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# Implementation of a portable module for assessing the eutrophication risk: initial evaluation in the upwelling-driven bay of Ria de Arousa (NW-Iberian Peninsula)

Paula C. Pardo[1,*], Susana F. Bastero[1], Laura Moreno[1], Carmen G. Castro[1]

[1] Instituto de Investigación Mariñas - CSIC (Rúa de Eduardo Cabello, 6, 36208 Vigo, Pontevedra, Spain)

* Corresponding author: pconde@iim.csic.es

## ABSTRACT

This study presents the implementation of a portable module designed for autonomous analysis of sea-surface inorganic nutrients onboard vessels of opportunity, as an additional tool for assessing the levels of eutrophication risk. The study was carried out during August-mid-September 2019 in the Ria de Arousa and outer shelf area (NW-Iberian coastal upwelling system). During this period, the distributions of the measured sea-surface concentrations of nitrate and phosphate were compared according to three Oceanographic Environments (OEs). The OEs were defined according to the interplay between upwelling/downwelling events and river discharge on the coastal system. The nutrient measurements agreed well with the OEs, showing that the portable module is a useful tool for opportune measurements of sea-surface nutrients and can serve as a complement for the available monitoring networks. An initial evaluation of the eutrophication risk in this area indicated low risk levels (following the Environmental European Agency criteria) for most of the measured points in summer, except for some vulnerable areas under certain OEs. Nutrient concentrations are sensitive to periods of *Sustained Upwelling* events, reaching medium risk levels (7.14 – 9.05 µmol $L^{-1}$ for nitrate and 0.39 – 0.64 µmol $L^{-1}$ for phosphate) in inner parts of the Ria de Arousa. These areas are characterized by abrupt bathymetric changes that channel and intensify the upwelling processes, increasing sea-surface nutrient concentrations. High eutrophication risk levels of phosphate (1.53 µmol $L^{-1}$) were detected close to the coastline during *Upwelling Relaxation* periods. Under these conditions, continental flows, previously retained by the upwelling, are able to expand. The location of these samples and the difference in concentration between phosphate and nitrate indicate a most likely source in wastewater outflows. Our results highlight the need for deeper studies on the synergy between upwelling/downwelling processes and the continental water discharges and its modulation of sea-surface nutrients.

**Descriptors:** Nitrate and phosphate; WIZ-4 probe; Upwelling system; Coastal environmental risks; NW-iberian peninsula.

## INTRODUCTION

Coastal systems are highly productive areas that account for 20-50% of the global ocean primary production while occupying only 7% of the ocean surface (Wollast, 1998). These regions are significant socio-economic areas that attract ~ 680 million people, a number expected to increase to one billion by 2050 (Oppenheimer et al., 2019). Therefore, coastal systems are going to be highly impacted by anthropogenic activities (Sale et al., 2014). Eutrophication is one of the environmental risks caused by human activities that can severely affect marine coastal ecosystems and that

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results from the increase in the concentration of nutrients (mainly nitrogen and phosphorous) in the water column (Nixon and Fulweiler, 2009; Malone and Newton, 2020). The most common cause of coastal nutrients increase is the use of fertilizers in agriculture, which brings nitrogen and phosphorous components to the sea transported by fluvial systems (Vitousek et al., 1997; Johnson and Harrison, 2015). In addition, wastewater not properly treated can also increase the nutrients supply in coastal waters as well as groundwater and atmospheric deposition (Galloway and Cowling, 2002; van Drecht et al., 2009; Nixon and Fulweiler, 2009).

The process of marine eutrophication implies different consecutive steps (Selman et al., 2008; Malone and Newton, 2020). In the first step, it promotes microbial community blooms, some of them toxic, and opportunistic macroalgae. These proliferations can lead to a decrease in the amount of light that penetrates into the water column and to an increase in organic matter content once the organisms die, with the consequent decrease in oxygen due to organic matter remineralization. In addition, the increase in abundance of autotrophic organisms can, in turn, increase the number of heterotrophs, increasing the oxygen demand of the ecosystem as well (Malone and Newton, 2020). Under these conditions, eutrophication processes are ultimately able to alter the trophic structure of coastal marine environments and deteriorate water quality, consequently affecting the coastal ecosystem services (Costanza et al., 1997; Millennium Ecosystem Assessment, 2005). The European Union (EU) has defined indicators to halt the loss of biodiversity and preserve the environmental status of marine coastal waters, including nutrient concentration in the water column (EEA, 2007; EEA 2009).

One way to measure dissolved inorganic nutrients is using automated probes such as the WIZ-4. These types of probes have been most frequently used in lakes and lagoons or fixed to moorings or coastal infrastructures in the marine environment (Wild-Allen and Rayner, 2014; Bodini, 2015). The main objective of this study is to implement a portable module (with an integrated WIZ-4 probe) onboard vessels of opportunity, as a complementary tool to assess eutrophication risk in the coastal upwelling system of the NW-Iberian Peninsula. The NW-Iberian coast is monitored by the observational network of the RAIA Observatory (www.marnaraia.org) that covers the Euroregion of Galicia - Northern Portugal. The observational network includes data from buoys, tide gauges, meteorological stations, HF radars, and hydrographic cruises. The hydrographic cruises are repeated weekly inside the bays and monthly on certain areas of the shelf, and include measurements of seawater nutrient concentrations. The portable module presented herein was designed to serve as a complementary tool for the existent hydrographic cruises repeats at RAIA Observatory. The module can be easily mounted on any vessel of opportunity, allowing for sampling different variables in areas of the shelf and during periods of time that the current RAIA's monitoring systems do not cover.

The reliability of the portable module was tested aboard the Tyba-III vessel during August-mid-September 2019, under the framework of the MarRISK project (https://keep.eu/projects/21783/Adaptation-to-climate-chang-EN/). The sampling cruises were carried out in an area of the NW-Iberian coast and adjacent shelf. The NW-Iberian coast and adjacent shelf belong to the northern extension of the Canary Eastern Boundary Upwelling Ecosystem and constitute the most important upwelling region in Europe (Fraga, 1981; Figueiras et al., 2002). The measured sea-surface concentration of nitrate and phosphate were validated in relation to different Oceanographic Environments (OEs). The OEs were identified by analysing the variability in the oceanographic and meteorological conditions (upwelling/downwelling processes, river discharge and thermohaline properties) during the period of study. Finally, we made an initial evaluation of the nutrient levels found to study the potential implications of the different OEs on the eutrophication risk in this coastal upwelling system during summer.

## METHODS

### Study area

The coast of the NW-Iberian upwelling system is characterized by numerous bays called rias, whose water biogeochemical properties result from the interaction between the dynamics of the river inputs and the open ocean (Vidal Romani, 1984; Evans and Prego, 2003). The term "*rias*" designates a certain type of incised valleys where the estuarine zone can move according to climatic changes. Regarding the NW-Iberian rias, only the inner part can be considered an estuary from both hydrographic and sedimentological points of view (Evans and Prego, 2003). Specifically, this study was carried out in one of the rias, Ria de Arousa, and on the continental shelf in front of it (Figure 1). The rias are characterized by a 2-layer circulation, with fresher water running off to the open ocean in surface layers (promoted by the rivers discharge on the head of the rias) and oceanic water entering the rias through deeper layers to compensate for the surface water transport (Fraga and Margalef, 1979).

In addition, the NW-Iberian coastal area is affected by upwelling/downwelling processes linked to the seasonality of the atmospheric pressure systems (Fraga, 1981; Bakun and Nelson, 1991; Castro et al., 2000). The upwelling season (when upwelling events are more frequent) usually extends from late spring to early autumn, produced by the location of the Azores High to the NW of the Iberian Peninsula (Wooster et al., 1976; Bakun and Nelson, 1991). At the end of this period, the Azores High moves southward between winter and spring, promoting southerly winds and favoring an increase in the frequency of downwelling events over the NW-Iberian coast. In general, however, wind regime variability can be relatively high during short-time periods, and upwelling and downwelling events can alternate during both seasons (Alvarez-Salgado et al., 2003).

Upwelling events involve the pumping up to the sea surface of cold and nutrient-rich deep waters, while downwelling events pile up nutrient-depleted open-sea surface water towards the coastline. Due to the effect of upwelling events, the NW-Iberian coast represents ~25% of the world mussel production (Figueiras et al., 2002), with Ria de Arousa having the highest raft density in the area. Ria de Arousa has a SW-NE orientation with a total surface area of ~ 239 km$^2$, length of ~33 km, and an average width of ~9 km (Figure 1). In the outermost part of the ria, Salvora island divides the entrance into two mouths: a narrow northern mouth ~10 m deep and a wider southern mouth 50–60 m deep (Figure 1). From the south mouth to the innermost parts of the ria, the water column depth progressively decreases to less than 20 m.

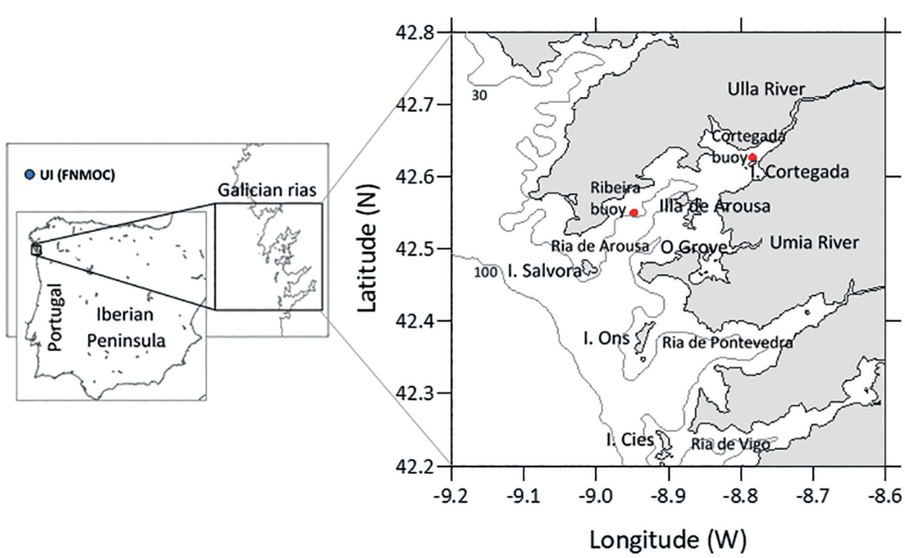


**Figure 1.** Study area in the NW-Iberian Peninsula with the locations of Ria de Arousa, Ria de Pontevedra and Ria de Vigo as well as the FNMOC point for the estimate of the Upwelling Index (data distributed by the US Navy Fleet Numerical Meteorological and Oceanographic Center). The names of the islands and the location of the Cortegada and Ribeira oceanographic buoys in Ria de Arousa are also shown.

Two main rivers flow into this estuary, the Ulla and the Umia, the prior being the main continental water discharge in the area. (Rosón et al., 1997).

The population of the Galician Rias (Figure 1) has increased more than 75% since the 1900s (Goerlich Gisbert et al., 2015), and its coastal areas are the most populated of the NW-Iberian Peninsula (Galician Institute of Statistics, IGE). Fishing is the main primary sector activity in this coastline (11% of Spanish fishing), together with aquaculture and shellfish harvesting and farming. These activities give employment to more than 20 thousand people (IGE, data from 2019). The secondary sector also generates significant employment through industries related to the production of canned, frozen, and processed marine products as well as shipbuilding. Tourism is also important in the area, with a mean occupancy of ~40% in hospitality establishments (IGE, data from 2019). All these activities can have different environmental implications that can alter the risk of eutrophication of the coastal area, specially through continental outflows.

## Multi-parameter module and WIZ-4 nutrient probe

Nutrient analysis technologies are based on optical sensors, ion selective electrodes, and wet chemistry analysis (Bende-Michl and Hairsine, 2010; Pellerin et al., 2016), the latter being the most suitable for detecting very low concentrations of nutrients in marine environments (Patey et al., 2008; Ma et al., 2014; Bodini, 2015). Most automated wet chemical analysers have been commonly deployed on moorings and coastal infrastructures (Wild-Allen and Rayner, 2014; Bodini, 2015). However, they require a fixed or floating platform with a power supply and constant maintenance, and involve the risk of loss during periods without surveillance. In the context of the MarRISK project, a portable module was designed for unattended and continuous analysis of surface nutrients aboard small vessels. This module involves an automated wet chemical analyser, the WIZ-4 probe (Systea S.p.A., Anagni, Italy) mounted on a continuous pumping circuit for collecting sea-surface water samples (Figure 2). Although the WIZ-4 probe was designed to be submerged up to 8 m, using it on board avoids dealing with biofouling risk (Chen and Crossman, 2021).

To ensure data quality, diligent maintenance, calibration, and data post processing by experts are required (Li et al., 2008; Wild-Allen and Rayner, 2014). Once the probe has been calibrated at the laboratory for each sampling cruise, the complete set is easily transportable and mountable onto small vessels by any user with basic training. Its versatility allows for different modes of operation for the automated sampling. The probe is programmable and activated via an RS-232 serial port with an external computer using the Sysmedia program. The configuration options to activate the probe also include the use of a datalogger via SMS with a Zetalog serial controller or via the Internet by the Systea Web App. Our module's circuit was also designed to be coupled to other equipment for continuous analyses, specifically to a SBE45 thermosalinograph by Sea-Bird Scientific, for sea surface temperature (SST) and sea surface salinity (SSS) measurements, and an AFT-pH sensor by Sunburst Sensors for sea surface pH measurements. However, the incorporation of these last two instruments in the module was not possible for this study due to limitations with the seawater pumping circuit on the vessel of opportunity.

The WIZ-4 probe consists of a lower analytical unit and an upper reagent canister (Figure 2). The analytical unit is composed of a peristaltic pump, hydraulic manifold, flow-cells, heating coil, and UV units (Copetti et al., 2017). The seawater sample is pumped through the module PVC circuit into a 250 mL flexible bag before entering the nutrient analyser. The sample is previously filtered by passing through a fiber cartridge and a 0.1 micron-filtration unit. When the nutrient analysis is finished, a washing cycle is activated. This probe model allows for the analysis of up to four parameters sequentially (nitrate + nitrite, nitrite, phosphate, and ammonium). In this study, it was programmed for sequential measurement of nitrate + nitrite and phosphate every 40 min, which implies long-duration cruises (10-14 hours).

The probe operates under the automated micro-loop flow analysis (µLFA) technology patented by Systea S.p.A (Moscetta et al., 2009; Azzaro,

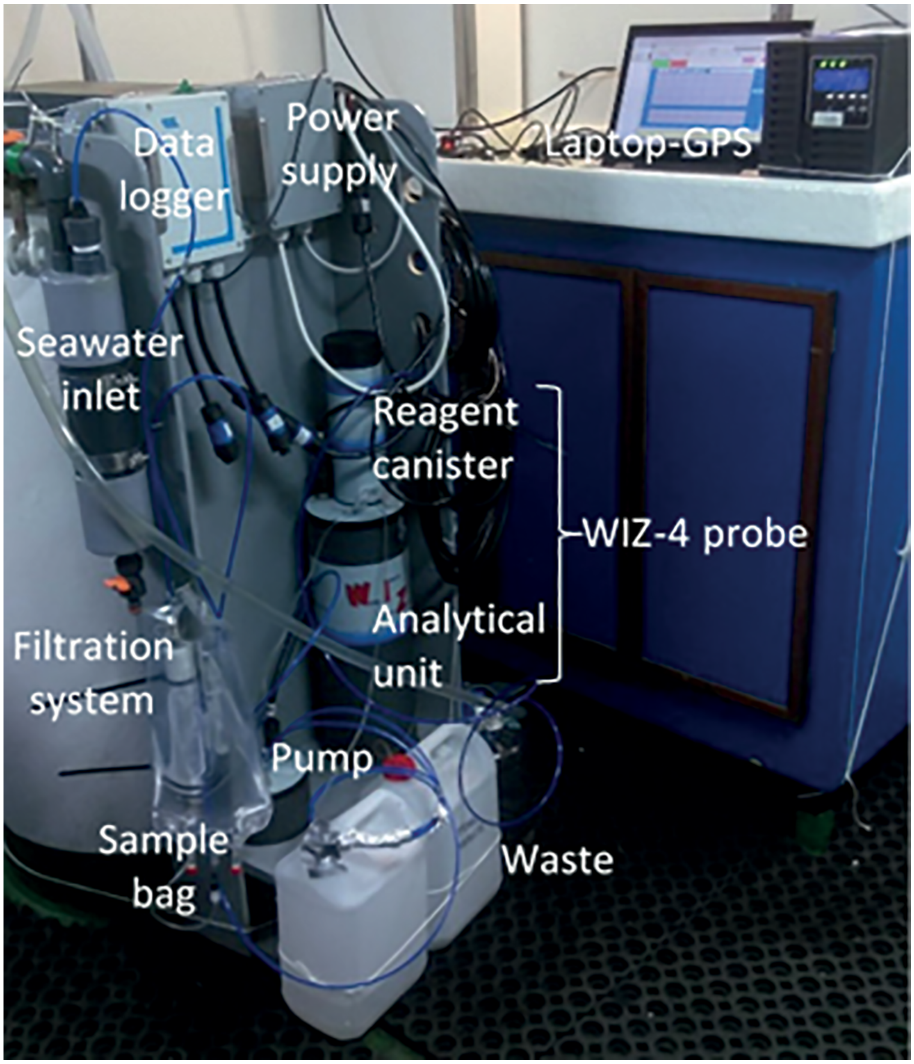


**Figure 2.** Multi-parameter module integrated by the WIZ-4 probe of Systea on a pumping circuit and a seawater filtration system.

2013). The species are analysed within the same circuit by means of opening-closing sequential valves for the inlet and mixing of chemical reagents with the sample. The main advantages of this technology are the low reagent consumption (~30-60 µL/analysis) and the analysis of up to four parameters using a single sample unit. Nitrate and nitrite are measured by UV-photoreduction of nitrate as nitrite and spectrophotometric quantification of a pink azo dye at 525 nm (Zhang and Wu, 1986; Grasshoff et al., 1999; Strickland and Parsons, 1968). DTPA solution and TRIS buffer are added, and nitrite react with NED and SAA to form a colored complex. Phosphate determination follows the phosphomolybdenum method by using molybdate solution and ascorbic acid, and blue complex is measured at 880 nm (Murphy and Riley, 1962; Strickland and Parsons, 1968; Grasshoff, et al., 1999). A set of standards of known concentration (12 µmol $L^{-1}$ N-$NO_3$; 10 µmol $L^{-1}$ P-$PO_4$) was previously measured to establish the relation between optical density and concentration. Testing with calibrant solutions was done both in the laboratory and in the field. Precision was evaluated from the relative standard deviation (% RSD) of the standard solutions measurements, with a % RSD average of 2.29 for nitrate and 0.94 for phosphate.

### Seawater sampling

Surface seawater samples were collected on different days during August-mid-September 2019 at different points in Ria de Arousa and the adjacent continental shelf (Figure 3A). Nitrate and phosphate concentrations were analyzed *in situ* with the WIZ-4 probe installed aboard the vessel Tyba III (11-meter-long Princess 37V Hull model) of the Bottlenose Dolphin Research Institute (BDRI) located at O Grove in Ria de Arousa (Figure 1). The BDRI performs systematic cruises to monitor marine mammals along the NW-Iberian coast, providing an opportunity to carry out oceanographic observations. The path of the cruises, which were dependent on the cetacean routes and the weather conditions, limited the area and frequency of sampling. The summer season was chosen for this testing because the weather conditions are better and the BDRI cruises are more frequent. Overall, the collaboration with BDRI was very useful and positive to test the new measurement equipment at a reduced cost.

Data in this study were the result of four cruises conducted on August 14th, 22nd and 30th and September 12th 2019 (Figure 3A). The location of the sampling stations was determined by a GlobalSat USB-GPS receiver for real-time navigation. On August 14th and 30th, the sampling stations were all located inside Ria de Arousa (Figure 3A). On August 22nd, most of the samples were taken in the continental shelf area close to Ria de Arousa, Ria de Pontevedra, and Ria de Vigo (Figure 3A, Figure 1). On September 12th, the sampling stations were located in the innermost area of Ria de Arousa, north of the inner island called Illa de Arousa (Figure 3A, Figure 1).

## Oceanographic and meteorological datasets

### Upwelling index

To estimate the volume of water transported towards and off the coast due to the action of northerly-southerly winds, we used the Upwelling Index (Bakun, 1973). The Upwelling Index is related to the Ekman transport (-Qx, $m^3\ s^{-1}\ m^{-1}$) by:

$$\mathrm{UI} = -\mathrm{Q_x} \times 10^3 = \frac{\rho air^{C}{}_{D} \,|\, V \,|\, V_y}{\rho_{sw}\ \mathrm{f}} \times 10^3 \qquad (1)$$

where UI is the Upwelling Index ($m^3\ s^{-1}\ km^{-1}$), $\rho_{air}$ is the air density (1,22 Kg $m^{-3}$) at 15 °C, $C_D$ is the empirical wind curl coefficient ($1{,}4 \cdot 10^{-3}$), $|V|$ is the mean daily wind velocity module ($m \cdot s^{-1}$), $V_y$ is the velocity of the component of the wind parallel to the coast, $f$ is the Coriolis parameter ($9{,}95 \cdot 10^{-5}$ $s^{-1}$) at 43° N, and $\rho_{sw}$ is the seawater density (1025 $Kg \cdot m^{-3}$).

Positive values of UI indicate the dominance of northerly winds responsible for upwelling events while negative values are related to downwelling

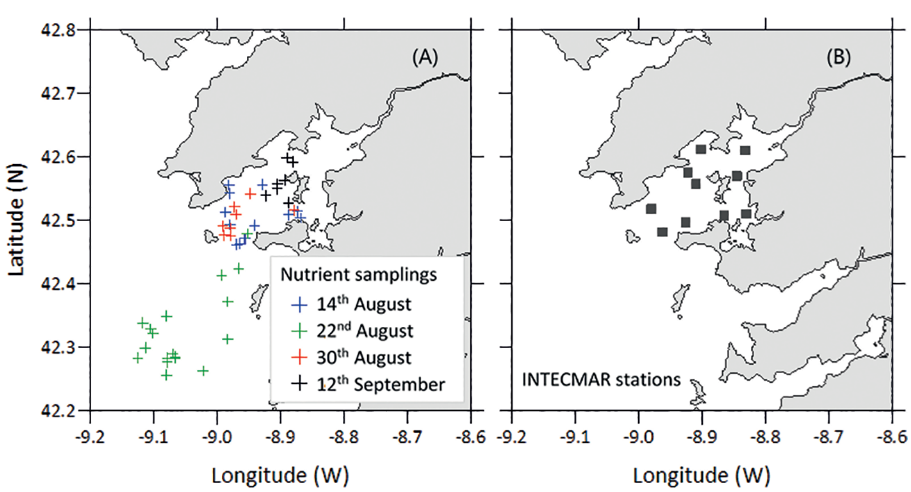


**Figure 3.** Location of (A) the nutrient measurement stations, with colors indicating the different sampling dates and (B) the INTECMAR stations where SSS and SST data were retrieved weekly for the same period.

processes. In this study, we used UI data for the NW-Iberian shelf (Figure 1) delivered by the Spanish Institute of Oceanography (IEO, www.indicedeafloramiento.ieo.es). Winds to obtain UI are estimated from surface atmospheric pressure fields (WXMAP atmospheric model) and distributed by the US Navy Fleet Numerical Meteorological and Oceanographic Center (FNMOC) in Monterey, California. 6-h UI data were downloaded from the IEO portal for the period August-mid-September 2019 and averaged to obtain daily UI data.

### River discharge

To analyse the fresh water input into the area of study, we downloaded the runoff data for the Ulla River that discharges at the head of Ria de Arousa (Figure 1). Daily flow from the Ulla River ($Q_R$) from August to September 2019 was obtained from the river gauging-station network (Ulla_Teo, 42.76°N 8.55°W) managed by Augas de Galicia and distributed by MeteoGalicia (Regional Bureau of Meteorology, http://www2.meteogalicia.gal/servizos/AugasdeGalicia/estacions.asp?request_locale=gl). The second most important river in Ria de Arousa is the Umia River. Data from the Umia River was not available at Augas de Galicia for the period of study. However, its input is only ~36% of the mean daily discharge from Ulla River (Otero et al., 2010).

### Time series of Sea Surface Temperature and Salinity

Time series of SST and SSS were obtained from two oceanographic buoys included in RAIA Observatory (www.marnaraia.org). The Ribeira buoy is located in the central area of Ria de Arousa, close to the northern coast in front of Ribeira village (Figure 1). The Cortegada buoy is located next to Cortegada island, close to the head of the ria, where the Ulla River discharges (Figure 1). 10-min data from both buoys were downloaded for the period August-mid-September 2019 and averaged to obtain daily time series of SSS and SST.

### Horizontal distributions of SST and SSS

SST and SSS were also obtained from the observational network at RAIA distributed by the Technological Institute for the Monitoring of the Marine Environment (INTECMAR) (http://www.intecmar.gal/Ctd/Default.aspx). INTECMAR is a public entity dedicated to the quality control of the marine environment and the implementation of policies related with the health control of sea products. INTECMAR carries out weekly samplings in 43 oceanographic stations distributed mostly in the coastal bays of the NW-Iberian coast, including Ria de Arousa (Figure 3B). The oceanographic stations cover the main mussel production areas and consist of vertical profiles done with Conductivity-Temperature-Depth (CTD) devices equipped with probes for different variables. SSS and SST were measured by INTECMAR in Ria de Arousa on August 5th, 12th, 20th and 26th, and September 3rd and 9th 2019.

### Eutrophication risk evaluation

According to several directives developed in the European Commission (Nitrates Directive 1991; Urban Wastewater Treatment Directive, 1991; Water Framework Directive WFD, 2000; Marine Strategy Framework Directive MSFD, 2008), the European Environment Agency (EEA) considers the trends in historical winter means of nutrient levels an environmental indicator for assessing eutrophication risk (EEA, 2009). Different nutrient concentration ranges for the Euroregions in Northern Europe and the Mediterranean Sea have already been proposed by the EEA (EEA, 2019). However, the EEA has not yet published any information on the eutrophication levels in the Euroregion of Galicia-Northern Portugal.

In this sense, in order to make an initial evaluation of the eutrophication risk in our study area, we use the nutrient concentration limits established for the Euroregion of Galicia-Northern Portugal by the working groups of the MarRISK project (https://marrisk.inesctec.pt/public/#!/indicators, Bastero et al., in prep.). These nutrient limits follow the EEA criteria, with different concentration ranges of nitrate and phosphate indicating low, medium, and high eutrophication risk levels. In terms of nitrate, values lower than 7.14 µmol L-1 indicate low risk, values between 7.14 and 60.71 µmol L-1 indicate medium risk, and values higher than 60.71 µmol L-1 indicate high risk. With respect to phosphate concentrations, values lower than 0.39 µmol L-1 are indicative of low risk, between 0.39 and 1.13 µmol L-1 indicate medium risk, and higher than 1.13 µmol L-1 indicate high risk.

## RESULTS AND DISCUSSION

### Oceanographic Environments and nutrient concentrations

Considering the evolution of the sea-surface oceanographic conditions of the area of study from August until mid-September 2019, we were able to identify three Oceanographic Environments (OEs): (1) *Downwelling event followed by relaxation (August 1st-17th)*; (2) *Sporadic upwelling event (August 18th-28th)*; and (3) *Sustained upwelling event (August 28th -September 15th)*.

These OEs represent relatively short time-periods (between 9-20 days) characterized by the different roles that the wind-driven circulation (upwelling/downwelling events) and river discharge have on the dynamics and thermohaline characteristics of the coastal system. The identification of the OEs was based on the time series of UI, $Q_R$, SST, and SSS at Cortegada and Ribeira buoys (Figure 4) and the horizontal distributions of SST and SSS obtained from the INTECMAR's observational network (Figures 1 and 3B). During the period of study, $Q_R$ (Figure 4B) showed little variability (mean value of 15.5 ± 3 $m^3s^{-1}$). Therefore, most of the OEs will be mostly modulated by the variability in the wind-driven circulation. These OEs also have an expected effect on the sea surface nutrient concentrations and will help us validate the concentrations of phosphate and nitrate measured by the portable probe.

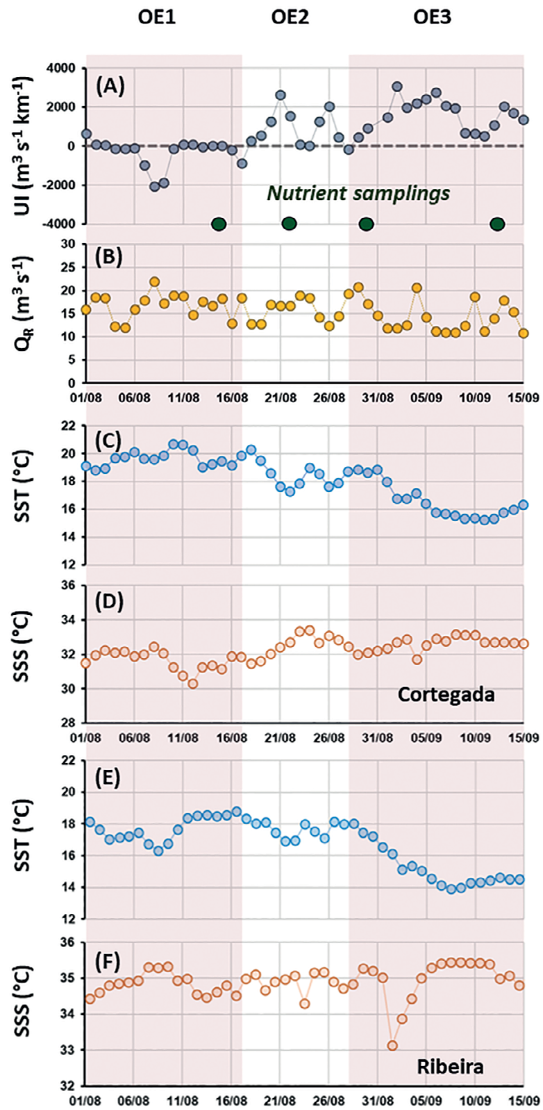


**Figure 4.** Time series of (A) Upwelling Index UI, (B) Ulla River flow QR, (C,E) SST and (D,F) SSS at Cortegada and Ribeira buoys. Green dots indicate the time of the nutrient samplings.

### OE1: Downwelling event followed by relaxation (August 1st-17th)

UI showed values close to zero at the beginning of August, indicating weak winds parallel to the coast (Figure 4A). From August 7th to 9th, UI showed negative values, with the lowest value on August 7th (-961 $m^3s^{-1}km^{-1}$), indicating a coastal downwelling event favored by predominant southerly winds over the shelf. SST at Ribeira buoy, in the outer parts of the ria, varied between 17.04-18.14 °C (Figure 4E) at the beginning of August, decreasing to a relative minimum on August 8th (16.30 °C), while SSS increased from 34.44 on August 1st to 35.33 on August 9th. Close to Cortegada island, at the head of the ria, SSS gradually decreased from August 8th to a value of 30.32 on August 12th (Figure 4D), and SST progressively increased from ~19.00 °C to ~20.60 °C from the beginning of August until August 11th (Figure 4C).

Under normal conditions, the water inside the ria is fresher close to the head, where the river discharges, saltier towards the mouths, and overall fresher than the water on the shelf (Rosón et al., 1997). These normal conditions in the ria can be seen in the horizontal distributions of SST and SSS on August 5th from the INTECMAR data (Figure 5A,B). On this date, SST in Ria de Arousa decreases from the inner to the outer areas, with values ranging from 15 °C to 18 °C, while SSS increases in the same direction, with values between 35.1 and 35.7. During a downwelling event (August 6th-10th), oceanic water enters the ria from surface layers, pushing inward water that was already inside the ria and limiting the effect of the river to the innermost parts. Under these conditions, SSS is expected to increase in outer parts of the ria and to decrease in inner parts. Also, during the downwelling event, SST could be expected to decrease in outer parts of the ria (entrance of usually colder open-ocean water) and to increase in inner parts (warming of restricted water). Therefore, the evolution of SST and SSS at Cortegada and Ribeira buoys during these dates agrees with the hydrographic conditions of a downwelling event in the ria.

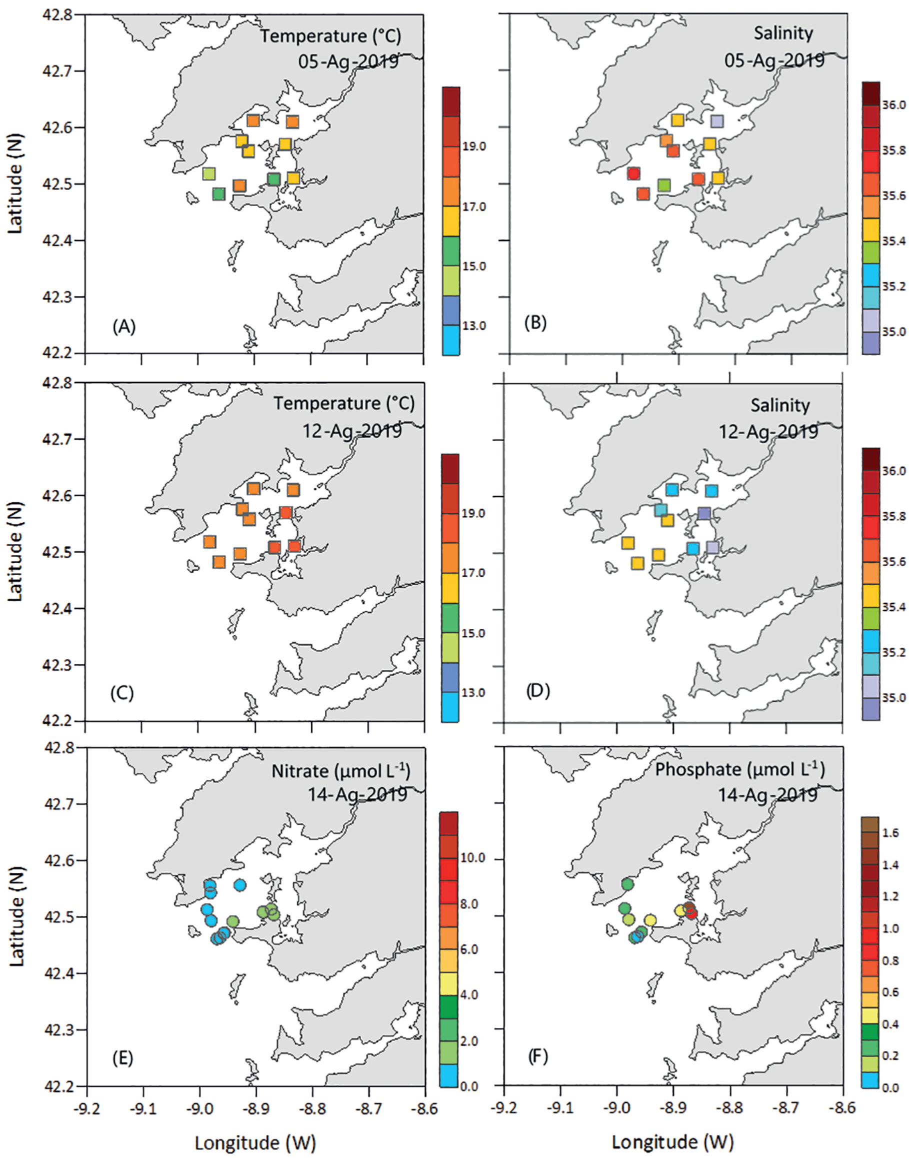


**Figure 5.** (A, C) SST (°C) and (B, D) SSS from the INTECMAR observation network on 5th and 12th August 2019, respectively. Sea-surface concentrations, in µmol L-1, of (E) nitrate and (F) phosphate on 14th August 2019.

The downwelling event was followed by a weakening on the southerly winds that lead to a relaxation period (August 11th–17th), with values of UI close to zero (Figure 4A). This relaxation in the wind forcing favored the reestablishment of the 2-layer estuarine circulation within the ria. The retreat of oceanic water to the shelf on surface layers agrees with the decrease and posterior stabilization of SSS at Ribeira buoy from August 9th until 17th (Figure 4F). The increase in SSS registered at Cortegada buoy (Figure 4D) between August 12th-17th also reflects the reestablishment of the 2-layer circulation in the ria. The river was stacked at the head of the ria during the downwelling event, and the fresher surface layer reached deeper levels (Rosón et al., 1995). During the re-establishment of the 2-layer circulation, the fresher surface layer became thinner, allowing for increased mixing with saltier waters underneath, which could increase SSS. SST increased at the locations of Ribeira (from August 8th) and Cortegada (from August 13th) buoys during the relaxation period due to summer heating and the expansion of warmed surface water previously limited to inner parts of the ria. The extension of this warmed surface water is also shown in the horizontal distributions of SSS and SST on August 12th (Figure 5C, D). SST is higher than 17 °C on the whole surface of the ria, with higher SST at inner shallower zones. On the other hand, SSS values are lower than 35.5 and decrease from the mouths to the head of the ria, suggesting waters with relatively high influence of the river runoff.

Nitrate concentrations measured on August 14th varied between 0.61-1.53 µmol $L^{-1}$ (Figure 5E). Low concentrations (0.61-1.00 µmol $L^{-1}$) were measured in the north and south mouths of the ria and in the northern coast close to Ribeira (Figure 1). High concentrations (1.00-2.00 µmol $L^{-1}$) were found in shallower areas western of the O Grove peninsula and between O Grove peninsula and Illa de Arousa (Figure 5E, Figure 1). Phosphate concentrations varied between 0.03-1.53 µmol $L^{-1}$ (Figure 5F). Similar to nitrate, high phosphate concentration values (>0.40 µmol $L^{-1}$) were measured in the vicinity of O Grove peninsula, with the highest value (1.53 µmol $L^{-1}$) between O Grove peninsula and Illa de Arousa. Relatively low concentration values in phosphate were found in the mouths of the ria and in the coastal area near Ribeira (Figure 5F). These surface nutrient distributions agree with the oceanographic conditions characterizing the relaxation period. During this period, the nutrient-depleted oceanic water retreats from inner parts of the ria towards the ocean while, at the same time, the nutrient-rich river flow extends far from the head of the ria, where it had previously been confined. Therefore, the sea-surface nutrient concentrations are expected to decrease from the head to the mouths of the ria.

The elevated concentration of phosphate close to O Grove peninsula at extremely high value compared to the rest of the concentrations is noticeable. Lindo-Atichati et al. (2019) located wastewater runoffs close to this sampling station, which could explain the high phosphate concentration found. River waters and runoffs have a relatively higher phosphates content compared to oceanic water, since phosphate concentrations in continental waters are related to the use of fertilizers in agriculture, detergents in laundry, as well as to soil leaching (Gago et al., 2005; Lombardo, 2006).

### OE2: Sporadic Upwelling event (August 18th–27th)

High intensity northerly-wind gusts characterized the last weeks of August, generating intense but short upwelling events (UI = 2629 $m^3s^{-1}km^{-1}$ on August 21st and UI = 2060 $m^3s^{-1}km^{-1}$ on August 26th (Figure 4A). The sporadic upwelling events forced the entrance of oceanic water in the ria from deep to surface layers. The signal of these upwelling events can be seen in the variability of SST and SSS registered by the Ribeira and Cortegada buoys (Figure 4C-F). Between August 18th-22nd, SST decreased approximately 3 °C at Cortegada, and from August 23th to 27th showed values between 17.60 °C and 19.00 °C (Figure 4C). At Ribeira, SST decreased less than at Cortegada, diminishing by 1 °C between August 18th-22nd and then varying between 17.10 °C and 18.20 °C from August 23th to 27th (Figure 4E). SSS at Cortegada increased ~2 units between August 18th-24th and then stabilized around 32.87±0.22 (Figure 4D), but at Ribeira SSS remained around 35.03±0.10 (Figure 4F).

These differences in SSS and SST variability between buoys were most probably due to the short duration of upwelling events. These sporadic upwelling events are caused by gusts of northerly winds that, though sometimes very intense (e.g., August 21st and 26th) and associated with high values of UI, rapidly cease. The thermocline in the ria is intensified during summer because of seasonal heating, and a sporadic upwelling event is unable to completely destroy the thermocline and drastically change the surface water conditions of the ria (Rosón et al., 1995; 1997; Alvarez-Salgado et al., 2003). The relatively intense upwelling events force the oceanic water to enter the ria through deep layers. Inside the ria, the oceanic water is channeled by bathymetry towards shallower inner parts at the head of the ria and in front of O Grove (Rosón et al., 1997). The progressive decrease in depth intensifies the inward flow of oceanic water that can more easily break the seasonal thermocline, leading to more abrupt changes in SST and SSS at Cortegada than at Ribeira buoy.

This process is easily observed when comparing the INTECMAR SST and SSS data on August 20th and 26th (Figure 6A-D). The surface waters of

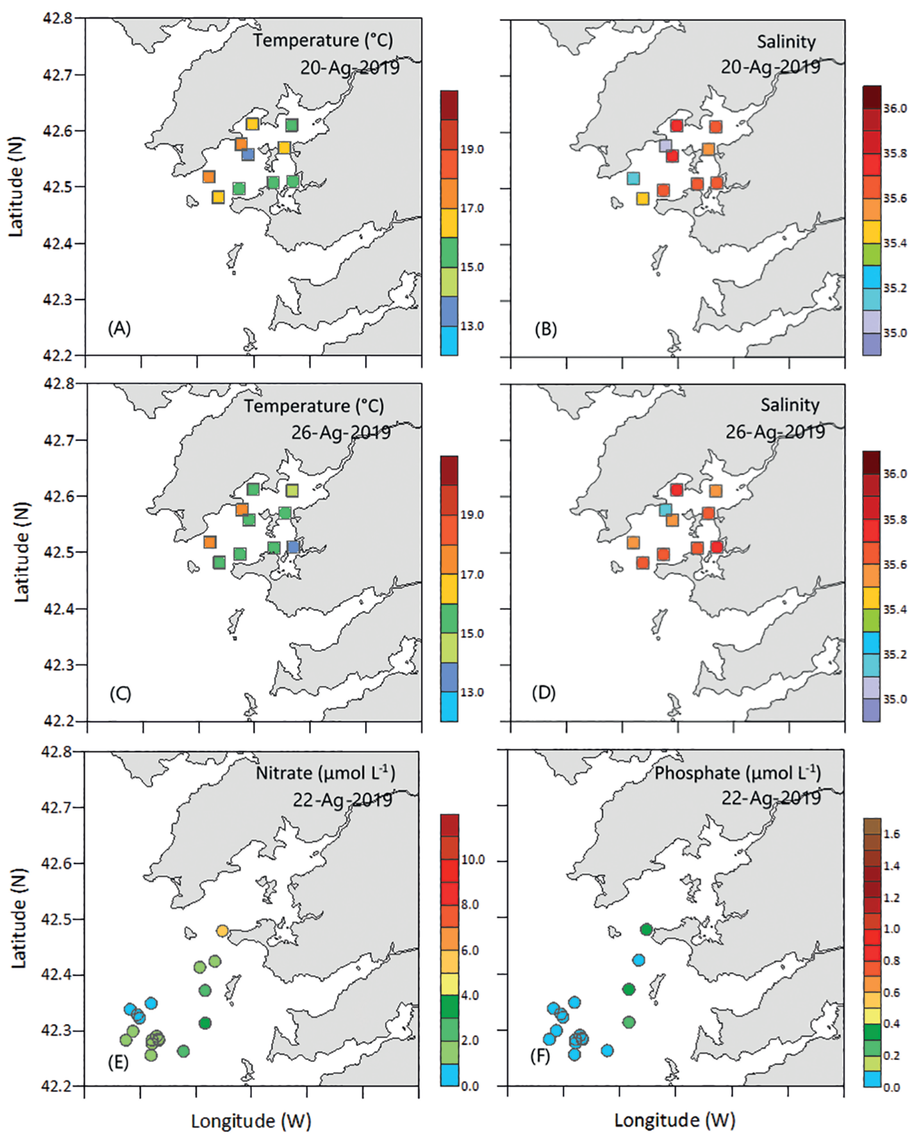


**Figure 6.** (A, C) SST (°C) and (B, D) SSS from the INTECMAR observation network on 20th and 26th August 2019, respectively. Sea-surface concentrations, in µmol L$^{-1}$, of (E) nitrate and (F) phosphate on 22th August 2019.

the ria were colder and saltier on the southern and innermost areas and warmer and fresher along the northern middle and outer areas, responding to the upwelling process. The warmer and fresher waters along the northern coast of the ria could be indicative of the surface layer being pushed out towards the ocean by the upwelling events (Rosón et al., 1997; Alvarez-Salgado et al., 2003). SST was lower and SSS higher on August 26th compared to August 20th, when the upwelling event was more intense.

The second sampling date of nutrients, August 22nd, is included in EO2. On this day, nitrate concentrations varied between 0.63-5.35 µmol $L^{-1}$ (Figure 6E), achieving higher values than on August 14th. The highest concentration measured on August 22nd (5.35 µmol $L^{-1}$) was found in the vicinity of O Grove peninsula. On the continental shelf, nitrate concentrations were lower (0.00-4.00 µmol $L^{-1}$) than those found close to O Grove peninsula, and lower in the offshore area of the shelf (< 1.00 µmol $L^{-1}$) than in the mid-shelf area (1.00-4.00 µmol $L^{-1}$). Phosphate concentrations on this date were lower than 0.40 µmol $L^{-1}$ and showed a similar distribution to that of nitrate (Figure 6F). Relatively high concentrations of phosphate (0.20-0.40 µmol $L^{-1}$) were found between O Grove peninsula and the inner shelf, while lower concentrations (< 0.20 µmol $L^{-1}$) were measured in the mid- and offshore shelf areas. Phosphate concentrations were, in general, lower than on August 14th.

The distribution of the concentrations of both nitrate and phosphate on the continental shelf also respond to OE2. On the shelf, the difference in depth between the open ocean and the shelf and between the shelf and the coast favors the upwelling of subsurface waters and their entrance in the ria (see Fig. 5 in Castro et al., 2000). Therefore, sea surface nutrients tend to renovate faster in those areas where the water is pumped up. The highest values of nutrient concentration on the August 22nd can be found over the 50 m isobath, in areas close to the Ons and Cies islands and O Grove peninsula (Figure 1). This fact indicates that the nutrient concentrations found respond to the occurrence of an upwelling event.

## OE3: Sustained Upwelling event (28th August–15th September)

During all OE3, winds over the shelf blew mainly from the north, favoring persistent upwelling in the area of study. The correspondent UI values were positive during this period and relatively high (highest UI= 3067 $m^3s^{-1}km^{-1}$, on September 2nd), with some fluctuations marked by a decrease on September 10th, when UI reached values close to zero (Figure 4A). SST and SSS at Cortegada and Ribeira buoys agree with OE3 and also responded to the fluctuations observed in UI (Figure 4C-F). Between August 28th and September 11th, there was a clear decrease of SST close to Cortegada Island, reaching the lowest value registered in the period of study (15.23 °C on September 11th), and an increase of SSS between August 18th and September 10th, with some fluctuations. SST at Ribeira buoy gradually decreased to a value of 13.91 °C on September 7th, the minimum value found during the period of study. Except for a sudden low value on September 1st (33.13), SSS at Riberia buoy progressively increased to values around 35.42 ± 0.04 between September 6th-11th.

These observations corroborate the upwelling of colder and saltier waters within the ria. After the minimum value of UI on September 10th, UI continuously increased but with less intensity in terms of its maximum value and duration (Figure 4A). After September 10th, SST increased in both buoys (+1.5 °C at Cortegada and +0.9 °C at Ribeira), while SSS remained quite stable (32.71 ± 0.06 at Cortegada and 35.10 ± 0.23 at Ribeira) (Figure 4C-F). This is due to a loss of inertia in the upwelling. Although conditions on the shelf were still favorable to upwelling between September 10th to 15th (SSS does not change), the intensity is not high enough to significantly change surface waters of the ria that, instead, warm up due to summer heating. These same findings can also be seen in the horizontal distributions of SST and SSS in the ria on September 3rd and 9th (Figure 7). SST drops between 14 -18 °C on September 3rd to between 13-15 °C on September 9th, while SSS is roughly unchanged on both days, between 35.5 and 35.9.

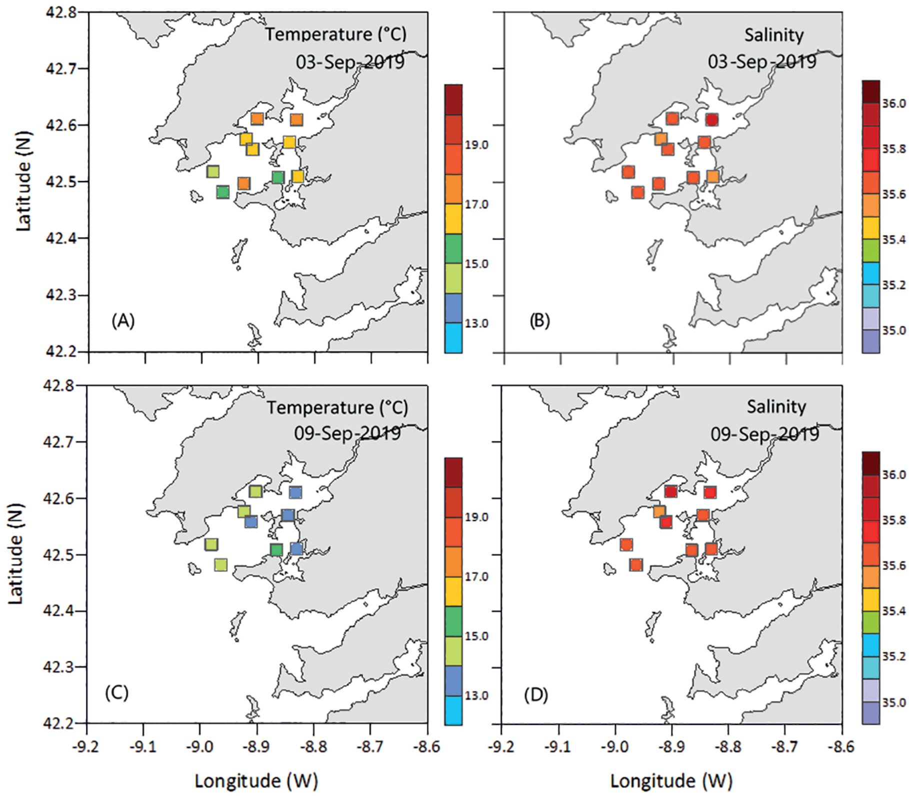


**Figure 7.** (A, C) SST (°C) and (C, D) SSS from the INTECMAR observation network on 3rd and 9th September 2019, respectively.

The last two nutrient-sampling dates are included in OE3: August 30th and September 12th. Nitrate concentrations on August 30th varied between 0.77-1.86 µmol $L^{-1}$ (Figure 8A). The higher concentration values (1.00-1.86 µmol $L^{-1}$) were measured in the northern coastal area close to Ribeira and the area between the Illa de Arousa and O Grove peninsula. Relatively low nitrate concentrations (< 1.00 µmol $L^{-1}$) were observed in the mouths of the ria. Phosphate concentrations were lower than 0.28 µmol $L^{-1}$ (Figure 8B). Again, relatively low concentrations (<0.10 µmol $L^{-1}$) were measured close to the mouths of the ria, while higher concentrations (>0.10 µmol $L^{-1}$) were observed in the coastal area of Ribeira and south of Illa de Arousa. These measurements respond to oceanographic conditions at the beginning of OE3, when the upwelling was not very intense. The SST near the coast of Ribeira had already began to decrease by this date but had not yet reached its minimum. This not fully-developed upwelling event only slightly increased the concentration of nutrients in the sampling stations located in inner parts of the ria.

On September 12th, nitrate concentrations varied between 2.78-9.05 µmol $L^{-1}$ (Figure 8C) and increased from the area south of Illa de Arousa (5.00-6.00 µmol $L^{-1}$) towards the west of the island (> 6.00 µmol $L^{-1}$). North of the island, nitrate concentrations were slightly lower (<3.00 µmol $L^{-1}$). Phosphate concentrations on this date varied between 0.17-0.64 µmol $L^{-1}$ (Figure 8D) and also showed values that increase from the south (<0.50 µmol $L^{-1}$) to the west (0.50-0.60 µmol $L^{-1}$) of Illa de Arousa. The lowest concentrations were measured north of the island (<0.30 µmol $L^{-1}$). Although samplings on August 30th and September 12th were carried out in different areas of the Ria de Arousa, it is clear that the mean concentration of nutrients in surface waters was higher on September 12th. In fact, the concentrations of both nitrate and phosphate on September 12th were the highest of

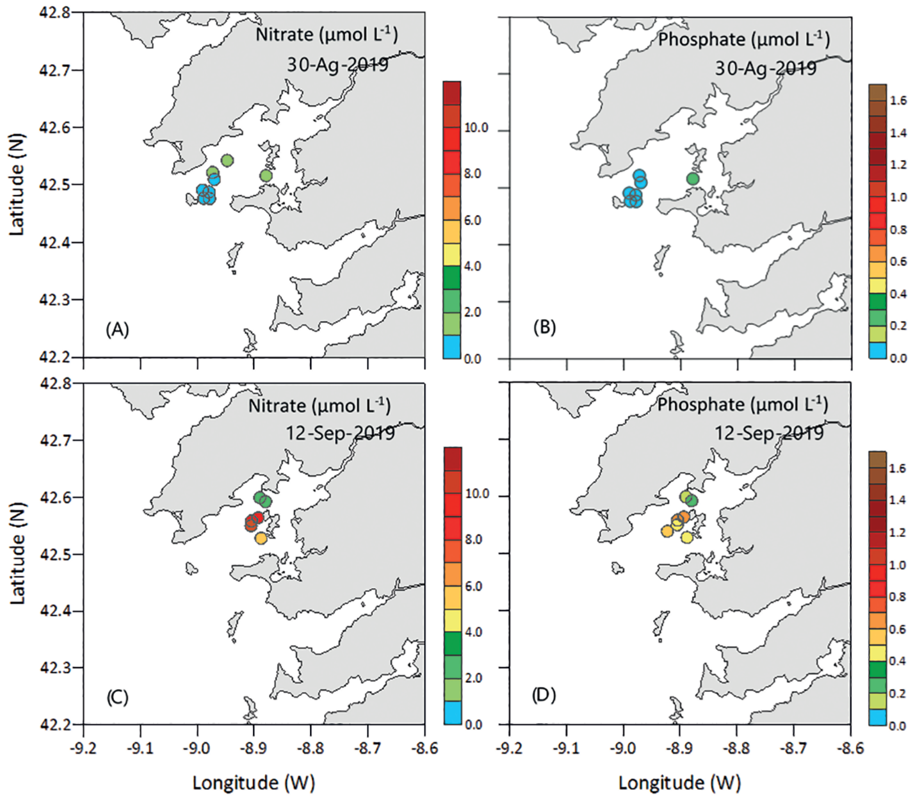


**Figure 8.** Sea-surface concentrations, in µmol L-1, of (A, C) nitrate and (B, D) phosphate on 30th August and 12th September 2019, respectively.

the period of study, corroborating the effect of the persistent upwelling on the properties of surface waters of the ria.

In summary, the results from this study indicate that nutrient concentrations obtained with the portable module responded to the 3 OEs identified. Also, the measurements done with the opportune sampling complement the INTECMAR sampling repeats, adding data from new areas, especially on the shelf, and on different dates. These results show that this equipment is both reliable and a useful tool for studies onboard vessels of opportunity on coastal upwelling ecosystems.

## Initial evaluation of the risk of eutrophication

The different levels of eutrophication risk for Ria de Arousa considered here were determined for the Euroregion Galicia-Northern Portugal under the MarRISK project (https://marrisk.inesctec.pt/public/#!/indicators, Bastero et al., in prep.). In this project, three risk levels (low, medium or moderate, and high) were established from the historical mean values of nitrate and phosphate during winter, following EEA criteria (EEA 2009). We compared these limits with our summer nutrient data (August-mid-September 2019) to make an initial evaluation of the potential implications of the OEs on the eutrophication risk of the ria. In general, for the Euroregions (EEA 2009), the studies on eutrophication risk levels are carried out during winter because concentration of nutrients is expected to be highest due to seasonal increases in continental water input (i.e, the anthropogenic nutrient sources). However, in coastal upwelling systems, in addition to the increase in nutrients due to the anthropogenic activities, it is also necessary to consider the natural nutrient rich conditions under upwelling events (Fraga, 1981; Alvarez-Salgado et al., 1996).

In general, nitrate values showed a range that indicates low risk of eutrophication in Ria de Arousa for most of the studied period (Figure 9A). However, some samples near the northwestern

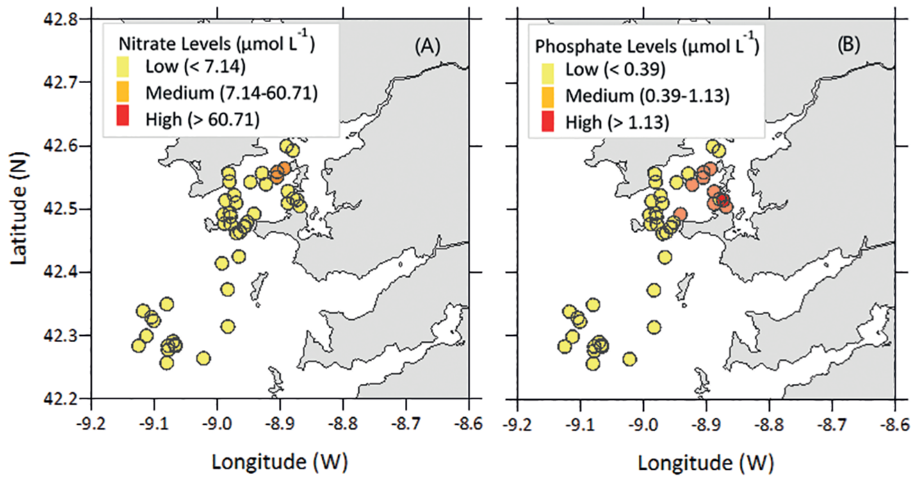


**Figure 9.** Eutrophication risk levels in the NW-Iberian Peninsula obtained from surface nutrient concentrations of (A) nitrate and (B) phosphate, measured between August and mid-September 2019. Nutrient ranges, in μmol $L^{-1}$, were established following the EEA criteria (EEA 2009).

part of Illa de Arousa (Figure 1) showed concentrations of nitrate indicative of medium risk level. Theses samples were obtained on September 12th, included in the period of *Sustained Upwelling Event* (OE3), indicating that the nitrate input due to the upwelling was significant. With respect to phosphate (Figure 9B), concentrations indicative of medium and high eutrophication risk levels were detected around O Grove Peninsula (Figure 1) on August 14th as well as in areas northwest of Illa de Arousa on September 12th. On September 12th, similarly to nitrate, the relatively high concentration of phosphate can be explained by the sustained upwelling event that took place around those dates (OE3). On August 14th, the ria was under a relaxation phase (OE1), and the high concentrations of phosphate found around O Grove peninsula are most likely linked to continental sources and the expansion of the river flow previously retained.

These results indicate that the eutrophication risk in this area of the NW-Iberian upwelling system was low for most of the measured points during this summer period. Although this study constituted an initial evaluation, with a small quantity of samples collected, our results have already pointed out specific vulnerable areas and oceanographic conditions that are prone to high levels of sea surface nutrient concentrations. In order to properly evaluate the potential risk of eutrophication in the area of study, it is necessary to know how long high nutrient concentrations persist over time on surface layers. In this sense, in addition to the hydrodynamic modulation, the role of phytoplankton consumption in surface-layers must also be considered. Therefore, future studies with the module, with higher spatial and temporal data density and combined with other measurements (i.e., chlorophyll, oxygen) and model results, could be of help to identify new OEs and their impact on the sea-surface nutrients concentration of coastal upwelling systems.

## CONCLUSION

Advances in innovative technologies are essential to study the dynamics of marine ecosystems. The potential of our portable module has been demonstrated by the results provided from the *in situ* measurements carried out on both coastal and shelf areas of the NW-Iberian coast. Our results also indicate the utility of the designed module as a complementing tool for monitoring networks available in the area. It should be noted that most studies based on nutrient probes, such as the WIZ-4 model, are usually performed in closed systems such as lakes, reservoirs, and semi-closed bays. The present study focused on the implementation of equipment as an autonomous, easily mountable, and usable module to be used aboard vessels of opportunity.

The results from this study allowed for an initial evaluation of the potential eutrophication risk that can be derived from sea-surface nutrient concentrations resulting from different OEs. Our results showed high-vulnerability regions in Ria de Arousa during summer related to areas of upwelling intensification and in proximity to local continental outflows. Our results are limited by the opportunistic nature of the sampling strategy, which did not allow us to have high-density sampling nor to sample the same stations along the time period. Future studies based on more frequent and wider opportune samplings should be done to better evaluate the eutrophication risk level on the NW-Iberian coast on the basis of different OEs.

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## AUTHOR CONTRIBUTION

P.C.P.: Conceptualization; Investigation; Data curation; Supervision; Writing-original draft; Writing-review & editing.

S.F.B.: Methodology; Samplings; Formal Analysis; Writing-original draft; Writing-review & editing.

L.M.: Samplings; Formal Analysis; Data curation; Writing-original draft; Writing-review & editing.

C.G.C.: Conceptualization; Investigation; Data curation; Visualization; Supervision; Resources; Funding acquisition; Writing-review & editing.

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