



SIQUIMAR

XX SEMINARIO IBÉRICO DE QUÍMICA MARINA



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ORAL COMMUNICATIONS



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BIOGEOCHEMICAL PROCESSES

SEASONAL DYNAMIC OF CO₂, CH₄, AND N₂O IN THE GUADALQUIVIR ESTUARY

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Abstract: The concentration of dissolved CH₄ and N₂O, and the partial pressure of CO₂ (pCO₂) have been studied in the Guadalquivir estuary. Samples were taken in July 2017, and during March and April 2018 and 2019 in different rainy and tidal conditions. Two different types of sampling were carried out: a longitudinal transect across the river and during a tidal cycle of 24 h in the mouth of the estuary. The concentration of CH₄ and N₂O was obtained by using a gas chromatograph, and pCO₂ was measured continuously with an infrared gas analyser. The higher values of the gases were found in the inner part of the estuary and during the low tide. These distributions of the gases are affected by the organic matter and nutrient inputs that the estuary receives, through the river itself, from lateral inputs related to salt marshes and irrigation drainage areas, and by the organic matter remineralisation processes in the sediments. Seasonal variations were observed in the Guadalquivir estuary between July 2017 (pCO₂: 386.3 – 5865.6 µatm, CH₄: 4.9 – 441.9 nM, N₂O: 7.1 – 101.6 nM), March and April 2018 (pCO₂: 376.3 – 1357.5 µatm, CH₄: 5.1 – 158.0 nM, N₂O: 7.6 – 71.6 nM) and March and April 2019 (pCO₂: 465.1 – 2776.5 µatm, CH₄: 6.3 – 73.7 nM, N₂O: 4.8 – 97.0 nM). The water - atmosphere fluxes of the pCO₂, CH₄ and N₂O are positive, so the estuary acts as a source of these gases to the atmosphere.

Key words: Greenhouse gases, tidal cycle, water - atmosphere fluxes, Guadalquivir estuary

Acknowledgments: This work was supported by the Spanish CICYT (Spanish Program for Science and Technology) under contract RTI2018-100865-B-C21.

FLUXES OF PARTICLES AND ORGANIC CARBON IN THE NORTH BALEARIC SEA

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Abstract: We present the total mass and organic carbon fluxes obtained from a mooring line with two levels, at -200 m and -2400 m deep. The mooring was located at the base of the northern continental slope of the island of Menorca (western Mediterranean), at a depth of 2425 m. Framed by the ATHAPOC project (2015-2018), we maintained the mooring line for three sampling periods (I from 09/2015 to 03/2016; II from 12/2016 to 05/2017; and III from 06/2017 to 02/2018), with a total of 473 days.

Particle fluxes in the deepest trap show higher values, with average values up to 4.6 times higher than the surface. The average flux for the entire period was 113.2 and 172.2 mg·m⁻²·d⁻¹ at 200 and 2400 m of water depth, respectively. Temporal evolution of particle fluxes shows how the greatest difference between surface and bottom fluxes is inversely proportional to the magnitude flux, with larger differences between the surface and the bottom when the mass fluxes are lower.

The average organic carbon content of the fluxes was 9.8% for the surface trap and 4.6% for the deep trap, but fluxes at both levels were similar of 11.37 and 9.39 mg OC·m⁻²·d⁻¹, at 200 and 2400 m depth, respectively. The origin and evolution of organic matter has been studied through the isotopic composition ($\delta^{13}\text{C}_{\text{OC}}$ and $\delta^{15}\text{N}$) and the N:C ratio. In general, the $\delta^{13}\text{C}_{\text{OC}}$ isotopic signal shows values in the range of organic matter of continental origin or refractory organic matter, between -21.5 and -33.8‰. This signal was surprisingly more depleted in the deeper trap (average value of -29.2‰) than in the surface trap (25.5‰). The N: C ratio shows a dispersion of values (0.01 to 0.22) resulting from the mixture of organic materials of continental and marine origin.

Key words: Particle fluxes, Organic carbon, Key word 3 (3 to 5 key words)

GREENHOUSE GASES DYNAMICS IN MAR MENOR

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Abstract:

This study focuses on the characterization of the processes affecting the exchange of greenhouse gases (CO₂, CH₄ y N₂O) through the sediment-water and water-atmosphere interfaces. Two campaigns have been carried out in winter and summer of 2018 to evaluate the distribution of these gases in the water column and their exchange with the sediment (benthic chambers), as well as a set of complementary variables (salinity, temperature, dissolved oxygen, nutrients and chlorophyll) that allow a better interpretation of the processes that affect their concentrations. The partial pressure of CO₂ has been calculated from the pH and total alkalinity values, while the concentration of CH₄ and N₂O has been quantified by gas chromatography.

Benthic fluxes have an important seasonal variation, with an increase of dissolved inorganic carbon and methane fluxes during summer. If the total area of Mar Menor is considered, the sediment produces an input of $45.3 \cdot 10^8$, $2.0 \cdot 10^5$ and $0.25 \cdot 10^4$ mol year⁻¹ of dissolved inorganic carbon, methane and nitrous oxide to the water column, respectively. Surface water is oversaturated with CO₂ and therefore, Mar Menor acts as a source of this gas emitting $1.5 \cdot 10^8$ mol CO₂ year⁻¹ to the atmosphere. The water-atmosphere fluxes of CO₂ are lower in summer, as a result of the increase of the photosynthetic activity of phanerogams meadows. Regarding to CH₄, there is an increase of the concentration in summer due to an intensification of mineralization processes of organic matter with temperature. The system is supersaturated with CH₄ and acts as a source to the atmosphere, with an emission of $4.0 \cdot 10^5$ mol CH₄ year⁻¹. On the other hand, Mar Menor is undersaturated by N₂O due to its consumption in denitrification processes, acting as a sink of this gas ($3.5 \cdot 10^4$ mol N₂O year⁻¹).

Key words: Methane, Nitrous Oxide, Carbon Dioxide, Air-Water exchange, benthic fluxes, coastal lagoon.

Acknowledgments: This work was supported by “Dirección General del Mar Menor (Murcia)” under contract “Estudio biogeoquímico de los fondos del Mar Menor” (TRAGSA, OT2018/024).

CU AND FE REDOX INTERACTIONS IN SEAWATER

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Abstract: The current investigation studies the redox chemistry of Cu under different concentrations of oxygen, H₂O₂ and Fe, both Fe(II) and Fe(III). According with these experimental results, the Cu(I) oxidation rate under oxygen saturation conditions linearly decreased in the presence of Fe(II) and increased in the presence of Fe(III). The effect of Fe(II) was one order of magnitude higher than that for Fe(III). On the other hand, Cu(II) was rapidly reduced to Cu(I) in the presence of Fe(II) in seawater under air-saturated and anoxic conditions. The concentration of Cu(I) formed was affected by the concentrations of both Fe(II) and H₂O₂ in seawater.

However, in order to fully understand the Cu and Fe interaction in seawater, the role of Cu ([Cu]₀=0-200 nM) on the Fe(II) oxidation has to be studied. The experimental results demonstrated that these redox processes have to take into account: a) competition between both metals by the reaction intermediates; b) direct redox reactions between Cu and Fe; c) the formation of Fe-Cu species that is directly involved in the oxidation of Cu and Fe in seawater.

According to the experimental results, a kinetic model was developed. This inorganic kinetic model is the previous step to be able to incorporate the role of organic binding ligands in the Fe and Cu redox interaction in natural waters and represents an advance in the Fe and Cu coupled marine biogeochemical cycles.

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

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THE ROLE OF GENTISIC ACID ON THE Fe(III) REDUCTION IN SEAWATER

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Abstract: Natural organic ligands control the speciation and distribution of Fe in the ocean where >99% of dissolved Fe exists as organic complexes (Gledhill and van den Berg, 1994; Rue and Bruland, 1995). Gentisic acid (GA) is a phenolic compound excreted by marine microalgae and has been reported as a part of the ligand pool in natural waters (López *et al.*, 2015; Rico *et al.*, 2013; Santana-Casiano *et al.*, 2014).

The goal of this investigation was to study the Fe(III) reduction to Fe(II) in seawater under different GA concentrations (100 – 1000 nM) and pH (7.00 – 8.01). In order to elucidate the effect of the ionic composition of the seawater on the Fe(III) reduction process, the experiments were also carried out in 0.7 M NaCl (+ 2mM NaHCO₃) taking into account the same GA concentrations and pH range. In addition, studies for individual ions (K⁺, Br⁻, F⁻, Mg²⁺, Ca²⁺, B³⁺, SO₄²⁻) were performed. On the other hand, the Fe(III)-GA complexes were studied via formation and dissociation experiments.

The experimental results demonstrated that GA is able to reduce Fe(III) to Fe(II) in seawater in a pH-dependent process that is faster in seawater than that in NaCl solutions. This reaction is affected by the major ions in seawater favouring the Fe(II) regeneration in this medium. The complexes Fe(III)-GA was characterized by a formation rate constant of $k_f = 1.023 (\pm 0.24) \cdot 10^4 \text{ (M}^{-1}\text{s}^{-1})$ and a dissociation rate constant of $k_d = 2.06 (\pm 0.45) \cdot 10^{-4} \text{ (s}^{-1})$. The conditional stability constant of Fe(III)-GA complex was $\log K'_{\text{FeL}} = 7.79 \pm 0.04$. This study shows that phenolic compounds exudated by marine microalgae as GA are influencing the Fe marine biogeochemical cycles promoting the persistence of Fe(II) in solution and keeping in solution to be bioavailable longer periods.

Key words: Fe(III), Fe(II), Fe-binding ligands, Complexation, Seawater.

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ORAL COMMUNICATIONS

CHEMICAL OCEANOGRAPHY

TRACE METAL AND MICROBIAL PLANKTON IN THE SURFACE MICROLAYER OF THE MEDITERRANEAN SEA

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Abstract: Traditionally, studies of trace metals in the open ocean have focused in the first top meters, whereas the role of the ocean surface microlayer (SML) has been largely ignored. The present work investigates the trace metal (i.e. Cd, Co, Cu, Fe, Ni, Mo, V, Zn and Pb) composition, distribution and partitioning in the top meter (including the SML) of the central and western Mediterranean Sea. Our results indicate that residence times of particulate metals derived from aerosols deposition ranged from a couple of minutes (e.g. for Fe) to a few hours (e.g. for Cu) and where microbial uptake seems to play an important role. Our results show a strong negative correlation between Ni concentration and heterotrophic bacterial abundance in the SML and SSW, but whether this correlation reflects a toxicity effect or results from some other process cannot be ascertain.

Key words: Sea Surface Microlayer, Trace Metals, Mediterranean Sea, Neuston, Aerosols

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TEMPORARY EVOLUTION OF THE CARBON DIOXIDE SYSTEM IN A NORTHEAST ATLANTIC TRANSECT

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Abstract: The anthropogenic CO₂ emissions raise since the Industrial Revolution has increased its atmosphere concentration by approximately 40% (IPCC, 2013), which has had a significant impact on the Earth's climate (Solomon et al., 2007); as well as in the ocean chemistry, an important CO₂ sink that represents about one third of the total CO₂ emission (Sabine et al., 2004). In general terms, the anthropogenic CO₂ uptake by the ocean decreases the pH of seawater and alters the natural chemical balance of the CO₂-carbonate system, producing a decrease of calcium carbonate (CaCO₃) saturation, in a process termed “ocean acidification” (Caldeira & Wickett, 2003; Doney et al., 2009). In order to understand and model the dynamics of the carbon cycle and evaluate the biological effects and possible regional and temporal variations, it is important to study the CO₂ ocean system in time series in stations and transects.

This work focuses on the temporary evolution of CO₂ system in the transect “Las Palmas de Gran Canaria - Santa Cruz de Tenerife - Arrecife – Sagunto”, which corresponds to the RENATE P container ship itinerary. Specifically, it is evaluated the variation of the parameters that characterize the CO₂ ocean system: partial pressure of CO₂ (pCO₂), total dissolved inorganic carbon (DIC), total alkalinity (TA) and pH. The study region, in the Northeast Atlantic, has special interest from the chemical oceanography point of view. It is an oceanic transition region between the the African coast upwelling and the oligotrophic waters of the subtropical turn, influenced by the North Atlantic Oscillation (NOA) and the atmospheric deposition of earth's crust materials, which represents one of the main sinks in this basin and that has the strongest seasonal variation of CO₂ fugacity (fCO₂) (Landschützer et al., 2013; Schuster et al., 2009).

Key words: CO₂-system, CO₂ ocean sink, Ocean Acidification.

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SOLID PHASE EXTRACTION OF OCEAN DOM WITH PPL CARTRIDGES: EFFICIENCY AND SELECTIVITY

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Abstract: At an amount of 662 Pg C, dissolved organic matter (DOM) in the ocean, represents the Earth's largest reservoir of bioreactive organic carbon (Hansell et al., 2009), comparable to the atmospheric CO₂ pool (828 Pg C; Joos et al., 2013). Despite the size of this pool, its chemical composition is still poorly characterized, because of the low concentrations of DOM and the elevated salinity of seawater. Solid-phase extraction (SPE) using styrene divinyl benzene polymer cartridges (PPL) is one of the most extended methods to concentrate DOM and proceed to its molecular characterization (Dittmar et al., 2008). In this context, the main purpose of this work is to assess the efficiency and selectivity of this DOM isolation method in the ocean. The C and N content of DOM and its optical properties have been determined before and after SPE-PPL concentration on samples collected from surface to bottom in the Cape Vert Frontal Zone (CVFZ), where North and South Atlantic Central water masses converge, and the giant upwelling filament of Cape Blanc introduces coastal DOM into the open ocean. SPE-PPL average recovery was 52±8% for C and 29±10% for N, evidencing a much lower recovery of N compounds. The mean absorbance recovery was 60±42%, presenting the highest values at 340 nm (proxy for aromatic compounds). The average humic-like fluorescence efficiency was 96±50%, whereas protein-like fluorescence recovered by SPE-PPL was 55±23%. Horizontally, the northern and western transects presented higher recoveries than the eastern and southern ones for all the variables. Nevertheless, vertically, these recoveries were not affected by depth. Our results indicate that SPE-PPL does not extract the DOM in seawater evenly but the recovery varies among different DOM fractions. This information is fundamental when conducting studies oriented to specific DOM fractions, to know the limitations of SPE-PPL and improve it. Conversely, different recoveries among samples can be useful to infer molecular changes between them.

Key words: SPE, DOM, CDOM, FDOM, Cape Vert Frontal Zone

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THE NORTHEAST ATLANTIC IS RUNNING OUT OF EXCESS CARBONATE: THE FRAGILE FUTURE OF COLD-WATER CORAL COMMUNITIES

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Abstract: Ocean acidification decreases the excess carbonate, that is, the amount of carbonate available for marine calcifiers. Here, the chemical status of the Northeast Atlantic and its cold-water corals (CWC) communities is examined by means of a high-quality database of carbon variables based on the GO-SHIP A25 section. The database covers a two-decade period (1997-2018), where the mean annual atmospheric carbon dioxide (CO₂) increased from 364 to 409 parts per million of volume. The running out of excess carbonate, that is, the progression of undersaturation with respect to aragonite, could compromise the conservation of the habitats and ecosystem services developed by CWC communities. We find that the anthropogenic perturbation in the ocean carbon cycle is significantly decreasing the concentration of excess carbonate in the waters surrounding CWC communities at a rate of $-0.17 \pm 0.02 \mu\text{mol kg}^{-1} \cdot \text{ppm}^{-1}$. The optimal chemical conditions for development of CWC communities in the Northeast Atlantic are maintained by the interplay between the northward spreading of recently conveyed Mediterranean Water with excess of carbonate available and the arrival of subpolar-origin waters close to undersaturation. Given the current acidification rate, the living CWC communities would be exposed to undersaturated waters before the end of the century, if atmospheric CO₂ concentration reached ~ 700 ppm. Therefore, the future of the CWC communities in the Northeast Atlantic is closely linked to the accomplishment of global climate policies to limit global warming below 1.5-2°C, which would preserve chemically optimal conditions of CWC growth in this particular oceanic region.

Key words: Ocean acidification, cold-water corals, deep-sea, Vulnerable Marine Ecosystem, Northeast Atlantic.

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SPOT SAMPLING VERSUS PASSIVE SAMPLING: ADAPTING THE EXISTING ENVIRONMENTAL QUALITY STANDARDS (EQS) FOR DIFFUSIVE GRADIENTS IN THIN FILMS (DGT), FOR THE CHEMICAL ASSESSMENT OF METALS IN TRANSITIONAL AND LITTORAL WATERS

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Abstract: Since the adoption of the Water Framework Directive (WFD, Directive 2000/60/EC) for the protection and management of European waters, Member States are required to assess the chemical status of their water bodies by the comparison of the

concentrations of priority substances with Environmental Quality Standards (EQS). Accordingly, regulatory monitoring adopted by Member States is mainly based upon the collection of spot water samples and posterior analysis of the dissolved metal concentrations, which presents several advantages and limitations. In the context of the European INTERREG project MONITOOL, Diffusive Gradients in Thin films (DGT) passive samplers have been deployed in estuaries and coastal areas to i) investigate their potential to overcome some of the limitations of spot sampling, providing time integrated labile metal concentrations, and ii) adapt the already existing dissolved metal EQSs for water for DGTs, enabling their use for regulatory monitoring. Two sampling campaigns were carried out in winter (rainy season) and in summer (dry season) 2018, by simultaneous deployment of DGTs and high-frequency collection of spot water samples at several sites from the Bay of Biscay and other Atlantic and European regions (including Mediterranean and Irish Sea). DGTs and water samples were analysed for the dissolved (by ICP-MS), chemical labile (by voltammetry) and DGT labile (by ICP-MS) concentrations of priority (Cd, Ni, Pb) and other specific metals (Cu, Co, Fe, Mn, Zn). The metals concentration measured by DGT and by spot sampling were strongly correlated, except for Co. In general, these relationships were not explained by the studied environmental variables (salinity, pH, DOC/TOC, turbidity), although some exceptions were observed. From this data, adapted EQSs will be suggested, following a transparent and scientific procedure, to ensure that they are at least as protective as EQSs laid down for water. Ultimately, their consideration for regulatory purposes within the WFD will be proposed.

Key words: metals, passive samplers, DGT, EQS, marine waters, chemical status

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HOW HEAT WAVES AFFECT THE SEDIMENT-WATER INTERFACE IN SHALLOW AQUATIC AREAS?

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Abstract: The ongoing climatic change, caused by the anthropogenic production of greenhouse gases (GHG), is increasing the average temperature of the planet and the frequency of extreme climatic events such as heat waves. Shallow aquatic environments can be sources or sinks of such gases but are also highly vulnerable to short term climatic variations due to their low thermal inertia. In order to quantify the consequences of altered temperatures on the net metabolism, fluxes of dissolved inorganic nitrogen and GHG in these systems, sediment cores from the saltmarshes of the Bay of Cadiz were exposed to a wide range of temperatures (10, 18, 26, 34, 42 °C) in the laboratory during 5 days. Sediment-water fluxes were measured by core incubation and oxygen microprofiles.

Our results showed that higher respiration rates within the sediment decreased oxygen penetration depth in the sediment up to 40% with temperature (from 10 to 42 °C) and resulted in higher emissions of CO₂ with increasing temperatures. Sediments consumed ammonium from the water column and rates increased with increasing temperatures, likely reflecting a stimulation of nitrification rates. The GHG (CH₄ and N₂O) fluxes revealed a net release to the water column during the whole experiment at any temperature. N₂O release from the sediment increased with temperature up to 26-32°C, but decreased at higher temperatures. The N₂O emissions were also higher during the first days, showing an uncoupling of processes that enhanced net release from the sediment. The release of methane from the sediment increased exponentially with temperature, revealing a large impact of short-term temperature increases in the emissions of both GHG from shallow environments. Therefore, the increase in the frequency and duration of heat waves could significantly increase the net release of GHGs such as CO₂, CH₄ and N₂O with unknown consequences in further feedbacks with global warming.

Key words: Climate change, Greenhouse gases, Heat waves, Sediment-water fluxes alteration

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SEASONALITY OF DISSOLVED ORGANIC CARBON EXCHANGE ACROSS GIBRALTAR STRAIT

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Abstract: Exchange of mass, heat and dissolved materials across the Strait of Gibraltar are fundamental to understand the hydrography, circulation and biogeochemistry of the Mediterranean Sea and the North Atlantic Ocean (Huertas et al., 2012; Schneider et al., 2014; Barbosa et al., 2015). Here we focus on the exchange of dissolved organic carbon (DOC) across the strait. A marked bimodal distribution is observed, with exchange minima around $5 \cdot 10^9 \text{ g C d}^{-1}$ in late June and late October and maxima around $15 \cdot 10^9 \text{ g C d}^{-1}$ in mid April and late August. This temporal pattern is mainly due to seasonal variation of the DOC gradient between the Atlantic surface water (ASW, salinity < 37.5) that enters the Mediterranean Sea and the opposite-flowing Mediterranean Overflow Water (MOW, salinity > 37.5) (Huertas et al., 2012). This gradient is primarily controlled by the different seasonal cycles followed by the concentration of DOC in the two layers. Seasonal variability at the strait is not only autochthonous but caused by biogeochemical processes occurring during the transits of ASW and MOW to the Gibraltar strait too. Water exchange across the strait also varies seasonally, from a maximum of 0.90 Sv by early April and a minimum of 0.75 Sv by mid August (Sammartino et al., 2015), having a secondary impact on the variability of DOC fluxes. The annual average DOC exchange across the Strait of Gibraltar, $4.2 \pm 1.5 \cdot 10^{12} \text{ g C y}^{-1}$, represents 55% of the external DOC inputs and supports 32% of the net heterotrophy of the Mediterranean Sea.

Key words: DOC, exchange fluxes, net heterotrophy, Gibraltar strait

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SIGNIFICANT RELEASE OF DISSOLVED INORGANIC NUTRIENTS FROM THE SHALLOW SUBMARINE VOLCANO TAGORO (CANARY ISLANDS) BASED ON SEVEN-YEAR MONITORING

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Abstract: Tagoro, the shallow submarine volcano that erupted south of El Hierro (Canary Islands, Spain) in October 2011, has been intensely monitored for over 7 years, from the early eruptive stage to the current degassing stage characterized by moderate hydrothermal activity (Fraile-Nuez et al., 2012; Santana-Casiano et al., 2013; Santana-Casiano et al., 2016; Fraile-Nuez et al., 2018). Here, we present a detailed study of the emissions of inorganic macronutrients ($\text{NO}_2^- + \text{NO}_3^-$, PO_4 , and $\text{Si}(\text{OH})_4$) comprising a dataset of over 3300 samples collected through three different sampling methodologies. Our results show a significant nutrient enrichment throughout the whole studied period, up to 8.8-fold (nitrate), 4.0-fold (phosphate), and 16.3-fold (silicate) in the water column, and larger enrichments of phosphate (10.5-fold) and silicate (325.4-fold), but not of nitrate, in the samples collected directly from the vents. We also provide some preliminary results showing ammonium (NH_4^+) concentrations up to 1.97 μM in the vent fluids as compared to 0.02 μM in the surrounding waters. Nutrient fluxes from the volcano during the degassing stage were estimated as $3.19 \pm 1.17 \text{ mol m}^{-2} \text{ year}^{-1}$ ($\text{NO}_2^- + \text{NO}_3^-$), $0.02 \pm 0.01 \text{ mol m}^{-2} \text{ year}^{-1}$ (PO_4), and $0.60 \pm 1.35 \text{ mol } 234 \text{ m}^{-2} \text{ year}^{-1}$ ($\text{Si}(\text{OH})_4$), comparable to other important nutrient sources in the region such as fluxes from the NW-African upwelling (Barton et al., 1998). Nutrient ratios were affected, with a minimum ($\text{NO}_2^- + \text{NO}_3^-$): PO_4 ratio of 2.36:1; moreover, a linear correlation between silicate and 324 temperature enabled the use of this nutrient as a mixing tracer. This study sheds light on how shallow hydrothermal systems impact the nutrient-poor upper waters of the ocean.

Key words: hydrothermal vents, Tagoro submarine volcano, inorganic nutrients, Canary Islands,

nutrient fluxes

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COMBINED BIOTIC AND ABIOTIC EFFECTS ON FDOM COMPOSITION DYNAMICS

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Abstract: Fluorescent Dissolved Organic Matter (FDOM) composition is known to be subjected to modification by multiple processes, both biotic and abiotic. This work examines the combined effect of sunlight exposure and phytoplankton nutritional state on the evolution of FDOM composition along a 23-day mesocosm experiment, carried out at the University of Bergen Mesocosm Centre (Norway) during late spring 2018.

The experiment setup consisted on seven 11 m³ bags, three of which were covered with a transparent plastic lid that limited UV-radiation. All bags were enriched with nitrate and phosphate at different ratios and frequency throughout the experiment and the surrounding fjord water was used as a control. Multiple optical parameters were examined daily along with various biogeochemical variables (Chlorophyll-a, DOC and nutrient concentration and phytoplankton composition).

Thanks to the experimental design, we were able to attribute changes in FDOM composition to both biotic and abiotic effects. Photobleaching played a major role in the exposed bags, reducing significantly the humic-like components fluorescence (peaks A, C & M), while the production of protein-like components (peaks T & B) was mainly controlled by the nutritional state of the phytoplankton community. Phytoplankton responded to sunlight and nutrient limitation stress by increasing the production of humic-like components as a photoprotection strategy.

These findings underline the importance of considering not only environmental and biological factors but also their possible synergetic effects to better understand the forces driving FDOM composition dynamics.

Key words: FDOM, Mesocosm, Photobleaching, Phytoplankton.

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SIQUIMAR
XX SEMINARIO IBÉRICO DE QUÍMICA MARINA



ORAL COMMUNICATIONS

GLOBAL CHANGE

EFFECTS OF CLIMATE CHANGE AND ANTHROPOGENIC PRESSURES IN THE WATER QUALITY OF THE RIA FORMOSA (PORTUGAL)

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Abstract: The Ria Formosa, a coastal lagoon located in the South coast of Portugal, is a very important ecosystem that supports diverse economic activities in the region. Understanding how climatic and anthropogenic drivers will influence this coastal lagoon is fundamental to guarantee its sustainability. Thus, this study aimed to assess the influence of climate change and anthropogenic pressures in the water quality of the Ria Formosa using a numerical modelling approach. The 3D coupled hydrodynamic-biogeochemical model SCHISM (Zhang et al., 2006) was validated and used to simulate several scenarios of climate change and anthropogenic pressures in the Ria Formosa. Besides a reference scenario (S0), three scenarios were simulated: i) S1 - mean sea level rise of 0.5 m; ii) S2 - increase of the air temperature of 1.68°C and iii) S3 - increase of 50% of the ammonium and phosphorous loads from the wastewater treatment plants (WWTP) discharging into the lagoon. For the mean sea level rise scenario (S1), results suggest an increase of the salinity near the area of influence of the WWTP. The simulated increase of the air temperature (S2) leads to changes in the water temperature that range from 0°C to +1°C. Similarly to scenario S1, the influence of the increase of the nutrients loads (S3) is more significant near the area of influence of the WWTP. Overall, in comparison to the reference scenario minor differences are observed in the trophic index (TRIX) of the lagoon for the analyzed scenarios. The exception are some areas near the WWTP discharges, where the TRIX tends to increase for scenario S3. These results provide further insight about the response of the Ria Formosa to future changes and can support its management.

Key words: Ria Formosa, sea level rise, temperature, nutrients

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MODELLING THE IMPACTS OF CLIMATE AND LAND USE CHANGES ON WATER QUALITY IN THE GUADIANA BASIN AND THE ADJACENT COASTAL AREA

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Abstract: The increasing pressure on water resources and the management problems related to it, highlight the need of a multidisciplinary approach in the hydrological, social, economic and ecological field, applicable to every considered catchment.

Changes in land use means changes in quantity and quality of water resources; this scenario could be more severe with the intensification of some chemical and physical processes, as a consequence of climate change. Based on this concept, the present work has been developed to support the use of information systems tools in the decision making process, from integrated river basin management to the integrated coastal zone management. For this purpose, it is proposed a hydrological model, using the Guadiana catchment as case study. The model has been calibrated and validated for river flow with satisfactory results, and then it was used for water quality simulation. In this way, a first estimate can be presented about the impact of outflow from the Guadiana River on nitrate concentrations in the coastal area adjacent to its estuary. Furthermore, simulations were done under two future Climate Change (CC, Representative Concentration Pathway - RCP 4.5 and RCP 8.5) and Land Use (LU) scenarios to evaluate their contribution on nutrient concentration that reaches the estuary.

With this support, it can be sought solutions, linked to the modification of different crops, with policies and incentives that are considered convenient and that allow to control, prevent or correct the deterioration of water bodies and thereby accomplish with the quality levels required by European Directives.

Key words: water quality, hydrological model, integrated management, Guadiana, Climate Change

CARBON AND CALCIUM DYNAMICS IN THE GUADALQUIVIR RIVER ESTUARY

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Abstract: The longitudinal variation of the different species associated with the carbon cycle has been studied during the spring of 2019 in the estuary of the Guadalquivir river. This study has been carried out with two different tidal coefficients. For achieving this purpose, two campaigns were carried out aboard the B/O UCADIZ., the first one was in March from 19th to 22nd and the second one was in April from 9th to 11st.

Total alkalinity (TA) and dissolved inorganic carbon (DIC) increase into the estuary, where they reach maximum concentrations of 4034 and 3760 μmolkg^{-1} respectively. These high values in the river area are due to processes derived from biological activity such as breathing, and mainly the leaching of the carbonated basin and the dissolution processes of CaCO_3 , as indicated by the values above the unit registered for the TA/DIC ratio. The contribution of organic bases to the TA (AOrg) has maximum values in the most fluvial zone, contributing up to 19% in the TA. The apparent oxygen utilization (AOU) varies between -8,35 and 208,92 μmolkg^{-1} , presenting positive values in most stations. This indicates the predominance of the processes of degradation of organic matter throughout the estuary, especially in the most river area, coinciding with the highest values of DOC (335 μmolkg^{-1}) and nutrients. Equally, the high correlations between the DIC and nutrients indicate an intense remineralization of organic matter in the system, especially in the internal zone. The concentration of Ca^{2+} has been measured by potentiometric titration, and its value decreases towards the internal estuary area, with a variation range between 2,54 y 10,59 mmolkg^{-1} . On the other hand, the degree of saturation of CaCO_3 (Ω) has values greater than unit in all sampling station (Ω_{Ar} : 2,08-14,56; Ω_{Ca} : 3,23 - 24,99). DOC, DIC and nutrients have the highest concentrations at low tide, which is indicative than the Guadalquivir estuary acts an exporter of these substances to the Gulf of Cadiz. On the other hand, the difference in the tidal coefficient between the two campaigns does not seem to have affected the behavior of the different variables studied in the longitudinal or circadian sampling.

Key words: dissolved inorganic carbon (DIC), degree of saturation (Ω), Guadalquivir estuary, organic alkalinity (A_{Org})

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SIQUIMAR
XX SEMINARIO IBÉRICO DE QUÍMICA MARINA



ORAL COMMUNICATIONS

MARINE ECOTOXICOLOGY AND POLLUTION

MARINE XENOBIOTIC MONITORING VIA THE SMALL-SPOTTED CATSHARK (*Scyliorhinus canicula*): A MONTHLY TRAIT AND SPATIAL DISTRIBUTION EVALUATION

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Abstract:

The small-spotted catshark *Scyliorhinus canicula* (Linnaeus, 1758), is a Scyliorhinid shark species commonly found in Mediterranean and Northeastern Atlantic waters, at depths ranging between 10 and 400 meters (Compagno, 2001). The philopatric and sedentary nature of female *S. canicula*, along with its high abundance among bottom trawl bycatch; the resilience of its stocks to regular exploitation and its widespread distribution could support to some extent the biomonitoring potential of this species (Sims, Nash and Morritt, 2001; Massutí and Moranta, 2003; Ruckstuhl and Neuhaus, 2005; Pennino *et al.*, 2013; Gubili *et al.*, 2014; Kousteni *et al.*, 2015; Kousteni, Karachle and Megalofonou, 2017; Barragán-Méndez *et al.*, 2019).

Pb, Cd and Cu were extracted and quantified in Western Mediterranean (Alicante, Spain) fisheries sourced *S. canicula* muscle tissue via Microwave Assisted Extraction (MAE) and Graphite Furnace Atomic Absorption Spectrometry (GF-AAS). A monthly assessment is being performed on the spatial distribution of the studied elements via interpolation of georeferenced capture data and muscle tissue analysis results.

Preliminary results are consistent with the existence of regular, time persistent traits regarding element-specific concentration hotspots and their spatial distribution. However, the magnitude of these appeared to vary in time with only Cd showing concentration peaks surpassing during 2018 surveys the 0.05 $\mu\text{g}\cdot\text{g}^{-1}$ (ww) threshold established by the European Commission. The source and nature of this phenomena is yet to be revealed by future sampling and analysis of *S. canicula* specimens and environmental samples from the study area, nevertheless, the regularity of the observed traits offer further promising feedback towards the establishment of this species as a cost-effective, fishery-based heavy metal biomonitor.

Key words: Biomonitor, Fisheries, Catshark, *Scyliorhinus canicula*, Heavy metal

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WATER QUALITY OF THE RIA FORMOSA LAGOON (SOUTH PORTUGAL): UNRAVELLING THE EFFECTS OF URBAN WASTEWATER TREATMENT PLANTS

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Abstract: Ria Formosa is a productive coastal lagoon system located in the south Portuguese coast and represents the largest national producer of the clam *Ruditapes decussatus*. Effluents from urban wastewater treatment plants (UWWTP) have a critical impact on the lagoon water quality. This study aims to assess the impact of five main UWWTP on the Ria Formosa, particularly over shellfish farming ground areas. Water quality assessment was based on chemical variables, phytoplankton composition (including potential harmful species), and fecal contamination. Water sampling was conducted along dominant longitudinal gradients of the effluent dispersion, from the discharge point down to 1-2 km, during the period September 2018 - September 2019. Key variables indicative of sewage influence, such as salinity and dissolved oxygen, were measured *in situ* using a multiparametric probe (YSI EXO 2). Surface water (20-30 cm) samples were collected at both high and low tide (both at spring and neap tide from April to September, and only at neap tide between October and March) and analyzed for nutrients, chlorophyll-*a* concentration (Chl*a*) phytoplankton abundance and species composition, and indicators of fecal contamination. Nutrients and Chl*a* were quantified using Grasshoff *et al.* (1983) and Lorenzen (1967) methods, respectively. Samples for phytoplankton analysis were preserved with Lugol's solution and observed using inversion microscopy (Utermohl, 1958). Bacteriological indices of fecal contamination, *Escherichia coli* and enterococci (most probable number) were assessed using the Quanti-Tray method, following manufacturer guidelines. The impact intensity and spatial domains affected by the five UWWTPs varied, depending not only on effluent discharge and characteristics, but also on local hydrodynamics and circulation patterns. UWWTP impacts also varied over the annual cycle. Globally, the major detrimental impacts were observed at Faro UWWTP, and Spring-Summer represented the period of highest impact.

Key words: Ria Formosa, bivalves, sewage impact, urban wastewater treatment plants

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INCIDENCE OF MICROPLASTICS IN URBAN AND INDUSTRIAL WASTEWATER TREATMENT PLANTS

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Abstract:

Wastewater treatment plants (WWTPs) have been appointed as one of the main sources of microplastics (MPs) into marine ecosystems. In the present study, the influent and effluent of two WWTPs of different wastewater origin (industrial and urban) were investigated for 1 year. Both WWTP are situated in the province of Cádiz (Spain).

MPs were collected and extracted from wastewater matrixes following the method recommended by the National Oceanic and Atmospheric Administration (NOAA). The analysis of the samples was performed according to the abundance, shape, size and type of polymer, along with the removal rates of MPs in the plants.

Subsequently, the data obtained on both WWTPs were compared, to determinate the difference and similitude between the samples analysed. The main difference among the WWTP was the amount of microplastics found in the wastewater, as well as the presence of polymers with resins from industrial activities.

The results from this study established that the most representative form was fibers, followed by fragments and flakes (similar abundance) and low proportion of filaments and spheres; in reference to the size of MPs with highest abundant was between 100-355 μm , after the size from 355-1000 μm and finally the size among 1000-5000 μm was the lesser present, in all the samples. Regarding to the type of polymers a total of 13 were identified using attenuated total reflection Fourier-transformed infrared spectroscopy (ATR-FTIR). Further, PVC, PE, EAA and HDPE were the largest found polymers.

The presence of MPs in the influent varied from 632 ± 102 MPs/L to 1567 ± 413 MPs/L in the urban and industrial WWTP respectively; in the effluent, it varied from 16 ± 7 MPs/L to 131 ± 58 MPs/L. The removal rate overcome the 90% in all the samples.

Despite the elimination efficiency in the water line of the WWTPs the number of MPs discharged into aquatic ecosystem is important.

Key words: Microplastics (MPs), Wastewater treatment plants (WWTPs), wastewater, ATR-FTIR

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SEARCHING FOR HIGH TROPHIC LEVEL SPECIES IN MARINE POLLUTION MONITORING

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Abstract: Pollution monitoring is frequently undertaken in sedentary lifestyle organisms inhabiting coastal environments. However, there is a need to assess chemical exposures in predatory fish as key components of the marine ecosystem and largely responsible for its sustainability. In this study, the suitability of carboxylesterases (CEs), enzymes responsible for xenobiotic and endogenous metabolism, as potential biomarkers of chemical exposures, was explored in four predatory tuna species of commercial interest: little tunny (*Euthynnus alletteratus*), Atlantic bonito (*Sarda sarda*), bullet tuna (*Auxis rochei*) and albacore tuna (*Thunnus alalunga*). CE activities were measured in liver, the main metabolic organ, employing five commercial substrates: 4-nitrophenyl acetate (4NPA), 4-nitrophenyl butyrate (4NPB), 1-naphthyl acetate (1NA), 1-naphthyl butyrate (1NB) and 2-naphthyl acetate (2NA). The highest hydrolysis rates were obtained with butyrate ester substrates (4NPB and 1NB). CE activity differed between species (e.g. 1NB activity values: bullet tuna > little tunny > Atlantic bonito ≥ albacore tuna). Within the same species, activity values were largely variable depending on the substrate. Variations of CE activity revealed that body size was an important factor in modulating the enzymatic responses, while the trophic level, estimated with $\delta^{15}\text{N}$, had no influence. Geographical differences in CE activity of little tunny were not evidenced, but important inter-annual differences were found in the individuals collected off Cartagena, with lower activities in 2016. In vitro inhibitions by the pesticide dichlorvos, an inhibitor of CEs, gave complementary information on the sensibility of the different species to this pesticide. Based on the enzyme characterization and in vitro sensibility to chemical exposures, the little tunny is proposed as a potential bioindicator species for their combined characteristics of high enzymatic activity and sensibility to dichlorvos.

Key words: carboxylesterases, biomarkers, trophic level, dichlorvos

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D.N. All work procedures followed Spanish and EU legislation.

**(PHOTO)-FENTON PROCESSES FOR DECONTAMINATION OF
HIGH SALINITY EFFLUENTS**
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Abstract: During the last decade, Fenton-based processes have shown a great ability to decontaminate different types of waste effluents. The generation of highly oxidizing species in the presence of iron salts and H₂O₂, via Haber-Weiss reaction, demonstrate high performance in the removal of different types of environmental pollutants (Pignatello et al. 2006). However, the ability to maintain the iron active during this process is the main challenge step, which is greatly influenced by operational parameters, such as pH (García-Negueroles et al., 2019), because iron can be deactivated by decreasing its solubility via formation of (oxy)-hydroxides and consequently decrease its efficiency. One alternative to avoid this problem is the addition of diverse Fe-binding ligands, which are able to complex iron and assist Photo-Fenton processes at a wider pH range (Ahile et al., 2020). Also, toxicity and biodegradability of these substances must be taken into account since they are not normally naturally present in the aqueous matrices and have to be artificially added (Ahile et al., 2020). In this scenario, the main goal of this study is to assess the efficacy of (photo)-Fenton processes for decontaminating high salinity effluents derived from aquaculture or maritime industry. Six different Contaminants of Emerging Concern have been selected as model compounds. In an attempt to biomimetics, several phenolic compounds (e.g. Gallic Acid, Catechol, etc.), have been assessed as iron chelates for assist (photo)-Fenton processes by contemplating important factors such as pH and salinity. These phenolic compounds have been detected from phytoplankton exudates and bacterial siderophores (Santana-Casiano et al. 2010; Avdeef et al. 1986). In order to deep on mechanistic aspects, several tests have been performed with model molecules, such as Hydroquinone or Veratric Acid. Also, scavenging •OH radical tests have been briefly assessed with optimal conditions.

Key words: Fe-binding ligands, seawater treatment, phytoplankton exudates, Contaminants of Emerging Concern (CECs)

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MERCURY IN TWO TUNNA SPECIES FROM GULF OF CADIZ (*THUNNUS ALALUNGA* AND *THUNNUS THYNNUS*)

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Abstract: Mercury (Hg) is a global pollutant which is widely distributed in the environmental compartments. Its occurrence in oceans and coastal ecosystems is well documented and can be related to natural or anthropogenic sources. The contribution of anthropogenic sources has changed the figures of natural cycles fluxes of Hg on the Earth, increasing its presence from the beginning of industrialization. The main route of Hg exposure to the human being is related to food consumption. Species of larger fish (e.g. tuna, swordfish, etc.) accumulate significant amounts of Hg and mono methylmercury (MMHg) which are a risk for human health. In this work, we have analysed Hg concentrations in muscle and liver in two tuna species (i.e. *Thunnus alalunga* and *Thunnus thynnus*) collected in the Gulf of Cadiz. These specimens did not have a commercial size and the weight ranged between 1.12-1.43 kg and 0.22-0.37 kg for *T.alalunga* and *T.thynnus*, respectively. Similar Hg concentrations in both target tissues were reported in each species. *T. alalunga* bioaccumulated higher amounts of Hg in the muscle (0.51-1.22 mg/kg) than *T. thynnus*, (0.18-0.33 mg/kg). Although, only *T. alalunga* had concentrations higher than legal limits (1.0 mg/kg). A preliminary exam of the weekly intake of Hg considering both species did not show risk for the general population. However, a more detail exam of Hg intake for fish consumption should be carried out according to the last recommendations of the Spanish Food Security and Nutrition Agency (AESAN, 2019) which reduced the amount recommended for fish consumption with high Hg concentrations, especially for risk groups.

Key words: mercury, accumulation, *Thunnus alalunga*, *Thunnus thynnus*

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GEOGRAPHIC Hg PATTERN ALONG THE MEDITERRANEAN SEA: INSIGHTS FROM A SENTINEL SEABIRD

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Abstract: The usefulness of seabirds as sentinels of marine pollutant levels remains unclear due to several drawbacks such as the inherent influences of trophic ecologies at both individual and population levels. To understand the geographic variability and the influence of seabird trophic ecology in pollutant levels, we determined total mercury (THg) concentrations and stable isotope ratios in specific tissues of Scopoli's shearwaters (*Calonectris diomedea*) throughout its vast breeding range in the Mediterranean Sea (from the Strait of Gibraltar to Crete). Specifically, we obtained estimates of THg, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ of the first primary feather (P1, known to be moulted at the end of the breeding season, between August and September) of 320 individuals from 11 breeding colonies, and sampled from 2014 to 2018. THg concentrations were higher in birds from the eastern Mediterranean than in those from the westernmost colonies, showing a longitudinal gradient within the Mediterranean basin. Our results are in line with previous studies pointing out that current large-scale patterns in pollutant levels are the convergence between historical European discharges of pollutants in the Mediterranean basin and the almost confined nature of this basin, which diffuses towards Atlantic waters in the area of the Strait of Gibraltar. In addition, the positive relationship we found between THg concentrations and $\delta^{15}\text{N}$, even within each sampled colony, points out the great influence of the trophic ecology of the individuals in explaining exposure to pollutant, showing the strength of the biomagnification process even at intra-specific level. This second result emphasizes the need to understand diet specializations and trophic ecology of a given species before using it as a proper sentinel of environmental pollution. Our study highlights the potential of wide range breeding seabirds as suitable organisms for biomonitoring large geographic trends of pollutants in the marine environment.

Key words: Mediterranean, Mercury, Pollution, Seabirds

SORPTION AND DESORPTION OF TRICLOSAN AND METHYL-CHLORPYRIFOS ON HIGH-DENSITY POLYETHYLENE MICROPLASTIC IN SEAWATER

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Abstract: Microplastics (MP's) have been recognized as emergent problem of the marine and coastal environments on pollution. This is due to the threat they pose largely associated with their composition, size and their potential to sorb, release and partition toxic substances in the marine ecosystems (Ramirez *et al.*, 2019). The role of plastics as pollution vector can favour the transfer of the chemical contaminants of emerging concern through different environmental compartments (León *et al.*, 2019) and their bioavailability will depend on their sorption interactions and reversibility.

In this work, the sorption and desorption kinetics of triclosan, an antimicrobial product, and methyl chlorpyrifos, a current use insecticide, on high-density polyethylene (HDPE) in seawater was characterized. HDPE is the most common polymer used, and these selected contaminants are commonly found in marine organisms, water, and sediment from coastal areas. A constant amount (100 mg) of HDPE (non uniform particles, <22 µm) has been used in 100 mL seawater. The tested concentrations of the emerging contaminants ranged from 10 to 200 ng/L to get sorption isotherms. The incubation was carried out in dark conditions per triplicate. The effect of temperature was tested (15 and 25°C) during 24 hours in continuous agitation, which was established as the steady state time. After the incubation, the samples were filtered and seawater and HDPE fractions were analyzed separately. Extraction of contaminants from HDPE was performed with methanol following the method proposed by León *et al.*, (2019). The concentrations in seawater and HDPE extracts were determined by stir-bar sorptive extraction coupled to gas-chromatography with mass-spectrometry (SBSE/GC/MS). The partition coefficients calculated on HDPE at tested conditions ranged between 200 and 2500 (mL/g) for both contaminants and they were affected by temperature. Sorption was reversible process for both contaminants in first 24 h (15-70%), being dependent on temperature and analyte concentration.

Key words: triclosan, methyl-chlorpyrifos, microplastic, sorption, seawater

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R) project and by the European Union through the European Regional Development Fund (ERDF). M. García Pimentel acknowledges the Spanish Ministerial Science, Innovation and University for her predoctoral fellowship (PRE2018-085502).

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OCCURRENCE OF SOLAR CARE PRODUCTS IN MARKET FISH

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Abstract: Ultraviolet (UV) filters and stabilizers are two examples of emerging pollutants used to protect polymers, pigments and our skin against the sun damage, so they are incorporated into personal care products (PCPs), plastics and textiles. Owing to their wide production, the increase in their use and their poor elimination in the wastewater treatment plants (WWTPs), there is a continuous discharge of these compounds into rivers, lakes and seas (Montesdeoca-Esponda et al., 2018). Their presence and negative effect in fishes have been demonstrated. Because of their high persistence in tissues, that cause bioaccumulation and biomagnification in the trophic chain, and their importance in our diet, it is necessary to know their occurrence in fishes bought from local markets (Cunha et al., 2018).

In this study, a Microwave-Assisted Extraction (MAE) and Ultra-High Performance Liquid Chromatography with tandem mass spectrometry detection (UHPLC-MS/MS) method was successfully applied for the determination of 6 UV stabilizers and 7 UV filters in 9 different fish species from two markets (Tarragona and Las Palmas de Gran Canaria, Spain).

Among the studied compounds, the most detected was BP-3 (in 7 of the species) followed by UV-329. They also presented the highest concentrations in fish tissues, 682.5 ng g⁻¹ dry weight (dw) of BP-3 and 364 ng g⁻¹ (dw) of UV-329 in *Thunnus thynnus* samples. The trophic level which they belong and the location where the fish species come from could be related with the levels of compounds found.

Key words: UV stabilizer, UV filter, fish, MAE, UHPLC-MS/MS

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ORAL COMMUNICATIONS

TRACERS IN OCEANOGRAPHY

NEODYMIUM ISOTOPES AND RARE EARTH ELEMENTS AS NEW GEOCHEMICAL TRACERS IN THE CENTRAL MEDITERRANEAN SEA

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Abstract:

The present study aims at shedding light on the central Mediterranean Sea (MS) functioning in terms of water mass mixing and potential lithogenic sources by means of new geochemical tracers such as dissolved Nd isotopes (ϵ_{Nd}) and Rare Earth Element (REE: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) concentrations. Although proved to be valuable tracers of oceanographic processes, their measurements are basically lacking in the MS water column. We analyzed 9 stations around the Tyrrhenian, Ionian and Ligurian seas. Dissolved REE were measured with an Agilent 7500 ICP-MS and ϵ_{Nd} using a Nu Plasma-III MC-ICP-MS at UB. The obtained REE do not display nutrient-like profiles, likely suggesting relatively young waters with limited accumulation of remineralized REE. Light REE (LREE: from La to Gd) present a non-conservative behavior, largely peaking at surface waters and rapidly decreasing with depth. The negative linear correlation of surface LREE enrichment with offshore distance indicates their release from lithogenic sediments of the Italian coast to the Tyrrhenian waters. In contrast to other regions, this process does not modify the ϵ_{Nd} values. On the other side, distributions of dissolved heavy REE (HREE: Tb to Lu) and ϵ_{Nd} exhibit a conservative behavior that can be explained by mixing of western- (MAW and WMDW) and eastern- (LIW and EMDW) originated waters. We test this hypothesis with an Optimum Multi-Parameter Analysis (OMPA) including HREE and ϵ_{Nd} parameters. Even though the limited data set, consistent results of water mass fractions are obtained for the four main water masses although with some particularities. While LIW take on major importance when considering HREE in the model, EMDW fractions are preferentially detected with ϵ_{Nd} . This latter finding implies a noticeable deep-water flux across the Sicily Strait into the Western Mediterranean that was not clearly evidenced before.

Key words: Central Mediterranean, Rare Earth Elements, Nd isotopes, water mass advection

Acknowledgments: Samples were collected during the NextData Cruise on R/V Minerva I in June 2016. The authors thank financial support from the OPERA Project (CTM2013-48639-C2-1-R), the CHIMERA Project (CTM2016-75411-R) and Generalitat de Catalunya (2017 SGR 315). This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 683237).



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POSTER COMMUNICATIONS

BIOGEOCHEMICAL PROCESSES

REACTIVE SOLUTE TRANSFER THROUGH TWO CONTRASTING SUBTERRANEAN ESTUARY EXIT SITES OF RÍA DE VIGO, NW IBERIAN PENINSULA

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Abstract: Subterranean estuaries are highly reactive interfaces locus of the interaction between seawater and continental groundwater, actively mediating the transfer of solutes to surface waters through Submarine Groundwater Discharge (SGD).

Using radioisotope tracers, Ibánhez et al. (2019) recently identified significant SGD loads into Baiona Bay (Ría de Vigo, NW Iberian Peninsula), locus of the two subterranean estuaries studied here (Panzón and Ladeira beaches). Porewater samples were collected from both subterranean estuaries with push-pull piezometers installed at different depths along the permanently saturated zone during February, May, July and October 2019. Porewater ²²²Rn, ²²⁶Ra and salinity were used as tracers of porewater flow within the sediment and to quantify resulting SGD. The different coastal aquifer influence, wave exposure and configuration of these subterranean estuaries seem to drive highly contrasting biogeochemical dynamics at different spatial and time scales. On one hand, Ladeira beach showed generally reduced porewaters throughout the studied period. Low nitrate (<1 µM) and high phosphate (>50 µM) concentration porewaters were observed there, with high ammonium peaks (>100 µM) at specific depths during May and October. Porewater ammonium appeared to be generally linked with phosphate distribution, except in July. Observations suggest that organic matter mineralization within the sediment could be a main source of nutrients to this subterranean estuary. On the other hand, oxygen levels in Panzón beach reached near saturation levels in depth at high ²²²Rn-low salinity porewaters. There, high nitrate levels were strongly linked to brackish waters, suggesting its continental origin. Large modulation of porewater nutrient levels was observed at both subterranean estuaries, significantly altering its composition prior to discharge to Baiona Bay.

Key words: Submarine Groundwater Discharge, Subterranean Estuaries, Ría de Vigo, permeable sediment biogeochemistry

Acknowledgments: This research is supported by the SUBACID project (SUBmarine groundwater discharge (SGD) impact on coastal ACIDification processes in contrasting European Atlantic Shores: towards securing ecosystem services and food production) that has received funding from the Irish Research Council and the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 713279 through the CAROLINE program (CLNE/2017/210).

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DISSOLVED ORGANIC MATTER PRODUCED BY MARINE HETEROTROPHIC BACTERIA SHAPES THE ACTIVITY AND COMPOSITION OF NATURAL PROKARYOTIC COMMUNITIES

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Abstract: Marine bacterioplankton play a key role in organic matter processing in all aquatic ecosystems (Azam et al., 1983). However, the view of bacterioplankton as DOM sources remains underexplored (Jiao et al. 2010). In this study, we assessed how DOM produced by single bacterial strains was degraded by in situ Mediterranean Sea communities. We characterized DOM produced by two model bacterial strains: *Photobacterium angustum* and *Sphingopyxis alaskensis*. Grown with glucose as the sole carbon source, the two strains released up to 24% of the consumed glucose as bacterial derived DOM (BDOM), whose quality differed between strains. Significant growth of natural prokaryote communities on BDOM suggested that it was partly labile, however BDOM always promoted lower prokaryotic growth efficiency than in situ DOM. In addition, BDOM changed prokaryotic metabolism with an enhancement of aminopeptidase activities when degrading *P. angustum* DOM, and that of phosphatase activities when using *S. alaskensis* DOM. The different DOM sources also shaped prokaryotic community composition towards a relative enrichment in the orders Alteromonadales, Rhodobacterales and Oceanospirillales when growing on *P. angustum* DOM vs. relatively more Vibrionales and Rhodospirillales growing on *S. alaskensis* DOM. We conclude that bacterioplankton as DOM sources highly affect in situ prokaryotic communities, thus changing the pathways for DOM storage and cycling in the ocean.

Key words: dissolved organic matter, bacterioplankton, microbial carbon pump

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THE INFLUENCE OF HALOPHYTE PLANTS ON SEDIMENT REE MOBILITY FROM A MEDITERRANEAN SALT MARSH

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Abstract: The dispersion of rare earth elements (REE) in the environment has been leveraged over the last decades due to its increasing use in different areas (industry, agriculture and medicine) (Balaram, 2019). Estuarine marshes act as natural contaminant sinks, whereas halophyte plants may play an important role as phytoremediation agents. The REE mobility in sediments depends on several environmental factors, such as pH, redox potential or the presence of vegetation (Tyler, 2004). The main goal of this work was to evaluate the influence of three halophyte plants species, *Spartina maritima* (Curtis) Fernald, *Halimione portulacoides* (L.) and *Sarcocornia fruticosa* (L.), from a South European marsh (Tagus estuary, Portugal), on the mobility and bioavailability of sediment REE. A colonised sediment core with each plant species plus one non-colonised (bulk sediment) were sampled early April 2019 and sectioned into 2 cm layers. The sediments were characterised for pH, redox potential, moisture, organic matter content and major elements content (Al, Fe, Mn, Ca, Si). Total and leached REE concentrations obtained by a modified sequential extractions (Mittermüller et al., 2016) were quantified by ICP-MS. Total levels of major elements and REE obtained in this work are within the range of values previously reported by Brito et al. (2018). The highest levels of REE were observed in the colonised sediments (with a higher prevalence of fine-grained material), while the non-colonised and coarser sediment showed significant lower REE contents. The results obtained from the sequential extractions point to different REE fractionation and levels of association in the various fractions (easily soluble and exchangeable, carbonate bound and mobilised by complexation, reducible, oxidable and residual fractions) within the light (LREE), medium (MREE) and heavy-REE (HREE). This study also showed that the sediment REE mobility and bioavailability is influenced by the presence of halophytes plants and it is also species-dependent.

Key words: REE, mobility, sediments, halophytes, salt marsh

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TEMPORAL VARIABILITY OF RARE EARTH ELEMENTS CONTENT THROUGH THE CASCAIS SUBMARINE CANYON: DOMINANCE OF LITHOGENIC SOURCES

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Abstract: Temporal variations of Rare Earth Elements (REE), major elements (Al, Ca, Fe, Mn), Pb and Hg were determined in two multicores (252-35 (445mwd) and 252-32 (2100mwd)) collected along the axis of Cascais Submarine Canyon (CSC). Both cores were dated using ²¹⁰Pb and ²²⁶Ra determinations. The major elements, Hg, Pb and REE contents were determined by WD-XRF on fusion bead, CV-AAS, GF-AAS and ICP-MS after total decomposition, respectively.

The CSC is adjacent to the Tagus estuary, one of the largest European estuaries historically contaminated by trace metals (Figuères et al., 1985; Vale et al., 2008). Brito et al. (2018) characterized spatial distribution of REE contents in the Tagus estuary surface sediments identifying the main potential anthropogenic REE sources associated with deposition of fine-grained particles derived from the inactive chemical-industrial complex and wastewater treatment plants. Previous studies (Mil-Homens et al., 2009, Costa et al., 2011) identified that trace metal historical contamination is not constrained to the estuary but also transferred to adjacent shelf area by the hydrodynamic regime. The REE temporal variability is not being analysed at present.

Aluminium shows a down-core trend towards the surface in both cores in opposition to Ca. Iron, Mn and REE in core 252-35 follow the Al-pattern. Core 252-32 shows a sharp enrichment for Fe, Mn and REE suggesting early diagenetic processes associated with redox sensitive elements. The L-REE (La-Pr series) dominates the REE contents in both cores. The Post-Archean Australian Shale normalized pattern is marked by a positive Eu-anomaly that was also identified in the Tagus sediments reflecting dominance of lithogenic

components associated with feldspar minerals. This arises in opposition to Pb and Hg. The trace-metal normalized profiles show an increasing up-core trend not associated with sediment texture suggesting the extension of anthropogenic contamination derived from the estuary through the canyon to deeper parts of the margin.

Key words: Portuguese Margin, marine sediments, Temporal variability, Rare Earth Elements, trace metals

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INFLUENCE OF BENTHIC REGENERATION IN MAR MENOR

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Abstract: Two campaigns were carried out, in winter and summer of 2018, in the coastal lagoon Mar Menor in order to evaluate the importance of benthic fluxes and to determine the mechanisms that are producing the degradation of the accumulated organic matter in their sediment. In 6 stations were taken sediment cores and benthic fluxes were quantified with a benthic chamber.

Oxygen consumption from the sediment is a consequence of aerobic oxidation of the OM (organic matter) of the surface sediment, and the oxidation of other reduced compounds that are diffused from greater depths in all stations ($-33,8$ to -67.5 $\text{mmol m}^{-2} \text{d}^{-1}$). In contrast, the fluxes of TA (total alkalinity) (38.9 - 92.6 $\text{mmol m}^{-2} \text{d}^{-1}$) and DIC (dissolved inorganic carbon) (53.1 - 158.9 $\text{mmol m}^{-2} \text{d}^{-1}$) indicate the release of species involved from the sediment. Marked seasonal variation is observed, with intensified benthic fluxes with temperature, increasing TA and DIC fluxes by 33.6 and 14.2% respectively, while DO (dissolved oxygen) fluxes decrease by 27.2% in summer. The ratio between DIC and DO fluxes has value of approximately 2 and suggest that an important part of OM oxidation in sediments occurs by anaerobic pathways. The sediment is characterized by Eh values decrease considerably with depth, presenting high negative values from the first cm, which confirms the importance of anaerobic degradation, and high OC (organic carbon) content (10%). TOC (total organic carbon) in interstitial water has high values (up to 12.5 mM), about 40 times higher than that of the water column. TN (total nitrogen) values are also high, and the TOC/TN ratio of 4.9 indicates that the OM has a high relative content of N.

Key words: benthic fluxes, benthic regeneration, coastal lagoon, Mar Menor

Acknowledgments: This work was supported by “Dirección General del Mar Menor (Murcia)” under contract “Estudio biogeoquímico de los fondos del Mar Menor” (TRAGSA, OT2018/024).

LINK BETWEEN GREENHOUSE GASES (CO₂, CH₄, AND N₂O) AND DISSOLVED ORGANIC MATTER IN GUADALETE ESTUARY (BAY OF CÁDIZ, SPAIN)

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Abstract

Coastal zones receive large amounts of organic matter that enhanced the production of greenhouse gases (GHG), such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). CO₂ is produced by both aerobic and anaerobic degradation of organic matter, while CH₄ and N₂O are mainly produced in anaerobic conditions. However, recent studies showed “oxic” production of CH₄ related to bacterial degradation of dissolved organic matter (DOM) (Repeta et al., 2016, Donis et al., 2016). This study aimed to assess the distribution of DOM and CH₄, N₂O, and CO₂ in Guadalete estuary (Bay of Cadiz, Spain) and determine the relationship between different fractions of DOM with the production of GHG. We measured DOM, using its optical properties, and GHG using gas chromatography (CH₄, N₂O) or from total alkalinity and pH (CO₂) during four cruises. Excitation-emission matrixes were used to identify the different fractions of DOM (e.g., humic-like and protein-like). The concentration of CO₂, CH₄ and, N₂O ranged between 332.8-4275.6 μatm, 20.8- 6440.1 nM, and 8.8- 283.9 nM, respectively. The system was oversaturated with GHG. Thus, acting as a source of GHG to the atmosphere. DOM increased upstream, indicating that allochthonous origin predominates. We found strong linear relationships between the excess of the GHG (ΔCO₂, ΔCH₄, ΔN₂O) and the main groups of DOM. ΔCH₄ and ΔN₂O showed a positive relationship with the protein fraction (R² > 0.62, p > 0.05) while ΔCO₂ was related to the terrestrial humic fraction of DOM (R² = 0.52, p > 0.05). Our results indicated that the production of GHG in this estuary was also related to the degradation of DOM.

Key words: dissolved organic matter, greenhouse gases, estuary.

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POSTER COMMUNICATIONS

CHEMICAL OCEANOGRAPHY

TOTAL AND SOLUBLE METAL CONTENT OF TOTAL SUSPENDED PARTICLES (TSP) IN RURAL AND COASTAL AREAS IN GRAN CANARIA ISLAND.

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Abstract: Total and soluble Co, Cu, Pb, Mn, Al, Fe, Zn, V and Cd concentrations were measured in two different sites in Gran Canaria island: Port of Las Palmas (LP) and Pico de la Gorra (PG). The LP station is a coastal station influenced by the maritime traffic and also the city activities. On the other hand, the PG is a rural station placed at 1930 m above sea level. In this work, the samples of total suspended particulate (TSP) were simultaneously collected in both stations over a 2-year period. The main aim of this research was to identify the natural and anthropogenic sources and the anomalous enrichment of the trace metals. The filters (Whatman-41) were digested following GEOTRACES hot plate protocol and subsequently measured by ICP-MS. Because the elemental composition of the atmospheric aerosol is source-dependent, the air mass back trajectories from NOAA HYSPLIT model were calculated starting from different heights (200, 750, 1000, 1500, 2000, 2500, 3000 and 3500m in steps of 6 h) to determine the origin of the air masses and their influence on the trace metal content of TSP in the stations (Stein et al. 2015; Rolph et al. 2017) A high soluble Cu, Fe, Zn and V concentrations were observed in the aerosol samples with urban and industrial sources. Except for soluble V, a strong relationship between the trace metal solubility and the TSP concentration was exhibited. The higher solubility values corresponding to the lowest TSP concentrations and the presence of anthropogenic aerosol components.

Key words: TSP, trace metals, solubility, dust

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SEARCHING FOR pH VARIABILITY DRIVERS AT THE RIA DE VIGO (NW SPAIN) IN HIGH-FREQUENCY TIME-SERIES

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Abstract:

We study the link between seawater pH trends and upwelling drivers at the Ría de Vigo (NW Spain).

Many works show that negative pH trends and ocean acidification are linked in open-ocean. However, in upwelling areas, some factors obscure that link, and the information about pH drivers is limited.

A new study at the Ría de Vigo (Herrera et al., 2020) made openly available a new dataset of four high-frequency pH time-series obtained between 2017 and 2019, using a SAMI-pH sensor. They also provided time-series of temperature and salinity.

The data show trends associated with the seasonality of the Ría. On top of that, we observe a notable short-term variability that reveals an unexpected response of the pH during upwelling and downwelling events. The metabolic activity of the Ría, the temperature fluctuation, and fresh-water plume events are some explanations for such deviations.

Key words: pH, Upwelling, Ria de Vigo, Ocean Acidification

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LA-ICP-MS ANALYSES OF BORON IN THE CALCAREOUS ALGA *LITHOTHAMNION CORALLIOIDES*

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Abstract: Boron is incorporated in the mineral lattice of marine carbonates during precipitation (Hemming and Hanson, 1992). The B/Ca ratio gives information about past seawater CO₃ concentrations (Yu and Elderfield, 2007). However, it was also suggested a temperature influence on B/Ca in foraminifers (Wara et al., 2003; Yu et al., 2007) and in *Neogoniolithon* sp. (Donald et al., 2017).

B and Mg concentrations in the coralline algae *Lithothamnion corallioides* (P.Crouan & H.Crouan) P.Crouan & H.Crouan 1867 have been investigated by LA-ICP-MS at the Institute of Geosciences and Earth Resources (IGG) of the National Research Council (CNR) in Pavia (Italy). The samples were collected in the Western (Aegadian Islands; Corse; Elba; Pontian Islands; Sardinia) and Eastern (Othonoi Island) Mediterranean Basin and in the Atlantic Ocean (Morlaix, Brittany and Galway, Ireland). Spearman's correlation and the Kruskal-Wallis test followed by the Dunn's test for comparisons were performed in R 3.6.3 software.

B/Ca showed a positive correlation with Mg/Ca in Morlaix (R=0.58; p=0.0036), the shallowest habitat (12 m depth). The difference among sampling sites was statistically significant (p<0.001). The sample from Pontian Islands, the deepest sampling site (66 m depth), differed from the other sites (p<0.025) and had the lowest B/Ca mean value (462.8 μmol/mol).

Since Mg incorporation increases with temperature (Moberly, 1968; Berner, 1975; Ries, 2006), the correlation between B/Ca and Mg/Ca support the hypothesis that B incorporation is function of both pH and temperature. This trend was verified only in Morlaix, where strong seasonality occurs. More likely, the very low B/Ca of the sample from the Pontian Islands, where temperature is almost constant throughout the year, was influenced by the lower growth rates, that have been proven to decrease B/Ca (Kaczmarek et al., 2016; Donald et al., 2017) and may reflect the lower light availability.

Key words: coralline algae, B/Ca, boron incorporation, marine carbonates, *Lithothamnion corallioides*

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CaCO₃ SATURATION STATE AND ANTHROPOGENIC CARBON IN THE GULF OF CÁDIZ (2014-2017)

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Abstract:

CaCO₃ saturation states were studied during twelve oceanographic cruises between March 2014 and December 2016 along transects perpendicular to the coastline among Guadiana river and Cape Trafalgar on the eastern shelf of the Gulf of Cádiz, on board the R/V's Ángeles Alvariño and Ramón Margalef, and during one cruise in three estuaries of the Gulf Cádiz (Guadiana, Tinto and Odiel and Guadalquivir) in July 2017 on board R/V UCADIZ. pH, total alkalinity (TA) and calcium concentrations (Ca²⁺) were analysed through potentiometric titration. pH, TA and Ca²⁺ varied between 7.8 and 8.2, 2304.3 and 2585.6 μmol kg⁻¹, and 10.4 and 11.3 mmol kg⁻¹, respectively in the Gulf of Cádiz. The highest values of TA and Ca²⁺ were found in deep waters related to the presence of the Mediterranean Outflow Water. In the estuaries, the values of pH, TA and Ca²⁺ presented a greater variation range, being between 7.5 and 8.3, 1653.7 and 3720.4 μmol kg⁻¹, and 1.0 and 11.7 mmol kg⁻¹, respectively, with an increase of TA and a decrease of Ca²⁺ through the inner estuaries area. CaCO₃ saturation state in the Gulf of Cádiz is highest in the surface waters due to the photosynthetic activity and lowest in deep waters for the decrease of pH, with mean values of 3.8 ± 0.5 and 2.5 ± 0.3 for calcite (Ω_c) and aragonite (Ω_a) saturation states, respectively. However, Ω_c and Ω_a reached values of 25 and 15 in the internal areas of the estuaries. Spatio-temporal variations of anthropogenic carbon (C_{ANT}) were estimated using TrOCA method (Touratier et al., 2007) in the Gulf of Cádiz, having a mean value of 88.9 ± 13.9 μM, and with the highest values during autumn (101.0 ± 14.6 μM). C_{ANT} presented the greater values in surface waters and decreased with the distance to the coast.

Key words: Calcium, calcium carbonate, anthropogenic carbon, Gulf of Cádiz.

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SEA STORM ENHANCEMENT OF PARTICLES AND TRACE METAL FLUXES IN SUBMARINE CANYONS, VERA GULF, SW MEDITERRANEAN SEA

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Abstract: Quantifying actual fluxes of particulate trace metals from coastal and shallow marine environments to the deep sea is critical to understand to which extent, how and when these are transferred across continental margins down to ocean basins. The Gulf of Vera, in the SW Mediterranean Sea, is a particularly suitable where to assess such transport of metals given the presence, in its northeastern part, of a large metal-bearing mine tailings deposit resulting from the exploitation of sulphide ores inland. The deposit was formed from 1957 to 1990 and totals about 57 million tons. To answer to the metal transfer question we deployed five mooring lines including sediment traps and current meters from March 2015 to March 2016. The moorings were distributed as follows: 3 in the mid course of submarine canyons (1000m depth), 1 in the open slope (1000m depth) and 1 in the deep basin (2500m depth). Such a 1-year long deployment strategy allowed us to measure both the temporal variability of particle fluxes and the concentrations of Zn, Pb, As, Ni, Al, Cd, Cu, Co, Fe, Mn and Ti in settling particles.

First results point to sea storms as the main process in triggering particulate matter and metals transfer to the deep margin and basin. Storms lead to the development of thick nepheloid layers (100's m) that tend to focus in submarine canyons, although they also spread over the continental slope. After storms metal fluxes up to 120.4 mg/m²d of Pb, 282.3 mg/m²d of Zn and 40.4 mg/m²d of As at 1000 m of water depth within canyons point to these geomorphic features as efficient conduits for transferring metal pollution from shallow to deep.

Key words: Trace metals, dispersal, particle fluxes, Gulf of Vera, Mediterranean Sea

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PHOSPHORUS LIMITATION AFFECTS THE QUANTITY AND QUALITY OF DISSOLVED ORGANIC MATTER PRODUCED BY MARINE PROKARYOTES

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Abstract: Dissolved organic matter (DOM) is one of the largest reservoirs of reduced carbon (C) in the ocean. Heterotrophic bacterioplankton play a key role in organic matter remineralization in all aquatic ecosystems. But, they also release DOM; and a fraction of it can be recalcitrant; therefore, being sequestered in the ocean's interior through the so-called microbial carbon pump (MCP)¹. The mechanisms leading to this DOM production and the factors influencing them are scantily studied. Nutrients availability would be a key factor affecting these mechanisms². This study aimed to determine the effect of phosphorus (P) limitation on heterotrophic bacterial-DOM production and its quality. Mono-specific bacterial cultures were conducted using glucose as the sole carbon source under 2 different treatments: P replete (Media C:N:P=45:9:1) vs P-limiting (Media C:N:P=374:75:1). At the stationary growth phase, DOM was harvested by filtration and characterized by its optical properties (chromophoric and fluorescent DOM) and by their elemental ratios (C:N:P). The strains produced DOM, that represented up to 28 % of initial carbon. DOM quality differed among bacterial taxa and nutrient conditions: P limitation lead to higher C:N:P ratios and higher FDOM production, particularly for humic-like FDOM compounds, likely recalcitrant. We hypothesize that P limitation would enhance C sequestration by the MCP and could play an important role in nutrient limited systems.

Key words: Dissolved organic matter, heterotrophic bacteria, P limitation, microbial carbon pump

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THE AMINO ACIDS PROFILE ON THE MARINE DIATOM *Phaeodactylum tricornutum* UNDER DIFFERENT COPPER LEVELS

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Abstract: Marine microalga can regulate the reactivity, speciation and mobility of trace metals in seawater through the synthesis and release of organic ligands affected by environmental conditions such as the concentration of metals in solution (Hamed et al., 2017; López et al., 2015). This research is part of ATOPFe project (Effects of ocean acidification, temperature and organic matter on Fe (II) persistence in the Atlantic Ocean). The aim of this investigation is to study the influence of copper levels in amino acid production by marine diatom cells (*Phaeodactylum tricornutum*). Cells were harvested under axenic conditions under different Cu concentrations until 1.57 mM. The concentration of 10 different amino acids in cells were measured by RP-HPLC on C18 column with a photo diode array detector (PDA) following a modified method from Shi et al. (2013). The experimental results demonstrated that the production of amino acids by the marine diatom *P. tricornutum* is sensitive to the copper concentration in seawater. In this sense, under Cu stress conditions, the cells showed significant differences in glutamic acid, aspartic acid, proline, lysine and isoleucine respect to the control (seawater without any Cu additions). Furthermore, arginine, valine and phenylalanine were found in the control, whereas in the cells exposed to Cu were not detected. On the other hand, histidine was not detected in both extracts.

In conclusion, copper level in solution affects the amino acid profile in *P. tricornutum* cells. Further studies with amino acids are required to understand their Cu-complexing properties and its implication in the marine environment.

Key words: Amino acid, microalgae, HPLC, copper, *Phaeodactylum Tricornutum*.

Acknowledgments: This study received financial support from the ATOPFe project (CTM2017-83476-P) given by the Ministerio de Economía y Competitividad from Spain. The participation of Paula Santiago was funded by the PhD scholarship from the Universidad de Las Palmas de Gran Canaria (PIFULPGC-2019).

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IMPACTS OF GLOBAL CHANGE ON OCEAN DISSOLVED ORGANIC CARBON (DOC) CYCLING

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Abstract: The marine dissolved organic carbon (DOC) pool is an important player in the functioning of marine ecosystems. The DOC pool is at the interface between the chemical and the biological worlds, it fuels marine food webs, and is a major component of the Earth's carbon cycling. We reviewed the research showing impacts of global change stressors and disturbances on the DOC cycling, specifically: ocean warming, acidification, deoxygenation, glacial and sea ice derived material, changed inflow from rivers, changing ocean circulation, and wet/dry depositions. A unified outcome of the future impacts of these stressors/disturbances on the global ocean DOC production and degradation was not possible, due to e.g. regional difference and difference in stressors/disturbances impacts, but general patterns for each stressor/disturbance will be presented.

Key words: DOC, production, degradation, global changes (3 to 5 key words)

KINETICALLY-HINDERED METALS: IMPLICATIONS FOR TOXICITY STUDIES AS REVEALED FROM PT INTERACTIONS WITH *DUNALIELLA SALINA*

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Abstract: It is widely accepted that adverse effects of metals greatly depends on its speciation; therefore bioaccumulation and ecotoxicological studies must be carried at equilibrium conditions where the speciation of the (spiked) target metal reflects that of the ambient environmental conditions. Achieving equilibrium may, however, become complicated for those elements displaying extremely slow reaction kinetics, which is the case of Pt. In such cases, it is common that the speciation of the freshly-spiked metals (generally in the form of soluble salts) is different from that in real systems.

Despite of the fact that Pt(IV) is well known be kinetically-hindered with extremely low reaction kinetics, little information is available on the kinetics of Pt reactions in environmental systems. Thermodynamic approaches suggest that Pt(IV) hydroxychloride complexes may be the dominant form of dissolved Pt in low temperature brines that are strongly oxidized, such as seawater. In ecotoxicological studies, Pt(IV) is generally spiked to the test solutions in the form of its hexachloride complex (PtCl₆²⁻). However, the time required of this Pt(IV) form to reach its speciation at equilibrium conditions is yet unknown. To this aim, we have i) studied the changes in the Pt(IV) speciation during different periods after spiking (ageing) measured by UV-vis spectroscopy, and ii) conducted toxicity test with the green microalgae *Dunaliella salina* using both freshly-spiked test media and after a period of spike pre-equilibration of 10 days under controlled conditions. Results will be discussed in terms of how equilibration time of the spiked Pt on the exposure media, before performing any bioaccumulation or ecotoxicological experiment is started, may impact the ecotoxicological effects observed.

Key words: Platinum, Toxicity, Speciation

Acknowledgments: This is a contribution to the COST Action TD 1047 – NOTICE (www.costnotice.net). This work was partially funded by the Xunta de Galicia (ref. IN607A 2016/11). ARF acknowledges a postdoctoral grant (Juan de la Cierva) from the Spanish Ministry of Science.



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XX SEMINARIO IBÉRICO DE QUÍMICA MARINA



POSTER COMMUNICATIONS

MARINE ECOTOXICOLOGY AND POLLUTION

TEMPORAL EVOLUTION OF THE IMPACT OF URBAN WASTEWATER DISCHARGES ON CONTRASTING AREAS OF RIA FORMOSA (SOUTH PORTUGAL)

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Abstract: Ria Formosa is a highly productive coastal lagoon located on the south coast of Portugal, being the largest national source of shellfish. Within the scope of CONPRAR Project the impact of two contrasting urban wastewater treatment plant effluents upon Ria Formosa water quality was studied based on several chemical variables. One, in Faro, discharges a flow of *ca.* 4000 m³/d *ca.* 1 km away from shellfish beds, in a narrow and shallow channel, while the other, in Olhão, discharges *ca.* 500 m³/d in a major wider channel close to shellfish beds. During one year (starting in September 2018) water sampling was conducted along dominant longitudinal gradients of the effluent dispersion from the discharge point down to 1 km. Key variables indicative of sewage influence, such as salinity and dissolved oxygen, were measured *in situ* (using multiparametric probe YSI (EXO 2)) and surface water (20-30 cm) samples collected at both high and low tide (at spring and neap tide from April to September and only at neap tide from October to March) were analysed for nutrients (Grasshoff *et al.*, 1983) and chlorophyll *a* (Lorenzen, 1967). A trophic State Index, TRIX (aggregating chlorophyll-*a*, nutrients of nitrogen and phosphorus and dissolved oxygen) was applied for low water conditions, when sewage impact might be maximal (i.e., worst water quality scenario). Data shows that the water quality at ON is better than at FNW, associated not only with a lower effluent flow but also with a higher dilution effect promoted by stronger hydrodynamic conditions. Results were compared with historical data from 1991/1992 and 1996/1997 and point out for a slight decrease of the water quality. Given the importance of Ria Formosa, a continuous monitoring is imperative, in order to contribute to a better management and preservation of this ecosystem and its biodiversity.

Key words: Ria Formosa, water quality, sewage impacts, wastewater treatment plant

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HIGH FREQUENCY MEASUREMENT OF METALS: STEPS TOWARDS THE ACCEPTANCE OF PASSIVE SAMPLERS FOR REGULATORY MONITORING

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Abstract: There is an increasing interest in the use of passive samplers (PS) for the environmental assessment of water bodies, within European policies requirements. In the regulatory context of the European Water Framework Directive (WFD) (2000/60/EC), the main barrier for the acceptance of PS is the lack of appropriate Environmental Quality Standards (EQSs). Regulatory EQSs for metals in water are defined in the dissolved fraction, preventing the use of PS-labile concentrations for the establishment of the chemical status of water bodies. The specific objectives of this study are: (i) to investigate the relationship between dissolved metal concentrations from spot sampling with Diffusive Gradient in Thin Films (DGT) labile metal concentrations, (ii) to evaluate the reliability of the techniques for the measurement of metal concentrations in estuaries and (iii) to provide recommendations for the use of DGTs to develop environmental guidelines. In November 2019, five samplings were carried out in the Oiartzun estuary (Basque Country, Bay of Biscay), an area with high presence of industrial and port activities. DGTs (triplicates) were deployed and retrieved after 12 hours. During that period, hourly spot water samples were taken, at the same depth than DGTs. Water samples were filtered for the posterior analysis of metals, dissolved organic carbon and the quantification of suspended particulate matter. Priority metals (Cd, Ni, Pb) and other specific metals (Al, Ag, Cu, Cr, Co, Fe, Mn, Zn) were analysed in the 2 defined fractions (dissolved and DGT fraction) by ICP-MS. Hydrographic variables were measured at each sampling time. The relationships between dissolved and labile metal concentrations and the environmental factors influencing such correlations were studied. Statistical analysis highlighted the relationships between metal concentrations in DGT and in spot water samples, together with the variability in relation to the hydrographic variables.

Key words: Diffusive Gradient in Thin Films, spot sampling, environmental assessment

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TEMPORAL AND SPATIAL PATTERNS OF TRACE METALS AND RARE EARTH ELEMENTS (REE) IN THE GUADALQUIVIR ESTUARY

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Abstract: Estuaries are ecosystems with a high dynamic where sea and freshwaters are mixed affecting physicochemical and biological processes. The Guadalquivir River is the main river basin of the South of the Iberian Peninsula and its estuary is a zone of high ecological productivity although is affected by many pressures as agriculture, fluvial transport, wastewater, and mining activities. This ecosystem is very close to the Iberian Pyrite Belt and in the past has been affected by the release of metals or mining accident (e.g. Aznalcóllar disaster). Sediment act as sink of metals and rare earth elements, although they cannot be considered a final repository because changes of physical and chemical conditions can provoke the release of metals from sediment to the water column and to re-introduce them in the trophic web. In this work, the spatial pattern of trace metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn), metalloid (As) and rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were analysed in surface sediments. For the temporal evolution, two sediment cores (vibracores) were collected in the fresh and seawater areas. The level of contamination by trace metals in the Guadalquivir estuary can be considered low and the spatial pattern showed that low and middle estuary zones had higher concentrations than upper estuary area. Concerning the temporal evolution, a tendency to decrease has been reported. Finally, the study of REE fractionation pattern identified four different types. However, a more detail study could be convenient to determine the background levels and to determine the origin of analysed sediments.

Key words: trace metals, rare earth elements, distribution, sediment, estuary,

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HOW SENSITIVE IS THE ESCAPE RESPONSE FROM CONTAMINATION TO ASSESS ENVIRONMENTAL RISK? TRACKING A SENSITIVITY PROFILE TO TRICLOSAN

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Abstract: Avoidance response might prevent organisms against toxicity caused by the exposure to contamination. This approach requires the use of non-forced exposure system, providing different concentrations to be chosen by organisms. Two systems have been used for this proposal: the linear multi-compartmented system and the HeMHAS (Heterogeneous Multi-Habitat Assay System). In the current study, we assessed the ability of the estuarine shrimp *Palaemon varians* to detect a triclosan gradient and avoid the most contaminated areas. Organisms were exposed in those two systems (linear system and HeMHAS) to a triclosan gradient and their sensitivity to detect and avoid triclosan was checked. The comparison of the sensitivity of the avoidance response in relation to other responses was made based on (i) the sensitivity profile by biological groups and (ii) the species sensitive distribution (SSD). The gradient of triclosan simulated in both systems showed clearly that the shrimps (ca. 25% of the population) moved to the cleanest areas; shrimps' density did not exceed 3% for 54 µg/L in the linear system and 7% for 81 µg/L in the HeMHAS. The threshold of triclosan able to trigger an avoidance of 20% was ca. 18 µg/L. The profile of sensitivity to triclosan showed that avoidance is among the most sensitive ecotoxicological responses to triclosan. Considering the concentration established as safe for more than 95% of the species (HC₅ based on the SSD), in natural environments avoidance might occur even at lower levels than the HC₅, representing a risk to the ecosystems.

Key words: avoidance, HeMHAS, *Palaemon varians*, species sensitive distribution

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METAL DISTRIBUTION IN SEAFLOOR SEDIMENTS OFF PORTMÁN BAY, SE SPAIN: MULTIPROXY CHARACTERIZATION OF A SUBMARINE MINE TAILINGS DEPOSIT

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Abstract: Disposal of mine waste in the coastal environment may represent a critical source of metals and metalloids into the water column and the sediments, which potentially could lead to ecotoxicological effects. Portmán Bay, in SE Spain, is one of the most severe cases of mine-derived metal contamination worldwide. During 33 years, 57 million tons of mine waste rich in metal(loid)s (e.g. Mn, Fe, Zn, As and Pb) were directly discharged in the near coastal domain, which lead to the infill of the original bay and spread out into the adjacent inner continental shelf. Here, we present the first physical and geochemical characterization of the uppermost part of the submarine mine tailings deposit off Portmán Bay and of the sediments deposited on top during the 25 years following the cessation of mining. 52 short cores were analysed by means of non-destructive and continuous high resolution and techniques to determine the elemental chemical composition and the physical properties of the materials. Metal(loid) in the tailings deposit are higher in the innermost continental shelf, close to the infilled bay, than in other regions of the Mediterranean Sea. Post-dumping deposits present lower metal(loid) concentrations, although these are significantly higher than pre-anthropogenic loading background levels, with mean enrichment factors in the sediments of 8 for Mn, 56 for Fe, 22 for Zn, 9 for As and 5 for Pb, respectively. Such large values evidence a persistent flux of meta(loid)s to marine sediments atop of the mine tailings s.str. since the cessation of the mine waste dumping. We will also present the metal(loid)s dispersion patterns, which is a key aspect to assess the potential impact of their remobilization associated to the bay's environmental remediation plan.

Key words: Mediterranean Sea, Portmán Bay, mine tailings, metal contamination

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SEASONAL OCCURRENCE OF CURRENT-USE PESTICIDES AND PERSONAL CARE PRODUCTS IN EBRO DELTA AND MAR MENOR LAGOON WATERS

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Abstract: The occurrence and distribution of current-use pesticides (CUPs), personal-care products, plastic additives, polycyclic aromatic hydrocarbons (PAHs) and organochlorinated contaminants were characterized in surface waters from Ebro Delta and Mar Menor lagoon in summer of 2018 and winter/spring of 2019. Specifically 95 contaminants were determined by stir-bar sorptive extraction coupled to gas-chromatography with mass-spectrometry (Moreno-González et al., 2013). All contaminant groups (triazines, organophosphorus pesticides, organochlorinated pesticides, other pesticides, plastic additives, synthetic musks, UV-filters, PAHs and the antimicrobial triclosan) were found in both areas. In general, the highest concentrations were found close to the main pollution sources such as wastewater effluents discharges and surface watercourses. The highest concentrations in Ebro Delta waters corresponded to UV-filters and plastic additives in both seasons. However, the highest levels in Mar Menor lagoon were found for UV-filters, synthetic musks and CUPs in summer and plastic additives, UV-filters and CUPs in winter. PCBs were only detected in Ebro Delta waters. The observed distribution profiles were consequence of the predominant anthropogenic activities in every season (tourism, agriculture, urban nuclei and transport), the physicochemical properties of the considered substances (mainly hydrophobicity and persistence), the hydrodynamic transport and the environmental conditions in each study area. In fact the concentrations of UV-filters and synthetic musks were higher in summer than in winter in both areas due to their extended use in sun-screens and cosmetics in this season.

Key words: Current-use pesticides, Personal-care products, Plastic additives, Seawater, Coastal ecosystems

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PRESENCE OF BENZOTRIAZOLE ULTRAVIOLET STABILIZERS THE COAST OF GRAN CANARIA (CANARY ISLANDS, SPAIN)

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Abstract: The presence of emerging compounds in the environment must be characterized in order to determine their impact. In particular, benzotriazole ultraviolet stabilizers (BUVSs) are compounds found in personal care products (PCPs) and as plastic stabilizers, which may reach the sea through marine discharges from treated waters or directly in bathing areas. They are of great interest because they could be bioaccumulated and have adverse effects in marine organisms.

Gran Canaria is an island with a high population density and an important tourist activity. For that, it could be a strategic location to study the effects and consequences of the inputs of BUVSs in the coast.

In this context, we have developed environmentally sustainable analytical methods for the analysis of different marine matrices and have applied these methodologies to evaluate the presence of BUVSs in seawater, sediments and fish sampled near to different submarine outfalls during two years of sampling. Algae samples taken in the coast of Gran Canaria were also analyzed.

The results obtained provide information about the presence and distribution of BUVSs in the marine environment of this geographical area.

Key words: Benzotriazole ultraviolet stabilizers, seawater, sediments, fish, algae, Gran Canaria.

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PRELIMINARY RESULTS ON THE ADSORPTION AND EXTRACTION OF ORGANIC UV FILTERS IN MICROPLASTICS

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Abstract: Organic UV filter compounds in sunscreens generate great interest for their continuous use among the population. These substances could have harmful effects on aquatic ecosystems. Microplastics (MPs) have been shown the ability to accumulate these compounds (Camacho et al. 2019, Hartmann et al. 2017, Teuten et al., 2019), thus increasing their own impact to the marine environment. The aim of this work is to evaluate the capacity of adsorption of UV compounds in microplastics. The adsorption of five filters, 4-Methylbenzilidene Camphor (4-MBC), Homosalate (HMS), Benzophenone-3 (BP3), Octocrylene (OC) and Isoamyl p-methoxycinnamate (IMC), were tested on virgin polypropylene pellets in deionized water and seawater for six days.

The amount of adsorbed analytes was evaluated by means of the analysis of the solution by ultra-high performance liquid chromatography with tandem mass spectrometry.

In 24 hours, the highest level of adsorption of the compounds was observed. These spiked pellets were then subjected to ultrasound extraction with methanol and evaluated individually and in a mixture.

In view of the results, it has been demonstrated that polypropylene pellets are able to act as vectors of pollution. Because it seems there may be competition between the compounds, the aqueous medium and the polymer, further studies are necessary to know the behaviour of target analytes in contact with MPs.

Keywords: Microplastics, adsorption, UV filters, sunscreens, polypropylene

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ASSESSMENT ON THE OCCURRENCE AND DISTRIBUTION OF PERSISTENT AND EMERGING ORGANIC CONTAMINANTS IN THE MALTESE COAST

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Abstract:

Oceans are the ultimate sink for many of the thousands of synthetic chemicals produced every year. Among them, there are organic compounds that are regulated due to their persistence and toxicity (e.g., persistent organic pollutants, or POPs) and new emerging substances for which information on their environmental behavior is not available yet. In this work we have monitored the occurrence and distribution of a wide number of both classes of contaminants along the coast of Malta. By using a previously developed analytical method (Pintado-Herrera et al., 2014), we detected concentrations of synthetic fragrances and organophosphate flame retardants in the water column at concentrations up to 1250 ng/L. The most prevalent contaminants were: tris-n-butyl phosphate (a flame retardant at concentrations up to 80 ng/L), octocrylene (an UV filter used in sunscreens, detected at > 40 ng/L), and OTNE (a synthetic fragrance that was present in all samples at concentrations between 10 and 180 ng/L). Additionally, the insect repellent DEET was occasionally detected (70% of the samples) at levels above 100 ng/L in those sample stations closer to urban areas (San Julian, Sliema, La Valeta, and Birgu). POPs such as polychlorinated biphenyl (PCBs) and polycyclic hydrocarbons (PAHs) were often between 1 and 2 orders of magnitude lower than the aforementioned emerging contaminants. Further research is encouraged to identify specific sources for all these organic pollutants in Malta and their possible effects in the receiving marine ecosystems.

Key words: Emerging contaminants, seawater, persistent organic pollutants

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TROUBLESHOOTING IN STUDIES OF ADSORPTION OF POPS TO PLASTICS: A-ENDOSULFAN, A CASE STUDY

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Abstract: Sorption of contaminants to plastics could affect to the bioavailability, stability, and hazard of the contaminants, and therefore studies about sorption of organics on plastics are relevant. Nevertheless, some problems can affect the reliability of these studies.

In this work sorption assays for α -Endosulfan (α -EnS) were performed with LDPE and PHB at 4°C and 20°C, during a contact time of 7 days, in seawater. Adsorption was measured analysing water and plastics samples. Control water samples were included to ensure the stability of α -EnS over all the experiment.

Filtration to separate plastics from water can be an important source of errors, due to sorption or blank problems. Frequently this step it is not studied, and the adsorption of the analytes to the filters can be wrongly attributed to adsorption to plastic. The typically used filters adsorb α -EnS (cellulose filters: 100% sorption) whereas using glass columns with 20 μ m teflon frits only 3% was retained. Concentration of α -EnS in control samples remain stable in the 4°C. But in the 20°C assay, a reduction in concentration was observed (94% degraded at 7d). Regarding the analysis of plastics, PHB acquire a thick texture after contact with water and the extraction recoveries were reduced. These results bring to light the relevance of the quality of the analytical extraction methods by take into account all the steps involved, and all the parameters affecting the reliability of the results compromising the sorption studies.

Key words: Sorption, Polymers, PHB, α -endosulfan, Troubleshooting

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