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ON MARINE SCIENCES
VALENCIA, JULY 10-12

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VALENCIA, JULY 10-12



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ORAL COMMUNICATIONS ~ BIOGEOCHEMICAL PROCESSES

ENHANCING ALKALINITY IN RIA FORMOSA BY DEPLOYMENT OF ALKALINE SUBSTRATES: VARIABILITY IN NUTRIENT CONCENTRATION AND FLUXES

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Abstract: Reducing atmospheric CO₂ levels is crucial in combating global warming. Mineral weathering naturally maintains ocean alkalinity, removing CO₂ from the atmosphere over geological time scales. To accelerate this process, alkaline substrates can be introduced into coastal areas, but their effectiveness depends on factors such as substrate type, grain-size, temperature, pH, and salinity. In addition, the marine biota can be affected by the release of nutrients and trace elements. An *in situ* experiment in Ria Formosa productive coastal lagoon, Portugal, Europe's first, initiated in September 2022, examines the effects of olivine and basalt (coarse and fine) application on alkalinity, nutrient and metals. The experiment was installed in an undisturbed zone colonised by *Spartina maritima* with monthly measurements of temperature, salinity, oxygen concentration, pH and determination of total alkalinity, nutrients and trace metals in supernatant and porewater samples. The aim of the present work was to assess the variability of nutrient concentrations, during the first year. Nutrients were determined spectrophotometrically (Grasshoff et al., 1999), using the OSIL Marine Nutrient Kit as reference material. Following mineral application, there was a notable rise in nutrient levels, particularly in porewater (up to 15-fold higher than the supernatant). Sediments acted as a nutrient source, influenced by organic matter remineralization, bioturbation, and mineral dissolution. Nutrient concentrations in porewater relative to control were up 2-fold for silicate and phosphate and 50% higher for ammonium and nitrate. After 3-4 months, concentrations stabilized, resembling control levels and fluxes also decreased, except silicate and nitrate. Nutrients were higher in olivine treatments than in basalt despite no significant differences occurred between substrates. No significant differences were also found between grain-size. Data variability can also be due to seasonal effects including of biological activity, and heterogeneity in the composition of the sediments. Data show that substrates have potential to increase alkalinity, with manageable nutrient impacts, attributed to Ria Formosa's high-water renewal rate.

Key words: Alkalinity enhancement, nutrients, Ocean acidification, Ria Formosa lagoon.

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Grasshoff, K., Erhardt, M., Kremling, K. (1999). *Methods of Seawater Analysis*. Third, Completely Revised and Extended Edition. Wiley-VCH, New York, 598 pp.

MICROBIAL PROCESSES IN A DEOXYGENATING OCEAN: COEXISTENCE AND DOMINANCE AT LOW O₂ LEVELS

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Abstract: As a consequence of Global Warming and the eutrophication of coastal areas, the oxygen reservoir in the oceans is progressively decreasing. In permanent or seasonally stratified water masses, the respiration of the biological community decreases the dissolved oxygen, eventually leading to the formation of hypoxic and anoxic conditions. The progressive ocean deoxygenation is increasing the extension of these areas with unclear impacts on the global biogeochemical cycles. The microbial community inhabiting these marine areas respond to the changing redox conditions by altering the composition of the microbial community as well as modifying the main metabolic processes. Some components have metabolic plasticity, allowing physiological adaptations, such as increasing their affinity for oxygen to pursue with aerobic processes at trace O₂ levels or eventually shifting to anaerobic metabolic pathways such as denitrification. The balance of these processes determines the role of the ecosystem in the regeneration or loss of nitrogen nutrients and the production of relevant greenhouse gases such as nitrous oxide. During a series of oceanographic cruises to a coastal anoxic fjord and the oceanic Oxygen Minimum Zones, we measured some of the most relevant aerobic processes such as aerobic respiration and nitrite oxidation, as well as other anaerobic processes such as denitrification and anammox. Our results show that the aerobic community consumes the oxygen at nanomolar levels and that nitrite oxidation rather than aerobic respiration may be the most efficient processes consuming oxygen at trace levels. The constant exposure of the microbial community to low oxygen levels induces the use of higher affinity enzymes, increasing the affinity for oxygen of these communities for oxygen. In addition, anaerobic processes such as denitrification and anammox remain active in the presence of low oxygen levels, challenging the tight coupling of these processes to the absolute absence of oxygen.

Key words: Microbial metabolism, Oxygen, Respiration, Microbial community

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INFLUENCE OF DISSOLVED ORGANIC MATTER ON THE QUANTIFICATION OF WATER-ATMOSPHERE CO₂ FLUXES IN ESTUARINE SYSTEMS

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Abstract: Total alkalinity (TA) and pH are variables commonly used for characterizing the inorganic carbon system in coastal and estuarine systems. However, total alkalinity is not a specific method for measuring dissolved inorganic carbon (DIC), and the influence of different acid-base equilibria in water can be corrected based on its analytical concentrations and available thermodynamic information (e.g., silicate, phosphate, ammonium, or borate). In this study, a methodology is presented that allows estimating the influence of dissolved organic matter on total alkalinity (A_{org}) and is applied to assess its impact on quantifying CO₂ fluxes with the atmosphere in the Guadalquivir estuary. The approach involves successive acid-base titrations on the same sample while maintaining an intense N₂ bubbling to remove produced CO₂.

The Guadalquivir estuary exhibits intense gradients of TA (2500 - 4000 $\mu\text{mol kg}^{-1}$) and dissolved organic carbon (DOC, 100 - 450 $\mu\text{mol kg}^{-1}$) with salinity. The results obtained indicate that organic alkalinity (A_{org}) increases toward the interior of the estuary, contributing between 50 and 100 $\mu\text{mol kg}^{-1}$ to TA. However, there is no linear relationship with DOC, and this dependence varies based on the nature of the organic matter. These variations are interpreted in terms of the relative abundance of humic and protein compounds characterized using spectrofluorometric techniques. The presence of dissolved organic matter in the Guadalquivir estuary causes an apparent increase in CO₂ partial pressure when AT is not corrected for this effect, reaching levels above 100 μatm in the inner part of the estuary. This methodology helps to avoid overestimation of CO₂ fluxes to the atmosphere in systems with high DOC concentrations.

Key words: Total alkalinity, dissolved organic matter, water-atmosphere CO₂ fluxes, estuaries

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DISSOLVED REEs IN THE RIVER ULLA BASIN: SOURCES AND TRANSPORT TO THE RIA OF AROSA (NW IBERIAN PENINSULA)

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Abstract: The land-sea transport of Rare Earth Elements (REEs), recognized as emerging contaminants, is insufficiently studied. No research has focused on the eighteen Galician Rias, where to identify the geogenic and anthropogenic sources is a key issue. The Ulla-Arousa system is the biggest river-ria network in the northwest Iberian Peninsula, which is fed by tributaries like Lañas, Brandelos, Deza, and Sar, post-Portodemouros dam. Monthly water samples, including tributaries, the Ulla River and the dam outflow, were collected throughout October 2018 to September 2019. In situ measurements of temperature, conductivity, and pH were conducted. Fluvial water samples underwent processing in a clean laboratory, and dissolved lanthanides (Ln) and Y were determined in the “Analytical Service for the Determination of Metals in the Environment” of IIM-CSIC.

	Dam	Lañas	Brandelos	Deza	Ulla	Sar	Unit
Flow	23.7	1.5	3.1	13.5	51.5	8.4	m ³ ·s ⁻¹
Ln	173	24,400	1750	118	383	198	ng·L ⁻¹
Y	56	8270	826	53	161	63	ng·L ⁻¹

The outflows from the Portomouros dam and the Deza tributary exhibited lower annual average concentrations of dissolved REEs, as shown in the table. Conversely, the Lañas and Brandelos tributaries, situated near the amphibolite massif of the Arinteiro unit, displayed the highest concentrations. At the head of the Ria of Arousa, during the hydrological year addressed, the Ulla River discharged 748 kg-Ln·yr⁻¹ (47.8 kg-Gd·yr⁻¹), with an additional 57 kg-Ln·yr⁻¹ from the Sar River. This river, flowing alongside the city of Santiago de Compostela, exhibited a Gd anomaly, Gd/Gd* of 9.6, compared to 1.2 in the Ulla and other tributaries. This anomaly could be attributed to its use as an MRI contrast agent for cancer detection. In the Sar, the estimated anthropogenic input into the ria was 3.6 kg-Gd·yr⁻¹, constituting 58% of the total output (6.2 kg-Gd·yr⁻¹).

Key words: Lanthanoids, Yttrium, Gadolinium, concentration, fluxes, contamination.

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GREENHOUSE GAS DYNAMICS (CO₂, CH₄ AND N₂O) IN COASTAL SYSTEMS OF SOUTHWEST SPAIN: RIO SAN PEDRO TIDAL CREEK AND BARBATE ESTUARY

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Abstract: Coastal areas are experiencing significant anthropogenic pressure, leading to the influx of substantial amounts of organic matter and nutrients into these systems. A large portion of this organic matter reaches the sediments, where it is mineralized through various diagenetic processes, resulting in benthic fluxes of nutrients, carbon, and greenhouse gases (GHGs) into the water column. Consequently, the water column becomes supersaturated with greenhouse gases, causing coastal zones to act as GHG emitters. Concentrations of carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) in the water column and sediments have been analyzed in two coastal systems in the southwest of the Iberian Peninsula: Río San Pedro tidal Creek and Barbate Estuary. To examine seasonal variations, two samplings were conducted under winter and summer conditions in 2023. In the sediment, CO₂, CH₄ and N₂O concentrations generally increased with depth at almost all stations and exhibited seasonal variations associated with the intensification of mineralization processes with temperature. In the water column, GHG concentration increases towards the interior of both systems. These variations have been attributed to the high rates of organic matter mineralization both in the sediment and that entering the system through lateral inputs, mainly from the effluents of a fish farm in the San Pedro River and agricultural practices in the Barbate Estuary. Water-atmosphere fluxes increase towards the interior of both systems, generally being more intense during the summer. Both the Río San Pedro and Barbate Estuary serve as sources of CO₂, CH₄, and N₂O to the atmosphere. Annual average emissions for Río San Pedro were estimated at 5.4 10⁶ mol/year for CO₂, 1.6 10⁴ mol/year for CH₄, and 5.6 10² mol/year for N₂O, while for the Barbate Estuary 1.7 10⁷ mol/year for CO₂, 3.5 10⁴ mol/year for CH₄, and 2.5 10³ mol/year for N₂O.

Key words: greenhouse gases, air-water fluxes, sediment profile, coastal systems

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DISTRIBUTION OF GREENHOUSE GASES (CH₄ AND N₂O) IN SOUTH AMERICAN ATLANTIC COASTAL LAGOONS (URUGUAY)

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Abstract: Coastal regions receive inputs of organic matter and nutrients, leading to the production of greenhouse gases (GHG) such as methane (CH₄) and nitrous oxide (N₂O). While coastal ecosystems emit varying amount of CH₄, their role as a net source or sink of N₂O is uncertain, in particular in the southern hemisphere (Rosentreter et al., 2023). Here, we investigated the distribution of CH₄ and N₂O in three coastal lagoons located on the Atlantic coast of Uruguay (Laguna de Rocha, Laguna Garzón, Laguna José Ignacio). These lagoons integrate the UNESCO biosphere reserve "Reserva de Biosfera Bañados del Este", and are designated as protected landscapes under the National System of Protected Areas, as well as being part of the Ramsar Convention for wetlands. Samplings were conducted seasonally, during February, May, August, and November in 2021, 2022 and 2023. The concentration of CH₄ and N₂O were determined by gas chromatography. CH₄ concentrations ranged from 8.0 to 332.6 nM, with CH₄ saturation levels ranging from 285.9% to 11663.0%, indicating oversaturation of CH₄. On the other hand, N₂O concentrations ranged from 6.0 to 22.3 nM, with saturation levels between 70.3% and 781.0%. Overall, in the three lagoons water-atmosphere fluxes of CH₄ were positive throughout the study period (from 5.6 to 3319.0 μmol m⁻² d⁻¹). In contrast, N₂O fluxes exhibited seasonal variability, with mean positive fluxes during February and May, and negative fluxes during August and November (from -77.3 to 1194.8 μmol m⁻² d⁻¹). The study revealed that the Uruguayan coastal lagoons act as a source of CH₄ to the atmosphere consistently, as source of N₂O in summer and autumn, while acting as a sink of N₂O in winter and spring. This work is the first GHG characterization in these lagoons, and its results are expected to improve our understanding of regional variations from coastal systems.

Key words: greenhouse gases, atmospheric flux, coastal lagoons, South Hemisphere

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EVOLUTION OF THE FE(II) OXIDATION KINETIC CONSTANTS DURING THE 2021 LA PALMA ERUPTION

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Abstract: The eruption of La Palma, Canary Islands, Spain, in September 2021 was the longest in the island's recorded history. During 85 days, lava entered the sea on the west coast of the island four times, forming two lava deltas. The oxidation kinetics of iron(II) in this environment are poorly constrained, particularly in relation to the dependence on physico-chemical parameters such as temperature (T), pH and the effect of organic matter. Seawater samples were collected at 10 time points in the proximities of the forming lava deltas from the time of the eruption until 2024. Iron(II) oxidation kinetic studies were performed to analyse the effects of seawater characteristics on Fe(II) oxidation rate constants and $t_{1/2}$ (half-life). The experimental methodology is based on the Flow Injection Analysis by Chemiluminescence (FIA-CL) method at fixed conditions of pH, temperature and oxygen saturation (pH=8, T=15°C and Sat[O₂]=100%) resulting in $t_{1/2}$ times ranging from 2 to 11 minutes. In the case of a sample in which a rapid complexation was observed with the lowest $t_{1/2}$, further analyses were performed. The analysis of the Fe(II) oxidation rate constants at several stations revealed that factors, apart from T and pH, controlled the oxidation process. In a biogeochemical context, nutrients were analysed in order to elucidate the observed deviations.

Key words: Fe(II) oxidation kinetics, volcanic eruption, lava, GEOTRACES.

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ASSESSMENT OF THE MAIN DRIVERS CONTRIBUTING TO PCO₂ AND PH GRADIENT FORMATION ALONG THE GALICIAN RIAS BAIXAS (NW PENINSULA)

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Abstract: The Rías Baixas (NW Spain) are four coastal embayments lied within the Iberian Upwelling System that support important socioeconomically activities as aquaculture and small-scale fisheries (Fraga, 1981). In coastal upwelling regions the seasonal variation in wind direction results in an upwelling-downwelling regime that modulates CO₂, nutrient concentration, water temperature and primary production. This, together with the interaction with freshwater sources, such as river discharge, can result in CO₂ and pH gradients that can affect the response of plankton microbial community and calcifying bivalve production, among others (Álvarez et al. 1999; Nogueira and Figueiras, 2005). However, assessing the relationship of the main drivers on the CO₂ and pH gradients remains challenging (Duarte et al. 2013). In the framework of the ACID project, monthly sampling was carried out at the Ría de Vigo from April 2023 to April 2024 with the objective of addressing this uncertainty. Hydrographic profiles and samples for the determination of pH, dissolved inorganic carbon (DIC) and pCO₂, as well as samples for the assessment of the biological response, were collected throughout a longitudinal transect early morning during low tide. 2023-2024 results were also compared to preliminary data from October 2019 to February 2020. Results from both datasets showed that pCO₂ and pH along the Ria were regulated by wind-driven circulation and the intrusion of freshwater. 2019-2020 data revealed more pronounced pCO₂ gradients compared to 2023-2024 ACID findings. The inner stations exhibited higher pCO₂ concentrations (~5400 ppmv in January 2020), gradually decreasing towards outter stations (~430 ppmv in October 2019). In contrast, pH showed an opposite pattern to pCO₂, with similar values observed in both datasets and ranging from 8.29 to 6.61. DIC concentrations remained relatively uniform throughout the longitudinal transect, although slightly lower in 2023-2024 ACID findings. Hydrographic properties also showed consistently lower salinity conditions during 2023-2024 ACID samplings due to regular precipitation events and higher

river freshwater discharge than in 2019-2020 period. The latter seems to explain the main differences observed between both periods regarding the occurrence of pCO₂ and pH gradients and arise as important drivers of coastal acidification in Rías Baixas.

Key words: pCO₂, coastal acidification, upwelling region, gradients, Rías Baixas.

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REACTIVITY AND FLUXES OF INORGANIC NUTRIENTS FROM AN AGRICULTURALLY AFFECTED ESTUARY (GUADALQUIVIR ESTUARY)

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Abstract: The Guadalquivir Estuary receives significant inputs of nutrients from agricultural fields and from different urban centres, which causes a disturbance of the natural biogeochemical cycles of the system. For this reason, this study has been carried out to determine the longitudinal, tidal and seasonal influence on dissolved inorganic nitrogen (DIN), silicates (SiO₂) and phosphates (PO₄⁻³), as well as their transport to the Gulf of Cadiz. The study consists of a total of 12 samplings carried out between 2017 and 2022, ensuring different hydrodynamic and environmental conditions. The concentration of the nutrients increases inwards, reaching maximums in the innermost zone for DIN (416.2 μmol L⁻¹) and SiO₂ (156.3 μmol L⁻¹), while PO₄⁻³ has maximums in the intermediate zone (4.0 μmol L⁻¹), at the turbidity maximum zone (TMZ). Both DIN and SiO₂ show maximums associated with growing seasons and higher river flows. However, PO₄⁻³ shows its maximums in summer, suggesting a production favoured in the system by higher temperatures. The calculated maximum net transport shows clear dependence on the discharge regime, showing the maximum transport in the sampling where extreme rainfall occurred. Tidal height is the second variable that influences transport, which influences the inundation area, and therefore the greater transport of inorganic nutrients compared to other samplings with similar river flows. The range for the net transport is $1.7 \cdot 10^5 - 6.3 \cdot 10^6$ mol d⁻¹ for DIN, $1.4 \cdot 10^5 - 3.6 \cdot 10^6$ mol d⁻¹ for SiO₂ and $3.6 \cdot 10^3 - 3.0 \cdot 10^4$ mol d⁻¹ for PO₄⁻³. The results obtained indicate the Guadalquivir Estuary acts as a source of inorganic nutrients to the Gulf of Cadiz.

Key words: Guadalquivir Estuary, inorganic nutrients, net transport.

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RECENT ADVANCES IN THE BIOGEOCHEMISTRY OF PLATINUM-GROUP ELEMENTS IN IBERIAN ECOSYSTEMS

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Abstract: Over the past decade, studies on Platinum-Group Elements (PGEs) in the coastal ecosystems of the Iberian Peninsula have fulfilled significant knowledge gaps using various analytical strategies. Voltammetry has played a crucial role in understanding PGEs' biogeochemistry, particularly for platinum (Pt) and rhodium (Rh). The introduction of signal transformation using the second derivative improved voltammetric measurements, revealing new insights on their occurrence in aquatic media. Combining voltammetry with inductively coupled plasma mass spectrometry (ICP-MS) enhanced the understanding of Pt and Rh speciation analysis. In filtered samples (<0.45 µm) of road dust leachates and riverine waters, truly dissolved species determined by voltammetry comprised a significant portion of total dissolved species. Additionally, wetland vegetation's seasonal activity controls Pt geochemistry in sediments, influencing its solid/dissolved chemical species. Comparison of Pt and Rh concentrations in biota from urbanized coastal systems support their export to adjoining coastal areas. Therefore, further research on PGEs' biogeochemistry should encompass voltammetry due to its ability to provide additional information on the species and to cope with some analytical limitations that other techniques face during PGE analysis.

Key words: Platinum-Group Elements, Analytical advances, Environmental biogeochemistry

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ARE RARE EARTH ELEMENTS CLIMBING THE FOOD CHAIN? A CLOSER LOOK AT THE RÍA DE VIGO

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Abstract: Rare earth elements (REEs) are the subject of current economic and political attention due to their essential role in many essential industries and day-to-day technologies. These elements share very similar physico-chemical characteristics, show consistent behaviour in the environment and differ from each other due to the natural fractionation they undergo from their lithogenic origin to natural waters. The growing interest for this group, the issues related to their exploitation and the consequent increase in their presence in the aquatic environment highlight their potential role as new pollutants. This, together with the limited studies available on their effects and environmental problems that may affect several species, many of which are of important commercial value, indicates the need for further studies. The present work focuses on the determination of REEs (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) concentrations in the species studied along two trophic chains in the Ria de Vigo (NW Spain). The trophic levels of the collected species were established by stable isotope analysis (SIA) and trace elements concentrations, mainly in muscle tissues, were measured using ICP-MS. The results reflect intraspecific variability with different patterns of accumulation within the same group. The observed REEs variabilities are consistent with previous studies, showing higher concentrations in benthic or detritivorous species than in filter-feeding or pelagic species. Similarly, no pattern of biomagnification was observed in the trophic chains studied, as reported in reviews on this subject. The new data presented here on REEs concentrations in a wide range of marine species present in NW Spain can be used as a reference for future studies.

Key words: REEs, Stable isotopes, biomagnification, bioaccumulation

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UNVEILING THE COMPLEXATION DYNAMICS OF PLATINUM WITH DISSOLVED ORGANIC MATTER IN ESTUARINE ENVIRONMENTS

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Abstract: In the last decade, research on the behaviour of Platinum in aquatic systems has become a growing trend due to its increasing anthropogenic demand, especially linked to its use in catalytic converters in cars (Rauch and Peucker-Ehrenbrink, 2015). However, several aspects of the biogeochemical behaviour of Pt remain largely unknown; in particular, studies of the interaction with dissolved organic matter (DOM), a key factor in determining the speciation and reactivity of trace elements, are scarce for this metal. In order to assess the potential organically-bound fraction of Pt, we studied the concentration of dissolved organic carbon (DOC), dissolved Pt and other trace metals in the longitudinal axis of the Vigo Ria (NW Spain), from freshwater to the seawater end-member at different seasonal conditions. Concentrations of total dissolved and solid-phase extractable (SPE) DOC and trace metals of interest (Pt, Cu, U, Zn, Ni, Co, Fe, V, Mn, Cd, Pb) were determined in filtered (0.2 µm) water samples. SPE procedure used a styrene-divinylbenzene polymer sorbent (Bond Elut PPL). Results obtained in the extraction efficiencies for DOM (67.6 ± 6.4 %) and some of the ‘common’ trace metals (i.e. Cu (8-15%), Co (5-10%)), as well as the order of binding strength of these elements (Cu>U>Co>Ni>Fe>V>Cd) are consistent with previous studies (Dittmar et al., 2008; Waska et al., 2015; Ksionzek et al., 2018). On the other hand, extraction efficiency for Pt ranged from 10 to 30% (Pt). Thus, considering the differences existing between the metal-DOM complexation in water and extraction efficiencies reported in the literature (i.e. Cu >90% and 10-20% respectively), we can expect similar behaviour for Pt with comparable or higher extraction efficiencies in their association with DOM (Prego and Cobelo-García, 2003). Overall, our study provides new evidences on the effective complexation of Pt with DOM in natural waters that will allow a better assessment and understanding of its biogeochemical behaviour in estuarine systems.

Key words: Pt, trace elements, DOM, complexation, estuarine mixing

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EVOLUTION OF IRON SIZE FRACTIONATION IN SURFACE WATERS DURING AN AERIAL VOLCANIC ERUPTION

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Abstract: Life on land and at sea drastically changed on La Palma, Canary Islands, Spain in September 2021. For 85 days, the longest eruption in its recorded history took place. The aerial eruption produced tons of tephra which covered the whole island. This tephra reached the ocean liberating moles of iron. Concurrently, the lava flow reached the ocean, further liberating more iron. These two iron sources combined with the continuous iron sources found in these coastal areas such as sediment resuspension and underground water discharge.

Pre-lava-arrival and post-eruptive samples showed the lowest concentrations (averaging 77 ± 33 nM). The highest concentrations were observed 5 m from the lava-sea interface, when incandescent lava was observed to be forming laze plumes (2008 ± 75 nM on October 1, 2114 ± 41 nM on November 12 during LPV6 and 2008 ± 49 nM on November 14 during LPV7). Similar increases were observed in the dFe size fraction. Soluble Fe ($<0.02 \mu\text{m}$) did not present the same behaviour. The measured results confirm the importance of these two iron sources, where lava arrival produces a strong input, while ash deposition acts as a more continuous but lower iron source.

Key words: Iron size fractionation, volcanic eruption, lava, GEOTRACES

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ISOTOPIC CHARACTERIZATION OF DISSOLVED INORGANIC CARBON IN ESTUARY WATERS

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Abstract: Dissolved inorganic carbon (DIC) is the primary carbon reservoir in natural waters, and its quantification is essential for studying the global carbon cycle. Measurement of the stable isotope of DIC ($\delta^{13}\text{C-DIC}$) is a valuable tool for determining sources and sink of DIC providing a better understanding of the biogeochemical processes affecting the carbon cycle in aquatic ecosystem. This study aims to develop a methodology for the precise characterization of $\delta^{13}\text{C-DIC}$ in estuarine waters from coastal marine zones to fluvial waters. The study was carried out in several coastal systems of the southwestern of the Iberian Peninsula, taking Guadalquivir estuary as an example, which show an increase in DIC concentration from 2400 $\mu\text{mol kg}^{-1}$ at the mouth to 4300 $\mu\text{mol kg}^{-1}$ in the inner region. Measurements of $\delta^{13}\text{C-DIC}$ were conducted using a water-gas equilibration system coupled to an Isotope Ratio Mass Spectrometer (IRMS). Helium flow was optimized (100 mL min⁻¹) to purge air from the samples, and phosphoric acid was added to maintain a pH below 2. It was determined that 1 mL of sample acidified with 30 μL of 2 M H_3PO_4 in 10 mL vials, with 24-hour equilibration, was optimal for the determinations. Ten consecutive measurements were taken to enhance precision in of $\delta^{13}\text{C-DIC}$ measurements. Applying the developed methodology to Guadalquivir estuary revealed a significant $\delta^{13}\text{C-DIC}$ decrease along the salinity gradient. Values were -0.12 at the mouth and dropped to -5.95 ‰ in the inner zone. These variations in $\delta^{13}\text{C-DIC}$ along the estuarine salinity gradient, with more negative values in the inner region, are attributed to mixing processes and the intensity of mineralization processes within the estuary. This study underscores the importance of accurate $\delta^{13}\text{C-DIC}$ characterization for understanding carbon cycling in estuarine ecosystems and highlights the utility of the developed methodology for future research in similar environments.

Key words: estuarine waters, DIC, carbon isotope, southwestern Iberian Peninsula.

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VARIABILITY AND VERTICAL FLUXES OF CARBON DIOXIDE IN THE GUADALQUIVIR ESTUARY

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Abstract: Spatiotemporal variability of carbon dioxide (CO₂) in the Guadalquivir Estuary has been studied considering the influence of temperature, salinity, water-atmosphere fluxes, benthic fluxes and lateral inputs. The data correspond to tidal and longitudinal samplings carried out in September 2021, February 2022 and July 2022. The pCO₂ always increases inland, with values of 490 µatm at the mouth, and 2790 µatm in the inner zone. The influence of temperature in the variability of pCO₂ ranges between -3.1 and 4.3 µatm km⁻¹, contributing positively or negatively to CO₂ variability depending on the sampling. The effect of salinity always contributes negatively to pCO₂ variability, varying between -33.1 and -3.6 µatm km⁻¹. The system acts as a source of CO₂ to the atmosphere, with water-atmosphere fluxes of CO₂ increasing inland and ranging between 2.8 and 122.1 µatm m⁻² d⁻¹. The sediments of the Guadalquivir Estuary are a source of CO₂ to the water column, with benthic fluxes of CO₂ ranging between 0.3 and 7.2 mmol m⁻² d⁻¹. Based on the information obtained, it seems that lateral inputs would be the main factor controlling CO₂ variability, above thermodynamic effects and sediment-water-atmosphere fluxes. However, the uncertainty associated with the quantification of these processes does not allow a precise assessment of the influence of lateral inputs, despite their great importance in the Guadalquivir Estuary.

Key words: Carbon dioxide, water-atmosphere fluxes, benthic fluxes, lateral inputs, Guadalquivir Estuary

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DISSOLVED IRON CYCLING IN THE MAR MENOR (SE SPAIN) UNDER DIFFERENT SINGULAR ENVIRONMENTAL EVENTS: LEVELS AND ORGANIC SPECIATION

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Abstract: The Mar Menor is a shallow coastal lagoon with high salinity located in the southeast of the Iberian Peninsula. This area is highly affected by various impacts generated by human activity, especially of agricultural and mining origin, leading to the introduction of metals, organic matter, nutrients and contaminants into the lagoon. However, total metal concentrations are not precise indicators of their biological availability, so it is crucial to consider the chemical speciation of these metals, as is the case with iron (Fe), which also plays a crucial role in phytoplankton growth. The presence of elevated levels of dissolved organic matter (DOM), which may be due to eutrophication or associated to precipitation events, leads to the formation of organic complexes with Fe. In order to understand the Fe cycle in the lagoon, multiple stations were measured during 2021 including physico-chemical parameters (temperature, salinity, dissolved oxygen, pH and turbidity) as well as the dissolved Fe concentration (dFe) and Fe-binding ligands (LFe) that were characterized by the conditional stability constant ($K_{\text{condFe}^{3+}\text{L}}$). Fe concentration and speciation was measured by using Competitive Ligand Exchange-Adsorptive Stripping Voltammetry (CLE-AdCSV), employing TAC (2-(2-thiazolylazo)-p-cresol) as a synthetic competitive ligand (Croot et al., 2000). Total dissolved iron and speciation results show variations among different environmental events. The concentration of dissolved iron ranged from 12.99 nM to 72.38 nM. It is observed that the concentration of dFe is directly influenced by the presence of organic compounds. The conditional stability constant ranged from 21.57 to 19.68, and the concentrations of the complexing capacity (LFe) ranged from 13.60 nM to 58.50 nM. Both variables correlated with optical properties of organic matter such as fluorescence (humic substances) and absorbance at different wavelengths. This study highlights the importance of both the quantity and quality of dissolved organic matter in the

biogeochemical cycling of a micronutrient element such as iron.

Key words: Mar Menor, iron, stability constant, metal speciation, dissolved organic matter.

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FE(III) REDUCED TO FE(II) BY TRIPTOPHAN IN SEAWATER

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Abstract: Iron (Fe) is an essential micronutrient for marine productivity and can be found as Fe(III) and Fe(II), being the first one the most abundant but Fe(II) is easily used by microorganisms. In this sense, natural organic ligands play an important role in the Fe chemistry and can reduced Fe(III) to Fe(II) making it available for longer. Among all the ligands, tryptophan (Trp), an amino acid, is found in seawater and can form complexes with metal ions via chelation involving the α -amino ($-\text{NH}_2$) and α -carboxylate ($-\text{CO}_2^-$) groups. Then, the Fe(III) reduction by Trp has been studied as a function of pH (7.0 – 8.0), temperature (10°C – 25°C) and Trp concentrations (50 – 500 nM). In addition, a comparison with 0.7 M NaCl 2 mM NaHCO_3 solutions has been carried out for the same pH range. The Fe(III) reduction rate ($\log k'_{\text{Fe(III)-red}}$) in seawater was from -4.36 to -4.71 at pH 7.0 and 7.8, respectively, while at pH 8.0 the Fe(II) was not detectable. While in NaCl- HCO_3 solutions it was from -4.19 to -4.59. In the case of temperature, the Fe(III) reduction was studied at two pH values. The $\log k'_{\text{Fe(III)-red}}$ followed an inverse dependence when the temperature change from 10°C to 25°C and ranged from -5.06 to -4.36 and from -5.22 to -4.71 at pH 7.0 and 7.8, respectively. The concentration of Trp also affected the Fe(III) reduction in seawater. At pH 7.0, 10.12% and 18.64% of Fe(III) were reduced to Fe(II) when added Trp increased from 50 to 500 nM, respectively, while at pH 7.8, this Fe(III) was reduced between 5.06% and 16.67%.

According to the current results, in a situation of global warming and ocean acidification, changes in the physico-chemical conditions promote impacts on the Fe(III) reduction by organic ligands, such as amino acids, and influence the Fe marine biogeochemical cycles promoting the formation of bioavailable Fe(II) in seawater.

Key words: Iron, Amino acid, Kinetics, Seawater, Fe(II) regeneration

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INTERANNUAL AIR-SEA CO₂ FLUXES IN THE NW IBERIAN UPWELLING SYSTEM

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Abstract: Assessment of air-sea carbon dioxide (CO₂) fluxes are a requisite to evaluate carbon budgets and to inform policy and decision-making. In the coastal area the spatio-temporal heterogeneity of surface pCO₂ is larger in zones with seasonal variability, episodes of intense primary production, land-coastal fluxes and upwelling events. All these processes exist and usually co-occur in the upwelling region off NW-Iberian, but their long-term response to climate change is still uncertain. Here, a new assembled database of in-situ and remote observations collected from 1991 to 2022 has been curated and analysed for the South of Galicia coastal zone (43-42°N, 10-8°W). We produce an ensemble average of new development machine-learning models of variate complexity and adjusted for each Ría. The average uncertainty of this new pCO₂GalicIA ensemble, establishes a root mean square error of ~5-10 µatm when checked with independent datasets. The higher variability in the inner Rías, combined with a lower amount of observations for these zones, results in a lower confidence in the predictions compared with the offshore area. The interannual air-sea CO₂ exchange variability observed in Galicia was mostly related with the seasonal cycle, positive temperature anomalies, salinity, and chlorophyll. Although air-sea CO₂ exchanges are highly variable, surface waters off NW Iberian Upwelling System are net sinks for atmospheric CO₂ all year-round. This is an ongoing effort to characterize air-sea CO₂ fluxes at high resolution scale in the upwelling system of the NW Iberian Peninsula, a first step to characterize long-term responses in a highly productive marine ecosystem within the framework of anthropogenic climate change. This challenge will be even more relevant as it is an upwelling region that seems to be at a tipping point about its future evolution as climate projections suggest future wind intensification¹ while in situ observations still show contradictory results²⁻⁴.

Key words: air-sea CO₂ fluxes, upwelling system, machine learning

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COMPARISON OF VOLTAMMETRIC METHODS TO DETERMINE THE CHEMICAL SPECIATION OF DISSOLVED COPPER IN SEAWATER

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Abstract: The total metal concentrations are not suitable predictors of their bioavailability, therefore, the chemical speciation of metals should be considered. Speciation of dissolved Cu in seawater is mainly dominated by organic ligands, such as dissolved organic matter (DOM) (Sánchez-Marín et al., 2020). The present study aims at studying the chemical speciation of Cu in a coastal lagoon, affected by mining and eutrophication, and presenting high Cu and high DOC levels (Santos-Echeandía et al., 2023). The chemical speciation of dissolved copper (Cu) was studied using two different voltammetric methods known as cathodic stripping voltammetry (CLE-ACSV), using salicylaldoxime (SA) as competing ligand, and anodic stripping voltammetry (ASV). For this purpose, 36 water samples were taken in different locations of the Mar Menor lagoon at different events in 2021 and 2022. The Cu speciation parameters (complexation capacity and conditional stability constant) were calculated using ProMCC software, and the obtained values for the different samples were related with physicochemical variables (pH, salinity) and with different variables related with DOM such as DOC, fluorescence and absorbance of the DOM, by means of correlation and multiple regression analysis. The results of Cu complexation capacity (L_{Cu}) ranged from 15.89 to 90.82 nM for the CLE-ACSV method and from 40.37 to 205.50 nM for the ASV method. Additionally, the values of conditional stability constant ($\log K_{Cu^{2+}}$) varied between 11.36 and 12.92 for the CLE-ACSV and 8.19 and 10.09 for the ASV method. The parameters derived from both methods did not correlate between them, suggesting that these techniques might detect different ligand classes having different sources and behaviors. Clear relationships were observed between complexation parameters obtained by CSV and DOC and fluorescence peaks related with humic matter. The application of a unified multiwindow approach to these data is hampered by the important difference in Cu speciation obtained in both analysis methods.

Key words: Mar Menor, copper, complexation capacity, voltammetry, dissolved organic matter.

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SPONTANEITY OF THE DISSOLUTION REACTION OF BTEX COMPOUNDS IN A DEEP SPILL

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Abstract: The use of dispersants in deep hydrocarbon spills can have unfavorable consequences regarding pollution by BTEX compounds. In this context, it is important to be able to combine the effects of dispersants and their coupling with oceanographic dynamics to generate knowledge in the development of possible alternatives for the treatment of this type of contaminant in deep hydrocarbon spills. Based on the aforementioned, in a deep spill, the Gibbs potential of the benzene dissolution reaction in the water column, ΔG , will be a function of the hydrocarbon composition of the spill and the behavior of the plume(s), which, in turn, depends on the physical characteristics of the environment, such as bathymetry, stratification, depth, and absolute salinity SA. Currently, there is no coupling of thermodynamic aspects in mesoscale models, and, in that sense, the incorporation of thermodynamic variables into a hydrodynamic model becomes a research challenge. The dynamics and spatial distribution of the thermodynamic potential of Gibbs, ΔG , will provide information about the spontaneity of the dissolution reaction of BTEX compounds in seawater, which may vary during the ascent and evolution of the plume.

IRON BINDING LIGANDS IN THE SOUTHERN OCEAN, WINTER, AND SPRING (SCALE CRUISE 2019)

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Abstract: The Southern Ocean acts as a motor for the global oceanic circulation with the downwelling of water masses and its influence on the climate. This ocean is known to be a High Nutrient Low Chlorophyll region with iron (Fe) limitation. Fe-organic speciation and distribution knowledge is necessary to understand the Fe biogeochemical cycle. This work presents the first study of Fe-organic speciation in the Atlantic sector of the Southern Ocean in winter and spring (SCALE cruises 2019), measuring the Fe-binding ligand concentration (L_{Fe}) and their characteristics via conditional stability constant ($K^{cond}_{Fe \cdot L}$) in the water column. The L_{Fe} were measured by competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV) method, using TAC as a competitive ligand. Different detection windows (5 and 10 μ M TAC) were used to determine the optimal experimental conditions for winter and spring samples, being 5 μ M TAC the most convenient for comparing all the samples. The L_{Fe} concentrations ranged from 0.74-2.42 nM in winter and 0.57-2.03 nM in spring, and $\log K^{cond}_{Fe \cdot L}$ varied between 9.44 and 11.38 in the same period. According to the $\log K^{cond}_{Fe \cdot L}$ most of the L_{Fe} are L_2 (weak ligands) in the entire region. The L_{Fe} maxima were found in the lower intermediate waters and were higher in winter compared to spring. The maximum L_{Fe} concentration was found across the Antarctic Circumpolar Current (ACC), near Bouvet Island. The enrichment in L_{Fe} during the transport of the water masses can be linked to important remineralization processes, sediment leaching, sea ice melting, the proximity to the Antarctica shelf or the island effect.

Key words: Iron, Fe-binding ligands, Complexation, Southern Ocean.

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ORAL COMMUNICATIONS ~ ECOTOXICOLOGY AND MARINE POLLUTION

COMPARATIVE STUDY PB, CD AND CU CONCENTRATIONS IN *SCYLIORHINUS CANICULA* (LINNAEUS, 1758) AND *MERLUCCIIUS* *MERLUCCIIUS* (LINNAEUS, 1758) FROM THE WESTERN MEDITERRANEAN FOR FUTURE XENOBIOTIC MONITORING

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Abstract: The small-spotted catshark, *Scyliorhinus canicula* is a demersal Scyliorhinid shark species commonly found in the Mediterranean and Northeastern Atlantic waters. The philopatric and sedentary nature of adult female individuals, along with its high abundance among bottom trawl bycatch, stock exploitation resilience, and widespread distribution, could support the species xenobiotic biomonitoring potential. Previous research concluded that *S. canicula* muscle tissue is capable of reflecting space-time persistent Pb, Cd, and Cu hotspots. To further explore its biomonitor potential, interspecific monitoring has been conducted between *S. canicula* and the commercially valued species *Merluccius merluccius*, both of which can be found coexisting within the same habitat. A total of 50 individuals of each species were collected, and data correlation was performed among the individuals captured within the same trawl. High significant interspecific correlation values were observed in Cd and Pb concentrations between both species (Spearman $r = 0.817$ and 0.833 respectively) as well as moderate positive correlation for Cu ($r = 0.633$). Higher Cd and Cu concentrations were generally observed in *S. canicula* however, Pb concentrations were higher in *M. merluccius*. Such differences were attributed to trophic and physiological interspecific differences. High correlation values between both species supports their utilization for interspecific monitoring, which could pose a significant advancement towards xenobiotic biomonitoring in marine foodstuffs.

Key words: Biomonitor, GFAAS, Heavy metals, Marine pollution, *Scyliorhinus canicula*, *Merluccius merluccius*

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PHYSIOLOGICAL RESPONSE OF *P. ELEGANS* TO ANTHROPOGENIC STRESSORS: SYNERGISTIC IMPACTS OF HEATWAVES AND UV FILTERS FROM SUNSCREENS

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Abstract: Heatwaves are prolonged periods of unusually high temperatures which have emerged as a significant environmental threat to marine organisms. Their intensification has raised concerns about the impacts on aquatic organisms and ecosystem dynamics. On the other hand, the rapid escalation of tourism particularly in tropical and subtropical regions and the greater awareness of photoaging and photodamage caused by solar UV radiation increased the use of sunscreens. However, UV filters found in sunscreen have recently been identified as emerging pollutants in coastal waters due to their accumulation in the marine environment. Exposure to these components has been proven toxic to many aquatic species, both invertebrates and vertebrates. UV filters are a cause of substantial levels of reactive oxygen species (ROS) and the liberation of inorganic micronutrients, interacting with coastal habitats.

This study analyses the effects of extreme weather temperatures with two different sunscreens. Two temperatures (20, and 32°C) and two different sunscreens (one labelled as eco-friendly and the other not) were tested in a full factorial experiment for 12 hours. Shrimps were sampled at 0, 6 and 12 hours of exposure. The combined effect of temperatures and sunscreens was tested at each sampling time on shrimps' muscle and hepatopancreas. Cellular stress biomarkers associated with oxidative stress (CCO – Cytochrome-C oxidase,

ETS – Electron transport system, GST – Glutathione-S-Transferase, SOD – Superoxide Dismutase and LPO – Lipid) were used as indicators of the shrimp's physiological response to the stressors. Incorporation and bioaccumulation of the UV filters along the exposure period will also be investigated using high-performance liquid chromatography, clarifying if such a short time is sufficient to observe significant effects on the organisms.

By elucidating these mechanisms, this study will clarify these organisms' physiological resilience and vulnerabilities, which are fundamental for understanding the impact of environmental changes on marine ecosystems.

Key words: Heatwaves, oxidative stress, UV sunscreens filters, biomarkers, environmental stressors, *P.elegans*

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THE UNPREDICTABLE RESPONSE OF *IN VIVO* AND *IN VITRO* BIOLOGICAL MODELS TO MIXTURES OF POLYCYCLIC AROMATIC HYDROCARBONS

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) are complex compounds commonly encountered in the environment, formed through the fusion of aromatic rings. Their limited solubility in water leads to environmental persistence, accumulation within organisms, and induction of adverse effects such as oxidative stress, inflammation, genotoxicity and cellular damage. The complexity inherent to their toxicology arises from their existence in environmental matrices as complex mixtures, presenting challenges for risk assessment. This study aims to understand the mode of action (MoA) of environmentally relevant PAH mixtures using several biological models including fish primary hepatocytes, zebrafish immortalized hepatocytes (ZFL), immortalized human hepatocytes (HepG2), and juvenile fish.

In vitro experiments involved exposing cells to three PAHs (Benzo[a]pyrene - B[a]P, Phenanthrene - Phe, and Benzo[b]fluoranthene - B[b]F) individually and in mixtures (1:1, 1:2, 2:1). Toxicological responses, encompassing metabolism-related genes expression and activity, as well as DNA damage, were evaluated after 24h and 48h at concentrations ranging from 5 to 100 μ M.

For the *in vivo* bioassay, *Sparus aurata* juveniles were exposed for 42 days to Phe and B[a]P individually and in mixtures (1:2, 2:1), followed by biochemical analyses related to oxidative stress and PAH detoxification pathways.

In vitro assays revealed that B[a]P upregulated CYP1A1, enhancing its activity and inducing genotoxic DNA damage. Mixtures of Phe and B[a]P showed elevated CYP1A1 mRNA levels and DNA damage. In the *in vivo* bioassay, it was observed that PAH mixtures exerted

diverse effects on antioxidant enzymes and CYP1A1 expression compared to individual compounds in adult *S. aurata*. Nonetheless, no significant increase in DNA damage or lipid peroxidation was noted.

This study underscores the unpredictable nature of PAH mixtures and highlights the underestimation of the associated risks. Thus, there is a pressing need to enhance environmental guidelines, as the potential synergistic or antagonistic effects of various PAH mixtures may be miscalculated.

Key words: PAHs, Mixtures, Metabolism, CYP1A, Biological Models

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EFFECTS OF UV-C EXPOSURE ON LARVAL PERFORMANCE: IMPLICATIONS FOR BALLAST WATER TREATMENTS AND INVASIVE SPECIES MANAGEMENT

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Abstract: Bioinvasions are the second major threat to world biodiversity, after habitat destruction [1]. On marine environment, ballast water (BW) from ships stands out as the most significant introduction vector of allocthonous species into other biogeographic regions [2]. Although not all these introductions are successful, some could cause important ecological, socio-economic and health impacts [3]. In this sense, the International Maritime Organization (IMO) established the International Convention for the Control and Management of BW and Sediments to restrict the spread of organisms via BW [4;5]. According to these regulations, ships must install BW Treatment Systems to comply with the D-2 standard, which sets limits on the concentration of viable organisms in BW.

Ultraviolet irradiation is the most common method used on vessels and most studies focus on bacteria or phytoplankton rather than zooplankton species [6;7], while recent reports indicate that various BW treatments are ineffective for organisms larger than $\geq 50\mu\text{m}$. Thereby, studies on larval ecology are crucial since larval survival is a critical factor for the successful establishment of exotic species [8], acting as a bottleneck for the overall adult population [9].

This study aims to test the effect of different UV-C exposure treatments (1, 3 and 5 minutes) on physiological traits of *Carcinus maenas* larvae, a native species in the Gulf of Cadiz. Longer UV-C time exposure resulted in a decrease of larval survival, movement and oxygen consumption, suggesting UV irradiation as an efficient BW treatment for larger organisms ($\geq 50\mu\text{m}$ fraction). This analysis aimed to compare these traits with larvae from other crustacean species, especially the invasive ones (generally more tolerant) [10], p.e. the American blue crab *Callinectes sapidus*. This outcome could make positive contributions to blue economy, ensuring an environmentally safe shipping trade reducing biological invasions, according to sustainability objectives and the EU Biodiversity Strategy for 2030.

Key words: invasive species, ballast water, larval ecology, management, UV-LED.

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OPTIMIZING (PHOTO)-FENTON FOR EFFLUENT DECONTAMINATION: SALINITY, pH & PHENOLIC LIGANDS

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Abstract: Fenton-based processes have shown remarkable effectiveness in decontaminating various waste effluents worldwide, including high salinity effluents from aquaculture or maritime industries. However, maintaining active iron during the process poses a significant challenge. This study focuses on six different Contaminants of Emerging Concern selected as a model mixture. Phenolic compounds that mimic those found in phytoplankton exudates, have been investigated as iron chelates to assist (photo)-Fenton processes (González et al. 2019). The presence of phenolics, especially those with -OH groups in the ortho-position, enhances ligand efficiency, correlating with their ability to reduce Fe(III) to Fe(II). Catechol proves effective in suppressing chloride interference, preventing the formation of FeCl_2^+ and improving treatment outcomes even in saline conditions (Vallés et al. 2023). Moreover, the complex composition of the effluent matrix, including anions and organic pollutants, significantly influences iron speciation. These insights underscore the importance of phenolic compounds in (photo)-Fenton processes for marine pollution remediation, highlighting their role in overcoming challenges posed by high salinity and enhancing treatment efficiency for sustainable marine environmental protection.

Key words: Marine pollution, Contaminants of Emerging Concern, Fenton, Phenolics

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STABLE ISOTOPE DETECTION OF THE INFLUENCE OF MARINE AQUACULTURE ON SUBMERGED NATURAL HERITAGE: THE CASE OF THE BOU-FERRER ROMAN SHIPWRECK OFF THE COAST OF LA VILA JOIOSA (ALICANTE, SPAIN)

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Abstract: The impact of aquaculture on the marine environment has been extensively studied. However, there are fewer studies that analyse the impact on cultural heritage. The Bou Ferrer is a Roman wreck from the 1st century AD, discovered in 1999 off the coast of La Vila Joiosa at a depth of 24 m (Alicante, Spain). This site has been legally protected by Spanish law as an Asset of Cultural Interest since 2014, and in 2017 UNESCO included it in its International Register of Good Practices in Underwater Archaeology. In 2023, the Directorate General for Culture and Heritage of the Generalitat Valenciana commissioned the University of Alicante to carry out a study on the Evaluation and analysis of the impact of the aquaculture facility in La Vila Joiosa on the archaeological site of the Bou Ferrer Wreck (Code C.P.I 23-CECE19-03-195-UT-O). The present study was carried out to determine the influence of the aquaculture activity of a facility located 800 meters from the site, based on the isotopic signal of Carbon ($\delta^{13}\text{C}$) and Nitrogen ($\delta^{15}\text{N}$), comparing different sampling methods on the 24 m isobath. Four sampling localities were determined: Bou Ferrer, a locality close to the facility (< 500 m) and two controls (> 1 km), to the north and south of the facility. Niskin bottles (particulate matter near the bottom), sedimentation traps (water and sediment matter near the bottom) and cores (bottom sediment) were used for sampling. The influence of aquaculture was detected mainly by changes in $\delta^{13}\text{C}$ in the sediment obtained with the sedimentation traps and in the sediment itself. Fish-farming aquaculture may have a significant impact on this Roman wreck.

Key words: fish farm, stable isotopes, impact, cultural heritage, Vila Joiosa.

POTENTIAL HAZARDS OF OCTINOXATE (ETHYLHEXYL METHOXYCINNAMATE) EXPOSURE IN THE SEAGRASS *POSIDONIA OCEANICA* (L.) DELILE: EXPERIMENTAL EVIDENCE

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Abstract: Interest has risen in recent years to assess the fate and impacts of organic ultraviolet (UV) filters in aquatic environments, after being recognized as contaminants of emerging concern. Octinoxate, also known as ethylhexyl methoxycinnamate (EHMC), is among the widely used UV filters in sunscreen formulations, and its potential toxicological effects in aquatic biota has led to precautionary actions in some jurisdictions, such as restricting and even banning its presence in commercial sunscreens. However, research data is lacking for effective regulation of sunscreen ingredients in Mediterranean countries. Our study evaluated the response of the seagrass *Posidonia oceanica* to EHMC under a short-term experimental setup, recreating summer conditions in aquaria subjected to different environmentally relevant concentrations for the Mediterranean Sea (minimum: 31 ng L⁻¹, intermediate: 710 ng L⁻¹ and maximum: 1420 ng L⁻¹) and a control (no addition). Negative responses were evidenced in the physiology of *P. oceanica* due to EHMC exposure, with decreased gross primary production rates, loss of leaf chlorophyll content and inhibition of the overall nitrogen fixation associated with the seagrass tissues. Elevated oxidative stress biomarkers in *P. oceanica* under EHMC addition (*i.e.*, catalase activity, polyphenols concentrations and alkaline phosphatase activity in leaves) reflect the activation of antioxidant defenses to counteract oxidative damages possibly induced in cellular components by the presence of the contaminant. Our results may conservatively imply the high ecological risk imposed to *P. oceanica* by maximum concentrations of EHMC in Mediterranean coastal waters. Moreover, they contribute as experimental evidence of the potentially detrimental effects of sunscreen pollution in a keystone species, such as *P. oceanica*, which is the main structural component of a priority habitat for conservation in the Mediterranean Sea, currently affected by multiple stress factors leading to its recession in recent years.

Key words: organic ultraviolet filters, contaminants, octinoxate, sunscreen pollution, seagrass.

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EVALUATION OF TBT CONTAMINATION BY PASSIVE SAMPLERS IN THE BIDASOA ESTUARY (BAY OF BISCAY - NORTHEAST SPAIN) IN THE CONTEXT OF THE WATER FRAMEWORK DIRECTIVE

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Abstract: Tributyltin (TBT) and its degradation products are persistent substances that at very low concentrations ($\text{ng}\cdot\text{L}^{-1}$) can produce toxic effects in a wide spectrum of organisms (Beyer et al. al., 2022), being considered one of the most toxic xenobiotics that have ever been introduced into the environment (Goldberg, 1986). In the European Union, its use in the coating of ships was prohibited two decades ago. However, despite this, and due to its persistence in the environment, some water bodies still fail to meet the good chemical status for TBT.

Since 2014, in the Bidasoa estuary, the Basque Water Agency (URA), in collaboration with AZTI, has carried out quarterly monitoring of TBT following the conventional method of spot sampling, using an oceanographic bottle, and subsequent analysis to evaluate the degree of compliance with environmental quality standards (EQS). However, on many occasions, TBT concentrations are lower than the quantification limits of the analytical techniques used, which represents a limitation for evaluating the chemical status of the water body. Due to these difficulties, the use of passive samplers, recognized by Directive 2013/39/EU as novel and complementary techniques for the evaluation of chemical status, was proposed as an alternative.

In this study, the chemcatcher passive sampler was selected to determine contamination by TBT and DBT in the Bidasoa estuarine waters. For this purpose, in 5 stations, passive sampling (chemcatchers) and spot sampling (using bottles) were simultaneously carried out, in the dry season (May-June 2022) and in the rainy season (November 2022). The results obtained through spot sampling show great variability, both spatially and seasonally, with TBT and DBT concentrations from values below the limit of quantification to values higher than the EQS-Annual Average ($0.2 \text{ ng}\cdot\text{L}^{-1}$), which makes it difficult to assess the chemical status. On the contrary, with chemcatchers, in all stations and periods it was possible to quantify and determine time-integrated concentrations of TBT and DBT, making it possible to estimate the chemical status and determine a pattern of contamination by TBT and DBT in the estuary, showing the advantages of these techniques over the conventional ones.

Key words: Tributyltin (TBT), Chemcatchers, Spot sampling, WFD

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ALTERATIONS IN THE MICROBIOME OF THE CLAM DIGESTIVE GLAND AFTER EXPOSURE TO DRUGS

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Abstract: Aquatic ecosystems cover more than two-thirds of our planet and are the ultimate sinks for pollutants. The consumption of pharmaceuticals compounds in the last years has increased notably, and, consequently, the occurrence of these compounds in the aquatic environment. Their presence may be of concern, because although lethal concentrations are not usually approached, sublethal effects have been reported at cellular and molecular levels, even affecting physiological functions. In this work, we have investigated the effect of two different pharmaceuticals which have been described as compounds of environmental concern: carbamazepine (CBZ) and sulfamethoxazole (SMZ). To do so, multispecies/microcosm aquatic experimental set-ups were used to expose to 1 µg/L of the chemicals, individually or mixed, for 10 days. Using *Scrobicularia plana* clams as bioindicator organism, the microbiome associated to their digestive gland was identified and analysed by 16S rRNA metagenomics. At the highest taxonomic level, the phyla with the highest number of identifications were Proteobacteria, Tenericutes and Bacteroidetes. The *Mycoplasmataceae*, *Ectothiorhodospiraceae* and *Flavobacteriaceae* families were substantially abundant in every condition. Exposure to SMZ resulted in a significant decrease in the families *Pseudonocardiaceae*, *Thioalkalispiraceae* and *Xanthomonadaceae* when compared to the control. Exposure to the mixture of drugs resulted in an increase of the *Clostridiaceae* and *Pseudonocardiaceae* families when compared to SMZ exposure. The alpha diversity was calculated using the Shannon-Wiener index, but no significant change was observed after exposure to any drug/mixture. The potential biological functions of the microbiome were analysed with the FAPROTAX algorithm. “Chemoheterotrophy”, “Aerobic chemoheterotrophy” and “Phototrophy” functions were highly represented in each

condition. However, no significant changes were observed in the functional pattern after any of the exposures. Our final goal is to assess changes in the structure and functionality of the microbiome upon pharmaceuticals exposure to use them as biomarkers of pollution

Key words: Bacteria, Carbamazepine, Metagenomics, Pharmaceuticals, *Scrobicularia plana*, Sulfamethoxazole

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IMPACT OF NATURAL UV RADIATION ON THE TOXICITY OF PLASTIC LEACHATES TO MARINE ZOOPLANKTON

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Abstract: The presence of plastic waste in marine environments poses significant ecological threats. Leachates from plastic materials can contribute to the chemical stress experienced by marine organisms (Gunaalan et al. 2020, Almeda et al. 2023). This study investigates the influence of natural ultraviolet (UV) radiation on the toxicity of leachates from various plastic materials to marine zooplankton, using the nauplius larvae of the copepod *Acartia tonsa* as a model species.

Leachates of different plastic materials (beach-collected plastics, bioplastics, and tire wearparticles) were exposed to natural sunlight for two or five days. Post-exposure leachates were then tested on *A. tonsa* larvae for 48 hours and the number of surviving nauplii was recorded at the end of the exposure period. Results revealed a notable decrease in toxicity in leachates subjected to UV exposure compared to those kept in dark conditions. The decrease in leachate toxicity after UV exposure varied depending on the plastic material. Nauplii survival increased, and Lowest Observed Effect Concentration (LOEC) and No Observed Effect Concentration (NOEC) consistently decreased across all tested plastic types after five days of exposure. However, after only two days of exposure, no significant difference was observed between UV-exposed leachates and those kept in dark conditions.

The reduction in toxicity is hypothesized to result from photodegradation processes facilitated by UV radiation, which alters the chemical properties of the leachates, reducing their harmful effects. Further chemical characterization is being conducted to understand the specific transformations occurring in the leachates.

This study highlights the importance of UV radiation in reducing the ecological risks of plastic pollution. By revealing a natural factor that reduces plastic toxicity, these findings contribute to a better understanding of marine pollution dynamics. This knowledge is crucial for predicting the environmental risks associated with plastic debris and for developing effective strategies to manage and remediate plastic pollution in marine environments.

Key words: Plastic Pollution, Leachates, Photodegradation, Zooplankton, Copepods

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VERTICAL DISTRIBUTION OF ORGANIC MICROPOLLUTANTS IN SEDIMENTS FROM EUROPEAN BAYS AND ESTUARIES

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Abstract: Contamination of marine ecosystems by organic micropollutants may lead to a significant risk for inhabitant species. In order to assess such contamination, we have monitored several European estuaries and bays during the oceanographic campaign carried out within the SEA-EU in 2022 on board R/V OCEANOGRAPH. Such research was conducted in 9 sampling sites along the Baltic Sea, North Sea and the Atlantic Ocean. Sediment cores were collected, divided in 1 cm sections and analysed by gas chromatography – tandem mass spectrometry (GC-MS/MS) using a multiresidue method that covers > 100 target contaminants: polycyclic aromatic hydrocarbons (PAHs), UV filters, fragrances, organophosphorus flame retardants (OPFRs), polybrominated diphenyl ethers (PBDEs), phthalates, pyrethroids, among others. The most prevalent target contaminants were PAHs (anthracene or phenanthrene), followed by traces of UV-filters (4-MBC or octocrylene) and fragrances (tonalide or galaxolide), revealing different contamination sources in our study area. Vertical profiles for contaminants differed depending on the sampling site and target compound, with surficial or sub-surficial concentration maxima in most cases. Our study covers a very wide area and shows new data on the occurrence and distribution of a very high number organic contaminants, some of them of emerging concern (e.g., fragrances and UV-filters), for which available information is still scarce.

Key words: PAHs, micropollutants, marine environments, gas-chromatography.

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FROM NECROPSIES TO CONSERVATION: INVESTIGATING MASS MORTALITY EVENTS IN ALCID SEABIRDS

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Abstract: The migration patterns of seabirds, including those in the Alcidae family, are influenced by climatic phenomena and resource availability. These factors can have a significant impact on their survival and breeding success [2]. Our study was conducted along the southern coast of Spain to investigate mass mortality events of Atlantic Puffins (*Fratercula arctica*) and Razorbills (*Alca torda*) during the winter of 2022-23. Stranded seabirds were necropsied, and samples of muscle and liver tissue were collected to assess their body and metabolic state. A total of 95 specimens were collected, with Razorbills being the most abundant species and with a higher percentage of juveniles (74.5 %), as has been observed in other seabird stranding events [1]. The results revealed no significant differences in body condition between the two species, but metabolic analysis on both species indicated low carbohydrate levels and elevated lactate in muscle tissues, suggesting potential exhaustion or hypoglycaemia [3]. In this study, we also proposed a standardised body condition index based on biometric measurements and tissue analysis, offering a comprehensive approach to understanding the body condition at death of these unique species. Comparison with global data has highlighted similar mortality events in other regions, emphasizing the need for standardized protocols to assess possible causes of death through seabird necropsies. These findings underscore the importance of understanding the factors affecting seabird mortality to contribute on the implementation of conservation measures to protect these vulnerable species.

Key words: Seabird mortality, Mass stranding events, Physiological assessment

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ORAL COMMUNICATIONS ~ GLOBAL CHANGE

pH AND CO₂ COASTAL MONITORING IN THE CANARY ISLANDS

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Abstract: Carbon dioxide (CO₂) transferred from the atmosphere to the ocean is causing the ocean acidification. This monitoring initiative, in the Gando Bay, focuses on multiple variables within the CO₂ system, such as CO₂ fugacity ($f\text{CO}_2$), pH (in total scale, pH_T), total inorganic carbon (C_T), and other hydrographic variables including sea surface salinity (SSS), sea surface temperature (SST), wind intensity and direction. In addition, the CO₂ flux (FCO_2) between the surface waters and the atmosphere was computed. The lowest SST values were recorded in March, with a range of 18.8-19.3°C, while the highest SST were observed in September and October (24.5-24.8°C). SST exhibited an annual increase with a rate of 0.007°C yr⁻¹. Warmer months increased SSS, while colder periods, influenced by extreme events like tropical storms, led to lower salinity (SSS=34.02). The predominant Trade Winds facilitated the arrival of deeper water, replenishing seawater. Atmospheric $f\text{CO}_2$ averaged 415±4 µatm (2020-2023) while surface water $f\text{CO}_{2\text{sw}}$ presented variability, with the highest values recorded in September and October, peaking at 437 µatm in September 2021. The lowest values for $f\text{CO}_{2\text{sw}}$ were found in February 2021 (368 µatm). From 2020 to 2023, surface water $f\text{CO}_{2\text{sw}}$ values displayed an increasing rate of 1.9 µatm yr⁻¹ in the study area. The assessment of $f\text{CO}_{2\text{sw}}$ decomposition into thermal and non-thermal processes revealed the importance of SST on the $f\text{CO}_{2\text{sw}}$. Our findings highlight the influence of physical factors such as tides, and wind effect to horizontal mixing in these areas. The C_T showed a mean concentration of 2113±8 µmol kg⁻¹ and pH at *in-situ* temperature ($\text{pH}_{\text{T,IS}}$) has a mean value of 8.05±0.02. The mean FCO_2 from 2020 to 2023 was 0.34±0.04 mmol m⁻² d⁻¹ (126±13 mmol m⁻² yr⁻¹) acting as a slight CO₂ source. Extrapolating to the 6 km² of Gando Bay, the region sourced 33±4 Tons of CO₂ yr⁻¹.

Key words: CO₂ observations, coastal waters, times-series, Canary Islands, acidification

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SEASONAL VARIABILITY OF GREENHOUSE GASES (CO₂, CH₄ AND N₂O) AT THE EDGES OF RIA FORMOSA COSTAL LAGOON, SOUTH PORTUGAL

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Abstract: Coastal lagoons are highly productive ecosystems affected by anthropogenic pressures and climate change. The coastal lagoon Ria Formosa (southern Portugal) has been studied in terms of greenhouse gases (pCO₂, N₂O and CH₄), particularly at its western and eastern edges, where water quality has been found to be more variable. These parameters help to understand the environmental dynamics and the response of this ecosystem as a source or sink of greenhouse gases. The seasonal variability of partial pressure of CO₂ (pCO₂) and concentrations of dissolved methane (CH₄) and nitrous oxide (N₂O) were assessed over complete tidal cycles with 24 h sampling at the two edges of Ria Formosa (Site 1 and Site 2). pCO₂ was calculated from total alkalinity (TA) and pH, while N₂O and CH₄ were measured by gas chromatography. Site 1 had the highest values of both pCO₂ and N₂O, while site 2 had the highest concentrations of CH₄. However, globally, the variability of greenhouse gases was higher at site 2 than at site 1. Daily variations were observed to be in antiphase with the tidal cycles at both stations, with highest concentrations during ebb to low tide, suggesting that the coastal lagoon exports CO₂, CH₄ and N₂O to the adjacent coastal ocean. Changes in greenhouse gas concentrations were influenced by various environmental factors (e.g. salinity, temperature, gas reactivity, exchanges with the atmosphere) as well as biological processes (photosynthesis and respiration), which apparently are different at the two sites. Positive fluxes of pCO₂ and CH₄ indicate that the study areas acted as a source of these gases to the atmosphere. However, the fluxes of N₂O were negative, except during the summer campaign, indicating that the water was a sink for this greenhouse gas.

Key words: Greenhouse Gases, Coastal Lagoon, Ria Formosa

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IMPACT OF OCEAN WARMING AND ACIDIFICATION ON THE STATOLITHS OF THE MEDITERRANEAN JELLYFISH *RHIZOSTOMA PULMO*

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Abstract: Ocean acidification, along with rising water temperature, are both processes whose occurrence has increased alarmingly in recent decades, threatening the biogeochemistry of marine ecosystems (Flecha *et al.*, 2019). The gradual diminution of pH in the water column due to ocean acidification results on a lower stability of certain solid structures, affecting both directly and indirectly organisms that make use of them (Doney *et al.*, 2009; Billé *et al.*, 2013). Here we analyze the effects of both individual and combined increases of acidification and temperature on the statoliths of newly released ephyrae of the Mediterranean Jellyfish *Rhizostoma pulmo* Macri (1778). These structures, composed of calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), are used for equilibrium and are essential for the correct development and adaptation of the organisms to the marine environment, so their malformation could mean a decrease in their survival capacity and also could end up impacting negatively the planktonic food webs. In this work, six combinations of temperature and pCO_2 (18°C, 24°C and 30°C with a pCO_2 of 500 ppm and 1000 ppm each), according to the projections of the SSP5-8.5 (IPCC, 2021) scenario for the year 2100, were applied during 32 days to different groups of polyps. Statoliths of the ephyrae released during this period were counted and measured by inverted optical microscopy and SEM, as composition analyses were performed via EDX. Our results suggest the variation of both variables influence on the size of the structures but not their composition, where the increment of temperature causes the synthesis of bigger statoliths, while the increment of pCO_2 is responsible for the production of smaller structures. The way in which the development of different sized statoliths under warming and acidification conditions affect the equilibrioception and adaptation capacity of *R. pulmo*, as well as how it may impact the ecosystem of a warmer and more acidic Mediterranean is currently under study.

Key words: Jellyfish, Ephyra, Statolith, Acidification, Ocean warming

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ORAL COMMUNICATIONS ~ TRACERS IN OCEANOGRAPHY

GEOCHEMICAL TRACERS OF MEDITERRANEAN OUTFLOW WATERS: ND ISOTOPES, CARBON CYCLE AND NEW EXPORT CONSTRAINTS

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Abstract: The North Atlantic Ocean plays a critical role in the global circulation system, regulating the penetration of surface waters into the deep ocean, but also in key ocean biochemical cycles (e.g. carbon, oxygen, nutrients). Meridional heat and salt transport (i.e. buoyancy) drive the formation of different water masses and their circulation pathways. A relatively unknown but important element controlling the net meridional export of heat, salt and other chemical species into the North Atlantic is the Mediterranean Outflow Water (MOW): the salt injector. In this work, we present the first high resolution systematic study of traditional (T, S, Nutrients) and novel (Nd isotopes, alkalinity, pH) geochemical parameters of MOW waters from its source area at the Strait of Gibraltar up to the northern Iberian margin (Cantabric Sea). During the TRANSMOW cruise in 2021, over 500 seawater samples were collected along the main MOW pathway following its northward flow. A comprehensive suite of geochemical parameters including ϵ_{Nd} , alkalinity, pH and preformed nutrients were analyzed for these samples. We show that MOW can be 'traced' unequivocally using ϵ_{Nd} as a conservative tracer, a feature that opens a new set of possibilities to better estimate the contribution of MOW export to higher latitudes in the North Atlantic Ocean. Other parameters directly linked to the carbon cycle (alkalinity, pH) are also controlling the distinctive chemical properties of the MOW. One of the key advantages of these geochemical tracers is that they allow to better quantify export and mixing rates of MOW with North Atlantic waters. Using statistical tools such as a newly developed Monte Carlo Optimum Multi-Parameter Analysis (MC-OMPA) on an array of conservative tracers we have quantified mixing rates and exports between different water masses. These results will be fundamental to better constrain paleoreconstructions in the sedimentary record.

Key words: MOW, Nd isotopes, Carbon Cycle, geochemical tracers, OMPA

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THE IMPRINT OF ANTHROPOGENIC CLIMATE CHANGE IN THE SW IBERIAN UPWELLING SYSTEM: A WARMER, MORE ACIDIC AND LESS OXYGENATED OCEAN

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Abstract: The imprint of anthropogenic climate change on the ocean is unequivocal. Warming, ocean acidification, and deoxygenation stand out as the main biogeochemical stressors at global scale. At regional scale, Eastern Boundary Upwelling Systems are hotspots of climate change, threatening their valuable ecosystem services. Currently, predictions of how and when anthropogenic changes will emerge in coastal upwelling systems in response to biogeochemical stressors are uncertain. Furthermore, the potential widespread of biogeochemical compound events, that is, several extreme events co-occurring simultaneously (Gruber et al., 2021) is still unknown.

In this study, we assessed the changes in biogeochemical stressors in the Southwest Iberian coastal upwelling system in the last three decades with recent high-quality observations (1989-2022) from the interior ocean. Here, we show with two independent methodologies, a biogeochemical back-calculation anthropogenic carbon method (ϕCT°) and an analysis of carbon isotope values for the dissolved inorganic carbon ($\delta^{13}\text{C-DIC}$), that the surface-intensified anthropogenic imprint already reached two-thousand meters depth. Warming, acidification, and deoxygenation align closely with this burden of anthropogenic imprint, pushing ocean tracers out of their preindustrial local variability. These new observations confirm that in September 2022 there was a biogeochemical extreme and compound event in the surface waters of the Southwest Iberian coastal upwelling system: a marine heatwave,

an ocean acidity extreme and a low-oxygen extreme occurring together. Furthermore, at intermediate depths, the layer of Eastern North Atlantic Central Water (around 100-500 m depth) shows a significant decrease in pH ($\sim -2 \times 10^{-3}$ pH units yr^{-1}) and dissolved oxygen ($\sim -0.3 \mu\text{mol kg}^{-1}\text{yr}^{-1}$) even when is actually colder and fresher than it was in 1989.

Key words: ocean acidification, ocean deoxygenation, coastal upwelling system, biogeochemical extreme events

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POSTER COMMUNICATIONS



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POSTER COMMUNICATIONS ~ BIOGEOCHEMICAL PROCESSES

MULTI-COAST: MULTIPARAMETRIC STUDY OF THE CO₂ CHEMISTRY IN COASTAL WATERS

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Abstract: Coastal systems host a large amount of biodiversity, play a fundamental role in socio-economic development, and are highly affected by human activities. In addition, coastal zones connect terrestrial and oceanic systems being the interface where many chemical reactions and processes occur and are directly related to the carbon cycle. However, the coastal environment is very complicated to study due to the number of processes involved. In fact, the coastal contribution to the global carbon budget has been historically neglected even in such important reports such as the Intergovernmental Panel on Climate Change (IPCC). Accordingly, the Multi-Coast project is focused, for the first time, on a multidisciplinary analysis that involves the quantification of CO₂ transfer from coastal surface waters to sediments in three different areas: seagrass beds, algal covers and sandy zones. This work presents the overview of the preliminary results in terms of monthly measurements of sea surface temperature (SST), sea surface salinity (SSS), partial pressure of CO₂ (pCO₂), pH, total alkalinity (A_T), total inorganic carbon (C_T) and dissolved oxygen (DO). In addition, the % of CHN, metals in sediments, total dissolved metals in seawater and Fe-binding ligands have also been measured.

Accordingly, the results of this project try to identify a multiparametric relationship between CO₂ observations, hydrographic measurements and metal concentrations to be able to quantify the inventory of carbon sinks in coastal waters. The results of this project will be a decision-making tool for regional and national agencies to conserve those ecosystems where there is greater CO₂ capture.

Keywords: CO₂ observations, coastal waters, blue carbon, Canary Islands, trace metals

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ENHANCED GREENHOUSE GAS PRODUCTION BY DISSOLVED ORGANIC MATTER IN THE GUADALQUIVIR ESTUARY

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Abstract: Estuarine systems are characterized by receiving large amounts of organic matter, which can enhance the production of greenhouse gases (GHG) such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). Therefore, a study is conducted to relate the composition of dissolved organic matter (DOM) to these GHG based on various samplings carried out between 2018 and 2022 in the Guadalquivir Estuary. Excess values of CO₂ (Δ CO₂), CH₄ (Δ CH₄), and N₂O (Δ N₂O) are calculated as the differences between the dissolved gas concentration and the expected equilibrium concentration in the water column. This approach removes the effects of temperature and salinity on the GHG distribution. In all cases, there is an increase towards the interior, with values ranging from 1.6 to 101.5 μ mol L⁻¹ for Δ CO₂, -2.5 to 368.7 nmol L⁻¹ for Δ CH₄, and -3.0 to 91.4 nmol L⁻¹ for Δ N₂O. Of the six PARAFAC components identified in this study, four are humic-like components of terrestrial or microbial origin and two are protein-like components, corresponding to tryptophan and tyrosine. The humic-like components account for 85.8 $\pm$ 5.8% of the FDOM, while the protein-like components account for 14.2 $\pm$ 5.9%. Using multiple linear models, significant links are found between the GHG and the DOM composition. The Δ CO₂ is related to humic compounds and aromaticity, indicating that CO₂ is influenced by terrestrial inputs. Δ CH₄ shows relationships with the humic fraction associated with photodegradation and the protein-like fraction. Finally, Δ N₂O appears to be explained only by the humic components and the Apparent Oxygen Utilization (AOU), suggesting that lateral inputs of DOM and high nitrate concentrations promote N₂O production in the Guadalquivir Estuary.

Key words: Carbon dioxide, Methane, Nitrous oxide, Dissolved organic matter.

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SIMULTANEOUS VOLTAMMETRIC ANALYSIS OF PALLADIUM AND NICKEL USING SIGNAL TRANSFORMATION

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Abstract: Palladium (Pd) is a technology-critical element that even used at trace levels raises environmental concern. In aquatic media, its concentrations can range from 0.04 ng/L to 3.2 µg/L, with wastewaters containing the highest concentrations. Nickel (Ni) is a priority pollutant with concentrations reaching up to 16 µg/L in wastewaters. Also, Ni is the main interferent in Pd determination using voltammetry, a cost-effective technique for metal analysis.

In this work, we investigated the determination of Pd while monitoring Ni simultaneously by cathodic stripping voltammetry, which can be achieved in an optimal pH, taking advantage of the formation of complexes with dimethylglyoxime (DMG) by modulating its concentration. To improve the sensitivity of the determination, square wave voltammetry with the second derivative signal transformation was used. The experimental conditions were optimized in terms of electrolyte composition, frequency (Hz), deposition time (t_d) and deposition potential (E_d). After setting Pd and Ni concentrations at 1.5 and 10 µg/L, respectively, a decrease of pH (in the range 5.0 – 3.4) resulted in a lower Ni signal without affecting Pd signal, while an increase in DMG concentration improved Ni sensitivity without affecting Pd signal. Thus, it was possible to control Ni interference on Pd signal by modulating the DMG concentration. Additionally, the best separation of Pd and Ni voltammetric signals was attained with a frequency of 30 Hz keeping the E_d at -0.2V. A linear increase in both signals with the t_d was noted. For $t_d = 180$ s, and in the working range up to 0.25 and 1.5 µg/L for Pd and Ni, respectively, the limit of detection for Pd was 0.02 µg/L and for Ni was 0.20 µg/L. The improved method was tested for interferences from other metal ions, and applied to different environmental matrices.

Key words: Palladium, Nickel, Square Wave Voltammetry, Second Derivative

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DISTRIBUTION, SOURCES AND FLUXES OF DISSOLVED ORGANIC MATTER IN SEDIMENTS OF THE GUADALQUIVIR ESTUARY (SW IBERIAN PENINSULA)

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Abstract: The Guadalquivir Estuary, is located in the SW of the Iberian Peninsula. In this estuary there is an exchange between the Atlantic and fluvial water masses. This region is characterized by a high anthropogenic pressure.

Sediment samples up to 30 cm depth taken with meso-boxcorer during 3 oceanographic cruise onboard R/V UCADIZ. Sediment samples were collected at 5 stations along the estuary. The objective of this research, is the characterisation of DOM by studying of its optical properties and its different fractions as well as an estimation of the diffusive flux of dissolved organic carbon (DOC) in the estuary.

To obtain quantitative and qualitative information about DOM their optical properties (absorbance and fluorescence) were characterised. PARAFAC analysis validated six fluorescent components, four humic-like or allochthonous (C1, C2, C4 and C5) and two protein-like or autochthonous (C3 and C6) The composition of DOM in the estuary is predominantly allochthonous, with humic components accounting for 64 ± 17 % of the fluorescent DOM (FDOM), while protein components, associated with autochthonous processes, account for 36 ± 17 % of the FDOM. Two indexes were further derived from the EEMs (Excitation-Emission matrixes): the humification index (HIX), with homogeneous high values average of 0.82 ± 0.06 , and the index of recent autochthonous contribution (BIX), with average values of 0.60 ± 0.03 . Calculated diffusive fluxes of DOC indicate positive values towards the water column with a wide range from 2.1 to 23.5 (mmol/ m²d) along the estuary.

Key words: dissolved organic carbon, sediment, estuary, optical properties.

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COUPLING GLOBAL OCEAN DEOXYGENATION AND ACIDIFICATION TROUGH MACHINE LEARNING PRODUCTS

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Abstract: Climate change is altering ocean chemistry, posing serious threats to marine ecosystems through warming, ocean deoxygenation and acidification. These alterations, driven by heat uptake, changing ocean dynamics and anthropogenic carbon dioxide uptake, require sustained, long-term monitoring efforts for proper detection and attribution, that sometimes are not available. Machine learning spatio-temporal resolved fields are a promising alternative.

Here, we analysed the GOBAI-O2 dataset, a 0-2000 m water depth monthly time series (2004 - 2022) of temperature, salinity and dissolved oxygen (DO) in the global ocean (Sharp et al., 2022). From that, we estimated inorganic carbon and nutrients with CANYON-B (Bittig et al., 2018) and, for the Atlantic Ocean, the anthropogenic carbon content with the biogeochemical back-calculation ϕCT° method (Vázquez-Rodríguez et al., 2009). Following best practices for assessing trends of ocean acidification time series, we removed seasonal variability and fitted a linear model over the detrended data (Sutton et al., 2022) to investigate deoxygenation and acidification trends.

Our analysis indicates a statistically significant decline in dissolved oxygen content in the subtropical North Atlantic ($-0.6 \mu\text{mol.kg}^{-1}.\text{year}^{-1}$) and Northeast Pacific ($-1.0 \mu\text{mol.kg}^{-1}.\text{year}^{-1}$) between 100m and 500m depth. In the North Atlantic, comparisons between our inorganic carbon trends with trends based exclusively on observations validated our approach. In the subtropical North Atlantic there are some of the largest total carbon rates of increase. We also analysed the relationship between DO and total carbon trends in the Eastern North Atlantic Central Water layer, revealing differences in carbon dynamics relative to oxygen consumption between high and low latitudes.

Our case study presents a systematic procedure for detecting deoxygenation and acidification patterns in areas with limited time series, and analyse the relationship between total carbon and oxygen content change, offering valuable insights for understanding the full scope of the ocean's biogeochemical state trough machine learning products.

Key words: ocean deoxygenation, ocean acidification, machine learning, ocean chemistry, carbon

cycle

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DIAGENESIS OF ORGANIC MATTER IN THE ESTUARY OF THE GUADALQUIVIR RIVER

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Abstract: Three campaigns were conducted in the Guadalquivir River estuary (September 2021, February, and June 2022), collecting sediment cores at 3/5 stations to study the diagenesis of organic matter and its effect on the diffusive fluxes at the sediment-water interface.

The sediment is fundamentally anoxic, with only the stations near the estuary mouth showing positive Eh values at the surface. The organic carbon content is high at the internal stations (up to 90% of total carbon), decreasing towards the marine stations. The concentrations of dissolved organic carbon and nitrogen in pore water are high (DOC > 6000 μM ; DON > 400 μM), often surpassing those of dissolved inorganic carbon and nitrogen.

The diffusive fluxes of DIC (0.25-6.51 $\text{mmol}\cdot\text{m}^{-2}\text{d}^{-1}$) are highest at the innermost station, decreasing towards the mouth. For NH_4^+ , the fluxes range between 0.13 and 1.17 $\text{mmol}\cdot\text{m}^{-2}\text{d}^{-1}$, with no clear longitudinal or seasonal variations. High NO_3^- concentrations in the water column result in negative diffusive fluxes (-0.975 to 0 $\text{mmol}\cdot\text{m}^{-2}\text{d}^{-1}$), indicating the importance of denitrification in organic matter diagenesis, more intense at the inner stations. The diffusive fluxes of Si (0.014-0.187 $\text{mmol}\cdot\text{m}^{-2}\text{d}^{-1}$) and HPO_4^{2-} (0.00021-0.00543 $\text{mmol}\cdot\text{m}^{-2}\text{d}^{-1}$) show higher at the more internal stations and during summer samplings compared to winter.

The low concentrations of sulfate and sulfide in the pore water suggest that aerobic oxidation, denitrification, and methanogenesis are the main mechanisms of organic matter diagenesis in the Guadalquivir estuary sediment. Generally, no clear seasonal variation is observed. The amount and type of organic matter received by the sediment and the characteristics of the water column seem to be the variables most influencing the estimated diffusive fluxes in this system.

Key words: organic matter diagenesis, Guadalquivir estuary

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UPTAKE OF ATMOSPHERIC CO₂ DURING DEEP-WATER FORMATION IN THE NORTHWESTERN MEDITERRANEAN SEA

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Abstract: The ocean's absorption of carbon dioxide (CO₂) from the atmosphere takes up around 25% of anthropogenic CO₂ emissions. In particular, regions where open ocean deep convection takes place provide large sequestration of anthropogenic CO₂ in the deep ocean. However, the Gulf of Lion in the Mediterranean Sea, where the winter formation of the Western Mediterranean Deep Water (WMDW) takes place, has been insufficiently evaluated due to the scarce measurements taken of its carbonate system. The FAMOSO project (FAte of the northwestern Mediterranean Open sea Spring bLOom) gathered biogeochemical information from underway pCO₂ measurements, vertical profiles and satellite observations in the Northwestern Mediterranean Sea from the ending of a deep-convection event (8th March 2009) to a restratification phase (23rd March 2009). The surface waters in the inner Gulf of Lion reached mean CO₂ undersaturation values of 54±10 µatm. The mean CO₂ uptake of the shelf and ocean waters during this period was -3±3 mmol m⁻² d⁻¹ and -10±5 mmol m⁻² d⁻¹, respectively. In the first half of March 2009 a large extension of homogeneous dense waters recently ventilated filled the water column of the Gulf of Lion from surface to bottom. The intense penetration of atmospheric CO₂ during these ventilation events is coincident with winter deep convection events that could foster ongoing ocean acidification.

Key words: air-sea CO₂ flux, winter deep convection, Western Mediterranean Deep Water

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POSTER COMMUNICATIONS ~ CHEMICAL OCEANOGRAPHY

BASELINE STUDY OF SULFUR LEVELS IN THE COASTAL ZONE OF THE BAHÍA BLANCA ESTUARY (ARGENTINA)

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Abstract: Estuaries are among the world's most productive zones. The sulfur cycle is crucial in the ocean, serving as an important reservoir of SO_4^{2-} and minerals such as pyrite (FeS_2). Under oxygenated conditions, SO_4^{2-} is the most stable form, while anoxic conditions lead to high concentrations of inorganic sulfur forms in sediments and bottom waters, affecting to entire water column. The aim of this study was to evaluate the inorganic sulfur levels and its relationship with the physical-chemical parameters in the seawater from the Bahía Blanca estuary, Argentina. Surface water samples were collected at the end of winter and early spring (August-November) during 2022 and 2023 in five sampling sites along the estuary: Brown (B), Ingeniero White (IW), Villa del Mar (VM), Puerto Rosales (PR) and Punta Ancla (PA). The concentration of sulfides (S^{2-}), sulfates (SO_4^{2-}), dissolved oxygen (DO), chlorophyll *a* (Chl*a*), phaeopigments (Phaeo), turbidity, pH, and temperature were determined. Results showed significant differences between months for SO_4^{2-} ($p < 0.01$) and DO ($p < 0.001$), between years for DO, Chl*a* and Phaeo, and between sites for S^{2-} (all with $p < 0.001$). In both years, positive correlations between temperature and SO_4^{2-} , turbidity and S^{2-} , and negative correlations between DO and temperature were detected. Chl*a* levels (7.29 ± 5.84 and 1.35 ± 1.09 , $\mu\text{g L}^{-1}$), pH (8.44 ± 0.67 and 8.03 ± 0.18), and DO (9.65 ± 1.17 and 8.30 ± 0.84 , mg L^{-1}) were significantly higher in 2022 than 2023. SO_4^{2-} monthly variations were registered, peaking during warmer months (3029.95 ± 294.09 mg L^{-1} , November). S^{2-} mean concentration was 2.83 ± 4.48 μM and 2.35 ± 3.77 μM for 2022 and 2023, respectively. The positive correlation between turbidity and S^{2-} could indicate that the suspended particulate matter contributes this species to the water column. A decreasing trend in DO levels was detected.

Key words: sulfide, sulfate, seawater, dissolved oxygen, Bahía Blanca estuary

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PRIORITY METAL CONCENTRATIONS IN TRANSITIONAL AND COASTAL WATERS BY CONCURRENT SPOT WATER SAMPLING AND PASSIVE SAMPLERS (DGT)

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Abstract: The MONITOOL project was conceived to provide a robust database for total dissolved and labile metal concentrations in transitional and coastal waters supported on concurrent spot water sampling and Diffusive Gradients in Thin films (DGT) deployments. Thus the chemical forms of the priority metals Ni, Cd and Pb, regulated by Environmental Quality Standards (EQS) under the Water Framework Directive (WFD), were determined by different methodologies across a broad geographical area. In total, 712 spot water samples were collected, and 238 DGT devices concurrently deployed and retrieved. Then, were analyzed the relationships between metal concentrations in DGT (*i.e.*, DGT-labile concentration) and i) Pb and Cd conditional labile fractions determined in discrete water samples by Anodic Stripping Voltammetry (ASV); ii) total dissolved Ni in discrete water samples by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and also measured by Cathodic Stripping Voltammetry (CSV). As to the labile fractions, ASV and DGT were well suited for the simultaneous determination of Cd and Pb dynamic speciation in the marine environment. Similar labilities were measured for Cd, while for Pb, the ASV labile fraction was lower than the one determined by DGT. As to Ni, results confirmed that both ICP-MS and CSV are suitable for determining Ni dissolved concentrations through proper control of precision and accuracy of the analytical procedures. Despite the high variability, priority metal dissolved concentrations across locations remained below the EQS values.

Key words: Priority metals, Passive and spot sampling, DGT, Voltammetry, ICP-MS

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AIR SEA CO₂ EXCHANGE IN THE ALGARVE SHELF IS UNDERESTIMATED IN CURRENT COASTAL CO₂ FLUX ASSESMENTS

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Abstract: The ocean can be a source or a sink for carbon dioxide (CO₂). Whether it acts as a source or sink depends on a variety of hydrographic variables: from water temperature and salinity (which vary CO₂ solubility) to biological uptake of CO₂ or mixing of water masses. Robust assessment of air-sea CO₂ fluxes in space and time is a key knowledge for global and regional carbon budgets. This is relevant as inform-based decisions to mitigate climate change require well constrained carbon budgets.

The air-sea flux of CO₂ (FCO₂) from the west coast of the Iberian Peninsula (42.5-37.3°N, 12.5-7.5°W) was quantified using the partial pressure of carbon dioxide in surface seawater (pCO₂^{sw}), which was obtained during the EUROFLEETS+ SINES cruise (9th-21st September 2022). The data have been compared with previous data from the Surface Ocean CO₂ Atlas (SOCAT, Bakker et al., 2023) and the latest global coastal ocean pCO₂ product (Roobaert et al., 2023). In general, the ocean acted as a moderate source of CO₂ during the study days, with the exception of the Algarve shelf region (36.7-37.3°N, 9.0-7.5°W), where conditions of low temperatures (<19°C) and salinities (<36) where concurrent with large wind speeds and a strong CO₂ uptake. The occurrence of short-lived event of high wind speed in the area, in conjunction with a low pCO₂ in surface seawater, led to an increase in the sink intensity, resulting in mean FCO₂ values of -3.97 molC m⁻² yr⁻¹.

These findings were unseen in the previous measurements available in SOCAT and in the monthly climatology for coastal sea surface pCO₂ conditions likely due to sparse spatial and temporal observations. The September sink of CO₂ could be higher than previously thought. This serves to highlight the necessity for further data to be collected on the area in question, as well as for in situ samples to be analysed.

Key words: air-sea CO₂ fluxes, Algarve shelf region, partial pressure of CO₂ in sea surface.

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CONTRIBUTION OF ORGANIC MATTER TO TOTAL ALKALINITY IN THE ESTUARY OF THE BARBATE RIVER AND IN THE RÍO SAN PEDRO CREEK (SW SPAIN)

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Abstract: This work addresses the influence of organic matter on the inorganic carbon cycle when it is established on the basis of total alkalinity (TA) and pH measurements. The work has been carried out in two coastal systems in the south of the Iberian Peninsula, the Barbate estuary and the Río San Pedro tidal channel in winter and late spring situations. To quantify the contribution of organic matter to TA (Aorg), two consecutive potentiometric titrations were performed on the same sample. The first one allows the calculation of AT by means of Gran functions, and once finished, it is bubbled intensely with N₂ to eliminate the CO₂ produced. Subsequently, the pH is increased by addition of a NaOH solution to the initial values of the sample, and then titrated again with HCl to see the contribution to TA of all the acid-base equilibria present (phosphate, ammonium, silicate, borate, fluoride, sulfate and organic bases) once the dissolved inorganic carbon has been eliminated.

In general, TA values and concentrations of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) increase towards the interior of both systems. However, the results obtained show a clear difference between winter and spring sampling. In this respect, the contribution of organic bases remains relatively constant, with mean values of 65.8 ± 6.1 $\mu\text{mol/kg}$ in the Barbate River and 65.1 ± 1.9 $\mu\text{mol/kg}$ in the San Pedro River. In summer, a considerable increase in DOC is observed, as well as a greater contribution of organic matter to TA values, which can reach maximum values of up to 800 $\mu\text{mol/kg}$ in Barbate river and 450 $\mu\text{mol/kg}$ in Río San Pedro.

The correction of TA values considering the contribution of organic compounds (Aorg) is important to avoid an overestimation of CO₂ fluxes through the atmosphere - ocean interface.

Key words: Organic alkalinity, DOC, estuarine system, SW Iberian Peninsula.

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POSTER COMMUNICATIONS ~ ECOTOXICOLOGY AND MARINE POLLUTION

IMPACTS OF AGRICULTURAL PLASTIC WASTE IN PORTUGAL - CONTRIBUTION TO THE AGRI-PLAST PROJECT

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Abstract: Plastics are one of the environmental problems (OECD, 2022), and a recent FAO report (2021) points out that the amount of plastic waste in soil is higher than in the sea, with implications for the entire food chain, and recommends urgent implementation of measures for its reduction and better management. Since the 1970s, the use of plastics in agriculture has increased.

The massive use of agricultural plastic waste (APW) and its mismanagement is causing environmental impacts; large amounts of APW are lost to the soil, which eventually fragments, producing micro- and nanoplastics that persist for long periods in the environment, contaminating soil, water and plants, and affecting agricultural yields (Boots et al. 2019, Gao et al., 2019).

Portugal lacks an integrated solution for managing APW and has limited knowledge about the actual extent of the agricultural plastics value chain, its impacts, and potential management solutions. Mulch film waste stands out as a significant type of agricultural plastic by weight. A growing concern revolves around the generation and fate of microplastics from agricultural plastic materials, which can infiltrate various trophic levels, potentially endangering human health (FAO, 2021).

The Agri-Plast Project involves a consortium of 14 entities, which aims to develop organizational and economic solutions tailored to the different sectors that extensively use plastic films in their farming practices, and comprises five tasks: diagnosing the APW issue, capacity building and stakeholder engagement, experimentation for innovation and demonstration, organizational models for APW management, and post-project governance and policies. The first task has already initiated with the sampling campaign and the macro and microplastics analyses in the soil samples of the six partner entities with cultivated fields, which will contribute to the knowledge of the magnitude of the pollution associated with APW.

Key words: Agricultural plastic waste, Macro and Microplastic in soil, Production organization,

Innovation.

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TOXICITY OF THIRTEEN ELEMENTS PRESENT IN TECHNOLOGICAL WASTE RESIDUES ON THREE MARINE MICROALGAE SPECIES

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Abstract: The occurrence and levels of elements from technological wastes have increased in aquatic media, as a consequence of the rapid evolution of those technologies (Pibul et al., 2023). Although hazard and risk associated to some of those elements (such as Cu, Cd or Zn) have been studied for years and are well-established, the consequences of increased concentrations of other components (such as Lanthanum, Neodymium or Gadolinium) in aquatic environments are not well understood yet (Bergsten-Torralba et al., 2020). In this work, wide-range toxicity of thirteen elements (Li, Al, Mn, Ni, Co, Zn, Cu, Cd, La, Ce, Nd, Gd and Pb), common in residues from technological products, have been tested on three marine microalgae: *Phaeodactylum tricornutum* (Bacillariophyceae), a standard species in microalgae bioassays (ISO, 1975); *Nannochloropsis gaditana* (Eustigmatophyceae), representative of the microplankton; and *Pleurochrysis roscoffensis* (Haptophyceae), a coccolithophorid. Results from those experiments reveal that, among the species assayed, *P. tricornutum* was the most sensitive species to the elements tested, while *P. roscoffensis* was the least sensitive. Cu proved to be the most toxic element assayed, although Zn, Cd, La, Nd, Gd and Pb also demonstrated toxicity to some of the assayed microalgal species at the concentrations assayed (up to 1 mg·L⁻¹). A short-range toxicity test was then carried out for *P. tricornutum* and three rare earths (La, Nd and Gd), revealing that other endpoints measured by flow cytometry, apart from cellular density, (e.g., chlorophyll fluorescence,

forward or side scatter) can also generated useful responses in toxicity studies involving microalgae.

Key words: Technological residues, Phytoplankton, Toxicity tests, Rare earths, Flow cytometry

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HOME-MADE AFFORDABLE UV-DIGESTOR FOR THE ELIMINATION OF ORGANIC MATTER IN WATER SAMPLES PRIOR TO VOLTAMMETRIC HEAVY METAL DETERMINATION

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Abstract: The presence of heavy metals in marine environments is a universal concern since they tend to accumulate in aquatic organisms. Amongst these, Pb and Cd are of special interest because of their toxicity. Voltammetry is a suitable technique for both qualitative and quantitative analysis of heavy metals with very low limits of detection. However, the organic matter (OM) present in these samples can compromise the trueness of the results since it can form stable complexes with the metals and, thus, underestimate their total concentration. Therefore, OM must be eliminated, and this is usually done by UV digestion. Few UV- digestion systems are commercially available, but they are expensive and have small capacities. For that reason, we developed an in-house UV-digester to simultaneously digest 12 60 mL samples consisting of 6 commercial UVC (Hg vapor discharge, 250 nm Λ_{max}) lamps of 90W nominal power (20W/100 h radiated power) surrounding a rack holding 12 quartz tubes. Its performance was tested using tannic and humic acids as OM. Different carbon concentrations, radiation times and the need of H₂O₂ to improve the digestion were evaluated. Finally, the performance of the UV-digester was tested with both synthetic samples spiked with Pb and Cd, and real river and estuarine samples. Results showed that the addition of small amounts of H₂O₂ fastened the digestion of the organic matter and 2h were enough to eliminate 10 mg/L C. Pb and Cd concentrations decreased in the presence of organic matter and after the digestion, their full concentrations were recovered.

Key words: home-made UV digester, voltammetry, trace analysis, heavy metals

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IN SITU EXPERIMENTAL EVIDENCE OF THE EFFECTS OF COMMERCIAL SUNSCREENS AND THEIR ULTRAVIOLET FILTERS ON POSIDONIA OCEANICA IN A MEDITERRANEAN ISLAND (FORMENTERA) DURING SUMMER

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Abstract: Sunscreen products usually contain a wide range of substances, including inorganic and organic ultraviolet (UV) filters, which belong to the main groups of contaminants of emerging concern for marine ecosystems. Research on the effects of sunscreen pollution in the Mediterranean marine biota is scarce, limiting the information necessary to promote a sustainable coastal tourism through environmental policies that protect priority species for conservation against potentially harmful substances. The impacts of sunscreen components on the primary productivity of *Posidonia oceanica* was assessed through short-term (48 h) in situ field experiments, using bell jar chambers during July of 2023 in Formentera, Balearic Islands, Spain. Environmentally relevant concentrations of a mixture of commercial sunscreens (6.080 mg L⁻¹), benzophenone-3 (BP-3; 246.990 and 1115.000 ng L⁻¹) and titanium dioxide (TiO₂; 0.042 and 37.600 µg L⁻¹) were tested against a control (without addition of contaminants). Both UV filters promoted greater respiration rates in *P. oceanica* than in the controls, resulting in a negative net carbon gain for the seagrass. Although the whole sunscreen mixture also induced respiration in the plants, the net primary productivity was higher under sunscreen addition, possibly enhanced by the nutrients released from the mix. These results provide pioneering evidence on the potential hazards of UV filters for *P. oceanica*.

Key words: Sunscreen, UV filters, Mediterranean, pollution, seagrass.

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**BIOCHEMICAL AND PHYSIOLOGICAL BIOMARKERS IN
SPECIMENS OF *CASSIOPEA XAMACHANA* (BIGELOW, 1892)
AND *AURELIA AURITA* (LINNAEUS, 1758) FROM
L'OCEANOGRÀFIC**

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Abstract: There is a need to develop efficient tools to prevent damage to marine ecosystems due to pollution. The use of scyphozoans as biomonitors is proposed using biomarkers as sensitive early warning tools for the detection of contaminants. The common jellyfish (*Aurelia aurita*) and inverted jellyfish (*Cassiopea xamachana*) are species widely distributed in their natural habitats and are reproduced and exhibited in aquariums worldwide. *Cassiopea spp.* are epibenthic and incorporate the photosynthetic zooxanthella *Symbiodinium* within their mesoglea during the polyp stage.

The objectives of this study were a) to establish the practical procedures and the basal levels of a battery of biochemical and physiological biomarkers of *C. xamachana* and *A. aurita* and b) to characterize the carboxylesterase enzymes using different substrates and to quantify the degree of inhibition in the presence of model inhibitors.

Biomarkers related to the biotransformation of xenobiotics (enzymatic activity of CbE and GST), oxidative stress (LPO levels and enzymatic activity of CAT and GR), secondary metabolites (glucose, lactate and ammonia levels) and density of zooxanthellae in tissues of the umbrella and oral arms were studied. For the basal values of the studied biomarkers, ranges varied between 0.83 and 3.18 nmol g⁻¹ of wet weight for LPO, 3.30 and 8.36 nmol min⁻¹ mg⁻¹ of protein for GR, 0.78 and 3.17 µmol mg⁻¹ of protein for glucose, 0.36 and 1.14

$\mu\text{mol mg}^{-1}$ protein for lactate, 0.029 and 0.073 $\mu\text{mol mg}^{-1}$ protein for ammonia, 14.55 and 195.02 $\text{nmol min}^{-1} \text{mg}^{-1}$ protein for CbE, 5.8 and 83 $\text{nmol min}^{-1} \text{mg}^{-1}$ of protein for GST and 18.07 and 22.2 $\mu\text{mol min}^{-1} \text{mg}^{-1}$ of protein for CAT. These results were compared with those of species of scyphozoans, other cnidarians and marine invertebrates, showing inter and intraspecific variability.

Key words: Jellyfish, lipid peroxidation, antioxidant enzymes, metabolites, biotransformation enzymes.

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SEASONAL MICROBIAL CHANGES IN THE SEDIMENTS ALONG THE HUELVA COAST (SW SPAIN)

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Abstract: The ocean and coastal areas are subjected to many drivers of environmental changes, mostly associated with human activities. Some coastal areas are particularly stressed due to the nearby presence of impacting human activities, such as: mining, industry, or agriculture. Microorganisms have been proposed as good indicators of response to environmental pollution. In this regard, the wide distribution and rapid adaptation of the microbiome in response to environmental stressors lead to changes in their structure, diversity, and functionality. In this work, we have studied aquatic sediments from three different locations along the Huelva coast (Andalusia, Southwest Spain): “Isla Cristina” salt marsh (H1), “Carreras” river (H2) and “El Terrón” port (H3) in two different seasons: spring and autumn. The 16S rDNA gene was sequenced for the identification of bacteria. Statistical analyses were carried out to compare the number of bacterial identifications between the two seasons in each location. The phyla of bacteria with the highest number of identifications were Proteobacteria and Bacteroidetes in both seasons. In H1, the Planctomycetes phylum significantly decreased in autumn when compared to spring. In the case of H2, the Chlamydiae and Planctomycetes phyla significantly decreased in autumn. With respect to H3, the Cyanobacteria and Planctomycetes phyla significantly decreased in autumn, whereas the Firmicutes phylum increased in this season when compared to the spring sampling. A total of 96 bacterial families were identified considering the two seasons. In H1, 4 bacterial families showed significant changes; in H2, 12 families; and 16 families showed significant changes in H3. The Shannon-Wiener index was calculated to evaluate the alpha diversity, but no significant changes were observed in any of the three locations. Metagenomics allows us to assess the changes in the microbiome structure, which can be

related with the sampling seasons and chemical characteristics of the sites in field studies.

Key words: Bacteria; Environmental samples; Metagenomics; Seasonal variations

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USE OF OYSTER (*MAGALLANA GIGAS*) AS AN INDICATOR ORGANISM FOR PAHS CONTAMINATION ON THE SPANISH ATLANTIC COAST

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Abstract: Mussel *Mytilus galloprovincialis* have been used as a key species for assessing marine pollution in the Spanish coast during the last decades. However, the increasing scarcity of this species in some parts of the coastline is pushing the search for other species that can be used as sentinel organisms for pollution. Thus, the aim of this study is to examine the suitability of the introduced oyster *Magallana gigas* as sentinel for PAHs. We compare concentrations of PAHs in *M. galloprovincialis* and *M. gigas* (at six sampling sites along the Atlantic Spanish coast). Additionally, we compared PAHs concentrations between two oyster size, 4,5-9cm and 9-12cm, and between two control groups, each one made of 25 randomly selected individuals. Both species displayed consistent pollutant concentration patterns, facilitating site pollution identification. In general, oyster concentrations showed similar assimilation and accumulation patterns than mussels. Also, we found similar assimilation and accumulation patterns across different sizes and control groups. In conclusion, oyster *M. gigas* seems to be suitable for effective pollution assessment and merits further consideration in environmental monitoring strategies, particularly for continuing historical monitoring records.

Key words: Polycyclic aromatic hydrocarbons (PAHs), oyster, indicator organism.

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EFFECT OF MUSSEL BODY SIZE ON BIOLOGICAL RESPONSES TO FLUORANTHENE EXPOSURE

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Abstract: Environmental monitoring programs use wild mussel as bioindicator to assess the levels of chemical pollutants and the biological responses related to pollution. In IEO monitoring programs (González-Fernández, et al., 2015), organisms from a specific size range are used to reduce the influence of size on bioaccumulation and effects responses of the pollutants (30-50 mm). Nevertheless, differences in mussel size could be related to age, since mussels are animals with unlimited growth. Therefore, mussel size might act as a “confounding factor” affecting biological responses to pollutants (Zhong et al., 2013).

The aim of this study was to evaluate the effect of mussel size on biochemical responses to the polycyclic aromatic hydrocarbon (PAH) fluoranthene (FLU). For that purpose, mussels of different body sizes (S, small 30 mm; M, medium 40 mm; L, large 50 mm) were exposed to 30 µg L⁻¹ of FLU. After 21 days of exposure, the following biochemical biomarkers were measured: catalase (CAT), superoxide dismutase (SOD), glutathione reductase (GR), glutathione peroxidase (GPx), glutathione-S-transferase (GST) and lipid peroxidation (LPO). FLU bioaccumulation was quantified together with biological variables such as anatomical indices, gonadal development, and body reserves. Biochemical biomarkers were affected by the mussel size and also the effect of toxicant exposure was size-dependent. In general, small mussels were more sensitive to the oxidative stress of FLU. These results highlight the significance of endogenous factors, such as animal size, in the biological responses to pollutants and in assessing the biomarkers used in biomonitoring programs.

Key words: marine pollution, biomarkers, monitoring programs

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POSTER COMMUNICATIONS ~ GLOBAL CHANGE

OCEAN ACIDIFICATION FORCING DRIVERS IN THE IBERIAN BASIN OVER THE LAST 25 YEARS

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Abstract: High-quality measurements of CO₂ chemistry collected during 12 cruises along the GO-SHIP section A25-OVIDE between 1997 and 2023 have been utilized to assess long-term ocean acidification in the Iberian Basin. The section was divided into five layers based on thermohaline criteria: North Atlantic Central Water (NACW) as the surface layer, Mediterranean Water (MW) and Labrador Sea Water (LSW) as intermediate layers and upper and lower North Atlantic Deep Water (uNADW and lNADW) as the deepest layers. Results showed a pH decline across the water masses, with more pronounced acidification trends at the surface. The acidification rates in the three upper water masses were $-0.0021 \pm 0.0002 \text{ yr}^{-1}$ (NACW), $-0.0013 \pm 0.001 \text{ yr}^{-1}$ (MW), and $-0.0008 \pm 0.0001 \text{ yr}^{-1}$ (LSW). The trends observed in NACW and MW were nearly double the published trends for the Eastern North Atlantic (1981-2008) by Vázquez-Rodríguez et al. (2012). The pH decrease in the two deepest layers of the North Atlantic Deep Water was not significant, showing near steady-state values of 7.958 ± 0.003 (uNADW) and 7.916 ± 0.002 (lNADW) over the past 25 years. The main drivers of these pH trends were quantified using a decomposition approach based on temperature, salinity, total alkalinity, and total dissolved inorganic carbon (DIC) changes. DIC was split into natural and anthropogenic components using the ϕC_T method (Pérez et al., 2008). The sum of all percentages of these forcings, positive and negative, was practically 100% considering methodological uncertainties. The increase in the anthropogenic DIC fraction was identified as the primary driver, representing $84 \pm 3\%$ of the net pH decline in NACW, $73 \pm 7\%$ in MW, and $78 \pm 8\%$ in LSW. Significant decreases in total alkalinity, around $-0.2 \text{ } \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ in MW and LSW, reinforced ocean acidification by $43 \pm 19\%$ and $73 \pm 17\%$, respectively. In contrast, cooling mitigated acidification in the intermediate layers, with a higher impact of $-21 \pm 7\%$ on the pH trend in MW.

Key words: ocean acidification, North Atlantic Ocean, GO-SHIP section A25

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POSTER COMMUNICATIONS ~ TRACERS IN OCEANOGRAPHY

CONSTRAINING DENMARK STRAIT OVERFLOW WATER EXPORT USING ND ISOTOPES

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Abstract: The Denmark Strait is a gateway region between the Arctic and Atlantic oceans that plays a crucial role in the Atlantic Meridional Overturning Circulation (AMOC) and global climate dynamics. The Denmark Strait Overflow Water (DSOW) forms as a result of the admixture of Atlantic, Greenland Sea and Icelandic Sea sourced waters transported southward by the East Greenland Current (EGC) and by the North Icelandic Jet (NIJ). Once DSOW crosses the Denmark Strait, it becomes a precursor of the densest component of North Atlantic Deep Waters (NADW). Among the various geochemical tracers used to investigate ocean circulation, neodymium isotopes (ϵNd) have emerged as powerful tools due to their ability to serve as tracers for water mass origins, circulation patterns and mixing processes in the ocean. This study focuses on the characterization of DSOW export and mixing between the different water masses present in the Denmark Strait using neodymium isotopes and traditional tracers such as salinity and temperature. During the FAR-DWO cruise in 2023, approximately 250 seawater samples were collected for neodymium isotopes and rare earth elements analysis, aiming to characterize the water masses in the area, their mixing processes and tracing their circulation patterns. Initial results from ϵNd analysis reveal a very distinctive isotopic signature between DSOW ($\epsilon\text{Nd} \sim -10.9$) and adjacent water masses ($\epsilon\text{Nd} \sim -14.0$) thus enabling to track the path of this deep water formation and the mixing processes occurring along its export pathway. Using statistical tools such as a newly developed Monte Carlo Optimum Multi-Parameter Analysis (MC-OMPA) we will identify the relative abundances of the different water masses described in the Denmark Strait.

Key words: Nd isotopes, Denmark Strait, DSOW

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