- Line 32: It is not good to start a sentence with a symbol. I suggest to write: Emission of anthropogenic origin CO2 ...
The suggestion has been included in the new version of the manuscript

- Line 49:IOC is a UNESCO body. To be more precise substitute United Nations with UNESCO
The suggestion has been included in the new version of the manuscript

- Line 326: following the suggestion of a referee, here I am recommending to change the sentence in: ... error was 0.003, using the equation of practical salinity given by UNESCO (1981) ...
The suggestion has been included in the new version of the manuscript

- Line 413: A quality flag ... Please, specify in parenthesis what QC flags convention are you using (SeaDataNet? WOCE? ...)
The quality control flags in the previous version was a mixture of WOCE bottle flagging and SEADATANET codes, since following a reviewer's recommendation we assigned a flag of "6" to values below the detection limit. As we are using WHP-Exchange bottle format for the database, we believe it would be best to use an unique convection, namely WOCE bottle. Therefore, we will assign a code of "2" to those values that were flagged as "6" according to the SEADATANET flags. We will make this change in the repository, as soon as we know your opinion on this issue. The new sentence is:
" A quality control flag value following the recommendations from WOCE bottle data flagging quality codes was assigned to each measurement available from the repository sites (Table 1)."

ARIOS: a database for ocean acidification assessment in the Iberian Upwelling System (1976 - 2018).

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1. Abstract

A data product of 17,653 discrete samples from 3,343 oceanographic stations combining measurements of pH, alkalinity and other biogeochemical parameters off the North-western Iberian Peninsula from June 1976 to September 2018 is presented in this study. The oceanography cruises funded by 24 projects were primarily carried out in the *Ría de Vigo* coastal inlet, but also in an area ranging from the Bay of Biscay to the Portuguese coast. The robust seasonal cycles and long-term trends were only calculated along a longitudinal section, gathering data from the coastal and oceanic zone of the Iberian Upwelling System. The pH in the surface waters of these separated regions, which were highly variable due to intense photosynthesis and the remineralization of organic matter, showed an interannual acidification ranging from -0.0016 yr^{-1} to -0.0039 yr^{-1} that grew towards the coastline. This result is obtained despite the buffering capacity increasing in the coastal waters further inland as shown by the increase in alkalinity by 1.1±0.7 µmol kg^{-1} yr^{-1} and 2.6±1.0 µmol kg^{-1} yr^{-1} in the inner and outer *Ría de Vigo* respectively, driven by interannual changes in the surface salinity of 0.0193±0.0056 psu yr^{-1} and 0.0426±0.016 psu yr^{-1} respectively. The loss of the vertical salinity gradient in the long-term trend in the inner ria was consistent with other significant biogeochemical changes such as a lower oxygen concentration and fertilization of the surface waters. These findings seem to be related to a growing footprint of sediment remineralization of organic matter in the surface layer of a more homogeneous water column.

Data are available at: http://dx.doi.org/10.20350/digitalCSIC/12498 (Pérez et al., 2020).

2. Introduction

Emissions of anthropogenic origin CO_2 (fossil fuels, land use and cement manufacturing) into the atmosphere are the main cause behind the warming of the Earth due to the greenhouse effect (IPCC, 2013). Given the constant exchange of gases through the air-sea interface, the oceanic reservoir plays a key role as a sink for about

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31% of anthropogenic CO_2 emissions (Sabine et al., 2004), controlling the partial pressure of carbon dioxide in the atmosphere and regulating global temperatures.

The CO_2 uptake by the oceans produces changes in the inorganic carbon system in spite of being partially dampened by the seawater buffering capacity. This ability of seawater to withdraw anthropogenic CO_2 becomes more limited as more CO_2 is absorbed, which will make it difficult to stabilize atmospheric CO_2 in the future (Orr et al., 2009). The gradual absorption of atmospheric CO_2 by the oceans decreases seawater pH, causing ocean acidification, which conditions the buffering capacity of seawater and in turn the exchange of CO_2 between the ocean and the atmosphere (Caldeira and Wickett, 2003; Raven et al., 2005). This effect of CO_2 absorption, which is known as ocean acidification, conditions the buffering capacity of seawater and to some extent the exchange of CO_2 between the ocean and the atmosphere. The Intergovernmental Oceanographic Commission of the UNESCO identified the chemical change in seawater brought about by ocean acidification as an indicator of a stressor on marine ecosystems with a negative impact on socio-economic activities such as fishing and shellfish farming. Hence, it was necessary for the oceanography community to observe and gather data about pH and other parameters of the marine carbon system to conduct accurate measurements of pH and ancillary parameters and provide data products to help a sustainable management of the marine resources. The effect of ocean acidification on marine ecosystems has stimulated impetus in the international community for gathering high quality time-series measurements of the marine inorganic carbon system (Hofmann et al., 2011; Andersson and MacKenzie, 2012; McElhany and Busch, 2013; Takeshita et al., 2015; Wahl et al., 2016) and for predicting the future evolution of the pH caused by climate change.

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The threat for oceanic acidification of marine ecosystems is especially significant in regions like coastal upwelling areas, which are more sensitive and appear to respond faster to anthropogenic perturbations (Feely et al., 2008; Gruber et al., 2012; Lachkar, 2014; Hauri et al., 2013). These ecosystems are characteristic for their complex physical and biogeochemical interactions and for sustaining enormous biological productivity and productive fisheries (Pauly and Christensen, 1995; Haury et al., 2009). The photosynthetic activity in these regions is also an important mechanism for the seawater CO_2 uptake, converting most of these areas into atmospheric CO_2 sinks (Pérez et al.,

1999; Cobo-Viveros et al., 2013). However, the high physical/chemical variability in short temporal and spatial scales of upwelling systems and the lack of regular sampling in these waters prevents a complete picture of the acidification of these ecosystems.

In the Iberian Upwelling System, the researchers of the Instituto de Investigaciones Mariñas (IIM-CSIC) since 1976 commenced accurate measurements of marine inorganic carbon system and associated parameters. As a result, a collection of pH observations and ancillary biogeochemical information along the Galicia coast (40ºN and 45ºN, 11ºW) has been gathered under the framework of different projects over the past 40 years. The current database, hereinafter called ARIOS (Acidification in the rias and the Iberian continental shelf) database, holds biogeochemical information from 3,357 oceanographic stations, giving 17,653 discrete samples. This unique collection is a starting point for evaluating the ocean acidification in the Iberian Upwelling System characterized by intense biogeochemical interactions as an observation-based analysis, or for use as inputs in a coupled physical-biogeochemical model to disentangle these interactions at the ecosystem level.

3. Data provenance

3.1. Data spatial coverage

The main characteristic of the Galician coastline, located in the north-west of the Iberian Peninsula, is the *Rías Baixas*, four long coastal estuaries or rias (>2.5 km^3) between 42ºN and 43ºN (Fig. 1). The water exchange between the *Rías Baixas* and open waters is drastically affected by the coastal wind pattern as part of the Canary Current Upwelling System (Wooster et al., 1976; Fraga 1981; Arístegui et al., 2004). Under the predominance of northeasterly winds (Blanton et al., 1984) during spring-summer, the surface offshore transport of surface waters leads to a rising cold, nutrient-rich, deep water mass called the Eastern North Atlantic Central Water (ENACW) (Ríos et al., 1992). Under these conditions, the *Rías Baixas* act as an extension of the continental shelf (Rosón et al., 1995; Souto et al., 2003; Gilcoto et al., 2017), where upwelling filaments extending westward export primary production from the coast into the ocean (Álvarez-Salgado et al., 2001). In the opposite direction, the prevalence of northward winds (Blanton et al., 1984) moves the surface waters towards the coast, where they accumulate, sink and thus isolate the coast. This process, known as downwelling, is typical during the autumn-winter along with other characteristics such as the warm,

salty waters from the Iberian Poleward Current (IPC) of subtropical origin (Fraga et al., 1982; Alvarez-Salgado et al., 2006) that flows constrained to the Iberian shelf break (Frouin et al., 1990). The run-off from local rivers also contributes to the presence of river plumes over the shelf (Otero et al., 2008). These hydrodynamic conditions, the meteorological forcings and the alternation of periods of upwelling and downwelling (Álvarez, 1999; Gago et al., 2003c; Cobo-Viveros et al., 2013) stimulate the development of intense primary production and high rates of recycling and downward carbon export (Alonso-Pérez and Castro, 2014). The result of this biogeochemical variability in terms of air-sea CO_2 exchange is that the surface waters act as a net CO_2 sink that is especially intense and variable over the shelf compared to offshore or in the inner *Rías Baixas* (Padin et al., 2010).

Besides the short-term and seasonal variability, significant changes in the long-term scale have been reported in this region. In addition to changes such as the weakening and shortening of the upwelling events (Lemos and Sansó, 2006; Pérez et al., 2010; Alvarez-Salgado et al., 2009), the warming (González-Pola et al., 2005; Pérez et al., 2010) and changes in the composition of phytoplankton (Bode et al., 2009; Pérez et al., 2010), the acidification in the first 700 metres for the geographical area from the Iberian Peninsula to the 20º W meridian and from 36ºN to 43ºN has also been observed at a rate of -0.0164 pH units per decade (Ríos et al., 2001; Castro et al. 2009).

3.2. Distribution of sampling

According to the type of region under study, different areas were identified in order to classify the measurements gathered in the oceanographic cruises (Fig. 1). The latitude of 43ºN where Cape Finisterre is located was used as the dividing line between northern and southern waters. Subsequently, a criterion of depth also split the waters to the north of 43ºN into north oceanic (below 250 m), north shelf (between 205 m and 75 m) and north coast (75 m to the surface). The southern shelf waters were divided by latitude 42ºN into Portuguese and the *Rías Baixas* (RB) shelves, whereas the shallower waters were identified by the main rias, where three different zones were defined using longitude boundaries (outer, middle and inner) according to Gago et al. (2003c) in the *Ría de Vigo*, and just two zones in the other rias (*Ría de Pontevedra*, *Ría de Arousa*, *Ría de Muros*). Southern waters between the isobath at 75 metres and the mouth of the estuaries were identified as the Portuguese and RB coast.

The discrete measurements gathered in the ARIOS dataset were mainly found in different regions' waters around 42ºN latitude (Fig 1; Fig. 2a), especially in the outer and middle areas of the *Ría de Vigo*, which accounted for 15% and 21% of the total measurements respectively due to the proximity to the *Instituto de Investigaciones Mariñas* (IIM-CSIC). Most of the measurements (85%) carried out by many of these cruises to study the coastal ecosystems concentrated on shallow waters between the seawater surface and 75 metres in depth (Fig. 2b). Although waters below 4,900 metres deep were also sampled, observations below 900 metres only account for 1% of the ARIOS database.

The observations made over more than 40 years in every region of the ARIOS database were irregular on both an interannual and seasonal scale (Fig. 2a). The period of most sampling activity was the 80s and 90s, whereas samples were especially scarce in the early 2010s. On a seasonal scale, summer and autumn were the preferred seasons to address the different research purposes, with 37% and 36% of the total samples respectively. The observations taken during less favourable winter conditions, especially aboard the coastal vessels usually available, only accounted for the 10% of the ARIOS database.

3.3. Data sources

The ARIOS database is a compilation of biogeochemical properties with discrete measurements of temperature, salinity, oxygen, nutrients, alkalinity, pH and chlorophyll that were sampled in waters off the northwest of the Iberian Peninsula from 1976 to 2018 and measured by IIM-CSIC (Table 1). This data collection is part of the research by 24 projects and oceanographic cruises conducted in response to different aims. The different sampling strategies built up an irregular biogeochemical database whose particular frequency and spatial coverage is shown in Figure 2.

The contribution to the ARIOS database from the oceanographic cruises and projects over the different decades is described below.

Cruises in the 70s and 80s:

The first three cruises were carried out over three periods (1976, 1981-1983 and 1983-1984), sampling the *Ría de Vigo*. These cruises were designed to provide environmental information (upwelling events, estuarine circulation, continental inputs, etc.) for research into the biology of some fish species. They measured identical parameters in the Vigo estuary but at different stations and frequency.

In the summer of 1984, the *Galicia VIII* cruise studied the summer upwelling events occurring on the contact front between the two ENACW water masses off Cape Finisterre from short sections perpendicular to the Galician coast with 85 stations offshore and 35 stations over the shelf. This cruise marked a milestone in the oceanographic research of IIM-CSIC because it was the first time that the parameters of the carbon system were measured on-board in offshore waters. Moreover, measurements of a particular station on the shelf break with a bottom depth of 600 metres were taken every two days for a month, including two-day continuous samplings.

Two years later, the Ria de Vigo 1986 sampled along the main axis of the Ria de Vigo in 7 monthly repetitions during the first half of the year in which the primary production and the organic matter exchange between the estuary and the shelf was studied in relation to the hydrographic regime. Shortly afterwards, the same topic was also researched by the Galicia IX project in September and October 1986 from 145 stations, 50 of which were coastal and 80 located in ocean waters (Prego et al., 1990).

The following year, the 1987 Provigo project (Nogueira et al., 1997) initiated a periodic study from a fixed site (42º14.5'N, 8º45.8'W) located in the main channel in the middle zone of the *Ría de Vigo*. This oceanographic station was selected as suitable for evaluating the main processes that occur in the inner ria associated with external forcing changes (Rios, 1992; Figueiras et al., 1994). Although the Provigo project finished in 1996, the fixed station was repeatedly included in subsequent cruises, extending the time series at this location until today, when it is currently sampled every week by INTECMAR (www.intecmar.gal). An example of the subsequent sampling repetition of this station occurred the following year when one of the three stations in the Vigo estuary in the Luna 1988 project (Fraga et al., 1992) took a sample every two weeks to

study the environmental control over the phytoplankton populations throughout an annual cycle (February 1988 - February 1989).

At the end of 80s, the carbon system monitoring by the IIM-CSIC was extended to the *Ría de Arousa* throughout 1989 (Álvarez-Salgado et al., 1993; Perez et al., 2000) in order to learn the effect of upwelling on the water circulation pattern, community production and the fluxes and net budgets of biogenic constituents in this ria with the highest mussel production in Europe. For 5 months, 11 stations' samples were repeated twice a week in the ria that is the most productive, housing intense cultivation of mussels on rafts (Blanton et al., 1984).

Cruises of the 90s:

In the first half of this decade, studying the phytoplankton communities was the oceanographic cruises' most relevant aim, concentrating particularly on harmful algae blooms. The hydrodynamic and biogeochemical conditions controlling the growth, development and migration of the phytoplankton were analysed both in the interior of the estuary and on the continental shelf.

For five days in September, the 1990 *Ría de Vigo* cruise (Figueiras et al., 1994) sampled five stations distributed along the longitudinal axis of the ria and one at the northern mouth. The next year, the cruise Galicia XI was carried out in May, sampling at 39 stations along eight transects perpendicular to the coastline; and Galicia XII (Alvarez-Salgado et al., 1998, 2002, 2003; Castro et al., 1994) in September, sampling at 37 oceanic stations and 7 coastal stations.

The *Ría de Vigo* cruise in 1993-4 (Miguez et al., 2001), with four stations using 24 repetitions with a CTD-SBE25, investigated the hydrodynamic and biogeochemical effect on the evolution of phytoplankton communities in the *Ría de Vigo*. Six samples were taken in approximately two weeks corresponding to two different periods (27 September to 8 October 1993, and 6 March to 24 March 1994).

Ría de Vigo 1994-95 (Alvarez et al., 1999; Doval et al., 1998, 1997a, 1997b) and *Ría de Vigo* 1997 (Gago et al., 2003a, b, c) were two cruises that took place in the second half of the decade. These campaigns' objective was no longer the ecology of the plankton,

but the factors behind the variation of the carbon pools during the upwelling and downwelling events along the central axis of the *Ría of Vigo*. During the 1997 cruises on board the *B/O Mytilus*, a systematic observation of the pCO_2 was carried out for the first time in Spanish coastal waters, using an autonomous continuous system with additional measurements of temperature, salinity and chlorophyll.

Cruises in the 2000s and recent years:

After a period of poor sampling at the end of 90s, the first decade of the 21st century gave new impetus to biogeochemical monitoring of Galician waters. As shown below, several projects dealt with various objectives, focussing on particular issues in the dynamics of these waters:

The DYBAGA project (Galician Platform's Annual Dynamics and Biochemistry: short-scale variation) (Álvarez-Salgado et al., 2006; Castro et al., 2006; Nieto-Cid et al., 2004) analysed the phenomena of upwelling and downwelling in the Galician shelf opposite the *Ría de Vigo* weekly and their impact on the different biogeochemical and carbon system variables including organic dissolved matter. Three stations were sampled weekly from May 2001 to April 2002 between the shelf break (1,200 m deep) to the middle of the *Ría de Vigo* (45 m deep).

The REMODA (Reactivity of dissolved organic matter in a coastal upwelling system) (Álvarez-Salgado et al., 2005; Piedracoba et al., 2005; Nieto-Cid et al., 2006) project concentrated on learning the origin and destination of dissolved organic matter in the *Ría de Vigo* as well. Three stations along the main axis of the *Ría de Vigo*, including the fixed station as the central one, took samples with short (3-4 days) and seasonal time scales.

The FLUVBE project (Coupling of benthic and pelagic fluxes in the *Ría de Vigo*) added to knowledge about the productivity and the benthic fluxes of oxygen and inorganic nutrients in the Ría de Vigo from 16 oceanographic surveys with four stations between April 2004 and January 2005.

The ZOTRACOS project studied the biogeochemical and hydrodynamic characterization of the coastal transition zone in NW Spain during the downwelling period (Teira et al., 2009).

The CRIA (Circulation in a RIA) (Barton et al., 2019) project examined the layout of the two-layer circulation and propagation of upwelled and downwelled waters in order to estimate the flushing and vertical velocities in the *Ría de Vigo* in repeated hydrographic surveys between September 2006 and June 2007 (Barton et al., 2015, 2016; Alonso-Perez and Castro, 2014; Alonso-Perez et al., 2010; Alonso-Perez et al., 2015).

The RAFTING project (Impact of mussel raft cultivation on the benthic-pelagic coupling in a Galician ria) (Frojan et al., 2018; Frojan et al., 2016; Froján et al., 2014) assessed for the first time how mussel cultivation influences the quality of particular organic carbon fluxes in the *Ría de Vigo*. Over the four seasons, two stations were visited every two to three days during each period, meaning 24 oceanographic cruises in 2007 and 2008.

The CAIBEX (Continental shelf-ocean exchanges in the marine ecosystem of the Canary Islands-Iberian Peninsula) (Villacieros-Robineau et al., 2019) project compared the dynamics and biogeochemical activity between the coastal zone and the adjacent ocean in the study zone during the summer upwelling events. As part of the CAIBEX project, a mooring at the LOCO (Laboratory of Ocean and Coastal Observation) (Zuñiga et al., 2016, 2017) site located on the continental shelf was deployed and visited monthly for one year to monitor the vertical profiles of biogeochemical variables.

After these projects were completed in 2009, new measurements were not provided until 2018. The aim of the ARIOS project (Acidification in the rias and on the Iberian continental shelf) was to evaluate the impact of ocean acidification and learn about potential impacts on the mussels and their adaptation (Lassoued et al., 2019) to the new climate change.

3.4. Methods

To assess of the level of acidification in the ocean adjacent to the Galician coast, variables of the carbon system (pH and alkalinity), nutrient concentration, dissolved oxygen, chlorophyll-a, salinity and temperature were measured in each cruise. The variables measured in each oceanographic cruise gathered in the ARIOS dataset are shown in Table 1. The main changes in the material and methods throughout these years are detailed below.

T-S measurements

Temperatures from 1976 to 1984 were measured using a Wallace and Tiernan bathythermograph. Reversing thermometers that had a precision of 0.02ºC were used, attached to the water samplers between 1984 and 1990, correcting the temperature between the protected and unprotected thermometers according to Anderson (1974). During those years, the depth was calculated from the thermometric readings, rounding the result off to the nearest ten. After 1990, different models of CTD instruments that measured the seawater temperature with a precision of 0.002ºC were used to obtain the thermohaline profile.

The first measurements of salinity were determined with a Plessey Environmental Systems 6230N inductive salinometer calibrated with normal IAPSO water and calculated from the equations given in the NIO and UNESCO International Oceanographic Tables (1981). The precision of these salinity measurements was 0.005 psu. After using this equipment, the salinity was determined with an AUTOSAL 8400A inductive salinometer calibrated with normal IAPSO water whose estimated analytical error was 0.003 using the equation of practical salinity given by UNESCO (1981). CTDs began to be used in 1990 to record the vertical salinity profiles, calibrated using the salinity samples, whose possible deviations in the measurements were estimated from the discrete measurements from the AUTOSAL salinometer.

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pH measurements

The pH measurements were originally taken with a Metrohm E-510 pH meter with a glass electrode and a Ag/ClAg reference one calibrated with 7.413 NBS buffer. All pH values were converted to values at 15 ºC using the temperature correction from the Buch and Nynas tables published by Barnes (1959). In 1984, the method was modified and the temperature normalization was carried out following Pérez and Fraga (1987b).

Two years later, the measurement equipment was the Metrohm E-654 pH meter with an Orion 81-04 Ross combined glass electrode, with the pH converted to the SWS scale using the hydrogen activity coefficient given by Mehrbach et al. (1973) at 25ºC with the parameterization given by Pérez and Fraga (1987b). The error in this potentiometric method was 0.010. In 2001, the seawater pH measurements were determined with a spectrophotometric method following Clayton and Byrne (1993), subsequently adding 0.0047 to the pH value according to DelValls and Dickson (1998). The precision of the spectrophotometric measurements was 0.003 pH units.

The pH values were reported on total pH scale at 0 dbar of pressure and both at 25ºC and in situ temperature (pH_T) following the same procedure of GLODAP v2 (Olsen et al., 2019). A total of 12,220 measurements of pH on NBS scale were converted to the total scale using CO2SYS (Lewis and Wallace, 1998) for MATLAB (van Heuven et al., 2011) with pH and total alkalinity as inputs. The conversion was conducted with the carbonate dissociation constants of Lueker et al. (2000) and the borate-to-salinity ratio of Uppström (1974). Whenever total alkalinity data were missing, these values were approximated as 66 times salinity that is the mean ratio between the total alkalinity and the salinity of every in situ measurements compiled in the ARIOS database. Data for phosphate and silicate are also needed and were, whenever missing, a constant values of 10 μmol kg^{-1} for silicate and 1 μmol kg^{-1} for phosphate were used. These approximations were tested on 8,296 samples with complete biogeochemical information showing a bias of less than 0.0004 pH units for 99.95% of the samples.

Alkalinity measurements

The seawater alkalinity was measured for the first time in 1981 by potentiometric titration with HCl 0.1M at final pH 4.44 following Pérez and Fraga (1987a) with an analytical error of 2 μmol kg^{-1} and a precision of 0.1%. Sodium tetraborate decahydrate (Borax, $Na_2B_4O_7$ $10H_20$, Merck p.a.) was used for standardizing the HCl (0.13 M). The pH measurements were carried out with a combined glass electrode (Metrohm E-121) with Ag/AgCl (KC1 3M) as the reference. The pH was calibrated using the NBS buffers assuming the theoretical slope. As of 2001, the accuracy of alkalinity measurements was determined using samples of certified reference material (CRM) provided by Dr. A. Dickson, University of California, improving the precision to ±1.4 mol kg^{-1} and an

accuracy of <0.1% recently established by (Ríos and Pérez, 1999) from cross-calculation with measured Certified Reference Materials (Dickson et al., 2007).

Nutrient measurements

Except for the Galicia cruises (Table 1), in which nutrient samples were analysed on board, samples were kept in the dark and cold (4ºC) after collection for further analyses in the shore based laboratory. Nutrient concentration was determined by a flow-segmented autoanalyzer (Technicon AAII and Alpkem after 1995) as described in Strickland and Parsons (1968) with the particularity that the reduction of nitrate to nitrite with Cd column was done using a citrate buffer according to Mouriño and Fraga's modification (1985). Phosphates and silicates were measured following Grasshoff (1983), and ammonium as described by Grasshoff and Johannsen (1972). This method was maintained in the subsequent cruises, achieving a precision of 0.02 μmol/kg for nitrite, 0.1 μmol/kg for nitrate, 0.05 μmol kg^{-1} for ammonium and silicate, and 0.01 μmol/kg for phosphate.

Oxygen measurements

The dissolved oxygen was determined via the Winkler titration method for the first time in 1981 following the procedure published later by Culberson et al. (1991). The oxygen concentration in the samples in this method was fixed with $MnCl_2$ and NaOH/NaI, which were kept in the dark until analysis in the laboratory 12-24 hours later. The measurements were made by titration of iodine with thiosulfate using an automatic titrator. During the 80s and early 90s, the titration was carried out with Metrohm instruments (E-425 or E-473), which had an analytical error of 1 μmol kg^{-1}. The oxygen concentration after 1997 was estimated using a Titrino 720 (Metrohm) analyser with an accuracy of 0.5 μmol kg^{-1}.

Chlorophyll measurements

The chlorophyll-a values were measured following SCOR-UNESCO (1966) using a 6 cm diameter Schleicher and Scholl 602eh filter covered with magnesium carbonate. The absorption was measured in 1 cm optical path cuvettes using a Beckman DU spectrophotometer. In 1984, discrete water samples of the chlorophyll-a samples were filtered through Whatman GF/F filters of 2.5 cm, which were preferred from then on, and measured fluorometrically following Strickland and Parsons (1972) without

correction for concentration by pheophytes. The fluorescence readings were carried out with a Turner Designs 10,000 R fluorometer (Yentsh and Menzel, 1963) obtaining a precision of 0.05 g L^{-1}.

Quality control

Every cruise gathered in Table 1 passed 1st quality control (QC1) to ensure truly confident results. The GO-SHIP software for quality control of hydrographic data (Velo et al., 2019) that compile several QC1 procedures was applied to ARIOS dataset. That procedures consist on reviewing the property profiles and property-property plots generated by that application, adequate for each variable. A quality control flag value following the recommendations from WOCE bottle data flagging quality codes was assigned to each measurement available from the repository sites (Table 1). This method was preferred over applying a very stringent flagging process because it is difficult to rule out some extreme values associated with low salinities or that could be supported by the high variability of an ecosystem characterized by an intense biological activity. Nutrients and chlorophyll with values inferior to the precision were flag=2. Some very low pH associated to very low salinity waters were flagged as doubtful.

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The ARIOS database includes the cruise corrections for pH data of the -0.017 for the Galicia VIII cruise (29GD19840711) and +0.032 for Galicia IX cruise (29GD19860904) detected during the second level quality control of CARINA project (Velo et al., 2010).

4. Results

Some of the most obvious results provided by the ARIOS database are shown below. The purpose is to describe the environmental context and the main oceanographic processes that affect the variability of these discrete measurements and offer preliminary information for future detailed biogeochemical research.

4.1. Vertical distribution

The vertical profile of the temperature, salinity, pH on total scale at in situ temperature (pH_T), NO_3^- and oxygen concentration in the ocean region between 41ºN and 43ºN was estimated for each oceanographic station as the mean value of the depth ranges described in Figure 2b. These measurements were gathered attending to the collection periods (December-February, March-May, June-August and September-November) and

443 averaged to describe winter, spring, summer and autumn respectively (Fig. 3, Table A1
444 in the Appendix).
445
446 The vertical distribution of the temperature (Fig. 3a) showed the presence of warmer
447 saline waters throughout the water column in winter with the exception of the surface
448 waters during summer, which showed intense heating due to the radiant solar energy.
449 Below the maximum temperature observed during the summer, cold central waters of
450 subpolar origin occupied the water columns with lower salinity (Fig. 3b). The vertical
451 variation of temperature is typical for a temperate region with relatively homogenous
452 deep water below the seasonal thermocline, reaching maximum SST values in summer
453 and autumn, and minimums in spring and winter. The winter temperature profile is
454 relatively warmer than in spring because of the presence of the IPC (Alvarez-Salgado et
455 al., 2006), which reaches a depth of 300 metres. The maximum salinity is also found in
456 winter due to the presence of the IPC, whereas the minimum values are found in autumn
457 (Fig. 3b). Below 500 metres in depth, the increase in salinity points to the presence of
458 Mediterranean Water. These differences reach a minimum at 500 metres deep, where
459 the salinity values coincided. From this depth down to 1,100 metres, the differences in
460 temperature and salinity throughout the four seasons were minimal, with the mean
461 values converging to 11.03±0.07ºC and 36.117±0.009 psu, respectively (Fig. 3ab).
462
463 The vertical profiles of pH_T, NO_3^- and oxygen concentration (Fig. 3cde) also showed a
464 variation lower than 1% within this depth range with annual means of 15.2±0.1 μmol
465 kg^{-1}, 8.025±0.005 and 188±1 μmol kg^{-1} respectively. The pH values from a maximum
466 subsurface located at around 40 metres deep showed a clear inverse correlation with the
467 depth down to a depth of 500 metres throughout the seasonal cycle, where the annual
468 minimum value of 8.018±0.005 was reached. The higher pH values could be attributed
469 to the biological reduction of CO_2 by phytoplankton activity, which brought the pH to a
470 maximum value of 8.13 to 40 meters during the spring bloom. After the intense
471 photosynthetic activity observed in surface waters during spring and summer, pH values
472 reached minimum values in the first 200 metres of depth during autumn due to
473 respiration of organic matter. However, it was at a depth of 500 metres that the
474 minimum pH values were measured in all seasons where is found the subpolar Eastern
475 North Atlantic Central Water proceeding from the northeastern cyclonic gyre (Harvey,
476 1982; Ríos et al., 1992). The influence of phytoplankton growth on biogeochemistry

during spring can be also evidenced by the oxygen concentration pattern (Fig. 3e). In the upper layer above 250 metres depth, spring oxygen levels exceeded those in winter, whereas a decrease in oxygen concentration was found from this depth down to 1000 metres, possible due to enhanced respiration from cascading organic matter. The impact on the growth of the phytoplankton community during the spring was also evident, judging by the oxygen concentration. So, in the upper waters the spring oxygen concentration values exceeded those of the winter values, while oxygen consumption was found from a depth of 300 metres to 1,000 metres due to respiration from organic matter arriving from above. The minimum values for oxygen concentration throughout the water column were found during summer and autumn. The nitrate concentration displayed a particularly vertical distribution, growing with depth from minimum values in the upper layer of the ocean region, which was practically zero during the first 50 metres. Below 100 metres, the nitrate concentration showed the maximum values in the vertical distribution during summer and autumn coinciding with the presence of waters of subpolar and subtropical origin respectively, whereas the minimum values appeared in winter. Towards the bottom, the seasonal values of NO_3^- concentration were almost coincident at a mean value of 15.2±0.1 μmol kg^{-1}.

4.2. Seasonal cycle

The seasonal cycle of the biogeochemical properties (temperature, salinity, pH_T, oxygen concentration, nitrate concentration and chlorophyll) in the surface waters (0 to 5 metres) of five geographical boxes was estimated as a monthly average previously filtering values outside of two standard deviations of the mean (Table A2 in the Appendix). Five regions that were located as a longitudinal transect between the inner Ría de Vigo and the ocean zone are shown in Fig. 4.

In general terms, the seasonal variability of the temperature was very similar in every area, ranging between 12 and 19ºC (Fig. 4a). Only particular features observed on a short-term scale as in the examples below differ between each region. The warmer waters were usually found in the oceanic zone, reaching a maximum monthly averaged temperature of 18.6ºC in September, while the coldest surface waters of 12.6ºC were located in the inner stations closer to the mouth of the *Ría de Vigo* in January. Another secondary minimum averaged temperature was also found in the shelf and the outer area of the *Ría de Vigo*, which was remarkably low in August due to the entry of cold

511 upwelled waters in the surface layer (Alvarez-Salgado 1993).
512
513 The monthly salinity averages (Fig. 4b) clearly showed significant differences between
514 the offshore and coastal waters. Sharp salinity changes were seen in the estuary during
515 winter, especially in the inner area where values lower than 28 psu were reached with
516 the arrival of continental inputs in December. The weak seasonal cycle of salinity in the
517 shelf and ocean waters showed high values in December due to the influence of warm
518 saline water from the IPC, usually located on the shelf slope even though it may even
519 enter the rias depending on the relative intensity of shelf winds and the intensity of the
520 continental runoff (Alvarez-Salgado et al., 2003). In this sense, the slight salinity
521 minimum observed in the shelf waters in March could be consequence of the offshore
522 spreading of the maximum discharges from the River Miño and Douro (Otero et al.,
523 2010) at the end of downwelling season. After this, the shelf and ocean waters showed
524 minimum values in summer due to the arrival of cooler and fresher subpolar waters
525 (Rios et al., 1992; Alvarez-Salgado et al., 2003, 2006). In August, coinciding with the
526 maximum salinity of the surface waters in the interior of the *Ría de Vigo* due to the
527 minimum river runoff, the surface waters between the inner *Ría de Vigo* and the ocean
528 region were almost homogeneous, with minimum differences in salinity of 0.2 psu.
529
530 Like salinity, there was little seasonal variability in pH in the offshore waters, but large
531 seasonal variability in coastal waters, with maximum and minimum pH values in spring
532 and autumn, respectively, and in all regions (Fig. 4c). The net balance between
533 production and respiration of organic matter and the estuarine circulation caused a
534 maximum pH of 8.19 in the outer region of the *Ría de Vigo* in May and a minimum of
535 7.96 in the inner waters in November.
536
537 The oxygen concentration (Fig. 4d) in the coastal ecosystems is also controlled by the
538 remineralization of the organic matter and photosynthetic activity of the phytoplankton
539 community, with the effect of salinity and temperature on the oxygen saturation level.
540 The variability in the oxygen concentration, like the pH distribution, showed a growing
541 seasonal amplitude towards the coastline, with maximum values in the outer and middle
542 *Ría de Vigo* and lower values in the inner waters, especially during the second half of
543 the seasonal cycle. Hence, the dissolved oxygen concentration mirrored the seasonal
544 cycle of pH, showing growing seasonal amplitude towards the coastline with a range

between 284 μmol kg^{-1} found in the outer region of the *Ría de Vigo* in May and 205 μmol kg^{-1} in the inner waters in November. These results seem to reinforce the importance of the oxygen consumption in this shallow area, where the water column is less than 10 metres deep and therefore it would also be influenced by benthic respiration (Alonso-Pérez and Castro, 2014).

The monthly means of nitrate concentration (Fig. 4e) could be summarized as high values during autumn and winter due to the nutrients delivered from the continent and the vertical mixing, and as minimum nitrate values from March to September because of phytoplankton consumption. The nitrate concentration was markedly higher in the inner *Ría de Vigo*, where it exceeded 9 μmol kg^{-1} in February and decreased towards the open ocean, where the highest monthly value was seen to be 2.5 μmol kg^{-1}. Some notable aspects can be seen in Fig. 5d, such as water poor in nitrate in the ocean region between the two peaks of 3.5 μmol kg^{-1} in March and 1.3 μmol kg^{-1} in October. This shows the presence of the IPC waters, which are warmer and saltier than the shelf waters. Also noteworthy was the particular fact that while the nitrate concentration in other areas was practically zero in summer, the nitrate amount in the surface waters within the *Ría de Vigo*, and especially in the inner *Ría de Vigo*, was not completely consumed. This indicates a constant supply throughout the year, either through upwelling events or the continental inputs. This in turn means that while the chlorophyll values were at a minimum in the offshore waters in summer, the phytoplankton community in the estuary grew in summer during the upwelling relaxation periods (Pérez et al., 2000). The nutrient concentration during spring and summer was only detectable in the newly upwelled waters that can show values up to 6 μmol L^{-1} (Fraga, 1981; Castro et al., 1994). During the cessation of the upwelling season in September and October, the chlorophyll concentration (Fig. 5f) increased again, sustained by nutrients that entered from deeper waters through vertical mixing. It should be noted that there was a coincidence of high chlorophyll in the water column and low oxygen concentration in the inner *Ría de Vigo* from May to November, indicating the potential importance of benthic fluxes and vertical fluxes (reference).

4.3. Long-term trends

The long-term trends of the biogeochemical properties in the surface waters along the described longitudinal transect between the inner Ría de Vigo and the ocean zone were

579 estimated to be the interannual linear rate of the deseasonalyzed time series, previously
580 removing the monthly means in these regions and assuming a null spatial variability.
581 The significant trends in the ARIOS database, meaning long-term variability, should be
582 interpreted as a combination of the natural variability on a decadal scale (Pérez et al.,
583 2010; Padin et al., 2010) and anthropogenic forcings (Wolf-Gladrow et al., 1999;
584 Anderson and Mackenzie 2004; Bakun et al., 2010).
585
586 No long-term temperature variability was found in the surface waters of any region
587 despite the known warming previously reported on the Northern Iberian coast (Pérez et
588 al., 2010; Gesteira et al., 2011; González-Pola et al., 2005). Unlike the temperature, the
589 other expected consequence of climate change in marine ecosystems, namely ocean
590 acidification (Caldeira and Wickett, 2003) was observed along the longitudinal transect,
591 with a greater decrease in the long-term trend of pH towards the coast (Table 2). The
592 long-term pH variation of -0.0039±0.0005 yr^{-1} in the inner waters was about three fold
593 higher than the change observed in the ocean zone, equivalent to -0.0012±0.0002 yr^{-1} in
594 the ocean zone, explaining the 34% and 22% variation in pH in situ respectively, and
595 representing 1-3% of the seasonal pH variation in all zones. These pH decrease rates
596 found in both coastal and open ocean regions of the Iberian Upwelling System lie
597 within the range of other acidification rates estimated in different sites of the North
598 Atlantic Ocean (Lauvset and Gruber, 2014; Bates et al., 2014), being also coherent with
599 the mean rates calculated for the global ocean and for the Eastern North Atlantic and
600 equal to -0.018 and -0.0164 $decade^{-1}$, respectively (Lauvset et al., 2015; Rios et al
601 2001).
602
603 The long-term trend in salinity was also seen to be evidently dependent on the distance
604 to the mouth of the *Ría de Vigo*. The interannual rate of sea surface salinity in the outer
605 and inner ria previously reported by Rosón et al. (2009) was 0.0426±0.016 psu yr^{-1} and
606 0.0193±0.0056 psu yr^{-1} respectively. These changes were observed in parallel to an
607 interannual alkalinity increase that is cancelled out in the normalized alkalinity,
608 estimated as the difference between the alkalinity measured and the alkalinity calculated
609 using the linear regression with salinity in each region. Therefore, the interannual
610 salinity increase was the forcing that explains the increase in the buffer capacity of the
611 surface waters (Sarmiento and Gruber, 2006).
612

Other significant long-term variations were found in other biogeochemical parameters in the ARIOS database. The long-term trend of the concentrations of nutrients in the inner Ría de Vigo that had been previously reported for the period 2001-2011 by Doval et al. (2016) showed a significant increase in nitrate, phosphate and ammonium concentrations of 0.0559±0.0158 μmol kg^{-1} yr^{-1}, 0.0076±0.0016 μmol kg^{-1} yr^{-1} and 0.0560±0.0011 μmol kg^{-1} yr^{-1} respectively. This fertilization on a long-term scale in the surface waters of the inner ria estimated from ARIOS database was observed in parallel to the deoxygenation of -0.7±0.2 μmol kg^{-1} yr^{-1}. The apparent oxygen utilisation (AOU), calculated using the concentration of O_2 at saturation calculated according to Benson and Krause (1984), underwent an equivalent significant long-term change of 0.7±0.2 μmol kg^{-1} yr^{-1}, indicating that either the biological consumption rates, or a change in the amount of time that the waters are ventilated, or even its interaction or exchange with the sediment, cause the the long-term reduction of oxygen.

This fertilization on a long-term scale estimated from ARIOS database in the surface waters of the inner ria was observed in parallel to the deoxygenation of -0.7±0.2 μmol kg^{-1} yr^{-1}. The apparent oxygen utilisation (AOU), calculated using the concentration of oxygen at saturation calculated according to Benson and Krause (1984), underwent a long-term change of 0.7±0.2 μmol kg^{-1} yr^{-1} equal to the observated in the measurements of oxygen concentration. This coincidence may indicates that the long-term reduction of oxygen is due to the changes in the biological consumption rates, in the rates of the waters ventilation or even in sediment-water interactions rather than due to the effect of temperature. and salinity on oxygen saturation.

These findings found in the shallower waters of the *Ría de Vigo* allow us to hypothesize that the long-term increase in salinity would produce an increasingly weak vertical salinity gradient in the water column that would favour the vertical fluxes between the bottom and surface waters. Therefore the observed changes of oxygen and remineralized nutrient inputs in the surface waters could be due to an increasing footprint of benthic respiration, that has a major importance in the net ecosystem metabolism of this coastal region (Alonso-Pérez et al., 2015). This hypothesis would also explain the intense acidification in the inner waters in spite of growing alkalinity buffering.

The mean values at each station of the ARIOS database estimated for each depth range described in Figure 2, resulting in 8,384 values, were used to estimate a general value of the long-term trend in pH. The historical pH values in situ from the ARIOS database showed a general decrease in seawater pH in the Iberian Upwelling between 1976 and 2018, with an acidification rate of -0.012±0.002 yr^{-1} that significantly explains 2% of the total pH variation (Fig. 5a). The apparent oxygen utilisation was also shown as function of pH over time, revealing the association of higher AOU values with lower pH. The relationship between pH and AOU (Fig. 5b) showed an inverse linear correlation of -399±5 μmol kg^{-1} and a coefficient of determination (r-squared) of 0.52. The strong biological activity of the upwelling systems is the main driver of pH changes, explaining 52% of the observed variation in the discrete measurements. The distribution of nitrate seen in relation to the distribution of pH and AOU (Fig. 5b) showed the association of higher pH values with negative AOU values and a nitrate decrease, reinforcing the importance of biological processes in these marine carbonate system. Although the different processes controlling the AOU values were not separated in this analysis, the oxygen concentration in addition to the remineralization of the organic matter and the photosynthesis is conditioned by changes in temperature and salinity, ventilation events, water masses mixing and other processes (Sarmiento and Gruber, 2006). Therefore, the long-term drop in seawater pH measurements estimated from the ARIOS database presented here confirms that the future evolution of ocean acidification in this productive region is likely to depend on both the CO_2 increase in the atmosphere and other long-term changes (of natural and/or anthropogenic origin) affecting the seawater's carbonate system.

5. Data availability

The ARIOS dataset (Pérez et al., 2020) is archived at DIGICAL CSIC under the Digital Object Identifier (DOI): http://dx.doi.org/10.20350/digitalCSIC/12498.

The data are available as WHP-Exchange bottle format (arios_database_hy1.csv). A documentation file (readme_ARIOSDATABASE.txt) provides an description of the material and methods of the measurements and the parameters of the dataset. In both files, a table similar to the Table 1 of this manuscript include the DOI and the EXPOCODE of the original cruise files gathered in the ARIOS dataset.

These data are available to the public and the scientific community with the aim of that their wide dissemination will lead to new scientific knowledge about the ocean acidification and the biogeochemistry of the Galicia Upwelling System. The dataset is subject to a Creative Commons License Attribution-ShareAlike 4.0 International (http://creativecommons.org/licenses/by-sa/4.0/) and users of the ARIOS dataset should reference this work.

6. Conclusions

The ARIOS database is a unique compilation of biogeochemical discrete measurements in the Iberian Upwelling Ecosystem from 1976 to 2018. This data set comprises more than 17,653 discrete samples from 3,357 oceanographic stations (but not always for all parameters) of pH, alkalinity and associated physical and biogeochemical parameters (e.g., temperature, salinity, and chlorophyll and oxygen concentrations). The material and methods varied throughout the sampling period due to logistical and analytical issues such as those described in Table 1, where different sites are mentioned to download these measurements and detailed information.

Among the results described as preliminary and relevant information to learn the environmental and oceanographic context of the ARIOS database, we can mention the following main points concerning the pH characteristics of the Iberian Upwelling System:

- A decrease in seawater pH in the Iberian Upwelling between 1976 and 2018, with an acidification rate of -0.012±0.002 yr^{-1} that significantly explains 2% of the total pH variation
- An interannual pH variation of -0.0039±0.0005 yr^{-1} in the inner waters and -0.0012±0.0002 yr^{-1} in the ocean zone.
- An inverse linear correlation between pH and AOU of -399±5 $\mu mol\ kg^{-1}$ that explained 52% of the observed variation in the discrete measurements.

This published ARIOS database is a useful and necesseary tool to confirm and study biogeochemical changes in the seawater at long term trend. Likewise, we understand that it is a starting point to which to add future observation projects to continue increasing the knowledge about the impact of climate change in the Iberian Upwelling Ecosystem.

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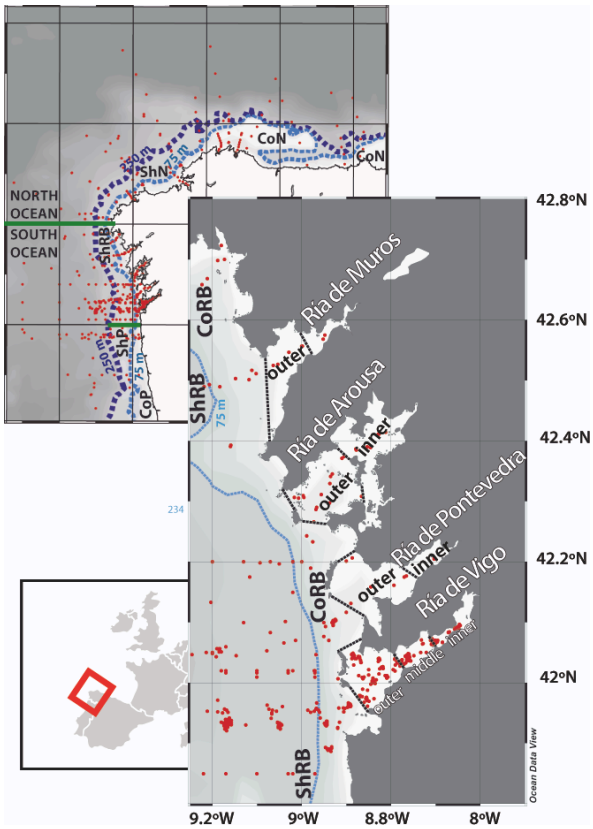

Figure 1. Map of all stations (red dots) including the geographical areas selected to classify the ARIOS database from isobath of 250 m (dark blue line) and 75 metres (light blue line), latitudinal criterion (green lines) and geographical lines (black lines).

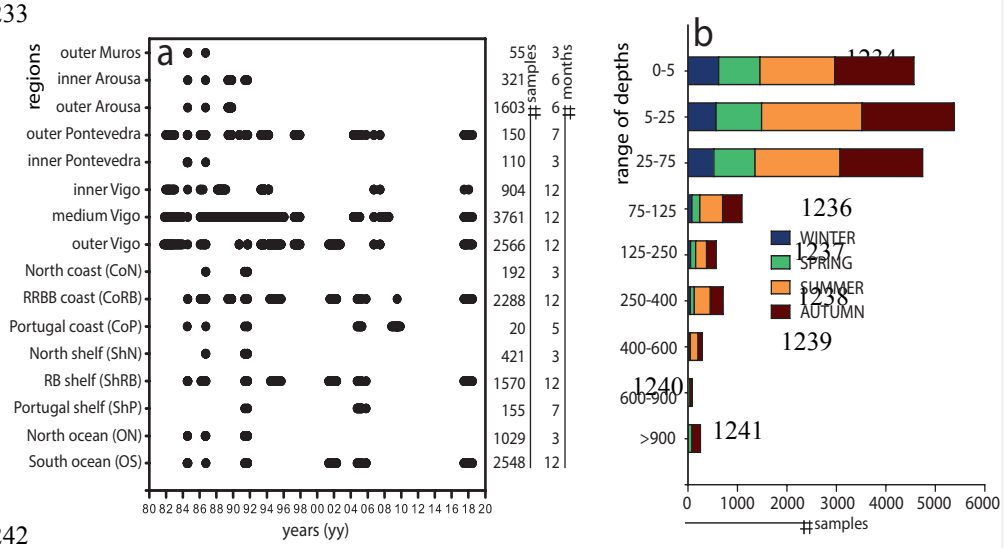

Figure 2. a) Temporal distribution of the observations in the geographical boxes included in the ARIOS dataset. b) Seasonal distribution of the measurements in relation to depth.

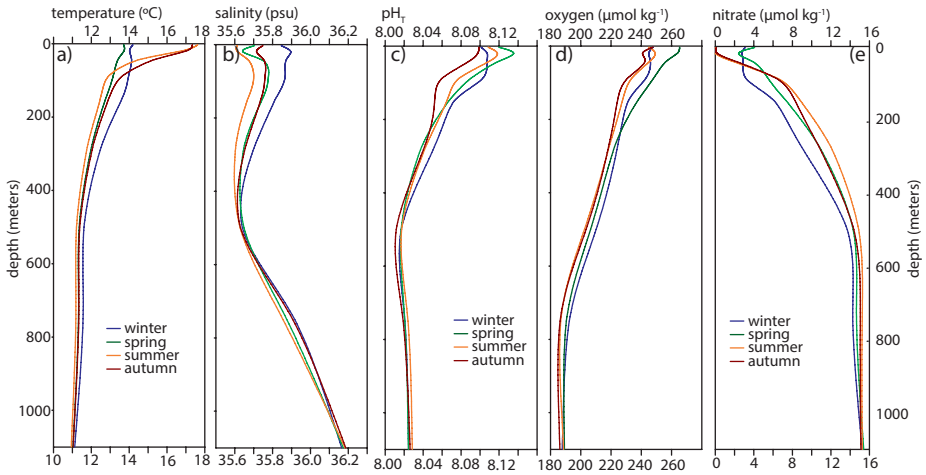

Figure 3. Profiles of seasonal means of temperature (a), salinity (b), pH_T (c), oxygen (d) and nitrate concentration (e) in the first 1100 meters of the region South Ocean shown in Fig. 1.

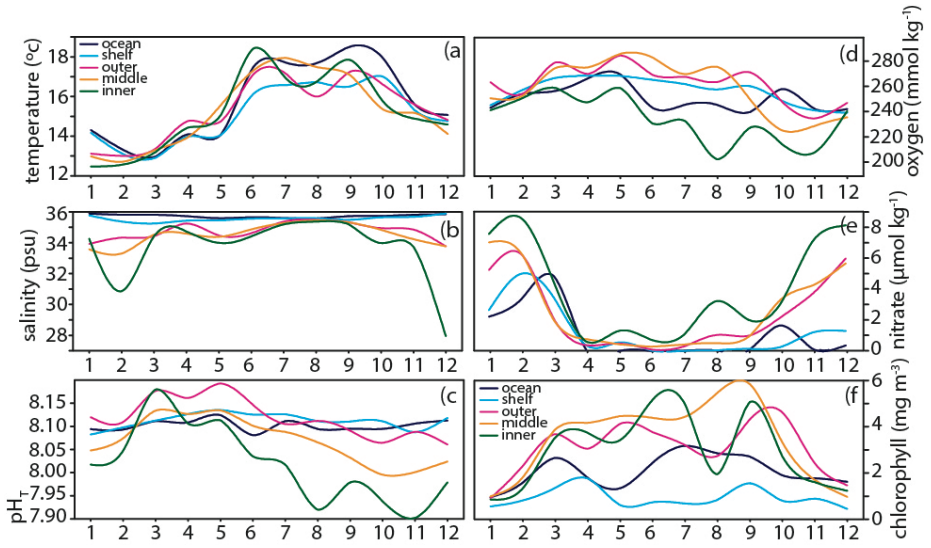

Figure 4. Sea surface (<5 meters depth) seasonal cycles in 1976 - 2018 of temperature (a), salinity (b), pH_T (c), oxygen concentration (d), nitrate concentration (e) and chlorophyll (f) at sea surface for five geographical boxes shown in Fig. 1: South Ocean, RB shelf and outer, middle and inner Ria de Vigo for the entire period of the ARIOS database.

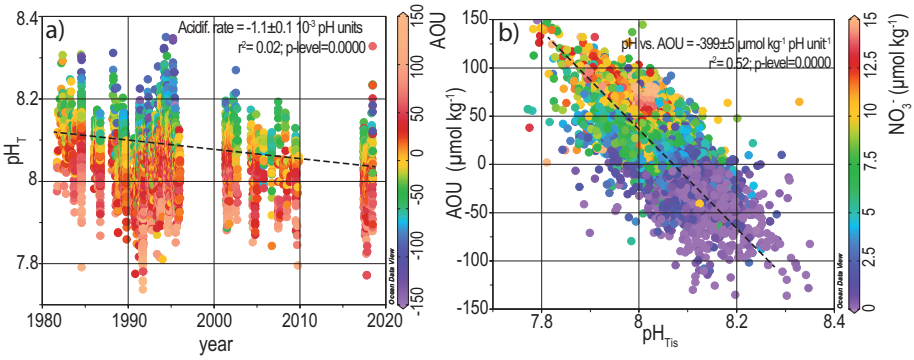

Figure 5. Time-series of pH ARIOS data. The black line depicts the long-term trend. Scatter diagram of AOU vs pH_T including the nitrate concentration shown as colour of every dot.

Table 1. Discrete measurements of projects gathered in the ARIOS database and associated information: including dates, the number of days between the start and the end of sampling period (#d), sample number (#), the principal investigator (PI), measured parameters, link to data repository and the sampled geographical area.

- All projects include measurements of T, S. Others as pH, alkalinity (Alk), nutrient (Nut), oxygen (O_2) concentration, chlorophyll (Chla) are indicated.

- The concentration units of these variables are μmol kg^{-1} or μmol L^{-1} (*) and the pH measurements in NBS scale (^{o}) or in total scale.

- Regions are identified as ocean (O), shelf (Sh), coastal (Co), Ría de Vigo (RV), Ría de Pontevedra (RP), Ría de Arousa (RA) and Ría de Muros (RM) while the superscript index means south (^{S}), north (^{N}), Portugal (^{P}), Rías Baixas (^{RB}), outer (^{O}), middle (^{M}) and inner (^{I}).

	SS_{range}	r^2ss	$t_{interannual}$	r^2	p-value
OCEAN	0.050	0.17	-0.0012±0.0002	0.21	0.0000
SHELF	0.050	0.06	-0.0017±0.0003	0.15	0.0009
OUTER	0.120	0.24	-0.0027±0.0003	0.21	0.0000
MIDDLE	0.130	0.28	-0.0022±0.0005	0.03	0.0000
INNER	0.260	0.47	-0.0039±0.0005	0.34	0.0000

Table 2: Seasonal amplitude of monthly pH means (SSrange) and long-term trends ($t_{interannual}$) of pH in five regions and significant regression coefficients between the in situ pH measurements and the monthly mean pH values (r^2ss) and the regression coefficient of the temporal variability of the deseasonalyzed pH measurements (r^2).

Appendix A

Table A1: Vertical distribution of seasonal mean values and standard deviation (mean ± standard deviation) of temperature, salinity, pH_T, oxygen and nitrate in the region South Ocean shown in Fig. 1.

	z (m)	winter	spring	summer	autumn
temperature (°C)	0-5	13.6±0.5	13.4±0.7	17.9±0.7	17.7±1.5
	5-25	13.8±0.7	13.6±0.6	17.1±0.7	17.2±1.5
	25-75	13.9±0.6	13.2±0.4	14.1±0.5	14.9±1.0
	75-125	13.7±0.6	13.0±0.5	12.8±0.3	13.2±0.4
	125-200	13.5±0.6	12.6±0.4	12.3±0.3	12.6±0.3
	200-400	12.6±0.3	11.9±0.3	11.6±0.3	11.9±0.3
	400-600	11.5±0.1	11.3±0.1	11.1±0.2	11.2±0.2
	600-900			11.4±0.1	11.4±0.2
	900-1300	11.2±0.1	11.1±0.2	10.9±0.3	11.0±0.3
salinity	0-5	35.82±0.06	35.72±0.11	35.62±0.07	35.71±0.08
	5-25	35.85±0.06	35.67±0.15	35.62±0.07	35.69±0.09
	25-75	35.85±0.05	35.74±0.09	35.71±0.06	35.76±0.08
	75-125	35.86±0.07	35.76±0.07	35.70±0.04	35.76±0.07
	125-200	35.80±0.10	35.73±0.06	35.64±0.04	35.72±0.06
	200-400	35.71±0.04	35.65±0.04	35.59±0.05	35.64±0.05
	400-600	35.64±0.04	35.65±0.05	35.64±0.05	35.64±0.03
	600-900			35.89±0.09	35.99±0.06
	900-1300	36.17±0.02	36.18±0.02	36.19±0.03	36.17±0.07
pH_T	0-5	8.10±0.02	8.12±0.02	8.11±0.02	8.09±0.02
	5-25	8.11±0.02	8.14±0.02	8.12±0.02	8.09±0.02
	25-75	8.11±0.01	8.12±0.01	8.11±0.02	8.08±0.02
	75-125	8.10±0.01	8.09±0.02	8.08±0.03	8.06±0.02
	125-200	8.07±0.03	8.07±0.03	8.06±0.03	8.05±0.02
	200-400	8.05±0.01	8.04±0.01	8.04±0.02	8.03±0.01
	400-600	8.02±0.01	8.017±0.002	8.02±0.02	8.01±0.01
	600-900			8.01±0.02	7.984±0.003
	900-1300	8.025±0.004	8.024±0.002	8.03±0.01	8.01±0.02
oxygen (µmol kg^{-1})	0-5	249±6	265±17	250±12	244±12
	5-25	250±7	267±13	253±10	240±7
	25-75	249±8	255±9	247±7	236±8
	75-125	247±9	247±9	232±4	227±7
	125-200	230±11	237±9	226±6	224±6
	200-400	227±11	224±8	213±7	220±8
	400-600	209±6	205±5	196±7	200±4
	600-900			186±2	184±2
	900-1300	187±1	189±3	188±4	185±3

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Table A2: Monthly mean values and standard deviation (mean ± standard deviation) of temperature, salinity, pH_T, oxygen concentration, nitrate concentration and chlorophyll at the surface waters for five geographical boxes shown in Fig. 1: South Ocean, RB shelf and outer, middle and inner Ría de Vigo.

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	month	OCEAN	SHELF	OUTER	MIDDLE	INNER
temperature (ºC)	Jan	14.3±0.4	14.2±0.4	13.1±0.8	13.0±0.7	12.5±0.4
	Feb	13.3±0.2	13.1±0.6	13.0±0.7	12.7±0.7	12.6±0.7
	Mar	13.0±0.6	12.9±0.5	13.4±0.4	13.3±0.6	13.2±0.6
	Apr	14.1±0.4	14.0±0.3	14.8±1.2	14.0±0.9	14.4±1.1
	May	14.1±0.9	14.1±1.1	14.7±1.0	15.6±1.5	15.1±1.3
	Jun	17.5±1.1	16.1±0.9	17.1±1.0	17.3±1.3	18.4±1.1
	Jul	17.7±0.6	16.6±1.0	17.2±1.0	17.9±1.5	16.9±1.2
	Aug	17.7±0.9	16.7±0.6	16.0±1.7	17.5±1.5	16.8±1.7
	Sep	18.5±1.3	16.5±1.3	17.3±1.3	17.1±1.2	17.8±1.4
	Oct	17.9±0.4	17.0±0.6	16.6±0.9	15.4±1.1	15.8±1.0
	Nov	15.6±0.6	15.3±1.1	15.6±1.4	15.2±0.9	14.9±1.2
	Dec	15.1±0.3	14.8±0.2	14.8±1.3	14.1±0.9	14.6±1.1
salinity	Jan	35.88±0.13	35.77±0.18	33.92±0.82	33.57±2.37	34.26±1.44
	Feb	35.81±0.04	35.37±0.84	34.33±1.63	33.30±2.51	30.86±4.78
	Mar	35.81±0.04	35.24±0.71	34.43±0.77	34.52±1.12	34.42±1.25
	Apr	35.72±0.07	35.43±0.47	35.24±0.29	34.58±0.90	34.72±0.74
	May	35.59±0.12	35.45±0.25	34.47±1.37	34.38±1.09	33.99±2.29
	Jun	35.64±0.13	35.56±0.12	34.62±0.81	34.87±0.74	34.42±0.54
	Jul	35.60±0.07	35.58±0.08	35.36±0.26	35.27±0.38	35.19±0.50
	Aug	35.57±0.05	35.59±0.05	35.48±0.22	35.45±0.21	35.37±0.17
	Sep	35.72±0.12	35.48±0.18	35.33±0.19	35.32±0.29	35.20±0.27
	Oct	35.74±0.05	35.65±0.10	34.94±0.56	34.84±0.88	33.98±1.45
	Nov	35.81±0.06	35.67±0.11	34.85±0.77	34.23±0.85	33.73±2.80
	Dec	35.85±0.06	35.89±0.26	33.76±1.36	33.77±1.51	27.95±5.50
pH_T	Jan	8.09±0.03	8.08±0.03	8.12±0.06	8.05±0.05	8.02±0.04
	Feb	8.09±0.02	8.10±0.03	8.11±0.05	8.07±0.05	8.05±0.06
	Mar	8.11±0.01	8.11±0.03	8.18±0.08	8.13±0.07	8.18±0.08
	Apr	8.11±0.02	8.13±0.03	8.16±0.05	8.13±0.05	8.11±0.07
	May	8.12±0.02	8.14±0.04	8.19±0.04	8.13±0.08	8.11±0.07
	Jun	8.08±0.03	8.13±0.03	8.15±0.04	8.10±0.07	8.04±0.09
	Jul	8.11±0.02	8.13±0.02	8.11±0.06	8.09±0.07	8.02±0.07
	Aug	8.09±0.03	8.11±0.03	8.11±0.07	8.07±0.09	7.92±0.05
	Sep	8.09±0.02	8.11±0.03	8.09±0.05	8.03±0.07	7.98±0.11
	Oct	8.09±0.01	8.11±0.03	8.06±0.06	8.00±0.08	7.94±0.09
	Nov	8.11±0.02	8.09±0.02	8.09±0.07	8.00±0.06	7.90±0.12
	Dec	8.11±0.01	8.12±0.01	8.06±0.03	8.02±0.04	7.98±0.02

Table A2: Continued

	month	OCEAN	SHELF	OUTER	MIDDLE	INNER
oxygen (µmol kg^{-1})	Jan	244±6	246±5	265±8	252±16	242±11
	Feb	255±5	259±12	255±13	254±15	252±14
	Mar	258±16	268±19	280±27	276±23	260±28
	Apr	268±5	270±7	271±13	276±25	249±26
	May	271±13	269±14	286±22	287±25	260±12
	Jun	244±3	266±11	270±17	284±26	232±19
	Jul	247±12	263±11	269±23	271±25	234±23
	Aug	247±9	259±8	265±23	277±27	204±21
	Sep	241±9	261±14	272±18	251±26	228±34
	Oct	259±13	250±12	249±20	226±21	215±16
	Nov	243±11	242±4	236±9	230±16	209±26
	Dec	243±10	240±12	248±11	237±14	242±16
nitrate (µmol kg^{-1})	Jan	2.3±0.5	2.7±0.8	5.3±2.6	7.1±3.8	7.6±2.0
	Feb	3.4±0.7	5.0±2.6	6.3±3.0	6.3±3.4	8.6±4.5
	Mar	4.9±2.4	3.5±2.9	2.1±2.5	2.0±2.4	4.5±2.3
	Apr	0.1±2.4	0.4±0.7	0.4±0.5	0.8±1.0	0.6±0.6
	May	0.02±0.03	0.6±0.4	0.5±0.4	0.5±0.8	0.7±1.3
	Jun	0.04±0.02	0.1±0.1	0.1±0.3	0.3±0.4	0.8±0.8
	Jul	0.1±0.1	0.0±0.1	0.3±0.6	0.5±0.7	1.1±0.8
	Aug	0.08±0.03	0.1±0.1	1.1±1.6	0.6±0.9	3.3±3.2
	Sep	0.1±0.1	0.2±0.7	1.0±0.9	0.9±1.1	2.1±1.4
	Oct	1.7±0.8	0.3±0.7	2.2±2.4	3.4±2.7	3.1±1.5
	Nov	0.1±0.1	1.2±2.9	3.8±2.9	4.3±2.3	7.2±3.2
	Dec	0.4±0.9	1.3±1.0	6.0±3.1	5.7±2.7	8.2±4.1
chlorophyll (mg m^{-3})	Jan	0.5±0.1	0.6±0.1	0.9±0.2	1.0±0.9	0.9±0.3
	Feb	0.5±0.1	0.8±0.3	2.3±1.5	1.8±1.6	1.3±0.9
	Mar	0.5±0.2	1.4±1.5	3.7±2.8	3.9±3.2	3.5±2.3
	Apr	2.6±1.1	1.8±1.4	3.0±1.8	4.2±2.4	3.7±2.1
	May	0.5±0.2	0.6±0.6	4.1±3.0	4.5±4.5	3.4±2.6
	Jun	0.8±0.8	0.7±0.6	3.8±1.7	4.4±2.7	5.2±3.2
	Jul	0.4±0.2	0.7±0.7	3.2±1.9	4.4±2.5	5.0±2.2
	Aug	0.5±0.2	0.8±0.5	2.7±2.3	5.5±4.1	2.0±2.3
	Sep	0.5±0.3	1.6±1.0	4.3±2.4	5.8±3.6	5.1±3.7
	Oct	0.3±0.1	0.8±0.5	4.6±4.1	3.3±3.5	2.7±1.9
	Nov	0.8±0.3	0.9±0.8	2.4±1.1	1.7±2.4	1.6±1.0
	Dec	0.5±0.2	0.4±0.6	1.5±0.8	1.0±0.6	1.2±0.3

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