



Colección Congresos y Homenajes Serie Congresos

# XXI INTERNATIONAL IBERIAN MARINE CHEMISTRY

LAS PALMAS DE GRAN CANARIA, JULY 06-08





# XXI INTERNATIONAL IBERIAN MARINE CHEMISTRY (SIQUIMAR 2022)

Libro de Abstracts

Las Palmas de Gran Canaria 06-08 de julio de 2022

Coordinación: María Esther Torres Padrón Decana de la Facultad de Ciencias del Mar UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA



2023

#### Colección Congresos y Homenajes Serie Congresos

INTERNATIONAL IBERIAN MARINE CHEMISTRY (21°. 2022. Las Palmas de Gran Canaria)

XXI International Iberian Marine Chemistry (SIQUIMAR 2022) [Recurso electrónico] : libro de abstracts : Las Palmas de Gran Canaria, 06-08 de julio de 2022 / coordinación, María Esther Torres Padrón. -- Las Palmas de Gran Canaria : Universidad de Las Palmas de Gran Canaria, Servicio de Publicaciones y Difusión Científica, 2023

1 archivo PDF (108 p.). -- (Congresos y Homenajes. Serie Congresos) ISBN 978-84-9042-478-0

1. Oceanografía química – Congresos y conferencias 2. Península Ibérica I. Torres Padrón, María Esther, coord.. II. Universidad de Las Palmas de Gran Canaria, ed. III. Título IV. Serie

551.464(46)(063)

Thema: RBKC, PNC, 4CTM

#### XXI INTERNATIONAL IBERIAN MARINE CHEMISTRY (SIQUIMAR 2022)

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#### Las Palmas de Gran Canaria, 06-08 de julio de 2022

© 1ª edición, 2023

Universidad de Las Palmas de Gran Canaria Servicio de Publicaciones y Difusión Científica serpubli@ulpgc.es https://spdc.ulpgc.es/

Primera edición [electrónica PDF], Las Palmas de Gran Canaria, 2023

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Editorial: Servicio de Publicaciones y Difusión Científica de la ULPGC

ISBN: 978-84-9042-478-0

#### DOI: https://doi.org/10.20420/1716.2023.580

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Abstracts Volume XXI International Iberian Seminar on Marine chemistry held under the umbrella of the VIII International Symposium on Marine Sciences, July 2022.



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# ORAL COMMUNICATIONS











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# ORAL COMMUNICATIONS

# CHEMICAL **OCEANOGRAPHY**













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# THE EFFECTS OF ORGANIC MATTER CHARACTERISTICS ON FE(II) OXIDATION KINETICS IN COASTAL SEAWATER

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**Abstract:** The iron (II) oxidation kinetic process was studied at 25 stations in coastal seawater of the Macaronesia region (9 around Cape Verde, 11 around the Canary Islands, 5 around Madeira). In a physicochemical context, experiments were carried out to study the pseudo-first order oxidation rate constant (k', min<sup>-1</sup>) over a range of pH (7.8, 7.9, 8.0, 8.1) and temperature (10, 15, 20, 25°C). Deviations from the calculated  $k'_{cal}$  at the same T, pH and S were observed for most of the stations. Measured  $t_{1/2}$  ( $\ln 2/k'$ , min) values at the 25 stations ranged from 1.82-3.47 min (mean 1.93±0.76 min) and for all but two stations were lower than the calculated  $t_{1/2}$  of  $3.21\pm0.2$  min. In a biogeochemical context, nutrients and variables associated with the organic matter spectral properties (CDOM and FDOM) were analyzed to explain the observed deviations. The application of a multilinear regression model indicated that k' can be described (R=0.921, SEE=0.064 for pH=8 and T=25°C) from a linear combination of three organic variables.

 $k^{OM} = k'_{cal} - 0.11* \text{ TDN} + 29.9 * b_{DOM} + 33.4 * C1_{humic}$ 

where TDN is the total dissolved nitrogen,  $b_{\text{DOM}}$  is the spectral peak obtained from colored DOM analysis when protein-like or tyrosine-like components are present and C1<sub>humic</sub> is the component associated to humic-like compounds obtained from the parallel factor analysis (PARAFAC) of the fluorescent DOM. Results show that compounds with N in their structures principally explain the observed k' increase for most of the samples. Although other components could also present a relevant role. Experimentally, k' provides the net result between the compounds that accelerate the process and those that slow it down.

Key words: Iron(II), oxidation kinetics, coastal waters, CDOM, FDOM.

# IRON (II) OXIDATION KINETICS VARIABILITY IN THE ATLANTIC OCEAN AND DEVELOPMENT OF AN IMPROVED THEORETICAL EQUATION

# David González-Santana<sup>1\*</sup>, Melchor González-Davila<sup>1</sup>, Maeve C. Lohan<sup>2</sup>, Lise Artigue<sup>3</sup>, Alessandro Tagliabue<sup>4</sup> and J. Magdalena Santana-Casiano<sup>1</sup>

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**Abstract:** During the GEOTRACES GA13 section cruise (FRidge), the iron(II) oxidation rate constants at six hydrothermal vent sites along the Mid-Atlantic Ridge were studied. Results showed high variability between samples collected within and outside the hydrothermally affected regions. Further iron(II) oxidation rate constant analysis experiments revealed that the presence of organic ligands and colloidal size particles delayed the oxidation process, while not affecting the overall pH dependency.

High volume samples were analysed across a range of temperatures (2-25 °C) and pH (7-8) to extend the range of the existing multiparametric equation describing the oxidation rate constant change as a function of pH and temperature. The new equation covers a larger range of temperatures than previous published equations and provides consistently better statistical results, thus improving its applicability for global biogeochemical models.

Key words: Iron, iron(II) oxidation, hydrothermal, GEOTRACES.

## SPATIO-TEMPORAL VARIABILITY OF THE AIR-SEA CO2 FLUXES IN THE STRAIT OF GIBRALTAR BASEDON HIGH-FREQUENCY DATA COLLECTED BY A VOS.

David Curbelo-Hernández<sup>1,\*</sup>, J. Magdalena Santana-Casiano<sup>1</sup>, Aridane G. González<sup>1</sup>, Melchor González-Dávila<sup>1</sup>

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#### Abstract:

The spatio-temporal variability of the surface ocean CO<sub>2</sub> system and the air-sea CO<sub>2</sub> fluxes were studied in the Strait of Gibraltar based on high-resolution underway field data collected between February 2019 and March 2021 by a surface ocean observation platform (SOOP) aboard a volunteer observing ship (VOS). The changes in the depth of the Atlantic-Mediterranean Interface layer and the upwelling of deep-water drove by tidal and trade winds strongly influenced the surface CO<sub>2</sub> distribution. The variability of the CO<sub>2</sub> fugacity (fCO<sub>2,sw</sub>) and fluxes were mainly driven by temperature despite the significant influence of non-thermal processes in the southernmost part. The  $fCO_{2,sw}$  increased with temperature by  $9.02 \pm 1.99 \text{ \mu atm }^{\circ}\text{C}^{-1}$  (r<sup>2</sup>=0.86) and  $4.51 \pm 1.66 \text{ \mu atm }^{\circ}\text{C}^{-1}$  (r<sup>2</sup>=0.48) in the northern and southern sections, respectively. The thermal to non-thermal effect ratio (T/B) was higher in the northern section (>1.8) compared with the southern section (<1.30) due to the enhancement of biological activity and vertical mixing related to the seasonal wind-induced upwelling along the African coast. The annual cycle (referenced to 2019) of total inorganic carbon normalized to a constant salinity of 36.7 (NC<sub>T</sub>) was attended. The net community production processes described 93.5-95.6% of the total NC<sub>T</sub> change, while the contribution of air-sea exchange and horizontal and vertical advection was found to be minimal (<4.6%). According to the seasonality of air-sea  $CO_2$  fluxes, the region behaved as a strong  $CO_2$  sink during the cold months and as a weak CO<sub>2</sub> source during the warm months. The Strait of Gibraltar acted as annual net CO<sub>2</sub> sink, with higher net ingassing along the southern section (-1.01 mol C m<sup>-2</sup>) compared to the northern section (-0.82 mol C m<sup>-2</sup>). The calculated average CO<sub>2</sub> flux for the entire area was -7.12 Gg CO<sub>2</sub> yr<sup>-1</sup> (-1.94 Gg C yr<sup>-1</sup>).

**Keywords:** Air-sea CO<sub>2</sub> fluxes, CO<sub>2</sub> system, VOS line, Surface Ocean Observation Platform, Strait of Gibraltar.

#### Acknowledgments:

This study was supported by the Canary Islands Government and the Loro Parque Foundation through the CanBIO project, CanOA subproject (2019–2022), and the CARBOCAN agreement (Consejería de Transición Ecológica, Lucha contra el Cambio Climático y Planificación Territorial, and Gobierno de Canarias). We would like to thank the RENATE P ship owner, the NISA-Marítima company and the captains and crew members for the support during this collaboration. Special thanks to the technician Adrian Castro-Alamo for biweekly equipment maintenance and discrete sampling of total alkalinity aboard the ship. The VOS line will be part of the Spanish contribution to the Integrated Carbon Observation System (ICOS), European Research Infrastructure starting in 2021.

# INFLUENCE OF COASTAL PROCESSES ON THE ORGANIC COMPLEXATION OF IRON AND COPPER IN THE MACARONESIA REGION

# V. Arnone<sup>\*1</sup>, D. González-Santana<sup>1</sup>, M. González-Dávila<sup>1</sup>, A.G. González<sup>1</sup> and J.M. Santana-Casiano<sup>1</sup>

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**Abstract:** Coastal environments around islands are characterized by the combination of physical, chemical, and biological interactions, such as water mixing, wind stress, dust deposition, and resuspension from sediments that have impacts on the biogeochemistry of trace metals like iron (Fe) and copper (Cu). Therefore, the coastal waters and the influences of their processes on the organic complexation of Fe and Cu have to be studied to fully understand the biogeochemical cycles of these metals in the marine environment.

Dissolved iron (dFe) and copper (dCu), the concentration and the conditional stability constants of organic binding ligands ( $L_{Fe}$ ,  $L_{Cu}$ , log  $K^{cond}_{Fe3+L}$  and log  $K^{cond}_{Cu2+L}$ ) were studied in the surface coastal waters of the Macaronesia region (Cape Verde, Canary Islands, and Madeira). Samples were collected during the POS533 cruise (2019) and analysed by competitive ligand exchange adsorptive cathodic stripping voltammetry. More than 98% of dFe (0.46-1.32 nM) was organically complexed with  $L_{Fe}$ , whose concentration range was between 0.56-2.96 nM. The logK<sup>cond</sup><sub>Fe3+L</sub> presented values between 20.77 and 21.90 (L<sub>2</sub>-type ligands). In the case of dCu (0.07-4.03 nM), more than 99% was complexed and  $L_{Cu}$  concentration was in the range of 0.54-2.59 nM. The logK<sup>cond</sup><sub>Cu2+L</sub> showed values between 13.40 and 14.42 ( $L_1$ -type ligands). The results suggest that, along the region, physical processes related to the water mixing could influence Fe and Cu speciation. Dissolved metals and ligand concentrations were greater at the coastal stations than in oceanic water related to biological activity and water mixing induced by the wind. Furthermore, greater concentrations were observed on the eastern parts of Fogo, Tenerife and Gran Canaria than on the western coast, due to stronger wind incidence.

Key words: Iron, Copper, Organic ligands, Cathodic stripping voltammetry, Coastal water.

**Acknowledgments:** We want to express our gratitude to Dr. Birgit Quack from GEOMAR for inviting us to participate in the AIMAC project. Special thanks go to Rui Caldeira, Cátia Azevedo, Claudio Cardoso, Ricardo Faria and Jesus Reis from the Oceanic Observatory of Madeira for the CTD- deployments and data. To acknowledge the GEOMAR funds for POS533 and Kastriot Qelaj for the nutrient analysis. This study received funding from the

European Union's Horizon 2020 research and innovation program under grant agreement No 820989 (project COMFORT, Our common future ocean in the Earth system–quantifying coupled cycles of carbon, oxygen, and nutrients for determining and achieving safe operating spaces with respect to tipping points). We also acknowledge the financial support for the ATOPFe project (CTM2017-83476-P) from the Ministerio de Ciencia e Innovación (Spain). Veronica Arnone's participation was funded by the PhD grant (PRE 2018-084476). The participation of Aridane G. González was within the Programa de Cooperación INTERREG V-A España-Portugal MAC (Madeira-Azores-Canarias) 2014-2020 (PLANCLIMAC project).

# THE USEFULNESS OF REAL TIME MONITORING OBSERVATORIES – THE CASE OF RIA FORMOSA LAGOON (SOUTH PORTUGAL)

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Abstract: At coastal lagoons, complex dynamics of physical-chemical-biologicalgeological parameters (e.g., temperature, salinity, dissolved gases, pH, nutrients, chlorophyll a, suspended matter and sediments) occur over a variety of temporal scales (diurnal, tidal, seasonal and annual). Disentangling variability over different spatial and temporal scales, at a time of rapid change, is crucial to understand the importance of the interplaying processes. This work aimed to provide insights into temperature, salinity, pH, Dissolved oxygen (DO), chlorophyll-a and turbidity variability, through a real time monitoring station installed, for the first time in Ria Formosa, during 2017-2020, acquiring data at a high frequency (every 15 min). The monitoring station was equipped with an YSI EXO 2 multiparameter probe with water temperature, salinity, pH sensors, together with optical ones to measure DO, chlorophyll-a and turbidity, which were maintained and calibrated along their deployment. This allowed a continuous surveillance of the system during this period, able to capture distinct temporal signatures, including episodic mesoscale and meteorological events, usually not captured when using only sampling spot strategies. Data showed that DO was highly variable along time with an evident seasonal distribution pattern and reactive to physical-chemical-biological interplaying processes. Critical values < 5 mg/L were only recorded in 3% of the global data. Upwelling events were also captured, mirrored on the distribution of water temperature, DO and pH. The high frequency data acquisition, also allowed to assess the influence of pulses of organic matter inputs and benthic remineralization, particularly after rainfall and land runoff. The knowledge driven from this observatory, covering short (hourly) to long temporal scales (yearly), provides a broad range of conditions for a better understanding of the functioning of this ecosystem and represents a key source of information that can contribute to support coastal management and protection, which is imperative for building knowledge-based societies.

Key words: Monitoring Observatories, Ria Formosa, Coastal lagoons

**Acknowledgments:** The authors would like to thank to APSines for the gracious logistic support provided for the installation and deployment of the multiparameter probe, and allowance for its maintenance since May 2017. The work was funded by Fundação para a Ciência e Tecnologia FCT - UBEST project (ref: PTDC/AAG-MAA/6899/2014).

## MODELLING NORTH-ATLANTIC WATER COLUMN RESPIRATORY CO<sub>2</sub> PRODUCTION, VERTICAL CARBON FLUX, NUTRIENT RETENTION EFFICIENCY, AND BENTHIC RESPIRATION

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**Abstract:** New North Atlantic rates of carbon-flux  $(F_c)$ , oxygen utilization (OUR), and mineralization, when combined with new oceanographic concepts, can provide new insight into the dynamics of metabolic ocean biogeochemistry. Here, data from heliumtritium dating, advection-diffusion modeling, apparent oxygen utilization, respiratory electron transport activity (ETS), and three different types of sediment traps were used to calculate new metabolic-based rates. First, we used OUR to calculate CO<sub>2</sub> remineralization  $(J_c)$  profiles.  $J_c$ , at 100m, ranged from 0.4 to 109 millimol CO<sub>2</sub> m<sup>-3</sup> yr<sup>-1</sup>and from 1000m, it ranged lower, from 0.001 to 4.3 millimol CO<sub>2</sub> m<sup>-3</sup> yr<sup>-1</sup>. Secondly, we used J<sub>c</sub> to calculate carbon flux ( $F_c$ ) profiles. These, plus measured  $F_c$ , ranged from 1.5 to 17.8 millimol C m<sup>-2</sup> yr<sup>-1</sup> at 100m and to 0.03 to 12.1 millimol C m<sup>-2</sup> yr<sup>-1</sup> at 1000m. Thirdly, integrating  $J_c$  from the bottom of the mixed layer to the seafloor yielded New Production (NP) and Export Production (E). The two are considered equal. We found a North Atlantic NP range of 0.07 to 23.3 mol C m<sup>-2</sup> yr<sup>-1</sup>. Fourth, from the ratio,  $J_c/F_c$ , we calculated the nutrient retention efficiency (NRE =  $(J_c/F_c)$ \*100) that predicts future regenerated production. NRE is inversely related to carbon-flux transfer efficiency ( $T_{eff}$ ) and both NRE and  $T_{eff}$  are related to b, the attenuation exponents of J<sub>c</sub> and F<sub>c</sub>. For a 50m water column centered at 125m, NRE ranged from 51 to 27% while Teff ranged from 49 to 73%. In a 50m water column at 1025m, NRE ranged, much lower, from 8 to 4 % while T<sub>eff</sub> ranged, much higher, from 92 to 96%. Fifth, benthic J<sub>c</sub> was calculated, using different limits of integration, from F<sub>c</sub>. It varied indirectly with water column NRE. For the North Atlantic, we found that benthic  $J_c$  ranged from 2.1 to 7040.0 millimol C m<sup>-2</sup> yr<sup>-1</sup>.

Key words: OUR, AOU, respiratory ETS, ocean metabolism, ocean particle flux.

**Acknowledgments:** This research was funded by TIAA-CREF and Social Security (USA) to TTP.

# WATER MASSES AND NUTRIENTS VARIABILITY IN THE SOUTH IBERIAN PENINSULA (GULF OF CADIZ)

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Abstract: This study addresses the seasonal variability of water masses and inorganic nutrients in continental margin of the Gulf of Cadiz (South Iberian Peninsula) during 2017. Samples were collected seasonally at transects located perpendicular to the coast along the continental margin within the framework of the STOCA project. The results of the data analysis indicated that there was a marked seasonal variability in the nutrient concentrations and the thermohaline features of water masses throughout the water column during 2017. Below the upper layers the presence of North Atlantic Central Water (NACW) was observed during all cruises, although its influence was greater in September. The lower influence of the NACW was observed in December, showing the T-S plots an eroded thermohaline signature. The variability observed in the thermohaline features of the water masses coincided with different wind regime. Thus, favourable upwelling winds (westerlies) predominated in June and September, while in March and December easterlies prevailed. Nitrate and phosphate concentrations were low in the surface layers of the water column. Nevertheless, some exceptions were observed in a few stations in September, March and December, coinciding with low salinities. In June, due to the intense thermal stratification, these nutrients were exhausted at most of the stations. At depths >250 m the higher nutrient concentrations were detected in June and September associated to the signature of NACW at intermediate depths. Also high concentrations were associated to the NACW in March and December, although these were lower than in June- September. The results show that the seasonal variability of NACW observed in 2017 had a marked impact on the seasonal dynamics of nutrients in the continental margin of the Gulf of Cadiz.

Key words: NACW, nutrients, continental margin, Gulf of Cadiz

Acknowledgments: We acknowledge the financial support provided by IEO and also the ESMARES2 project

# RECENT DEVELOPMENTS BY VOLTAMMETRY IN THE QUANTIFICATION OF THE ROLE OF HUMIC SUBSTANCE IN THE SOLUBILITY OF IRON IN THE OCEAN

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Abstract: Iron is the most relevant micronutrient in ocean waters because of its limiting role in primary productivity and CO<sub>2</sub> uptake over vast areas of the global ocean. At the physicochemical conditions of seawater, inorganic iron is extremely insoluble, but the presence of ligands permits concentrations in the nanomolar and subnanomolar range. Although ligands concentrations can be achieved by iron titration and determination by voltammetry, the characterization of such ligands has proved elusive to date. One of the main candidates to constitute the bulk of iron ligands in the ocean is the heterogeneous mix known as humic substances (HS). HS are the product of degradation of vegetal tissues and are ubiquitous in natural waters. HS are usually measured by fluorescence or voltammetry. Iron-HS complexes can be directly detected on a mercury electrode in the presence of a specific catalytic reagent (bromate). New developments have shown that in open ocean waters is possible to determine not just the concentration of HS but also the concentration of humic iron (the concentration of iron naturally bound to HS). In this presentation, we will describe the technique and show past and recent analysis of samples in the Arctic and North Atlantic Ocean that show the power of the analytical approach. We could observe how in some surface waters (Transpolar Drift) most of iron is in the form of humic complexes and in other water masses this contribution is important but not the main component of iron speciation.

Key words: iron solubility, iron speciation, organic complexation, humic substances

Acknowledgments: HUFENAO project (PID2020-115291GB-I00 ) funded by MCIN/ AEI /10.13039/501100011033

# Severe deoxygenation event caused by the 2011 eruption of the submarine volcano Tagoro (El Hierro, Canary Islands)

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Abstract: The shallow, near-shore submarine volcano Tagoro erupted in October 2011 at the Mar de las Calmas marine reserve, south of El Hierro island. The injection of lava into the ocean had its strongest episode during November 2011 and lasted until March 2012 (Fraile-Nuez et al., 2012). During this time, *in situ* measurements of dissolved oxygen were carried out, using a continuous oxygen sensor constantly calibrated with water samples. A severe deoxygenation was observed in the area, particularly during October-November 2011, which was one of the main causes of the high mortality observed among the local marine ecosystem (Santana-Casiano et al., 2013). The measured O<sub>2</sub> concentrations were as low as 7.71 µmol kg<sup>-1</sup>, which represents a -96% decrease with respect to unaffected waters. The oxygen depletion was found in the first 250 m of the water column, with peaks between 70-120 m depth. The deoxygenated plume covered an area of at least 464 km<sup>2</sup>, distributed particularly south and south-west of the volcano, with occasional patches found north of the island. The oxygen levels were also monitored through the following years, during the degassing stage of the volcano, when oxygen depletion was no longer observed. Additionally, during the eruption, an island-generated anticyclonic eddy interacted with the volcanic plume and transported it for at least 80 km (Eugenio et al., 2014), where the O<sub>2</sub> measurements still showed a -8% decrease after mixing and dilution. This feature draws attention to the permanence and transport of volcanic plumes far away from their source and long after the emission.

Key words: Tagoro, submarine eruption, dissolved oxygen, deoxygenation, Canary Islands.

Acknowledgments: This research was funded by the Ministerio de Economía y Competitividad del Gobierno de España (MINECO), FEDER through VULCANO-I (CTM2012-36317), VULCANO-II (CTM2014-51837-R), and CETOBAPH (CGL2009-13112) projects, and The Spanish Institute of Oceanography (IEO) through BIMBACHE

(IEO-2011-2012), RAPROCAN-III (IEO-2010-2012), VULCANA-I (IEO-2015- 2017), and VULCANA-II (IEO-2018-2020) projects. We would also like to thank the officers and crew of the R/V *Ramón Margalef* and *Ángeles Alvariño* from the IEO for their help at sea.

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# ORAL COMMUNICATIONS BIOGEOCHEMICAL PROCESSES













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# LAVA-SEAWATER INTERACTION EFFECTS IN THE CARBONATE SYSTEM DURING THE ERUPTION OF THE LA PALMA VOLCANO 2021

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**Abstract:** The effect of the lava arriving to the sea in the carbon dioxide system was studied during the eruption of the volcano located in Cabeza de Vaca (La Palma, Canary Islands) on September 19<sup>th</sup>. The affected area was a shoreline below a cliff with heights between 80-100m with a sandy beach in the southern part. The lava reached the coastal waters three times since the eruption began. An increase in temperature and salinity was observed due to seawater heating and water vapor formation, followed by an important decrease in pH<sub>T</sub>, related to the release of magmatic volatiles and water-rock reactions. A portion of the magmatic acidic volatiles (CO<sub>2</sub>, SO<sub>2</sub>, HCl, HF, HBr) that remains after the lava transit to the ocean is released in contact with seawater and moving out, mixed with the water vapor, but also affecting the seawater pH. Changes in the alkalinity (A<sub>T</sub>) and total dissolved inorganic carbon (C<sub>T</sub>) were also observed, producing a decrease in both variables. In September 30<sup>th</sup>, the NC<sub>T</sub> decreased by 90 µmol kg<sup>-1</sup> while the NA<sub>T</sub> decreased in 224 µmol kg<sup>-1</sup>, reaching 2180 µmol kg<sup>-1</sup>. This result indicates the effect is not only due to strong acid addition but to the loss of carbonate species, affecting both variables, together with silicate and phosphate precipitation with metals from the lava, changing the A<sub>T</sub>.

The anomalies found in the carbon dioxide and hydrography properties were localized in the frontal seawater that moved up and displaced out as a tongue of 4-6m depth with anomalous values observed as far as 1.5 km in the first meter. When the lava was not arriving to the sea or was falling on previously formed rocks, the area affected was strongly limited to the first few tens of centimeters of the column and at distances of 10-15 m.

Key words: Carbonate system, lava-seawater interface, acidification.

# COPPER AND LEAD COMPLEXATION BY DISSOLVED ORGANIC MATTER IN MAR MENOR COASTAL LAGOON

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Abstract: Mar Menor coastal lagoon is a shallow system with a reduced exchange with the open sea, that is affected by several anthropogenic pressures, mainly agriculture and mining. The mining sierra of Cartagena-La Unión has been historically discharging mining waste rich in heavy metals in the south area of Mar Menor, resulting in high metal concentrations in sediments (García and Muñoz-Vera., 2015). The nutrients reaching the lagoon, together with the high temperatures, also provoke phytoplankton blooms that lead to high concentrations of dissolved organic matter (DOM). It is well known that total metal concentrations are not good predictors of their bioavailability, and metal speciation should be taken into account. The presence of ligands, such as DOM in the water, may form metal-DOM complexes and protect against the deleterious effects of metals. The present study aims at studying the effect of DOM on the speciation of dissolved metals (Cu and Pb) in Mar Menor waters. With that aim, filtered water was sampled at five sites in Mar Menor lagoon at several sampling periods. Metal concentration was analysed by ICP-MS with Argon gas dilution, DOC was analysed in a carbon-specific infrared gas analyser and optical characterization of DOM was obtained from absorbance and fluorescence spectra. Complexiometric titrations of Cu and Pb were performed by anodic stripping voltammetry following Durán and Nieto (2011). Preliminary results show that Cu and Pb concentrations in Mar Menor waters are higher than in other coastal areas, especially in the south area of the lagoon, reaching concentrations of tens of nanomolar. DOC concentrations are also very high in Mar Menor waters, leading to high complexation capacities for Cu, therefore protecting aquatic biota from the deleterious effects of Cu. Pb, on the contrary, is poorly complexed by DOM, and almost all dissolved Pb is present in inorganic forms.

Key words: Metal speciation, ASV, cDOM

**Acknowledgments:** This work has been supported by the Spanish Ministry Science and Innovation and by the European Union through the European Regional Development Fund (ERDF) through 'SEEME' (PID2019-109355RA-I00) project.

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# CONSEQUENCES OF SINGULAR ENVIRONMENTAL EVENTS ON THE CYCLE OF METALS IN COASTAL LAGOONS AND THEIR INFLUENCE ON THE INCORPORATION OF METALS BY PRIMARY PRODUCERS

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Abstract: Coastal areas are valuable and sensitive environments subjected to great anthropogenic pressure. Among these pressures, metal pollution is of priority concern as these pollutants can reach concentrations that exceed the levels established to protect sensitive organisms in the ecosystem. In coastal lagoons, shallow systems with a reduced exchange with the open sea, metal concentrations are one or two orders of magnitude higher than in open-waters. In addition, these systems are subjected to physicochemical variations that can alter the biogeochemical cycling of the metals. Singular environmental events such as strong winds cause metal resuspension, torrential rain events provoke the entrance of solutes and pollutants, and phytoplankton blooms dramatically increase the concentration of organic matter. These events provoke alterations in the concentration and speciation of metals in the water column. This will have a direct impact in the organisms living in the area, since metal toxicity and bioavailability depends on the chemical speciation. Dissolved organic matter (DOM) is the most important variable influencing metal speciation and bioavailability in seawater. However, the effects of DOM on metal bioavailability have not been yet unravelled and contrasting results have been reported, some showing that DOM protects against metal toxicity and others showing the opposite. The present study was designed to study how the biogeochemical cycling of trace metals in the water column of coastal lagoons is influenced by these singular environmental events and how this affects the incorporation of metals by the primary producers, in this case, microalgae, with particular focus on the effect of dissolved organic matter on metal biouptake. The proposed work combines field sampling and analytical work in the Mar Menor lagoon (SE Spain). This project will substantially contribute to widen our knowledge about the behaviour of metals in coastal areas and to determine how the presence of DOM affects their toxicity.

Key words: coastal lagoons, singular environmental events, metals, bioavailability

**Acknowledgments:** This work has been supported by the Spanish Ministry Science and Innovation and by the European Union through the European Regional Development Fund (ERDF) through 'SEEME' (PID2019-109355RA-I00) project.

# EFFECT OF DISSOLVED ORGANIC MATTER ON COPPER BIOAVAILABILITY TO A COASTAL DINOFLAGELLATE

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Abstract: Metal complexation by dissolved organic matter (DOM) is considered to decrease metal bioavailability by lowering the free metal ion concentration, therefore protecting organisms from the deleterious effects of metals (Campbell et al., 2002). In coastal lagoons like Mar Menor, with high terrestrial influence and low exchange with open sea, the levels of both DOM and metals are one or two orders of magnitude higher than in open-waters. In order to verify the free ion activity model (FIAM), copper internalization by Prorocentrum micans, a cosmopolitan dinoflagellate also present in the Mar Menor, was tested in the absence and presence of two types of DOM, commercially available fulvic acids from riverine origin (SRFA) and coastal DOM obtained by ultrafiltration (UF-DOM). The microalgae were exposed to artificial sea water enriched with increasing amounts of Cu<sup>65</sup> isotope, at levels from 5 to 100 nM Cu, solely and in combination with DOM. After onehour exposure, samples were centrifuged and washed and pellets were digested with nitric acid at 90°C, following Sánchez-Marín et al (2010) and Croteau and Luoma (2005). In parallel, careful measurements of metal complexation by anodic stripping voltammetry (ASV) were performed and total Cu concentrations were measured by ICP-MS. Preliminary results show that copper internalization by the microalgae increases linearly as a function of labile Cu, both in the absence and presence of DOM, in agreement with FIAM and with labile Cu measurements performed by ASV. Future work might include testing the influence of competing metals, such as Pb or Zn, on Cu internalization, and to study Cu bioavailability in natural samples collected in the Mar Menor, in order to shed light into the factors that control Cu bioavailability in coastal lagoons.

Key words: Metal complexation, Cu uptake, ASV, DOM, ICP-MS.

**Acknowledgments** This work has been supported by the Spanish Ministry Science and Innovation and by the European Union through the European Regional Development Fund (ERDF) through 'SEEME' (PID2019-109355RA-I00) project.

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## THE ROLE OF GALIC ACID AND OCEAN ACIDIFICATION IN THE REDOX CHEMISTRY OF IRON IN SEAWATER Norma Pérez-Almeida<sup>\*1</sup>, Aridane G. González<sup>1</sup>, J. Magdalena Santana-Casiano<sup>1</sup>, Melchor González-Dávila<sup>1</sup>

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**Abstract:** The biogeochemistry of iron (Fe) is affected by ocean acidification, both in terms of redox and complexation reactions. Accordingly, it is directly linked with ecosystems because Fe is an essential trace metal for microorganisms. Within the pool of organic ligands present in the ocean, polyphenols are exudated by marine microalgae and can complex Fe(III) and reduce it to Fe(II) in seawater (SW).

Among all the polyphenols, Gallic Acid (GA; 3,4,5-trihydroxy benzoic acid) has been studied in terms of oxidation and reduction of Fe in natural seawater. The presence of GA decreased the oxidation rate of Fe(II) in SW, ([Fe(II)]<sub>0</sub>=25 nM, Fe:GA ratio from 1:1 to 1:4), increasing the permanence of Fe(II) in solution with increasing GA concentration. The decrease in Fe(II) oxidation rate is related to the Fe(III) reduction in the presence of GA. In this sense, Fe(III) is reduced to Fe(II) in a pH-dependent process, in both SW and NaCl-NaHCO<sub>3</sub>. The Fe(III) reduction rate increased with pH, with a slope of 0.46 ± 0.03 in NaCl-NaHCO<sub>3</sub> and 0.91 ± 0.14 in SW. The addition of the major ions of SW, such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, to the NaCl-NaHCO<sub>3</sub> solution showed a decrease in the Fe(III) reduction rate in the presence of Ca<sup>2+</sup> and in the pH range 7.0-8.0. When the studies were carried out with different GA concentrations, the Fe(III) reduction increased with the GA levels. Accordingly, at pH = 7.0, an increase in the Fe(III) reduction rate was observed over the entire range of Fe:GA ratios studied (from 1: 2 to 1:20; [GA]=50-500 nM). At pH = 8.0, Fe(II) was only detected at ratios from 1:3 to 1:10, because the Fe(II)-FZ<sub>3</sub> was not observed by the interference of GA peaks under that experimental conditions.

This study shows that the presence of GA significantly increases the residence time of Fe(II) in SW due to the reduction of Fe(III) to Fe(II) and it has to be considered in the Fe biogeochemical cycles.

Key words: Gallic acid, Iron, Complexation, Redox, Seawater, Ocean acidification

Acknowledgements: This study received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 820989 (project COMFORT) and financial support for the ATOPFe project (CTM2017-83476-P) from the Ministerio de Ciencia e Innovación (Spain).

# TRANSPORT OF THE BUFFER PROPERTIES FROM THE GUADALQUIVIR ESTUARY

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**Abstract:** The Guadalquivir estuary is one of the main sources of continental water to the Gulf of Cádiz, which has an important role in the biogeochemical cycles due to the export of different species. Especially, the carbon system transport can lead to an increase in the buffer capacity of the coastal, which makes it less sensitive to the ocean acidification processes described (Jiménez-López et al., 2021). To study this possible effect on the carbonate system, a total of 11 campaigns on board of R/V UCádiz have been carried out during the years from 2017 to 2022. All samplings include longitudinal transects and tidal cycles in different environmental and tidal conditions. In general terms, Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC) shows an increase in their concentration upstream, while calcium (Ca<sup>2+</sup>) presents the highest values in the more marine waters. The variations intervals found for these three variables are  $2180-5140 \mu$ M,  $430-3950 \mu$ M and  $1.30 - 10.9 \text{ mmol kg}^{-1}$  for TA, DIC and Ca<sup>2+</sup> respectively. Together with the pCO<sub>2</sub> dataset from previous works (Sánchez-Rodríguez et al., 2022; Sierra et al., 2020) different buffer factors were calculated in order to analyze the Guadalquivir influence in the coastal zone. In a first approach, the results indicated that, towards the mouth, the waters are more capable of storing anthropogenic carbon in the mouth of Guadalquivir. A nonlinear hydrodynamic model is used to estimate the transport of AT, DIC and  $Ca^{2+}$  to the Gulf of Cadiz. Net export variations between the dry season and extreme rains are of the order of  $1.1 \cdot 10^7 - 1.5 \cdot 10^8$ Gmol d<sup>-1</sup>,  $9.9 \cdot 10^6 - 1.8 \cdot 10^8$  Gmol d<sup>-1</sup> and  $4.5 \cdot 10^7 - 1.3 \cdot 10^5$  Gmol d<sup>-1</sup> for TA, DIC and  $Ca^{2+}$  respectively.

Key words: Inorganic Carbon, Buffer Factors, Guadalquivir estuary, Hydrodynamic model

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

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# INFLUENCE OF OXIDATION PROCESSES IN CH<sub>4</sub> AND N<sub>2</sub>O EMISSIONS TO THE ATMOSPHERE IN THE GUADALQUIVIR ESTUARY (SW, SPAIN)

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**Abstract:** The distribution and reactivity of methane and nitrous oxide have been studied along the salinity gradient in the Guadalquivir Estuary (SW Spain). Samples were taken in March and September 2021 and February 2022. This study complements the work carried out by Sierra *et al.* (2020) and Sánchez-Rodríguez *et al.* (2022). The concentrations of these gases were quantified by gas chromatography. It has been observed that the concentration of CH<sub>4</sub> and N<sub>2</sub>O increases towards the interior of the estuary, with maximum values in the turbidity maximum zone. Values of up to 250 nM for CH<sub>4</sub> and 70 nM for N<sub>2</sub>O have been reached in September 2021. This distribution is influenced by inputs of organic matter and nutrients to the estuary, mainly lateral inputs from the salt marsh areas and the organic matter remineralization processes in the sediments.

The fluxes of CH<sub>4</sub> and N<sub>2</sub>O through the water-atmosphere interface are positive in all seasons and increase towards the interior of the estuary (10-300 and 0-80  $\mu$ mol-m<sup>-2-</sup>d<sup>-1</sup>, respectively). This system acts as a source of these gases to the atmosphere.

In addition, the reactivity of these gases in the water column at different salinities has been studied by means of a constant temperature incubation experiment. From preliminary results, it has been found that  $CH_4$  oxidation rates and  $N_2O$  consumption rates become more important at lower salinities.

Key words: methane, nitrous oxide, reactivity, estuary.

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

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# DYNAMICS OF CO<sub>2</sub>, CH<sub>4</sub>, AND N<sub>2</sub>O IN RIA FORMOSA LAGOON

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Abstract: Coastal environments are highly productive systems which receive significant amounts of organic matter and nutrients. This inputs enhance the production of greenhouse gases and are affected by the anthropogenic activity in these areas, such as fertilisers use on agriculture, livestock farming, fish farms or wastewater treatment plants (Burgos et al., 2015; Ferron et al., 2009; Vallejo et al., 2021). A first characterization had been carried out to study the role and impact of greenhouse gases in selected coastal systems of the southern Portugal. To this purpose, the partial pressure of  $CO_2$  (pCO<sub>2</sub>) and the concentration of dissolved CH<sub>4</sub> and N<sub>2</sub>O have been measured in Ria Formosa lagoon, one of the most productive transitional systems of the south coast of Portugal. Two surveys were carried out during 2020, at low tide under typical conditions of Spring (March) and end of Summer (October). The samplings sites were distributed along the costal lagoon covering: i) inner areas with strong human impact (influence of different flows of treated wastewater discharges); ii) different vegetation coverage; and iii) main channels in connection with the main inlets to study the exchanges with the ocean. pCO<sub>2</sub> was calculated from pH and Total Alkalinity (TA), measured by potentiometric titration, and the dissolved concentration of CH<sub>4</sub> and N<sub>2</sub>O was obtained by using a gas chromatograph. In general, the highest values of the three greenhouse gases were found in October (pCO<sub>2</sub>: 536.4 - 6314.5 µatm, CH<sub>4</sub>: 5.1 -334.7 nM, N<sub>2</sub>O: 2.2 - 93.2 nM) and in the inner studied areas, especially affected by the human activity. The mean water - atmosphere fluxes of the pCO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O are positive, showing that the study area acts as a source of these gases to the atmosphere.

Key words: Greenhouse gases, water - atmosphere fluxes, Ria Formosa, Coastal lagoon.

**Acknowledgments:** This work was supported by PO MAR2020 (ref: Mar-01.04.02-FEAMP-0003) and by the Spanish CICYT (Spanish Program for Science and Technology) under contract RTI2018-100865-B-C21.

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# CHARACTERIZATION OF IRON-POLYPHENOLS COMPLEXES IN SEAWATER

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**Abstract:** Marine microorganisms like microalgae, can produce organic ligands with the capability to complex trace metals in the ocean such as iron (Fe) and copper (Cu). Among all the possible organic compounds, polyphenols have been measured and identified in the exudates of marine microalgae such as *Phaeodactylum tricornutum* and *Dunaliella tertiolecta*. Among all these polyphenols, catechin, sinapic acid, gallic acid and gentisic acid have been studied in terms of Fe complexation via kinetics of formation ( $k_f$ ) and dissociation ( $k_d$ ).

The  $k_f$  of these organic ligands was  $1.2 \times 10^4 - 4.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_d$  was  $1.8 \times 10^{-4} - 4.4 \times 10^{-4} \text{ s}^{-1}$ . Therefore, the conditional stability constant (log K'<sub>Fe'L</sub>) was from 7.8 to 9.2. Then, these polyphenols can be considered weak ligands (L2-type).

These results demonstrated that the microalgae can excrete functional groups to complex Fe in seawater, increasing its solubility and keeping for longer in solution. This work improves our knowledge about the Fe biogeochemical cycle and characterizes the pool of organic matter in terms of interactions with Fe.

Keywords: Complexation, organic ligands, polyphenols, iron, ocean, biogeochemical cycle

**Acknowledgements:** We would like to thank the ATOPFe (CTM2017-83476-P) project given by the Ministerio de Economía y Competitividad from Spain. Veronica Arnone's participation was funded by the PhD grant (PRE 2018-084476).

# ANTHROPOGENIC SOURCES AND MICROBIAL ACTIVITY HIGHLY DETERMINATE DISSOLVED ORGANIC MATTER COMPOSITION IN THE WATER COLUMN AND SEDIMENTS OF A COASTAL LAGOON: MAR MENOR, SPAIN

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Abstract: The Mar Menor is one of the largest coastal lagoons in Europe and the Mediterranean Basin, with salinity values ranging from 41.9 to 45.5. It's subjected to strong anthropogenic pressure that caused an intense eutrophication process. We studied the characteristic of dissolved organic matter (DOM) using its optical properties in the water column and in poor water sediments during two oceanographic cruises (March and September 2018). In the water column, five components/fluorophores were identified; three microbial humic-like associated with microbial activity (C1<sub>WS</sub>) and effluents from anthropogenic sources (urban and agriculture,  $C2_W$  and  $C3_{WS}$ ) (e.g. Amaral et al. 2020, Wang et al. 2021, Williams et al. 2013, Cohen et al. 2014) and two protein-like that resembles the amino acids tryptophan and tyrosine (C4<sub>w</sub> and C5<sub>w</sub>, Catalá et al. 2015) (Table 1). All components showed no vertical differences (surface/bottom, p > 0.05) and higher intensities during summer, except for  $C5_W$  which was higher during winter (p < 0.05). The dominant fluorophore was  $C1_{WS}$  during both seasons (33% ± 1%), and  $C4_{W}$ showed the highest increase between seasons (6% winter, 27% summer). These results indicated changes in the DOM quality and sources between seasons mainly associated with biological and anthropogenic activities. In sediments poor water samples, we identified  $C1_{ws}$  and  $C3_{ws}$ , and three new components; two protein-like related with black odor waters, dissolved organic nitrogen loading from argo-urban coastal systems, the activity of sulfatereducing bacteria, and highly reactive DOM ( $C2_S$ ,  $C4_S$  and  $C5_S$ ) (Lu et al. 2022, Amaral et al. 2021, Osburn et al. 2016, D'Andrilli et al. 2019). Protein-like C2<sub>8</sub> and C4<sub>8</sub> accounted for > 60 % of the total fluorescent DOM. Our results highlight the importance of anthropogenic sources, such as urban and agricultural runoff, and microbial activity in DOM composition in this coastal lagoon.

Key words: Mar Menor, Fluorescent DOM, urban and agriculture runoff, microbial activity

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

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### LABILE ORGANIC MATTER IN SURFACE MARINE SEDIMENTS FROM THE SOUTHWESTERN IBERIAN PENINSULA

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Abstract: In this work, we study the variability of the labile organic matter (including detrital phytopigments, carbohydrates and proteins) in marine sediments from the Southwestern Iberian Peninsula (Gulf of Cadiz). Samples were collected in 2019 at stations located on the continental margin. The different components of the labile organic matter in surface sediments (0-1 cm) presented a high variability, with large differences in concentrations between stations. Thus in some stations, phytopigment concentrations were much higher compared to other stations. On the other hand, the more easily extractable fractions (i.e. the water-soluble fraction) of proteins and carbohydrates showed a similar distribution pattern, existing a positive correlation between these two fractions. The watersoluble fraction of proteins correlated highly with phytopigments, while the correlation between the water-soluble fraction of carbohydrates and phytopigments was weaker. On the other hand, the alkaline extractable fractions of proteins and carbohydrates were in general higher than the water-soluble fractions of these biogeochemical components. The concentration of the alkaline fractions of proteins and carbohydrates presented a similar distribution they were highly correlated. The protein/carbohydrate ratio also shows high spatial variability, although the ratio in the water-soluble fraction was lower compared to the ratio in the alkaline-soluble fraction. The results suggest the existence of an accumulation zone, as indicated the higher detrital phytopigment concentrations observed at some stations. The correlation between water-soluble proteins and phytopigments suggests that both components may come from the same sources. In addition, the variability in the protein/carbohydrate ratio suggests differences in the lability of organic matter among stations, which may affect the biogeochemical transformations in sediments.

Key words: Labile organic matter, biogeochemistry, marine sediments, Gulf of Cadiz

**Acknowledgments:** This work has been supported with funding from the Spanish State Research Agency through the project INPULSE (CTM2016-75129-C3-1-R) and from IEO through the project BIOGEOMOSE.



# ORAL COMMUNICATIONS ECOTOXICOLOGY AND MARINE POLLUTION













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## ASSESSING THE EFFECTS OF UV-A/H<sub>2</sub>O<sub>2</sub> PROCESS ON THREE DIFFERENT PHOTOSYNTHETIC MARINE MICROORGANISMS

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Abstract: Harmful Algal Blooms (HABs) impacts ecosystems on different ways. One of the reasons is the species translocation trough ballast water, as it can potentially drive HABs in coastal ecosystems. To minimize the potential transfer of *bloom* forming species, water treatment systems able to inactivate harmful phytoplankton species are necessary, either at the source (to prevent the discharge of microorganisms via ballast water -IMO Convention) or at industrial activities that need to produce water with certain quality, such as desalination systems or aquaculture activities. Among oxidative treatments, H2O2 has become an emerging reagent with environmental-friendly characteristics, which show promising results for cyanoHABs mitigation in freshwater ecosystems [1]. However, their potential application for the seawater scenario, and specifically for inactivate harmful phytoplankton, is still to be explored. Accordingly, in this study we aim to assess the effectiveness of H<sub>2</sub>O<sub>2</sub>based process for the inactivation of three different photosynthetic organisms, including HABs related eukaryotes (Prymnesium parvum and Amphidinium carterae) and a ubiquitous cyanobacteria (Synechococcus sp.). The effect of different H<sub>2</sub>O<sub>2</sub> concentrations (0-10 mg·L<sup>-</sup> <sup>1</sup>) were evaluated in single species but also in a multispecies approach. H<sub>2</sub>O<sub>2</sub> by itself can promote oxidative stress in the three selected organisms (specially in cyanobacterial species), suggesting a species-specific response, as the EC50% differs from the different microalgae. Multispecies experiments have been also carried out, suggesting that some interspecific protection from eukaryotes can protect cyanobacteria [2]. Additionally, the effect of single UV-A radiation and its combination with H<sub>2</sub>O<sub>2</sub> has been assessed, in order to promote the formation of Reactive Oxygen Species in an extracellular environment, but more importantly, intracellularly [3]. It would enhance cell damage and increase the water treatment efficiency based on H<sub>2</sub>O<sub>2</sub>.

Key words: Harmful Algal Blooms, hydrogen peroxide, UV radiation, oxidative stress

Acknowledgments: 2014–2020 ERDF Operational Programme of the Regional Government of Andalusia (FEDER-UCA18–108023). Grant IJC2020–042741-I funded by MCIN/AEI/ 10.13039/501100011033 and by European Union NextGenerationEU/PRTR.

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## ARE PASSIVE SAMPLERS USEFUL TOOLS TO EVALUATE THE IMPACT OF DREDGING ACTIVITIES IN PORT WATERS?

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**Abstract:** Port waters are usually under different anthropic pressures that affect their physico-chemical quality. In Spain, the R.O.M. 5.1-13 (Recommendations on the Quality of Littoral Waters in Port Areas) establishes the methods and criteria to evaluate the quality of port waters. These Recommendations establish the need to monitor the quality of water by periodical spot water sampling using oceanographic bottles. However, in the last years, alternative novel tools, as passive samplers (PS), have shown to present several advantages compared to traditional spot sampling, and thus, have been suggested as complementary tools to improve the quality of the assessment (CIS 2009). While spot sampling provides contaminant concentrations at the moment of sampling, PS can be deployed for several days/weeks, providing time-integrated concentrations that represent the entire exposure time.

In this context, the aim of this study was to evaluate the applicability of PS to assess the impact of dredging activities in the quality of port waters in the Royal Maritime Club of Abra (Bilbao Port, North Spain). For this purpose, Diffusive Gradient Thin Film (DGT) PS were deployed (5 days) at five stations at increasing distance from a dredging area, in 3 different periods: before, during and after dredging activities. Simultaneously, spot water samples were collected at the same stations. Hydrographic parameters were measured *in situ*. Priority (Cd, Ni, Pb) and other specific metals (Cu, Co, Zn) were analysed in the DGTs and in the water samples by ICPMS. Total organic carbon, turbidity and suspended matter were also analysed in the water samples. Preliminary results show that most of metals were below the detection limit in the discrete water samples while DGTs provided quantifiable concentrations for all metals. Besides, DGTs enabled to assess the temporal and spatial distribution of metals in the water column following dredging activities, providing more meaningful information than traditional water sampling (discrete water samples).

Key words: passive samplers, spot sampling, port waters, dredging

Acknowledgments: Authors wish to acknowledge the Bilbao Port Authority for funding this study. The technical and human support provided by the Geochronology and Isotope Geochemistry-SGIker facility (UPV/EHU, MINECO, GV/EJ, ERDF and ESF) is also gratefully acknowledged.

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### EFFECTS OF BIOLOGICAL AND ENVIRONMENTAL FACTORS ON BIOMARKER ACTIVITIES OF TWO SMALL PELAGIC FISH

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Abstract: Biomarkers have been proved useful tools for monitoring chemical pollution in marine ecosystems. More frequently, biomarkers are measured in benthic organisms inhabiting coastal environments. However, marine pollution can affect areas far from the coast and accumulate through the food web, originating a need to find new indicator species with ecological relevance inhabiting pelagic marine environments. Biological and environmental factors could affect biomarker responses, masking the real effects of pollution. Therefore, it is crucial to unravel how these factors are affecting the biomarker values. In this study, we explored the effects of some important biological and environmental parameters on three hepatic biomarkers of xenobiotic exposure, namely carboxylesterases (CEs), glutathione-S-transferase (GST) and catalase (CAT) in two small pelagic fish, the European anchovy (Engraulis encrasicolus) and the European sardine (Sardina pilchardus). These two species inhabit pelagic environments, and are key elements in the Mediterranean food web. They were also selected for their different feeding strategies and reproductive periods. Results showed significantly higher enzymatic activities in sardine and these were sex-dependent. Moreover, CEs and GST activities were significantly affected by reproduction in both species. These biomarker activities were also influenced by temperature in anchovy. CEs in vitro incubations with the model pesticide dichlorvos caused up to 90% inhibition of basal activity, and gave complementary information on the differential species sensibility to this pesticide. The additional in vitro incubation with a battery of pesticides and plastic additives revealed significant CEs inhibition. This work has shown that reproduction and sex, as well as temperature variations had a significant effect on biomarker activities, and despite the ecological proximity of both species the influence of these parameters was species-dependent.

Key words: biomarkers, carboxylesterases, pollution monitoring, small pelagic fish

Acknowledgments: The sampling was funded by the project PELWEB (RETOS-2017-

CTM2017-88939-R; Ministerio de Economía, Industria y Competitividad, Proyectos de I+D+I, Spanish Goverment) leaded by Marta Coll. Thanks to Elena Lloret, Elena Fernández, Marta Albo and Joan Giménez for their help in the sample collection. Nixon Bahamon helped in the statistical analysis. This study is part of the PhD-thesis of D.N.

### THE INFLUENCE OF THE DEGASSING PHASE OF THE TAGORO SUBMARINE VOLCANO (CANARY ISLANDS) ON THE METAL CONTENT OF THREE SPECIES OF CEPHALOPODS

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**Abstract:** Underwater volcanic eruptions are a type of natural contamination that seriously affect all marine organisms at a local level (Eugenio et al., 2014). These eruptions usually end and begin a degassing stage of the volcano that, although they do not affect the magnitude of magma emanation, they do affect organisms to a lesser degree locally, such as cephalopods that, due to their metabolism and trophic level, are good bioindicators of contamination (Lozano-Bilbao et al., 2018; Penicaud et al., 2017; Santana-Casiano et al., 2016). A total of 180 samples of three species of cephalopods were caught for the study: sixty *Sepia officinalis*, sixty *Octopus vulgaris* and sixty *Loligo vulgaris* in the area of the

submarine volcano in El Hierro, Tenerife and Lanzarote in the Canary Islands (twenty samples per species in each location), and the metal concentrations (Al, Cd, Cr, Cu, Fe, Li, Ni, Pb and Zn) in each of the samples were analyzed. All species showed significant differences for all metals in El Hierro compared to Tenerife and Lanzarote.

All the analyzed species from El Hierro had higher concentrations of the nine studied metals,

this is due to the fact that they were caught near the Tagoro submarine volcano, which at the

time was in a state of degassing and discharged many metal-rich compounds.

Keywords: Volcano, metal, cephalopod, Canary Islands, bioindicators

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### LEAD ACCUMULATION AND SUBCELULAR DISTRIBUTION IN THE SCALLOP AEQUIPECTEN OPERCULARIS

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Abstract: The scallop Aequipecten opercularis accumulates high concentrations of lead (Pb) in its tissues, what has led to the ban of its extraction in the Ría de Vigo (Galicia, Spain) for feeding purposes. The Ría de Vigo presents higher levels of Pb than other industrialized Galician Rías, mainly due to a ceramic factory that was operating in the inner part of the Ría from 1961 to 2001 (Álvarez-Iglesias et al., 2003). This study aims at testing the dynamics of bioaccumulation of Pb in this species, its tissue distribution and the subcellular partitioning Pb, with the aim of enhancing our understanding of the mechanisms that provoke the high Pb levels reached in its tissues. Scallops originating from a clean area were exposed in cages in two places in the Ría de Vigo (one harbour and a less impacted location) and 10 individuals were collected every month over a three months period. The bioaccumulation of Pb and other metals was studied including its distribution in several tissues: gills, digestive gland, kidney, muscle, gonad and rest. The results showed that scallops accumulated similar levels of Pb in both locations, and that about 76% of the Pb was found in the kidney. Subcellular partitioning of kidney samples additionally showed that around a 60-70% of Pb in the kidneys was included in metal rich granules, indicating that this is probably the reason of the high levels of Pb observed in this species, as occurs for other bivalves (Darriba and Sánchez-Marín, 2013). Concerning other metals analysed, it was observed that Zn was also mainly accumulated in the kidney, while Cd content was highest in the digestive gland. Cu and Ni were preferentially accumulated in the digestive gland or kidney, depending on the location, and As was mainly found in the muscle. Results will be discussed on the basis of metal pollution in both locations and according to detoxification strategies used by scallops.

Key words: metal bioaccumulation, metal rich granules, bivalves

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### COPPER, LEAD AND CADMIUM MONITORING VIA THE SMALL-SPOTTED CATSHARK (Scyliorhinus canicula): SPACE TIME DRIVEN VARIABILITY IN WESTERN MEDITERRANEAN POPULATIONS

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

Pb, Cd and Cu were extracted and quantified in Western Mediterranean (Alicante, Spain) fisheries caught *S. canicula* muscle tissue via Microwave Assisted Extraction (MAE) and Graphite Furnace Atomic Absorption Spectrometry (GF-AAS). A monthly assessment has been performed on these three analyte's concentrations from November 2019 to November 2020 and compared to results previously gathered data during 2017 and 2018 surveys.

Results are consistent with the existence of regular time persistent traits regarding elementspecific concentration peaks in particular months, with relatively high concentrations of Cd and Cu being observed during March 2020 ( $\bar{x} = 0.4229$  and  $0.01342 \ \mu g \cdot g^{-1}$  (*ww*) respectively) and Pb concentration peaks for Pb being found during December 2019 ( $\bar{x} = 0.05354 \ \mu g \cdot g^{-1}$  (*ww*)). Significant differences in analyte concentrations were also found between nonconsecutive months implying gradual concentration variability in time. Regarding each elements spatial distribution among *S. canicula* populations, time persistent concentration hotspots were observed throughout the sample area from 2018 to 2020. Despite the source and nature of this phenomena is yet to be, the regularity of the observed traits offers further promising feedback towards the establishment of this species as a costeffective, fishery-based heavy metal biomonitor.

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

**Acknowledgments:** This work was supported by funds of IMEDMAR-UCV (Spain). Special thanks to Calp's fishing guild.

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### INFLUENCE OF TOURISM ON MICROPLASTIC CONTAMINATION AT WASTEWATER TREATMENT PLANTS IN THE COASTAL MUNICIPALITY OF CHICLANA DE LA FRONTERA

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Abstract: The close relationship between the Andalusian coasts and tourism is one of the most important sources of the economy in the Bay of Cádiz. Specifically, the municipality of Chiclana de la Frontera, with a population lower than 90,000 citizens, located in the southeast of Spain, duplicates its population during the summer season leading to an increment in flow at wastewater treatment plants (WWTPs). WWTPs have been reported as a source of microplastics (MPs) into marine ecosystems, therefore the aim of the present study is to investigate if the tourism affects the presence, discharge and in the receiving environment. Samples were taken at the influent and effluent of the municipal WWTPs (one located at the urban area and other located at resort area) during 2021 (including low and high season). MPs were collected and extracted from wastewater matrixes following the method recommended by the National Oceanic and Atmospheric Administration (NOAA) and UTS treatment to reduce organic matter and cellulose, respectively. The analysis of the samples was performed according to their abundance, shape, size, and type of polymer, along with the removal rates of MPs at WWTPs. The results showed heterogeneous MPs abundance ranging from 2246 to 345 MPs/L and 72.9 to 4.6, in the influent and effluent, respectively, increasing the presence of MPs during high season. Fibers were the predominant shape within all the samples. A total of 17 polymers were identified, by ATR-FTIR, where Acrylates, PE and PA were the largest polymers found. Despite the high MPs retention performance of the WWTPs analysed (71.8 - 99.9 %), a combined contribution of approximately  $2.1 \times 10^5$  MPs per day to the aquatic environment was estimated. Finally, the increase in population during high season had a direct relationship with the increase on the MPs discharged to the aquatic environment through the WWTPs.

Key words: Wastewater Treatment Plant (WWTPs), Tourism, Microplastics.

**Acknowledgments:** We thank the financial support provided by Regional Government of Andalusia (P18-RT-2947).

### PRESENCE OF MICROPLASTICS IN AQUACULTURE AND POSSIBLE ENTRY ROUTES

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### **Abstract:**

The presence of plastics in all matrices is raising global concern about plastics. This makes it necessary to study how plastics and in particular microplastics affect aquaculture systems. In aquaculture, a complete knowledge of the water line, the feed and the organisms (sea bass) is required to understand how microplastics interact in the system. Knowing the amount of microplastics that are found in the receiving environment and accumulate in aquaculture facilities, as well as the effectiveness of inlet water purification and sterilisation technologies affecting microplastics is essential to get an idea of the distribution of microplastics in the aquaculture aquatic environment. It is noted that the available purification systems reduce the amount of microplastics entering from the receiving environment. However, new microplastics was observed in the sea bass tank, which may be largely due to those added via the feed, as well as in pipes and other materials used in current aquaculture systems. Among all the water samples, 16 types of polymers were detected, 14 have been identified in the receiving environment. The study shows that the feed may be a source of microplastics input to the environment as a total accumulated of 28 MPs/kg (dry weight) was detected in the 5 feed samples analysed. Having analysed the possible routes of entry of microplastics in aquaculture, 15 sea bass samples were studied, each sample consisting of a set of 3 sea bass to obtain a considerable dry weight mass for the study. In all 15 samples, heads and muscle were observed along with skin. Polystyrene, Teflon, Polyethylene and Polyamide were found in head and muscle samples. These studied showed that although the water purification and sterilisation systems at the beginning of the plant operated properly, there were other pathways of microplastics to enter the system and ending up in the sea bass and entering the food chain.

Key words: microplastics; sea bass; treatment; feed

**Acknowledgments:** We thank the financial support provided by the Spanish Ministry of Science, Innovation and Universities (RTI2018-096771-B-I00).

### ACCUMULATION AND TROPHIC TRANSFER OF MERCURY IN MEDITERRANEAN PLANKTONIC FOOD WEBS

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Abstract: Humans, especially around the Mediterranean Sea, are exposed to mercury (Hg) and mainly via the consumption of seafood, containing methylmercury (MeHg). Methylmercury biomagnifies up to harmful levels in marine top predators, but little is known about the uptake processes at the base of the food web. Their large biomass, fast growth rates and their capacity to uptake contaminants, makes plankton a key compartment in the accumulation and transfer of Hg through food webs. However, those processes are poorly understood. The HIPPOCAMPE cruise to the western Mediterranean Sea was conducted during spring 2019 and covered 10 sampling stations along a meridional transect from Marseille, France to Gabès, Tunisia. We sampled three size classes of phytoplankton (0.7-2.7, 2.7-20, 20-60  $\mu$ m) and five size classes of zooplankton (60-200, 200-500, 500-1000, 1000-2000 and > 2000  $\mu$ m). All samples were measured for Hg and MeHg, carbon and nitrogen concentrations and their stable isotopes ( $\delta^{13}$ C and  $\delta^{15}$ N).

Overall, Hg concentrations in phytoplankton were higher than previously reported. However, differences between stations were not explained only by seawater concentrations. Picophytoplankton, the most abundant species in oligotrophic regimes like the Mediterranean Sea, contained higher Hg concentrations than nanophytoplankton, probably due to larger specific surface area ( $236 \pm 206$  and  $151 \pm 100$  ng g<sup>-1</sup> respectively). Phytoplankton and zooplankton Hg concentrations were negatively correlated with chlorophyll *a*, highlighting the influence of the trophic regime on bioconcentration, and evidencing a successive impact on consumers. In addition, mercury concentrations in zooplankton were also correlated with  $\delta^{15}$ N, revealing the possible influence of predation, enhanced in low productive ecosystems.

Bioconcentration and plankton food web interactions play a determinant role in the Hg transfer to top predators. Thus, the reduction of Hg emissions may not result directly in lower Hg levels in fish. Climate change impacting primary producers by possibly reducing their size and changing their trophic dynamics may increase this transfer in the future.

Key words: Mercury, Plankton, Food webs, Mediterranean Sea

### SPATIAL DISTRIBUTION AND TEMPORAL TRENDS OF BUTYLTINS (TBT, DBT & MBT) IN SHORT SEDIMENT CORES OF THE SW PORTUGUESE MARGIN (WESTERN IBERIAN MARGIN, NE ATLANTIC)

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### Abstract:

The spatial patterns and temporal trends of butyltin compounds (BTC), including tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT), were assessed along the SW Portuguese Margin. Due to a lack of information of BTC in sediments, they were not considered in the first assessment cycle of the Portuguese Marine Strategy Framework Directive which occurred in 2012. In this assessment, the shelf area between Lisboa and Sines did not reach the Good Environmental Status. BTC were measured only recently in this area during an assessment in 2019-2021, in a set of surface samples and short sediment cores collected within the scope of the CSS project. BTC compounds were measured by SPME-GC-MS. To support the interpretation of the BTC, grain-size and organic carbon contents were also determined. Sediment chronology was based on the down-core distribution of <sup>210</sup>Pb, and sedimentation rates were calculated using the Constant Flux and Constant Sedimentation Rate model, including a surface mixed layer (SML).

Monobutyltin and DBT were the predominant organotin species detected, with DBT

showing the highest concentrations. Only 4 out of a total of 35 surface samples contained TBT above the detection limit (DL, 5 ng/g), with maximum concentrations around 30 ng/g in the vicinities of the Sines harbour and in the Sado and Tagus dredge disposal sites for Class 3 (slightly contaminated dredged material) of the Portuguese Regulatory Legislation 1450/2007. At those locations, TBT was also detected slightly deeper within the SML, reflecting sediment reworking. In all other subsurface sediments TBT was below DL. Despite the toxicity of BTC, they are not part of the mandatory substances included in the Portuguese legislation for monitoring of the quality of dredged sediments. Their inclusion is recommended because they represent a serious environmental risk when relocating dredged material, especially when dredged sediment is derived from shipyards and harbour areas.

**Key words:** Portuguese continental shelf, marine sediments, butyltin compounds, Marine Strategy Framework Directive (MSFD)

**Acknowledgments:** This study was supported by the Fundo Europeu dos Assuntos Marítimos e das Pescas (FEAMP) through the CSS project (MAR-01.04.02-FEAMP-0013). The MINEPLAT project (ALT20-03-0145-FEDER-000013) supported the 2019 sampling campaign. CIIMAR thanks to the Strategic Funding UIDB/04423/2020 and UIDP/04423/2020 through national funds provided by FCT and ERDF. We are grateful to the crews of the NI Noruega and NRP Gago Coutinho and the technical staff of the Universidade de Évora and Instituto Hidrográfico for their contribution to the sediment sample collection and sample preparation.

The authors would like to thank the technical staff of the Laboratório de Contaminantes, Laboratório de Macrobentos and Laboratório de Sedimentologia (IPMA), for their assistance during sampling, sample preparation, and grain-size analysis.

### OCCURRENCE AND DISTRIBUTION OF CONTAMINANTS OF LEGACY AND EMERGING CONCERN SORBED ON FLOATING PLASTIC DEBRIS FROM MAR MENOR LAGOON AND EBRO RIVER SURFACE WATERS

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**Abstract:** Plastic acts as passive samplers of organic and inorganic contaminants from the surrounding environment (air, water, soil, sediment, etc) (León et al., 2018) and they can be used as integrative matrix for these contaminants in the marine environment. Previous studies have confirmed the concentration of organic contaminants in continental (León et al., 2018) and beached plastics (León et al., 2019) along the SE Iberian coast, but no information is available in relation to their concentrations in floating plastics.

In this study the occurrence and distribution of current-use pesticides (triazines, organophosphates and others), personal-care products (fragrances, UV-filters,..), pharmaceuticals, plastic additives, polycyclic aromatic hydrocarbons (PAHs) and organochlorinated contaminants were characterized in floating plastics sampled in different sampling points from Ebro River and Mar Menor lagoon in winter of 2019. The polymeric nature of plastic debris was characterized by attenuated total reflection Fourier-transform infrared spectrometry, showing that polyethylene (PE) and polypropylene (PP) were the most frequently found plastic polymers.

Contaminants were extracted from plastic following the proposed method by León et al., (2019), which consists of three successive ultrasonic extractions with MeOH and the analysis of the extract by stir-bar sorptive extraction coupled to gas-chromatography with mass-spectrometry. The presence and distribution profiles of these contaminants were consequence of the predominant anthropogenic pollution sources in each coastal ecosystem (tourism, agriculture, urban nuclei and transport) and some differences were found in their distribution profiles depending on the considered polymer and the physicochemical properties of the substances. Plastic additives, UV-filters, pharmaceuticals and PAHs were the groups of contaminants most commonly detected in these samples, being found at the highest concentrations near the main urban and touristic nuclei.

**Key words:** Current-use pesticides, Personal-care products, Plastic additives, Pharmaceuticals, Floating Plastics, Coastal ecosystems

Acknowledgments: This study is funded by the Spanish State Research Agency of the

Spanish Ministry of Science, Innovation and Universities and the European Fund for Regional Development (FEDER-MCIU-AEI/ CTM2017-89701-C3) and by Spanish Ministry of Science and Innovation and EU Next Generation Funds (PharmaSea JPI project, PCI2021-121933). M. García Pimentel acknowledges the Spanish Ministerial Science, Innovation and University for her pre-doctoral fellowship (PRE2018-085502).

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## **CHEMICAL OCEANOGRAPHY**













Universida<sub>de</sub>Vigo

### BENEFITS OF USING WATER QUALITY INDICES TO ASSESS THE IMPACT OF TREATED WASTEWATER IN RIA FORMOSA

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Abstract: Coastal lagoons are the most productive ecosystems, with ecological and economic value (Kennish and Paerl, 2010), providing various services. The degradation of these ecosystems has increased over the last decades due to multiple anthropogenic impacts (Barbier et al., 2008), including the disposal of treated wastewaters and consequent water quality alteration. Application of water quality indices can represent a benefit, since these could be an effective tool for assessing its state as they integrate/aggregate key water quality parameters. Thus, these indices convey information in a simplified way that can be easily used by environmental managers/decision makers to protect these systems. Ria Formosa is a shallow multi-inlet coastal lagoon, a main centre for bivalve production, located along the south Portuguese coast, where four Wastewater Treatment Plants (WWTP) from three main cities (two in Faro, one in Olhão and one in Almargem/Tavira, with ca. 1250000 inhabitants) are currently discharging their treated effluents. This work intended to evaluate the impact of the discharge of the main WWTP in Ria Formosa, during 2018-2020. For that, two water quality indices were applied: 1) TRIX (Vollenweider et al, 1998), which assesses the trophic status of waters, by aggregating oxygen, chlorophyll *a*, inorganic nitrogen and phosphorus data; and 2) CCME WQI (CCME, 2001, Uddin et al., 2021), adapted to consider the salubrity of bivalves of Ria Formosa, aggregating salinity, % oxygen saturation, chlorophyll a, NH<sub>3</sub>, Escherichia coli and Pseudo-nitzschia spp., Dinophysis sp. and Gymnodinium catenatum data. These indices showed to be valuable, indicating an improvement of water quality with increasing distance to the discharge points. Among study areas, Faro presented the worst classification (poor classification at 500 m from the discharge point in summer), followed by Almargem/Tavira and then by Olhão area where a good classification was achieved.

Key words: Coastal Lagoons, Water Quality, Ria Formosa, Wastewater disposal

**Acknowledgments:** This work was funded by the research project PO Mar2020 (ref MAR-01.04.02-FEAMP-0003).

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### QUANTIFICATION OF CAROTENOIDS AND CHLOROPHYLLS IN ALGAE

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**Abstract:** Chlorophylls (Chl) and carotenoid intake has been correlated with a chemoprotective effect (Ferruzzi and Blakeslee, 2007; Tanaka et al., 2012). They are abundant pigments in algae and were quantified in extracts from macroalgae mix biomass and pure strain of *Lobophora variegate* (*L. variegate*) collected from Las Canteras Beach (Gran Canaria). The contents of Chl a and b,  $\beta$ -carotene and lycopene were determined by extracting 500 mg of biomass with 5 mL of acetone-hexane (2:3) and measuring the absorption at 453, 505, 645 and 663 nm; Chl a and b, and total carotenoids were also quantified by extracting 500 mg of biomass with acetone-water (4:1), and recording the absorbance at 663.6 nm for Chl a, 646.6 nm for Chl b and 470.0 nm for total carotenoids. The effect of sonication on extraction yield was also studied (Branisa et al., 2014). Therefore, samples prepared as described above were sonicated before extraction. The results are summarized in the following table:

	Solvent: acetone-hexane			
	Chl a	Chl b	β-carotene	Lycopene
L. variegate	51,1±0.1*	7.07±0.3*	-	6.8±0.1*
	39.6±1	3.2±0.7	$2.47 \pm 0.06$	4.09±0.03
Mix biomass	30±2*	2.9±0.1*	2.1±0.2*	2.73±0.1*
	20.3±0.7	2.0±0.2	1.23±0.08	$1,94{\pm}0.09$
	Solvent: acetone-water			
	Chl a	Chl b	Total carotenoids	
L. variegate	50.1±0.1*	5,625±0.003*	15,9±0.3*	
	48±2	3.73±0.01	$15.28 \pm 0.02$	
Mix biomass	40.2±0.5*	11±1*	13,05±0.03*	
	35.4±0.8	7.2±1	12.9±0.4	
*Samples were soni	icated before extr	action		
The results are expr	essed as $\mu g g^{-1}$ of	biomass		

Sample sonication increased the extraction yield of natural pigments. *L. variegate* strain showed higher content of pigments than the mix biomass. These pigments have great commercial value.

Key words: Algae, Chlorophylls, Carotenoids, Commercial value.

**Acknowledgments**: Our thanks to the Spanish Bank of Algae (BEA) in Gran Canaria for providing algal strains. Ana M<sup>a</sup> Baracaldo thanks the scholarship ref.21AE1/195628. The participation of Paula Santiago was funded through a PhD scholarship from the Universidad de Las Palmas de Gran Canaria (PIFULPGC-2019) to join the Ph.D. Program in Oceanography and Global Change (DOYCAG). This Ph.D. Program is promoted by the Institute of Oceanography and Global Change (IOCAG).

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### HYDRODYNAMIC MODEL APPLIED TO THE CALCULATION OF NUTRIENT TRANSPORT IN THE GUADALQUIVIR ESTUARY.

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### Abstract:

The Guadalquivir River Estuary is a highly mixed and quite channelized Estuary in southwest of Spain (Siles-Ajamil et al., 2019) mainly dominated by tides. The multiples anthropogenic activities developed along the river such as dredging, dams, etc., may originated significant changes in the hydrodynamic pattern of the Estuary. In this work, we analyze the transport of nutrients (Nitrate, Nitrite, Phosphate and Silicate) along the Estuary using a set of observations and a non-linear one-dimensional hydrodynamic model, to which has been coupled a transport and dispersion module allowing us the study of the variability of nutrients concentration in two climatic seasons: dry season (July 2017) and wet season (April 2018). Our model has a high horizontal and temporal resolution of 25 m and 1 s respectively using the most recent available bathymetry. The sea surface elevation and current simulations performed by the model show a high reliability against the observations  $(R^2 > 0.8, R^2 > 0.93, respectively)$ . Nutrient concentrations increase upstream of the river, except for ammonium, which displays higher concentrations at the mouth of the Estuary. Silicate shows a conservative behavior, while nitrate and phosphate present a maximum in the turbidity plug zone (300  $\mu$ M and 5  $\mu$ M, respectively). The calculated net transports for the two seasons show notable differences;  $2.6 \cdot 10^4$  and  $1.3 \cdot 10^7$  Gmol d<sup>-1</sup> (Nitrate);  $2.2 \cdot 10^4$ and  $3.2 \cdot 10^6$  Gmol d<sup>-1</sup> (Nitrito);  $8.9 \cdot 10^2$  and  $2.8 \cdot 10^4$  Gmol d<sup>-1</sup> (Phosphate);  $8.9 \cdot 10^2$  and  $2.8 \cdot 10^4$  Gmol d<sup>-1</sup> (Silicate). Besides, nutrient transport is intrinsically linked to phytoplankton concentration, as they interact with each other. Therefore, at wet season the plume will be more enriched with a greater discharge of nutrients than in the dry season. This could contribute to a greater growth of phytoplankton in the coastal strip of the Gulf of Cadiz (Gomiz-Pascual et al., 2021).

Key words: Guadalquivir River, hydrodynamic model, nutrient concentration, net transport.

Acknowledgments: Sara Sirviente is supported through a doctoral grant at the University of Ferrara and University of Cádiz, also by the Spanish National Research Plan

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# POSTER COMMUNICATIONS

## BIOGEOCHEMICAL PROCESSES













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### EFFECTS OF ANTARCTIC PENGUINS GUANO ON MARINE PHYTOPLANKTON COMMUNITY STRUCTURE

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Abstract: The Southern Ocean is characterized by the worldwide largest area defined "HNLC" (High-Nutrient, Low-Chlorophyll) where phytoplankton growth is constrained by the limitations of some essential trace metals, especially Iron (Fe), resulting in a lower resource supply for the entire marine food web (de Baar et al., 2005; Martin, 1990). Penguin colonies can contribute to increase the biodiversity of land vegetation (mosses and lichens) by fertilizing the soil with their nutrient-rich (i.e., nitrogen) excretion products, called "guano" (Otero et al., 2018). However, recent studies indicate that penguin guano also contains high concentrations of bioactive trace metals that are necessary for several biological processes (i.e., Fe, Cu, Zn and Mn) (Sparaventi et al., 2021). Given the large population of penguin colonies and the extraordinary amount of guano excreted on land every breeding season, these metals could potentially boost primary production when either lixiviated to coastal waters or directly excreted in the sea. During austral summer 2020-21, we assessed the trace metal content in Chinstrap penguin (Pygoscelis antarcticus) guano, and its influence in phytoplankton biomass and community structure. An enrichment incubation experiment with controlled exposure to different guano concentrations was carried out. Results showed clear response of all phytoplankton size-fractions to penguin guano, with a particular increase in abundance of picoplankton cells (0.2 - 2 µm). These results show that penguin guano not only increases phytoplankton biomass but also influences the structure of plankton communities in the Antarctic environment.

Key words: Penguins guano, Antarctic, Trace Metals, Phytoplankton communities

Acknowledgments: This research is a contribution of the project PIMETAN funded by the Spanish Government (ref. RTI2018-098048-B-I00), EQC2018-004275-P and EQC2019-005721-P. E. Sparaventi is supported by the Spanish FPI grant (Ref: PRE2019-089679) and A. Rodríguez-Romero is supported by the Spanish grant, Juan de la Cierva Incorporación (Ref: IJC2018-037545-I). We thank I. Carribero, M.C. Agulló and R. Gutierrez for their support with the instrumental and methodological analyses.

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### COUPLED WATER-ATMOSPHERE EXCHANGE OF GREENHOUSE GASES IN THE GULF OF CADIZ

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Abstract: Continental platforms act, all in all, as systems that capture part of the anthropogenic carbon dioxide (CO<sub>2</sub>) from the atmosphere and emit methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). If we consider the different Global Warming Potential of these gases, we can find some controversy on the effect of the exchange combination of these gases on the radioactive capacity of the atmosphere. This paper presents the seasonal evolution of the joint emissions of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O in the Gulf of Cádiz from 2014 to 2016. The database corresponding to the fluxes with the atmosphere for the years 2014 and 2015 are part of the works of Sierra et al. (2107a, b) and Jiménez-López et al. (2019). Additionally, CH4 emissions in 2016 have been described by Sierra et al. (2020). As a new database, the seasonal variations of the CO<sub>2</sub> (pCO<sub>2</sub>) partial pressure distribution and the N<sub>2</sub>O concentration during 2016, as well as their corresponding water-atmosphere fluxes, are included. In 2016, the pCO<sub>2</sub> in surface waters showed a linear variation with temperature (8.0  $\mu$  atm °C<sup>-1</sup>) and chlorophyll concentration (r<sup>2</sup>=0.42), in addition to a mean flux to the atmosphere of  $-0.17 \pm 4.21$  mmol m<sup>-2</sup> d<sup>-1</sup>. On the other hand, the relationships between the  $N_2O$  concentrations with the Apparent Oxygen Utilization (r<sup>2</sup>=0.68) and nitrate concentration ( $r^2=0.84$ ) indicate a production by nitrification in the water column, which generates a mean flow to the atmosphere of  $0.8 \pm 0.3$  µmol m<sup>-2</sup> d<sup>-1</sup>. For the 2014-2016 period, average annual emissions have been estimated in the studied area of the Gulf of Cadiz  $(69.1 \cdot 10^2 \text{ km}^2)$  resulting in 23.7 Gg CO<sub>2</sub> y<sup>-1</sup>, 0.5 Gg CH<sub>4</sub> y<sup>-1</sup> and 0.1 Gg N<sub>2</sub>O y<sup>-1</sup>.

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

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### **BENTHIC PRODUCTION OF NUTRIENTS IN THE MAR MENOR**

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**Abstract:** The Mar Menor is a wide hypersaline coastal lagoon (135 km<sup>2</sup>) subjected to a high anthropic pressure that causes an intense eutrophication process, followed by a recovery of the macrophyte meadows. This study focuses on the distribution of the nutrients benthic fluxes and their influence on the system's waters quality. Therefore, 2 intensive campaigns were carried out in extreme seasonal conditions (winter and summer 2018) including the characterization of the water column, the exchange of nutrients with the sediment through benthic chambers, in addition to the study of the diagenetic routes associated with the degradation of the accumulated organic matter in its sediments.

The NO<sub>3</sub><sup>-</sup> average fluxes present an inversion, with positive values in winter (0.57 mmol m<sup>-2</sup> d<sup>-1</sup>) and negative in summer (-0.28 mmol m<sup>-2</sup> d<sup>-1</sup>); which show an intensification of the denitrification processes in the sediments with the increase in temperature. For NH<sub>4</sub><sup>+</sup> and HPO<sub>4</sub><sup>2-</sup> benthic fluxes, results show a seasonal variation, with mean values of 10.18 and 0.72 mmol m<sup>-2</sup> d<sup>-1</sup> in summer, and 4.9 and 0.08 mmol m<sup>-2</sup> d<sup>-1</sup> in winter, respectively. This increase is also consistent with the intensification of the oxidation processes of organic matter with temperature, which produce a release of these nutrients from the sediment, resulting in an increase of the benthic oxygen fluxes of up to a 27.2% in summer. These benthic fluxes represent an annual net input to the water column of 2354.25 t y<sup>-1</sup> of P and 8376.75 t y<sup>-1</sup> of N to the Mar Menor.

Although the contents of organic matter in the Mar Menor surface sediments are high (4.8–6.6%), the benthic fluxes values obtained are relatively common in coastal systems and explain the intense eutrophication processes that occur in the system.

Key words: Benthic fluxes, nutrients, eutrophication process, Mar Menor

Acknowledgments: This work was supported by Dirección General Mar Menor under contract TRAGSA – OT2018/024, and by the Spanish CICYT (Spanish Program for Science and Technology) under contract RTI2018-100865-BC21.

### BENTHIC PRODUCTION OF GREENHOUSE GASES IN THE GUADALQUIVIR ESTUARY (SW SPAIN)

### T. Ortega<sup>\*1</sup>, J. Sánchez-Rodríguez<sup>1</sup>, A. Sierra<sup>1</sup>, R. Ponce<sup>1</sup>, MC. Fernández-Puga<sup>2</sup>, A. Gómez-Parra<sup>1</sup> and J. Forja<sup>1</sup>

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Abstract: Benthic fluxes of dissolved oxygen (DO), inorganic carbon (DIC), total alkalinity (TA), dissolved methane and nitrous oxide were estimated by benthic chamber deployments at five stations along the salinity gradient in the Guadalquivir Estuary (SW Spain). The samplings were carried out in the extreme seasonal conditions of summer (September 2021) and winter (February of 2022). Sediment oxygen uptakes resulted moderate and ranged up to 80 mmol O<sub>2</sub> m<sup>-2</sup>d<sup>-1</sup>. Total alkalinity and inorganic carbon fluxes reached maximum values in summer affected by the high temperatures showing a similar behaviour to other coastal systems (Forja et al., 2004, Ferrón et al., 2009). DIC and DO benthic flux quotients were far in excess of unity, indicating the significance of the anaerobic degradation of organic matter processes. A great part of DIC benthic fluxes are due to CaCO<sub>3</sub> dissolution processes, which constitute, in some sampling stations, up to more than 50% of the total DIC flux. Benthic fluxes of methane varied from 0.2 to 170 µmol CH<sub>4</sub> m<sup>-2</sup>d<sup>-1</sup>. The highest values were observed in the innermost stations of the estuary highlighting the greater importance of methanogenesis compared to sulphate reduction. Benthic fluxes of N2O reached maximum values of 0.10  $\mu$ mol N-N<sub>2</sub>O m<sup>-2</sup> d<sup>-1</sup> in summer and, like methane, resulted with the highest values in the most riverine stations. These results highlight the importance of benthic production in the distribution of greenhouse gases in the Guadalquivir Estuary.

**Keywords**: Benthic fluxes, greenhouse gases, dissolved inorganic carbon, Guadalquivir estuary.

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

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# WET AND DRY DEPOSITION FLUXES OF SOLUBLE ELEMENTS IN THE CANARY REGION (2002-2022)

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Abstract: In this work, a data set of 20 years of dry (DD) and wet (WD) depositional fluxes in the Canary Islands region for the period February 2002 to February 2022 is presented. This is the longest time series of depositional fluxes in the eastern North Atlantic to our knowledge. The samples were collected at urban background site located in Tafira (269 m a.s.l), Gran Canaria. A total of 424 DD and 329 WD samples were collected. The average DD and WD fluxes were  $33.82 \pm 59.43$  and  $28.89 \pm 89.90$  mg m<sup>-2</sup> d<sup>-1</sup>, respectively. The DD and WD fluxes were determined by the seasonal patterns of the African dust inputs to the region. The air masses responsible for the highest depositional fluxes affect Canary Islands during the winter-early spring and summer in agreement with previous studies (López-García et al., 2013; 2017; 2021). The major ions (fluoride, chloride, bromide, nitrite, nitrate, phosphate, and sulphate), the dicarboxylic organic acids (acetate, formate and oxalate), the soluble trace metals (Ti, Fe, Mn, Co, Ni, Zn and Cu) and the pH were measured in the dust deposition samples using surrogate surfaces. Using the results obtained from Principal Component Analysis (PCA), a multivariate statistical method, three main sources from DD fluxes have been determined: marine (Na<sup>+</sup>, Cl<sup>-</sup>, K<sup>+</sup>, Mg<sup>2+</sup>), crustal-anthropogenic mixed  $(Ca^{2+}, PO_4^{3-}, C_2O_4^{2-}, HCOO^-, CH_3COO^-)$  and anthropogenic source  $(NO_3^-, nssSO_4^{2-})$ . Besides WD fluxes were characterized mainly by a marine component (Na<sup>+</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup>) and two different anthropogenic sources: (HCOO<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, NH<sub>4</sub><sup>+</sup>) and (NO<sub>3</sub><sup>-</sup>, nss-Ca<sup>2+</sup>, nss-SO<sub>4</sub><sup>2-</sup>). Although WD accounted for only 8.42 % of the total particle flux in the study period, the amount of atmospheric soluble metal inputs to the Region increased significantly during the raining seasons (more than 50% of the total Fe flux).

Key words: Particle Fluxes, Dry deposition, Wet deposition, major ions, trace metals

#### Acknowledgments:

This study was funded by the European Regional Development Fund through the Madeira-Açores-Canarias Territorial Cooperation Operational Program (POMAC) 2014-2020 through the ECOMARPORT (MAC/1.1b/081) and MAWADIPOL (MAC2/3.5B/334) projects. We would like to thank Drs. Matthew Patey and Patricia López García for his assistance in sampling collection and analysis.

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# INFLUENCE OF THE DIAGENETIC PROCESSES IN THE GREENHOUSE PRODUCTION IN THE ESTUARY OF GUADALQUIVIR

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**Abstract:** The Guadalquivir Estuary, the largest of the Gulf of Cadiz, 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, mainly due to a high poblation density, an important agricultural activity and navigation activities. Aditionally, this estuarine sector is located in the Doñana National Park, region with great environmental significance.

In 2021 September, an oceanographic cruise were carried out onboard R/V UCADIZ. Sediment samples were collected at 5 stations along a 67 km transect from the vicinity of La Puebla del Río, in the inner part to Sanlúcar de Barrameda, in the mouth of Guadalquivir. It was used a meso box-corer dredge, which was sub-sampled with polycarbonate tubes of about 50 cm in length and 9.5 cm in diameter. Methane and nitrous oxide concentrations were determined by gas chromatography.

The objetive of this research, is the study of the behaviour of the greenhouse gases CH4 and N2O in the sediment from the surface to 40 cm depth and across the estuarine system.

In general, methane profiles exhibit a concentration increase from the external sector towards the interior of the estuary system, with a very wide dispersion of values. The concentration range from 0.26 nM at the station closest to the mouth and 2453.48 nM at the

station furthest from the mouth.

Nitrous oxide profiles show a concentrations range from 0.015 nM at the station closest to the mouth and 3.658 nM at a station located in the intermediate sector between the mouth and the upper estuary.

The increase in methane concentration with depth in the sediment and the occurrence of subsurface maxima in nitrous oxide concentration highlight the relative importance of methanogenesis and denitrification/nitrification processes along the estuary.

Key words: methane nitrous oxide, sediment, Guadalquivir Estuary

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

# GUADALQUIVIR ESTUARY AS A MAJOR SOURCE OF DISSOLVED ORGANIC MATTER TO THE GULF OF CÁDIZ

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Abstract: The Gulf of Cádiz connects the North Atlantic Ocean and the Mediterranean Sea through the Strait of Gibraltar and receives freshwater input from different estuaries. Previous work found that Guadalquivir was the major contributor of dissolved organic matter (DOM) to the adjacent coast with a net flux of  $1.5 \times 10^5$  Gmol d–1 for dissolved organic carbon (DOC) (Amaral et al. 2020a). However, the fluxes estimated by the authors were during the dry season (n = 50), in the absence of precipitation, and when the lower discharge occurs. Here, we evaluated DOM composition using its optical properties along the salinity gradient and tidal cycles during seven oceanographic campaigns (n = 349). FDOM modeling was carried out by combining excitation-emission matrixes and the multivariate parallel factor analysis. We used a non-linear hydrodynamic model to estimate the net flux of DOC from the estuary to the coastal zone of the Gulf of Cadiz. Six fluorescent components were identified: two humic-like (terrestrial and microbial), two terrestrial photoproducts, and two protein-like, previously identified in the coastal and ocean zone of the Gulf of Cádiz (Amaral et al. 2020b). Overall, the humic fraction was the most abundant followed by the photoproducts and the protein-like material accounting for  $63\% \pm 8\%$ ,  $23\% \pm 5\%$ , and  $14\% \pm 8\%$ , of the total fluorescence, respectively. The net transport of DOC varies from  $6.8 \times 10^5$  Gmol d-1 in the dry season to  $2.3 \times 10^7$  Gmol d-1 in periods of intense precipitation. Around 70% of the FDOM exported was humic. Our results indicate a net transport of humic-like DOM from the Guadalquivir estuary to the Atlantic Ocean.

Key words: Dissolved organic carbon, Fluorescent DOM, tides, net transport, Guadalquivir estuary

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

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# POSTER COMMUNICATIONS ECOTOXICOLOGY AND MARINE POLLUTION













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# CHEMICAL, BIOLOGICAL, AND OCEANOGRAPHIC FACTORS AFFECTING LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS IN WESTERN AND CENTRAL MEDITERRANEAN SEAFOOD

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Abstract: in this work, we collected and harmonized the results of several studies achieved over the years, in order to obtain a database of georeferenced observations on polycyclic aromatic hydrocarbons (PAHs) in Western and Central Mediterranean seafood. For each observation in the database, we reported several information on the taxonomy and the ecology of the sampled species, as well as details on the investigated hydrocarbon, and spatial and temporal information on sampling. Moreover, we calculated two health risk indexes (i.e., Target Hazard Quotient – THQ – and Excess Lifetime Cancer Risk – ELCR) for each PAH record. Through several statistical methods, we conducted a meta-analysis of the data on some of the species in the database, identifying trends that could be related to the biology of the investigated organisms (e.g., reproductive cycle), as well as to the physicochemical properties of each hydrocarbon (e.g., solubility) and to the oceanographic characteristic of this part of the Mediterranean Sea (e.g., water masses circulation). The analysis of the data showed that, at a consumption rate like the one typical of the Italian population, seafood caught from the area considered in the present work seems to pose a minimal risk to health. However, we also found evidence of an increasing trend of PAHs concentrations in Mediterranean mussels, pointing to the need of a constant monitoring.

Key words: polycyclic aromatic hydrocarbons, seafood, Mediterranean Sea, meta-analysis, contaminants

**Acknowledgments:** The research leading to these results was conceived under the collaboration between the University of Bologna and the National Research Council for the implementation of the International PhD Program "Innovative Technologies and Sustainable Use of Mediterranean Sea Fishery and Biological Resources" (www.FishMed-PhD.org).

# PHYTO-TREATMENT OF AQUACULTURE EFFLUENTS USING MICROALGAE- BACTERIA TECHNOLOGY.

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#### Abstract:

Marine aquaculture has considerably increased its production growth in recent decades. Intensive aquaculture farms generate currents of concentrated solids corresponding to uneaten feed remains and fish feces [1]. These residues contain big amounts of organic matter and nutrients; species of nitrogen and phosphorus, which worsen water quality and produce eutrophication, facilitating the appearance of pathogens that endanger aquatic plants and animals, even the risk to public health [2].

In the present study, a purification treatment for the concentrated current of solids in an aquaculture farm dedicated to the cultivation of soles (*Solea Senegalensis*) with recirculation aquaculture systems (RAS) were studied [3]. The current was treated by a consortium of microalgae-bacteria. This consortium was cultivated in 8-liter reactors and operated in a discontinuous and semi-continuous mode to determine the kinetic modeling of the biological process (organic matter, nutrients removal, and production of biomass). Concerning the nutrient removal rate, a yield of 87% for N and 98% for P was achieved and 52% in the case of C.

The algal biomass was harvested by coagulation-flocculation and the final separation of biomass from the water was tasted by two techniques: flotation and decantation. The decantation was the best harvesting technique, using a concentration of 60 mg/L of coagulant and obtaining a greater biomass recovery efficiency of 93%. Furthermore, the biomass obtained was dehydrated by centrifugation, and the water obtained in this process was filtered through a sand filter to obtain a quality effluent.

The composition of algal biomass will be analyzed to use as a biofertilizer in agriculture. In this way, the life cycle impacts of microalgae systems will be able to get environmental and economic benefits.

Key words: renewable resources, wastewater treatment, nutrient removal, photobioreactor.

**Acknowledgments:** This work was carried out within the RECOVER Project "Recovery and valorization of surplus nutrients from the intensive marine aquaculture through biotechnology microalgae" (N° P18-RT-3406). Project co-financed 80% by the European Union, within the framework of the Operational Program ERDF Andalusia 2014-2020 «Intelligent growth: an economy based on knowledge and innovation".

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# DISTRIBUTION OF LEGACY AND EMERGING ORGANIC CONTAMINANTS IN COASTAL ENVIRONMENTS: A CASE STUDY IN THE TROPICAL COAST (GRANADA, SPAIN)

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Abstract: Contamination of aquatic systems by regulated or banned organic compounds and newly detected chemicals, represents a rising concern. The knowledge of their distribution and fate is more limited in marine than in freshwater ecosystems, especially true in sediments and suspended solids as their bioavailability and toxicity are severely reduced. This work is focused on investigating the spatial distribution of a wide range of both legacy and emerging compounds in water and sediment from a marine system (Tropical Coast of Granada, Spain) including polycyclic aromatic hydrocarbons, UV-filters, fragrances, organophosphorus flame retardants, organochlorine pesticides, polychlorinated biphenyls, polybrominated-biphenyls, polybrominated diphenyl-ethers and nonylphenol). 17 sampling sites to collect surface sediment and water from Cerro Gordo, La Herradura and Punta de la Mona. For aqueous samples, analyte extraction was carried out by stir bar sorptive extraction (SBSE) to determined non or less polar contaminants (Pintado-Herrera et al., 2012). For solid samples, extraction and clean-up were integrated into one step using pressurized liquid extraction (in-cell PLE) (Pintado-Herrera et al., 2016). Separation and quantification of target analytes were carried out by gas chromatography tandem mass spectrometry (GC-MS/MS). Organic matter was determined to find a correlation with concentrations of organic contaminants along the coast. The most prevalent contaminants belonged to PAHs (anthracene or phenanthrene) NP has attracted attention for its prevalence and potential effect as an endocrine disruptor. UV-filters (4-MBC or octocrylene) and fragrances (tonalide or galaxolide) were also found. Detected concentrations were associated to direct discharges of a sewage pipe in La Herradura. Areas which high levels of UV-filters and fragrances were associated to touristic activities (e.g. Cerro Gordo) specially in summer. Exceptionally, small fragments of coral tissues found were analysed to study the bioaccumulation of these contaminants. To the best of our knowledge, it presents the first data for some chemicals in the study area, detecting lower concentrations in water than in sediment and comparing the influence of the sampling period in the distribution of different contaminant classes. Further research is required to identify others organic compounds and the environmental status of the area.

Key words: Organic contaminants, Water, Sediment, Coral, Tropical Coast of Granada

**Acknowledgments:** Financial support was provided by Spanish National Project BIOCEMAS, RTI2018-096211-B-100. This research was partly supported by Coral soul NGO and Coral guardian NGO under special coordination for the sampling programme and marine conservation.

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Seminario Ibérico de Química Marina (SIQUIMAR) Las Palmas de Gran Canaria (Spain), 6-8<sup>th</sup> July 2022

# TEMPORAL AND SPATIAL VARIABILITY OF CHEMICAL INGREDIENTS RELEASED BY SUNSCREENS IN TWO URBAN BEACHES: INFLUENCE OF BEACHGOERS ON THE BEACH CONTAMINATION

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**Abstract:** With almost 30 millions of visitors each year, Andalusia is one of the most important tourist destinations in Spain. Most of these tourists make an intensive use of the coastal areas, particularly of beaches, which undoubtfully has environmental consequences in the coastal ecosystems. The growing awareness of the risks associated with skin exposure to ultraviolet (UV) radiation over the past decades has led to increased use of sunscreen products which are introduced mainly in the coastal waters, via release from the skin during swimming. In this work, the presence of the main organic (methylbenzylidene-camphor - 4MBC, benzophenone 3 - BP3, octinoxate -EHMC 2-ethylhexyl salicylate -EHS, homosalate- HMS and octocrylene-OC) and trace metals (V, Fe, Co, Ni, Cu, Zn, Cd, Mo, Pb and Ti) used some of them (Ti and Zn) in the formulation of sunscreen as inorganic ultraviolet filters, and with known environmental toxicity, were assessed in two representative beaches of Andalusian coast. The influence of bathers on the presence and levels of these UV filters were also studied. Two seasonal samplings (summer and winter) of different seawater compartments (surface microlayers and water column) were conducted in two urban beaches (one situated at the coastal area of the Mediterranean in Marbella and

other located in the Atlantic coast in Cádiz). Results indicated that the studied organic UV filters widely occur in urban beaches during summer. Differences in organic UV filters concentrations were observed between the surface microlayer and the rest of the water column, with higher values found in the first case. However, trace metals did not show significant concentrations among season and water compartments. Concentrations of organic UV filters were influenced by the weather and sea conditions, such as wind and wave action, which enhance the water exchange and minimize the residence time, enabling the detection of most of them in Marbella beach. Organic UV filters in seawater were undetectable in both beaches during winter season as a consequence of the lack of bathers during this season. In Cádiz beach, the concentrations of organic UV filters and some metals such as Fe and Mn in seawater were strongly correlated with the number of bathers present in each point. In the case of trace metals, it could be related with the sediment resuspension whiles that organic UV filters are released directly from the beachgoers skin during bath.

Key words: Ultraviolet filters, Skin care products, Sun and beach tourism, Marine contamination

**Acknowledgments:** This work is funded by the 2014–2020 ERDF Operational Programme and by the Department of Economy, Knowledge, Business and University of the Regional Government of Andalusia (project reference: FEDER-UCA18-106672) and by the Plan Andaluz de Investigación, Desarrollo e Innovación PAIDI 2020 (project reference: P20\_00271). A. Rodríguez-Romero is supported by the Spanish grant Juan de la Cierva Incorporación referenced as IJC2018-037545-I. We thank the Town Halls of Cádiz and Marbella, David Roque and Antonio Moreno for their support with the sampling in the field.

# DETERMINATION OF SUNSCREEN IN SEAWATER BY ULTRAVIOLET ABSORPTION SPECTROPHOTOMETRY

#### Antonio Tovar-Sánchez<sup>1</sup>, Erica Sparaventi<sup>2</sup>, Amandine Gaudron<sup>3</sup>, Araceli Rodríguez-Romero<sup>4</sup>

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Abstract: Sunscreen is released into the marine environment and is considered toxic for marine life. The current analytical methods for the quantification of sunscreen are specific to individual chemical ingredients and based on complex analytical and instrumental techniques. A simple, selective, rapid, reproducible and low-cost spectrophotometric procedure for the quantification of commercial sunscreen in seawater is described here. The method is based on the inherent properties of these cosmetics to absorb in the wavelength of 300-400 nm. The absorption at 303 nm wavelength correlates with the concentration of most commercial sunscreens. This method allows the determination of sunscreens in the range of 2.5 - 1500 mg/L, it requires no sample pretreatment and offers a precision of up to 0.2 %. The spectrophotometric method was applied to quantify sunscreen concentrations at an Atlantic Beach with values ranging from 10 to 96.7 mg/L in the unfiltered fraction and from the undetectable value to 75.7 mg/L in the dissolved fraction. This method is suggested as a tool for sunscreen quantifications in environmental investigations and monitoring programs.

Key words: Sunscreen, UV absorption, spectrophotometry, seawater, marine pollution

Acknowledgments: This work is funded by the 2014–2020 ERDF Operational Programme and by the Department of Economy, Knowledge, Business and University of the Regional

Government of Andalusia (project reference: FEDER-UCA18-106672). A. Rodríguez-Romero is supported by the Spanish grant Juan de la Cierva Incorporación referenced as IJC2018-037545-I. We thank the Town Hall of Cádiz, David Roque and Antonio Moreno for their support with the sampling in the field.

# HEAVY METAL BIOMONITORISATION VIA SMALL-SPOTED CATSHARK (Scyliorhinus Canicula (Linnaeus, 1758)) EMBRYOS: A VIABILITY ASSESMENT

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**Abstract:** A viability assessment on the heavy metal biomonitor potential of small-spotted catshark (*Scyliorhinus canicula* (Linnaeus, 1758)) embryos. Egg capsules were obtained from bottom trawl captured females which were excluded as bycatch by Calp's fishing fleet.

Lead and cadmium concentrations were analyzed in embryos from two treatment groups after a two and a half months exposure period. Dissolved heavy metal concentrations ranged from 0.05ppb to 12.49ppm for Cd and from 3ppb to 74ppm for Pb with a blank concentration treatment for both elements. Concentrations remained constant throughout the experiment.

Prior to sample analysis the matrix was pre-treatment and extracts were obtained via microwave assisted extraction (MAE). For the pre-treatment of the samples, each of them was frozen at -80°C, dried at 60°C for 48h or until o completely dry, and finally crushed to obtain a homogeneous sample. Subsequently, sample analysis was performed via graphite furnace atomic absorption spectrometry (GF-AAS)

Preliminary results suggest certain potential of this matrix for its use in heavy metal environmental biomonitorisation, with embryos being able to withstand and accumulate high analyte concentrations.

Key words: Scyliorhinus canicula, embryos, heavy metals, biomonitor

# PRESENCE OF MICROPLASTICS IN LOWER BASIN OF GUADALETE RIVER

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Abstract: Due to growing environmental concern, in recent times, the scientific community has focused more than ever on investigating the impact generated by anthropogenic activity on the environment and health. One of the issues on which the most efforts have been focused is that of microplastics that end up in aquatic ecosystems, and that, due to their small size and physical-chemical characteristics can cause serious damage to organisms that interact with them. Microplastics (MPs) are globally recognized as an issue of emerging concern in the environment. Microplastics are widely dispersed in the coastal and marine environment, and sediments are considered to be sinks for microplastics. This study highlights the presence of MPs in different matrices (water and sediment) from the lower basin of the Guadalete River, situated on the South of Spain. The sampling stations were selected due to their different exposure to anthropogenic activities and/or pressures. Sediment samples were collected using a box corer dredge and water samples were collected using neuston net. The samples (water and sediments) were physically and chemically characterized. The physical characterization consisted in visual examination of the samples, counting the number of MPs collected according to their size and shape abundance. For the physical analysis, the samples were examined under a Carl Zeiss Axio Imager M1m optical microscope. Chemical characterization comprised identification of the polymers that compose the microplastics. Chemical analysis was performed using Fourier Transform Infrared Spectroscopy (FTIR). The results clearly show the presence of MPs in all samples (waters and sediments). The main MPs shape was fibers (88.8%) followed by fragments (5.80%). Among the more of 20 polymer types identified by FTIR, the most prevalent ones were, polypropylene (PP) polyethylene(PE), ethylene vinyl alcohol (EVOH), polyvinyl chloride (PVC) and polyamide (nylon). These results show the influence of the population in the lower Guadalete River basin, as well as its impact on the environment.

Key words: Microplastics; polymers; estuary.

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

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**Abstract:** The protection of waters in Europe is regulated by the Water Framework Directive (WFD), mandatory for all European Union members. Detecting and monitoring the level of contaminants in seawater and inland waterways is a key element of this Directive [1]. In many cases, they are very difficult to determine by traditional techniques (spot sampling), particularly in transitional and coastal waters, and so there is an urgent need to find accurate, reliable, easy and cost-efficient alternatives. Passive sampling devices have several advantages compared to conventional monitoring methods, since this methodology can provide time weighted average concentrations integrated over a period of time, among others [2]. The aim of the MONITOOL project [3] is to adapt existing metal Environmental Quality Standards (EQS) for passive sampling devices (DGT-type), thus allowing their use to evaluate the chemical status of waters under the WFD and improving

the quality of the overall assessment in dynamic marine and estuary waters. To do this, in MONITOOL, two successful campaigns (wet and dry conditions) for DGT sampling were conducted, in addition to spot sampling and *in situ* parameter measurements. Common guidelines were produced [4,5] and followed by all partners to ensure the comparability and reproducibility of data obtained in different partner regions, covering a high variety of environmental conditions across the Atlantic and Mediterranean marine regions. After laboratory analysis and data treatment, results have provided a robust MONITOOL dataset on dissolved (spot sampling) and labile (passive sampling) metal concentrations [6]. MONITOOL has successfully adapted the existing metal EQS by DGT passive sampling devices for cadmium, nickel and lead, as well as for other metal ions under study. During the granted 18-month project-extension (January 2022-June 2023), the study will be extended searching for higher metal concentrations in order to validate and improve the obtained results.

**Key words:** Water Framework Directive (WFD), Passive sampling, DGT, Environmental Quality Standards (EQS), metals

**Acknowledgments:** The MONITOOL project is co-financed by the European Regional Development Fund through the Interreg Atlantic Area Programme (no contract: EAPA\_565/2016). We would also like to thank the other researchers involved in the project for their contribution to obtaining the results that are presented in this paper.

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# BIOACCUMULATION OF ORGANOCHLORINATED AND CURRENT USE PESTICIDES IN SEDIMENTS AND FISH SPECIES (CYPRINIFORMES, MUGILIFORMES AND SILURIFORMES) FROM EBRO DELTA (NE SPAIN)

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**Abstract:** The accumulation of contaminants in sediments and organisms is a recurrently observed process due to the presence and persistence of many of them in the environment, such as organochlorines and some current use pesticides (CUPs). In this study, the concentrations of polychlorinated biphenyls (PCBs: 28, 52, 101, 105, 118, 138, 153, 156 y 180) and organochlorinated pesticides (OCPs: p,p' DDT and metabolites p,p'DDD and p,p'DDE, hexaclorobenzene, lindane, aldrin, endrin, isodrin and dieldrin), together with some CUPs (pendimethalin, trichloronate, DCPA, tokuthion, prothiophos, fenchlorphos and chlorpyrifos) were determined in sediments and fish species from Ebro Delta.

Two sampling campaigns (summer 2018 and winter 2019) were performed for sediments with four sampling points in lower Ebro (from Miravet village to Deltebre village), four sampling points in Alfacs bay (south of the Delta), and four sampling points in Fangar bay (north of the Delta). Two sampling areas were considered in the lower stretch of Ebro Delta for the following fish orders: cypriniformes, mugiliformes and siluriformes. The sediment and fish muscle samples were freeze-dried, powdered and stored at -20°C. The extraction and purification of the compounds was carried out with Soxhlet method and analyzed by GC-MS/MS. PCBs, organochlorinated pesticides and some CUPs were found in sediments and fishes from Ebro Delta. In general, the concentrations found of organochlorinated compounds both in sediments and biota, were higher than those detected for CUPs, thus evidencing the high persistence of these compounds in the environment.

Key words: sediment, fish, pollution, persistent pollutants, CUPs

Acknowledgments: This work was supported by the Spanish Inter-Ministerial Science and Technology Commission through the 'PLAS-MED' (CICYT, CTM2017-89701-C3) project and by the European Union through the European Regional Development Fund (ERDF). M. García Pimentel acknowledges the Spanish Ministerial Science, Innovation and University for her pre-doctoral fellowship (PRE2018-085502).

# BIOACCUMULATION OF PERSONAL CARE PRODUCTS IN MARINE ORGANISMS

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**Abstract:** Personal Care Products (PCPs) are widely used in daily life and contribute to improve its quality. Many of these compounds are not efficiently removed by conventional sewage treatment plants (STPs) and thereby they are discharged into the environment making these chemicals ubiquitous in many aquatic ecosystems, including oceanic and coastal settings (Lara-Martín *et al.*, 2020). This, together with their physicochemical properties, could suppose a risk for wild organism exposed to them.

Three PCPs were considered for this study: triclosan (TCS) is a preservative and broadspectrum antimicrobial agent extensively used in household and personal care products; N,N-diethyl-meta-toluamide (DEET) is one of the most commonly used active ingredients in insect repellents and it has been largely detected in water samples; benzophenone-4 (BP-4) is a UV filter widely used in sunscreen formulations and as an anti-UV agent in many products, thus being commonly detected in aquatic ecosystems.

Gilt-head sea bream (*Sparus aurata*) and manila clam (*Ruditapes philippinarum*) were exposed to a nominal concentration of 10  $\mu$ g L<sup>-1</sup> of TCS, BP-4 and DEET in separated tanks using a continuous flow-through seawater system under controlled laboratory conditions for 22 days. Concentration of pollutants in the water was monitored during the whole experiment.

Fish and clam tissue samples were used to analyse pollutants bioaccumulation.

To optimize the extraction method, for the three compounds in the two biological matrices, automated (i.e., pressurized liquid extraction) and manual (i.e., sonication followed by a solid phase extraction clean-up step) extraction techniques, both implemented with different solvents with different polarities, were tested and compared. The results allowed to choose the best extraction method for each compound and showed that they accumulate in the organisms' tissue, ranging between 6 ng g<sup>-1</sup> d.w. and 3869 ng g<sup>-1</sup> d.w. in clam and between 36 ng g<sup>-1</sup> d.w. and 324 ng g<sup>-1</sup> d.w. in fish.

Key words: personal care products (PCPs), clam, gilt-head sea bream, bioaccumulation

**Acknowledgments:** This study was carried out with the support of a Spanish regional research project (P20-00953). G.Burbui was supported by the Erasmus + programme (KA 107).

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## EXPOSURE OF MICROPLASTICS AND PHARMACEUTICAL PRODUCTS TO Lactuca sativa

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Abstract: One of the sources of plastics into the environment are WWTPs, since, during water treatment processes, plastics transformed into microplastics are able to evade treatment and are released into the environment. Most of the microplastics that are captured during treatment in WWTPs are retained in sludge, 80% of which is used as fertiliser in agricultural sectors (Priyanka and Saravanakumar, 2019). Pharmaceutical products are another emerging pollutant of major concern. Much of our society relies on the use of these compounds. For all these reasons, in this study we have determined the effects caused by exposure to microplastics (polyethylene fibres) and drugs (simvastatin and carbamazepine) in Lactuca sativa. For this purpose, several germination tests were carried out with Lactuca sativa seeds (germination and elongation), with the aim of determining the possible alterations produced by these pollutants. The concentrations applied in the tests were concentrations found in the literature, in sewage sludge (Dierkes et al., 2019; Mahon et al., 2016; Yan et al., 2014), as this sludge is used as fertiliser in agriculture. The concentrations used were: Polyethylene: 0.3125; 0.625; 1.25; 2.5; 5 mg/mL, Carbamazepine: 0.415 ng/ML and Simvastatine: 63.34 ng/mL in different assays separately. After 5 days of exposure, the data were processed and it was found that there were no significant differences between the contaminants and the control, which allows us to assume that the concentrations of both drugs, available in sewage sludge, do not have acute toxicity effects on germination and elongation in these organisms. On the other hand, other concentrations of drugs higher than the previous ones were used in combination with microplastics (Polyethylene: 2.5 mg/mL; Carbamazepine: 5; 10; 20; 40; 40; 80 mg/L; Simvastatine: 2.5; 5; 10; 20; 40 mg/L), and growth alterations and signs of tissue necrosis were observed in the latter.

Key words: Microplastics, Simvastatine, Carbamazepine, Lactuca sativa,

**Acknowledgments:** We thank the financial support provided by the Junta de Andalucía (Secretaría General de Universidades, Investigación y Teconología) (P18-RT-2947)

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# DETERMINATION OF STEROID HORMONE RESIDUES IN SEA URCHINS

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The fact of preserving our environment from human impact has turned into a real challenge, in part due to the inefficient removal of toxic substances in WWTP, such as steroid hormones. This problem leads to the contamination of marine habitats, resulting on the degradation of ecosystems, leaving the need of developing methodologies to evaluate which compounds are affecting marine organisms (Parida et al., 2021). The study of the presence of steroid hormones in marine organisms such as sea urchins is very interesting because it could be used as bioindicators, since they feed on algae, and they are constantly in contact with the sediment (Parra-Luna et al., 2020). Because of the low concentrations of steroid hormones in marine environments, it is necessary to develop an extraction procedure that allow to extract and preconcentrate these pollutants. Microwave-assisted extraction (MAE) has been used due to many advantages in comparison with traditional extraction techniques. In this regard, MAE uses low volumes of organic solvents, easy handling of samples and the use of microwaves provides very selective extractions.

This study presents the optimization of an analytical method to determine 15 hormones in sea urchins. The different variables (type of solvent, solvent volume, extraction time and extraction temperature) that affect the extraction procedure have been studied following factorial experimental designs. The extraction method, coupled to ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS), showed very appropriate analytical parameters and it was applied to samples of 3 different species of sea urchins of the Canary Islands (*Arbacia lixula, Paracentrotus lividus and Sphaerechinus granularis*) found in different locations around the island of Gran Canaria (Spain).

Key words: Steroid hormones, microwave-assisted extraction, sea urchins

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# A COMPARATIVE STUDY OF TROPHIC INDEXES IN COASTAL WATERS OF THE NW ALBORAN SEA

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Abstract: This study analyses the behaviour of different trophic indexes (TRIX, UNTRIX, and Eutrophication Index) in coastal waters of the northwestern Alboran Sea in response to the oceanographic variability throughout a seasonal cycle. The study is based on data collected in autumn, winter, spring and summer at several locations stations off the Malaga coast. UNTRIX values were always lower than TRIX values and both presented a relatively high variability with similar seasonal patterns. Likewise, both index showed higher values in spring, coinciding with upwelling and higher clorophyll-a and nutrient concentrations. The TRIX-UNTRIX difference was not constant. The higher difference was in summer and autumn, coinciding with the presence of a marked thermocline and low nutrient concentrations. The lower TRIX-UNTRIX difference was found in spring, coinciding with the upwelling. The results of the statistical analysis (PCA) indicate that the difference TRIX-UNTRIX was highly and negatively correlated to nutrients, while the variability of dissolved oxygen and chlorophyll-a contributed less to the variability of the difference TRIX-UNTRIX. These outcomes indicate that nutrient variability have a noticeable influence on the difference between these two trophic indexes. As to the Eutrophication Index (EI), the value was also largely dependent on nutrient concentrations. The higher mean value of EI was in spring, coinciding with the upwelling, although in general the variability was extremely high throughout the seasonal cycle. The results show that the high oceanographic variability in the area of study led to a high variability of the different trophic indexes. In particular, the extremely high variability of EI makes this index unsuitable for estimating the trophic status in the area of study.

Key words: TRIX, UNTRIX, EI, trophic indexes, Alboran Sea

# DISTRIBUTION OF LEGACY AND EMERGING ORGANIC CONTAMINANTS IN COASTAL ENVIRONMENTS: A CASE STUDY IN THE TROPICAL COAST (GRANADA, SPAIN)

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Abstract: Contamination of aquatic systems by regulated or banned organic compounds and newly detected chemicals, represents a rising concern. The knowledge of their distribution and fate is more limited in marine than in freshwater ecosystems, especially true in sediments and suspended solids as their bioavailability and toxicity are severely reduced. This work is focused on investigating the spatial distribution of a wide range of both legacy and emerging compounds in water and sediment from a marine system (Tropical Coast of Granada, Spain) including polycyclic aromatic hydrocarbons, UV-filters, fragrances, organophosphorus flame retardants, organochlorine pesticides, polychlorinated biphenyls, polybrominated-biphenyls, polybrominated diphenyl-ethers and nonylphenol). 17 sampling sites to collect surface sediment and water from Cerro Gordo, La Herradura and Punta de la Mona. For aqueous samples, analyte extraction was carried out by stir bar sorptive extraction (SBSE) to determined non or less polar contaminants (Pintado-Herrera et al., 2012). For solid samples, extraction and clean-up were integrated into one step using pressurized liquid extraction (in-cell PLE) (Pintado-Herrera et al., 2016). Separation and quantification of target analytes were carried out by gas chromatography tandem mass spectrometry (GC-MS/MS). Organic matter was determined to find a correlation with concentrations of organic contaminants along the coast. The most prevalent contaminants belonged to PAHs (anthracene or phenanthrene) NP has attracted attention for its prevalence and potential effect as an endocrine disruptor. UV-filters (4-MBC or octocrylene) and fragrances (tonalide or galaxolide) were also found. Detected concentrations were associated to direct discharges of a sewage pipe in La Herradura. Areas which high levels of UV-filters and fragrances were associated to touristic activities (e.g. Cerro Gordo) specially in summer. Exceptionally, small fragments of coral tissues found were analysed to study the bioaccumulation of these contaminants. To the best of our knowledge, it presents the first data for some chemicals in the study area, detecting lower concentrations in water than in sediment and comparing the influence of the sampling period in the distribution of different contaminant classes. Further research is required to identify others organic compounds and the environmental status of the area.

Key words: Organic contaminants, Water, Sediment, Coral, Tropical Coast of Granada

**Acknowledgments:** Financial support was provided by Spanish National Project BIOCEMAS, RTI2018-096211-B-100. This research was partly supported by Coral soul NGO and Coral guardian NGO under special coordination for the sampling programme and marine conservation.

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# POSTER COMMUNICATIONS

# **GLOBAL CHANGE**













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### METABOLOMIC RESPONSE IN A GLOBAL CHANGE CONTEXT: THE CASE OF MARINE SPONGE *Aplysia aerophoba* NARDO, 1843

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#### Abstract:

Many benthic invertebrates, such as sponges, are known to develop defensive strategies against potential predators and fouling. The constant and accelerated global change of our planet could have an effect on these functions, altering the normal relationships within organisms. The aim of this study, included in the MultiCab project, is to evaluate the potential effect of rising temperatures and ocean acidification due to climate change on the Mediterranean demosponge Aplysina aerophoba Nardo, 1843. Samples were collected in 2018 in Alcudia Bay (Mallorca), and transferred to Jaume Ferrer Station Research located in the South-East of Menorca, where the experiments were carried out. Sponges were kept alive at different temperatures (20°C, 25 °C, 30°C) and with two acidification situations (pH= 7,8 and pH= 7,65) along four months. Organic solvents were used for extracting the bromotyrosine derived compounds; additionally, HPLC and Liquid chromatography-mass spectrometry (LC-MS) were performed for further analysis and quantification. The current study has revealed a change in A. aerophoba chemical composition, and therefore in the amount of the different metabolites produced, against temperature and pH variations. These changes may affect their ability to survive in the field and, since Porifera are significant components of benthic biodiversity, the entire ecosystem could be compromised. Responses to stressors are very specific to each group of invertebrates, thus, further research about abiotic global change influencing them is required.

**Key words:** marine chemical ecology, marine benthos, global climate change, temperature stress, ocean acidification, metabolomics.

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VIII International Symposium on Marine Sciences 2022 (ISMS) Las Palmas de Gran Canarias (Spain), 6-8<sup>th</sup> July 2022

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