested and analysed by AdCSV and ICP-MS.
The highest PGE concentrations in the Tagus estuary were found at BRR in the deeper layers, between 10- and 20-cm depths. The industrial peak activities back in 1960/70s, mainly related to ore processing and metals extraction, may explain those enrichments. In addition, the significant correlations found also suggest that geochemical processes may have favoured PGE retention in sediments. The concentrations found at CN site suggest continuously input of PGE, presumably from catalysts used in hydrogen peroxide production.
These results evidence the clear signature from past industrial activities that occurred previously to the implementation of ACC in the early 1990s. This work significantly contributes to the current and limited knowledge of PGE emissions resulting from industrial sources.

Key words: Platinum-group elements, industrial activities, historical contamination

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SIMULATION OF THE EFFECTS OF DREDGING ON THE MOBILITY OF MERCURY AND ARSENIC IN RESUSPENDED CONTAMINATED ESTUARINE SEDIMENTS (ASTURIAS, SPAIN)

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Abstract: Metal ore extraction was active in the Nalón River drainage basin until the 1970s. The mining activity, abandoned before the introduction of environmental laws, led to the contamination of soil, water and sediments, where high concentrations of potentially toxic elements (PTEs) can be found. Estuarine sediments must be dredged in order to allow for navigation, and their destination must be managed following guidelines based only on the total concentration of contaminants. The effect of resuspension on the cycling of mercury (Hg) and arsenic (As) between the sediment and water column was investigated in a mesocosm study. Four experiments were conducted in three Asturian estuaries based on samples collected from sites impacted by Hg and As and periodically subjected to dredging activities. Designed to mimic the resuspension of particles, all the experiments revealed that the release of Hg and As species do not depend on the total concentration in the sediments. In summary, it is evident that following a resuspension event there is an increase in particulate and dissolved Hg and As which can be released from pore waters or from the dissolution of iron (Fe) and manganese (Mn) oxi-hydroxides depending on the redox conditions. In some cases, the concentrations of As and Hg in the water column remained high even at the end of the experiments, after 24 hours. Conversely, in other sites, the effects of resuspension lasted only a few hours and the restoration of pre-suspension conditions were observed. Part of the Hg and As released from porewaters and/or by desorption during resuspension was presumably removed by the subsequent adsorption onto the settling fine particles and/or was coprecipitated in association with oxi-hydroxides of Fe and Mn.

Key words: Estuarine sediments, mercury, arsenic, resuspension, dredging

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POLYBROMINATED FLAME RETARDANTS IN GALICIAN ESTUARINE SEDIMENTS

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Abstract: PBDEs were worldwide used as flame retardants added to a wide variety of materials including plastic, textile, furnishing, electronic products and building materials. Their principal sources were evaporation and leak into dust from products treated with PBDEs, emissions from manufacturing processes and leachate from waste disposal sites. Nowadays are globally distributed mainly associated with sediments and biota as PBDEs are highly hydrophobic. Despite the European Union restrictions starting in 2004, concentrations are still detected causing an environmental concern in coastal and estuarine areas.

In 2016 a sampling campaign was carried out covering four estuarine environments in the west coast of Galicia, NW Spain, these being Muros, Arousa, Pontevedra and Vigo rias. The different characteristics of the four estuaries including industrialised areas, medium-populated towns, intense shipping traffic and shipyard activities, mussel farming etc, make this four estuaries an ideal environment to compare different pollution sources affecting similar environments.

For a better description of the sediment type, sedimentological characteristics including grain size distribution and total organic content were measured. The analytical method used to analyse PBDEs in sediments is similar to that described elsewhere (Viñas et al 2018) and the analysis is under QA/QC to guarantee the quality of the results.

Levels found are in the order of those in similar estuarine environments and well below the FEQG, Canada.

Key words: Polybrominated flame retardants, PBDEs, sediments, Galician rias.

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POLYCICLIC AROMATIC HYDROCARBONS (PAHs) IN FOUR ESTUARINE AREAS

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Abstract: Polycyclic Aromatic Hydrocarbons (PAHs) pollution has been a matter of long-standing concern especially on estuarine and coastal areas. 90% of the material transported by rivers and rain waters drainage ends up in estuarine environments thus becoming a main sink for pollutants. In addition, coastal areas are generally affected by marine transport that also acts as an important source of PAHs. In the case of these compounds the atmospheric deposition also plays an important role in the transportation and fate of pollutants.

In this study 35 individual PAHs, both parent and alkylated, were analysed. This wide range of compounds allows the determination of possible sources of pollution.

Four estuarine environments in Northwest Spain, namely Muros, Arousa, Pontevedra and Vigo Rías were selected to conduct a PAHs contamination study in 2016. Sediment sampling sites were distributed along a central transect in the different estuaries in order to check both the spatial distribution of PAHs in each estuary and among estuaries.

Both grain size and TOC (Total Organic Carbon) were determined as complementary characteristics defining the sediment type. Sample preparation and analytical determination used for analysis are described elsewhere (Viñas *et al*, 2009; Pérez-Fernández, *et al* 2015) and they are under a QA/QC system that guarantees the quality of the results.

The general pattern of distribution of PAHs shows a clear gradient in all the estuaries with the highest values in the inner part of the estuaries and close to the main known anthropogenic inputs. These values decrease when approaching the outer part of the estuaries.
Muros is the less affected area, while Arousa, although less industrialized and populated than Vigo or Pontevedra, presents concentrations in the range of these last two. This fact, as previously described (Perez-Fernandez *et al*, 2018) is probably due to the intense mussel farming activities in the estuary.

Key words: Polycyclic aromatic hydrocarbons, sediments, Galician rias.

Acknowledgments: Authors would like to thank the technical staff at the Marine Pollution Department at Centro Oceanográfico de Vigo for their work during the sampling, storage and pretreatment of the samples. We would also like to thank the crew at the B/O Ramon Margalef for their help during the SECON16 sampling campaign.

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HUMAN IMPACTS ON ESTUARIES: HALOGENATED ORGANIC COMPOUNDS POLLUTION

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Abstract: Levels of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in sediments from estuarine locations were investigated to evaluate their pollution potential on the environment.

OCPs have been used in reducing crop damages from insects, diseases and weed. OCPs are among the more persistent pollutants; especially DDT is one of the less water soluble compounds. PCBs are industrial compounds with multiple applications; they have been used as coolants and lubricants in electrical equipment. PCBs have also been used in adhesives, paints, inks and as plasticizers. It has been estimated that globally 1.3 million tonnes of PCB compounds have been produced (Breivik et al., 2007) until they were banned in mid-1980s.

Four estuarine environments (Muros, Arousa, Pontevedra and Vigo) were checked to identify whether 40 years after being banned they were still present in the environment and, if so, the spatial distribution of these compounds in the estuaries and its relation with the probable sources of pollution.

Supplementary characteristics of the sediment such as grain size distribution and organic carbon content where also measured to allow interpretation of the data. The analytical method has been described elsewhere (Viñas et al., 2018). A QA/QC system is implemented in the lab to guarantee the quality of the results.

Distribution patterns identified differences among estuaries and also spatial gradients from the inner to the outer part of the estuaries. The values were compared with those environmental assessment criteria available.

Key words: organochlorine pesticides, polychlorinated biphenyls, estuarine pollution

Acknowledgments: Authors would like to thank the technical staff at the Marine Pollution Department at Centro Oceanográfico de Vigo for their work during the sampling, storage

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METAL ASSESMENT ON ESTUARINE AREAS

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Abstract: Metals are easily adsorbed on fine particles of sediments and remain retained in estuarine environments that act as a sink causing an increase in metals concentration and an ecological degradation.
Trace metals selected in this study constitute the core of the Spanish Marine Monitoring Program and were determined to identify estuarine distribution of these pollutants. The results can be used to evaluate some environmental protection activities undertaken after the Marine Strategy Framework Directive
Sediment surface samples were collected in four estuarine Galician rias: Muros, Arousa, Pontevedra and Vigo. Sample preparation and analytical determination used for analysis are described elsewhere (Besada et al., 2014; Quelle et al., 2011) and they are under a QA/QC system that guarantees the quality of the results. The spatial distribution of trace metals in the rías was closely related to the content of fine particles in the sediments and, accordingly, to the content of organic matter.
The joint pollution assessment revealed differences among the estuaries. The presence of most of metals, increased towards the inner part of the rías. Their concentrations reflect the influence of different anthropogenic factors in the estuaries, for example lead in Vigo and mercury in Pontevedra

Key words: trace metal, pollution,

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MONITOOL: NEW TOOLS FOR MONITORING THE CHEMICAL STATUS IN TRASITIONAL AND COASTAL WATERS UNDER THE WATER FRAMEWORK DIRECTIVE

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Abstract: MONITOOL[i] is a European project formed by 17 Partners covering the Atlantic region from the Canary Islands to the Scottish Highlands and Islands. The main driver of this project is to respond to European Directive[ii] demands for the assessment of the chemical status of transitional and coastal waters. Passive sampler (PS) like Diffusive Gradient in Thin Films (DGT) 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 (EQS). EQSs for metals are defined in the dissolved fraction, preventing the use of DGT-labile concentrations for the assessment of the chemical status of water bodies. Thus, the main objective of MONITOOL is to adapt the already existing EQSs for DGTs, enabling their use for regulatory monitoring. Two field campaigns were performed at 4 selected sites (transitional and coastal sites) in each consortium region (8 regions), in winter and in summer 2018, deploying DGTs and collecting high-frequency spot water samples simultaneously. All partners followed the same protocol for sampling and analysis to minimize the operational variability. Priority metals (Cd, Ni, Pb) and other specific metals were analysed in waters and in DGT resins. Obtained results were collected in a common database. Preliminary statistical analysis were applied to first results to study relationships between metal concentrations in DGT and in spot water samples. In a final step, suitable EQS for DGTs will be calculated on basis the statistical relations obtained previously. This will permit a better implementation of the Water Framework Directive in variable systems.

[i] https://www.monitoolproject.eu/
[ii] Directive 2000/60/EC of the European Parliament

THE AQUATIC PLANT *CYMODOCEA NODOSA* AS A TRACER OF TRACE METAL ANTHROPOGENIC INPUTS TO THE MAR MENOR COASTAL LAGOON (SE SPAIN)

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Abstract: Coastal lagoons are areas subjected to high anthropogenic pressures due to human settlements, agricultural activities and local industry. They represent transition areas between the land and the ocean, but due to the limited interchange of water with the ocean, coastal lagoons tend to accumulate great part of the contaminants derived from the anthropogenic pressures. The Mar Menor coastal lagoon is one of the biggest ones in the Mediterranean basin. The main anthropogenic activity carried out in this area is the historical exploitation of the La Unión mine area, located in the southern area of the lagoon. In addition, the numerous recreational and fishing ports and the inputs of agricultural waters coming from the adjacent field of Cartagena suppose extra contributions of contaminants to this coastal system. One of the most dangerous groups of contaminants in the environment are heavy metals. Each metal or group of metals can be usually associated to a different anthropogenic activity. In the present study, samples of the aquatic plant *Cymodocea nodosa* were collected in more than 40 points homogenously distributed along the Mar Menor coastal lagoon and several metals (i.e. Cu, Pb, Zn, Ni, Co, Fe, Mn, As, Hg) were analyzed in the plant tissues. The results obtained show that these plants can be used as bioindicators of the different metal sources to the lagoon, as they spatial distribution of trace metals in the plan was different depending on the diverse anthropogenic activities predominant at each area of the lagoon.

Key words: Cymodocea nodosa, bioindicator, metals, lagoon

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ROLE OF JUNCUS MARITIMUS IN THE MERCURY CYCLE OF A CONTAMINATED SALT MARSH

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Abstract: *Juncus maritimus* is the most abundant halophyte in the marshes of the Nalón estuary, a Spanish area contaminated by mercury (Hg) as a consequence of mining activities. With the purpose to clarify the role of this species in the salt marsh Hg cycling, sediments and plants were collected from seven locations differing in Hg contamination. Hg uptake and distribution between plant organs were evaluated, as well as the available, organic and total concentration in the bottom sediments. The results showed that *J. maritimus* may influence the sediment physic-chemical conditions increasing the potentially available Hg for uptake. In plants, most of the absorbed Hg (86.4-98.4%) was retained in the root system, phytostabilizing the metal and reducing the concentration of Hg in the sediments. *J. maritimus* had a high efficiency to accumulate mercury in their organs showing enrichments from 3 to 24 times the available metal concentration detected in sediments. This mechanism in the root system seems to be effective for inorganic Hg whereas organic Hg seems to be translocated to the aerial part of the plants. These results suggest that in salt marshes where organic mercury fraction is important, *J. maritimus* may act as a source of contamination transferring Hg from the sediments to the atmosphere. Conversely, *J. maritimus* can be used to immobilize Hg and store them in the root system when inorganic mercury is dominate, which could be usefull for phytoremediation and phytostabilization.

Key words: *Juncus maritimus*, Mercury, Bioaccumulation factors, Salt marshes

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RARE EARTH ELEMENTS AND YTTRIUM IN DIFFERENT SIZE FRACTIONS OF FOUR BOREAL RIVERS IN SWEDEN AND ICELAND

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Abstract: Rivers are an important source of trace metals to the ocean. As estuarine processes, such as salt-induced coagulation, remove particles and nanoparticles and colloids (NPCs) from the water column, it is important to gain a better understanding of the distribution of particle-reactive elements in the different "size-fractions" of river water: (i) suspended particles (> 0.2 µm), (ii) NPCs (0.2 µm - 10 kDa), and (iii) the truly dissolved fraction (< 10 kDa). Here, we present data for rare earth elements and yttrium (REY) in these different physical pools in four different boreal rivers in Sweden (Kalix, Råne) and Iceland (Markafjót, Þjórsá). The shale-normalized (subscript SN) REY patterns of the suspended particles and NPCs of Kalix and Råne rivers are rather flat with a small negative cerium anomaly, while the respective patterns of the Markafjót and Þjórsá rivers show a slight enrichment of middle REY_{SN} relative to light and heavy REY_{SN}. The REY_{SN} patterns of the truly dissolved fraction of these rivers are distinctly different from their suspended particles and their NPCs. All four rivers show almost seawater-like REY_{SN} patterns in the truly dissolved fraction with an enrichment of heavy REY_{SN}, a negative Ce_{SN} anomaly and a distinctively positive Y_{SN} anomaly. Our results of the truly dissolved fraction having a seawater-like REY_{SN} pattern are comparable to those of available ultrafiltration data from different rivers, suggesting that the truly dissolved fraction may have a major influence on the REY distribution in seawater. Currently, there is only a limited amount of ultrafiltration data for rivers, estuarine waters and seawater available. It is, therefore, crucial to collect more data in order to investigate the influence of estuaries on REY distribution in the open ocean.

Key words: rare earth elements, boreal rivers, ultrafiltration

TAGUS ESTUARY OBSERVATORY: SEASONAL MONITORING OF THE WATER QUALITY

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Abstract: The Tagus estuary (Portugal) supports diverse uses and activities and its ecological value is well recognized. This study aimed to characterize the water quality in the Tagus estuary during one year, as part of the Tagus estuary observatory. Three field campaigns were performed in 2018 covering distinct seasons (Spring – May; Summer – September; Autumn – November). Seven sampling stations were chosen, covering the whole estuary and its water bodies (WB). At each station, physical, chemical and biological data were collected during one semidiurnal tidal cycle (~12 hours). Temperature, salinity, pH and dissolved oxygen were measured *in-situ*. Water samples were collected to determine in laboratory the concentration of nutrients, chlorophyll-a and total suspended solids. Results showed marked spatial gradients, typically with larger concentrations of chlorophyll-a, nitrate and silicate upstream. Silicate and nitrate presented a conservative behaviour, contrarily to ammonium and phosphate. Seasonally, the highest nutrients and suspended solids concentrations were found in Autumn, after a period of rainfall, pointing out to the relevance of land runoff for material supply into the estuary. These conditions were favourable for phytoplankton development, once chlorophyll-a was maximum during this campaign (24 μg/l in the upper estuary – WB4). Following Caetano et al. (2016) the Tagus estuary was classified relative to the nutrients concentrations. Both the Tagus WB1 and WB2 presented "Good" status. The Tagus WB3 and WB4 presented "Medium" status due to, respectively, ammonium, and nitrate and phosphate concentrations. The data acquired will be combined with historical data and numerical modelling, to contribute to a better understanding of the biogeochemical buffering capacity of the Tagus estuary and its susceptibility to climate change and anthropogenic pressures.

Key words: Estuarine observatories, nutrients, chlorophyll-a, nutrients status classification

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PLATINUM ACCUMULATION AND TOXICITY IN MARINE BIVALVES

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Abstract: Despite expanding use and increasing release of platinum (Pt) into the coastal environment, almost no studies cover the transfer of this Technology Critical Element (TCE) to marine biota and its associated potential toxicity. Oysters (*Crassostrea gigas*) from an unpolluted estuary were exposed to the stable isotope ^{194}Pt in seawater at a range of concentrations (50, 100, and 10 000 $ng.kg^{-1}$ Pt) during 35 days. Seawater was renewed daily and spiked to respective nominal Pt concentrations for two replicate exposure series. Control conditions were also monitored. Fifteen oysters from each tank were sampled and dissected after 3, 7, 28 to 35 days of Pt exposure. Different endpoints were investigated throughout the exposure period being (i) Pt distribution between the different organs (organotropism) through analyses by ICP-MS, and (ii) modification of biomarkers at cellular (lipofuscin and lipid content, Black Silver Deposit accumulation) and tissue (digestive gland integrity) levels. Organotropism study revealed that gills, and to a lesser extent mantle, show the strongest Pt accumulation. A linear increase in Pt levels occurred in all the organs investigated (i.e. digestive gland, gonads, gills, mantle, and muscle) with the exposure period. In oysters exposed to Pt concentrations of 10,000 $ng.kg^{-1}$, significant biomarker impairments were detected, with a clear toxicological impact at cellular levels. They reflect altered lipofuscin and neutral lipid contents, as well as intra-lysosomal metal accumulation. These observations suggest the activation of excretion (detoxification) mechanisms, including Pt elimination through faeces and clearly support the importance of the digestive gland in the response to direct Pt exposure. The present work contributes to our understanding of Pt accumulation and biomarker responses in marine bivalves. Effects of emerging metallic contaminants such as Pt and other TCEs in aquatic organisms may be used as integrative tools between environmental monitoring and toxicological assessment.

Key words: Platinum; Isotopes; Marine Bivalves; Organotropism; Biomarker.

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DISPERSION SCENARIOS OF ANTIMONY AND TELLURIUM RADIONUCLIDES IN THE GIRONDE ESTUARY: A COMBINATION OF SOLID/LIQUID PARTITIONING, RADIONUCLIDE DECAY AND ESTUARINE HYDRODYNAMICS

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Abstract: Antimony (Sb) and tellurium (Te) radionuclides are nuclear fission products presenting non-negligible radioactive doses (Saito et al. 2015). However, their environmental dispersion is unknown and historical releases from Chernobyl and Fukushima major nuclear power plant (NPP) accidents were scarcely monitored, particularly in aquatic systems (Whitehead et al. 1988). A commonly accepted alternative approach to understanding radionuclide environmental dispersion and fate is to study the stable homologues in the field ("inherent") and/or laboratory experiments representing environmental conditions ("experimental"). However, differences between inherent and experimental element behaviour may occur due to element-dependent properties, speciation and spiking concentrations (Ciceri et al. 1988). This work compares inherent and experimental Sb and Te solid/liquid partitioning (Kd) and sorption kinetics on suspended particulate matter (SPM) from the Gironde Estuary in contrasting salinity (0 and 32) and turbidity (100 and 1000 mg L^{-1}) gradients. Matching inherent and experimental Kd values were found for Te (log_{10} Kd 4.9-5.3 L kg^{-1}; Gil-Díaz et al. 2019), whereas higher inherent (log_{10} Kd 3.5-4.4 L kg^{-1}; Gil-Díaz et al. 2016) than experimental (log_{10} Kd ~2.0 L kg^{-1}) Kds occurred for Sb. Coupling these results to temporal scales of Sb/Te radionuclide decay and estuarine seasonal hydrodynamics (e.g., water and SPM residence times) suggests that hypothetical radionuclide releases from the Blayais NPP in the Gironde Estuary may result in contrasting scenarios: (i) non-negligible transport of dissolved ^{125}Sb ($t_{1/2}$ = 2.76 y) to the coast in all hydrological conditions, and (ii) high sorption/retention of ^{129}Te ($t_{1/2}$ = 1.16 h), ^{132}Te ($t_{1/2}$ = 3.2 d) and ^{129m}Te ($t_{1/2}$ = 33.6 d) radionuclides within the estuarine SPM, especially in the maximum turbidity zone (MTZ, SPM>1000 mg L^{-1}) during high discharge conditions. These findings together with the upstream migration of the MTZ to the city of Bordeaux during drought conditions should be included in post-accidental nuclear risk assessment.

Key words: Blayais NPP, radioactivity, residence times, nuclear risk assessment

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CADMIUM FRACTIONATION IN DEPTH SEDIMENTS OF SAN SIMON BAY (NW IBERIAN PENINSULA)

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Abstract: Trace metals have a great ecological and environmental significance due to their toxicity and accumulative behavior. Most of them have increased their concentration due to human activities, impacting in their biogeochemical cycles and generating a high pressure, particularly in coastal environments. San Simon Bay is a shallow embayment located in the innermost zone of the Ría of Vigo (NW Spain). The bay supports mariculture activities of great economic importance hence, the presence of potentially toxic elements like Cd requires some vigilance. Their mobility, biological availability and potential toxicity is dependent on their chemical forms and partitioning within sediments.
A gravity core (230 cm depth) was retrieved in San Simon Bay and cut into 10-cm (n = 23). Sequential extraction was performed according to the method of Campanella, et al. (1995), 5 fractions were obtained: (F1) Cd present in ion-exchange form and bound to carbonates, (F2) Cd in the reductive phase bound to manganese-iron oxides, (F3) Cd weakly bound to organic matter, (F4) Cd strongly bound to organic matter, (F5) Cd bound to sulfides. The results showed that Cd concentrations ranged from 0.1 to 2.1 mg kg^{-1}. Cadmium exhibited considerable presence in the F1 (i.e. exchangeable and bound to carbonates) and F4 (i.e. strongly bound to organic matter) fractions. More than 75% of the total Cd was found in F1 fraction above 100 cm depth, involving a potential risk of contamination in the San Simon Bay. Moreover, Cd showed a high susceptibility to complexation with organic matter compounds, especially below 100 cm where F4 fraction reached more than 55% Cd total at some depths. In conclusion, Cd showed higher mobility and bioavailability in the surface layers remaining bound to organic matter in depth.

Key words: Cadmium geochemistry, San Simon Bay, sediments

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IDEALIZED MODELLING OF MICROPLASTIC TRANSPORT IN ESTUARIES

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Abstract: Microplastic pollution in marine environments is currently receiving much attention due to the increased awareness of its potential risks to human health and wildlife. Numerical simulations can be used to provide estimates of microplastic distribution, but so far this approach has been largely applied to coastal seas and the open ocean. In this work, we develop a 2D-vertical model to gain insight into the transport mechanisms and spatial distribution of both floating and suspended microplastics in estuaries. Firstly, three simplified synthetic cases, corresponding to a salt-wedge, a partially-mixed and a well-mixed estuary are devised and analysed. We show that the model is capable of reproducing the physical distribution mechanisms described in the conceptual model of Vermeiren et al. (2016). Secondly, we consider the Ria de Vigo estuary as a real case study. The relative importance of the circulation induced by various forcings (river discharge, wind, gravitational circulation and tidal straining) on microplastics distribution is evaluated. Forcing conditions that induce the seaward flushing of microplastics or, on the contrary, the trapping of microplastics within the estuary are identified. Based on time series of forcings, residence times of microplastics are estimated. It is argued that this modelling approach can guide field surveys and contribute to the implementation of measures to reduce microplastic pollution.

Key words: microplastics, estuary, idealized model, spatial distribution, transport mechanisms

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INTERACTION OF MERCURY WITH BEACHED PLASTICS WITH SPECIAL ATTENTION TO ZONATION, DEGRADATION STATUS AND POLYMER TYPE

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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, colour and degradation status 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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ENVIRONMENTAL DIAGNOSTIC OF THE IMPACT OF WASTEWATER DISCHARGES ON WATER QUALITY OF SHELLFISH WATERS IN THE RIA FORMOSA LAGOON: CONPRAR PROJECT

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Abstract: Ria Formosa (RF)is a productive coastal lagoon located along the South coast of Portugal. This ecosystem supports intensive shellfish farming, dominated by the bivalve species *Ruditapes decussatus* (ca. 90% national production), being thus highly relevant from both ecological and socio-economic perspectives. Despite providing significant goods and services, RF is subjected to various anthropogenic pressures, including the discharge of urban wastewater treatment plants (UWWTP), which represents a great concern on the water quality. In this context, this study, integrated in the project CONPRAR, aims to assess the impact of the five major UWWTP on RF water quality, specifically in the vicinity of shellfish farming grounds. Water quality has been evaluated since September 2018 and will be undertaken during a 2-year period. Sampling is conducted monthly (Winter) and bimonthly (Spring – Autumn), during both spring and neap tides, along a longitudinal gradient of the effluent dispersion (1-2 km), starting at the discharge point. Water quality of surface samples, representative of maximum effluent influence, included *in situ* analysis of temperature, salinity, pH and dissolved oxygen, using an EXO2 multiparameter sonde (YSI). In the laboratory, concentration of dissolved inorganic macro-nutrients and chlorophyll *a* (used as a proxy for phytoplankton biomass), phytoplankton composition and bacteriological contamination were further analysed. Our dataset will be explored to: (i) evaluate the spatial impact of each major UWWTP; (ii) identify periods of intensified UWWTP impacts; (iii) compare water quality across RF domains; and (iv) diagnose the global risk of UWWTP on water quality, using an integrative Quality Index for bivalves. This index will jointly consider chemical and microbial contamination, including both bacteriological data and potential harmful phytoplankton species. Overall, project information will be disseminated to groups of interest (e.g., end-users, decision makers, shellfish farmers) and aims at supporting the management and protection of RF valuable ecosystem and resources.

Key words: Ria Formosa, coastal lagoons, water quality, UWWTP, *Ruditapes desussatus*

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ANNUAL CYCLE OF INSHORE-OFFSHORE EXCHANGES OF NUTRIENTS AND DISSOLVED ORGANIC MATTER IN THE RIA OF VIGO

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Abstract: The exchanges between the Ria of Vigo and its adjacent shelf are mainly driven by seasonal upwelling events, which move ENACW inside the ria, and the river contributions that export water from the ria to the ocean. So, the ria is a biogeochemical reactor processing the ENACW and fluvial nutrients, exporting organic matter offshore where a subsurface remineralisation zone takes place. We hypothesise that both fluxes, from land and ocean, entering to the ria are contributing to support the shelf remineralisation process throughout the year. Hydrographical and meteorological information, together with dissolved oxygen saturation, nutrient salts (nitrate, nitrite, ammonium, phosphate and silicate) and dissolved organic carbon and nitrogen (DOC and DON, respectively) concentrations, were obtained from June 2017 to June 2018 in 19 ria-shelf water column sections with nine oceanographic stations sampled on-board the CSIC R/V Mytilus. The shelf remineralisation maximum has remained, with varying intensity, at the isobath of 125 m close the bottom (100-125 m depth), where 65-95% of oxygen saturation, 9-15 μM of nitrate, 0.6-1.0 μM of phosphate and 60-90 μM of DOC were measured.

Key words: nutrients, organic matter, upwelling, ENACW, remineralization, ria, Galicia.

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EFFECTS OF DIFFERENT NITROGEN SOURCES ON COASTAL MICROPLANKTON COMMUNITIES

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Abstract: Anthropogenic alteration of the nitrogen (N) cycle has importantly increased the inputs of organic and inorganic reactive N (Nr) into the coastal ocean. N controls the productivity of marine ecosystems over ecological time scales and therefore, significant responses of microbial communities to the incoming supply of Nr might be expected. The short-term effects of inorganic and organic nutrients, limited in phosphorus (P) and including different sources of N (nitrate, ammonium), on microplankton community structure and metabolism were studied in microcosm experiments conducted in a eutrophic coastal embayment in NW Spain under contrasting hydrographic conditions. Results obtained showed that micro- and nanophytoplankton positively responded to nutrient additions, and did not show a preference between distinct inorganic N forms. By contrast, picophytoplankton and heterotrophic bacteria clearly preferred ammonium to nitrate. These results are important in the context of increasing riverine and atmospheric inputs (with high N/P ratios and relatively different ammonium and nitrate concentrations) into marine coastal embayments.

Key words: anthropogenic inputs, nitrogen, ocean, phytoplankton, bacterioplankton.

BIOGEOGRAPHICAL DISTRIBUTION OF ANAMMOX BACTERIA IN NW PORTUGUESE ESTUARIES

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Abstract: Anthropogenic inorganic nitrogen inputs to aquatic systems are a major environmental concern in the EU and worldwide. The discovery of anaerobic ammonium oxidation (anammox) revealed the existence of a shortcut in the classic nitrogen cycle where ammonium is converted directly to dinitrogen gas (Mulder et al., 1995). In recent years, the importance of this process has been demonstrated in both engineered and natural ecosystems (Hu et al., 2013; Sonthiphand et al., 2014). Anammox reaction is performed by a distinct group of bacteria belonging to the *Planctomycetes* phylum. Anammox bacteria have been reported in a variety of habitats, from marine anoxic basins to freshwater lakes, but despite the widespread occurrence, low diversity of anammox bacteria has been reported so far (Sonthiphand et al., 2014). In this study, we aimed to examine the diversity and distribution of anammox bacteria in natural habitats along the NW Portuguese coast. Sediment samples were collected in different estuaries, coastal lagoons, and saltmarshes. Total community DNA was extracted and anammox bacterial 16S rRNA gene sequences were amplified using specific set of primers. The amplicons were cloned and sequenced. Sequences were compared to reference sequences, aligned, and submitted to phylogenetic analysis. Anammox-like sequences were recovered from samples from different locations including the Cávado, Ave, and Douro estuaries. Phylogenetic analysis of the 16S rRNA genes has revealed the presence of three of the five genera described so far, namely, *Candidatus Scalindua*, *Kuenenia*, and *Brocadia*. The broad anammox bacterial distribution indicates that anammox might play an important role in removing fixed nitrogen from those estuarine systems.

Key words: Anammox, Sediments, Biogeography

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PALAEOPRODUCTIVITY RECONSTRUCTION OF A SEDIMENT CORE FROM THE TRANSITIONAL ZONE OF THE GALICIA CONTINENTAL MARGIN

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Abstract: Biogenic Barium, Organic Phosphorous and Total Organic Carbon (TOC) proxies were calculated to obtain the palaeoproductivity reconstruction of the last 170 kyr BP of a core extracted at the Transitional Zone (TZ) in the Galician continental margin. Five-step sequential extractions analysis (Schenau et al., 2001) were performed in a 125 mg of freeze-dried of sixteen selected samples to determinate the different phases of barium (biogenic barium, Ba associated with Fe/Mn oxides and Ba associated with aluminosilicates) and phosphorous (biogenic apatite, iron-bound P, authigenic apatite, detrital apatite and organic P) by ICP-OES. Total acid digestions were performed in 216 samples to obtain the downcore Ba_{total} and P_{total} concentration. Duplicate samples and sediment reference materials standards monitored the validity and accuracy of the ICP-OES results. Biogenic Barium (Ba_{bio}) and organic phosphorous (P_{org}) were estimated subtracting detrital barium (Ba_{det}) and detrital phosphorus (P_{det}) fraction from the $[Ba]_{total}$ and $[P]_{total}$ respectively. The detrital fraction was estimated as the result of the $[Al]_{total}$ x $(Ba \text{ or } P/Al)_{det}$ equation, where $(Ba \text{ or } P/Al)_{det}$ values were obtained from the sequential extraction. Total Carbon (TC) and Total Inorganic Carbon (TIC) were determined with a LECO CNS2000 elemental macroanalyzer. The total organic carbon (TOC) was calculated by the difference between TC and TIC. Productivity Ba_{bio}, P_{org} and TOC fluxes were calculated for each proxy (Schoepfer et al., 2015). Productivity fluxes results and [Ba] and [P] of the different phases, allowed understanding the variation of the biological pump and the biogeochemical cycles in the Galicia continental margin attending to the glacial/interglacial cycles along the last 170 kyr BP.

Key words: palaeoproductivity, biogeochemical cycles, barium, phosphorus, Galicia continental margin

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TARENA EXPEDITION AN OCEANOGRAPHIC CAMPAIGN BIOGEOCHEMICAL IN TROPICAL ESTUARY

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Abstract: TARENA objective is to understand biogeochemically in the Gulf of Urabá an area of semi-enclosed estuaries, located in the southwest Caribbean Sea, Colombia (South America). The first oceanographic campaign, which explored areas in the south of estuary. Today, the expedition took place in about 15 stations in 80km of longitude along of estuary. Oceanographic research to show that there was a hypoxic event, high nutrients concentrations, chlorophyll-a, biomass, high diversity planktonic, and the outbreak of toxic algae. Finally, TARENA has allowed us to know the diversity of a few explored area within the coastal ecosystems of Colombia.

Key words: Estuaries, Oceanographic Campaign, Biogeochemical

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REVISITING THE CRITICAL TURBULENCE HYPOTHESIS IN THE UPWELLING REGION OFF NW IBERIA

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Abstract: The Critical Turbulence Hypothesis (CTH, Huisman et al., 1999) proposes that if turbulence is low enough, phytoplankton in the well-lit surface layer could bloom independently of the thickness of the mixed layer. Here use the theoretical framework of the CTH to investigate the variability of phytoplankton growth along a seasonal cycle in the NW Iberian Peninsula. Continuous recording of current velocity data were collected in the Ría de Vigo between March 2017 and May 2018. Vertical profiles of dissipation rates of turbulent kinetic energy, by using a microstructure profiler, and samples for the determination of inorganic nutrients, phytoplankton biomass and primary production were collected weekly. Phytoplankton growth rates were high and very variable during the spring-summer upwelling season, coinciding with shallow mixed-layers due to thermal stratification and relatively weak mixing ($\leq 10^{-4}$ m^2 s^{-1}). During autumn, when an alternance of downwelling-upwelling conditions was observed, growth rates declined to ≤ 1 d^{-1} along with an increase of the mixed-layer depth and strong mixing ($\sim 10^{-2}$ m^2 s^{-1}). From January to April downwelling conditions prevailed and growth rates remained low (≤ 1 d^{-1}) despite the shallow mixed layers, due to haline stratification and relatively weak mixing ($\leq 10^{-4}$ m^2 s^{-1}). A wavelet spectral analysis (Torrence et al., 1999) showed three maxima of covariace between phytoplankton growth rates and mixing at ~29-35 days, ~55-62 days and ~100-110 days. The first maximum was associated with high variability sampled during the upwelling season, the second was present through most of the year, and the third corresponded with the growth decline observed in autumn. Our results partially agree with the CTH and show the coupling of turbulence and phytoplankton growth at different temporal scales in this system.

Key words: Phytoplankton growth, turbulence, Critical Turbulence Hypothesis, Ría de Vigo, Upwelling region off NW Iberia

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NEPHELOID LAYER DYNAMICS IN A COASTAL UPWELLING SYSTEM (NW IBERIA)

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Abstract: The dynamics of the bottom boundary layer (BBL) and their effects on the development of nepheloid layers (NLs) on a high-energy and upwelling-affected margin, the NW Iberian continental shelf, was studied by means of ADP currents, wave time series and across-shelf hydrographic surveys covering an entire annual cycle. The BBL hydrodynamics showed that high levels of bottom shear stress in the inner shelf occurred mainly during the downwelling seasons, when there was a coupling between wave storms and intense currents. This wave-current coupling, promoting strong resuspension events, favored the generation of bottom nepheloid layers (BNLs) that were limited to the inner continental shelf inshore of a thermohaline front generated by the interaction of the Iberian Poleward Current (IPC) and the West Iberian Buoyant Plume (WIBP). The front prevents the offshore export of resuspended particles during the downwelling season. Indeed, resuspended material is directly transported northward within an inshore coastal current. In contrast, during the upwelling season only thin BNLs were developed, and surface nepheloid layers (SNLs), principally composed by biogenic particulate material, were advected offshore in the Ekman layer often as part of the development of upwelling filaments, becoming the principal offshore export pathway.

Key words: bottom boundary layer, nepheloid layers, wave-current bottom shear stress, coastal upwelling, NW Iberia.

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CHARACTERIZATION OF PHYTOPLANKTON COMMUNITY AND NON-LIVING PARTICLES BY CONVENTIONAL MICROSCOPY AND FLOWCAM® IN THE RIA DE VIGO

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Abstract: Most biological studies on the dynamics of pelagic ecosystems focus on the living components. However, natural non-living particles of mineral (e.g. clay particles) or biological origin (e.g. faecal pellets) as well as synthetic particles (e.g. micro-plastics) may play an important, but normally misleading, role in ecosystem function and biogeochemical cycles, for instances enhancing particle sinking or providing colonisable surfaces for certain organisms (Passow. U, 2002; Eerkes-Medrano et al, 2015). In the present communication we have carried out a combined study of the phytoplankton community, the thanatocoenosis (the assemblage of organisms or their parts brought together after their deaths) and synthetic particles (mainly plastic fibres).
The study was realized in a fixed station in Ría de Vigo, as a part of project REMEDIOS ('The role of mixig on phytoplancton bloom initiation, maintenance and disipation in the Galician rias').The samples were collected approximately once a week from 9 March 2017 to 10 May 2018, at 1m and 10m depth. Phytoplankton community composition was obtained by traditional microscopy (Uthermöhl).The flow imaging microscopy (FlowCAM®) provided collection of images of the living and non-living particles present in the samples, that were classified in several groups according to its morphometric characteristics (size, shape, colour or transparency): clay particles, faecal pellets, semi-transparent aggregates (possible transparent exopolymer particles (TEP)), parts of organisms (e.g. empty diatom frustules, parts of zooplankton corpses) and synthetic fibres. Preliminary analysis suggests that the combination of traditional and image-based approaches provides a broader view of ecosystem dynamics, and the relationships between living and non-living components.

Key words: Phytoplankton community, non-living particles, thanatocoenosis, FlowCAM®, Ría de Vigo.

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INORGANIC CARBON CYCLE IN THE RIA DE VIGO (NW SPAIN)

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Abstract: Inorganic carbon cycle in coastal environments plays a key role for the ecosystems (e.g. Guinotte and Fabry, 2008; Bauer et al., 2013). The most frequently measured variables of this system: total alkalinity (AT), total dissolved inorganic carbon (TCO2), pH and partial pressure of CO2 (pCO2), have a high variability in estuaries. Because of the difficulty of measuring these variables with a high time frequency, the understanding of this cycle becomes complicated. Furthermore, anthropogenic modifications add a degree of difficulty. In this study, we have used a database containing oceanographic measurements in the coastal waters of Galicia (NW Spain) to extract the relationships between different predictors and the most frequently measured variables of the inorganic carbon system with the help of feedforward neural networks (Russell and Norvig, 2010). The predictors were depth, temperature, salinity, phosphate, nitrate, silicate, oxygen, chlorophyll-a, week and year. The root-mean-square error (RMSE) obtained for the four modelled variables with the combination of predictors that resulted in a lower error was 11.5 µmol kg^{-1} for AT, 16.4 µmol kg^{-1} for TCO2, 0.026 for pH and 11.1 µatm for pCO2. Passing the data measured by the Instituto Tecnolóxico para o Control do Medio Mariño de Galicia (INTECMAR) at 7 locations in the Ría de Vigo, surface (0-5m) time-series were obtained in a weekly time resolution between 2006 and 2019. Time-series were adequately validated with data of different cruises. The unique validation dataset with a monthly and sub-monthly time resolution showed how time-series represent very good the annual cycle in all the variables. This product is a seed to analyze in detail the inorganic carbon cycle in the Ría de Vigo. It can be used to evaluate the variability of the last decade and as initial conditions and validation in biogeochemical models.

Key words: Inorganic carbon cycle, time-series, neural networks, Ría de Vigo.

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AUTONOMOUS NUTRIENT ANALYSIS MONITORING USING A PORTABLE SYSTEM ALONG COASTAL TRANSECTS

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Abstract: Eutrophication can cause adverse effects in the coastal ecosystems, this leads to an accelerated proliferation of opportunistic microbial and macroalgae communities, altering the trophic structure of the marine ecosystems and deteriorating water quality. Consequently, nutrient enrichment risk negatively affects to ecosystem services (Ferreira et al, 2011; Millennium Ecosystem Assessment, 2005; OSPAR, 2017).

The determination of eutrophication risk requires a continuous acquisition of time series of nutrient data to establish environmental trends (EEA, 2014). Most of nutrient probes are commonly used for fixed and floating platforms (Bodini et al, 2015). In the context of the MarRISK project (0262_MARRISK_1_E), we have designed an easy portable system to autonomously measure inorganic nutrients along with other parameters such as pH, temperature and salinity along transects on research vessels. In-situ measuring instruments of this system (SBE45 thermosalinograph, AFT-pH sensor, WIZ nutrient probe) are mounted on a pumping circuit collecting sea-surface waters.

Regarding nutrient analysis, seawater sample is filtered through a fiber cartridge and pumped with a peristaltic pump into a flexible bag before entering in the WIZ analyser. The nutrients probe is programmed for sequential measurement of nitrate+nitrite and phosphate every 40 min. The WIZ probe is based on the automated micro-Loop Flow Reactor technology (patented by Systea S.p.a., Italy) and it is composed of an analytical unit and a reagent canister. Nitrate+nitrite analysis is based on UV-phoreduction and phosphate is determined by OPA fluorimetric method. The main advantages of this probe are the low reagents consumption (in the order of µL) and the analysis of 4 parameters (nitrate+nitrite, nitrite, phosphate and ammonium) using one single unit.

This autonomous system integrated by the WIZ probe-pHmeter-thermosalinograph-GPS is activated manually by a single user only to start and to stop it. This multi-parameter system has been tested in several campaigns in automatic and continuous mode for more than 24 h, showing that it is a powerful tool for biogeochemistry studies in coastal areas.

Key words: Inorganic nutrients, Eutrophication, Coastal risks, WIZ probe; Autonomous analyses.

Acknowledgments: We are indebted to the crew of the R/V Mytilus (UTM-CSIC, Vigo) and Tyba III (BDRI, O Grove) for their assistance. This contribution has been funded by the European Union MarRISK project: Adaptación costera ante el Cambio Climático: conocer los riesgos y aumentar la resiliencia (0262_MarRISK_1_E), through EP-INTERREG V A Spain-Portugal (POCTEP) program, 2014-2020.

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BIOGEOCHEMICAL BUDGET OF NUTRIENTS AND ORGANIC MATTER IN THE RIA OF CEDEIRA. CHANGES DUE TO ANTHROPOGENIC DISTURBANCES AND SEASONAL UPWELLING

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Abstract: Biogeochemical processes in the Western Galician Rias are mainly driven by continental and marine inputs of nutrients. Upwelling usually supply nutrients during the dry season and fluvial loads can be disturbed by anthropogenic activities, a question scarcely treated in the literature. The objective is (i) to quantify the pristine, included upwelling contributions, and anthropogenic sources of nutrient salts and organic matter to the Ria of Cedeira and (ii) to explore the relevance of changes in the ria budget.
The Ria of Cedeira (area of 4.7 km^2) is a Middle Galician Ria were the upwelling influence was not yet established. Three rivers flow into this Ria: Condomiñas (wastewater inputs), Das-Mestas (pristine) and Forcadas (dammed). Seawater column at the ria mouth was sampled (10 cruises) on-board the R/V Lura. Rivers were monitored the same days. Nitrate, nitrite, ammonium, phosphate and silicate, dissolved and organic particulate carbon (DOC, POC) and nitrogen (DON, PON) were determined. River loads and ria-ocean exchanges were estimated.
Similar land use, population distribution and climate of Cedeira fluvial basins allowed applying the Das-Mestas River as reference to quantify the anthropogenic disturbances: Condomiñas-ria fluxes of DOC and DON increased two-fold, ammonium three-fold and phosphate 10-times; Forcadas-ria fluxes of phosphate, silicate and DOC decreased to the half. Offshore was the main source for phosphate, DOC and DON, while rivers contributed with the half of silicate and one-tenth of DIN reaching the ria. Nitrate and phosphate concentrations in the incoming seawater increased 2-3 times during upwelling events. The Ria of Cedeira as a biogeochemical reactor remains under oceanic control since continental discharges of nutrients and organic matter are comparatively low. However, the direct (wastewaters) and indirect (impoundments) anthropogenic impact is changing the dissolved silicate and ammonium river-ria fluxes, which may modify the diatom-dinoflagellates assemblage.

Key words: nutrients, budget, upwelling, damp, wastewater, ria, Galicia.

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BENTHIC FLUXES AND NET ECOSYSTEM METABOLISM IN A COASTAL UPWELLING EMBAYMENT (RIA DE VIGO, NW SPAIN)

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Abstract: Simultaneous direct measurements of primary production, pelagic and benthic respiration and vertical fluxes allowed, for the first time, the evaluation of the carbon metabolism in the Ría de Vigo (NW Spain) on seasonal and annual scales. With this aim, a total of 16 oceanographic cruises covering the main oceanographic conditions were carried out between April 2004 and January 2005. In addition, a 2D carbon budget, including extraction from mussel culture and fisheries activities, is proposed. The pelagic system was net autotrophic during the spring and summer periods and autotrophic or almost in balance during autumn and winter. Vertical fluxes of organic carbon were higher than net community production (NCP) during autumn and winter periods, probably due to resuspension processes and inputs of organic matter from continental runoff. Benthic mineralization is an important process in the Ría de Vigo, which gains significance during autumn and winter when benthic respiration accounts for 40% and 45% of the total respiration, respectively. The Ría de Vigo is net autotrophic on annual basis (317 ± 113 g C m-2 yr-1) even though the benthic metabolism reduces the NCP by 23%. Total annual carbon seafood harvest amounted 3% of the net ecosystem metabolism and it is dominated by mussel culture (89%). However, based on mean energy transfer efficiency between trophic levels of 10%, it is estimated that mussel culture and reported fish catches require up to 38% of the NCP. The organic carbon produced in situ at the Ría de Vigo and available for export to the adjacent shelf and/or to be buried in the sediment represents ¼ of the gross primary production and it is favoured during summer upwelling.

Key words: benthic fluxes, net ecosystem metabolism, primary production, vertical fluxes, coastal upwelling, mussel harvest

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EXPORT OF DISSOLVED AND SUSPENDED MATTER FROM THE MAIN ESTUARIES IN SOUTH PORTUGAL DURING WINTER CONDITIONS

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Abstract: Estuaries are essential drivers of primary productivity in coastal waters through the export of dissolved and suspended material. This study aims at quantifying this fertilisation process at the two main estuaries in South Portugal during the typical low river discharge conditions that prevail in winter, due to strong flow regulation by upstream dams and seldom-local rain events. Data were collected across the channel of the lower Arade (10/01/2018) and Guadiana (04/02/2019) estuaries during an entire semi-diurnal tidal cycle with intermediate tidal range (1.5 m and 2.2 m, respectively). Continuous current velocity records (with a ship-borne ADCP) were completed with hourly temperature, salinity, pH and O_2 measurements (with a multiparameter sonde) and water collection near the surface and bottom for suspended solids, chlorophyll *a* and nutrients determination. Nutrients and chlorophyll *a* were analysed by spectrophotometric methods (Grasshoff *et al*., 1983 and Lorenzen, 1967, respectively), while suspended solids by a gravimetric method (APHA, 1992). Concentrations were averaged vertically, as no vertical stratification was observed (except at the Guadiana at the end of low tide). The results show that the two estuaries were characterised by distinct water circulation patterns and tidal properties (e.g., standing wave at the Arade, mixed wave at the Guadiana). Nevertheless, the along-channel Lagrangean flux of dissolved and particulate matter displayed a general similar anti-phase pattern of transport variations with tidal height at both estuaries. Likewise, the residual mass transport (obtained from the integration of the Lagrangean flux over the tidal cycle and channel section) indicated that both estuaries generally contribute to fertilize adjacent coastal waters by exporting nutrients (order of kg), chlorophyll *a* (order of kg) and suspended solids (up to tons). The results at both estuaries reflect the typical discharge flow and environmental conditions as well as the different contamination sources close to the study areas.

Key words: Arade estuary, Guadiana estuary, transport, nutrients, Chlorophyll *a*

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DISSOLVED ORGANIC MATTER DISTRIBUTION IN THREE ESTUARIES OF THE GULF OF CADIZ: TIDAL EFFECT AND TRANSPORT TO THE COASTAL ZONE

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Abstract: The Gulf of Cádiz connects the North Atlantic Ocean and the Mediterranean Sea through the Strait of Gibraltar and receives freshwater input from three estuaries with very different chemical properties (Guadalquivir, Guadiana and Tinto-Odiel). Guadalquivir and Guadiana present high concentrations of dissolved organic matter (DOM, González-Ortegón et al. 2018) whereas Tinto-Odiel estuary is one of the most polluted areas in the world (Sainz and Ruiz, 2006). However, the chemical composition of DOM in these estuaries and their role in the Gulf of Cádiz biogeochemistry is still unknown.

DOM composition was evaluated using its optical properties along the three estuaries systems of the Gulf of Cádiz. Dissolved organic carbon (DOC), colored and fluorescent dissolved organic matter (CDOM, FDOM) was analyzed. FDOM modeling was carried out combining excitation-emission matrixes and the multivariate parallel factor analysis (PARAFAC). The main components identified were: two humic-like (terrestrial and microbial) and two protein-like, widely distributed in aquatic systems. FDOM and CDOM concentration increased toward low salinity, showing a conservative character in Guadiana and Tinto-Odiel, while in Guadalquivir a non-conservative character was observed. A clear effect of tidal in FDOM was observed in the mouth of Guadalquivir and Guadiana, with higher humic-like material during low tide, while with high tide an increase in protein-like fraction was observed. Our results indicate a net transport of humic-like DOM to the Atlantic Ocean, even during the dry season, with DOC values of 2.16 x 10^6 in Guadalquivir and 1.82 x 10^5 mol d^{-1} in Guadiana. The results obtained in this work highlight the importance of local conditions in FDOM distribution, reactivity and transport to the coastal ocean.

Key words: DOC, fluorescence, estuaries, tide, carbon flux.

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BENTHIC NUTRIENT FLUXES IN SEDIMENTS ALONG THE LIMA ESTUARY (NW PORTUGAL)

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Abstract: Benthic fluxes of dissolved inorganic nitrogen (NO_x and NH_4^+), and phosphorus (PO_4^{3-}) were measured in sediments from the Lima River estuary (NW Portugal), during the summer and winter seasons. Sediment samples were collected at eight locations, covering subtidal and intertidal areas, along the salinity gradient. Water–sediment fluxes of inorganic nutrients were measured in laboratory microcosms with intact sediment cores and continuous water flow. Sediments from the Lima estuary were mainly composed by sand, with the exception of two subtidal locations. NO_x, NH_4^+, and PO_4^{3-} levels in the water column entering the estuary were 80.7 µM, 1.09 µM and 0.211 µM during the winter, and 25.9 µM, 2.62 µM and 0.128 µM during the summer, respectively. Nutrient concentrations decreased gradually during the 24h incubation period in most of the microcosms. The negative fluxes were more accentuated in winter, with no significant differences ($p>0.05$) between intertidal and subtidal sediments. The Lima estuary acted as a sink for inorganic nutrients thus reducing the transport of N and P from land to the sea.

Key words: Nutrient fluxes, Estuary, Sediments

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HYPOXIA IN THE LOWER ST. LAWRENCE ESTUARY: IMPACTS ON BENTHIC OXYGEN DEMAND

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Abstract: A decrease in oxygen concentration has been observed, at an average rate of 1 µmol L^{-1} $year^{-1}$, between 1930 and 1990, in the bottom waters of the Lower St. Lawrence Estuary (LSLE), resulting in persistent hypoxia (O_2 < 62,5 µmol/L). Under hypoxic conditions, the metabolic processes of many aquatic organisms can be altered and significant changes in benthic community assemblages and activities can be observed. Oxygen is the most favourable electron acceptor for the microbial mineralisation of organic matter in natural aquatic environments and for the oxidation of metabolites (Mn (II), Fe (II), NH_4^+, HS^-) of anaerobic respiration. Oxygen uptake rates at the sediment-water interface (SWI) can be used as an indicator of overall benthic respiration rates. We investigated the impact of persistent hypoxia on the sediment oxygen demand by comparing oxygen penetration depths and oxygen fluxes in cores recovered between 1985 and 2019 along the oxygenation gradient in the LSLE. All the measurements were conducted by high-resolution profiling across the (SWI) using potentiometric microelectrodes. Based on more than 100 profiles, we carried out a multivariate statistical analysis of the spatial and temporal distribution of the sediment oxygen uptake rates in the LSLE..

Key words: Hypoxia, Oxygen uptake, Lower St. Lawrence Estuary (LSLE)

HIGH RESOLUTION ANALYSIS ON MARINE AND ESTUARINE SEDIMENTS BY ITRAX CORE SCANNING IN THE CACTI OF THE *UNIVERSIDADE DE VIGO*: DATA OPTIMIZATION

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Abstract: A facility dedicated to rapid high-resolution (HR) analysis of marine and estuarine samples is available for the scientific community at the Scientific and Technological Research Assistance Centre (C.A.C.T.I.) of the *Universidade de Vigo* since 2012. HR optical images, radiographic images and X-ray fluorescence data – both qualitative and quantitative – can be obtained on sediment samples from continuous analysis. Such analyses provide very detailed information for assessing and monitoring trace element inputs to coastal environments or identifying diagenetic processes, among other applications. Measuring conditions need to be adapted to the objectives of the different study cases as well to the kind of target sediments, being necessary to optimize scanning resolution and exposure times (usually 1-2 mm, and 10-20 s, respectively). One meter core can be analysed in a few hours. Element quantification is done by selecting adequate sediment reference materials (SRM). The capabilities of the C.A.C.T.I. Itrax core scanner and the advances done in data optimization are presented through several examples where sediments of different provenance, composition and grain size are analysed. Results obtained with the two available anodes (Mo, Cr) are considered. Tests on element quantification on selected SRM at different exposure time or stepsize showed very good results for elements generally used in XRF-scanning studies. Discrete core-samples were also analysed for optimizing quantification. Test showed that most light rare earth elements (REE) can be detected.

Key words: high-resolution analyses, core-scanning, EDXRF, reference material, coastal sediments

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