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"Dynamics of inorganic carbon and carbonate saturation in the Gulf of Cádiz (SW Spain)”

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A MI MISMA

“CAMINANTE SON TUS HUELLAS

EL CAMINO Y NADA MAS;

CAMINANTE, NO HAY CAMINO

SE HACE CAMINO AL ANDAR. “

1. INTRODUCTION

1.1 THE OCEANS AND CARBON DIOXIDE: ACIDIFICATION PROCESS AND THE GLOBAL CHANGE

In 1896 Svante A. Arrhenius claimed that the increase of emissions from fossil fuel-burning into the atmosphere could lead or accelerate global warming (Arrhenius, 1896) and established a relationship between atmospheric carbon dioxide and temperature. Only in the last four decades (Broecker, 1975), the phenomenon of climate change has been observed and has its origins in the increased atmospheric emissions of greenhouse gases, such as carbon dioxide(CO_2), methane (CH_4) and nitrous oxide (N_2O) and water vapour. These gases have the property of absorbing and re-emitting the infrared radiation (IR), which is what makes CO_2 an effective trap-heat greenhouse gas. In this way, these molecules gain extra kinetic energy, which may then be transmitted to other molecules and causes general heating of the atmosphere

The greenhouse effect works like this: First, the sun's energy enters the top of the atmosphere as shortwave radiation and makes its way down to the ground without reacting with the greenhouse gases. Then the ground, clouds, and other earthly surfaces absorb this energy and release it back towards space as longwave radiation. As the longwave radiation goes up into the atmosphere, it is absorbed by the greenhouse gases. The greenhouse gases then emit their radiation (also longwave), which will often keep being absorbed and emitted by various surfaces, even other greenhouse gases, until it eventually leaves the atmosphere. Since some of the re-emitted radiation goes back towards the surface of the earth, it warms up more than it would if no greenhouse gases were present (Figure 1). IR build-up in the lower layers of the atmosphere ultimately causes heating of this , as well as the earth's surface, causing the phenomenon known as global warming.

Anthropogenic greenhouse gas emissions have increased since the pre-industrial era, driven largely by dramatic changes in the economic, social and technological sectors. Since then, their effects have been detected throughout the climate system, and are likely to have been the dominant cause of the observed warming since the mid-20th century.

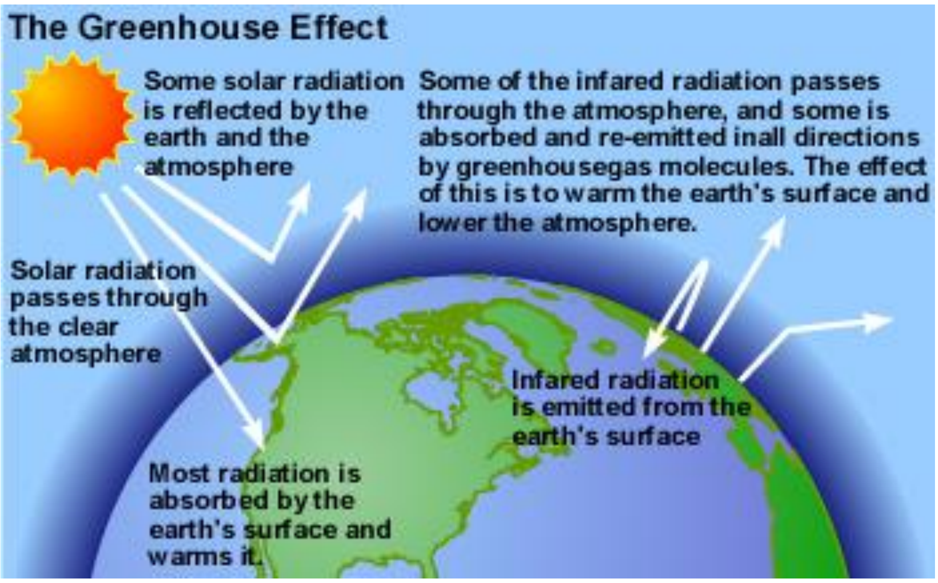


Figure 1. The Greenhouse Effect. Image captured by http://climate.ncsu.edu/edu/k12/.GreenhouseEffect

Recently, National Administration of Department of Aeronautics and Aeronautical National (NASA, National Aeronautics and Space Administration) has conducted a study on air bubbles trapped in ice that allowed to analyse how the earth and climate change have been modified over time. By this work emerged that levels of carbon dioxide (CO_2) in the atmosphere are higher than they have ever been at any time in the past 400,000 years. During ice ages, CO_2 levels were around 200 parts per million (ppm), and during the warmer interglacial periods, they hovered around 280 ppm. In 2013, CO_2 levels surpassed 400 ppm for the first time in recorded history (Figure 2). This recent relentless rise in CO_2 shows a remarkably constant relationship with fossil-fuel burning, and can be well accounted for based on the simple premise that about 60 percent of fossil-fuel emissions stay in the air (http://climate.nasa.gov/climate_resources/24/).

Great importance has been the creation of Intergovernmental Panel on Climate Change (IPCC), the leading international body for the assessment and the current state of climate change in 1988; thanks to the IPCC more attention has been driven on climate change and the negative effects it has on the surface temperature, vapour in the atmosphere , precipitation, ice cover , the frequency of extreme event , the sea level and changes in ocean chemistry Synthesis(IPCC,2014).

The anthropogenic CO_2 emitted into the atmosphere is largely captured by natural systems such as the terrestrial biosphere and oceans. Recent studies have estimated that in the past 200 years, the oceans have absorbed 525 billion tons of carbon dioxide from the atmosphere, or nearly half of the fossil fuel carbon emission over this period (Orr et al. 2005, Sabine et al. 2004).

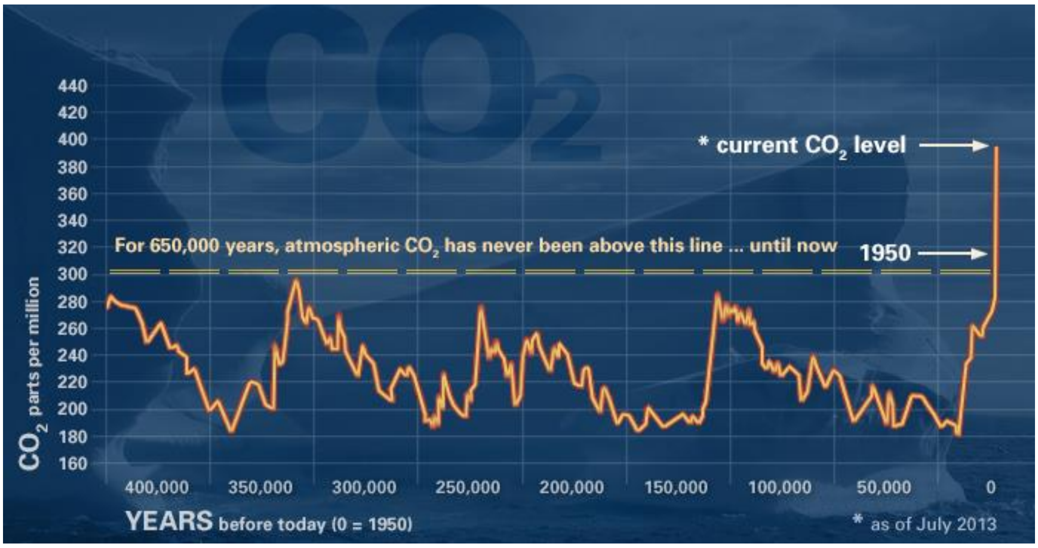


Figure 2. Register of annual concentrations of atmospheric CO2 for 800,000 years, conducted on air bubbles trapped in ice by the Administration of Department of Aeronautics and Aeronautical National. Image obtained from http://climate.nasa.gov/climate_resources/24/.

The oceans cover over two-thirds of the Earth's surface. They play a vital role in global biogeochemical cycles, contribute enormously to the planet's biodiversity and provide a livelihood for millions of people. Initial evidence shows that the surface waters of the oceans, which are slightly alkaline, are already becoming more acidic: this process is known as of ocean acidification (

Figure 3).

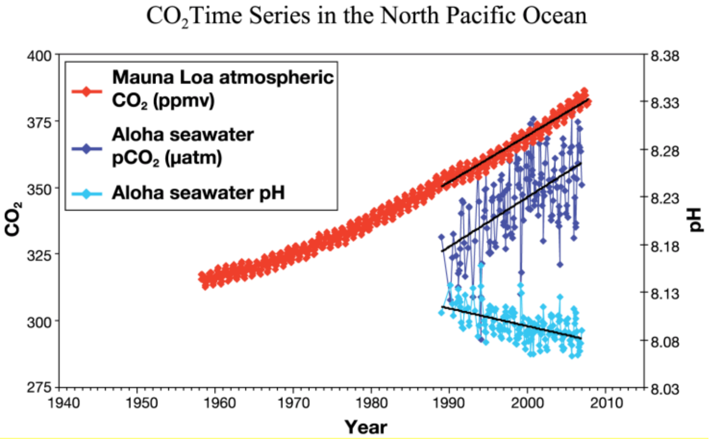

CO$_2$Time Series in the North Pacific Ocean

Figure 3. Times series of atmospheric at Manua Loa and surface ocean pH and pCO2 at ocean station Aloha in the subtropical North Pacific Ocean. Mauna Loa data: Dr. Pieter Tans, NOAA/ESRL; HOTS/Aloha data: Dr. David Karl, University of Hawaii (modified after Feely, 2008).

The absorption of anthropogenic CO$_2$ has caused a decrease on surface-ocean pH of ~0.1 units, from~8.2 to ~8.1 (Zeebe, 2012). Surface-ocean pH has probably not been below ~8.1 during the past 2 million years (Hönisch et al. 2009). This value may seem small; however this change represents an increase of about 30% in acidity, measured as hydrogen ion concentration (The Royal Society 2005). The increase of acidification will have significant effects on the marine system. If CO$_2$

emissions continue unabated, surface-ocean pH could decline by approximately 0.7 units by the year 2300 (Zeebe et al. 2008). Oceans also play a significant role in the regulation of global temperature and thus they affect a range of climatic conditions and other natural processes on the Earth (Zeebe et al,2001).

The Earth's climate is currently undergoing changes as a result of global warming, which is impacting many chemical and biological processes(Figure 4) shows the projected rise in temperature through 2100, compared to the rise in temperature we have already experienced since 1900 (the "thermometer" on the right shows warming since the late 1800s). On average, temperatures have risen less than one degree since then. The highest projections of greenhouse gas emissions, known as "Representative Concentration Pathways 8.5" (RCP8.5), indicate that temperatures could rise a full four degrees Celsius above recent temperatures. But if we're aggressive about mitigating the effect of climate change, we could wind up in a low-emission RCP2.6 scenario of a one- to two-degree temperature rise.

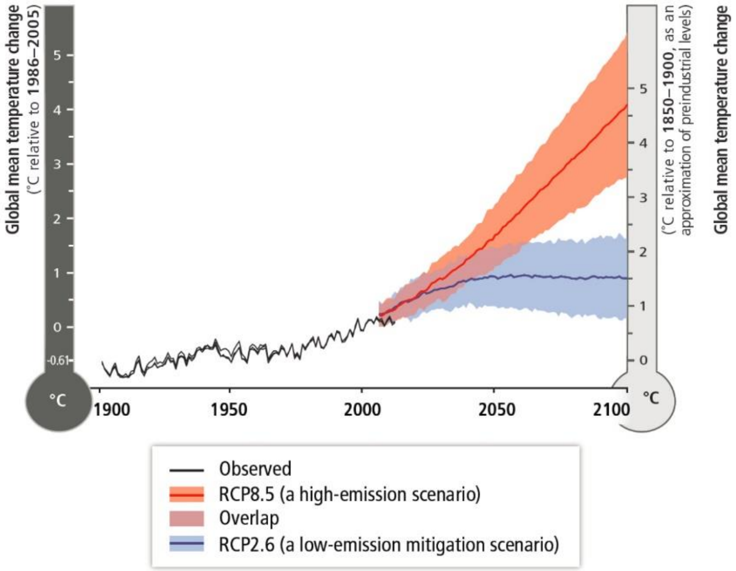


Figure 4. The projected rise in temperature through 2100, compared to the rise in temperature have already experienced since 1900. Image from Pachauri, R.K, et al. (2014)

Carbon dioxide in the atmosphere is chemically an unreactive gas but, when it is dissolved in seawater, it becomes more reactive taking part in several chemical, physical, biological and geological reactions, many of which are complex (The Royal Society, 2005).

When CO_2 dissolves in seawater forms a weak acid, called carbonic acid (H_2CO_3). Part of the acidity is neutralised by the buffering effect of seawater, but the overall impact is to increase the acidity that consequently decreases the concentration of the carbonate ion, whereas the bicarbonate ion ([HCO_3]) increases.

The pH of the ocean is also controlled by the temperature of the surface oceans and upwelling of CO_2-rich deep water into the surface waters in upwelling areas (The Royal Society 2005).

The solubility of CO_2 depends on the temperature so that low surface water temperatures increase the CO_2 uptake, while surface warming drives its release. When CO_2 is released from the oceans at constant temperatures, pH increases. The concentration of carbon dioxide is higher in deep ocean water because there is no photosynthesis to remove carbon dioxide from the water. Animal respiration and scavenger decomposition also increase the level of carbon dioxide in deep water. Since carbon dioxide solubility in ocean water increases with decreasing temperature and increasing pressure, this allows deeper water to store more carbon dioxide.

One of the most important implications of the changing acidity of the oceans is the effect on many marine photosynthetic organisms and animals, such as corals that make shells and plates using calcium carbonate ($CaCO_3$). This process is known as 'calcification' and it is important for the biology and survival of several marine organisms. Calcification is impeded progressively by to decrease of pH and declining [CO_3^{-2}]. Consequently the stability of calcium carbonate is reduced.

However, the complexity of the marine biogeochemical processes and the lake of the complete Knowledge of the effect on oceanic CO_2 chemistry have led to difficulties in predicting the consequences for marine life. It has also been difficult to set the appropriate threshold levels for a tolerable pH change (Zeebe et al.,2008). For the complete understanding of the effects of acidification, we need to assess all the aspects of the forcing of the marine CO_2 system. Model results have shown that the high latitude oceans will be the first to become undersaturated with respect to calcite and aragonite (Orr et al,2005)

1.2 CARBONATE CHEMISTRY IN THE AQUATIC SYSTEM

The reactions that take place when carbon dioxide dissolves in water can be represented by thermodynamic equilibrium where gaseous carbon dioxide [$CO_2(g)$] and [CO_2] are related by Henry's law:

$$CO_2\,(g) \rightleftarrows CO_2\,(aq)$$

$$CO_2\,(aq) + H_2O(l) \rightleftarrows H\,(aq) + HCO_3^-\,(aq)$$

The equilibrium relationships between the concentrations of these various species can then be written as:

$K_{0=}\, CO_2\,(g) = [CO_2]$

$K_1 = CO_2 + H_2O = HCO^-{}_3 + H^+$

K_2=HCO^{-}_{3} =$CO^{2-}{}_{3}$+ H^+

where K_0 is the temperature- and salinity-dependent solubility coefficient of CO_2 in seawater (Weiss 1974). The concentration of dissolved CO_2 and the fugacity of gaseous CO_2, fCO_2, then obey the equation $[CO_2] = K_0 \times fCO_2$, where the fugacity is virtually equal to the partial pressure, pCO_2 (within ∼1%). The dissolved carbonate species react with water, hydrogen ions (pH = −log([H+])), and hydroxyl ions and are related by these equilibria:

The pK*s [= −log(K*)] of the stoichiometric dissociation constants of carbonic acid in seawater are $pK_1^* = 5.94$ and $pK^*_2 = 9.13$ at temperature Tc = 15◦C, salinity S = 35, and surface pressure P = 1 atm (Prieto & Millero 2001). At a typical surface-seawater pH of 8.2, the speciation between $[CO_2]$,$[HCO_3^-]$, and $[CO_3^{2-}]$.In the Figure 5 is showed the distribution of carbonate species as a fraction of total dissolved carbonate in relation to solution pH.

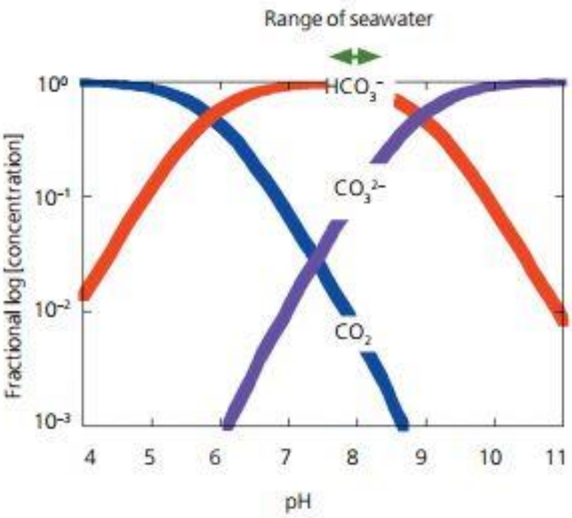


Figure 5. The distribution of carbonate species. Extract by Zeebe et all,2005

The concentrations of the individual species of the carbon dioxide system are ($[CO_2]$,$[HCO_3^-]$, and $[CO_3^{2-}]$). They can however be obtained from experimental parameters [pH, partial pressure of CO_2 (pCO_2), total dissolved inorganic carbon (DIC) and total alkalinity (AT)] along with the utilization of thermodynamic constants. In order to characterize the carbonate system, at least two parameters are required. As an example, consider the case in which DIC and $[H^+]$ (i.e. pH) have been obtained by direct measurement.

The total inorganic carbon (CT, or TIC) or dissolved inorganic carbon (DIC) is the sum of inorganic carbon species in a solution. The inorganic carbon species include carbon dioxide, carbonic acid, bicarbonate anion, and carbonate:

CID = $[CO_2^*] + [HCO_3^-], + [CO_3^{2-}]$

The concentrations of the different species of DIC (and which species is dominant) depends on the pH of the solution.

Alkalinity is an experimental value that has been used widely together with pH in the calculation of dissolved inorganic carbon speciation in sea water. Essentially, it consists in the measurement of the quantity of strong acid necessary to transform all inorganic carbon present to CO_2. Because there are a number of acid- base equilibriums in sea water apart from those involved in the carbonate system, the total alkalinity (AT) can be expressed in a general form as :

AT= [Weak Acids] – [Weak Protonised Acids] + $[OH^-]$ – $[H^+]$

The total alkalinity of a sample of sea water is a form of mass-conservation relationship for hydrogen ion. It is rigorously defined (Dickson, 1981) as “. . . the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10–^{4.5}$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10–^{4.5}$) in 1 kilogram of sample.” Thus

AT= $[HCO_3^-]+2[CO_3^{2-}]+[B(OH)_4^-]+[OH^-]+[HPO_4^{2-}]+2[PO_4^{3-}]+[SiO(OH)_3^-]+[NH_3]+[HS^-]-[H^+]_F$ $-[HSO_4^-] - [HF] - [H_3PO_4]$;

The concentrations are total concentration and include the multiple ionic associations formed by these species in sea water.

This expression is currently widely accepted for alkalinity in sea water. It is required for carrying out inorganic carbon speciation in complex marine system. When the expression is applied to oceanic waters, it simplified to:

AT= $[HCO_3^-]+]+2[CO_3^{2-}]+[B(OH)_4^-]$

The hydrogen ion concentration in sea water is usually reported as pH:

$$pH = -\log[H^+]$$

Although the concept of a total hydrogen ion concentration is somewhat confusing, it is needed to define acid dissociation constants accurately in sea water (Dickson, 1990). Total hydrogen ion concentration is defined as:

$$[H+] =[H^+]_F + (1+ S_T / K_S).$$

where $[H^+]$F is the *free* hydrogen ion concentration, S_T is the total sulphate concentration ($[SO_4^{2}]$+$[HSO_4^-$] and KS is the acid dissociation constant for HSO_4^-. At pH values above 4, previous equation can be approximated as:

$[H^+] = [H^+]_F + [HSO_4^-]$

The pH scale and the corresponding analysis of the proton transfer reactions in sea water constitute one of the most controversial issues in marine chemistry. This is due to the current use of 3 distinct scales for the expression of the hydrogen ion concentration each with their own corresponding dissociation constant for a particular proteolytic species (Dickson, 1984) (

Table 1).

Table 1.Nomenclature proposed by UNESCO (1987) for the pH scale. Where K´, K* and K_m are apparent, stoichiometric and in terms of molalities respectively

pH Scale	$[H^+]$	pH	K
NBS	a_H (NBS)	pH (NBS)	K´
Total hydrogen ion concentración (mol / Kg-soln)	$[H^+]_T$	pH_T	**K***
Free hydrogen ion concentration (mol / Kg-H)	m_H	pm_H	K_m

The difference between the distinct pH scales owes fundamentally to the different regulating solutions used for calibration of the pH meters. The international scale for pH is based on standard diluted solutions of low ionic strength as put forward by the National Bureau of Standards (NBS) (pH 4.00 and pH 7.02) and represents a normalized pH scale. This is without doubt the most commonly used scale for pH measurement in natural water bodies of low ionic strength such as rivers, lakes and aquifers (Bates 1973, 1975; Covington et al., 1985) as well as being the scale utilised by the majority marine studies.

The electro-chemical measurement of pH is affected by the state of the electrode and the variation in liquid union potential of the reference electrode when it passes from one medium to another, for the example standard solution and the sample. The value increases when the difference in composition between the two mediums is accentuated. This effect is patent in sea water, since its ionic strength (0.7 M) is different from the NBS standard solutions (I< 0.1M). The suitability of applying this pH scale in the marine environment has been questioned by various authors (Bates and Culberson, 1977; Dickson, 1984; UNESCO, 1987; Dickson, 1993).

The problem of the low reproducibility in the measurement of pH in sea water is currently solved using a standard solution of similar ionic strength. These solutions are used on scales known as "overall/total concentration" and "hydrogen ion free concentration" (pHT and pmH, respectively).The overall/total scale was defined by Hanson (1973) in terms of the total hydrogen ion concentration ($H^+ + HSO_4^-$) per kg of sea water. Following this, Bates and Macaskill (1975) defined the pm_H scale in hydrogen free ion molalities. This scale is converted directly to the overall/total scale by taking the bisulphate ion into account.

Dickson and Riley (1979) defined the Sea Water Scale (SWS), which differentiates itself from the overall scale by including the concentration of hydrogen fluoride. Currently, the use of this scale isn't widespread since the equilibrium constant in water for hydrogen fluoride is not well known. Nevertheless, the error produced by ignoring fluoride is negligible. Dickson (1993) defended the use of the overall/total scale and found that the difference in the hydrogen ion concentration given by the "overall/total" when compared to the "Sea Water" scale was around 2-3%.

The last three scales mentioned use standard solutions made up of artificial sea water and as a buffer system, an equimolar blend of tris-hydroxymethyl-methyl-amine and tris-hydroxymethyl-methyl-ammonium chloride, commonly known as TRIS and TRIS·HCl. These solutions have the advantage of not creating a significant variation in liquid union potential between the calibration solution and the samples.

The free and total hydrogen ion concentration scales are related by the following expression (Culberson, 1981):

$$pH_T = pH_F - \log(1 + \beta_{HSO4} [SO_4^{2-}])$$

Where β_{HSO4} is the association constant for the formation of HSO_4^-:

$$\beta_{HSO4} = [HSO_4^-] / [H^+] \cdot [SO_4^{2-}]$$

The value of β_{HSO4} has been determined in sea water at a range of temperatures by various researchers (e.g. Khoo et al., 1977; Bates and Calais, 1981; Millero, 1983).

The pH scales (NBS) and the total hydrogen ion concentration, are expressed in terms of one another via the apparent hydrogen ion activity (f_H^T), which is defined as:

$$f_H^T = \frac{a_H}{[H^+]_T}$$

where a_H is the apparent hydrogen ion activity and $[H^+]_T$ is the total hydrogen ion concentration ($H^+ + HSO_4^-$) in moles per kilogramme of sea water (UNESCO, 1985). The relation between the NBS and SWS scales is the same as that described, with the only difference being that for the total proton concentration, H^+, HSO_4^- and HF are considered. In the same way, the apparent activity coefficient for the free hydrogen ion concentration (f_H^F) is:

$$f_H^F = \frac{a_H}{m_H} \Big/ \left(1 - S/1000\right)$$

This equation relates the NBS and free hydrogen ion concentration (pm_H) scales where pm_H is the apparent hydrogen ion activity.

The partial pressure of carbon dioxide in an aquatic system is described by the Henry's law:

$$pCO_2 = K_0[CO_2]_{ac}$$

Since CO2 has not an ideal behaviour using the fugacity in place of the partial pressure:

$$fCO_2 = f\,pCO_2$$

It assumes f=0.997 at 25°C and that CO_2 has an ideal behaviour , and then $fCO_2 \approx f\,pCO_2$. Through the use of these two experimental parameters and the use of the dissociation of carbonic acid , it is possible to determine all the behaviours that describe the carbon in the seawater system

Some of the main basics of seawater carbonate chemistry are illustrated in the Figure 6 as total dissolved inorganic carbon (DIC), total alkalinity (TA), and $[CO_2]$ at temperature T = 15 °C, salinity S = 35, and pressure P = 1 atm .Contours indicate lines of constant $[CO_2]$ in μmol kg^{-1}. Invasion and release of CO_2 into/from the ocean changes only TCO_2, whereas photosynthesis and respiration also slightly change TA owing to nitrate uptake and release. $CaCO_3$ formation decreases T CO_2 and TA in a ratio of 1:2, and, counterintuitively, increases $[CO_2]$, although the total inorganic carbon concentration has decreased. $CaCO_3$ dissolution has the reverse effect. Modified from Broecker & Peng (1989) and Zeebe & Wolf-Gladrow (2001).

In the carbons equilibrium the temperature and salinity are so important particularly at the surface, in fact CO_2 is less soluble at higher temperatures, leading to outgassing to the atmosphere and hence locally reduced TCO_2.Conversely, CO_2 uptake takes place predominantly in colder waters, and TCO_2 is higher.

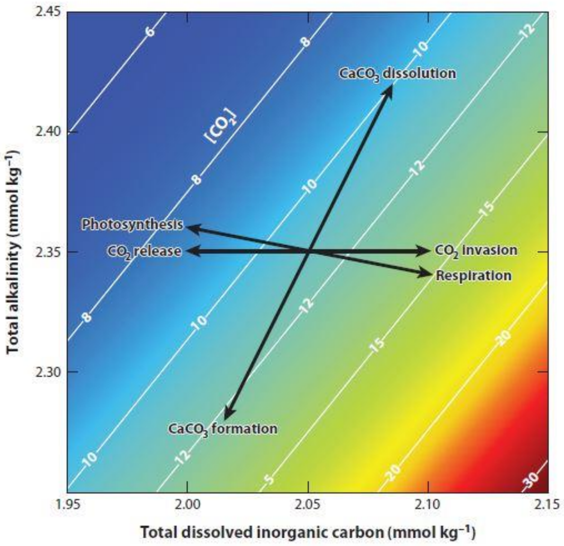


Figure 6. Basics of seawater carbonate chemistry as total dissolved inorganic carbon (DIC), total alkalinity (TA), and [CO_2] at temperature $T = 15$ °C, salinity $S = 35$, and pressure $P = 1$ atm. Image captured by Zeebe et al,2012

2. Calcium Carbonate: Chemical processes, functions of calcification and saturation state

Important issues have indicated the important role of calcium carbonate in the context of ocean acidification and calcifies.

Several studies have evidenced that biogenic calcification will decline and $CaCO_3$ dissolution will increase under rising atmospheric CO_2 and lowered seawater pH (Kleypas et al., 1999). Calcium carbonate becomes more soluble with decreasing temperature and increasing pressure, and hence with ocean depth.

The biological production and dissolution of $CaCO_3$ in the ocean result in changes in TA in the water column according to the following reaction:

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO^{-3} .$$

A change in the balance of this reaction in the ocean would have a significant impact on atmospheric CO_2 concentration (Zondervan et al., 2001). Dissolution of $CaCO_3$ particles increases TA in seawater and thus the capacity of the ocean to absorb CO_2 from the atmosphere, whereas the production of $CaCO_3$ leads to the opposite consequence (Zeebe et al.,2012)

The mineral $CaCO_3$ derives from shells and skeletons of marine organisms, including plankton, corals and coralline algae, and many other invertebrates. In pelagic environments, carbonates fall through the water column and are either dissolved or deposited in shallow or deep-sea sediments (Feely et al. 2004,Berelson et al. 2007)

The formation and dissolution of calcium carbonate ($CaCO_3$) is an important component of the oceanic carbon cycle. The $CaCO_3$ cycle modulates the oceanic dissolved inorganic carbon. Since the settling time of $CaCO_3$ particles is thought to be short if compared to dissolution rates, it was generally believed that much of the carbonate dissolution takes place upon or just beneath the surface of the sediments.

As a consequence of this process, the oceanic $CaCO_3$ export will decrease, which might further weaken its ballast effect for vertical transfer of organic carbon to the deep ocean (Armstrong et al., 2002; Barker et al., 2003).

However, evidence from a variety of sources suggests that as much as 60-80% of net $CaCO_3$ production is dissolved in depths that are above the chemical lysocline, the depth below which the rate of $CaCO_3$ dissolution distinctly increases (Milliman et al., 1999; Francois et al., 2002).

Calcium carbonate exists in two main structures. These are aragonite, which has orthorhombic symmetry in its structure, and calcite, which is trigonal. Both aragonite and calcite are abundant in organisms. However, because of its structure, calcite is less soluble than aragonite (Scott et al, 2009). Usually seawater is supersaturated with constituents for the formation of calcium carbonate (calcite or aragonite). Anyway, in many areas, immediately below the sediment-water interface, the release of protons produced by aerobic degradation processes of organic matter leads to the dissolution of $CaCO_3$.

This is mainly seen in the existence of an increased calcium concentration near the sediment-water interface. At greater depths, the degree of saturation of $CaCO_3$ in the interstitial water increases due to increased alkalinity producing anaerobic degradation processes of organic matter, primarily the sulphate reduction, which causes the precipitated $CaCO_3$. In coastal areas, where the contributions of organic matter usually high, these processes of dissolution/precipitation of $CaCO_3$ have great relevance (Jahnke y Jahnke, 2000; Mucci et al., 2000).

The carbonate saturation (Ω) depend on the carbonate concentration, pressure, temperature and salinity. Calcite and aragonite are examples of minerals whose solubility increase with decreasing temperature. e aragonite is more soluble, its saturation CO_3^{2-} is always higher than that of calcite. These data are plotted in Figure 7, which clearly illustrates the greater importance of pressure over temperature in determining calcium carbonate solubility for both calcite and aragonite. This unusual behaviour is referred to as retrograde solubility. Because of the pressure and temperature effects, calcium carbonate is far more soluble in the deep sea than in the surface waters. Most water masses are not at equilibrium with respect to either calcite or aragonite. The degree to which a water mass deviates from equilibrium for a particular mineral type can be expressed as its degree of saturation, which is defined as :Ca^{2+}

$$\Omega = \frac{[Ca^{2+}]observed \times [CO_3^{2-}]observed}{[Ca^{2+}]saturat \times [CO_3^{2-}]saturat} = \frac{Ion\,product}{K_{sp}^{*}}$$

Where [Ca^{2+}]$_{\text{observed}}$ and $[CO_3^{2-}]_{\text{observed}}$ are the in situ concentrations in the water mass of interest; K_{sp}^{*} of calcite in seawater of 35 ‰ at 25°C and 1 atm is 10$^{-6.4}$.Since aragonite is more soluble than calcite, Ω_{calcite} is always greater than $\Omega_{\text{aragonite}}$ for a given water mass.

If Ω is greater than 1, the water mass is supersaturated and calcium carbonate will spontaneously precipitate until the ion concentrations decrease to saturation levels. When Ω is less than 1, the water mas is under saturated. If calcium carbonate is present, it will spontaneously dissolve until the ion product rises to the appropriate saturation value. Although calcium is a bio intermediate element, it is present at such high concentrations that particulate inorganic carbon (PIC) formation and dissolution causes its concentration to vary by less than 1%. Thus, [Ca^{2+}]$_{\text{observed}}$ ≈[Ca^{2+}]$_{\text{saturation}}$ it is possible resume Ω as :

$$\Omega = \frac{[CO_3^{2-}]\text{observed}}{[CO_3^{2-}]\text{saturation}}$$

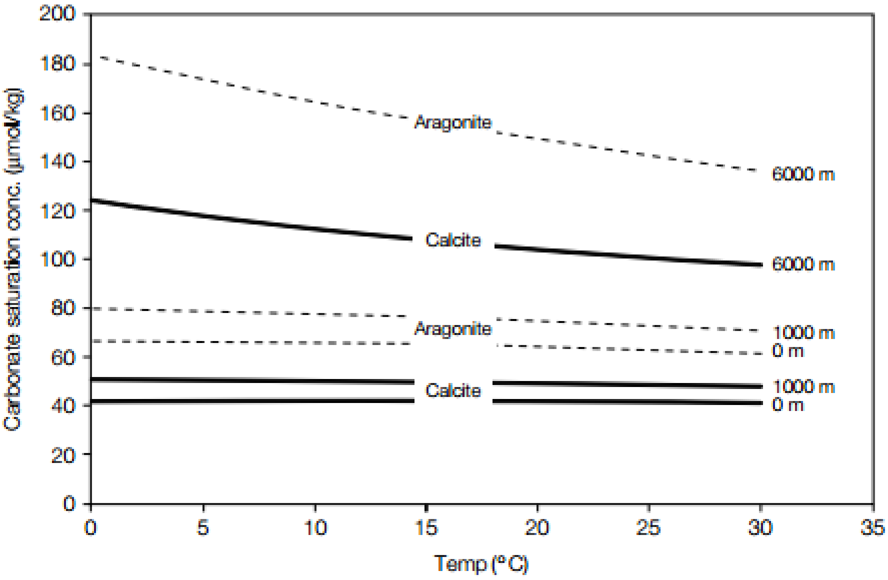


Figure 7.Saturation concentrations of carbonate ion in seawater as a function of temperature and pressure. Image by Susan M. Labes, 2009

The depth at which dissolution starts to have a significant impact on the sedimentary %CaCO$_3$ is termed the calcite lysocline (Susan M. Libes,2009).

Lysocline is defined as the depth in the water column where a critical undersaturation state with respect to aragonite or calcite results in a distinct increase in the CaCO3 dissolution rate (Morse, 1974). For want of a more robust definition, a chemical lysocline is sometimes defined at $\Omega = 0.8$, a value which marks a distinct increase in dissolution rate. The lysocline is the horizon where dissolution becomes first noticeable (a sediment property), and is typically below the calcite saturation horizon (Heiko et all., 2012).

Deeper still, and dissolution becomes sufficiently rapid for the dissolution flux back to the ocean to exactly balance the rain flux of calcite to the sediments. This is known as the calcite (or carbonate) compensation depth (CCD). Because in the real World the boundary in depth between sediments that have carbonate present and those in which it is completely absent is gradual rather than sharp, the CCD is operationally defined, and variously taken as the depth at which the $CaCO_3$ content is reduced to 2 or 10 wt.% (Ridgwell and Zeebe 2005).

At the CCD the rate of supply of calcite equals the rate of dissolution, and no more calcite is deposited below this depth. In the Pacific, this depth is about 4,5000 below the surface; in the Atlantic, it is about 6,000 m deep. This dramatic variation is due to differences in ocean chemistry. The Pacific has a lower pH and is colder than the Atlantic, so its lysocline and CCD are higher in the water column because the solubility of calcite increases in these conditions.

In the Figure 8 the relationship between CCD, sediment $CaCO_3$ content (dotted black line), carbonate accumulation rate (blue line) and lysocline, in comparison with cumulative ocean floor hypsometry (orange line) is showed. The CCD, a sediment property, is defined as where carbonate rain is balanced by carbonate dissolution. Previously, it has been operationally defined to coincide with a fixed content of $CaCO_3$ (for example, 10%) in sediments, or where the carbonate accumulation rate interpolates to zero (this second definition is advantageous as it is independent of non-carbonate supply or dilution effects).

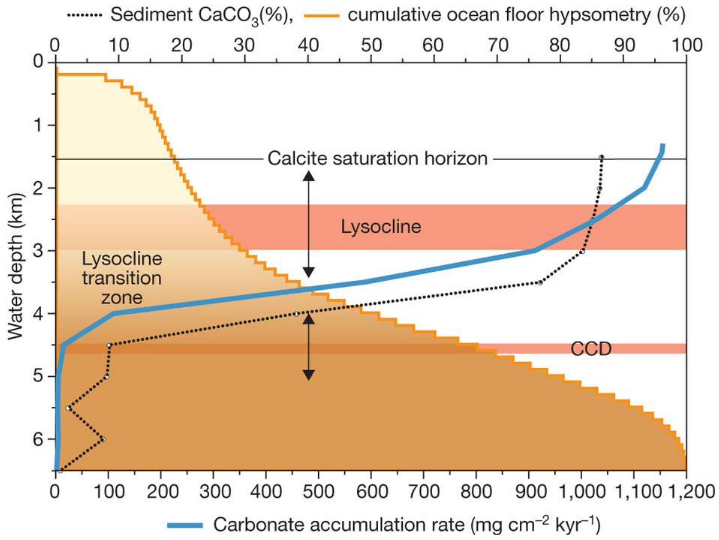


Figure 8. The position of the CCD and lysocline, and their relationship to ocean bathymetry, carbonate accumulation rate and $CaCO_3$ content. Image Heiko P et al., 2012.

The use [Ca^{2+}] to look into the marine $CaCO_3$ cycle is related to the variations of Ca^{2+} in the ocean interior that are almost solely controlled by $CaCO_3$ formation and dissolution on day-to-decade time scales. Ca^{2+}, one of the eleven major ions in seawater, has been recognized to be conservative in the ocean (Pilson, 1998; Millero, 2006).

Since calcium has a such fundamental role in biotic calcification there have been many studies about its distribution in the oceans. Dyrssen et al.(1968) and Whitfield et al.(1969) proposed a potentiometric titration methods using calcium selective electrodes but results had not have a high shown an high accuracy. However after this study Ruzicka et all (1973) and Lebel and Poisson(1976), developed this method until to get a precision 0.1%.

The aim of this study has been to improve the method of these authors to analyzed the calcium concentration in the open ocean.

It is known that the Ca^{2+} concentration is relatively small and it has a conservative state in ocean as proposed by Milliman (1993), Balch and Kilpatrick (1996), Pilson(1998) and Berelson et al.,(2007).

However, it is possible to assumed that in costal environments the calcium has a not stable state because of the river input, the rain the biological precipitation of calcium carbonate from the adjacent surface waters of the Gulf and other chemical or physical factors.

A non-conservative calcium state has been observed for some natural systems: the Persian Gulf (Wells,Illing,1964), small hard-water lakes (Wetzel 1966) and shallow carbonate marine environments (Broecker and Takahashi,1966)

In the seawater, Ca^{2+} concentration typically representing only 1% of its ambient concentration,~10,280 mmol kg^{-1} at a salinity of 35 (Pilson, 1998). For this reason there is lacke of data.

In support of these claims arguments different studies have been conducted to assess the investigate effects of acidification on carbonate production. It very difficult to evaluate this effect because the baseline estimates of how much carbonate is produced and rains through the water column has been shifting (Berelson et al., 2007).

Milliman (1993) estimated carbonate production in the entire ocean at 5 $x10^{13}$ moles $CaCO_3$ yr^{-1} (0.6 Gt PIC yr^{-1}), which included both neritic and open ocean environments. Later, Milliman et al. (1999) determined carbonate production in the open ocean at 6 x 10^{13} moles CaCO3 yr^{-1} (= 0.7 Gt PIC yr^{-1}) based on an inventory of alkalinity and the residence time of various water masses.This value was significantly higher than the one estimated with flux into deep traps and lead to the hypothesis that high rates of carbonate dissolution may occur within the water column.

Balch and Kilpatrick (1996) measured carbonate production in the equatorial Pacific and determined a ratio of PIC to POC (particulate organic carbon) production of 9%, which, if globally extrapolated would yield to estimate of carbonate production of 3.5 x 10^{14} moles $CaCO_3$ yr^{-1} (= 4.3 Gt PIC yr^{-1}).

Balch et al. (2007) reevaluated carbonate production from an assessment of satellite-determined parameters, calcification, and photosynthesis rate determinations, and this value is 1.3 $x10^{14}$ moles $CaCO_3$ yr^{-1} (1.6 Gt PIC yr^{-1}).

Recent estimates of both $CaCO_3$ production and export at a global ocean scale were roughly at the same order, at 0.4–1.8 Gt C yr−1, suggesting relatively high carbon export efficiency in the form of inorganic carbon (Berelson et al., 2007).

If the carbonate system is in steady state, the amount produced in the surface water should equal or exceed the amount falling out of the surface ocean (export), and this would equal the sum of what is remineralized and what is buried (Berelson et al.,2007).

The dissolution of one mole of calcium carbonate adds one mole of calcium and two equivalents of alkalinity to the sea water. The concentration of calcium and alkalinity in sea water are, therefore, expected to change in this proportion if other processes which change calcium concentration or alkalinity are absent (Kanamori et all, 1980).

Ca^{2+} does not suffer from such potential issues. The excess Ca^{2+} (Ca^{2+}_ex) in the ocean interior, if it exists, can only have originated from $CaCO_3$ dissolution, especially in waters at shallow depth being hardly influenced by hydrothermal inputs (de Villiers and Nelson, 1999). There is conjecture that dissolution or ion change of silicate material in the water might increase Ca^{2+} in the intermediate water (Tsunogai et al., 1973), however, until now there is no report of such processes. While we also recognize the potential of shallow depth $CaCO_3$ dissolution from many trap studies (e.g., Martin et al., 1993; Honjo et al., 1995; Wong et al., 1999), the magnitude and the causes accounting for shallow-depth $CaCO_3$ dissolution warrant further examination, in particular in the context of better predicting the response of oceanic buffer capacity to increasing penetrated anthropogenic CO_2. We argue that high-quality Ca^{2+}data from a proper study site with distinguishable preformed waters are required to better examine this shallow-depth $CaCO_3$ dynamics

3. AIM OF THIS STUDY

The main aim of this work is characterize the Dissolved Inorganic Carbon (DIC) dynamics and the saturation state of calcium carbonate in the north-eastern area of Gulf of Cadiz. The achievement of this aim defines the spatial and temporal distribution of DIC in the study area, as well as the saturation state of CaCO3.

These are the specific aims:

- Quantification of inorganic carbon from pH and total alkalinity measured in samples collected along transects in the gulf of Cadiz and different depths in every stations of sampling.
- Estimation of the saturation state of CaCO3 of calcite and aragonite, and their spatial and temporal variation in the Gulf of Cadiz
- Understanding data obtained considering the specific hydrodynamic and chemical characteristics of water mass and seasonal variations.

Calcium is a major element in seawater, and its concentration changes at ocean level. There are many studies where calcium is calculated from salinity (Pilson, 1998, Shadwick et al.2014). However in coastal areas due to the contribution of the rivers and to processes of CaCO3 dissolution

/ precipitation, this element may have variations in its concentration. The second aim of this work is to optimize the measurement of calcium in seawater, allowing a better quantification for future work of the saturation state of CaCO3.

2. THE STUDY AREA

This study was carried out in the nearshore north-eastern shelf of the Gulf of Cádiz (SW Iberian Peninsula), which is a wide basin between the Iberian Peninsula and the African continent where the North Atlantic Ocean and the Mediterranean Sea meet through the Strait of Gibraltar (Figure 9).

Figure 9. Satellite image of Gulf of Cádiz

The Gulf of Cádiz is a domain of considerable interest since it connects the Mediterranean Sea with the Atlantic open ocean and receives the outflowing Mediterranean seawater through the Gibraltar Strait. It therefore plays an important role in the North Atlantic circulation and climate in general (Reid, 1979; Price and O'Neil-Baringer, 1994; Mauritzen et al., 2001). First, in the Gulf of Cadiz there are several water masses mixing to form the ‘‘Atlantic inflow’’ which is responsible for the general oligotrophic and relatively well oxygenated regime of the north-western Mediterranean Sea (Packard et al., 1988; Minas et al., 1991). Second, this area is on the pathway of the ‘‘Mediterranean outflow’’ which thereafter enters to the open ocean and influences the circulation of the North Atlantic and climate in general (Rahmstorf, 1998). The study of the carbon exchange throughout this strait began only a few years ago and it has already been emphasized that the Gulf of Cadiz plays an important role in the carbon cycle of the. eastern North Atlantic (Parrilla, 1998) and the Mediterranean Sea (Dafner et al., 2001).

Only few biogeochemical studies have been done in this area (Minas et al., 1991; Minas and Minas, 1993; Echevarria et al., 2002), especially for the CO2 system (Dafner et al., 2001; Santana-Casiano et al., 2002; González-Dávila et al., 2003).

The Gulf of Cadiz is well documented from a physical point of view (Madelaine, 1967; Zenk, 1975; Ambar et al., 1976; Ochoa and Bray, 1991; Price et al., 1993). The general surface circulation in the Gulf of Cadiz is anticyclonic with short-term, meteorologically induced variations. Hydrodynamics in the Gulf of Cádiz is dominated by the exchange of water masses that occurs in the Strait of Gibraltar, between the Atlantic Ocean and the Mediterranean Sea. Thus the surface water enters the Atlantic Ocean to the Mediterranean, while the masses of water of the Mediterranean, denser, go through the Strait at greater depths (Gascard and Richez, 1985), thus producing a bilayer exchange flow through Strait of Gibraltar (Ochoa and Bray, 1991). This exchange is related to the warm, dry climate of the Mediterranean Sea and its basin has produced a negative water balance, with a predominance of evaporation over precipitation, and that favors the importation of water from outside (Margalef and Albaigés, 1989).

This circulation is maintained in the Gulf of Cádiz, where there are 3 main types of water masses of well characterized. From the surface and even the seasonal thermocline is a body of water of Atlantic origin modified platform-ocean exchanges (Criado-Aldenueva et al., 2006). The presence of NACW in the area is evident below 100 m depth, as described in previous studies (Navarro et al., 2006). This water mass has been categorized in two varieties, such as the warmer Eastern North Atlantic Central Water of subtropical origin (ENACt) and the colder subpolar Eastern North Atlantic Central Water (ENACs) (Ríos 157 et al., 1992; Pollard et al., 1996; Pérez et al., 2001; Alvarez et al., 2005). At shallower depths, NACW is modified by the atmospheric interaction and it has been defined as North Atlantic Surface Water (Gascard and Richez, 1985).

A general movement taking place in the Gulf of Cádiz, we must add the entry of inland water from various rivers, such as the Guadiana, Guadalquivir, Tinto and Odiel.

Another feature that can be highlighted in the Gulf of Cádiz is the existence of upwelling areas in capes of San Vicente and Santa Maria, located in the westernmost part of this area and also form part of the northern branch of outcrop Canary .These are produced by the wind that dominates the area, although Cape Santa Maria is a process rather short time, due to changes in wind patterns (García et al., 2002), leading to higher values biological production. In addition, areas such as the mouth of the Guadalquivir River and the Bay of Cádiz, have the highest values of primary production of the basin (Navarro and Ruiz, 2006).

3. MATERIALS AND METHODS

3.1 FIELD SAMPLING

This work is part of the investigation project of the Institute of Oceanography Spanish (IEO), STOCA (Series Temporales de datos Oceanográficos en el Golfo de Cádiz), in partnership with Campus de Excelencia Internacional del Mar (CEI MAR) and the University of Cadiz.

The aims of this project is to establish the effects of global change on the east part of the Gulf of Cádiz (from the Straits of Gibraltar to the mouth of the Guadalquivir River) based on a systematic sampling of radio or defined transect.

Water samples were collected during the STOCA cruises on board of the R/V Alvariño Angeles and Ramon Margalef. The data reported in this work were collected during 4 cruises that took place 28-31 March 2015 (STOCA 5), 15-18 June 2015 (STOCA 6), 15-18 September 2015 (STOCA 7) and 1-4 November 2015 (STOCA 8) 2015.The first two were on aboard the R / V Angeles Alvariño , while the latter on the R / V Ramón Margalef.

In each of the campaigns, three transects perpendicular to coast, were performed. The chosen transect of Guadalquivir was about 45 km, and water depth varied from 5 to 550 m. The chosen transect of Sancti Petri was about 53 km, and water depth varied from 5 to 600 m. The chosen transect of Trafalgar was about 40 km, and water depth varied from 5 to 250 m. Surveys were carried out continuously for 24 h (as long as weather conditions permitted).

Guadalquivir and Sancti Petri transects have six stations each, while Trafalgar has four set points (only for the cruise STOCA 7 5 stations) (Figure 10). At each sampling station STOCA profile CTD- O2 - LADCP was performed and water samples were taken to levels on surface , 25 m, 50 m, 75 m, 125 m and bottom.

Water samples were taken following the protocol described below. The equipment used for hydrographic measurements and sampling of water was Batisonda and rosette system for profiles of the water column while samples are taken at certain levels. Batisonda is integrated in the rosette which currently has 9 bottles of 10 L. We continuously registered currents with acoustic Doppler profiler (LADCP), temperature, salinity and fugacity of CO_2 (fCO_2) to provide real-time readings via the serial uplink channel.

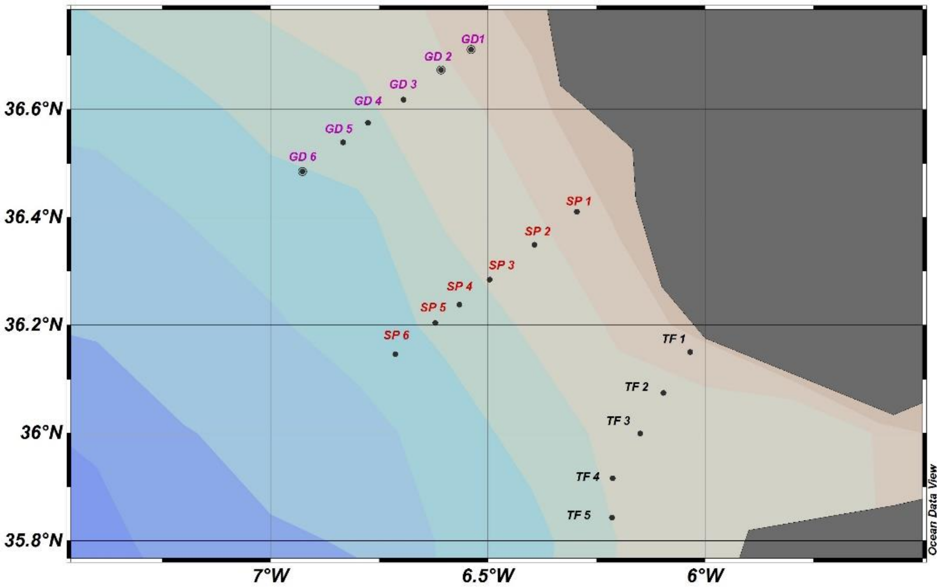


Figure 10. Distribution of transects in the study area . The GD points for the Guadalquivir River, SP for Sancti Petri Channel and TF to Cape Trafalgar

3.2. PHYSICAL-CHEMICAL CONDITION

In order to have a complete knowledge on the physical-chemical and oceanographic conditions of the water column for each cruise it was used the CTD- O_2 - LADCP sensor that has continuously recorded salinity (by measuring the conductivity) , temperature and depth (by pressure meter). The CTD sensor was associated with Niskins bottles, connected to each other to form a rosette . The Niskin bottles are designed so that they have the lids at the ends . When the probe is immersed in water , the lids of Niskins are open and there is a mechanism that is triggered to close electronically to the different depth chosen. The measured data are analyzed in real time by means of a conductor cable which connects the CTD to a computer on board the ship . Water samples were taken during the rise of the rosette (Figure 11)

Figure 11 Rosette incorporated with sensor CTD. Image captured during one of cruises.

3.3 TOTAL ALKALINITY

At each station samples were collected to analyse total alkalinity (TA) and pH.

Total alkalinity and pH were measured by endpoint potentiometric titration in an open cell (Metrohm 905) using a combined glass electrode (Metrohm , ref 6028300). The pH was calibrated in the Total pH Scale. The HCl titrant solution (0.1 mol kg^{-1}) was prepared in 0.7 M NaCl, to approximate the ionic strength of the sample, and calibrated against certified reference seawater by A. Dickson (Scripps Institution of Oceanography , University of California, San Diego, USA , Batch # 128). Accuracy and precision of the TA measurement on CRM was determined ±1.4 µmol kg^{-1}
In Figure 12 a typical titration curve is shown. The inflection points that correspond to the formation of bicarbonate and carbonic acid can be appreciated.

AT was determined from the second equivalence point (V_{e2}) , and the concentration of acid used in the tritation (C_A) and the volume of sample used (V_0) :

$$\frac{AT = V_{e2} \cdot C_A}{V_0}$$

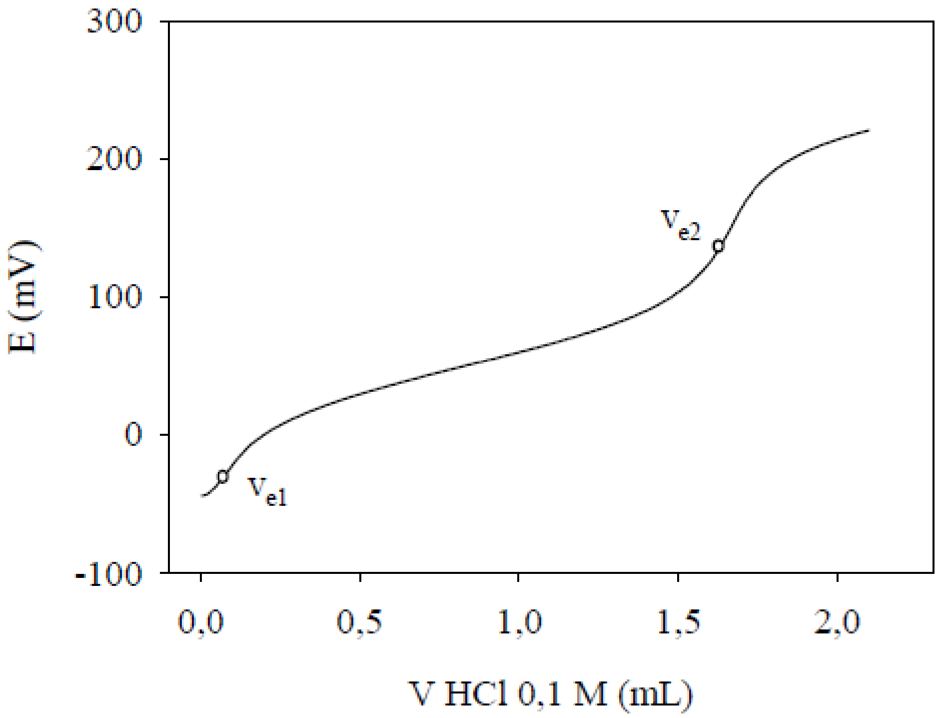


Figure 12. Titration curve. The inflection points correspond to two equivalent points.

3.4. THE CARBON SPECIATION

The calcium concentration [Ca^{2+}] is assumed to be conservative and proportional to the salinity, and is largely determined by variations in [CO_3^{2-}], which can be calculated from DIC and total alkalinity data. Following the determination TA, the pH (on the total scale), DIC and aragonite and calcite saturation state Ω were computed, using the standard set of carbonate system equation with CO_2SYS software (Pierrot et al., 2006). The thermodynamic solubility products for aragonite and calcite ($K_{C,A}^*$) are from Mucci (1983) corrected for in situ temperatures and pressures (Millero, 1983).

The expressions for the calculation of the solubility equilibrium for aragonite and calcite are:

$$\begin{aligned}\log K_C^* = \log K_C^0 + (-0.77712 + 2.8426 \cdot 10^{-3} \cdot T + \frac{178.34}{T}) \cdot S^{0.5} - \\ - 0.07711 \cdot S + 4.1249 \cdot 10^{-3} \cdot S^{1.5}\end{aligned}$$

$$\begin{aligned}\log K_A^* = \log K_A^0 + (-0.068393 + 1.7276 \cdot 10^{-3} \cdot T + \frac{88.135}{T}) \cdot S^{0.5} - \\ - 0.10018 \cdot S + 5.9415 \cdot 10^{-3} \cdot S^{1.5}\end{aligned}$$

We used the thermodynamic equation and constants for carbon, sulphate and borate of Lueker et al.(2000), Dickson (1990) and Lee at al.,2010, respectively. $K_{C,A}$ was calculated for both calcite and aragonite and the saturation states were given in terms :

$$\Omega_{C,A} = \frac{[CO_3^{2-}]\ X\ [Ca2+]}{K(C,A)}$$

The value of $\Omega_{C,A} < 1$ represent under saturated conditions, whereas the value of $\Omega_{C,A} > 1$ represent conditions of supersaturation.

The carbonate concentration, $[CO_3^{2-}]$, is calculated from TCO2, pH, and the values of K1 and K2 for carbonic acid. The effects of pressure on K1 and K2 are from Millero (1995).

The pressure correction for Ksp for calcite is from Ingle (1975) and that for aragonite is from Millero (1979).

We used AT, pH at 15 °C, salinity and sea surface temperature (SST) for each sample and the CO_2 calculation program CO2SYS (Lewis and Wallace, 1998) to calculate, total dissolved inorganic carbon (DIC), in situ pH, the carbonate ion concentration $[CO_3^{2-}]$, and the saturation state of aragonite (Ω_A) and calcite (Ω_C). The calculations were performed at the total hydrogen ion scale (pH mol/kg-SW) Lee et al. (2010). For KSO4 we used the constant determined by Dickson (1990) and K1, K2 from Lueker et al., 2000.

DIC is defined as the sum of $[CO_2]$+$[HCO_3^-]$+ $[CO_3^{2-}]$ and AT is defined as $[HCO_3^-]$+2$[CO_3^{2-}]$+ $[B(OH_3^-]$+$[OH^-]$−$[H^+]$. KSO_4 (Dickson 1990a; Khoo et al. 1977).

4. RESULTS

4.1 OCEANOGRAPHIC VARIABLES

Oceanographic [Salinity, S and Temperature, T (°C)] and biochemical variables (carbon system parameters) measured in the Gulf of Cádiz during the four STOCA sampling cruises accomplished in March, June, September and November 2015 (Table 2).

Guadalquivir

The highest values of temperature and salinity were observed in surface waters (~ 25 m top layer) in June and September and June and November, respectively, while lower temperatures were recorded in March. A sudden change of temperature is observed between March and June with a mean difference of about 3-4 °C, while differences between June and September, and September and November are of about 1-2 °C (Table 2).

Temperature decreased and salinity increased with depth, respectively. The thermocline was detected at 100 m depth and consisted of a sudden temperature decrease of about 1°C. Likewise, the halocline has been found at the same depth, extending down to a depth of 300 m, after which salinity started increasing again in deeper waters offshore. A slight increase in salinity was observed offshore in March and September (Figure 13)

Recorded temperatures were significantly different among seasons in the Guadalquivir, Sancti Petri and Trafalgar sampling areas ($p < 0.01$). In fact, March and November are significantly different, while September and November are not different. Minimum and maximum values were recorded

It is noteworthy that, the highest temperatures were recorded in June and November while in March and September tended to decrease, with the minimum value recorded in spring.

Overall, the oceanographic variables measured during March cruise reflected typical conditions recorded in Winter and June in Spring; conversely, September reflected the Summer conditions, and November represented the typical Autumn conditions.

Table 2. Mean, standard deviation and ranges of the in-situ oceanographic variables (T, salinity), and carbon system parameters (pH, $A_{T,}$ DIC, CO_3^{2-}, Ω_{Ca}, Ω_{Ar} Ca^{2+},) measured in the Gulf of Cádiz during four sampling cruises (March, June, September, November).

AREAS	PERIOD	Mean,± st.dv.	TEMPERATURE °C	SALINITY	TA (µmol kg^{-1})	pH	CO_3^{2-} (µmol kg^{-1})
GUADALQUIVIR	March	Mean± st.dv v.max-va.mi	14.3±0.89 12.73-15.76	36.0±0.85 35.6-36.6	2402 ±30 2354-2493	8.1 ± 0.080 8.2-7.9	172.40±30.49 133.2-261.5
	June	Mean± st.dv v.mi-va.max	18.1±2.9 13.1-21.7	36.2±0.17 35.8-36.6	2320 ± 32 2259-2429	7.92 ± 0.060 7.9-8	161.01±22.71 122.1-260
	September	Mean± st.dv v.mi-va.max	16.3±2.8 12.9-21.6	36.1±0.15 35.7-36.5	2402 ±37 2354-2493	7.90 ± 0.050 7.8-7.9	134.79±20.66 96.7-176.3
	November	Mean± st.dv v.mi-va.max	18.0±2.3 21-14.7	36.3±0.19 36.14-36.89	2288 ±20.6 2019-2331	8.02 ±0.020 7.7-8.3	169.98±14.84 145.8-189.3
SANCTI PEDRI	March	Mean± st.dv v.mi-va.max	14.5±0.81 11.9-15.9	36.0±0.20 35.7-36.9	2326 ± 36.3 2338-2446	7.97 ± 0.060 7.9-8.11	155.90±14.99 128.4-186.7
	June	Mean± st.dv v.mi-va.max	18.1±2.8 13.2-21.6	36.3±0.23 37.1-36.3	2326 ± 36.25 2275-2443	7.97 ± 0.060 7.9-8	175.87±22.77 138.5-207.2
	September	Mean± st.dv v.mi-va.max	16.2±2.8 13.03-21.5	36.1±0.18 35.9-36.9	2390 ±63.13 2160-2528	7.93 ±0.050 7.8-8.0	140.67±24.86 112-194.7
	November	Mean± st.dv v.mi-va.max	17.9±2.3 14.05-20.83	36.4±0.19 36.05-37.15	2282 ±23.49 2237-2361	8.01 ±0.060 7.7-8.05	168.62±20.71 107.8-189.03
TRAFALGAR	March	Mean± st.dv v.mi-va.max	14.6±0.60 13.7-15.7	36.1±0.22 36.0-36.9	2387 ± 40.0 2330-2462	7.96 ± 0.050 7.9-8.03	154.21±15.25 127.2-188.9
	June	Mean± st.dv v.mi-va.max i	17.8±2.1 13.8-21.1	36.4±0.32 36-37.5	2333 ± 37.20 2290-2414	7.97 ± 0.050 7.9-8.08	171.64±16.02 142.6-194.5
	September	Mean± st.dv v.mi-va.max	16.4±2.3 13.45-21.52	36.3±0.53 35.9-37.9	2417 ± 65.14 2300-2560	7.83 ±0.090 7.67-7.9	135.03±26.32 91.7-188.7
	November	Mean± st.dv v.mi-va.max i	18.7±2.02 14.84-20.65	36.5±0.28 36.27-37.5	2255 ±76.94 2019-2331	8.00 ±0.13 7.7-8.3	169.37±48.34 106.3-309.1

AREAS	PERIOD	Mean,± st.dv.	DIC(μmol kg^{-1})	Ω Ca	Ω Ar	Ca^{2+}
GUADALQUIVIR	March	Mean± st.dv v.mi-va.max	2161±42.65 2047-2247	4.02±0.75 3.1-6.2	2.59±0.48 2-4	10.6±0.12 9.9-10.7
	June	Mean± st.dv v.mi-va.max	2092±35.47 2048-2212	3.76±0.58 2.7-4.9	2.44±0.39 1.8-3.1	10.6±0.05 10.5-10.7
	September	Mean± st.dv v.mi-va.max	2224±40.00 2157-2307	3.14±0.52 2.1-4.1	2.03±0.35 1.4-2.7	10.6±0.05 10.5-10.7
	November	Mean± st.dv v.mi-va.max	2046 ±14.14 2002-2111	4.02±0.35 3.44-4.48	2.61±0.24 2.22-2.92	10.7±0.40 10.62-10.84
SANCTI PEDRI	March	Mean± st.dv v.mi-va.max	2172±32.90 2114-2228	3.63±0.40 2.9-4.4	2.33±0.26 1.8-2.8	10.6±0.05 10.5-10.7
	June	Mean± st.dv v.mi-va.max	2074±36.61 2017-2158	4.10±0.59 3.1-4.9	2.66±0.40 2.0-3.2	10.7±0.07 10.5-10.9
	September	Mean± st.dv v.mi-va.max	2201±49.87 2006-2286	3.33±0.59 2.65-4.62	2.15±0.40 1.7-3.01	10.6±0.06 10.5-10.8
	November	Mean± st.dv v.mi-va.max	2045±48.34 1970-2230	3.89±0.54 2.26-4.74	2.52±0.36 1.4-2.9	10.7±0.06 10.5-10.9
TRAFALGAR	March	Mean± st.dv v.mi-va.max	2173±38.0 2097-2240	3.61±0.38 2.9-4.5	2.32±0.24 1.9-2.9	10.6±0.06 10.5-10.6
	June	Mean± st.dv v.mi-va.max	2090±51.83 2041-2211	4.03±0.39 3.33-4.6	2.61±0.26 2.1-2.9	10.7±0.09 10.5-11.02
	September	Mean± st.dv v.mi-va.max	2243±65.40 2163-2413	3.20±0.63 2.17-4.48	2.09±0.41 1.42-2.93	10.7±0.16 10.57-11.15
	November	Mean± st.dv v.mi-va.max i	2013±104.77 1799-2192	3.97±1.2 2.51-7.31	2.58±0.76 1.64-4.76	10.7±0.08 10.66-11.02

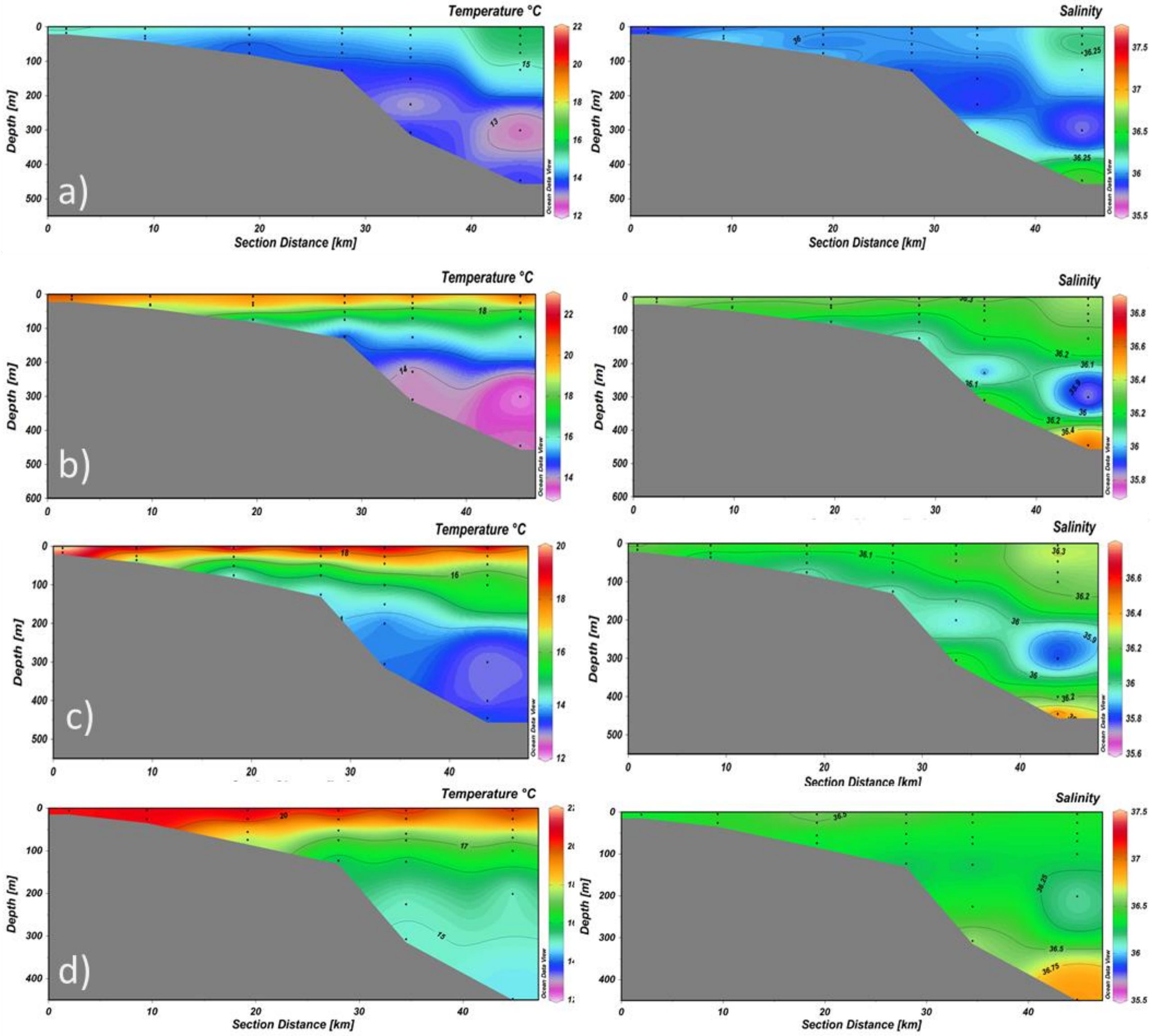


Figure 13. Vertical distribution of temperature and salinity of Guadalquivir transect : a) March, b) June, c) September, d) November. Imagines created by OceanDataView program.

Sancti Petri

In the section of Sancti Petri, both temperature and salinity showed a similar behaviour to what observed in the Guadalquivir transect (Table 2). A temperature change is observed between March and June, with a mean difference of about 3-4 °C, while differences between June and September, and September and November are about 1-2 °C (Table 2).

Figure 14 shows the vertical distribution of temperature and salinity for the Sancti Petri transect. In the surface water, the temperature tended to be higher in June to November (approximately around 22 °C), while in March it was lower. The thermocline occurred at about 100 m depth, then temperature decreased downward with depth during the year. Halocline was detected at about the same depth, extending down to a depth of 300 m, after which salinity started increasing again in deeper waters offshore. Salinity slightly increased offshore in surface water in March and September . In general, a colder water mass was detected between 300 and 400 m depth, being characterized by temperatures close to 13°C in March.

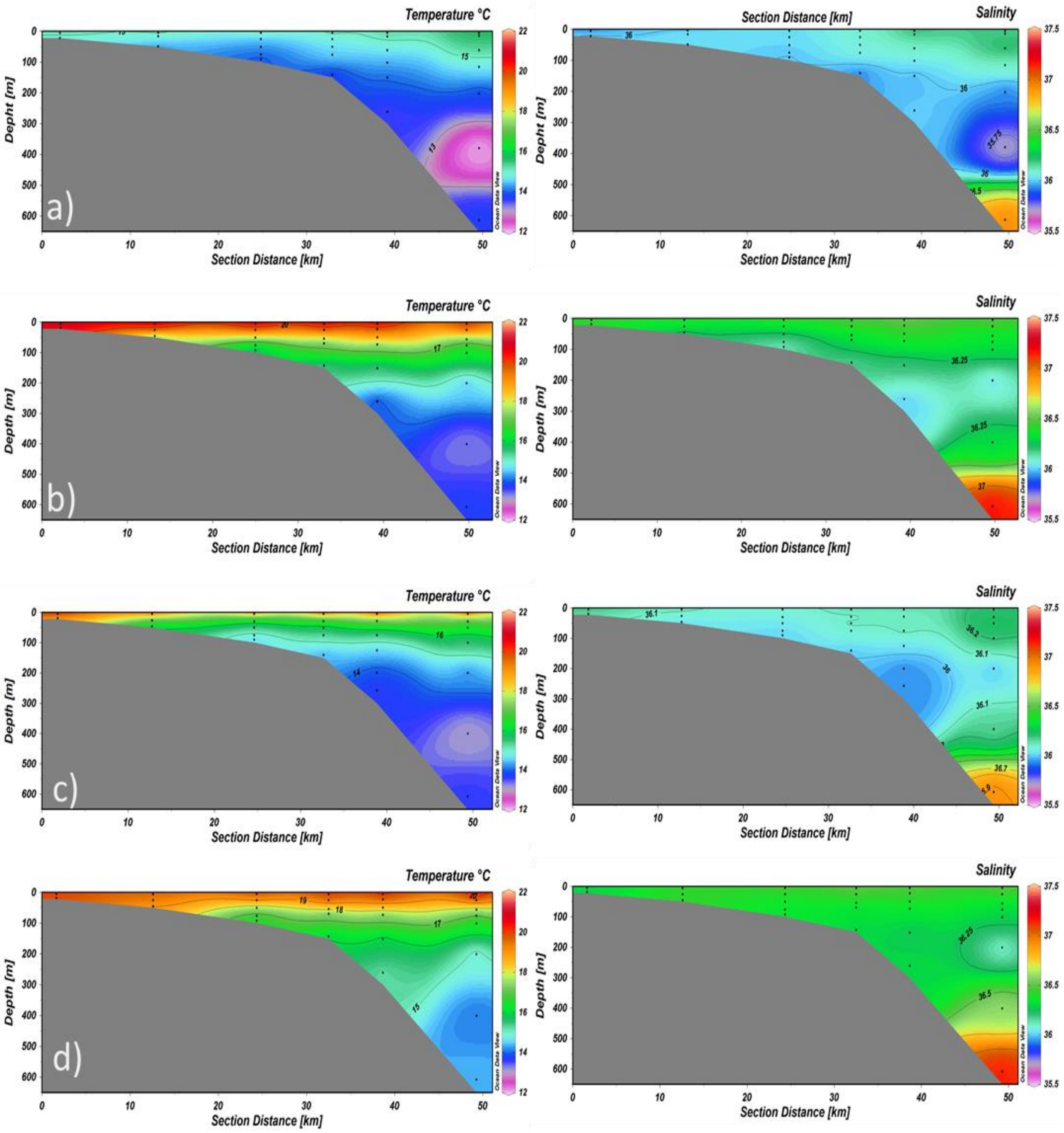


Figure 14.Vertical distribution of salinity and temperature of Sancti Petri transects: a) March, b) June) ,c) September, d) November

Trafalgar

Like the Guadalquivir and the Sancti Petri transects, the Trafalgar section showed higher temperature and salinity values in surface waters in June and September, while the lower temperatures were recorded in September. A sudden change of temperature was observed between March and June with a mean difference of about 3-4 °C, while differences between June and September, and September and November are of about 1-2 °C . Stratification was still absent, in March, along the water column, as indicated by the homogeneity of the temperature and salinity (Table 2).

Values of temperature and salinity recorded in winter were, in any case, statistically different ($p<0.01$) compared to summer and autumn.

Temperature decreased with depth, by becoming more evident at stations located in more depth from 20 km away to coast. The salinity is homogeneous in the superficial area while it increased at 200 m of depth. Contrary to the other sampling times, in which the thermocline was feasible observable at a depth of about 100 m, there were no clear evidences of a sudden temperature decrease during the cruise performed in March. The maximum salinity (37.5 and 38.0) was found in deeper waters offshore, contrary to what observed in stations close to the coast (Figure 15).

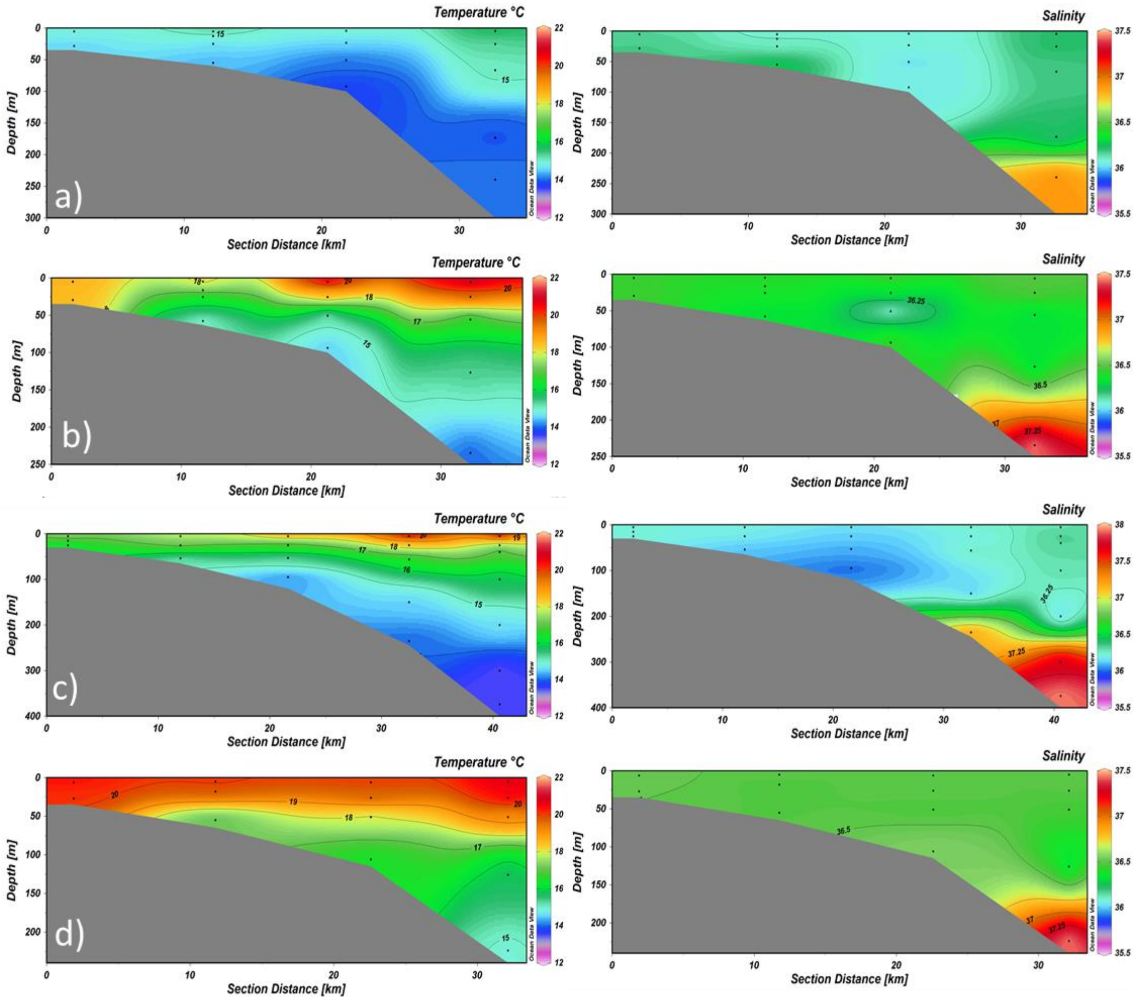


Figure 15. Vertical variation of salinity and temperature of Trafalgar: a) March, b) June), c) September, d) November

4.2. BIOCHEMICAL VARIABLES

Oceanographic [Salinity, S and Temperature, T (°C)] and biochemical variables (carbon system parameters) measured in the Gulf of Cádiz during the four STOCA sampling cruises accomplished in March, June, September and November 2015 (Table 2).

During one year the average variation in alkalinity and dissolved inorganic carbon was not marked, but it maintained almost constant values around 2326 ± 36 there is only a slight difference between average pH values in all three transepts; carbonate saturation showed a comparable behaviour with only minimal differences, while carbonate variability was more marked. Calcium average concentrations calculated by the salinity were constant in all samplings with values around 10.6±0.06.

Guadalquivir

The vertical variation of carbonate system parameters (pH, TA, DIC, CO_3^{2-}, Ω_{Ca}, Ω_{Ar}, Ca^{2+}) in March, June, September and November is depicted in figures 4-5-6-7 and in Table 1. In March, TA concentrations ranged from minimum values of 2350 µM kg^{-1} close to the coast, to maximum values of 2500 µM kg^{-1} in deeper waters of the continental shelf (Figure 16).

The pH values decreased in the deeper waters offshore. The carbonate ion (CO_3^{2-}) is ranging from 150 mmol/kg in deeper waters within the continental shelf to values approaching ~200 µmol/kg in surface waters. DIC values of ~2200 µmol/kg were recorded in surface and deeper waters of the Guadalquivir transect, except at the offshore station between 0 and 100 m depth (2150 µmol/kg).

In general, calcium (Ca^{2+}) displayed quite constant values of ~10.6 mmol kg-1; slight lower values were recorded near the coast (10.4 mmol kg^{-1}). Our results show that all waters in the Guadalquivir transect are strongly saturated with respect to both calcite and aragonite (>> 1). Figure 16 indicates that the saturation state of both minerals increased with distance from coast and decreased with depth. Calcite (Ω_{Ca}) showed a consistent change at ~75 m depth concomitant with a pH change.

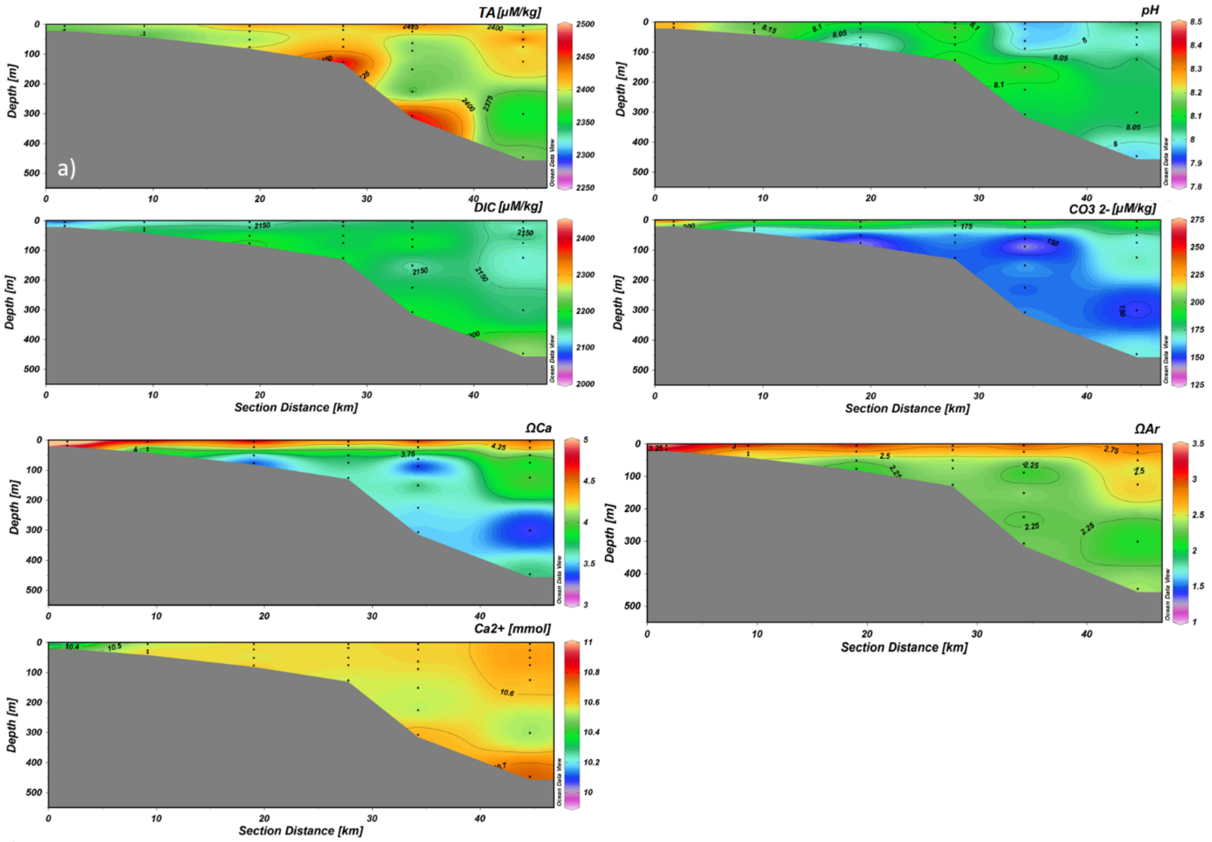


Figure 16. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Guadalquivir conducted in March .(STOCA 5)

Figure 17. In June, TA increased with distance from the coast and decreased with depth. It is possible to see an important decrease at nearly 200 m depth. TA concentrations ranged from minimum values of 2275 µM kg^{-1} along the continental shelf to maximum values of 2350 µM kg^{-1} at the offshore station and in superficial areas. pH increased with the distance from the coast and decreased with the depth. The carbonate behaviour was similar to pH and ranged from minimum values of 120 µmol/kg SW at a depth of 200-300 m to values approaching 220 µmol/kg SW in the surface waters. DIC concentrations ranged from minimum values of about 2000 µmol/kg/SW to maximum of 2150 µmol/kg/SW in surface and deeper waters, respectively.

In general, calcium (Ca^{2+}) displayed constant values in surface waters (~10.4 mmol kg^{-1}); conversely at the offshore station a decrease between 200 and 300 m followed by an increase between 300 and 400 m was observed. Calcite and aragonite saturation state (Ω_{Ca}, Ω_{Ar}) showed a supersaturated condition; both species increased with distance from coast and decreased with depth.

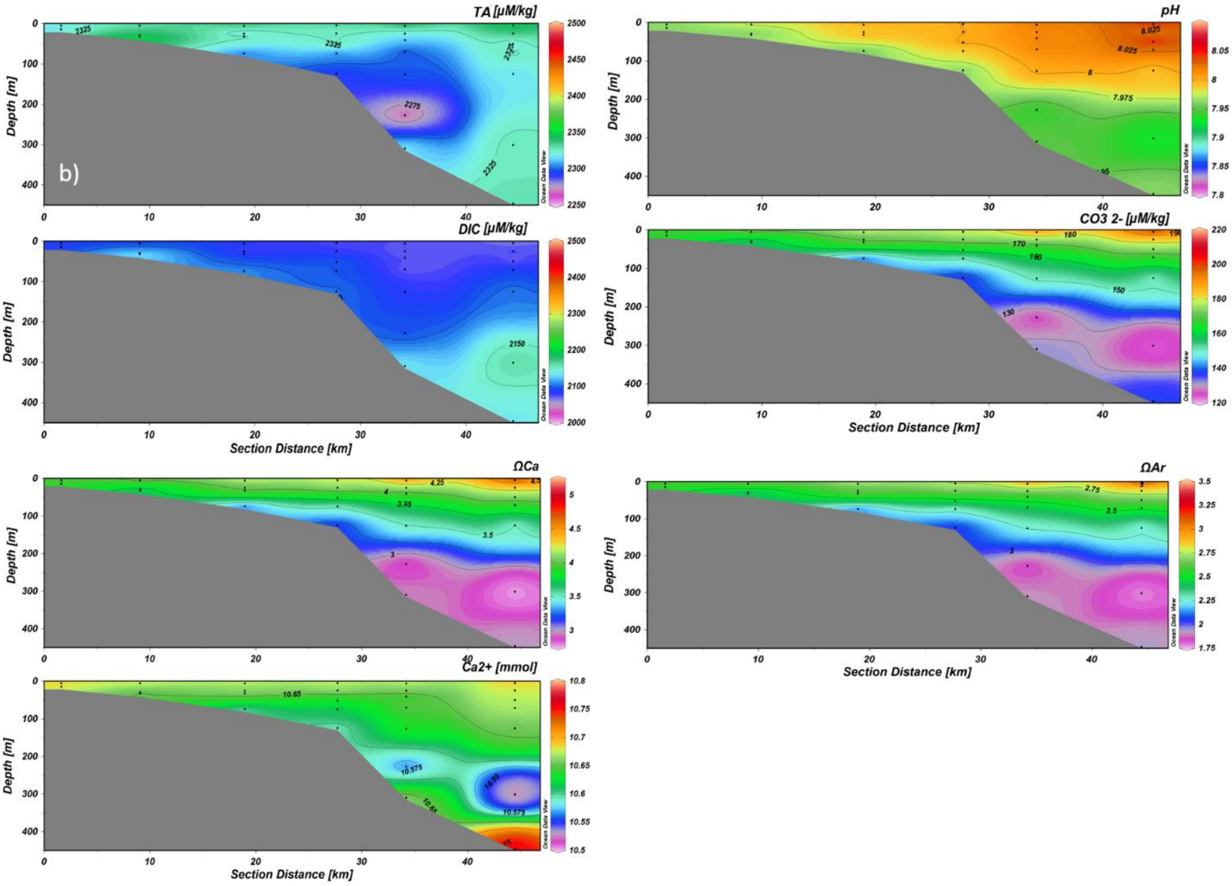


Figure 17. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Guadalquivir conducted in June (STOCA6).

Figure 18. In September, TA had the same behaviour with respect to March increasing offshore and decreasing with depth. TA concentrations ranged from minimum values of 2350 μM kg^{-1} in deeper waters to maximum values of 2450 μM kg^{-1} at the offshore station and in superficial area, mostly along the platform. The pH increased with distance and decreased with the depth with values ranging from 8.05 in surface waters to 7.95 in deeper. The carbonate behaviour showed a trend similar to pH and ranged from minimum values of 120 μmol/kg SW between 200-300 m, to values approaching 220 μmol/kg , in the superficial area. Surface and deeper DIC values were lower than what occurred in March and ranged from 2000 μmol/kg/SW for surface to about 2150 μmol/kg/SW at deeper waters.. Calcium concentrations had constant values in superficial area around 10.6 mmol kg^{-1}. At the last station calcium concentrations decreased between 200 and 300 m and increased between 300 and 400 m. Data related to carbonate saturation of calcite and aragonite showed a supersaturated condition; both species increased with distance and decreased with depth with a gradient steeper depth with degree calcite

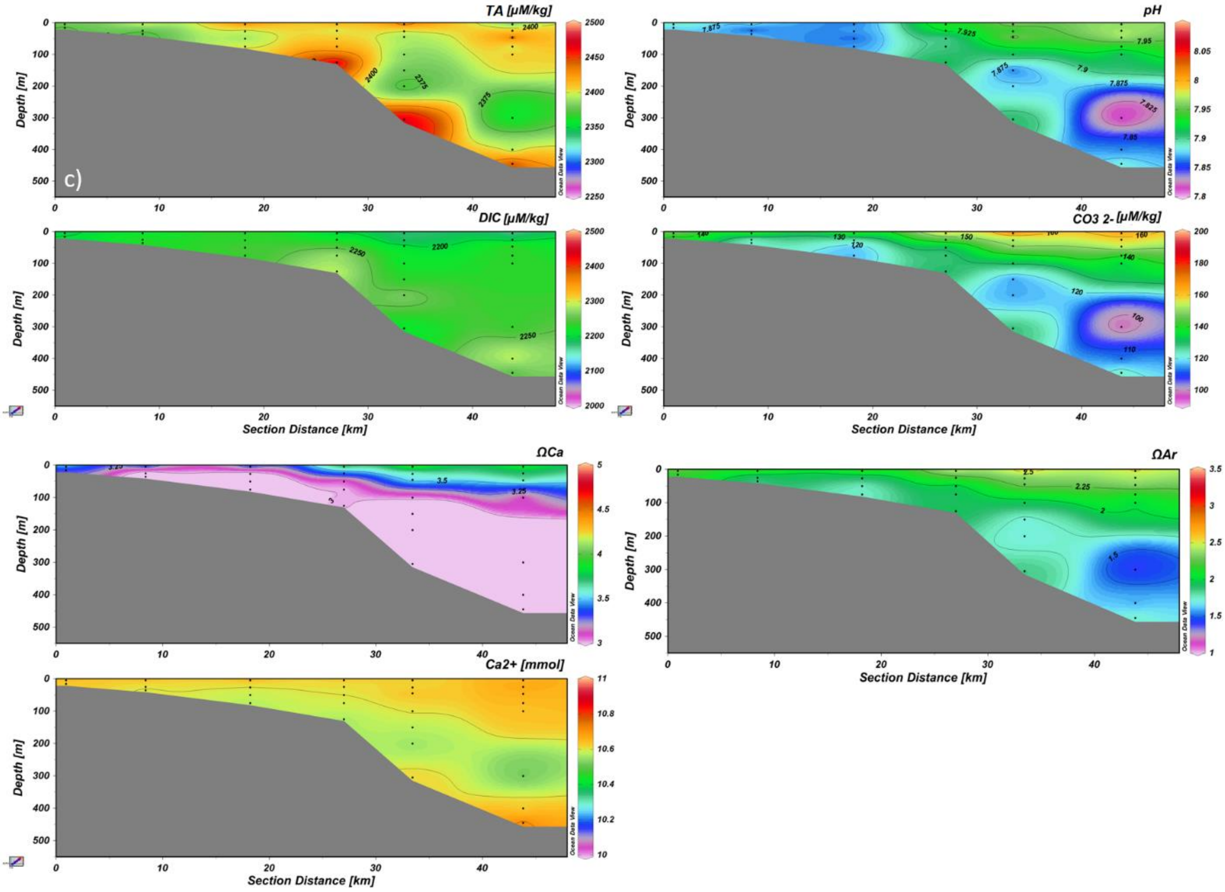


Figure 18.Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Guadalquivir conducted in September .(STOCA7)

Figure 19. In September, TA increasing with the distance to the coast and decreasing with depth. TA concentrations ranged from minimum values of 2250 μM kg^{-1} in the superficial water to maximum values of 2350 μM kg^{-1} close to the coast. The pH increased with distance and decreased with the depth with values ranging from 8.05 in surface waters to 8 in deeper. The carbonate ranged from minimum values of 150 µmol/kg SW between 200-300 m, to values approaching 190 µmol/kg , in the superficial area. Surface and deeper DIC values were lower than what occurred in September and ranged from 2025 µmol/kg/SW for surface to about 2100 µmol/kg/SW at deeper waters.. Calcium concentrations had constant values in superficial area around 10.7 mmol kg^{-1}. At the last station calcium concentrations increased between 300 and 400 m ~11 mmol kg^{-1}. Data related to carbonate saturation of calcite and aragonite showed a supersaturated condition; both species increased with distance and decreased with depth with a gradient steeper depth with degree calcite

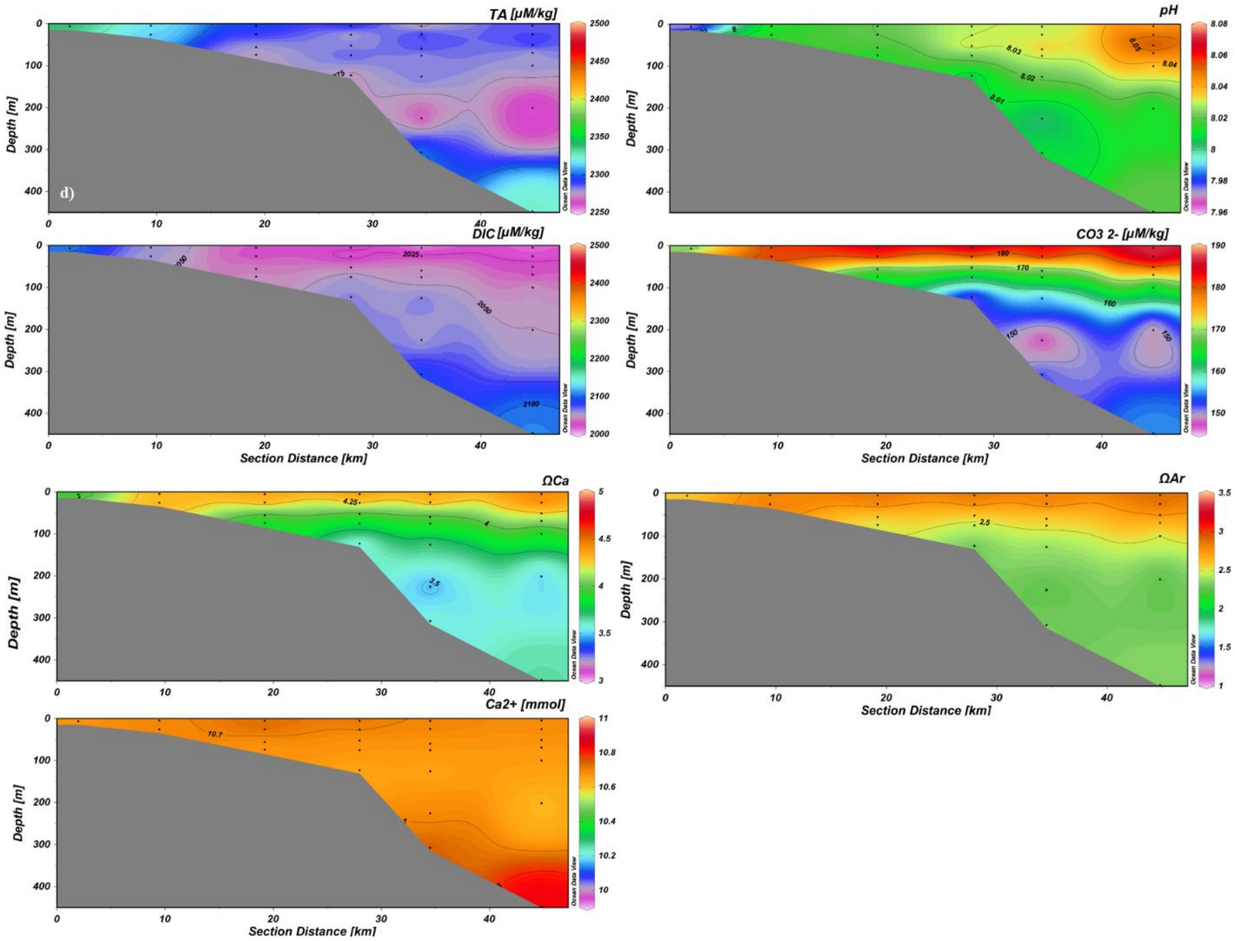


Figure 19. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Guadalquivir conducted in November (STOCA 8)

Sancti Petri

The vertical variation of carbonate system parameters (pH, TA, DIC, CO_3^{2-}, Ω_{Ca}, Ω_{Ar}, Ca^{2+}) in March, June, September and November is depicted in figures 8-9-10-11 and in Table 2. In March, TA increased with the distance to the coast and with depth. TA concentrations ranged from minimum values of 2350 μmol kg^{-1} at the last two stations while in superficial area and in deeper waters to maximum values of 2400 μmol kg^{-1} in proximity of the platform. The pH increased with the distance (values around 8.03) and decreased in the deeper water (values nearly 7.80).The carbonate behaviour was similar to pH and it ranged from minimum values of 150 µmol/kg SW at the offshore stations and values approaching 180 µmol/kg SW in the superficial area, proximally. DIC concentration increased with the distance around 2125 µmol/kg SW and increased with depth about 2225 µmol/kg/SW.. The calcite stratification showed an important change around 75 m depth to the ocean floor. Calcium concentrations (Ca^{2+}) in all sampling had a values around 10.6 mmol kg^{-1} except close to coast where they decreased and at 300 depth and after increased with values around 10.8 mmol kg^{-1}. Data related to carbonate saturation of calcite and aragonite reveal the occurrence of a supersaturated water; in any case, both species increased with distance and decreased with depth (Figure 20).

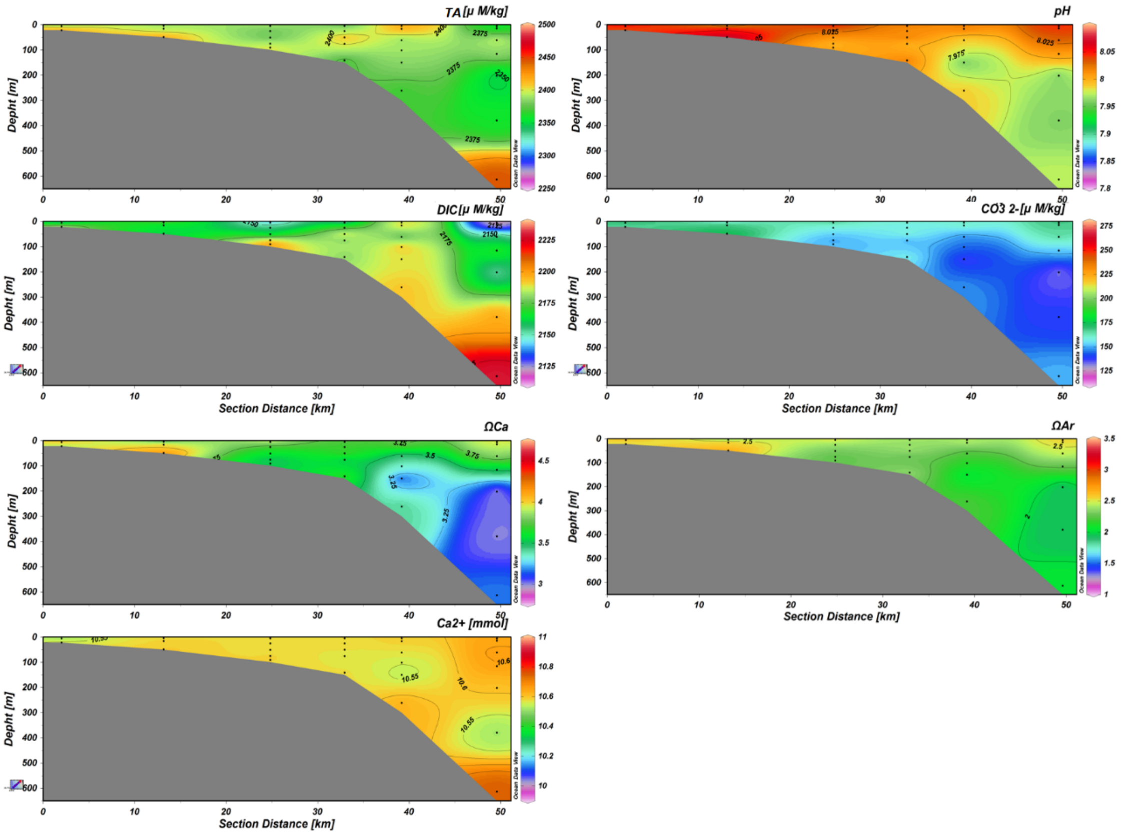


Figure 20. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Sancti Petri conducted in March (STOCA5).

Figure 21. In June, TA increased with the distance to the coast and with depth while between 100 and 300 m decreased. TA concentrations ranged from minimum values of 2300 μM kg^{-1} along the platform and at the last stations while in superficial area and in deeper waters to maximum values of 2400 μM kg^{-1} in proximity of the platform. The pH increased with the distance to the coast (values around 8.1) and decreased between 200 and 450 m (values nearly 8.0) and decreased to the ocean floor. The carbonate behaviour was similar to pH (and similar carbonate behaviour of March) and it ranged from minimum values of 150 µmol/kg SW at the offshore stations and values approaching 190 µmol/kg SW in the superficial area, proximally 175 µmol/kg. DIC concentration increased with the depht around 2100 μmol/kg SW and decreased in the superficial water about 2060 μmol/kg SW. Calcium concentrations in all sampling had a values around 10.6 mmol kg^{-1} increased in the deeper water with values around 10.8 mmol kg^{-1}. Data related to carbonate saturation of calcite and aragonite reveal the occurrence of a supersaturated water; in any case, both species increased with distance and decreased with depth. The calcite stratification showed an important change between 400 to 500 m depth.

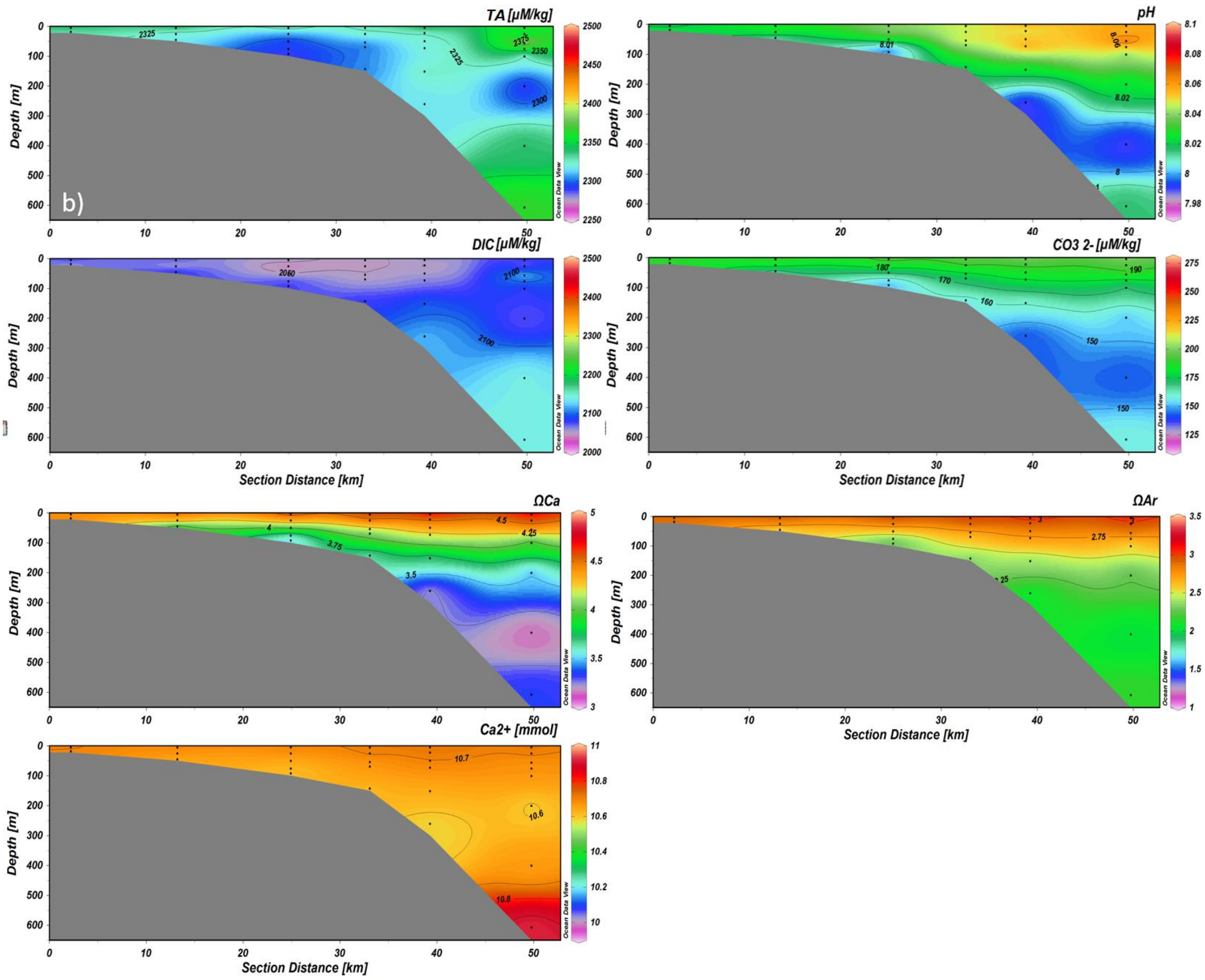


Figure 21. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Sancti Petri conducted in June (STOCA6).

Figure 22. In September, TA increased with the distance to the coast and decreased with depth. It is worthy that to 100 m TA decreased and between 150 and 400 m it is more evident in proximity of the platform. TA concentrations ranged from minimum values of 2250 μmol kg^{-1} along the platform while in superficial area values were around 2400 μM kg^{-1}.The pH values were constant in the superficial water and decreased with the distance (values around 7.9). The carbonate decreased with depth. It ranged from minimum values of 128 μM kg^{-1}from 100 m and values approaching 170 μM kg^{-1}in the superficial area, proximally. DIC concentration decreased in the proximity of the platform between 200 and 300 m around 2100 μmol kg^{-1}. The calcite stratification showed an important change at 100 m depth. Calcium concentrations in all sampling had a values around 10.6 mmol kg^{-1} increased in the deeper water with values around 10.8 mmol kg^{-1} , similar to the trend of Guadalquivir in November and Sancti Petri in June. Data related to carbonate saturation of calcite and aragonite had the same trend in

Guadalquivir transept in March. It reveal the occurrence of a supersaturated water; in any case, both species increased with distance and decreased with depth.

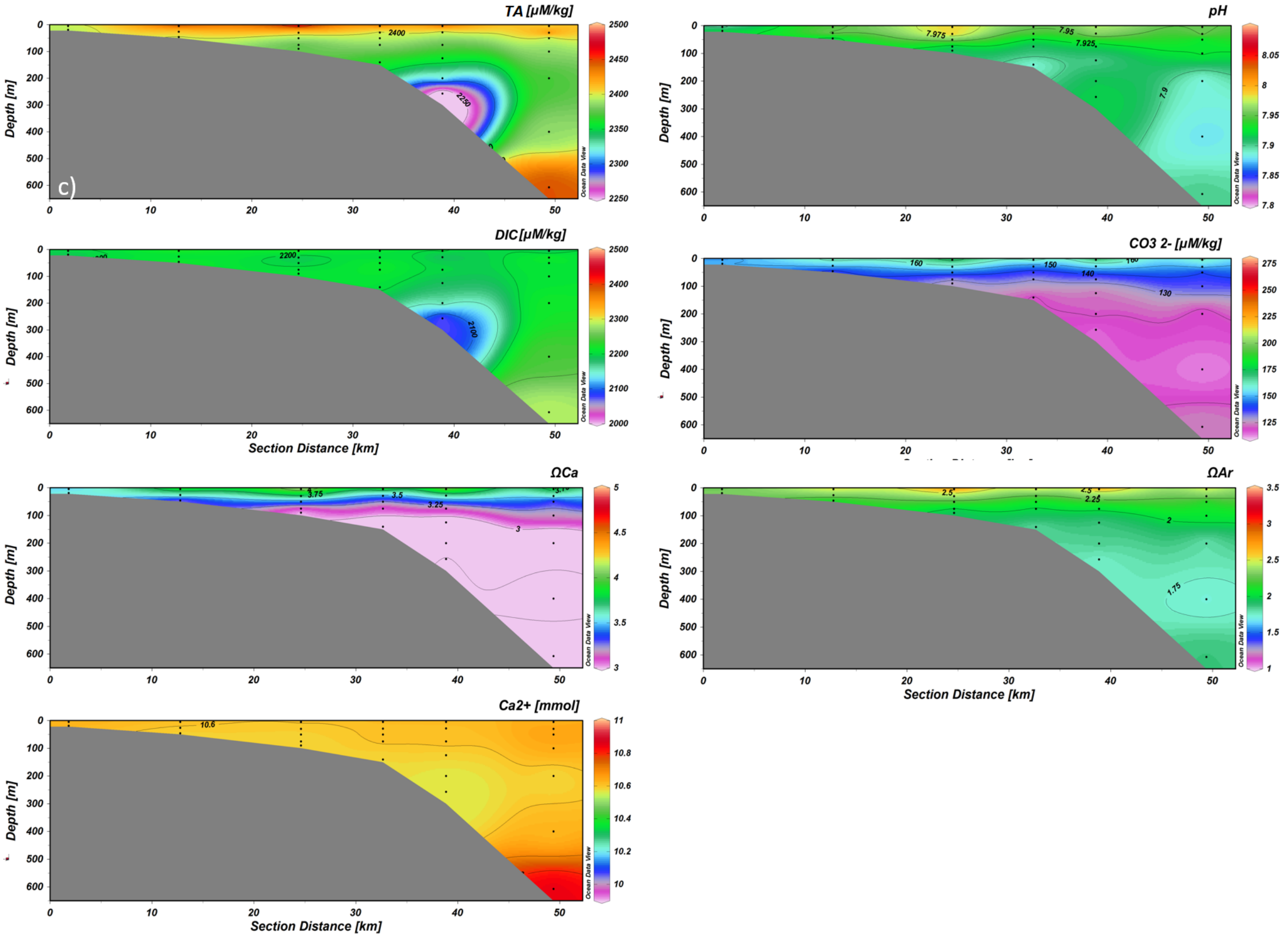


Figure 22. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Sancti Petri conducted in September.(STOCA7)

Figure 23.In November, TA increased to 200m and after increased to the ocean floor. TA concentrations ranged from minimum values of 2250 µmol kg^{-1} in superficial area and in deeper water values were around 2400 µM kg^{-1}.The pH values were constant in the superficial water and decreased with the depth (values around 7.8). The carbonate had the same behaviour of pH. It ranged from minimum values of 100 mmol/ks SW in deeper after and values approaching 200 µmol/kg SW in the superficial area, proximally. DIC decreased with the depth around 2000 µmol/kg SW. The calcite stratification showed an important change at 200 m at the last station. Calcium concentrations in all sampling had a values around 10.6 mmol kg^{-1} increased in the deeper water with values around 10.8 mmol kg^{-1} , similar to the trend of Guadalquivir in November and Sancti Petri in June and September. Data related to carbonate

saturation of calcite and aragonite reveal the occurrence of a supersaturated water; in any case, both species increased with distance and decreased with depth.

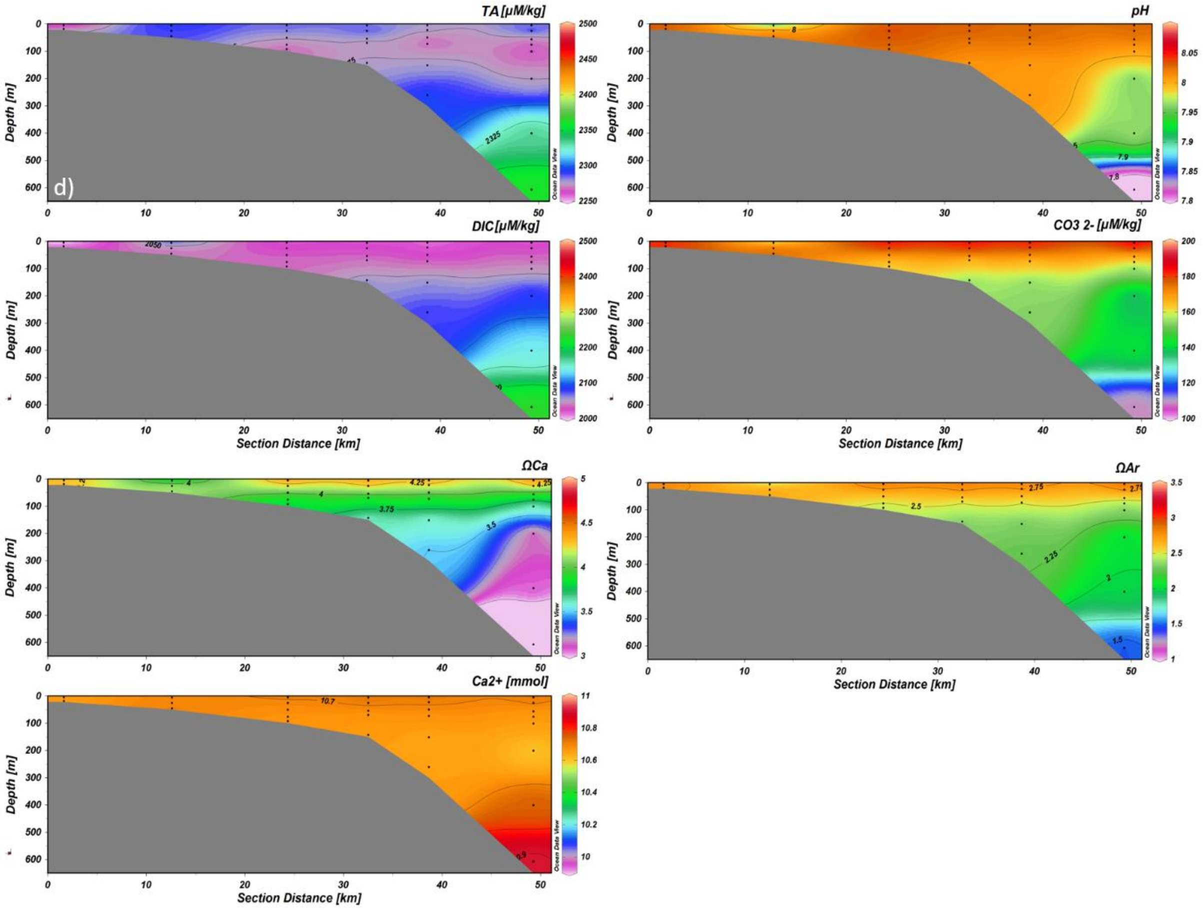


Figure 23. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Sancti Petri conducted in November.(STOCA8)

Trafalgar

The vertical variation of carbonate system parameters (pH, TA, DIC, CO_3^{2-}, Ω_{Ca}, Ω_{Ar}, Ca^{2+}) in March, June, September and November is depicted in figures 12-13-14-15 and in Table 1.

Figure 24. In March, TA concentration increased close to the coast ad with depth and decreased with the distance. TA ranged from minimum values of 2350 μmol kg^{-1} in superficial area and in deeper water values were around 2400 μM kg^{-1}.The pH values were constant in the superficial water and decreased with the depth (values around 7.8) and increased in ocean floor. The carbonate had the same behaviour of pH. It ranged from minimum values of 150 μmol/kg SW between 100 and 200 m and values approaching 170 μmol/kg SW in the superficial area. DIC concentration decreased with the depth around 2000 μmol/kg SW.. The calcite showed an important change at 150 m depth at the last station. Calcium concentrations in all sampling had

a value around 10.6 mmol kg^{-1} increased in the deeper water with values around 10.8 mmol kg^{-1}, similar to the trend of Guadalquivir in November and Sancti Petri in June and September and November. Data related to carbonate saturation of calcite and aragonite reveal the occurrence of a supersaturated water; in any case, both species increased with distance and decreased with depth.

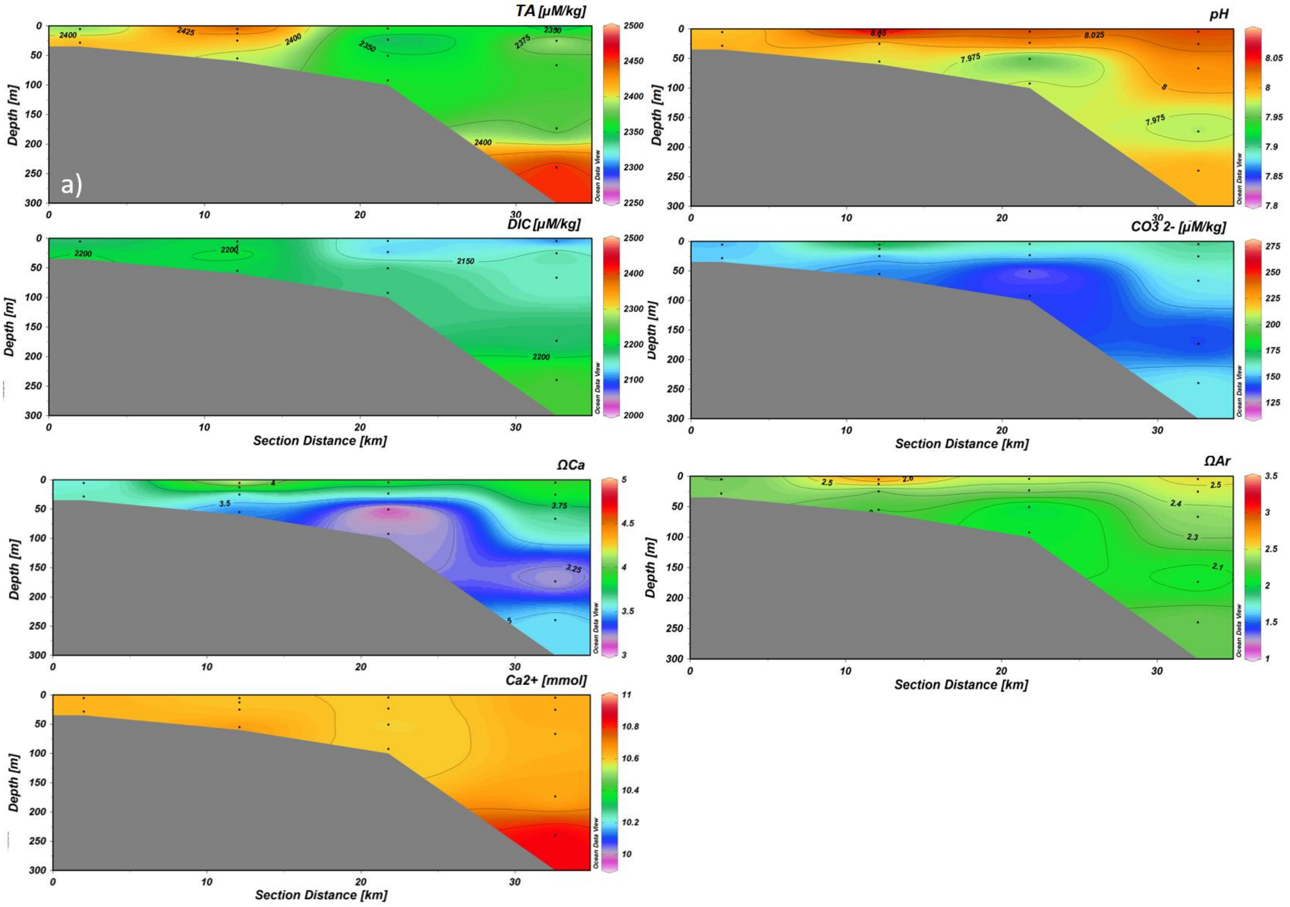


Figure 24. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Trafalgar conducted in March.(STOCA5)

Figure 25. In June, TA increased close to the coast and with depth while decreased with the distance, show the same behaviour in March. TA concentrations ranged from minimum values of 2225 µM kg^{-1} in superficial area and in deeper water values were around 2375 µmol kg^{-1}.The pH values were constant in the superficial water and with the depth (values around 7.8) and only in the proximity the platform decreased lightly at 50 m. The carbonate had the same behaviour of pH. It ranged from minimum values of 150 µmol/ks SW where pH is 8 and values approaching 200 µmol/kg SW in the superficial area. DIC concentration increased with the depth around 2500 µmol/kg SW while in superficial water was around 2050 µmol/kg SW. The calcite showed a similar behaviour than pH and has an important change at 150 m depth at the last station. Calcium concentrations (Ca^{2+}) in all sampling had a values around 10.6 mmol

kg^{-1} increased in the deeper water with values around 10.8 mmol kg^{-1}, similar to the trend of Guadalquivir in November ,Sancti Petri in June and September and November and Trafalgar in March. Carbonate saturation of calcite and aragonite s increased with distance and decreased with depth.

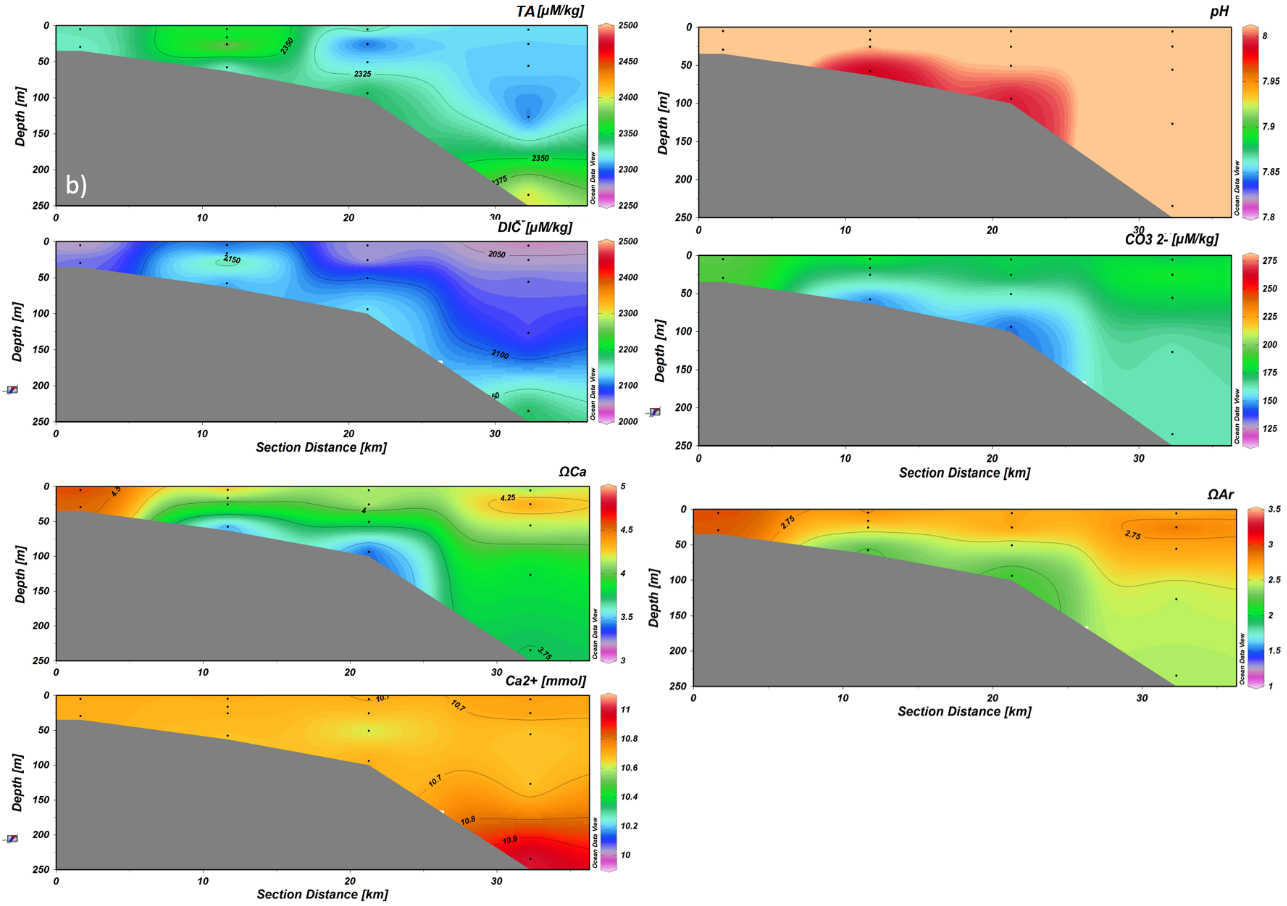


Figure 25. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Trafalgar conducted in June.(STOCA6)

Figure 26. In September, TA increased in the superficial area and in the deeper water with values approaching 2450 and 2425 µmol kg^{-1} respectively while decreased between 100 and 200 m. with values were around 2375 µM kg^{-1}.The pH varies in the first 100 meters after had value until to the bottom (≈8.0). The carbonate had the same behaviour of pH. It ranged from minimum values of 125 µmol/ks SW where pH is ≈8.0 and values approaching 150 µmol/kg SW in the superficial area. DIC concentration increased with the depth around 2400 µmol/kg SW while in superficial water was around 2200 µmol/kg SW. Calcium concentrations in all sampling had a values around 10.6 mmol kg^{-1} increased in the deeper water with values around 11 mmol kg^{-1}, similar to the trend of Guadalquivir in November ,Sancti Petri in June and September and November and Trafalgar in March. Data related to carbonate saturation of

calcite and aragonite reveal the occurrence of a supersaturated water; in any case, both species increased with distance and decreased with depth.

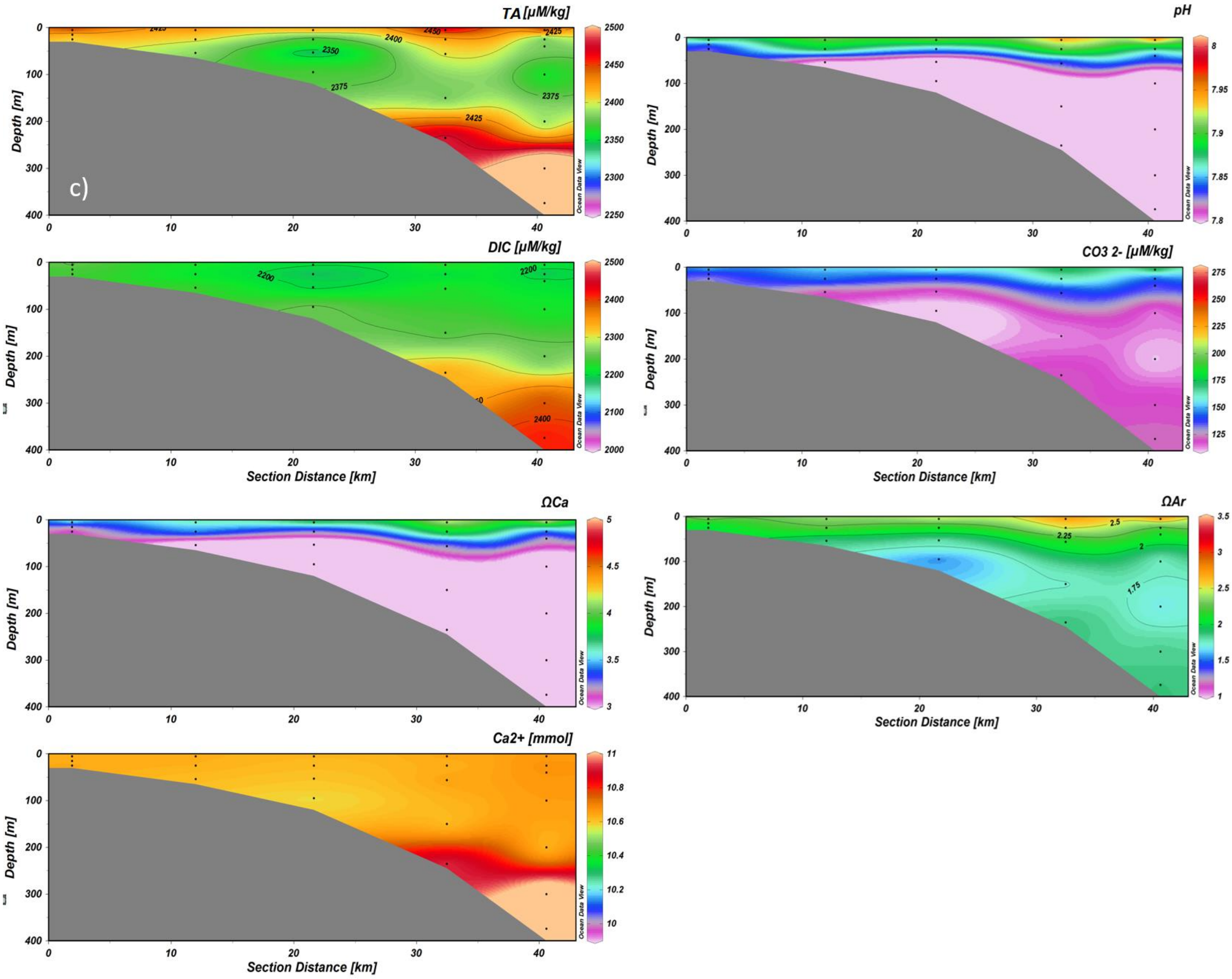


Figure 26. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Trafalgar conducted in September.(STOCA7)

Figure 27. In November, TA increased in the superficial area with values approaching 2300µM kg^{-1} while decreased in the deeper water with values around 2050 µmol kg^{-1}.The pH had a low values near the coast and increased with the distance and in the deeper water with a maximum value of 8.2. The carbonate present a similar behaviour of pH. It ranged from minimum values of 100 µmol/ks SW to maximum 250 µmol/ks SW near to the coast, at offshore values approaching 175 µmol/kg SW and in deeper water around 125 µmol/kg SW. DIC concentration decreased with the distance around 2000 µmol/kg SW in deeper and near to the coast while in offshore superficial water was around 2050 µmol/kg SW.. Calcium concentrations in all sampling had a values around 10.6 mmol kg^{-1} increased in the deeper water with values around 11 mmol kg^{-1}, similar to the trend of Guadalquivir in November

,Sancti Petri in June and September and November and Trafalgar in March. Data related to carbonate saturation of calcite and aragonite reveal the occurrence of a supersaturated water; in any case, both species increased with distance and decreased with depth. The calcite and aragonite stratification showed a similar behaviour of pH and carbonate

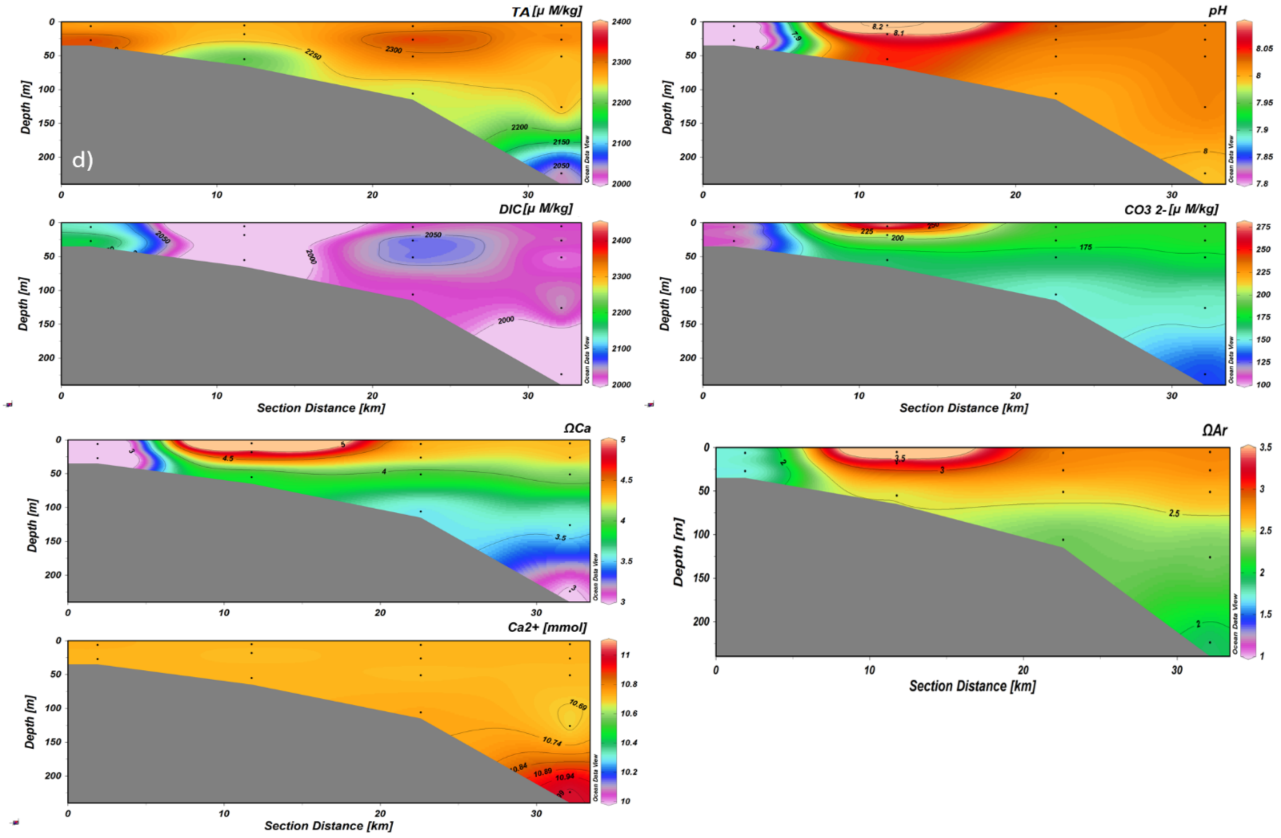


Figure 27. Seasonal variation with distance and with depth of pH, alkalinity, carbonate saturation, carbonate and calcium concentration of Trafalgar conducted in November.(STOCA8)

5. DISCUSSION

5.1 HYDROGRAPHY OF THE GULF OF CÁDIZ AND CARBONATE SYSTEM IN RELATION TO DIFFERENT WATER MASSES IN THE GULF OF CÁDIZ

In order to give a picture of the typical distribution of temperature and salinity in the Gulf of Cádiz, the offshore station within the Guadalquivir transect sampled in June (Figure 28) was taken as a model. In this station there was a very marked thermocline at a depth of 75 m delimiting the photic zone.

In general, within the Guadalquivir and Sancti Petri transects, both temperature and salinity showed a similar behaviour below ~100 m depth, decreasing approximately from 100 to 400 m, and increasing below 500 m depth; conversely, within the Trafalgar's transect, temperature and salinity increased below 175 m depth (Figure 28).

Three water masses were clearly identified in the Gulf of Cádiz according to their different thermohaline properties: the Atlantic Surface Water (SAW), the North Atlantic Central Water (NACW) and the Mediterranean Outflow Water (MOW). The MOW is a strong bottom-current which has been active since the Pliocene, when the Mediterranean basin was flooded after the Messinian salinity crisis (Mougenot and Vanney 1982): it is a strong, warm (13 °C), and saline (38) current, which flows out of the Mediterranean below the Atlantic waters (Ambar et al. 1976; Ambar 1983). It reaches core velocities > 2.5 m s^{-1} along the continental slope in front of Gibraltar, and still flows at 0.2 m s^{-1} off Cape St. Vincent, in Portugal (Meincke et al. 1975; Johnson et al. 2002).

Analysis of mixing water is conducted using three end members, as only salinity and temperature will be used as conservative variables (Pérez et al., 1998). Each water end member is defined by a single and fixed temperature and salinity while a water mass is conventionally characterized by the mixing of two end members, thus showing a rather fixed T-S relationship.

Sigma-t, is density of seawater calculated with in situ salinity and temperature, but pressure equal to zero, rather than the in situ pressure and 1000 kg/m3 is subtracted.

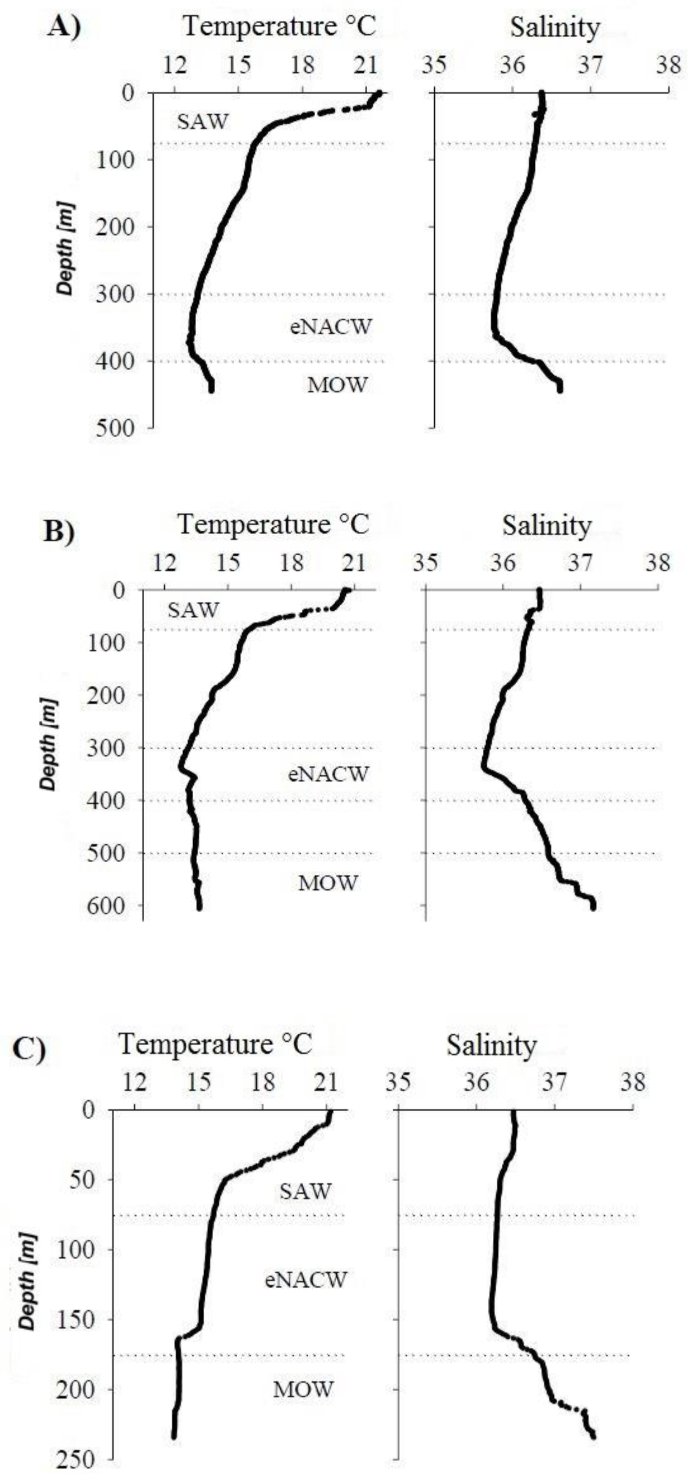
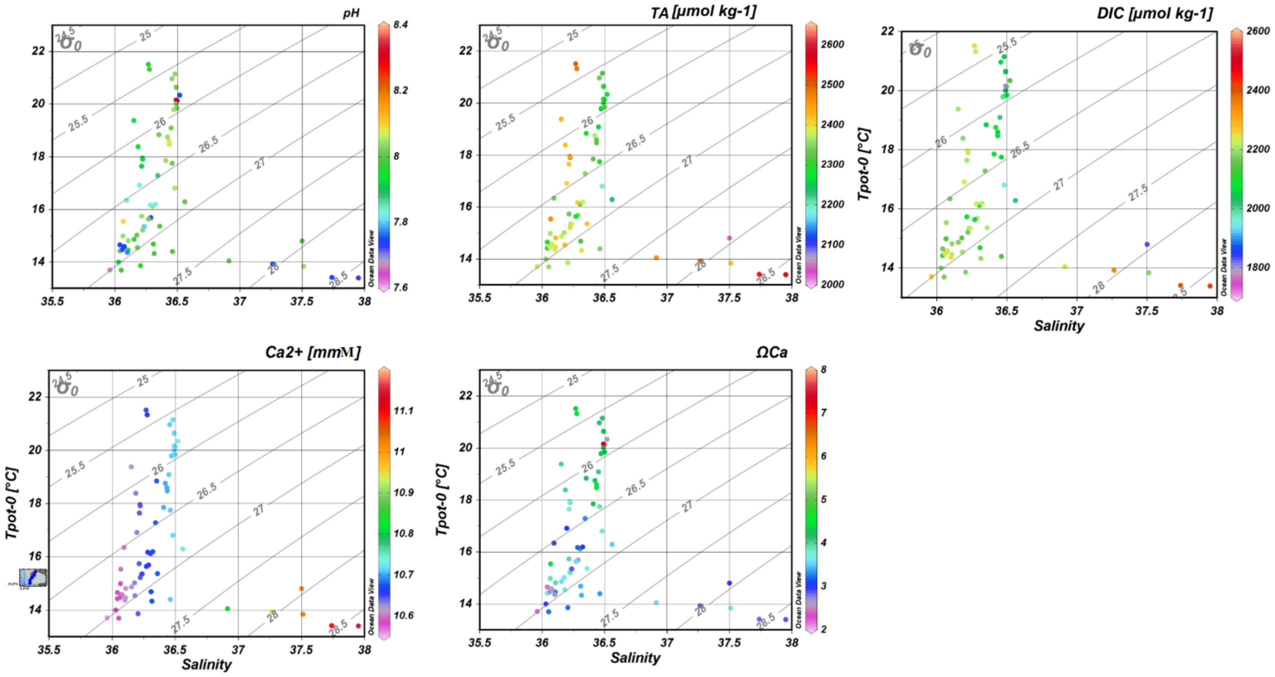


Figure 28 Vertical profiles of temperature and salinity to the deepest station on the section : A) Guadalquivir , B) Sancti Petri and C) Trafalgar, in June 2015. Depth-limits of the different water bodies (SAW: Surface Water Atlantic ; ENACW : Eastern North Atlantic Central Water ; MOW : Mediterranean Outflow Water) were also marked. Figures were plotted by the OCV program.

The Temperature-Salinity diagrams in Figure 29 shows the different three masses of water through the three sampling transects within the Gulf of Cádiz. SAW is distributed between 1 and 100 meters of depth. According to Criado-Aldenueva (2004), Huertas et al (2009) SAW has a characteristic temperature of ~16 °C, salinity of ~ 36.4, and sigma-t (σt) ≤ to 26.7 (Figure 30,Figure 31,Figure 32). The lower salinity detected in the Guadalquivir, Sancti Petri and Trafalgar suggests there is an influence of the Guadalquivir River discharge on the SAW within the Gulf of Cádiz. This is in agreement with previous observations by Van Geen et al. (1988, 1991), González- Dávila et al. (2003) and Criado-Aldeanueva et al.(2004).

The Eastern North Atlantic Central Water (ENACW) is detected in all three transects. The typical temperature range of ENACW is between 12°C and 16 ºC; salinity between 35.7 and 36.25 at depth between 300 and 400 m (**Errore. L'origine riferimento non è stata trovata.**,**Errore. L'origine riferimento non è stata trovata.**, Figure 32.). Generally ENACW shows a linear behaviour in the TS diagram to the 26,6 ≥ σt ≤ 27,3 values, in accordance with the findings of Knoll et al., 1999; Ambar et al., 2002. The coldest and less saline ENACW overlays the MOW and underlies NASW, producing a large thermohaline gradient (González- Dávila et al. (2003).



Mediterranean water (MOW) is characterized by high salinity (S > 36.4) and temperature (T > 12 ° C) values, increasing in density close to the bottom layer. In the TS diagram , this water mass shows two main peaks corresponding to the upper and lower cores with different densities (σ_t = 27.5 and σ_t = 27.8, respectively; Ambar and Howe, 1979a). The depth that appears MOW varies with distance from shore. In the most distal station, MOW is located at about 400 m depth in the Guadalquivir, at 500 m depth in the Sancti Petri , and at 175 m depth in Trafalgar transects. Similar results were obtained by Aït- Ameur et al. (2006). The authors reported that at the entrance of the Gibraltar Strait, in the eastern part of the E–W section, the Mediterranean Water (MW) between 300 and 400m depth is marked by maxima in salinity (> 38) and temperature (around 13 °C). This MW was earlier described by Ambar and Howe (1979), Ambar et al. (2002), Santana-Casiano et al. (2002), Johnson et al. (2002), and González-Dávila et al. (2003). In addition , Ambar and Howe (1979a, 1979b) observed that ‘‘the T-S distribution definitely reveals the initial stage in the subdivision of the MW into two cores. The lower main core (Ml) can be identified characteristically by the maximum salinity of 37.42 at a depth of 756 m (T = 13.16°C, σ_0= 28.28), whereas the upper core (MU) appears between 500 and 650 m, with a temperature as high as 13.72 °C at 650 m (S = 37.07, σ_0 = 27.88).

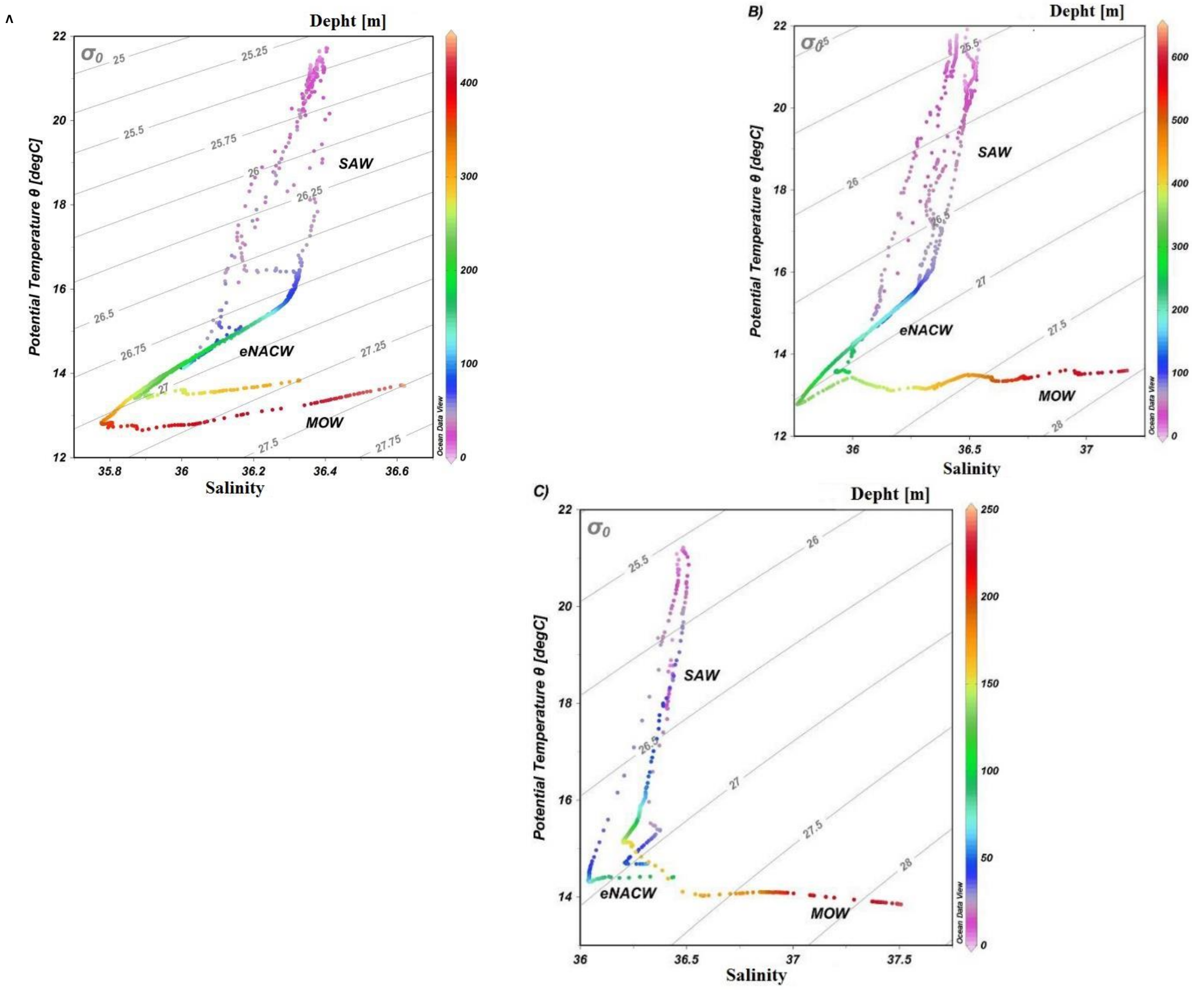


Figure 29. TS diagrams for different transects : A) Guadalquivir , B) and C Sancti Petri) Trafalgar in June 2015 . (SAW : Surface Water Atlantic ; ENACW : Eastern North Atlantic Central Water ; MOW : Mediterranean Water) . Figures plotted with the OCV program.

With reference to the Sancti Petri area, Lopez (2015) also detected the SAW and ENACW at 100 m and 250 m depth, respectively. SAW is influenced by solar heating and for this reason that is warmer and more saline, and hence flows in surface (Criado - Aldenueva , 2004). Below 400 m depth is detected the presence of a water mass of warm, saline water running along the continental slope corresponding to the MOW.

Carbonate System in Relation to Different Water Masses in the Gulf of Cádiz

The different water masses described above and defined by their thermohaline properties are also characterized by specific carbonate properties .(Figure 30,Figure 31,Figure 32) and chemical properties. Next we will describe their respective distribution along the three transects sampled during the cruises.

DIC, TA, pH and calcite saturation along the three sections sampled within the Gulf of Cádiz show a vertical gradient. TA and DIC increase with depth whereas O_2 decreases with depth in agreement with the findings of Aït-Ameur N., 2006. In addition, pH follows a pattern of decrease with depth, exhibiting a range of variation comprised between 8.037 and 7.875 in surface waters and above the seafloor, respectively, throughout the whole longitudinal section. The same behaviour has been detected by Huertas et al (2009) in the Gulf of Cádiz.

The distribution of both TA and DIC presents an evident variability in the water column along the Guadalquivir section due to characteristics of the calcareous soils of the Guadalquivir Valley that discharge in the tidal area of Gulf of Cádiz (Gonzalez- Garcìa, F et al.,1960). The SAW and ENACW, with low salinity, present high AT (>2350 µmol kg^{-1}) and DIC (>2250 µmol kg $^{-1}$). These high concentrations have been observed previously by Gonzalez-Davìla, et al. (2003) and they were attributed to the Guadalquivir River discharge. The river influence is traced by a relatively low pH value (~7.970). In the Guadalquivir section, the MOW is characterized by noticeable variability. Values of TA (>2300 µmol kg^{-1}) and DIC (>2250 µmol kg -1) at the bottom of the valley were detected, as reported by González-Dávila (2003) (Figure 30).

The distribution of both AT and DIC presents a evident variability also in the water column along to the Sancti Petri section due to influence of Guadalquivir River discharge and San Pedro River discharge. The SAW and ENACW present AT concentrations >2350 µmol kg^{-1}and DIC concentrations >2200 µmol kg $^{-1}$, as reports Gonzalez-Davìla, et al. (2003) and de la Paz (2007). The MOW is characterized by TA concentrations >2350 µmol kg^{-1} and DIC concentrations >2100 µmol kg $^{-1}$ (**Errore. L'origine riferimento non è stata trovata.**)

The distribution of both AT and DIC presents a clear variability also in the water column along the Trafalgar section due to influence of Guadalquivir river discharge. The SAW presents AT concentrations >2350 µmol kg-1 and DIC concentrations >2250 µmol kg^{-1} as reports Gonzalez- Davìla, et al. (2003).The ENACW presents TA (>2350 µmol kg-1) and DIC (>2200 µmol kg -1). The influence of river discharge on TA and DIC distributions was also discussed for the Mediterranean Sea by Pérez et al.(1986), Copin-Montégut (1993), and Huertas et al. (2006). Similar values of AT and DIC (~2360 and 2130 µmol kg-1, respectively) were detected at the Trafalgar transect, by Susana Flecha (2012).

The ENACW depth is characterized by higher and greatly variable pH values (ranging from 7.895 to 8.037), a circumstance possibly related to the biological processes taking place into the photic zone (as described in Macìas et al., 2008), and to seasonal atmospheric variations that affect both mixing and evaporation. The shallow core of MOW, which restricts the penetration of NACW to the slope, gives a large thermohaline differentiation, and also a significant gradient in the carbonate system. The MOW is characterized by the highest TA and DIC concentrations (> 2400 µmol kg $^{-1}$ and > 2300 µmol kg^{-1} respectively). The same concentrations along the transect are in agreement with those depicted in the same water mass by Aït-Ameur, (2006) and Huertas et al. (2009). The correlation between salinity and TA (TA=68.11 S–71.163, r^2=0:81) indicates that TA variability in the Gulf of Cádiz is mainly controlled by the mixing of Atlantic, Mediterranean, and riverine waters (Aït-Ameur, 2006) (Figure 32)

TA and DIC measurements are generally in good agreement with those of previous works performed in the Gibraltar Strait (Santana-Casiano et al., 2002; Dafner et al., 2001), the Gulf of Cádiz (González-Dávila et al., 2003), the Alboran Sea (Copin-Montégut, 1993), and the Canary Islands region (Pérez et al., 2001).

According to Ambar and Howe (1979), Ambar et al. (2002), Santana-Casiano et al. (2002), Johnson et al. (2002), González-Dávila et al. (2003) and Huertas et al (2009), in the Trafalgar section a pH minimum (7.849) is observed in highly saline deep waters (S>38), reflecting the active remineralization of organic matter that takes place in the Mediterranean Sea (Copin-Montégut, 1993; Dafner et al., 2001b; Béthoux et al., 2005).

To our knowledge no data for the carbonate saturation state in the Gulf of Cádiz have been found, but results obtained were compared with previous works conducted in similar areas as continental shelves or coastal areas. We have chosen to study the behaviour of calcite saturation state because is a good thermodynamic indicator of inorganic carbon chemistry changes providing a tool to predict the impact of increasing seawater CO_2 levels on the stability of the calcite mineral phase. For example, in the Pacific Ocean, an average 0.34% yr^{-1} decrease in the saturation state of surface seawater with respect to aragonite and calcite has been observed over a 14-year period. This has caused an upward migration of the aragonite and calcite saturation horizons toward the ocean surface on the order of 1–2 m yr^{-1}. These changes are the result of the uptake of anthropogenic CO_2 by the oceans, as well as other smaller scale regional changes in circulation over decadal time scales (Feely et al.,2012). Furthermore, there are decreases as large as 0.5-1 going towards the shore along the East coast of United States that are caused by combination of riverine outflow, vertical mixing and excess remineralization resulting from nearshore eutrophication (Wanninkhof et al., 2015).

In the upper ocean, the $\Omega_{ca\ and}$ Ω_{ar} are affected by processes such air-sea CO_2 exchange, biological production and respiration, physical mixing, freshwater input and changes in temperature (Chierici M. et al., 2009).

Surface seawaters, in the three transects of the Gulf of Cádiz, are supersaturated with respect to biogenic calcite (>> 1). At SAW depth(0 and 100 m), along the Guadalquivir transect , Ω_{ca} presents values between 4.5 and 5; along the Sancti Petri transect between 4.5 and 5, and along the Trafalgar transect between 4 and 5. Instead at the NACW depth (300 and 400m), along the Guadalquivir , Sancti Petri and Trafalgar transects, Ω_{ca} shows values ranging between 3 and 4. The MOW is characterized by values Ω_{ca} between 3 and 4 along the Guadalquivir transect, and Ω_{ca} values ranging between 2.5 and 3 along to the Sancti Petri and Trafalgar transects (**Errore. L'origine riferimento non è stata trovata.**,**Errore. L'origine riferimento** non è stata trovata.,

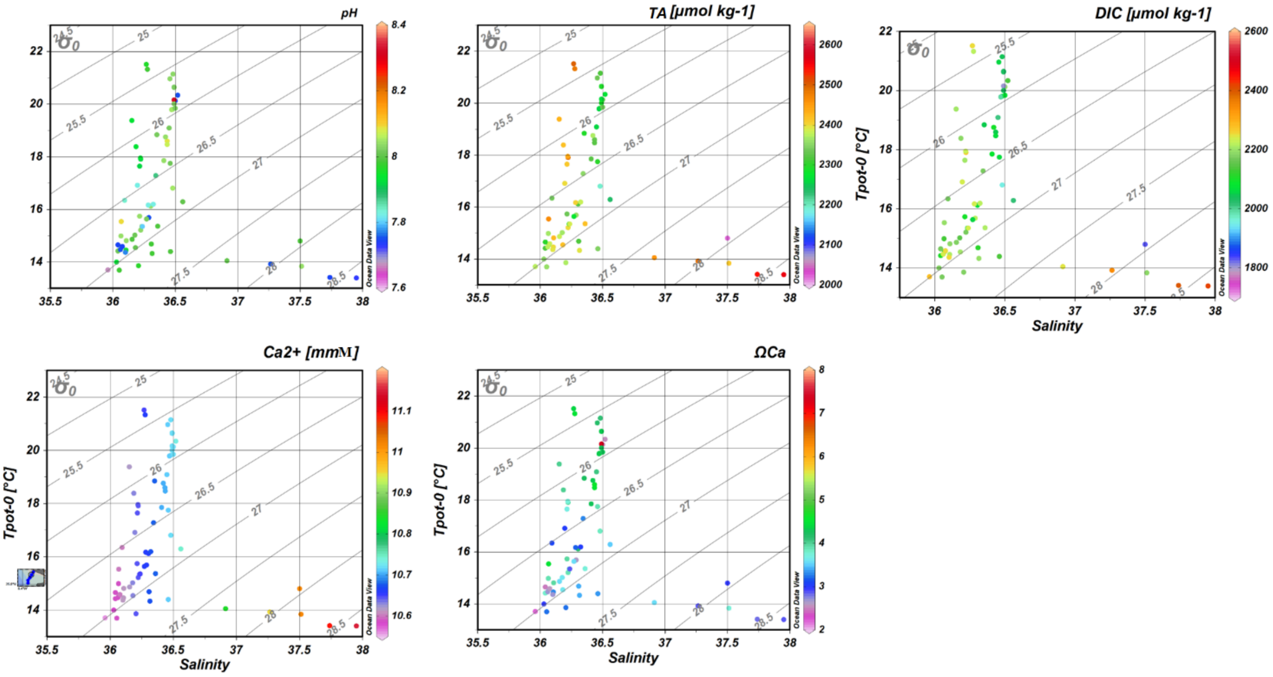


Figure 32.). Although there are no data on calcite saturation state for this area, we can refer to values reported by Susan M. Libes (2009) in which she describes the general behaviour of calcite saturation state in the Atlantic ocean. This work reports that all surface seawaters are presently supersaturated with respect to biogenic calcite ranging from 2.5 at high latitude and 6.0 at low latitudes. The elevated supersaturation at low latitude reflects higher $[CO_3^{2-}]$ due to the effect of temperature on CO_2 solubility and the K (constant dissociation) for $[HCO_3^-]$ and density stratification. Although surface waters are supersaturated with respect to calcium carbonate. It would be interesting to study the temporal evolution of saturation calcite state in tandem with the ocean acidification. A significant fraction of the CO_2 injected into the atmosphere as a results of fossil burning (that will dissolve in the surface ocean) might cause a decline in seawater pH (Caldeira et al.,2005) and Ω and to lead the ocean acidification. However, it should be noted that aragonite and calcite saturation conditions in coastal waters are more difficult to predict over the long-term because of higher degree of complexity of the physical and biogeochemical processes that cause enhanced localized spatial and temporal variability (Andersson et al., 2005, 2006; Feely et al., 2008; Bates et al., 2010; Shamberger et al., 2011).

According to T–S distributions, shelf waters of this coastal sector of the Gulf of Cádiz displayed considerable seasonal variations over an annual cycle, which seemed to depend mainly on the river discharge and meteorological conditions (wind regime and local temperature variations). Thus, the water mass present in the area can be identified as a modification of the NACW due to the influence of local climate fluctuations and fluvial inputs;

waters that have been classified previously as shelf waters (Criado-Aldeanueva et al., 2006). The discussion of results has been argued according to influence biological activity on chemical variables and the carbonate system. The inorganic carbon chemistry was affected by the interaction of the mineralization of organic material and different water masses.

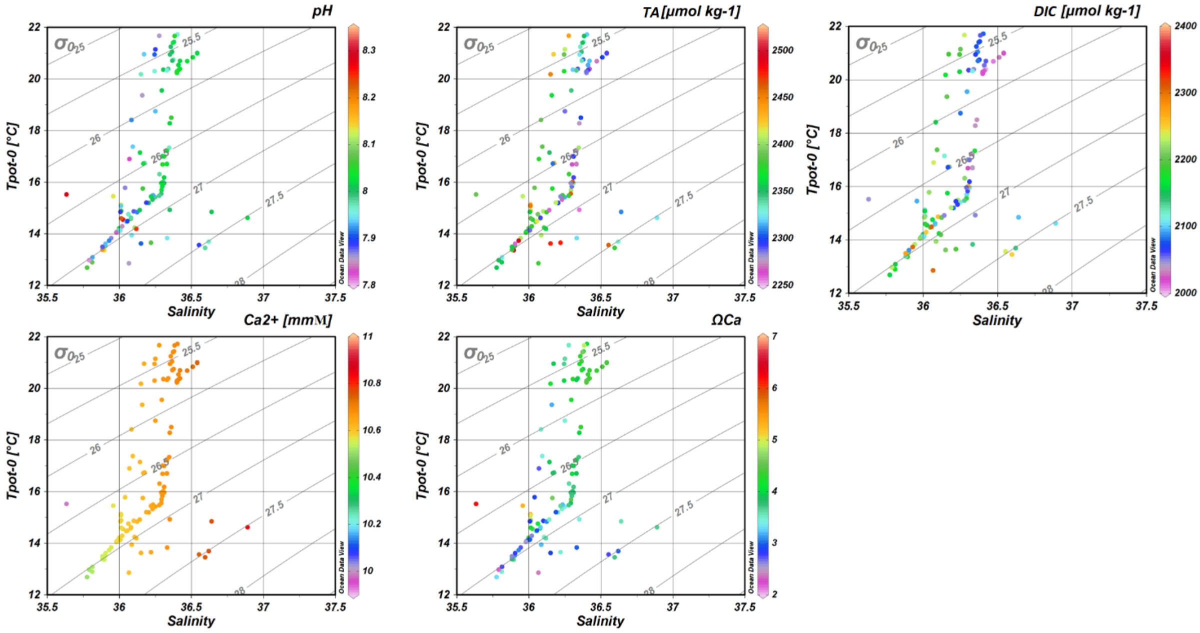


Figure 30. Carbonate system in relation to different water masses at the Guadalquivir station

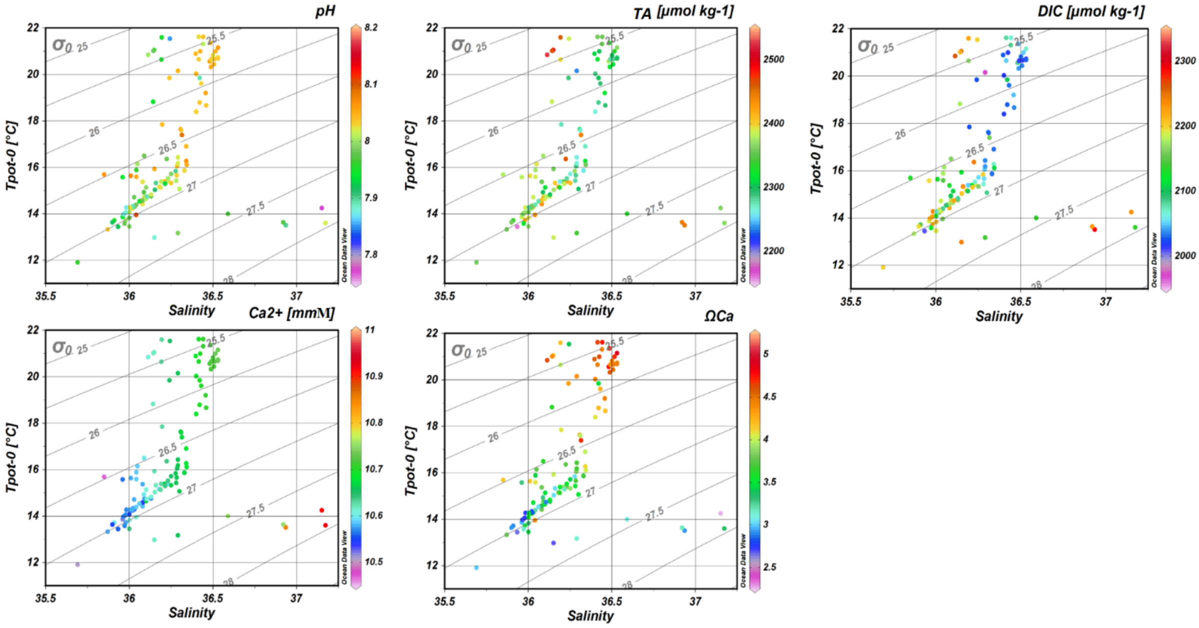


Figure 31. Carbonate system in relation to different water masses at the Sancti Petri station.

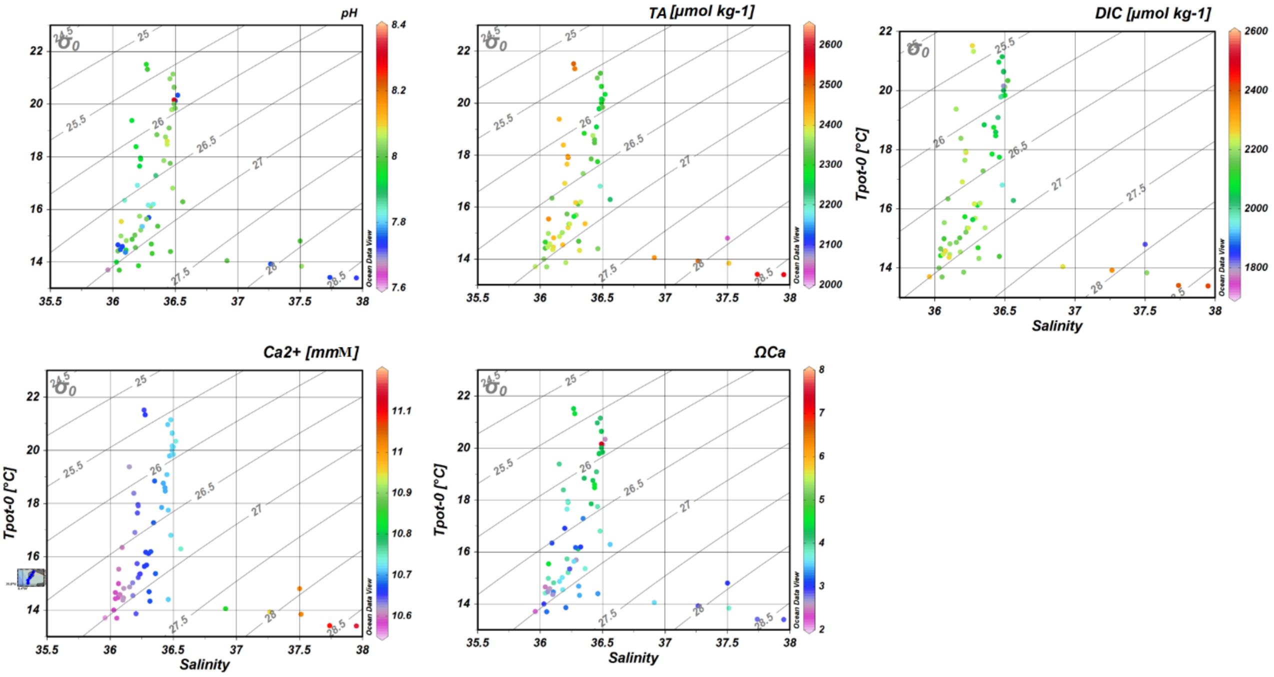


Figure 32. Carbonate system in relation to different water masses at the Trafalgar station.

5.2 SEASONAL VARIATION OF TA, DIC, PH AND Ω_{CA}

Previous studies reporting concentration of nutrients and chlorophyll in the Gulf of Cadiz (de la Paz et al., 2007; Macìas et al.,2009), indicate that it is possible to indirectly estimate the process of photosynthesis using values of DIC, AT, pH and Ω_{Ca}, referred to surface layers at depths between 0 and 50 m. DIC, AT, pH and Ω_{Ca} showed seasonal variations that may be a consequence of the different hydrodynamic regimes that characterise the Gulf of Cadiz and of coastal input of nutrients.

When photosynthesis was important in surface layers consequently DIC and TA decreased, and pH and ΩCa increased (Figure 6). Primary production processes removed CO_2 and hence determined the shift toward less acidic conditions that are well evidenced of the increase of both pH and Ω_{Ca} values. In winter and early spring (November- March), high values in the Guadalquivir Estuary and Cadiz Bay extended along and offshore from the coastline to form a plume (>1.3 mW/cm^2 µm sr) (Caballero et al., 2014) In March, TA and DIC showed the highest concentrations comparing to the other months.

In addition, the calcite and aragonite saturation solubility product and therefore the carbonate dissolution level increased when temperature decreased (Mucci, 1983). This explains why the highest TA concentration in the river endmember occured in winter, when the average temperature was 15 °C.

TA, DIC, pH and ΩCa trends in the Guadalquivir transect showed in March a clear gradient which decreased from the coastline towards offshore (Figure 33). Some authors have pointed out that during March the river has a great water discharge (Navarro et al., 2006). The stations of this transect which is nearest to coast presented high values of pH and ΩCa, probably as a consequence of enhanced photosynthesis and calcareous material from river inputs, respectively. The other two transect of Sancti Petri and Trafalgar did not present a clear trend on pH and ΩCa distribution because of the high distance from the Guadalquivir Estuary and the turbulence of the Strait of Gibraltar.

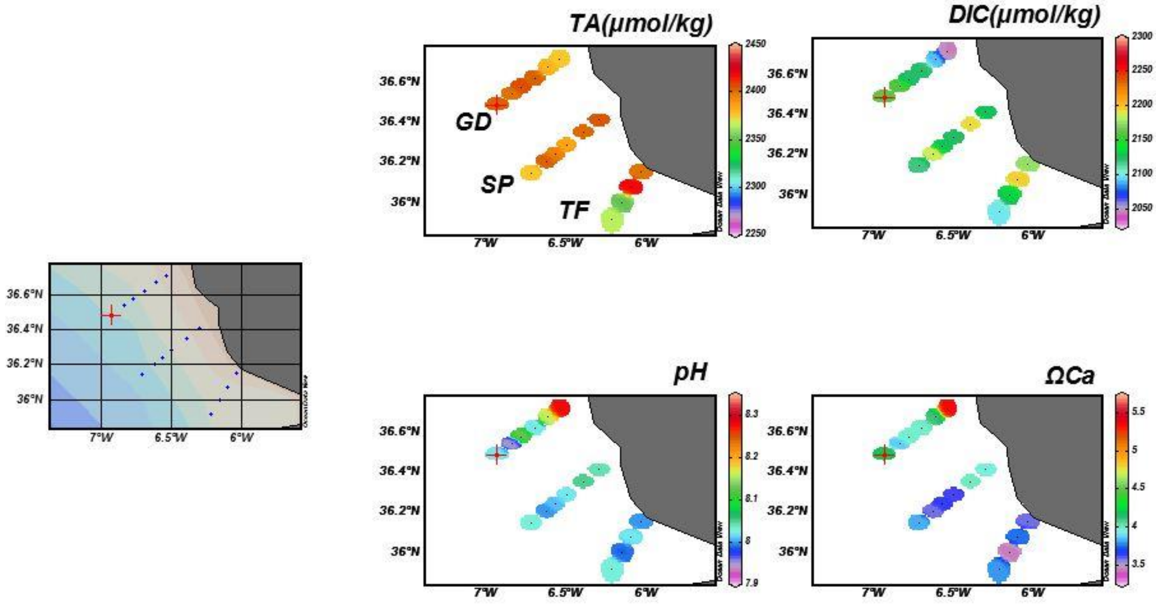


Figure 33.Total alkalinity (TA), dissolved inorganic carbon (DIC), pH and calcite saturation state (Ω_{Ca}) along the three transects sampled: Guadalquivir (GD), Sancti Petri (SP) and Trafalgar (TF) in March. Samples are from surface water values (<50m).

In June TA, DIC and pH concentrations were lower than the values measured in March. In the Guadalquivir transect, pH showed a clear gradient which increased from coast to offshore, probably as a consequence of respiration processes while in the Santi Petri and Trafalgar transects this pattern was less clear. Calcite saturation state was not influenced by the low pH. The station located close to coast, in the Guadalquivir transect, showed low values of AT, pH e Ω_{Ca}, most likely because of a deposit of organic matter (Figure 34)

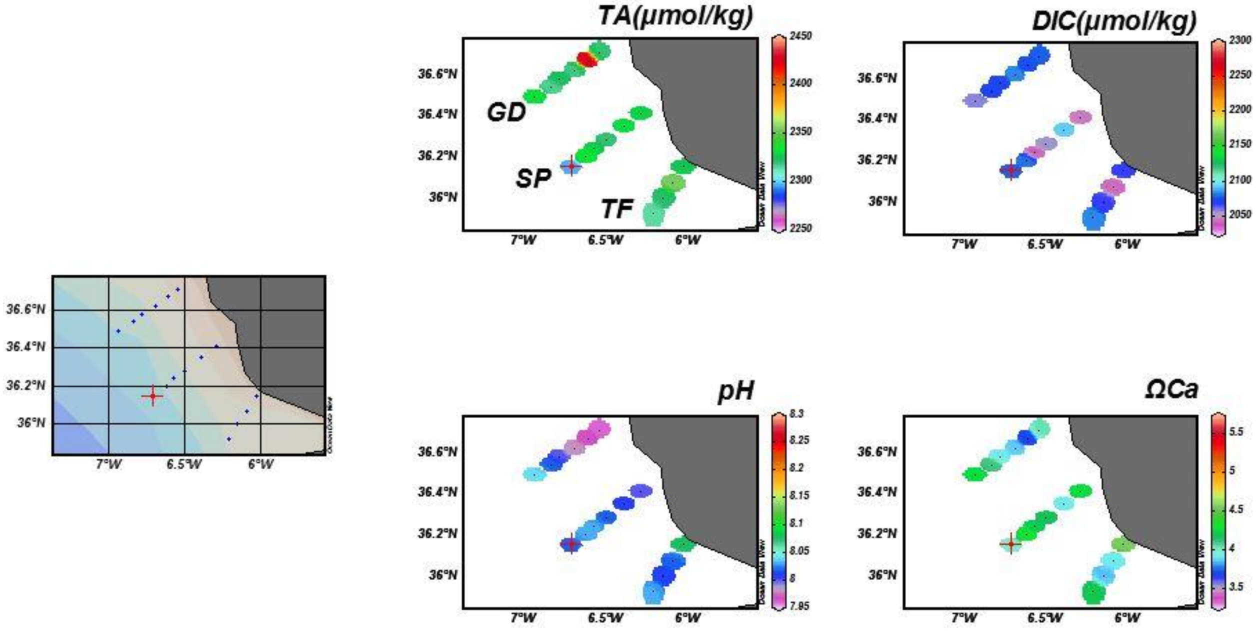


Figure 34**.** Total alkalinity (TA), dissolved inorganic carbon (DIC), pH and calcite saturation state (Ω_{Ca}) along the three transects sampled: Guadalquivir (GD), Sancti Petri (SP) and Trafalgar (TF) in June. Samples are from surface water values (<50m).

In September, TA and DIC increased with the distance to the coast while pH showed low values; around 7.95. Calcite values were also very low too, probably as a consequence of the remineralisation of the organic matter. In Trafalgar transect this process was more evident. Organic matter remineralisation processes in the Strait of Gibraltar have been previously reported by several authors such as Navarro et al., (2006), Huertas et al. (2009) and Macías et al. (2009) (Figure 35).

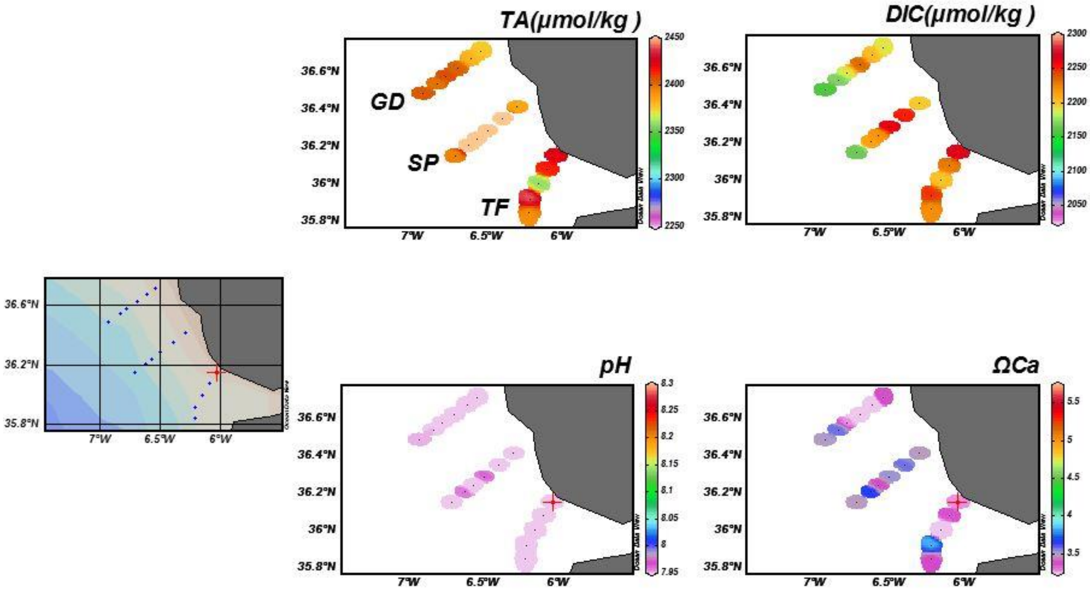


Figure 35. Total alkalinity (TA), dissolved inorganic carbon (DIC), pH and calcite saturation state (Ω_{Ca}) along the three transects sampled: Guadalquivir (GD), Sancti Petri (SP) and Trafalgar (TF) in September. Samples are from surface water values (<50m).

In November, we found a depletion of DIC that could be a consequence of an increase in primary production. TA at the Guadalquivir transect, showed a clear gradient decreasing from coast to offshore. This event was probably linked to an important water river discharge that occurred similarly to March. Navarro et al. (2006) reported an increased on the Guadalquivir River discharge in March and November. At the Sancti Petri and Trafalgar transects, TA increased from to the coast to offshore. A similar behaviour was reported in November by Ribas-Ribas et al. (2011).

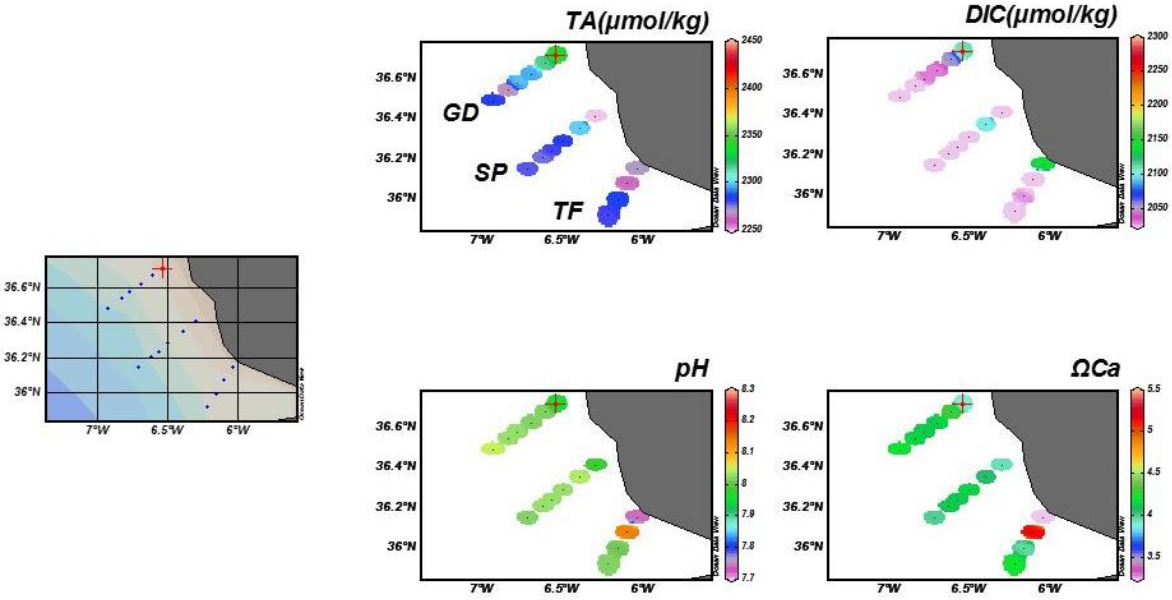


Figure 36**.** Total alkalinity (TA), dissolved inorganic carbon (DIC), pH and calcite saturation state (Ω_{Ca}) along the three transects sampled: Guadalquivir (GD), Sancti Petri (SP) and Trafalgar (TF) in November. Samples are from surface water values (<50m).

The coastal waters off the mouth of the Guadalquivir River and the Bay of Cadiz presented the highest primary production values within the Gulf of Cadiz (Navarro and Ruiz, 2006). Previous studies reported an intense biological activity in this area that is directly linked with the water discharge of Guadalquivir River and Rio San Pedro Creek (González-Dávila et al. 2003, Navarro et al. 2006, Prieto et al. 2009, Ribas-Ribas et al., 2010). Waters of the Guadalquivir River are highly alkaline and the Gulf of Cadiz is rich in DIC (de la Paz et al. 2007). The high TA concentrations found in waters of the Guadalquivir River may be due to the carbonatic composition of the drainage basin (de la Paz, 2007). Ingrosso et al. (2015) reports a similar situation for the Gulf of Trieste, where the Isonzo River represents a source of total alkalinity to the sea, due to a very high carbonate-weathering rate of its watershed (Szaramek et al. 2007, 2011). The DIC export from the river to the adjacent coastal areas is the product of the freshwater discharge and DIC concentrations in the Gulf. These authors reported that the observed DIC export varied from 5.7 × 106 mol d^{-1} in December 2000 to 14,2 × 106 mol d^{-1} in June 2003. In the Guadalquivir Estuary, the high DIC export was mainly due to the high TA concentration in the river as occurred in the Scheldt Estuary (Hellings et al., 2001), Loire Estuary (Abril et al., 2003), and several estuaries located in the Spanish coast (de la Paz et al. 2007). The photosynthesis activity was also confirmed by negative Apparent Oxygen Utilization (AOU) values in the water column at the Guadalquivir area relative to the SAW as reported by Aït-Ameur (2006). Negative values of AOU in surface waters of the continental shelf may indicate that these waters are over-saturated with oxygen and presents high values of Chorophyll-a concentration because it is affected by the photosynthetic activity of the phytoplankton. High productivity of waters along the continental shelf of the Gulf of Cádiz was likely the ecological cause of the high DOC concentration (concentration > 100 μM) observed in the Atlantic inflow in the north–western part of the Strait of Gibraltar suring summer and autumn (Dafner et al., 1999).

Seasonal variation of the measured values may be a balance between river inputs, water column mixing processes, primary production activity, and respiration and mineralization processes

6. FINAL REMARK

The formation and dissolution of calcium carbonate ($CaCO_3$) is an important component of the oceanic carbon cycle. Together with organic carbon metabolism, the ($CaCO_3$) cycle modulates the oceanic dissolved inorganic carbon system and eventually the CO_2 buffer capacity of the world ocean. Several studies have indicated that biogenic calcification will decline and ($CaCO_3$) dissolution will increase under rising atmospheric CO_2 and lowered seawater pH. To study the effect of ocean acidification on calcification it is necessary obtain a real picture of the distribution of (Ca^{2+}) along the section and, more important, not inferred by indirect approaches.

Ca^{+2} measurements

Ca^{+2} was determined using the classic ethylene glycol tetraacetic acid (EGTA) titration modified from Lebel and Poisson (1976). We have used selective ion electrode (ISE ref 6.0510.100). Samples for Ca^{2+} were filtered on GF/F membranes (47 mm). About 5 g di seawater and 10 gr di borate were weighed out. About 5.1 g of a concentrated EGTA solution (∼10 mmol L^{-1}) was added. The remaining Ca^{2+} was titrated by a diluted solution of EGTA (∼2 mmol L^{-1}) up to the end poit potential, wich was given by the Methrom 905 TITRANDO potentiometer. Instead of using the autogenerated value given by the Methrom TiAMO 1.1 software, the volume of the diluted solution of EGTA necessary for the remaining ∼5% of Ca^{2+} was obtained by manually fitting the first derivative of the titration curve, which proved to be optimal for better measurement precision (10,721 ± 0,007 mmol, n=24). EGTA solutions were standardized daily against a standard of $CaCO_3$, $MgCl_2$ and NaCl prepared in laboratory.

7. CONCLUSIONS

The Gulf of Cadiz is a unique area of the Eastern North Atlantic Ocean for understanding the carbon cycle with small spatial and temporal resolutions. Its wide and shallow shelf, the river discharges, the formation of the Atlantic inflow flowing into the Mediterranean Sea, and the transition of the Mediterranean outflow to the Atlantic Ocean make this area of unparalleled interest.

Results obtained during four seasonal cruises showed spatial variability: TA increased with the distance from the coast and decreased with depth, DIC increased with depth, pH increased with the distance from the coast and decreased with the depth, calcium concentrations (Ca^{2+}) in all sampling had values around 10.6 mmol kg^{-1}. except for those close to coast where they decreased and after increased in deeper water to higher salinity. Data related to carbonate saturation of calcite and aragonite revealed supersaturation in surface waters; in any case, both species saturation state increased with the distance to the coast and decreased with depth.

The analysis of T-S diagrams has allowed us to relate the different water masses present in the area. Distribution of total alkalinity (TA), dissolved inorganic carbon (DIC), pH, and calcite saturation state showed a vertical gradient which mainly depended on the influence of the Guadalquivir River discharges. The distribution of both TA and DIC presented a clear variability in the water column in all transects related to the riverine influence. Values of pH did not show any significant change except along the shelf as a consequence of the organic matter remineralization processes. Lower values of pH were detected at typical depths of the Eastern North Atlantic Central Waters ENACW. Data related to carbonate saturation of calcite revealed supersaturation of surface waters.

The distribution of TA, pH, DIC and Ω_{Ca}, refered to the surface layers of the water column, at depths between 0 and 50 m, showed temporal variability of the data. In March, June and November, TA and DIC concentrations were relatively low and pH and Ω_{Ca} were relatively high probably due to the organic matter remineralization processes. In November a depletion of DIC was found which may be related to an increase of the primary production. In September, TA and DIC concentrations were high regarding the pH and Ω_{Ca} values that may be a consequence of organic matter remineralization processes.

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