Interactive comment on "ARIOS: An acidification ocean database for the Iberian Upwelling Ecosystem (1976–2018)"
by Xosé Antonio Padin et al.
Anonymous Referee #1
Received and published: 9 May 2020

The manuscript is scientifically sound. With regard to the presentation, the paper is easily readable although some sentences are unclear, and there are a number of grammatical errors and typos in the text. If the authors have their text double-checked, I only have some small remarks, which need to be dealt with. Therefore, overall, I believe that the work is well suited for publication in ESSD.

Specific comments:
Title should be modified. I would suggest something like ARIOS: a database for ocean acidification assessment in the Iberian Upwelling System.
The title has been changed to the following:
ARIOS: a database for ocean acidification assessment in the Iberian Upwelling System (1976 - 2018).

Introduction
Line 41: change "fix" to "withdraw"
The suggestion has been included in the new version of the manuscript.

Lines 42-45: please rephrase "In any case, the rapid increase of CO2 in the atmosphere decreases the ocean's pH". I would suggest: The gradual absorption of atmospheric CO2 by the oceans decreases seawater pH, causing ocean acidification, which conditions the buffering capacity of seawater and in turn the exchange of CO2 between the ocean and the atmosphere.
The suggestion has been included in the new version of the manuscript

Lines 52-53: Please rephrase. "observe and gather data about pH and other parameters of the marine carbon system to produce global and regional data products in order to help sustainably manage the ocean's resources. I would suggest: to conduct accurate measurements of pH and ancillary parameters and provide data products for a sustainable management of marine resources.
The suggestion has been included in the new version of the manuscript

Line 55: change of marine ecosystems to for marine ecosystems
The suggestion has been included in the new version of the manuscript

Lines 63-65: I know what you mean but I would recommend to rephrase the sentence.
The sentence "However, the great spatial and temporal variability has been widely spaced and intermittent over time, preventing a complete view from being obtained of ocean acidification in the upwelling system" has been rewritten. The new sentence is: "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."

Line 67-72: remove the s at the end of effects for grammar consistency. I would also move this paragraph after line 53 for coherence with the text.
The following paragraph has been moved after line 53.
"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."

Lines 72-75: I would modify the entire paragraph as: In the Iberian Upwelling System, accurate measurements of carbon system parameters commenced more than 30 years ago.
The first sentence of the new paragraph is the following "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."

Lines 75-80: which changes? Results have not been presented yet. I would therefore, continue the statement as: Researchers of the Instituto de Investigaciones Mariñas (IIM-CSIC) have been collecting pH and biogeochemical data along the Galicia coast (40_N and 45_N, 11_W) under the framework of different projects. This has allowed to generate a database, ARIOS (Acidification in the rias and the Iberian continental shelf), containing 17,653 discrete records gathered in 3,357 sampling sites.
In response to the previous two comments, the paragraph has been rewritten in order to include the suggestions: "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."

Data provenance: I would remove provenance
Line 86: I would replace Region by Data Coverage
Region has been replaced by Data spatial coverage

Line 115: change In addition to for Besides
The suggestion has been included in the new version of the manuscript

Line 119: delete the article before acidification and it would be convenient to specify the exact region/s where the mentioned acidification rate was estimated
The suggestion has been included and the region was mentioned as "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"

Data sources:
In general, I very much appreciated the comprehensive explanation of the projects that provided data for the dataset. However, considering that explanatory information of the cruises is given in Table 1 and each individual project is associated to a database included in a public repository, I do not find section 3.2 essential for the manuscript, as all those details can be mentioned (and possible are) in the repository. The authors might re-consider to shorten this section by keeping the first paragraph and refer subsequent info to Table 1.

We understand that detailed information about the methods and materials of the oceanographic cruises that are part of the ARIOS database is mandatory according to the requirements of ESSD. Therefore, we prefer not to modify this section of the manuscript.

Methods:
Lines 337-338: Please rephrase. I would suggest: Except for the Galicia cruises (Table 1), in which nutrient samples were analysed on board, samples were kept in the dark and cold (4_C) after collection for further analyses in the shore based laboratory.
The suggestion has been included in the new version of the manuscript

Line 341: change is to was.
The suggestion has been included in the new version of the manuscript

Line 351: Same as above
The suggestion has been included in the new version of the manuscript

Line 371: remove the article before Table 1
The suggestion has been included in the new version of the manuscript

Line 374: You possibly mean Table 1 instead?
The suggestion has been included in the new version of the manuscript

Line 377: by the high variability present in a system characterized by an intense biological activity
The suggestion has been included in the new version of the manuscript

Line 384: This section should be moved and either merged with 3.1 or placed right below it for the sake of consistency and for a better introduction of the sampling region.
This section has been moved just below section 3.1. The other sections of the Material and Methods have been renumbered because of this change.

Results:
Line 424: vertical profile of what? Please indicate.
These sentences had been rewritten. The new text is: "The vertical profile of the temperature, salinity, 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"

Lines 420-445: why do not you show the standard deviations for T and S for all the depth ranges as you do for the water column comprised between 500m and 1100m?
The standard deviations were not included in Figure 3 simply to facilitate the clarity of the graphical representation of the vertical biogeochemical profiles. For the same reason, they were also not included in the monthly distribution of the biogeochemical variables shown in Figure 4. In any case, the mean values with their corresponding standard deviation values (mean±standard deviation) represented in Figure 3 and Figure 4 are shown in two Tables at the end of the reply to the referee. This information could be included as supplementary material to the manuscript if it deems this appropriate by the Editor.

Line 443: add : : :down to 1100m
The suggestion has been included in the new version of the manuscript

Line 447: change distribution to profile
The suggestion has been included in the new version of the manuscript

Line 448: replace at this depth by within this depth range
The suggestion has been included in the new version of the manuscript

Lines 452-454: Speculative as it is not demonstrated or shown in the graph. Therefore, I would just say: The highest pH values could be attributed to the biological CO2 drawdown by phytoplankton activity, which brought the pH to a peak value of 8.13 at 40 metres deep during the spring bloom.
The suggestion has been included in the new version of the manuscript.

Lines 454-457. Same as above. I would suggest to rephrase the paragraph as it is also confusing. Below 100 metres, respiration of organic matter possibly was responsible of lowering pH: : :.but anyhow the text s counterintuitive To me, pH values between 200 and 500 m depth seem to be lower than those from 500 m down to 1100m, which were also constant and similar within the entire depth range regardless of the season.
The commented lines: "Underneath this intense photosynthesis activity between the surface and 100 metres, the respiration of organic matter took the pH to lower values than those measured in winter between 200 to 500 metres, a depth at which the spring and winter values were practically equal." were rewritten. This was the new text: "The higher pH values could be attributed to the biological reduction of CO_2 by phytoplankton activity, which brought the pH to a maximum value of 8.13 to 40 meters during the spring bloom. After the intense photosynthetic activity observed in surface waters during spring and summer, pH values reached minimum values in the first 200 meters of depth during autumn due to respiration of organic matter. However, it was at a depth of 500 metres that the minimum pH values were measured in all seasons where is found the subpolar Eastern North Atlantic Central Water proceeding from the northeastern cyclonic gyre (Harvey, 1982; Ríos et al., 1992)."

Lines 458-462: Please rewrite: I would propose: The influence of phytoplankton growth on biogeochemistry during spring can be also evidenced by the oxygen concentration pattern during this season. In the upper layer (depth range?) spring oxygen levels exceeded those in winter, whereas a decrease in oxygen concentration was found from 300 m depth down to 1000 m, possible due to enhanced respiration from cascading organic matter. It would be helpful to add in this section a table with averaged concentrations and SD of each parameter within the different depth ranges and for each season.
The suggestion has been included in the new version of the manuscript. The new lines are the following: 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.

Line 473: seasonal cycle of what? Please specify. I would recommend to rewrite the whole paragraph, as in Fig 4 what you actually show is the seasonal cycle of different biogeochemical parameters in surface waters of 5 regions and not the five regions themselves, as it can be deduced from the text the way it is right now.
The suggestion has been included in the new version of the manuscript. The new lines are the following: "The seasonal cycle of the biogeochemical properties (temperature, salinity, pH, 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. Five regions that were located as a longitudinal transect between the inner Ría de Vigo and the ocean zone are shown in Fig. 4."

Line 506: replace seasonable by seasonal.. you could also rewrite the following sentence as: with maximum and minimum pH values in spring and autumn, respectively, and in all regions (Fig. 4c).
The suggestion has been included in the new version of the manuscript

Lines 541-549: considering change to past tense for consistency with the rest of the paragraph. Moreover, a reference could be well added at the end of the paragraph to reinforce your statement regarding the relevance of benthic and vertical fluxes in the Ria.
The suggestion has been included in the new version of the manuscript. The new lines are the following: "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).

Line 551: please add a “s” to trend
The suggestion has been included in the new version of the manuscript

Line 552: long term trends of what? Please specify. I assume the temporal trends are estimated over parameters and they do not refer to surface waters themselves. Therefore, it needs to be re-written.
The text has been re-written. "The long-term trends of the biogeochemical properties in these surface waters were estimated to be the interannual linear rate of the deseasonalyzed time series, previously removing the monthly means in these regions and assuming a null spatial variability"

Line 562: any suggestion why a warming trend is not found as it was previously reported?
The fact that we did not find a statistically significant warming trend as would be expected on the basis of the overall ocean behavior is mainly due to the fact that the warming trend was estimated for the surface waters of the study area. The first meters of the water column in this coastal zone are under the influence of important oceanographic phenomena that affect temperature such as coastal upwelling pulses, the presence of surface currents or river inputs. The different temporal variability of these processes together with the remarkable spatial variability of the study area prevents the characterization of the warming in a statistically significant way from measurements with the irregular frequency of the ARIOS database. Therefore, information from other temperature data sources and a more detailed statistical analysis should be considered for this specific purpose.

Line 563: consequence of climate change: : :I would add “in marine ecosystems”.. and move the reference by Caldeira and Wicket 2003 after ocean acidification.
The suggestion has been included in the new version of the manuscript

Line 565: What do you mean by pH number? Value? Number of measurements?
The text has been re-written. "with a greater decline in pH number towards the coast" has been changed by "with a greater decrease in the long-term trend of pH towards the coast

Line 566: please replace : : :was about triple the change of: : :by: : :.. was three fold higher than the

trend observed in the open ocean zone, equivalent to 0.0012_0.0002 yr-1
The suggestion has been included in the new version of the manuscript

Line 569-575: I would rephrase the paragraph as: These pH decrease rates found in both coastal and open ocean regions of the Iberian Upwelling System lie within the range of other acidification rates estimated in different sites of the North Atlantic Ocean (Lauvset and Gruber, 2014; Bates et al., 2014), being also coherent with the mean rates calculated for the global ocean and for the Eastern North Atlantic and equal to -0.018 and -0.0164 decade-1 , respectively (Lauvset et al., 2015; Rios et al 2001)
The suggestion has been included in the new version of the manuscript

Line 575: just indicate: Salinity exhibited an increasing long-term trend (value?) that was dependent on the distance to the mouth of the Ria (de Vigo? All of them?). I do not see the salinity trend indicated anywhere.
The suggestion has been included in the new version of the manuscript

Line 581: Change So to Therefore.
The suggestion has been included in the new version of the manuscript

Line 586: add a “s” to nutrient and remove the previous article
The suggestion has been included in the new version of the manuscript

Line 587: same as above: delete the article before nitrate. But anyhow, it is not clear if the trends in nutrients levelcome from the previous study by Doval et al (2016) or are the result of your analysis. Please clarify.
The rates had been estimated from ARIOS database. This paragraph has been rewritten in order to clarify the meaning. The new text is the following: " 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."

Lines 590-596: do you mean that your AOU temporal trend coincides with the deoxygenation rate calculated previously by Doval? It is not clear enough in the text.
Long-term trends in oxygen concentration and AOU were estimated from the ARIOS database. The paragraph was rewritten to clarify this information. This is the new text: "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.

Lines 598-604: Speculative. Please support with references
This paragraph was intended to provide an integrative hypothesis on observed large-scale trends. The text has been changed in the manuscript to the following paragraph: "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."

Line 614: correlation coefficient should be indicated even though it is contained in the Figure.
The coefficient of determination of 0.52 between pH and AOU was included in the sentence as follows: "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."

Line 606-619: To me, the entire paragraph is the highlight of the paper, as it evidences the relevance of the dataset and gives insight on the processes responsible for the mean decreasing pH trend found in the area. In my opinion, this finding gets somehow diluted between the other results when it should be emphasized by the authors.

Line 623: photosynthesis of organic matter???
The sentence has been corrected. The new text is: "... the oxygen concentration in addition to the remineralization of the organic matter and the photosynthesis is conditioned by changes..."

Line 627: I would finish as: Hence, the analysis performed over the database presented here confirms that the future evolution of ocean acidification in this productive region is likely to depend on both the potential CO2 increase in the atmosphere and other long-term changes (of natural and/or anthropogenic origin) affecting the seawater's carbonate system.
Following the suggestion, the new manuscript finish as follows: "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 potential CO2 increase in the atmosphere and other long-term changes (of natural and/or anthropogenic origin) affecting the seawater's carbonate system."

Interactive comment on "ARIOS: An acidification ocean database for the Iberian Upwelling Ecosystem (1976–2018)" by Xosé Antonio Padin et al.

Michele Giani (Referee)
mgiani@ogs.trieste.it
Received and published: 5 June 2020

The data set surely will be relevant also for the future understanding of the interactive effects on acidification in the Iberian Upwelling System of coastal processes and global changes. However there is a need of a careful revision of the data set and of improvements in the ms. In the abstract the author give acidification rates ranging from – 0.0016 to -0.0032 pH units/yr whereas in the ms (L. 566) they give a -0.0039 ph units/yr for the inner waters. This discrepancy should be resolved.
The discrepancy has been corrected. The correct acidification rate is -0.0039 pH units yr-1.

As the estimated acidification rate is higher than the average ocean acidification it would be important to discuss the potential effects of the gaps in the times series some spanning also 7 consecutive years.

It would be relevant to compare the trends on periods without long gaps of data, which could strongly affect the slope of the trend.

Following the reviewer's recommendation, the long-term trend in acidification was partially assessed in those periods best analysed, namely 1981-1998 and 2001-2009. The main conclusion of the results obtained was the loss of statistical significance of acidification rates. In fact, every interannual changes of deseasonalized pH time serie during the period 1981-1998 showed p-values> 0.05 while only the surface waters of the ocean and the continental shelf with pH trends of -0.0040±0.0006 yr^{-1} and -0.0140±0.0017 yr^{-1}, respectively, were significant. In any case, we understand that the inclusion of the data shown in Table 2 beyond an intense study on the evolution of acidification in an upwelling system want to highlight the fact that direct observations in the Iberian Upwelling System over the last 40 years indicate that pH is decreasing.

A comparison with other articles reporting ranges for coastal acidification trends could be interesting for improving the discussion of results.

Other measures of acidification rates in near-shore areas such as the well-known ESTOC or CARIACO stations show year-on-year trends of -0.0018±0.0001 yr^{-1} and -0.0025±0.0004 yr^{-1}, respectively. Other acidification rates like the one found at the DYFAMED station in the Mediterranean Sea was -0.0028±0.0003 yr^{-1} (https://hal.sorbonne-universite.fr/hal-01534516/document). In general these rates of change are in the range of the information obtained from the ARIOS database as well as the acidification rates used as reference by Lauvset et al. 2015.

Coastal acidification includes local changes in water chemistry from changes in temperature or salinity, high nutrient inputs or inputs from freshwater rivers, or excess nutrient runoff (e.g., nitrogen and organic carbon). An ecosystem's ability to cope with acidification is influenced by the number of local stresses it faces. Some ecosystems may be more resilient to ocean acidification by minimizing biogeochemical changes. Because of these characteristics, the impact of acidification between coastal areas is difficult to compare, and extensive work is needed to analyse the similarities and differences between coastal areas.

In the section "Cruises in the 2000s and recent years" (L. 261- 265), the information about each cruise is given but not always the months and years are given. I strongly suggest to provide similar information for each cruise or to refer to a more specific table where the time span of each cruise is given. In particular, regarding the last ARIOS project it is not clear in which months was carried out. **The number of days between the start and the end of the sampling period of each project was included in the Table 1.**

It would be important if the authors could be the precision for the temperature and salinity measurements in the period 1976-1984.
The information has been included in the new version of the manuscript. Namely, the precision of the temperature and salinity measurements in that period was 0.02ºC and 0.005 respectively.

For chlorophyll measurements, as different filters were used, could the authors provide an estimation of the pore size given and of potential effects of the change. The indication of the volume filtered (range) could be also important if available.
The 6 cm Schleicher and Scholl and Whatman GF/F 2.5 cm filters are made of glass fibre and have a similar nominal pore of 0.7 micron. The Schleicher and Scholl filters were used for chlorophyll measurements with spectrophotometers that needed a larger sample volume because of their lower detection sensitivity while the Whatman filters always for fluoremetric measurements.

Regarding the adopted Quality control procedure (L.370-L.382) it would be useful if the authors could provide a synthetic information on the first and second level of the quality control cited in this section.

Regarding the presented ARIOS data set there are some corrections to the data that the authors should consider as there are many negative concentrations for nitrites (n=4), nitrates (n=16), ammonia (n=13), and chlorophyll a (n=2).
The values of any parameter lower than the precision of those measurements as well as the negative measurements were replaced by zero and their corresponding flag by 6.

There are concentrations for nutrients and chlorophyll a in the range of 10-3 to <10-7 that should be correctly reported, presumably, as less than the detection limits given in the methods, and properly flagged with QF = 6.
The values of any parameter lower than the precision of those measurements as well as the negative measurements were replaced by zero and their corresponding flag by 6.

For all nutrients there are many values equal to 0 with QF= 2, these values presumably are below the detection limits and should be flagged with QF=6.
The values of any parameter lower than the precision of those measurements as well as the negative measurements were replaced by zero and their corresponding flag by 6.

There are three in situ pH values in the range 7-7.6 that should be checked to evaluate if they can be considered reliable or doubtful.
These 3 measurements of pH were flagged = 3

Below some minor comments are given:
L.52 I suggest to correct as follows: to help a sustainable management of the : : :
The suggestion has been included in the new version of the manuscript

L. 290 I think that "as well" should be omitted and I suggest to substitute "to create" with "to record".
The suggestion has been included in the new version of the manuscript

L. 306 "pH value to do so": unclear.
The sentence was rewritten as follows: "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)."

L325-327 it is unclear if for the titration the HCl concentration was 0.1 or 0.13 M.
0.1M

L.338, L.341 change the conjugation of verb to the past.
The suggestion has been included in the new version of the manuscript

L.351 "Cl2Mn" should be written as "MnCl2".
The suggestion has been included in the new version of the manuscript

L.352 change the conjugation of verb to the past.
The suggestion has been included in the new version of the manuscript

L. 382 check the year in the reference list is 2010.
The correct year is 2010. The manuscript has been corrected.

L. 506 "large seasonable variability" change with " large seasonal variability".
The suggestion has been included in the new version of the manuscript

L. 523 "and so it would" I suggest changing as: "and therefore it would".
The suggestion has been included in the new version of the manuscript

I suggest changing the yellow colour in Figure 1, as on the printed version is not clearly visible.
The suggestion has been included in the new version of the manuscript. The new line is a green line.

To enhance the readability of Figure 2, I suggest to enlarge them or to split the figure in two.

In Figures 3 and 4, for Salinity, I suggest omitting "psu" as it is not a real measurement unit, but a conductivity ratio. I suggest to indicate the pH is on the total scale similarly to figure 5.
The pH on the total scale was indicated as pH_T in every figure. The psu is mentioned to indicate salinity is reported in practical salinity scale. The new Figures 3 and 4 are attached to the reply to the referee.

There is the need to correct the units of oxygen in micromole kg-1 in figure 4.
The units of oxygen has been corrected.

The subscript of pHT in the Figure 5 is not well readable and should be explained in the caption.

I suggest, all over the figures, to indicate the pH as pHT for clarifying that is expressed on the total scale, moreover, to increase the readability, I suggest to enlarge or split the two graphs.

TABLE 1. According to the data set, the ARIOS cruises were carried out during different months of 2018 and not in one month of 2017. As some cruises/projects could span over more month perhaps it would be better to provide the period of the study instead of a single date.

The number of days (#d) between the start and the end of sampling period of each project was included in the Table 1 that is attached at the end of the reply to the referee.

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

Xosé Antonio Padin*^{1}, Antón Velo^{1} and Fiz F. Pérez^{1}

^{1,} Instituto de Investigaciones Marinas, IIM-CSIC, 36208 Vigo, Spain.

padin@iim.csic.es, avelo@iim.csic.es, fiz.perez@iim.csic.es

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

CO$_2$ emissions of anthropogenic origin (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

TONI PADIN 25/6/2020 14:25
Eliminado: **ARIOS: An acidification ocean database for the Iberian Upwelling Ecosystem (1976 - 2018)**

TONI PADIN 25/6/2020 11:15
Eliminado: 0032

through the air-sea interface, the oceanic reservoir plays a key role as a sink for about 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 United Nations 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.

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

TONI PADIN 22/6/2020 0:04
Eliminado: fix

TONI PADIN 22/6/2020 0:06
Eliminado: In any case,

TONI PADIN 22/6/2020 0:06
Con formato: Subíndice

TONI PADIN 22/6/2020 0:06
Con formato: Subíndice

TONI PADIN 22/6/2020 0:05
Eliminado: the rapid increase of CO_2 in the atmosphere decreases the ocean's pH

TONI PADIN 22/6/2020 22:38
Eliminado:

TONI PADIN 22/6/2020 22:38
Eliminado: produce global and regional data products in order to help sustainably manage the ocean's resources.

TONI PADIN 22/6/2020 0:07
Eliminado: of

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

TONI PADIN 24/7/2020 21:45
Eliminado:

TONI PADIN 22/6/2020 22:51
Con formato: Fuente: Sin Negrita

TONI PADIN 22/6/2020 22:51
Eliminado: However, the great spatial and temporal variability has been widely spaced and intermittent over time, preventing a complete view from being obtained of ocean acidification in the upwelling system.

TONI PADIN 25/6/2020 11:09
Con formato: Inglés (americano), No revisar la ortografía ni la gramática

TONI PADIN 22/6/2020 23:05
Eliminado: The effects of ocean acidification on marine ecosystems has awoken the interest of the international community and has stimulated global impetus 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. Researchers at the *Instituto de Investigaciones Mariñas* (IIM-CSIC) in Vigo (Spain) have already started this task, measuring the marine inorganic carbon system and associated parameters on the Galicia coast in the northwest of the Iberian Peninsula, since 1976. These biogeochemical changes, including the pH variation, have been gathered via different projects with particular objectives between 40ºN and 45ºN, 11ºW and the Galician coast over the past 40 years. The current database, hereinafter called ARIOS (Acidification in the rias and the Iberian continental shelf)

TONI PADIN 22/6/2020 0:08
Eliminado: Region

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

TONI PADIN 22/6/2020 23:39
Eliminado:

TONI PADIN 22/6/2020 0:11
Eliminado: In addition

TONI PADIN 22/6/2020 0:11
Eliminado: to

TONI PADIN 22/6/2020 23:53
Eliminado: in the surrounding waters of the Galician coast

TONI PADIN 22/6/2020 23:53
Eliminado: in the first 700 metres

TONI PADIN 23/6/2020 0:00
Movido (inserción) [1]

TONI PADIN 23/6/2020 0:01
Eliminado: 4

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:

TONI PADIN 25/6/2020 0:17
Eliminado:

TONI PADIN 23/6/2020 0:01
Eliminado:

TONI PADIN 23/6/2020 0:01
Eliminado: 2

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

TONI PADIN 23/6/2020 0:01
Eliminado: 3

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 psu, using the equations 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.

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).

TONI PADIN 25/6/2020 0:18
Eliminado: as well

TONI PADIN 25/6/2020 0:18
Eliminado: create

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.

TONI PADIN 25/6/2020 0:20
Eliminado: to do so (

TONI PADIN 25/6/2020 0:20
Eliminado: ,

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.

TONI PADIN 19/7/2020 23:58
Con formato: Subíndice

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

TONI PADIN 19/7/2020 22:49
Eliminado: N

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,

TONI PADIN 22/6/2020 23:58
Eliminado: Except in the campaigns called Galicia, where the samples were analysed on board, the samples collected are kept in the dark and cold (4ºC) to be analysed in the laboratory.

TONI PADIN 22/6/2020 0:12
Eliminado: i

TONI PADIN 22/6/2020 0:13
Eliminado: is

TONI PADIN 25/6/2020 0:30
Eliminado: Cl$_2$

TONI PADIN 25/6/2020 0:30
Con formato: Subíndice

TONI PADIN 25/6/2020 0:30
Eliminado: are

TONI PADIN 19/7/2020 23:33
Eliminado: C

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 flag 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=6. Some very low pH associated to very low salinity waters were flagged as doubtful.

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

TONI PADIN 22/6/2020 0:14
Eliminado: the

TONI PADIN 25/6/2020 12:39
Eliminado: QC

TONI PADIN 22/6/2020 0:15
Eliminado: 2

TONI PADIN 22/6/2020 0:20
Eliminado: with very

TONI PADIN 22/6/2020 0:20
Eliminado: high

TONI PADIN 23/6/2020 0:00
Subido [1]: **3.4. Distribution of sampling**

TONI PADIN 25/6/2020 0:35
Eliminado: 2009

TONI PADIN 23/6/2020 0:00
Eliminado: ... [1]

TONI PADIN 20/7/2020 0:02
Con formato: Subíndice

periods (December-February, March-May, June-August and September-November) and averaged to describe winter, spring, summer and autumn respectively (Fig. 3).

The vertical distribution of the temperature (Fig. 3a) showed the presence of warmer saline waters throughout the water column in winter with the exception of the surface waters during summer, which showed intense heating due to the radiant solar energy. Below the maximum temperature observed during the summer, cold central waters of subpolar origin occupied the water columns with lower salinity (Fig. 3b). The vertical variation of temperature is typical for a temperate region with relatively homogenous deep water below the seasonal thermocline, reaching maximum SST values in summer and autumn, and minimums in spring and winter. The winter temperature profile is relatively warmer than in spring because of the presence of the IPC (Alvarez-Salgado et al., 2006), which reaches a depth of 300 metres. The maximum salinity is also found in winter due to the presence of the IPC, whereas the minimum values are found in autumn (Fig. 3b). Below 500 metres in depth, the increase in salinity points to the presence of Mediterranean Water. These differences reach a minimum at 500 metres deep, where the salinity values coincided. From this depth down to 1,100 metres, the differences in temperature and salinity throughout the four seasons were minimal, with the mean values converging to 11.03±0.07ºC and 36.117±0.009 psu, respectively (Fig. 3ab).

The vertical profiles of pH_T, NO_3^- and oxygen concentration (Fig. 3cde) also showed a variation lower than 1% within this depth range with annual means of 15.2±0.1 µmol kg^{-1}, 8.025±0.005 and 188±1 µmol kg^{-1} respectively. The pH values from a maximum subsurface located at around 40 metres deep showed a clear inverse correlation with the depth down to a depth of 500 metres throughout the seasonal cycle, where the annual minimum value of 8.018±0.005 was reached. The higher pH values could be attributed to the biological reduction of CO_2 by phytoplankton activity, which brought the pH to a maximum value of 8.13 to 40 meters during the spring bloom. After the intense photosynthetic activity observed in surface waters during spring and summer, pH values reached minimum values in the first 200 metres of depth during autumn due to respiration of organic matter. However, it was at a depth of 500 metres that the minimum pH values were measured in all seasons where is found the subpolar Eastern North Atlantic Central Water proceeding from the northeastern cyclonic gyre (Harvey, 1982; Ríos et al., 1992). The influence of phytoplankton growth on biogeochemistry

TONI PADIN 22/6/2020 0:28
Eliminado: distribution

TONI PADIN 20/7/2020 0:02
Con formato: Subíndice

TONI PADIN 22/6/2020 0:29
Eliminado: at

TONI PADIN 23/6/2020 1:08
Con formato: Subíndice

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}.

TONI PADIN 23/6/2020 0:48

Eliminado: The highest values were related to the biological CO_2 drawdown, which brought the pH to a peak value of 8.13 at 40 metres deep during the spring bloom. Underneath this intense photosynthesis activity between the surface and 100 metres, the respiration of organic matter took the pH to lower values than those measured in winter between 200 to 500 metres, a depth at which the spring and winter values were practically equal.

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. Five regions that were located as a longitudinal transect between the inner Ría de Vigo and the ocean zone are shown in Fig. 4.

TONI PADIN 20/7/2020 0:02

Con formato: Subíndice

TONI PADIN 23/6/2020 9:40

Eliminado: The seasonal cycle of the surface waters (0 to 5 metres) was estimated as a monthly filtered means, accepting only values within two standard deviations. 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 upwelled waters in the surface layer (Alvarez-Salgado 1993).

The monthly salinity averages (Fig. 4b) clearly showed significant differences between the offshore and coastal waters. Sharp salinity changes were seen in the estuary during winter, especially in the inner area where values lower than 28 psu were reached with the arrival of continental inputs in December. The weak seasonal cycle of salinity in the shelf and ocean waters showed high values in December due to the influence of warm saline water from the IPC, usually located on the shelf slope even though it may even enter the rias depending on the relative intensity of shelf winds and the intensity of the continental runoff (Alvarez-Salgado et al., 2003). In this sense, the slight salinity minimum observed in the shelf waters in March could be consequence of the offshore spreading of the maximum discharges from the River Miño and Douro (Otero et al., 2010) at the end of downwelling season. After this, the shelf and ocean waters showed minimum values in summer due to the arrival of cooler and fresher subpolar waters (Rios et al., 1992; Alvarez-Salgado et al., 2003, 2006). In August, coinciding with the maximum salinity of the surface waters in the interior of the *Ría de Vigo* due to the minimum river runoff, the surface waters between the inner *Ría de Vigo* and the ocean region were almost homogeneous, with minimum differences in salinity of 0.2 psu.

Like salinity, there was little seasonal variability in pH in the offshore waters, but large seasonal variability in coastal waters, with maximum and minimum pH values in spring and autumn, respectively, and in all regions (Fig. 4c). The net balance between production and respiration of organic matter and the estuarine circulation caused a maximum pH of 8.19 in the outer region of the *Ría de Vigo* in May and a minimum of 7.96 in the inner waters in November.

TONI PADIN 23/6/2020 9:43
Eliminado: ble

TONI PADIN 23/6/2020 9:43
Eliminado: with peak pH in spring and minimum pH in autumn in every region (Fig. 4c)

The oxygen concentration (Fig. 4d) in the coastal ecosystems is also controlled by the remineralization of the organic matter and photosynthetic activity of the phytoplankton community, with the effect of salinity and temperature on the oxygen saturation level. The variability in the oxygen concentration, like the pH distribution, showed a growing seasonal amplitude towards the coastline, with maximum values in the outer and middle *Ría de Vigo* and lower values in the inner waters, especially during the second half of the seasonal cycle. Hence, the dissolved oxygen concentration mirrored the seasonal 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

TONI PADIN 25/6/2020 0:39
Eliminado: so

TONI PADIN 23/6/2020 9:50
Eliminado: is

TONI PADIN 23/6/2020 9:50
Eliminado: recently

TONI PADIN 23/6/2020 9:51
Eliminado: . It can reach up to

TONI PADIN 23/6/2020 9:51
Eliminado: rises

TONI PADIN 23/6/2020 9:52
Eliminado: entering

TONI PADIN 23/6/2020 9:52
Eliminado: i

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 estimated to be the interannual linear rate of the deseasonalyzed time series, previously removing the monthly means in these regions and assuming a null spatial variability. The significant trends in the ARIOS database, meaning long-term variability, should be interpreted as a combination of the natural variability on a decadal scale (Pérez et al., 2010; Padin et al., 2010) and anthropogenic forcings (Wolf-Gladrow et al., 1999; Anderson and Mackenzie 2004; Bakun et al., 2010).

No long-term temperature variability was found in the surface waters of any region despite the known warming previously reported on the Northern Iberian coast (Pérez et al., 2010; Gesteira et al., 2011; González-Pola et al., 2005). Unlike the temperature, the other expected consequence of climate change in marine ecosystems, namely ocean acidification (Caldeira and Wickett, 2003) was observed along the longitudinal transect, with a greater decrease in the long-term trend of pH towards the coast (Table 2). The long-term pH variation of -0.0039±0.0005 yr^{-1} in the inner waters was about three fold higher than the change observed in the ocean zone, equivalent to -0.0012±0.0002 yr^{-1} in the ocean zone, explaining the 34% and 22% variation in pH in situ respectively, and representing 1-3% of the seasonal pH variation in all zones. These pH decrease rates found in both coastal and open ocean regions of the Iberian Upwelling System lie within the range of other acidification rates estimated in different sites of the North Atlantic Ocean (Lauvset and Gruber, 2014; Bates et al., 2014), being also coherent with the mean rates calculated for the global ocean and for the Eastern North Atlantic and equal to -0.018 and -0.0164 decade^{-1}, respectively (Lauvset et al., 2015; Rios et al 2001).

The long-term trend in salinity was also seen to be evidently dependent on the distance to the mouth of the *Ría de Vigo*. The interannual rate of sea surface salinity in the outer and inner ria previously reported by Rosón et al. (2009) was 0.0426±0.016 psu yr^{-1} and 0.0193±0.0056 psu yr^{-1} respectively. These changes were observed in parallel to an interannual alkalinity increase that is cancelled out in the normalized alkalinity, estimated as the difference between the alkalinity measured and the alkalinity calculated using the linear regression with salinity in each region. Therefore, the interannual salinity increase was the forcing that explains the increase in the buffer capacity of the

TONI PADIN 24/6/2020 12:24
Eliminado: se

TONI PADIN 22/6/2020 0:41
Eliminado: (Caldeira and Wickett, 2003)

TONI PADIN 22/6/2020 0:49
Eliminado: decline

TONI PADIN 22/6/2020 0:49
Eliminado: number

TONI PADIN 22/6/2020 0:51
Eliminado: triple

TONI PADIN 22/6/2020 0:52
Eliminado: of

TONI PADIN 24/6/2020 12:22
Eliminado: Other acidification rates estimated in different sites of the North Atlantic Ocean (Lauvset and Gruber, 2014; Bates et al., 2014) including -0.018 decade^{-1} in the mean global ocean pH (Lauvset et al., 2015) or -0.0164 decade^{-1} in the Eastern North Atlantic by Ríos et al. (2001) are within the acidification range found in the ocean and coastal zones of these waters.

TONI PADIN 24/6/2020 12:22
Con formato: Superíndice

TONI PADIN 24/6/2020 12:26
Eliminado: ria

TONI PADIN 24/6/2020 12:26
Eliminado: *Ría de Vigo*

TONI PADIN 22/6/2020 0:54
Eliminado: So

surface waters (Sarmiento and Gruber, 2006).

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 observed 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

TONI PADIN 24/6/2020 12:40
Con formato: Superíndice

TONI PADIN 24/6/2020 12:40
Con formato: Superíndice

TONI PADIN 24/6/2020 12:40
Con formato: Superíndice

TONI PADIN 24/6/2020 12:40
Con formato: Superíndice

TONI PADIN 24/6/2020 12:40
Con formato: Superíndice

TONI PADIN 24/6/2020 12:40
Con formato: Superíndice

TONI PADIN 24/6/2020 12:40
Eliminado: The long-term trend of the nutrient concentration in the inner *Ría de Vigo* showed an increase in the nitrate, phosphate and ammonium concentrations of 0.0158±0.006 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 (Doval et al., 2016).

TONI PADIN 24/6/2020 21:48
Con formato: Superíndice

TONI PADIN 24/6/2020 21:48
Con formato: Superíndice

TONI PADIN 24/6/2020 21:48
Con formato: Superíndice

TONI PADIN 24/6/2020 21:48
Con formato: Superíndice

TONI PADIN 24/6/2020 18:39
Eliminado: .

TONI PADIN 24/7/2020 21:45
Con formato: Interlineado: 1,5 líneas

TONI PADIN 24/7/2020 21:39
Con formato: Fuente: Sin Negrita

TONI PADIN 24/7/2020 21:39
Con formato: Fuente: Sin Negrita

TONI PADIN 24/7/2020 21:39
Con formato: Fuente: Sin Negrita

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

TONI PADIN 24/7/2020 21:39

Eliminado: Attending to the interannual salinity changes in the shallower waters of the *Ría de Vigo*, these findings seem to be related to a weakening of the vertical salinity gradient and a growing exchange between the bottom and surface waters. So, the footprint of oxygen consumption and the remineralized nutrient inputs resulting from benthic respiration seem to reach the upper layer. The metabolic processes in a more homogeneous water column would also explain an intense acidification in the inner waters in spite of growing alkalinity buffering.

TONI PADIN 24/6/2020 21:59

Eliminado: .

TONI PADIN 19/7/2020 21:33

Eliminado: ... [2]

TONI PADIN 24/6/2020 22:07

Eliminado: and

TONI PADIN 24/6/2020 22:07

Eliminado: of organic matter

TONI PADIN 25/6/2020 11:32

Eliminado: in this region responding to the intrusion of atmospheric CO$_2$ may also be due to the impact of other interannual changes affecting the seawater pH, such as biological activity. So, the future evolution of acidification will respond both to the potential increase in CO$_2$ in the atmosphere and to other long-term changes affecting the seawater's carbonate system.

TONI PADIN 19/7/2020 21:33

Con formato: Subíndice

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.

Acknowledgements.

The compilation of this data set was funded by the ARIOS project (CTM2016-76146-C3-1-R) funded by the Spanish government through the Ministerio de Economía y Competitividad that included European FEDER funds. Part of the processing work was supported by the MarRISK project (European Union FEDER 0262_MarRISK_1_E) funded by the Galicia-Northern Portugal Cross-Border Cooperation Program (POCTEP). This project has also received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 820989 (project COMFORT, Our common future ocean in the Earth system – quantifying coupled cycles of carbon, oxygen, and nutrients for determining and achieving safe operating spaces with respect to tipping points). This data set encompasses decades of work conducted by an overwhelming number of people. We thank all of the scientists, technicians, personnel, and crew who were responsible for the collection and analysis of the over 22 000 samples included in the final data set. In addition to the PI cited in Table 1 we also thank to Trinidad Rellán, Antón Velo, Miguel Gil Coto, Marta Alvarez, Marylo Doval, Jesus Gago, Daniel Broullón and Marcos Fontela. We also thank Monica Castaño for starting this data compilation more than 10 years ago.

TONI PADIN 25/6/2020 0:33
Eliminado: ò

References

Alonso-Perez F., Ysebaert, T., and Castro, C. G.: Effects of suspended mussel culture on benthic-pelagic coupling in a coastal upwelling system (Ría de Vigo, NW Iberian Peninsula), Journal of Experimental Marine Biology and Ecology, 382–391, https://doi.org/10.1016/j.jembe.2009.11.008, 2010.

Alonso-Perez, F., and Castro, C. G.: Benthic oxygen and nutrient fluxes in a coastal upwelling system (Ria de Vigo, NW Iberian Peninsula): seasonal trends and regulating factors. Mar Ecol Prog Ser 511:17-32. https://doi.org/10.3354/meps10915. 2014.

Alonso-Perez, F., Zúñiga, D., Arbones, B., Figueiras, F. G., and Castro, C. G.: Benthic fluxes, net ecosystem metabolism and seafood harvest: Completing the organic carbon balance in the Ría de Vigo (NW Spain), Estuarine Coastal Shelf Science, 163, https://doi.org/10.1016/j.ecss.2015.05.038. 2015.

Alvarez-Salgado, X. A., Rosón, G., Pérez, F. F. and Pazos, Y.: Hydrographic variability off the Rías Baixas (NW Spain) during the upwelling season. Journal of Geophysical Research 98, 14447–14455, 1993.

Alvarez-Salgado, X. A., Figueiras, F. G., Villarino, M. L., and Pazos, Y.: Hydrodynamic and chemical conditions during onset of a red-tide assemblage in an estuarine upwelling ecosystem, Marine Biology, 130, 509–519, 1998.

Alvarez, M., Fernández, E., and Pérez, F. F.: Air-sea CO_2 fluxes in a coastal embayment affected by upwelling: physical versus biological control, Oceanologica Acta, 22, 5, 499–515, 1999.

Álvarez-Salgado, X. A., Doval, M.D., Borges, A.V, Joint, I., Frankignoulle, M., Woodward, E.M.S., and Figueiras, F.G.: Off-shelf fluxes of labile materials by an upwelling filament in the NW Iberian Upwelling System, Prog. Oceanogr., 51(2–4), 321–337, 2001.

Álvarez-Salgado, X. A., Beloso, X., Joint, I., Nogueira, E., Chou, L., Pérez, F. F., Groom, S., Cabanas, J. M., Rees, A.P., and Elskens, M.: New Production of the NW Iberian Shelf during the Upwelling Season over the period 1982-1999. Deep-Sea Res. 49(10), http://dx.doi.org/10.1016/S0967-0637(02)00094-8, 2002.

Álvarez- Salgado, X. A., Figueiras, F. G., Pérez, F. F., Groom, S., Nogueira, E., Borges, A. V., Chou, L., Castro, C. G., Moncoiffé, G., Ríos, A. F., Miller, A.E.J., Frankignoulle, M., Savidge, G., and Wollast, R.: The Portugal coastal counter current off NW Spain new insights on its biogeochemical variability, Progress in Oceanography, 56(2) http://dx.doi.org/10.1016/S0079-6611(03)00007-7, 2003.

Álvarez–Salgado, X. A., Nieto–Cid, M., Piedracoba, S., Crespo, B. G., Gago, J., Brea, S., Teixeira, I. G., Figueiras, F. G., Garrido, J. L., Rosón, G., Castro, C. G., and Gilcoto, M.: Origin and fate of a bloom of Skeletonema costatum during a winter upwelling/downwelling sequence in the Ría de Vigo (NW Spain), Journal of Marine Research, 63, 6, 1127–1149, http://dx.doi.org/10.1357/002224005775247616, 2005.

Alvarez-Salgado, X. A., Nieto-Cid, M., Gago, J., Brea, S., Castro, C. G., Doval, M., and Pérez, F. F.: Stoichiometry of the degradation of dissolved and particulate biogenic organic matter in the NW Iberian upwelling, Jourtnal of Geophysical Research, 111, C07017, http://dx.doi.org/10.1029/2004JC002473, 2006.

Anderson, L.: Correction of reversing thermometers andrelated depth calculations in Baltic water, Meddelande fran Havsfiskelaboratoriet. Lysekil, 166, 1974.

Andersson, A. J., and Mackenzie, F. T.: Revisiting four scientific debates in ocean acidification research, Biogeosciences, 9, 893–905, ww.biogeosciences.net/9/893/2012/, 2012.

Arístegui J., Barton, E. D., Tett, P., Montero, M. F., García-Muñoz, M., Basterretxea, G., Cussatlegras, A. S., Ojeda, A., and de Armas, D.: Variability in plankton community structure, metabolism, and vertical carbon fluxes along an upwelling filament (Cape Juby, NW Africa), Prog. Oceanogr., 62 (2-4), 95–113, 2004.

Bakun, A., Field, D. B., Redondo-Rodriguez, A., and Weeks, S. J.: Greenhouse gas, upwelling favorable winds, and the future of coastal ocean upwelling ecosystems. Global Change Biology, 16, 4, 1213–1228, https://doi.org/10.1111/j.1365-2486.2009.02094.x, 2010.

Barnes, H.: Apparatus and methods of oceanography. Part one: Chemical, Allen and Unwin. London, 335 p., 1959.

Barton, E. D., Largier, J. L., Torres, R., Sheridan, M., Trasviña, A., Souza A., Pazos, Y., and Valle-Levinson, A.: Coastal upwelling and downwelling forcing of circulation in a semi-enclosed bay: Ria de Vigo, Progress in Oceanography, 134,173–189. https://doi.org/10.1016/j.pocean.2015.01.014, 2015.

Barton, E. D., Torres, R., Figueiras, F. G., Gilcoto, M., and Largier, J.: Surface water subduction during a downwelling event in a semienclosed bay, Journal Geophys. Research, 121, 7088–7107, https://doi.org/10.1002/2016JC011950, 2016.

Barton, E. D., Castro, C. G., Alonso-Pérez, F., Zúñiga, D., Rellán, T., Arbones, B., Castaño, M., Gilcoto, M., Torres, R., Figueiras, F. G., Pérez, F. F. and Ríos, A. F.: Cria surveys: hydrographic and chemical data, Digital.CSIC, http://dx.doi.org/10.20350/digitalCSIC/9931, 2019.

Bates, N. R., Astor, Y. M., Church, M. J., Currie, K., Dore, J. E., González-Dávila, M., Lorenzoni, L., Muller-Karger, F., Olafsson, J., and Santana-Casiano, J. M.: A Time-Series View of Changing Surface Ocean Chemistry Due to Ocean Uptake of Anthropogenic CO_2 and Ocean Acidification, Oceanography, 27, 1, SPECIAL ISSUE ON Changing Ocean Chemistry, pp. 126–141, Published by: Oceanography Society https://www.jstor.org/stable/24862128. 2014.

Benson, B. B., and Krause, D. J.: The concentration and isotopic fractionation of oxygen dissolved in fresh water and seawater in equilibrium with the atmosphere. Limnology and Oceanography, 29(3), 620–632, 1984.

Blanton, J. 0., Atkinson, L. P., Fernandez de Castillejo, F., and Lavin Montero, A.: Coastal upwelling off the Rias Bajas, Galicia, Northwest Spain, I: Hydrography studies. Rapports et Proc-verbeaux Reun. Cons. into Explor. Mer, 183, 79–90, 1984.

Bode, A., Alvarez-Ossorio, M. T., Cabanas, J. M.: Miranda, A., Varela, M.: Recent trends in plankton and upwelling intensity off Galicia (NW Spain), Progress in Oceanography, 83, 342–350, 2009.

Caldeira, K., and Wickett, M.E.: Oceanography: anthropogenic carbon and ocean pH, Nature, 425, 365, https://doi.org/10.1038/425365a, 2003.

Castro, C. G., Pérez, F. F., Álvarez-Salgado, X. A., Rosón, G., and Ríos, A. F.: Hydrographic conditions associated with the relaxation of an upwelling event off the

Galician coast (NW Spain), Journal of Geophysical Research, 99, C3, 5135–5147, https://agupubs.onlinelibrary.wiley.com/doi/10.1029/93JC02735, 1994.

Castro, C. G., Nieto-Cid, M., Álvarez-Salgado, X. A., and Pérez, F. F.: Local remineralization patterns in the mesopelagic zone of the ENAW, Deep Sea Research Part I, 53 (12), 1925–1940, http://dx.doi.org/10.1016/j.dsr.2006.09.002, 2006.

Castro, C. G., Álvarez-Salgado, X. A., Nogueira, E., Gago, J., Pérez, F. F., Bode, A., Ríos, A. F., Rosón, G., and Varela, M.: Evidencias bioxeoquímicas do cambio climático. Edita: Xunta de Galicia. Consellería de Medio Ambiente e Desenvolvemento Sostible, Evidencias e impactos do cambio climático en Galicia, 303–326, 2009.

Clayton, T. D., and Byrne, R. H.: Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results, Deep Sea Research I, 40, 10, 2115–2129, https://doi.org/10.1016/0967-0637(93)90048-8, 1993.

Cobo-Viveros, A. M., Padin, X. A., Otero, P., de la Paz, M., Ruiz-Villareal, M., Ríos, A. F., Pérez, F. F.: Short-term variability of surface carbon dioxide and sea-air CO_2 fluxes in the shelf waters of the Galician coastal upwelling system, Scientia Marina, 77S1, doi: 10.3989/scimar.03733.27C, 2013.

Culberson, C. H., Knapp, G., Stalcup, M. C., Williams, R. T., and Zemlyak, F.: A comparison of methods for the determination of dissolved oxygen in seawater. WOCE Report 73/91, 77 pp, 1991.

DelValls, T. A., and Dickson, A. G.: The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol (“tris”) in synthetic sea water, Deep-Sea Res. I, 45, 1541–1554, 1998.

Dickson, A.G., Sabine, C.L., and Christian, J.R.: Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, 191 pp, 2007.

Doval, M., Nogueira, E., and Pérez, F. F.: Spatio-temporal variability of the thermohaline and biogeochemical properties and dissolved organic carbon in a coastal embayment affected by upwelling: the Ría de Vigo (NW Spain). Journal of Marine Systems, 14, 1-2, 135–150, https://doi.org/10.1016/S0924-7963(97)80256-4, 1998.

Doval, M. D., Alvarez-Salgado, X. A., and Perez, F. F.: Dissolved organic carbon in a temperate embayment affected by coastal upwelling, Mar. Ecol. Prog. Ser., 157, 21–37, doi:10.3354/meps157021, 1997a.

Doval, M. D., Fraga, F. and Perez, F.F.: Determination of dissolved organic nitrogen in seawater using Kjeldahl digestion after inorganic nitrogen removal, Oceanol. Acta. https://archimer.ifremer.fr/doc/00093/20429/18096.pdf, 1997b.

Doval, M.D., López, A., and Madriñán, M.: Temporal variation and trends of inorganic nutrients in the coastal upwelling of the NW Spain (Atlantic Galician rías), Journal of Sea Research, 108, 19–29, https://doi.org/10.1016/j.seares.2015.12.006, 2016.

Fraga F.: Upwelling off the Galician coast, northwest Spain. Coastal Upwelling, American Geophysical Union, Washington DC, pp. 176–182, https://doi.org/10.1029/CO001p0176, 1981.

Fraga, F., Mouriño, C., and Manriquez, M.: Las masas de agua en la costa de Galicia: junio-octubre. Result. Exped. Cient. Supl. Invest. Pesq., 10, 51–77, http://hdl.handle.net/10261/90380, 1982.

Fraga, F., Pérez, F. F., Figueiras, F. G., and Ríos, A. F.: Stoichiometric variations of N, P, C and O_2 during a Gymnodinium catenatum red tie and their interpretation, Marine Ecology Progress Series, 87, 1-2, 123–134, doi:10.3354/meps087123, 1992.

Figueiras, F. G., Jones, K., Mosquera, A. M., Álvarez Salgado, X. A., Edwards, A. and MacDougall, N.: Red tide assemblage formation in an estuarine upwelling ecosystem: Ria de Vigo, Journal of Plankton Research, 16 (7), 857–878, https://doi.org/10.1093/plankt/16.7.857, 1994.

Froján, M., Arbones, B., Zúñiga, D., Castro, C. G., and Figueiras, F. G.: Microbial plankton community in the Ría de Vigo (NW Iberian upwelling system): impact of the culture of Mytilus galloprovincialis, Mar Ecol Prog Ser, 498, 43–54, https://doi.org/10.3354/meps10612, 2014.

Froján, M., Figueiras, F. G., Zúñiga, D., Alonso-Pérez, F., Arbones, B., and Castro, C. G.: Influence of Mussel Culture on the Vertical Export of Phytoplankton Carbon in a Coastal Upwelling Embayment (Ría de Vigo, NW Iberia), Estuaries and Coasts, 39, 1449–1462, https://doi.org/10.1007/s12237-016-0093-1, 2016.

Froján, M., Castro, C. G., Zúñiga, D., Arbones, A., Alonso-Pérez, F., and Figueiras, F. G.: Mussel farming impact on pelagic production and respiration rates in a coastal upwelling embayment (Ría de Vigo, NW Spain), Estuarine, Coastal and Shelf Science, 204, 130–139, https://doi.org/10.1016/j.ecss.2018.02.025, 2018.

Frouin, R., Fiúza, A. F. G., Ambar, I., and Boyd, T. J._: Observations of a poleward surface current off the coasts of Portugal and Spain during winter, Journal of Geophysical Research, 95, 679–691, 1990.

Feely, R. A., Sabine, C. L., Hernandez-Ayon, J. M., Ianson, D., and Hales, B: Evidence for upwelling of corrosive “acidified” water onto the continental shelf, Science 320(5882), 1490–1492, doi:10.1126/science.1155676, 2008.

Gago, J., Alvarez-Salgado, X. A., Gilcoto, M., and Pérez, F. F.: Assessing the contrasting fate of dissolved and suspended organic carbon in a coastal upwelling system (Ría de Vigo, NW Iberian Peninsula), Estuarine, Coastal and Shelf Science, 56, 2, 271–279, http://dx.doi.org/10.1016/S0272-7714(02)00186-5, 2003a.

Gago, J., Alvarez-Salgado, X. A., Pérez, F. F., and Ríos, A. F.: Partitioning of physical and biogeochemical contributions to short-term variability of pCO_2 in a coastal upwelling system a quantitative approach, Marine Ecology Progress, 255, 43–54, http://dx.doi.org/10.3354/meps25504, 2003b.

Gago, J., Gilcoto, M., Pérez, F. F., and Ríos, A.F.: Short-term variability of fCO_2 in seawater and air-sea CO_2 fluxes, Marine Chemistry, 80, 4, 247–264, http://dx.doi.org/10.1016/S0304-4203(02)00117-2, 2003c.

Gilcoto, M., Largier, J. L., Barton, E. D., Piedracoba, S., Torres, R., Graña, R., Alonso-Pérez, F., Villacieros-Robineau, N., and de la Granda, F.: Rapid response to coastal upwelling in a semienclosed bay, Geophysical Reseach Letters, 44(5), 2388–2397, doi: 10.1002/2016GL072416, 2017.

González-Pola, C., Lavín, A., Vargas-Yáñez, M.: Intense warming and salinity modification of intermediate water masses in the southeastern corner of the Bay of Biscay for the period 1992–2003, Journal of Geophysical Research, 110, C05020, doi:10.1029/2004JC002367, 2005.

Grasshoff, K., Johannsen, H.: A New Sensitive and Direct Method for the Automatic Determination of Ammonia in Sea Water, ICES Journal of Marine Science, 34(3), 516–521, https://doi.org/10.1093/icesjms/34.3.516, 1972.

Grasshoff, K., Ehrhardt, M., Kremlin, K.: Methods of Seawater Analysis, 2nd. ed. Verlag Chemie, Weinheim, 419 pp, 1983.

Gruber, N., Hauri, C., Lachkar, Z., Loher, D., Frolicher, T. L., and Plattner, G. K.: Rapid progression of ocean acidification in the California Current System, Science, 337, 220–223, doi:10.1126/science.1216773, 2012.

Harvey, J.: θ-S relationship and water masses in the eastern North Atlantic. Deep-Sea Research, 29, 1021-1033, 1982.

Hauri, C., Gruber, N., Plattner, G. K., Alin, S., Feely, R. A., Hales, B., and Wheeler, P. A.: Ocean acidification in the California Current System, Oceanography, 22, 58–69, doi:10.5670/oceanog.2009.97, 2009.

Hauri, C., Gruber, N., Vogt, M. S., Doney, C., Feely, R. A., Lachkar, Z., Leinweber, A., McDonnell, A. M. P., Munnich, M., and Plattner, G.K.: Spatiotemporal variability and

TONI PADIN 19/7/2020 23:11
Eliminado:

long-term trends of ocean acidification in the California Current System, Biogeosciences, 10, 193–216, doi:10.5194/bg-10-193-2013, 2013.

Hofmann, G. E.: High-frequency dynamics of ocean pH: A multi-ecosystem comparison, PLoS One, 6(12), e28983, doi:10.1371/journal.pone.0028983, 2011.

IPCC: Climate Change 2013: the physical science basis Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change ed T F Stocker et al (Cambridge: Cambridge University Press) pp 1535, www.ipcc.ch/report/ar5/wg1/, 2013.

Lachkar, Z.: Effects of upwelling increase on ocean acidification in the California and Canary Current systems, Geophys. Res. Lett., 41, 90–95, doi:10.1002/2013GL058726, 2014.

Lassoued. J., Babarro, J., Padín, X. A., Comeau, L., Bejaoui, N., and Pérez, F.: Behavioural and eco-physiological responses of the mussel Mytilus galloprovincialis to acidification and distinct feeding regimes, Marine Ecology Progress Series, 626, 97–108, doi: 10.3354/meps13075, 2019.

Lauvset, S.K., and Gruber, N.: Long-term trends in surface ocean pH in the North Atlantic, Marine Chemistry, 162, 71–76, https://doi.org/10.1016/j.marchem.2014.03.009, 2014.

Lauvset, S. K., Gruber, N., Landschützer, P., Olsen, A., and Tjiputra, J.: Trends and drivers in global surface ocean pH over the past 3 decades, Biogeosciences, 12(5), 1285–1298, doi:10.5194/bg-12-1285-2015, 2015.

Lewis, E., Wallace, D.W.R.: Program developed for CO_2 system calculations, ORNL/CDIAC-105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1998.

Lemos, R. T., and Sansó, B.: Spatio-temporal variability of ocean temperature in the Portugal Current System, Journal of Geophysical Research, 111, C04010, doi:10.1029/2005JC003051, 2006.

Lueker, T. J., Dickson, A. G., and Keeling, C. D.: Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K-1 and K-2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium, Mar. Chem., 70, 105–119, 2000.

McElhany, P. and Shallin Busch, D.: Appropriate pCO_2 treatments in ocean acidification experiments, Marine Biology, 160, 1807–1812, https://doi.org/10.1007/s00227-012-2052-0, 2013.

Mehrbach, C., Culberson, C. H., Hawley, J. E., and Pytlowicz, R. M.: Measurements of the apparent dissociation constant of carbonic acid in seawater at atmospheric pressure, Limnology and Oceanography, 18, 897–907, 1973.

Miguez, B. M., Fariña-Busto, L., Figueiras, F. G., Pérez, F. F.: Succession of phytoplankton assemblages in relation to estuarine hdrodynamics in the Ria de Vigo, Scientia Marina, 65, S1, https://doi.org/10.3989/scimar.2001.65s165, 2001.

Mouriño, C., and Fraga, F.: Determinación de nitratos en agua de mar, Investigaciones Marinas, 49 (1), 81–96, 1985.

Nieto-Cid, M., Alvarez-Salgado, X. A., Brea, S., and Pérez, F. F.: Cycling of dissolved and particulate carbohydrates in a coastal upwelling system (NW Iberian Peninsula), doi:10.3354/meps283039, 2004.

Nieto-Cid, M., Alvarez-Salgado, X. A., and Pérez, F. F.: Microbial and photochemical reactivity of fluorescent dissolved organic matter in a coastal upwelling system https://doi.org/10.4319/lo.2006.51.3.1391, 2006.

Nogueira, E., Pérez, F. F., and Ríos, A. F.: Seasonal and long-term trends in an estuarine upwelling ecosystem (Ría de Vigo, NW Spain), Estuarine, Coastal and Shelf Science 44, 285–300, 1997.

Olsen, A., Lange, N., Key, R. M., Tanhua, T., Álvarez, M., Becker, S., et al.: GLODAPv2.2019: An update of GLODAPv2. Earth System Science Data, 11(3), 1437–1461. https://doi.org/10.5194/essd-11-437-2019, 2019.

Orr, F. M.: Onshore Geologic Storage of CO_2, Science, 25, 325, 1656–1658, doi: 10.1126/science.1175677, 2009.

Otero, P., Ruiz-Villarreal, M., and Peliz, A.: Variability of river plumes off Northwest Iberia in response to wind events, Journal of Marine Systems, 72(1-4), 238–255, 2008.

Padin X. A., Castro, C. G., Ríos, A.F., and Pérez, F.F.:Oceanic CO_2 uptake and biogeochemical variability during the formation of the Eastern North Atlantic Central water under two contrasting NAO scenarios, Journal of Marine Systems, 84, 3-4, 96–105, https://doi.org/10.1016/j.jmarsys.2010.10.002, 2010.

Pauly, D., and Christensen, V.: Primary production required to sustain global fisheries, Nature, 374(6519), 255–257, 1995.

Pérez, F. F., and Fraga, F.: A precise and rapid analytical procedure for alkalinity determination, Marine Chemistry, 21, 169–182, 1987a.

Pérez, F. F., and Fraga, F.: The pH measurements, in seawater on the NBS scale, Marine Chemistry, 21, 315–327, 1987b.

Pérez, F. F., Rios, A. F., and Rosón, G.: Sea surface carbon dioxide off the Iberian Peninsula North Eastern Atlantic Ocean, Journal of Marine Systems, 19, 27–46, 1999.

Perez, F. F., Alvarez-Salgado, X. A., and Rosón G.: Stoichiometry of the net ecosystem metabolism in a coastal inlet affected by upwelling. The Ría de H (NW Spain), Marine Chemistry, 69, 3-4, 217–236, 2000.

Pérez, F. F., Padin, X. A., Pazos, Y., Gilcoto, M., Cabanas, M., Pardo, P. C., Doval, M., D., and Farina-Busto, L.: Plankton response to weakening of the Iberian coastal upwelling. Global Change Biology, 16(4), 1258–1267, 2010.

Pérez, F. F., Velo, A., Padin, X. A., Doval, M. D., Prego, R.: ARIOS DATABASE: An Acidification Ocean Database for the Galician Upwelling Ecosystem, Instituto de Investigaciones Marinas, Consejo Superior de Investigaciones Cientificas (CSIC), doi: 10.20350/digitalCSIC/12498, 2020.

Piedracoba, S., Alvarez-Salgado, X. A., Rosón G., and Herrera, J. L.: Short timescale thermohaline variability and residual circulation in the central segment of the coastal upwelling system of the Ría de Vigo (northwest Spain) during four contrasting periods, https://doi.org/10.1029/2004JC002556, 2005.

Prego, R., Fraga, F., and Rios, A. F.: Water interchange between the Ria of Vigo and the continental shelf. Scientia Marina 54, 95–100, 1990.

Raven, J., Caldeira, K., Elderfield, H., Hoegh-Guldberg, O., Liss, P., Riebesell, U., Sphepherd, J., Turley, C., and Watson, A.: Ocean acidification due to increasing atmospheric carbon dioxide: Royal Society Policy Document 12/05, 68 p, 2005.

Ríos, A. F., Pérez, F. F., and Fraga, F.: Water masses in the upper and middle North Atlantic Ocean east of the Azores, Deep-Sea Res. Part I, 39, 645–658, 1992.

Rosón, G., Pérez, F. F., Alvarez-Salgado, X. A., and Figueiras, F. G.: Variation of both thermohaline and chemical properties in an estuarine upwelling ecosystem -Ría de Arousa. 1. Time evolution, Estauriane Coastal and Shelf Science, 41, 2, 195–213, doi 10.1006/ecss.1995.0061, 1995.

Rosón, G., Cabanas, J. M., Pérez, F. F., Herrera, J. L., Ruiz-Villarreal, M., Castro, C. G., Piedracoba, S., and Álvarez-Salgado, X. A.: Evidencias do cambio climático na Hidrografía e a dinámica das Rías e da plataforma galega. Edita: Xunta de Galicia. Consellería de Medio Ambiente e Desenvolvemento Sostible, Evidencias e impactos do cambio climático en Galicia, 287-302, 2009.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-

H., Kozyr, A., Ono, T., and Rios, A. F.: The oceanic sink for anthropogenic CO_2. Science 305, 367–371, 2004.

Sarmiento, J. L., and Gruber, N.: Ocean biogeochemical dynamics. Princeton Univ. Press. 2006.

Souto, C., Gilcoto, M., Fariña-Busto, L., and Pérez, F. F.: Modeling the residual circulation of a coastal embayment affected by wind-driven upwelling: Circulation of the Ria de Vigo (NW Spain), Journal of Geophysical Research - Oceans, 108 C11 (3340), doi: 10.1029/2002JC001512, 2003.

SCOR-UNESCO: Determination of Photosynthetic Pigments in Seawater. UNESCO, Paris, 1966.

Strickland, J. D. H., and Parsons, T.R.: A practical handbook of seawater analysis, Fisheries Research Board of Canada, Ottawa, Ontario, 1972.

Takeshita, Y., Frieder, C. A., Martz, T. R., Ballard, J. R., Feely, R. A., Kram, S., Nam, S., Navarro, M. O., Price, N. N., and Smith, J. E.: Including high-frequency variability in coastal ocean acidification projections, Biogeosciences, 12(19), 5853–5870, doi:10.5194/bg-12-5853-2015, 2015.

Teira, E., Martínez-García, S., Lonborg, C., and Álvarez-Salgado, X. A.: Growth rates of different phylogenetic bacterioplankton groups in a coastal upwelling system, Environmental microbiology reports, 1,6, 545–554, https://doi.org/10.1111/j.1758-2229.2009.00079.x, 2009.

UNESCO: Background papers and supporting data on the Practical Salinity Scale 1978. UNESCO Tech. Papers in Marine Science, 37, 144pp, 1981.

Uppström, L. R.: Boron = Chlorinity ratio of deep-sea water from Pacific Ocean, Deep-Sea Res., 21, 161–162, 1974.

Van Heuven, S., Pierrot, D., Rae, J.W.B., Lewis, E., Wallace, D.W.R. MATLAB Program Developed for CO_2 System Calculations. ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 2011.

Velo, A., Pérez, F.F., Lin, X., Key, R.M., Tanhua, T., de la Paz, M., Olsen, A., van Heuven, S., Jutterström, S., Ríos, A.F.: CARINA data synthesis project: pH data scale unification and cruise adjustments, Earth Syst. Sci. Data, 2, 133–155, doi:10.5194/essd-2-133-2010, 2010.

Velo, A., Cacabelos, J., Pérez, F.F., Ríos, A.F.: GO-SHIP Software and Manuals: Software packages and best practice manuals and knowledge transfer for sustained quality control of hydrographic sections in the Atlantic. (Version v1.0.0), Zenodo, http://doi.org/10.5281/zenodo.2603122, 2019.

Villacieros-Robineau, N., Zúñiga, D., Barreiro-González, B., Alonso-Pérez, F., de la Granda, F., and Froján, M.: Bottom boundary layer and particle dynamics in an upwelling affected continental margin (NW Iberia), Journal of Geophysical Research: Oceans, 124, https://doi.org/10.1029/2019JC015619, 2019.

Wahl, M., Saderne, V., and Sawall, Y.: How good are we at assessing the impact of ocean acidification in coastal systems? Limitations, omissions and strengths of commonly used experimental approaches with special emphasis on the neglected role of fluctuations, Mar. Freshw. Res., 67, 25–36, doi:10.1071/MF14154, 2016.

Wolf-Gladrow, D. A., Riebesell, U., Burkhardt, S., and Bijma, J.: Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton, Tellus, 51B, 461, 1999.

Wooster, W. S., Bakun, A., and McClain, D. R.: The seasonal upwelling cycle along the eastern boundary of the North Atlantic, Journal of Marine Research, 34, 131–141, 1976.

Zúñiga, D., Villacieros-Robineau, N., Salgueiro, E., Alonso-Pérez, F., Rosón, G., Abrantes, F., and Castro, C. G.: Particle fluxes in the NW Iberian coastal upwelling system: Hydrodynamical and biological control. Continental Shelf Research, 123 (2016), 89–98, http://dx.doi.org/10.1016/j.csr.2016.04.008, 2016.

Zúñiga, D., Santos, C., Froján, M., Salgueiro, E., Rufino, M. M., de la Granda, F., Figueiras, F. G., Castro, C. G., and Abrantes, F.: Diatoms as a paleoproductivity proxy in the NW Iberian coastal upwelling system (NE Atlantic), Biogeosciences, 14, 1165–1179, www.biogeosciences.net/14/1165/2017, 2017.

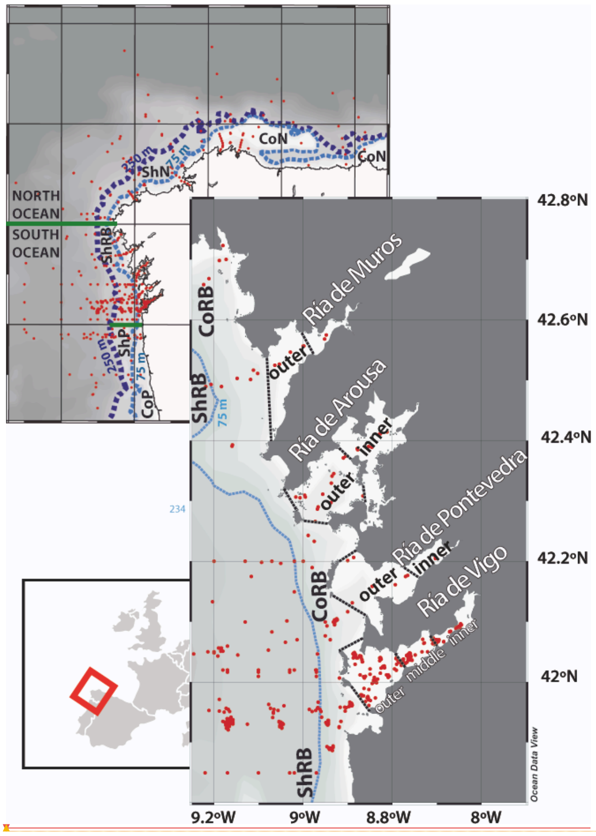
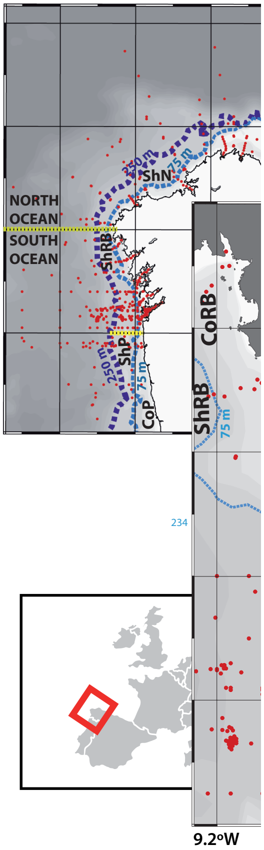


Figure 1. Map of all stations (red dots) including the geographical areas selected to classify the ARIOS database from isobath of 250 m (dark blue line) and 75 metres (light blue line), latitudinal criterion (green lines) and geographical lines (black lines).

TONI PADIN 25/6/2020 10:55



Eliminado:

Unknown

Con formato: Subíndice

TONI PADIN 25/6/2020 10:56

Eliminado: yellow

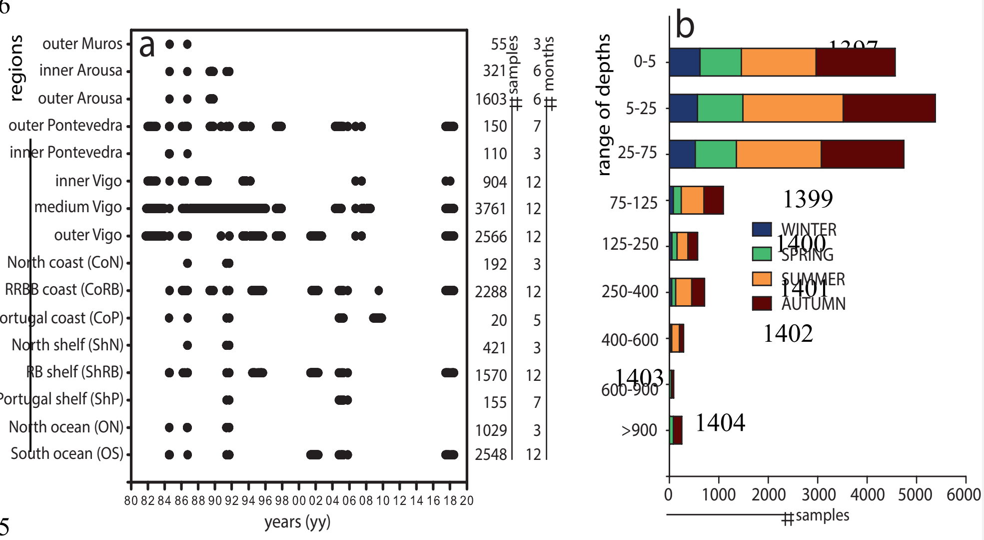


Figure 2. a) Temporal distribution of the observations in the geographical boxes included in the ARIOS dataset. b) Seasonal distribution of the measurements in relation to depth.

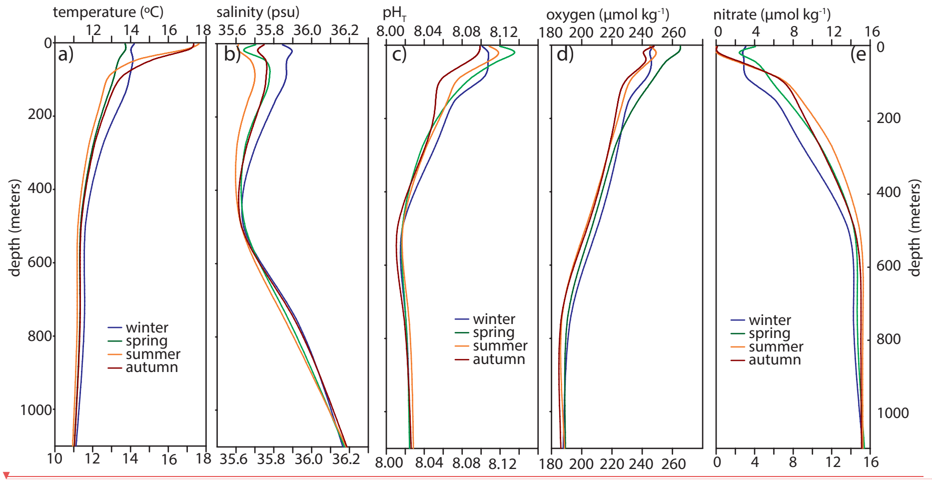
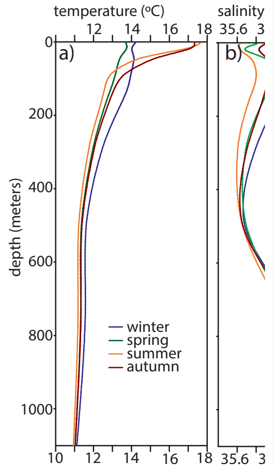


Figure 3. Profiles of seasonal means of temperature (a), salinity (b), pH$_T$ (c), oxygen (d) and nitrate concentration (e) in the first 1100 meters of the region South Ocean shown in Fig. 1.

TONI PADIN 25/6/2020 11:07

Eliminado:



TONI PADIN 25/6/2020 11:07

Con formato: Subíndice

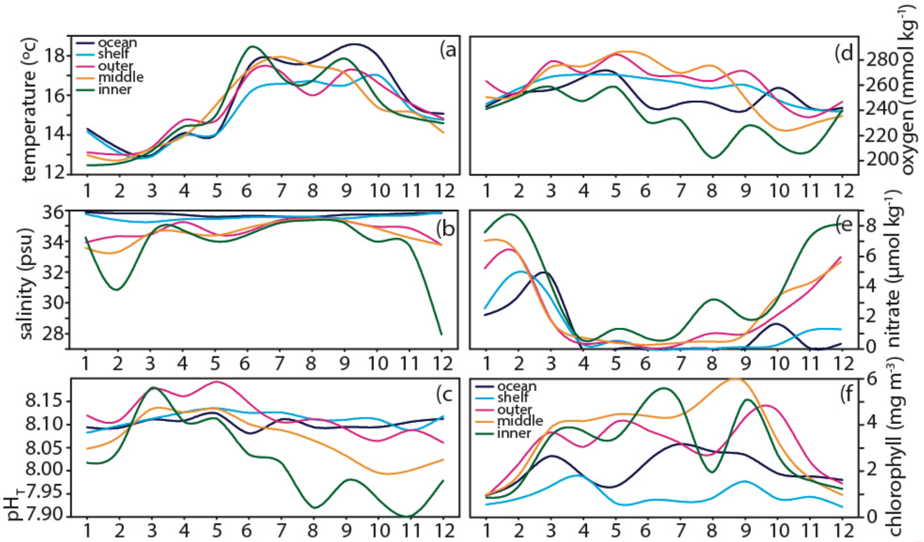
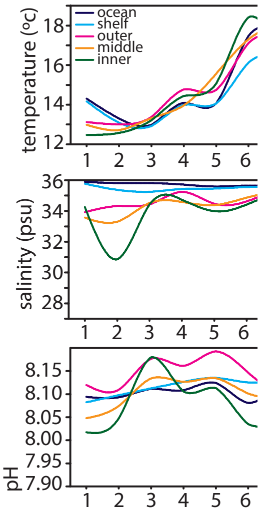


Figure 4. Sea surface (<5 meters depth) seasonal cycles in 1976 - 2018 of temperature (a), salinity (b), pH$_T$ (c), oxygen concentration (d), nitrate concentration (e) and chlorophyll (f) at sea surface for five geographical boxes shown in Fig. 1: South Ocean, RB shelf and outer, middle and inner Ria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

TONI PADIN 28/7/2020 16:47



Eliminado:

TONI PADIN 28/7/2020 16:47

Eliminado:

TONI PADIN 19/7/2020 23:56

Con formato: Subíndice

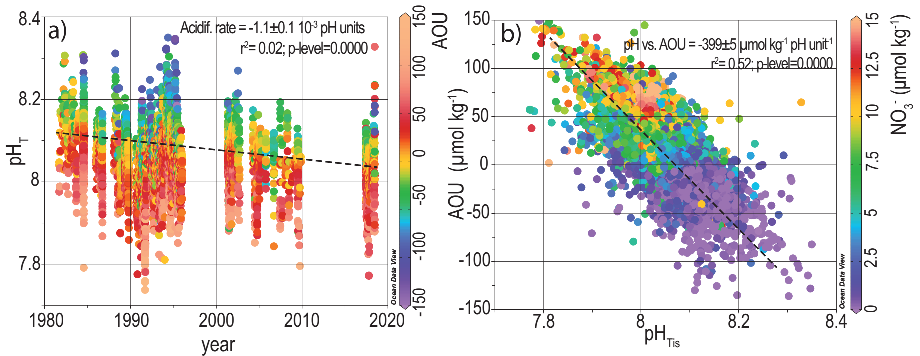
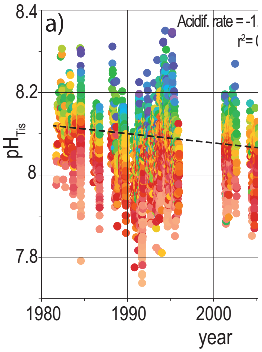


Figure 5. Time-series of pH ARIOS data. The black line depicts the long-term trend. Scatter diagram of AOU vs pH$_T$ including the nitrate concentration shown as colour of every dot.

TONI PADIN 25/6/2020 11:08



Eliminado:

TONI PADIN 20/7/2020 0:00

Con formato: Subíndice

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* $\mu mol\ kg^{-1}$ *or* $\mu mol\ L^{-1}$ *(*) 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}*).*

EXPOCODE	PROJECT	DATE	#d	IP	#	CTD	O$_2$	Nut	pH	Alk	Chla	CRM	Data Repository	REGIONS
29LP19761026	Ría Vigo 1977	26/10/76	413	F Fraga	135	N	N	S*	Sº	N	N	N	http://dx.doi.org/10.20350/digitalCSIC/9917	Co^{RB}
29LP19810929	Ría Vigo 1981-83	29/9/81	472	F Fraga	748	N	S*	S*	Sº	S	N	N	http://dx.doi.org/10.20350/digitalCSIC/9918	RV^{O,M,I}
29LP19830215	Ría Vigo 1983-84	15/2/83	322	F Fraga	312	N	S*	S*	Sº	S	N	N	http://dx.doi.org/10.20350/digitalCSIC/9919	RV^{O,M}
29GD19840711	GALICIA-VIII	11/7/84	28	F Fraga	1865	N	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9908	O^{N,S}, Sh^{RB}, Co^{P,RB}, RV^{O,M,I}, RA^{O,I}, RP^{O,I}, RM
29GD19860121	Ría Vigo 1986	21/1/86	203	F Fraga	332	N	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9910	Sh^{RB}, Co^{RB}, RV^{O,M,I}
29GD19860904	GALICIA-IX	23/9/86	5	F Fraga	1640	N	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9911	O^{N,S}, Sh^{RB,N}, Co^{P,RB,N}, RV^{O,M,I}, RA^{O,I}, RP^{O,I}, RM
29LP19870120	PROVIGO	17/9/87	3290	F F Pérez	2317	N	S	S	Sº	N	S	N	http://dx.doi.org/10.20350/digitalCSIC/9924	RV^{M}
29LP19880212	LUNA 88	12/2/88	367	A F Rios	468	N	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9907	RV^{M,I}
29IN19890512	GALICIA-X	5/5/89	171	F F Pérez	3113	N	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9920	Co^{RB}, RA^{O,I}
29IN19900914	Ría Vigo 1990	14/9/90	13	FG Figueiras	108	Y	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9921	RV^{O,M,I}
29IN19910510	GALICIA-XI	5/5/91	4	F F Pérez	327	Y	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9922	O^{N,S}, Sh^{P,RB,N}, Co^{P,RB,N}, RA^{O}
29IN19910910	GALICIA-XII	15/9/91	10	F G Figueiras	663	Y	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9923	O^{N,S}, Sh^{P,RB,N}, Co^{P,RB,N}, RV^{O,M,I}, RA^{O}
29LP19930413	Ría Vigo 1993-94	22/3/94	344	F G Figueiras	406	Y	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9927	RV^{O,M,I}
29JN19940505	Ría Vigo 1994-95	5/5/94	504	M Cabanas	669	Y	S	S	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9926	Sh^{RB}, Co^{RB}, RV^{O}
29MY19970407	CIRCA-97	7/4/97	248	F F Pérez	547	Y	S	N	Sº	S	S	N	http://dx.doi.org/10.20350/digitalCSIC/9928	RV^{O,M,I}
29MY20010515	DYBAGA	15/5/01	344	F F Pérez	1421	Y	S	S*	S	S	S	Y	http://dx.doi.org/10.20350/digitalCSIC/9929	Sh^{P,RB}, Co^{RB}, RV^{O}
29MY20010702	REMODA	2/7/01	451	X A Alvarez	203	Y	S	S*	S	S	S	Y	http://dx.doi.org/10.20350/digitalCSIC/9930	RV^{O}
29MY20040419	FLUVBE	19/4/04	283	C G Castro	187	Y	S	S*	S	S	S	Y	to be submitted	RV^{M,I}
29CS20041004	ZOTRACOS	4/10/04	389	M Cabanas	371	Y	S	S	S	S	S	Y	http://dx.doi.org/10.20350/digitalCSIC/9932	Sh^{P,RB}, Co^{P,RB}, RP^{O}
29MY20060926	CRÍA	26/9/06	275	D Barton	197	Y	S	S*	S	S	S	Y	http://dx.doi.org/10.20350/digitalCSIC/9931	RV^{O,M,I}
29MY20070917	RAFTING	17/9/07	301	C G Castro	287	Y	S	S*	S	S	S	Y	to be submitted	RV^{M}
29MY20081105	LOCO	5/11/08	378	X A Alvarez	72	Y	S	S	S	S	S	Y	http://dx.doi.org/10.20350/digitalCSIC/9936	Co^{RB}
29AH20090710	CAIBEX-I	16/7/09	11	D Barton	191	Y	S	S	S	S	S	Y	http://dx.doi.org/10.20350/digitalCSIC/9934	Co^{P,RB}
29MY20170609	ARIOS	9/6/17	382	FF Pérez	1114	Y	S	S*	S	S	S	Y	http://dx.doi.org/10.20350/digitalCSIC/9963	Sh^{P,RB}, Co^{RB}, RV^{O,M,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).