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## CLIMATE CHANGE AND OCEAN ACIDIFICATION

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### ABSTRACT

Carbon dioxide (CO<sub>2</sub>) is the greenhouse gas which ultimately causes ocean acidification. Oceans have approximately absorbed up to 30% of the released CO<sub>2</sub> to the atmosphere since the Industrial Revolution. The incessant increase in this gas concentration in the atmosphere and its consequent dissolution in the oceans have resulted in the decrease of several tenths of seawater pH. Scientists have intensely studied this process and its consequences for the last decade. Oceanographic cruises of data collection throughout the planet are essential for a correct evaluation of the state and consequences of ocean acidification. Similarly, laboratory studies are highly important for the evaluation of marine ecosystems.

The North Atlantic Ocean stands out globally due to the high accumulation of anthropogenic CO<sub>2</sub> (up to 25% of the total of all oceans, when it only constitutes a 15% of the total oceanic area). Other observed consequences have been the pH reduction and the consequent decrease in the organism capacity to build calcareous structures. The scarce studies carried out in the Baltic Sea have shown great capacity to buffer pH decrease. Despite them, several studies have verified the ocean acidification process and its effects on marine organisms.

Overall, positive, negative, and neutral responses have been found among the effects on organisms. Several species, such as plankton, mollusks, crustaceans, and corals, seem to be dramatically affected. These findings show the necessity of an ongoing investigation in order to acquire an accurate vision of the ecosystems health in this current volatile situation.

### KEYWORDS

Ocean acidification, carbonate system, impacts, biodiversity, climate change

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### General questions and concepts

**Anthropogenic:** related to or resulting from the human action. For example, the release of CO<sub>2</sub> to the atmosphere by the combustion of fossil fuels.

**Ocean acidification:** changes in the ocean water chemistry caused by the absorption of the CO<sub>2</sub> released to the atmosphere by human action, leading to a decrease in pH values.

**pH:** measure of the concentration of protons in a liquid. The range varies between 0 and 14, determining if the solution is basic (>7), neutral (=7) or acidic (<7).

**Water mass:** water body with defined hydrographic conditions, defined by salinity and temperature within certain ranges, for instance.

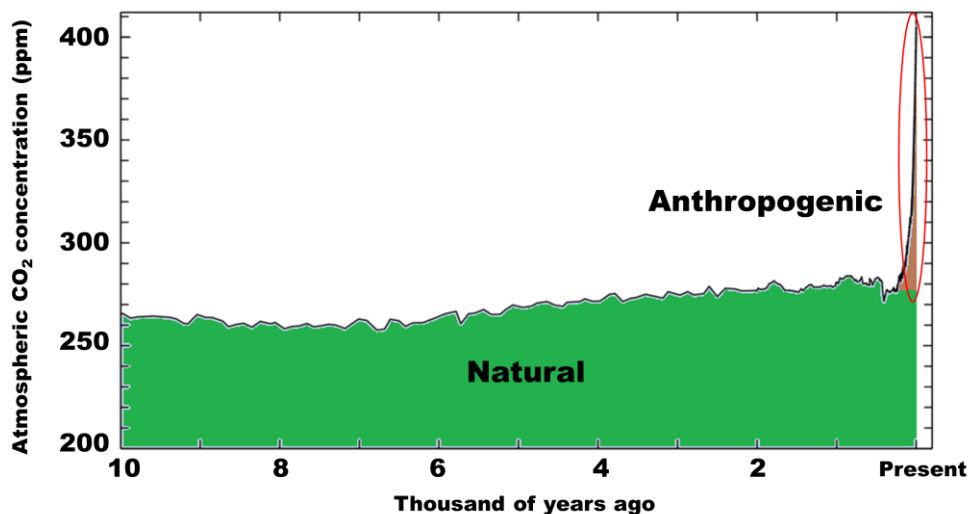
**Solubility:** measure of the capacity that a solid, liquid or gas has to dissolve in a medium.

**Calcareous structures:** anatomical parts of the organisms that are predominantly composed by calcium carbonate such as the valves (shell) of a mussel.

**Aragonite and calcite:** minerals composed by calcium carbonate that differentiates in its crystalline structure. Aragonite is more sensitive to the ocean acidification due to its higher solubility in the seawater.

### Introduction

Ocean acidification is the concept used to refer the changes happening in seawater chemistry related to Ph. The main cause of this process is increasing the amount of carbon dioxide (CO<sub>2</sub>) in the atmosphere. This gas has a natural component and an artificial one (anthropogenic) (Figure 1). The first one is due to the liberation from the ocean, the act of respiration of living beings, the decomposition of organic matter, fires and volcanic eruptions. This amount has hardly changed in the last 10000 years. The second one is the result of human activities since the Industrial Revolution (second half of the 18th century). The use of oil derivatives, cement production, agriculture and deforestation are the main causes that currently, the amount of CO<sub>2</sub> in the atmosphere has increased by 69% over the natural component.

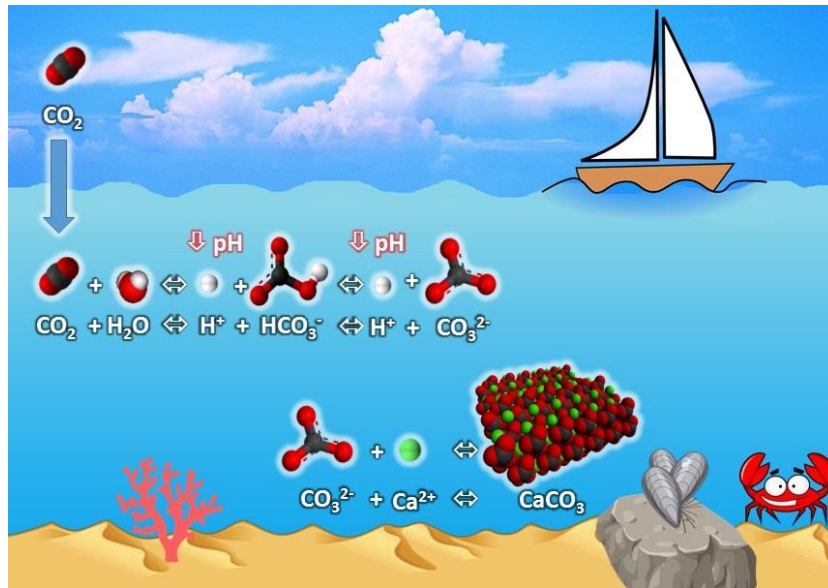


**Figure 1.** Concentration of CO<sub>2</sub> in the atmosphere over the last 10000 years.

CO<sub>2</sub> is a greenhouse gas, therefore absorbs heat. The initial concern of the scientific community was the increase of global temperature due to the rise in CO<sub>2</sub> levels, among others. Thanks to the ocean, this warming has been less accelerated than would be expected. The oceans have absorbed a 30% of anthropogenic CO<sub>2</sub>, giving rise to a lower concentration in the atmosphere than expected. But, at the beginning of this century, the scientists observed that this process had produced another problem: ocean acidification.

The oceans, as the atmosphere, contain CO<sub>2</sub>. The concentrations in both systems are kept in balance while there is no disturbance. The increase in the atmosphere makes this balance tends to break. The absorption capacity of the oceans (solubility) is the responsible for balance being restore again. As a result, CO<sub>2</sub> increases also in the ocean. Mainly, these changes produce modifications in certain chemical reactions of seawater. This important group of reactions is known as carbonate system (Figure 2).

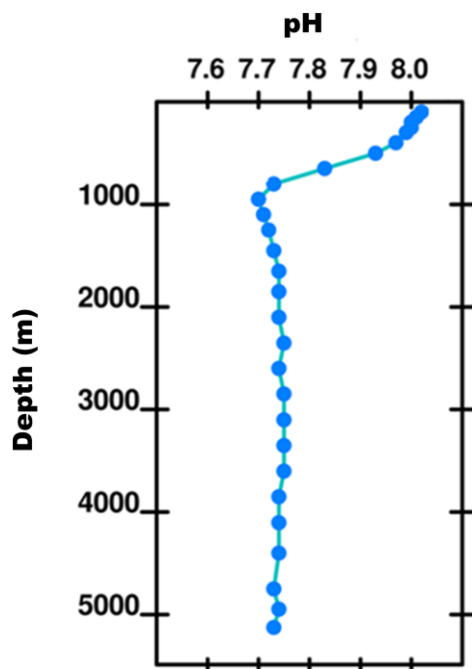
The first chemical reaction in the carbonate system occurs when the CO<sub>2</sub> from the atmosphere is absorbed by the ocean, becoming dissolved from its gaseous form. Once CO<sub>2</sub> is in the water, it reacts with water giving rise to protons (H<sup>+</sup>) and bicarbonate ions (HCO<sub>3</sub><sup>-</sup>). This last compound decomposes itself given rise to more protons and carbonate ions (CO<sub>3</sub><sup>-2</sup>). Finally, calcium carbonate (CaCO<sub>3</sub>) can be formed by combining the calcium ion (Ca<sup>+ 2</sup>) with the carbonate ion. All these reactions are balanced and, therefore, can take place in the reverse order described (Figure 2).



**Figure 2.** Chemical reactions of carbonate in the ocean system.

pH is the measure that allows us to know how is changing the concentration of protons in a liquid. Its calculation is performed as:  $\text{pH} = -\log [\text{H}^+]$ . The scale of measurement is a logarithmic one. Therefore, each increasing unit in pH represents that the concentration of protons has to be divided by 10 and vice versa. Conventionally, the values tend to vary in a range from 0 to 14. Intermediate, 7, is known as neutral. Above this value are known as basic and under this neutral value are named acids. The concentration of protons is in its minimum point when the pH is worth 14 and maximum when it is worth 0. In the ocean, this concentration varies depending on how these reactions described take place. When atmospheric  $\text{CO}_2$  is absorbed by the ocean, the balance is disturbed. In order to going back to the equilibrium state, the carbonate system's reactions generate a proton increase. This process leads to a progressive displacement of the ocean's pH towards lower values. This tendency of seawater to "acidify itself" has been named ocean acidification. Despite this appointment, the pH of the ocean is in the basic area of the scale. Currently, seawater pH has a value half of 8.1 on its surface. In the pre-industrial era, this value was of 8.2.

Figure 3 shows the pH values through the water column. In particular, this is an Atlantic typical profile. In general terms, oceans pH has its maximum value in surface and reaches its minimum at 1000m depth. These higher values are due to consumption of  $\text{CO}_2$  by photosynthetic organisms to produce organic matter. Generated in surface, this material progressively degrades on their way to the seabed. This process generates  $\text{CO}_2$  and therefore decreases pH.

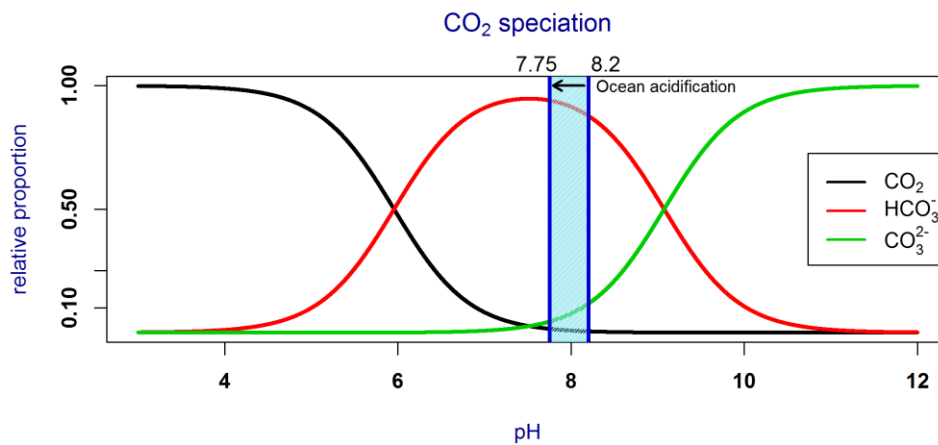


**Figure 3.** Profile of pH in the Atlantic Ocean at 24° N

The addition of the concentrations of the chemical species involved in the carbonate system in the Ocean ( $\text{CO}_2$  dissolved,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) is known as total dissolved inorganic carbon (equation: CID,  $\text{TCO}_2$  or  $\text{C}_T$ ).  $\text{CID} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  and its measurement unit is usually expressed in  $\mu\text{mol/kg}$ . Almost all of the carbon contained in the ocean is in this form. The remaining is carbon organic (living organisms). CID values change in the different oceans. With the increase of  $\text{CO}_2$  in the atmosphere and the consequent increase in the ocean, the CID value has increased since the Industrial Revolution. However, the concentration of each chemical species of this system does not increase proportionally to give rise to the increase of CID. Thanks to the creation of the Bjerrum diagram in 1914, we can observe how the concentration changes on the ocean acidification process. This diagram shows the concentration of each of the three species that form the CID depending on pH seawater has (Figure 4). Currently, the amount of the compounds present in the ocean is: 90%  $\text{HCO}_3^-$ , 9%  $\text{CO}_3^{2-}$  and 1%  $\text{CO}_2$  dissolved. Until the end of this century, in its latest report, the Intergovernmental Panel of the Climate Change (IPCC) estimates that the ocean surface pH will decrease, on average, 0.06 units (for a scene of emissions of  $\text{CO}_2$  reduced) and 0.32 units (for a scene of emissions of  $\text{CO}_2$  high). Bjerrum diagram shows how this decrease in pH will change the percentages of species forming the CID.  $\text{CO}_2$  dissolved and the  $\text{HCO}_3^-$  will

increase and the  $\text{CO}_3^{2-}$  will decrease (Figure 4). In addition, for the high emissions scenario, the change in pH will involve a 125% increase in the concentration of  $\text{H}^+$ .

The above changes have associated potential consequences. Most of the organisms that live in the oceans have structures of  $\text{CaCO}_3$ . This compound is also present in our bones. Their training is produced from the reaction between  $\text{Ca}^{2+}$  and the  $\text{CO}_3^{2-}$  (Figure 1). However,  $\text{H}^+$  ions bind more easily than the  $\text{Ca}^{2+}$  to the  $\text{CO}_3^{2-}$ . This process reduces the amount of  $\text{CO}_3^{2-}$  present and hinders the formation of  $\text{CaCO}_3$ . Therefore, the decrease of  $\text{CO}_3^{2-}$  expected with the reduction of pH (more  $\text{H}^+$  present to remove  $\text{CO}_3^{2-}$  available) will have consequences on the organisms that have structures of  $\text{CaCO}_3$  and they need certain amounts of this ion to form them. The effects will be detailed later.



**Figure 4.** Bjerrum diagram. It represents pH changes from the Industrial Revolution and estimates the end of the 21st century for a stage of high CO<sub>2</sub> emissions.

Another important effect of ocean acidification is the decrease of the Carbonate Compensation Depth (CCD). This depth is defined as the lowest limit where ocean waters are "corrosive" enough to dissolve  $\text{CaCO}_3$ . Therefore, the structures of  $\text{CaCO}_3$  only may retain above this limit. The position of the CCD varies in different oceans. This depends on the solubility of the  $\text{CaCO}_3$ . At the same time, solubility is determined by the pressure, the temperature and the amount of  $\text{CO}_2$  dissolved in the water. In low temperatures and high pressure, the solubility of the  $\text{CaCO}_3$  increases. This reflects the fact that the CCD is mainly located in great depths (between 4000m and 5000m). On the other hand, solubility of  $\text{CaCO}_3$  also increases with the rise of  $\text{CO}_2$  dissolved. Because of this, it is estimated that at the end of century the CCD will be placed at a lower depth. In addition, organisms located at a certain depth will be suffering the consequences of these changes.

Seawater has the ability to soften up changes of pH, anthropogenic and naturally formed. Besides these ions seen ( $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ), there are other ions in the seawater that are also able to combine with  $\text{H}^+$  and thus would reduce its concentration to give rise to an increment in pH. The difference between the total of those ions, and ions  $\text{H}^+$  is called alkalinity ( $A_T$ ).  $A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] - [\text{H}^+]$  and their units tend to be expressed as  $\mu\text{mol/kg}$ . Therefore, this concept refers to the quantity available of chemical species in the seawater capable of cushioning pH changes, and especially ocean acidification. The values of  $A_T$  don't change a lot between the different oceans and usually that is due to salinity. In contrast to the CID, the increase of atmospheric  $\text{CO}_2$  will not cause a significant change in the average value of  $A_T$ .

Ocean acidification affects with different magnitude throughout the oceans. The waters in high latitudes have a lower capacity to cushion the changes in pH than those at low latitudes. In part, this is because of the lower pH of the waters at high latitudes in relation to the low latitudes. As the ocean follow winning  $\text{CO}_2$ , water in general will see reduced its ability to buffer the pH.

### Methods of study

The measures of  $\text{CO}_2$  in the marine environment have experienced a large increase in the mid-20th century (Keeling et to the. 1965;) Takahashi et to the. 1961) with the development of different programs to increase knowledge of the oceans. Over the past decades, various conferences and international events focusing on the study of the climate and oceans showed the need to increase knowledge about the changes of our planet. These meetings laid the foundations for the study of climate change in the next decades. In these, they planned and developed global observing systems to obtain the needed information to improve current knowledge. In recent projects, it will attempt to optimize the evaluation of ocean acidification, their relation with other oceanographic variables, the impact on ecosystems and the modelling of its future evolution.

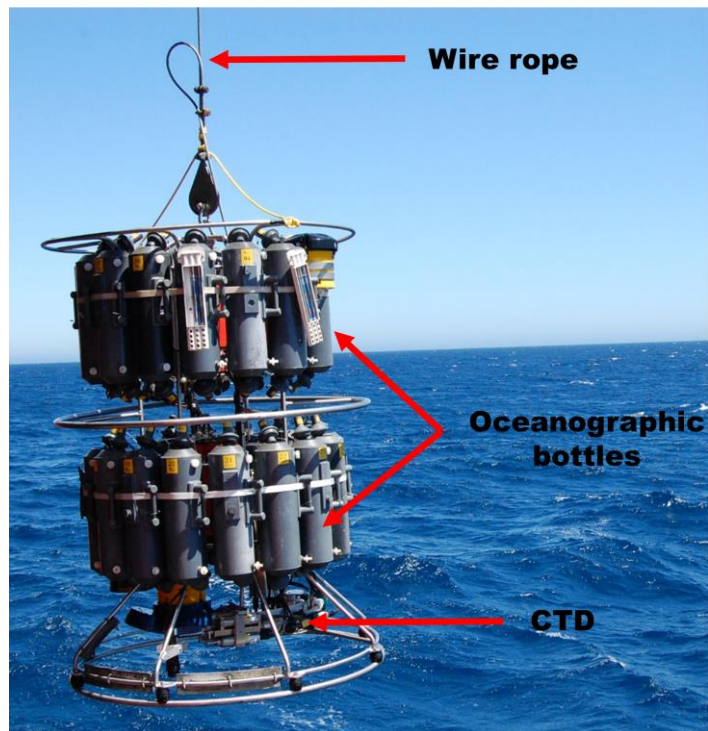
The main platforms for the study of ocean acidification are oceanographic research vessels. Usually, these research vessels are well prepared with laboratories where Scientifics are able to make experiments in those oceanographic campaigns. Measures in-situ and laboratory work developed on board are the main source of information of ocean acidification today. In addition, these data are used to compare and improve the different numerical models and measures of autonomous sensors.

Those Oceanographic campaigns performed for several decades are especially productive. In certain areas and in many cases supported by an international effort, these oceanographic campaigns were repeated periodically offering a real image of the variability of the system. In the same way and as part of campaigns or specific planning, pH and other variables of the system of carbonate in different points of the oceans are repeatedly analysed, reaching even the weekly frequency. These positions constitute the scarce but time series such valuable since they offer information of the impact of multiple processes on the pH of the region (Bates et al., 2014).

The work on research ships begins with taking seawater samples where we want to obtain the values of the variables related to the carbonate system at different depths. Oceanographic equipment CTD-rosette (Figure 5) is a complex device that allows us to simultaneously obtain samples of water in hermetic way (rosette) and register with high frequency and precision basic variables as pressure (depth), temperature and salinity (CTD). Currently, additionally built-in sensors allow also measured dissolved oxygen, chlorophyll, turbidity, distance to the bottom and visible radiation. Usually, the rosette consists of 24 bottles of PVC of 12L and is usually placed above the CTD. There are also other configurations with 12 or 28 bottles and with different capacities. This equipment is used on a routine basis since the 1990 currently constitute an essential element in every Oceanographic campaign.

The device is connected to the vessel using an electromechanical cable which sustains it at all times and serves as the umbilical cord to transmit all the information from sensors to control the boat room. In this way, the exact position of the team is known in real time as well as the thermohaline properties of water that surrounds it. In his descent through the water column, the bottles remain open and the CTD sensors are measuring the variables that allow the devices present in the configuration. Once the full profile has been done, CTD-rosette team is raised back to the ship. In this way it stops at certain interesting depths to scientists and each bottle closes electronically to obtain water from various depths. Once on the deck of the boat, water is extracted from each bottle to perform chemical or biological analysis. Based on the time available and the type of analysis, they can carry out in the laboratories of the boat or land. Variables to determine from these samples are dependent on every Oceanographic project objectives.





**Figure 5.** CTD-rosette.

During overseas campaigns, CTD-rosette team performs hundreds of times this action from surface to the bottom. The deep waters are cold ( $< 2^{\circ}\text{C}$ ) and pressure there is around 400 times higher than the surface pressure. These features require maintaining and a continuous monitoring on complex device sensors, the condition of the electromagnetic wire and the spool machine that repeatedly carries out lowering and hoisting of the sensors.

In particular, the study of acidification is variable analysis of the pH. Mainly, his determination in seawater is carried out using two methods (DOE 1996). The potentiometric method is based on the measurement of the electric potential with two electrodes immersed in the sample of seawater, a reference and other sensitive to pH (the electrode made of glass is used regularly). The Spectrophotometric method is based on the colour changes of a water sample which we have previously added a dye, m-cresol, which changes colour depending on the pH of the sample. The latter method is preferred because of its precision and speed although in many cases the available space aboard do not allow transporting the spectrophotometer (measure of the "colour" of sample instrument). Adaptations of this method are implemented in different autonomous sensors.

### The North Atlantic

The North Atlantic is one of the most important oceanic areas as a sink of anthropogenic CO<sub>2</sub>. Occupying 15% of all oceans, its waters stored 25% of all anthropogenic CO<sub>2</sub> that oceans contain (Sabine et al., 2004). The most influential process that occurs in this area is the formation of bodies of water as the sinking of ocean surface water. The water that reaches this area comes from subtropical areas where has temperatures exceeding 20° C. On their way to the high latitudes of the North Atlantic reduces its temperature to 4 ° C. Thus, the water becomes denser and therefore tends to sink. While on the surface, the concentration of CO<sub>2</sub> in the water is in equilibrium with the atmosphere. So, while the sinking movement this CO<sub>2</sub> tends to go to deeper areas of the ocean. This is why North Atlantic stores a higher quantity of anthropogenic CO<sub>2</sub> that its surface represents.

Recently, it has shown the magnitude of the process of acidification in the North Atlantic (García-Ibáñez et al., 2016). In particular, the process where studied in the Southeast of Greenland, the Irminger basin. Therefore, data from the carbonate system variables were measured and analysed in oceanographic campaigns between 1991 and 2015. The analysis was carried out in the different water masses present in the studied area, i.e. in different depth ranges. A body of water represents a volume of water which has a common history of formation and common physicochemical properties, different from the waters that surround it.

In this study it was observed that all bodies of water of the Irminger basin were winning anthropogenic CO<sub>2</sub>. In consequence, all bodies of water were decreasing its pH during the study period and that means they were more acid. PH measurements obtained in 6 years of study are shown in Figure 6. Each colour belongs to a body of water located in the corresponding range of depths indicated in the legend. Within each year, the pH decreases from surface to the bottom in a similar way as figure 3.

The results show that the rate of acidification (greater inclination of the straight, greater acidification rate) is quite similar between bodies of water (Figure 6). However, this decreased with depth. On the other hand, the deeper layer breaks that trend. The rate of high acidification of this body of water, that the overlying reflects, means this process is recent. Therefore, the found rate shows this mass has made contact with an atmosphere that has high concentrations of anthropogenic CO<sub>2</sub>. Finally, from this data was calculated that by the end of the century the decrease of pH in surface layers will be approximately 0.31 units. This value corresponds to the global average obtained in the IPCC for the higher emissions scenario.

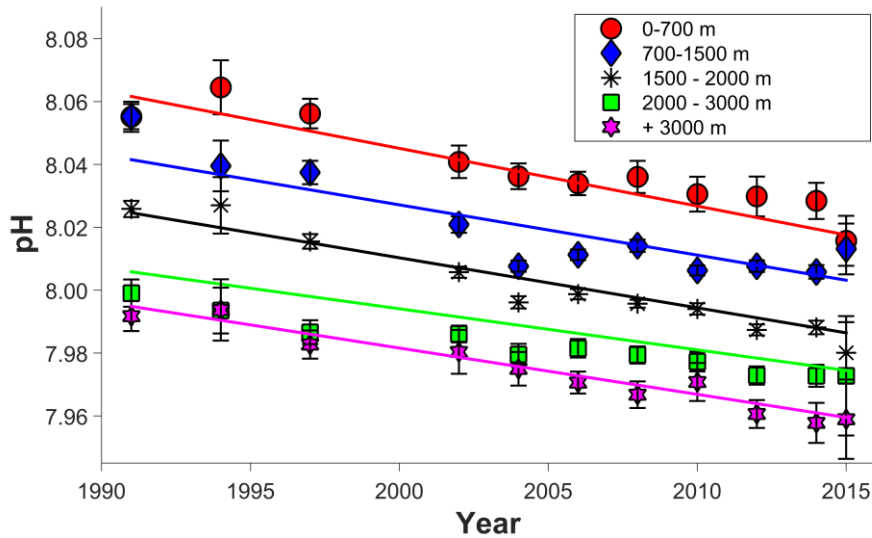


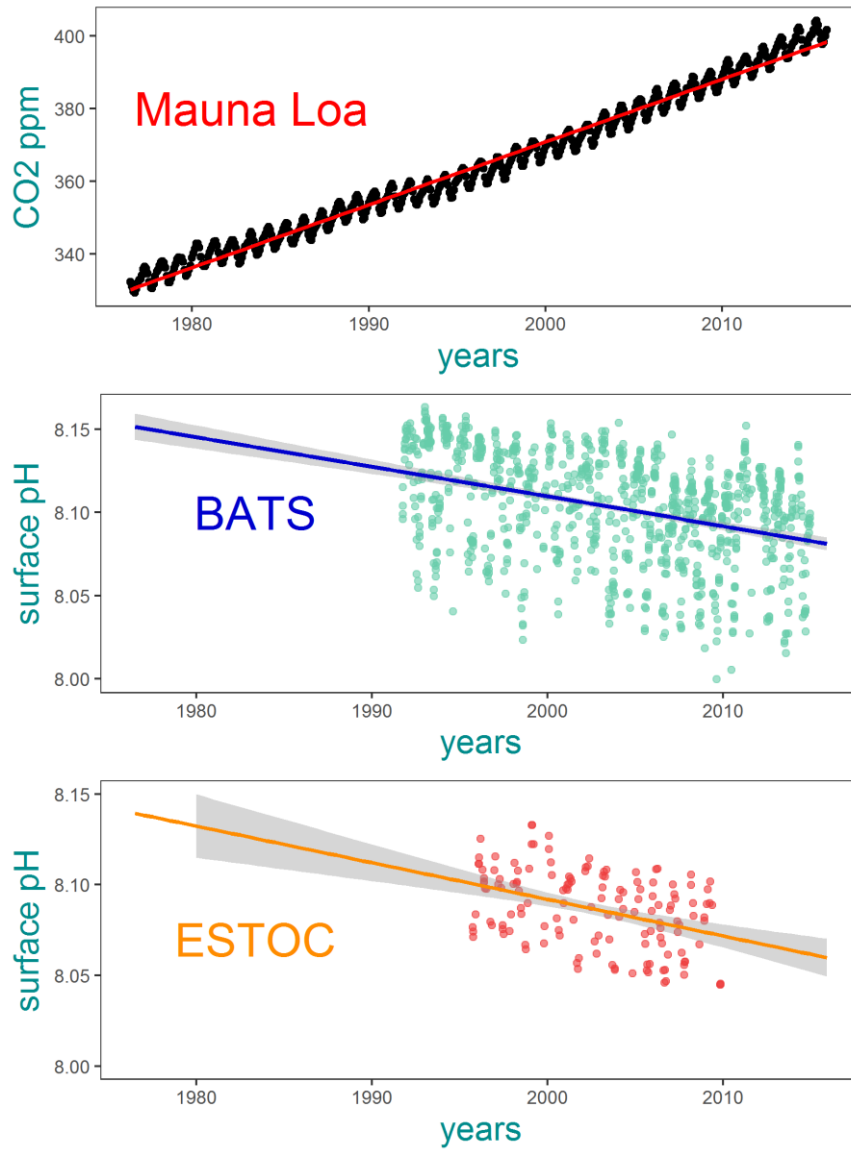
Figure 6. Acidification in the Irminger basin.

In this area it has been observed that aragonite saturation (variable that indicates the availability of  $\text{CO}_3^{2-}$  for organisms that form structures of aragonite, one of the crystalline forms of the  $\text{CaCO}_3$ ) has decreased in all the masses of water. Similarly, the distribution of pH in the water column, the aragonite saturation decreases with depth. In the intermediate waters of the Irminger basin has been found that the aragonite saturation horizon (depth below which the aragonite starts to dissolve) stood 10m closer to the surface each year. The changes of pH inferred by end of century will result in that the entire column of water of this basin is reagent. Therefore, organisms with aragonite structures that inhabit this area are affected.

Similarly, these changes have been observed in different time series located in the North Atlantic. Specifically, in BATS (located in the Bermuda Islands area) and ESTOC (located in the area of the Canary Islands). Data were collected from the 1980s and 1990s, respectively, in these stations where has been observed an increase of  $\text{CO}_2$  in the water. As a result, the changes caused in the carbonate system variables have been registered. It was found a decrease in pH buffer capacity, in the aragonite saturation and pH (Figure 7). The magnitude of this last change is very similar to the one shown by the study detailed previously in the Irminger basin.

Besides the pH decrease that has taken place in the two areas over the study period, the representation of the data shows variation in a smaller scale. PH values may vary

in the range seen in Figure 7a and 7b on timescales as diverse as days, weeks and seasons.



**Figure 7.** (a) Concentration of CO<sub>2</sub> in the atmosphere. (surface pH b) BATS and c) stock. The points represent observations and the straight lines the trend followed by the variable.

## The Baltic

The Baltic Sea is one of the world's largest estuaries. Its watershed comprises 14 countries and covers almost 20% of the European continent, being inhabited by some 85 million people. It drains one area four times larger than its own surface, and more than 250 rivers flow into it. The contribution of fresh water from the rivers (about 15,000 m<sup>3</sup>/s) and net precipitation of 1000 m<sup>3</sup>/s on the sea, make the total amount of fresh water to be added to the Baltic Sea is comparable to the total discharge of the Mississippi River. On the other hand, the connection with the North Sea is very limited to a shallow and narrow transition zone. This favours the formation of a shallow layer of low salinity, with a horizontal gradient of saline and a persistent vertical stratification which restricts the ventilation of deep waters. These are only renewed episodically (Jutterstrom et al. 2014;) Matthäus et al., 2008). Through rivers, huge amounts of carbon and nitrogen, inorganic and organic, fertilize the Baltic Sea (Kulinski and Pempkowiak, 2011;) Voss et to the. 2011). There is also a contribution by dissolution and deposition from the atmosphere of a similar amount of nitrogen. In this way, a large amount of micro-algae bloom in the surface layer which then settle on the seabed. In fact, the Baltic Sea is considered a eutrophic sea (high amounts of nutrients with possibility to produce massive increases of microalgae). Strong sedimentation of microalgae produced a great consumption of oxygen in the deep layers of the sea. As a result, large areas have very low oxygen concentrations (Conley et al., 2002).

The distribution of the CID in the surface waters of the Baltic Sea is widely controlled by alkalinity, which is caused mainly by the wear of the limestone in the drainage basin and the salt supply from the North Sea. The data of CID in surface waters along a transect across the Baltic Sea (Beldowski et al., 2010) show higher values (> 2000 µmol/kg) in the Kattegat and minimum values of approximately 600 µmol/kg in the Bothnian Bay. The annual range of pH for surface waters in the Kattegat region for the period 1992-2007 was 8.06-8.42; for the less saline the Central Baltic Sea area was 8.02-8.70; and for the northern region of Bothnian Bay, much less saline, was 7.40-8.37 pH (Havenhand 2012). In areas where deep values of oxygen they are close to zero, and even generates hydrogen sulfide, pH is approximately one unit less than the surface pH medium.

Precisely in the Baltic Sea, was where pioneers studied system of the CO<sub>2</sub> in seawater such as determining the constants of the equilibrium of the CO<sub>2</sub> in marine systems for the first time (Buch et to the. 1945). Also, a huge set of data from CO<sub>2</sub> were also compiled between 1927 and 1938 in the North of the Baltic Sea. These data indicate that in the Eastern Gotland basin alkalinity has increased at around 100µmol/kg during the last century. This was attributed to acid precipitation, which,

in a limestone basin, as the Neva River, intensify erosion and increases the alkalinity (Schneider et al., 2015). Climate change, due to its effect on the concentrations of nutrients in rivers, has accelerated the effects of eutrophication in the Baltic Sea. This fact increases the extent and volume of anoxic and hypoxic waters which cause an increase in alkalinity that dampen the effects of ocean acidification (Jutterstrom et al., 2014).

The high variability of the pH in surface waters, largely due to the high biological activity, hinders the detection of ocean acidification (Omstedt et to the., 2009). There are decreases in pH observed in almost all regions (Andersson et al., 2008), although only half of them have a statistically significant tendency in surface waters. Projections show a combined effect of eutrophication and ocean acidification indicating a decline in pH greater than expected, while changes in alkalinity are relatively uncertain depending on the changes of runoff in the different drainage basins with different compositions (calcareous or igneous). There is relative agreement that, despite any future changes in the intensity of eutrophication, the increase of atmospheric CO<sub>2</sub> will mainly handle the future changes of pH in surface waters of the sea.

### **Impact on marine organisms**

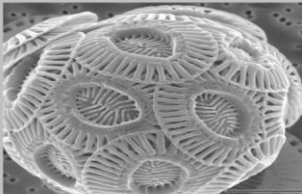









Ocean acidification, as well as modification of physic-chemical conditions of the environment, affects the sustainability of marine biodiversity. In particular, the entry of CO<sub>2</sub> oceans represents a potential risk for CaCO<sub>3</sub> producing marine organisms. Structures formed from this compound as shells have mainly structural and protection tasks against the environment and predators. These organisms include groups with a high ecological importance such as corals and plankton, together with molluscs, crustaceans and echinoderms, which have a remarkable economic importance through a growing industry in recent decades (Gazeau et al., 2007) with an annual value exceeding the 13 trillion dollar (FISHSTAT).

The need to analyse the impact of acidification on marine organisms is collected specifically in the guidelines Horizon 2020 programme of the European Union in which points out is the importance of knowing the potential effects of this problem emerging, particularly in aquaculture.

During the past years different studies by the Oceanographic community have been developed to analyse the potential impacts of acidification of the oceans in organisms (calcification, survival, growth, development, abundance, etc.). These results indicate that species that form CaCO<sub>3</sub> structures will be affected in different



degrees and different processes (Figure 8) and that impact will be moved to different extent along the food chains and in the different ecosystems. The majorities of these investigations are based on experiments for a single species in the laboratory and are relatively short. This shows a simplified view of the natural environment and offers a potential result making it difficult to conclude the situation for each species in a future ocean. Most studies focus on the impact of acidification on the production ability of CaCO<sub>3</sub>. However, changes in pH could determine success for obtaining energy from the environment and the effectiveness of physiological processes (reproduction, buoyancy, etc.) that could reduce its competitiveness and survival (Tyrrell et al., 1999; Gazeau et al., 2013).

Plankton		Molluscs	
	Survival		Survival
	Calcification		Calcification
	Growth		Growth
	Photosynthesis		Development
	Abundance		Abundance
	Survival		Survival
	Calcification		Calcification
	Growth		Growth
	Development		Development
	Abundance		Abundance
	Survival		Survival
	Calcification		Calcification
	Growth		Growth
	Photosynthesis		Development
	Abundance		Abundance
	Survival		Survival
Warm water Corals		Cold water Corals	
	Calcification		Calcification
	Growth		Growth
	Photosynthesis		Development
	Abundance		Abundance

**Figure 8.** Effects of ocean acidification on processes of different groups of organisms. Red: negative; Green: positive; White: no effect.

The production of CaCO<sub>3</sub> by certain marine organisms (bio formation) is based on the combination of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> obtained from sea water. As seen above, the concentration of CO<sub>3</sub><sup>2-</sup> decrease as it increases CO<sub>2</sub> in seawater. Therefore, these builder organisms must eliminate the H<sup>+</sup> of the areas of the body where to set their shell to have properly available CO<sub>3</sub><sup>2-</sup>. For that reason, they pump protons from small

internal spaces to the outside leaving  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ , which crystallize as  $\text{CaCO}_3$ . This process requires a high amount of energy at the expense of other critical processes of life, such as growth and reproduction (Irie et al., 2010), as well as being very sensitive to various environmental changes (Duarte, 2014;) Gestoso et al., 2016). Although identical chemical composition, marine organisms have mainly two types of different crystal structure and soluble minerals: calcite and aragonite. The last one is more soluble. Therefore, the organisms whose structures are composed of aragonite are more sensitive to the decrease of  $\text{CO}_3^{2-}$ .

In marine plankton, usually microscopic organisms that live in suspension in the oceans, find different groups with structures of  $\text{CaCO}_3$ . Despite its small size, they play a relevant role in ocean food chains and in the climate of the planet. These organisms have a special importance in the control and transport of  $\text{CO}_2$  from the surface to the ocean floor through the deposition of their bodies, representing a net withdrawal of  $\text{CO}_2$  from the atmosphere and therefore an attenuation of the greenhouse effect.

In particular, as part of the calcareous phytoplankton we find the coccolitoforidos. These algae, unicellular, is absent in the Baltic Sea because of its low saturation in  $\text{CaCO}_3$  (Tyrrell et al., 2008), they have an exoskeleton of  $\text{CaCO}_3$  and are the main producing limestone structures of the oceans. In addition, the coccolitoforidos are also the main source of dimethylsulphide (DMS) (Charlson et al., 1987), a gas in the atmosphere which has a role as a condenser of clouds increasing the reflectivity of the planet to the solar radiation and therefore tends to cool it. The impact on the climate and its trophic importance as primary producer make the coccolitoforidos' response to acidification an area of intense research and a decisive factor for the future climate. Although early studies in laboratory pointed to a less calcification in an acidified ocean (Riebesell, 2004), recent studies show discrepancies by pointing out that the coccolitoforidos will be adapted probably improving their growth (Jin et al., 2013; (KW et al., 2012).

As representatives of  $\text{CaCO}_3$  producer zooplankton, are the foraminifera and pteropods, being the latter especially relevant in polar latitudes. Experiments with these bodies indicate overall that do not support very well the changes of pH.

Among the marine organisms which produce skeletons of  $\text{CaCO}_3$ , corals are among the most vulnerable to the decrease in seawater pH. Studies suggest that the capacity-building of the coral skeletons is severely affected by ocean acidification. So much that coral reefs may erode faster than the time they need to reconstruct their structures. It has been estimated that the value of 560 ppm of  $\text{CO}_2$  in the atmosphere would lead to the beginning of this process, at the end of this century.



This process adds to the increase of the temperature of the planet, causing the coral bleaching and affecting their health. In this case they are zooxanthellae, symbiotic microscopic algae that give colour to the coral, which are affected by the warming of the waters. However, the corals that live in the North Atlantic are cold coral that live at great depths and do not depend on the zooxanthellae to develop (Figure 9). In this case, and unlike most water corals in the surface, its viability will depend on the penetration of atmospheric CO<sub>2</sub> to deeper layers and that recently has likened to the evolution of surface waters. It has been estimated that in 2100, 70% of cold-water corals will be exposed to a corrosive environment, and already in 2020 will dwell in waters with low saturation of CaCO<sub>3</sub> (Guinotte et al., 2006).



**Figure 9.** Cold-water coral *Lophelia pertusa*. © OCEANA

In the same way as corals, the formation of calcareous structures of molluscs, echinoderms and crustaceans will be committed to ocean acidification. So, these organisms will have a lower capacity of protection against predators and environmental risks. In this respect, various studies measured the growth rate of calcareous structures for some species of these groups, both in temperate waters as warm, finding significant differences. In relation to molluscs, studies show varying results. In general, the most representative pattern is a negative effect on the structures of protection. For mussels and oysters this effect has been described repeatedly (Kurihara et al., 2007;) Gaylord et al, 2011), especially in their early stages (Gazeau et al., 2007).

In addition to the effect of ocean acidification on the shells, studies show impacts on other structures. Specifically, for Mussel, we have obtained negative results on

the “biso” (O'Donnell et al., 2013). This filamentous structure mussels produce to cling to the substrate (rock, surface culture, etc.) through a natural glue that is a pH-dependent and determines its degree of commitment and resilience (ability to return to its original state after a perturbation) following the deformation (Harrington and Waite, 2007). Recent investigations have since revealed that the functionality of the “biso” is compromised by becoming weaker and less flexible under more acidic conditions.

The future impact on the group of echinoderms (sea urchins and starfish) is expected to be even more damaging than in molluscs. Their shells calcite has a high content in magnesium which makes them still more soluble than aragonite. Therefore, the chance of survival will be greatly diminished in the future.

However, this negative impact does not occur in all marine species with shells made of  $\text{CaCO}_3$ . Studies on crustaceans such as lobsters, crabs, and shrimp, showed that far from being disadvantaged in higher acidity means they developed stronger exoskeletons.

All indications are that the answer to acidification of these groups of organisms depends on the complexity of calcareous structures, as well as the protective layers presented on its coatings. Apart from the different taxonomic groups, the impact is also highly dependent on the type of species studied (Fernández-Reiriz et al., 2012), in the same geographical location (Range et al., 2014) and even the condition of individuals (Gazeau et al., 2013), if we had optimal conditions, it would dampen the negative impact of acidification. Also, the phase of the cycle life of each individual shows different responses, being its earliest stages the most sensitive to acidification. Thus, the larval stages come more committed their development by putting at risk the survival of populations. The impact in these stages of growth, where the aragonite is usually the predominant mineral, makes a potential risk factor for aquaculture. In the case of molluscs, they are one of the most sensitive groups to the acidification of the Ocean (Wittman and Portner, 2013).

Traditionally, it has been studied the impact of ocean acidification by testing the responses of individuals of a species to changes in the environment (Gazeau et al., 2013; Comeau et al., 2009). However, these responses both negative and positive are not always extrapolated to the natural environment since the impact within the population or community is much more complex because of the different relationships between species (Kroeker et al., 2010; Pörtner, 2008). Easily, the net impact on species also depends on the impact that this environmental change on the Predator (Hiebenthal et al., 2012). The impact on each species will be moved to the dynamics of the community in different ways, and the impact on these species

will amplify or attenuate over successive generations resulting in the reordering of the ecosystem.

Ocean acidification and climate change in general will play a key role in the distribution of  $\text{CaCO}_3$  productive species, which will occupy those areas where production of  $\text{CaCO}_3$  is sustainable. Also other non-  $\text{CaCO}_3$  productive species will be affected by changes in pH as shown, for example, the proliferation of jellyfish in the North Sea (Attrill et al. 2007). The competition for space could also lead to bioinvasions (Gestoso et al 2016;) Hoegh-Guldberg and Bruno, 2010) where the response to environmental change will determine the success within the community resident or alien species (Shea and Chesson, 2002;) Hochachka and Somero, 2002; Sorte et al., 2013). Examples of this fight were described in coral reefs inhabited by echinoderms and gastropods which came to be dominated by flowering plants and new invasive species (Hall-Spencer et al., 2008). In the same way, the climate on the coast of Galicia has shown varying degrees of vulnerability and resilience among the native Mussel, *Mytilus galloprovincialis*, and the invasive Mussel *Xenostrobus securis* (Babarro and Abbot, 2013; Gestoso et al., 2016), which shows a better adaptation to these environmental disturbances. The loss of these species would result in a lower biodiversity and therefore a loss of health for our oceans.

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