Contribution of submarine groundwater discharge (SGD) to the marine carbonate biogeochemistry of the Western Irish Coastal Sea

Trinity College Dublin
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The University of Dublin

A Thesis Presented to the Academic Faculty in Fulfilment of the
Requirements for the Degree of Doctor of Philosophy

2022

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Acknowledgements

As first, I have to thank the research body that gave me the possibility to get this financed project. This thesis is a result of research supported in part by the Science Foundation Ireland (SFI) under Grant Number 13/RC/2092 and co-funded under the European Regional Development Fund and industry partners of the Irish Centre for Research in Applied Geosciences (iCRAG). Specifically, this work was supported by PhD fellowships (TP MG2.3PhD2), co-funded by the SFI and the European Union, the project was awarded by the PI Carlos Rocha who gave me this opportunity. Many people from iCRAG have been helpful during this path, in particularly I thank Fergus McAuliffe for his useful training about science communication and to Professor Peter Croot who involved me and my colleague in the Marine Oceanographic Cruise in 2017 and Aoife Blowick which supported me particularly in the last year of the PhD.

I thank Jonathan Fin and Nathalie Lefevre for their technical support analysing samples and hosting me in the LOCEAN laboratory in Sorbonne Universités, where I acquired new laboratory skills. I thank the Marine Institute, Environmental Protection Agency and the Northern Ireland Environmental Agency, for some data used in this work. I thank Mark Kavanagh from the Trinity Centre of the Environment, Kevin Ryan and the Professor Alan O'Connor from the Civil Engineering Department of Trinity College Dublin for technical support to carry the analysis. I also thank professors: Mary Bourke, Susan Murphy and Cian O'Callaghan for their support as post-graduated advisor.

I thank Maebh Hughes and Leah Heron for assistance in field work. I am grateful towards Rainer Krause, Cyril Keane, Vincent Kane, and Simon Kennedy and his staff at Killary Fjord Shellfish, for providing their boat, and help during the transect surveys. I thank Philip Schuler for his kind support. I have to thank my colleagues who have been supportive Maxime, Ankit, Lauren, Jennifer. And all the other people that have been close to me during this challenging time and during this last year, even with social distance relationships but still close, Hilde, Maurice, Foteini, Josune, Victor. Last but not least, I thank Rino for everything, thanks to his help I found the energy to not give up, believing in myself. I thank all the people who have been around me in the last 4 years and support me during this challenging time, thank you all so very much!

Summary

The main objective of this study was to investigate the coastal carbonate chemistry in the Irish coastal seas, and specifically to understand the role of Submarine Groundwater Discharge (SGD) in the coastal biogeochemical cycles as a driver of coastal metabolism. From previous literature studies, SGD was recognised as an important source of nutrients and chemicals to the coast and also as an additional source of Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC). This project, therefore, aims to identify the role of SGD to the coast and this was addressed with a comparative approach. Two areas with contrasting watershed input (Kinvarra Bay fed by SGD and Killary Harbour fed by rivers) were selected for the study. The two selected systems were sampled at different times of the year, in order to capture freshwater discharge variability. The freshwater input to both study areas acts decreases pH in the low salinity areas. The question rising from the literature review on the influence of freshwater discharge in the TA:DIC ratio and therefore on the effect on coastal Net Community Production (NCP) was addressed. Carbonate system dynamics and NCP were analysed and compared.

Rivers flowing into Killary Harbour were a small source of TA (~20 - 450 µmol kg^{-1}), whilst SGD was a large source of TA (3111 - 4793 µmol kg^{-1}) and DIC (3241 - 4983 µmol kg^{-1}) into Kinvarra Bay. Both freshwater sources have low pH ($6.01 < \mathrm{pH} < 7.70$). Salinity-normalized TA-DIC slopes were compared, with reference to the open ocean. Freshwater inputs drove both systems into distinct metabolic (net autotrophy vs net heterotrophy) and biogeochemical (net $CaCO_3$ precipitation vs net $CaCO_3$ dissolution) states. The balance between organic and inorganic drivers of the TA:DIC ratio did not change in Killary Harbour with freshwater discharge or time of the year but did change in Kinvarra Bay. These results showed that both magnitude and typology of freshwater inputs affect the metabolic state of coastal carbonate systems. In groundwater-dependent systems, soil use might shift the TA:DIC compositional ratio in SGD.

High resolution sampling strategy was applied on the river and SGD end-member locations (sampled over a period of 24 hours every 30 minutes). The NCP was calculated following the dissolved oxygen dynamics. The diel variation of TA and DIC in the Erriff River were in the range of ~ 130 µmol kg^{-1} and pH changed of about 0.47 units. In Kinvarra Castle Spring diel fluctuations of TA and DIC were ~1200 µmol kg^{-1} and ~1800 µmol kg^{-1} respectively; the pH fluctuation was about of 0.85 units. Statistical analysis of the carbonate system parameters showed high positive correlation of TA with pH in the Erriff River and negative correlations of TA with pH in Kinvarra Castle Spring. The diel variation of TA and pH was correlated with the tidal excursion. The time-series analysis showed non-stationarity. Time-series in Kinvarra Castle Spring showed seasonality; therefore, in order to have a complete understanding of the diel carbonate system fluctuation, the trend analysis was combined with statistical decomposition to evaluate the possible drivers of the diel changes. Time-series in Erriff River showed a random pattern. The NCP at Aasleagh Bridge was 0.270±0.054 g m^2 d^{-1} and in Kinvarra Spring NCP was negative -0.037±0.006 g C m^2 d^{-1}. The result confirmed that Erriff River is an autotrophic and oligotrophic system as known from other literature studies. Kinvarra Castle Spring, conversely, has been identified as a heterotrophic system, since the dissolved oxygen dynamics during the day showed that the respiration processes exceeded the rate of photosynthesis.

In order to understand the retention fluxes of TA and DIC and DOC in two coastal embayments and to estimate NCP, LOICZ budgeting methodology was applied. Killary Harbour showed negative ΔTA and ΔDIC for all surveys and positive NCP, with an average value of ~ 14 mmol C m^2 d^{-1} (equivalent to 61 g C m^2 y^{-1}). Killary Harbour could be thus considered as an autotrophic system. On the other hand, Kinvarra Bay showed positive ΔTA and ΔDIC during the autumn and winter surveys implying a net export of TA and DIC to the open ocean, and a negative NCP. NCP in Kinvarra Bay was positive for the surveys taken during the other periods of the year, giving an average annual NCP of ~37 g C m^2 y^{-1}. These results suggest that freshwater inputs into Kinvarra Bay could seasonally drive the system into heterotrophy, intensifying ocean acidification trends. On an annual scale both areas can be considered autotrophic, although the net export of ΔTA and ΔDIC associated with negative NCP during the cold months in Kinvarra Bay moves the system into heterotrophy, intensifying ocean acidification.

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BOD	Biological Oxygen Demand
°C	Degrees Celsius
CA	Carbonate Alkalinity
$CaCO_3$	Calcium carbonate
CAP	Canonical Analysis of Principal Components
CCMs	Carbon Concentration Mechanisms
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
COP21	United Nations Climate Change Conference
CRMs	Certified Reference Materials
CTD	Conductivity Temperature Depth meter
CV	Celtic Voyager
DIC	Dissolved Inorganic Carbon
DIN	Dissolved Inorganic Nitrogen
DIP	Dissolved Inorganic Phosphate
dm^3	Cubic decimetres
DO	Dissolved Oxygen
DO%	Dissolved Oxygen saturation state
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
EC	Electrical conductivity
EPA	Environmental Protection Agency
F^-	Fluorine
fCO_2	Fugacity of carbon dioxide
GF	Gran Function
GPP	Gross Primary Production
gr	Grams
H^+	Hydrogen ion
H_0	Null hypothesis
H_1	alternative hypothesis
$H_2CO_3^-$	Carbonic acid
HAB	Harmful Algae Bloom
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate ion
HF	Hydrogen fluorine
$HgCl_2$	Mercuric chlorine
HSO_4^-	Sulfuric acid
kg	Kilograms
km	Kilometre
km^2	Square kilometre
Ks	Stability constant

Ksp	Solubility product constant
L	Litre
log	Logarithm
LOICZ	Land Ocean Interaction in the Coastal Zones
μmol kg^{-1}	Micromole per kilogram
µmol/l	Micromole per litre
m	Meter
mCP	Meta cresol purple
mg/l	Milligrams per litre
MI	Marine Institute
ml	Milliliter
mol kg^{-1}	mole per kilogram
NaCl	Sodium chloride
NBS	National Bureau of Standards
NCC	Net Community Calcification
NCP	Net Community Production
NEP	Net Ecosystem production
NH_4^+	Ammonia
NIEA	Northern Ireland Environmental Agency
nm	Nano meter
NO_2^-	Nitrite
NO_3-	Nitrate
OA	Ocean Acidification
ODV	Ocean Data View
OH^-	Hydroxide ion
org$^-$	Organic
PCA	Principal Components Analysis
pCO_2	Partial Pressure of Carbon Dioxide
PCOs	Principal Coordinates
pHF	pH free scale
pHo	pH ocean
pHr	pH coral reef
pHsws	pH sea water scale
pHT	pH total scale
PO_4^{3-}	Phosphate ion
POM	Particulate Organic Matter
PP	Primary Production
Ppm	Part per million
PQ	Photosynthetic Coefficient
PSU	Practical Salinity Unit
QCs	Quality Controls
R	Respiration
SGD	Submarine Groundwater Discharge
SiO_4^-	Silicate
SRP	Soluble reactive phosphate
SI	Saturation index

SW	Sea water
t/y	Tonnes per year
TA	Total Alkalinity
ToxN	Total oxidised Nitrogen
TP	Total Phosphorous
WFD	Water Framework Directive
yr^{-1}	per year
Ω	Calcium carbonate saturation state
Ω_{Ar}	Aragonite saturation state
‰	Part per thousand

1 General Introduction

Over the past 200 years, due to the burning of fossil fuels, human activities have altered the global carbon cycle leading to a 40% increase of CO_2 in the atmosphere , from 277 ppm in the pre-industrial era (Joos and Spahni, 2008) to nearly 413 ppm in 2021 (Dlugokencky and Tans, 2021). The consequent absorption of atmospheric CO_2 by the ocean has led to an alteration of marine carbonate chemistry with a 30% increase in H^+ concentration in sea water and the corresponding decrease of pH. This effect is called Ocean Acidification (OA) (Orr et al., 2005) and is the result of a long process fed by the evolution of the societies and of the technology. The pre-industrial ocean pH was slightly alkaline with a pH value of 8.2 (Caldeira and Wicket,t 2003). Following the industrial revolution the ocean pH decreased by 0.1 pH units, from approximately 8.21 to 8.10 (Raven, Caldera, et al., 2005), and is expected to decrease a further 0.3–0.4 pH units (Orr et al., 2005) by the end of the 21st century if atmospheric CO_2 concentrations will reach 800 ppm (Byrne et al., 2010; Caldeira and Wickett, 2005). This scenario is likely if CO_2 emissions will not be mitigated in time. Under the current circumstances, reasonable projections suggest that the global mean ocean pH will fall below 7.9 by 2100 (Zeebe and Wolf-Gladrow, 2001). The CO_2 concentration continues to rise at the rate of 2.73 ppm yr^{-1} (Bopp et al., 2013). In addition to the CO_2, fossil fuel combustion and agriculture also increase the atmospheric inputs of strong acids (nitric and sulfuric) and bases (ammonia), which in turn affects the coastal and open ocean carbonate geochemistry. These inputs are particularly important in the regions where the major sources are, primarily in the northern hemisphere, and are responsible of reduction in surface seawater alkalinity, pH, and Dissolved Inorganic Carbon (DIC) (Doney et al., 2009).

This thesis work focuses on the drivers that influence the carbonate chemistry of coastal areas, like river inputs and submarine groundwater discharge (SGD), and how they might contribute to modify the carbonate biogeochemistry of coastal seas. Coastal ecosystems may show acidification or basification: this depends on the balance between the invasion of coastal waters by anthropogenic CO_2 and the watershed export of alkalinity and organic matter. Furthermore, changes in the balance between primary production, respiration and calcification rates as a response to changes in nutrient inputs and losses of ecosystem components may also influence the acidification of coastal ecosystems (Duarte et al., 2013). The prolonged and intensive use of inorganic fertilizer in agriculture, changes in land use, for instance deforestation, and discharge of industrial and municipal waste have all contributed to the eutrophication of river water and of the coastal ocean, on a global scale. In karstic areas, subterranean waters play a significant role, modifying the biogeochemical cycles of the coastal ecosystems. This occurs because of the land usage and of the accumulations of nutrients and carbonate in the water that eventually are discharged into the coastal areas (e.g., the supply of nutrients through SGD is linked to the occurrence of red tides) (Hu et al., 2006; Lee et al., 2009; McCoy and Corbett, 2009). In this thesis work the nutrients that are measured and considered in the different chapters are: phosphate PO_4^{3-} , silicate SiO_4^-, ammonia NH_4^+, nitrate NO_3^-, nitrite NO_2^-. SGD is also a major source of carbon, in the form of DIC, which might decrease the coastal the capacity of the seawater inorganic carbon system to take up CO_2 from the atmosphere. SGD is also a source of Total Alkalinity (TA), that is introduced in the system by weathering of rocks, which might leads to an increase of coastal buffer capacity (De Weys et al., 2011; Cyronak et al., 2013; McMahon et al., 2013; Santos et al., 2014). According to the relation between TA and DIC the coastal areas system can contribute to offset or to intensify ocean acidification. SGD, being also a source of nutrients, has been consequently linked to severe degradation of water quality and alteration of the marine food web and community structure (Rabouille et al., 2001).

Since coastal marine systems are considered the most ecologically and socio-economically vital ecosystems on the planet (Costanza et al., 1998; Gazeau et al., 2007; Bopp et al., 2013), the safeguard of ecosystem services, such as aquaculture, is necessary. The increasing amount of CO_2 dissolved in the water column and the associated pH reduction result in a decrease of the metabolic activities of calcified organisms, from zooplankton to commercially valuable species like mussels (e.g., *Mytilus edulis*) (Hinga, 2002). In order to predict the pH trend in coastal areas, it is important to consider all the drivers that can affect the coastal carbonate chemistry. A biogeochemical approach is fundamental to avoid overlooking some important drivers such as SGD. In this sense, this thesis work also aims to emphasize the complexity of studies of this type in coastal areas, highlighting the need for a multi-disciplinary approach. In producing estimates of the impact of OA on aquaculture species, the scientific community has employed until now assumptions that are valid only for the open ocean and are not applicable on the coast; this should increase the interest about the coast especially in terms of future economic value loss. Indeed, a multi-disciplinary approach has been recognised by the scientific community to river, estuarine, coastal, open ocean observing and modelling. As early career scientist and member of the coast predict program, the knowledge acquired thanks to this project contributes to expand the discussion about global coastal ocean (https://www.coastpredict.org/steering-structure/).

1.1 The marine carbonate system

Carbon in the ocean is present in either inorganic or organic form, either dissolved or particulate. This thesis mainly focused on the inorganic forms of carbon and specifically the following carbonate system parameters were considered: dissolved inorganic carbon, the total alkalinity, pH, and the partial pressure of carbon dioxide (pCO_2). The knowledge of any two of these parameters, along with the temperature, salinity, pressure, phosphate and silicate concentrations, and the relevant equilibrium constants, allows the determination of the other two parameters (Lewis and Wallace, 1998).

1.1.1 Dissolved inorganic carbon and its cycle

Carbon dioxide dissolved in seawater exists in three main inorganic forms collectively known as DIC: carbon dioxide (CO_2), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) (Zeebe, 2012; Raven, Caldera, et al., 2005). The sum of CO_2 (aq) and H_2CO_3 is denoted as CO_2. At typical surface-seawater pH of 8.2, the speciation between CO_2, HCO_3^-, and CO_3^{2-} is 0.5%, 89%, and 10.5%, respectively, showing that most of the dissolved inorganic carbon is in the form of HCO_3^- and not in the form of CO_2. However, the amounts vary according to the temperature salinity and pressure of each system (Raven, Caldera et al., 2005), Figure 1-1.

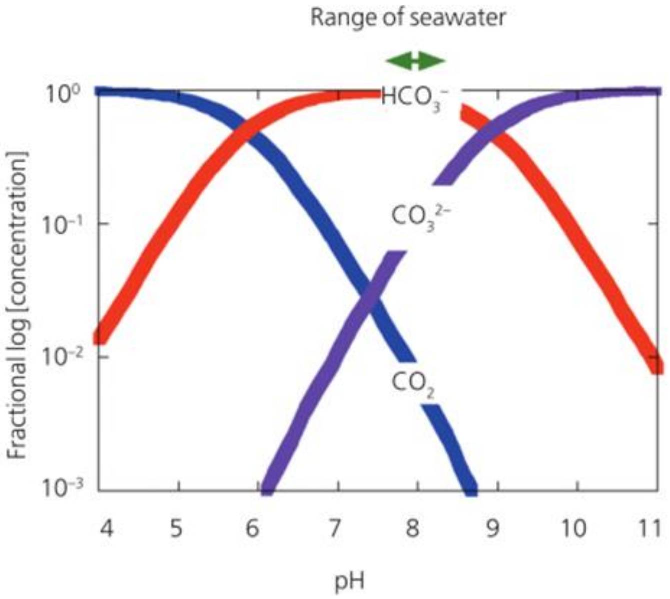


Figure 1-1 Relative proportions of the three inorganic forms of CO_2 dissolved in seawater. The green arrows at the top indicate the narrow range of pH (7.5–8.5) that is likely to be found in the oceans now and in the future (Raven, Caldera, et al., 2005).

All the three forms of dissolved CO_2 are important for the biological processes of marine organisms. These processes include:

- photosynthesis by marine algae (mostly phytoplankton);
- the production of complex organic carbon molecules from sunlight;
- calcification that creates structures such as $CaCO_3$ shells.

When these organisms die or are consumed, most of the carbon either stays in the surface waters or is released back into the atmosphere. However, some of this $CaCO_3$ and organic material falls as particle sediments to the deep oceans. The process by which the carbon is transferred from the atmosphere to the deep ocean waters and sediments, is referred to as the ‘biological pump’. By removing carbon from the surface waters and taking it to greater depths, the pump increases the capacity for the oceans to act as a sink for the atmospheric CO_2. Any changes in the strength of this pump would have significant consequences on the amount of carbon being sequestered to the deep ocean environments and therefore removed from the atmosphere (Raven et al., 2005; Wolf-Gladrow et al., 2007; Baird and Cann, 2012). When the atmospheric CO_2 dissolves in seawater, the additional hydrogen ions react with carbonate (CO_3^{2-}) ions and convert them to bicarbonate (HCO_3^-) (Figure 1-2). This reduces the concentration of hydrogen ions (the acidity) so that the change in pH is much less than would otherwise be expected. This results in oceans showing still alkaline pH values. The reactions described in (Figure 1-2) occur in the surface oceans (top few hundred meters). The capacity of the buffer to restrict pH changes diminishes as increased amounts of CO_2 are absorbed by the oceans. The ocean is called a "carbonate buffer system" because it is able to maintain the relative proportion of the three forms of CO_2, HCO_3^- and CO_3^{2-}, changing accordingly the pH of the seawater and keeping it within relatively narrow limits (see Figure 1-1).

The major source of the carbonate ion in natural waters are limestone rocks, which are largely made up of calcium carbonate, $CaCO_3$. Natural waters that are exposed to limestone are called calcareous waters. The CO_3^{2-} acts as a base, producing its conjugate weak acid, the bicarbonate ion, as well as hydroxide ion in the water (Orr et al., 2005; Le Quere et al., 2005; Sarmiento et al., 1998).

In modern marine sediments the presence of carbonate minerals can be divided between those found between 0 and 200 meters called shoal-to-shallow or more than 1000 meters considered as deep-water sediments (Morse et al., 2007). In the shoal-to-shallow water environment the source and diagenesis of carbonates derive or from rocks rich in carbonates or siliciclastic (composed mainly of detrital minerals such as clays and sands): these carbonates are produced by disintegration of the skeleton of benthic organisms (i.e. corals, echinoids, molluscs, benthic foraminifera, coralline algae) (Morse et al.,2007). In (Figure 1-2) the carbon saturation horizon is also represented: the conservation or the dissolution of the organisms previous listed, depends on the conservation of $CaCO_3$ ions in seawater (Raven, Caldeira, et al., 2005). *There is a critical concentration of carbonate ions in seawater (the saturation concentration) below which $CaCO_3$ will start to dissolve* (Raven, Caldeira, et al., 2005). Since the solubility of $CaCO_3$ increases with increasing of depth (pressure) and decreasing temperature, the saturation horizon represents that threshold below which the $CaCO_3$ dissolves (Raven, Caldeira, et al., 2005). With the increase of CO_2 in the atmosphere, due to the anthropogenic activity (this will be further explained in the next paragraphs), $CaCO_3$ decreases and, consequently, the saturation horizon will become shallower (Raven, Caldeira, et al., 2005; Morse et al.,2007).

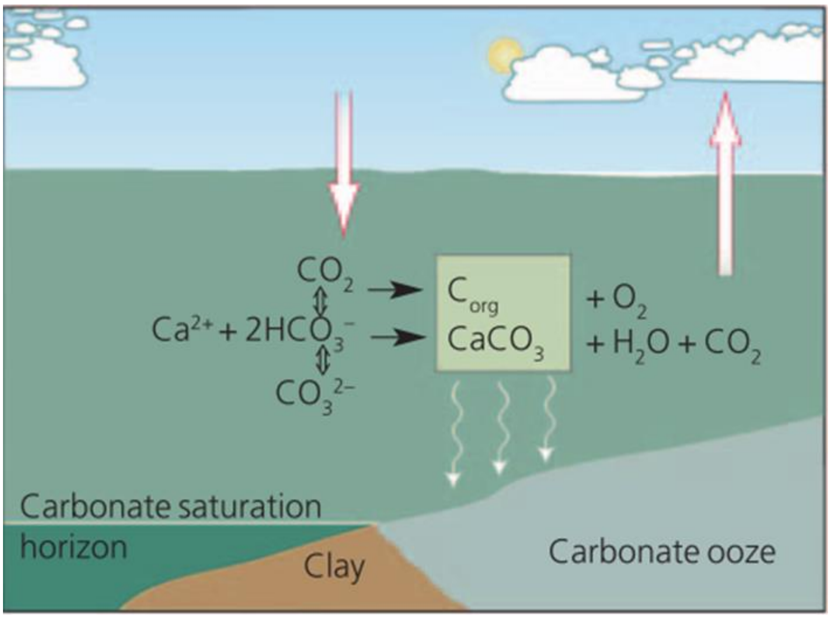


Figure 1-2 Atmosphere-Water-Soil chemistry interactions, the reactions involved in the carbon-dioxide carbonate-system. Three phases are involved: CO_2 in the air reacting with H_2O to form carbonic acid; at the same time calcium carbonate in the soil reacts with water and is dissolved in Ca^{2+} and CO_3^{2-}. The reactions described in the box occur in the top few hundred meters. The saturation horizon is located above: for calcite occur between 1.5. and 5 km depth and for aragonite between 0.5 and 2.5 km depth (Raven, Caldera et al., 2005).

1.1.2 Total alkalinity

Total alkalinity of a body of water is a measure of the capacity of the water body to neutralize all acids and hence to resist acidification. Historically the TA has been defined as the number of equivalents of strong acid required to neutralize 1 dm^3 ~ (or 1 kg) of seawater to the endpoint corresponding to the formation of carbonic acid from bicarbonate (Sverdrup, 1953). The total alkalinity in natural water is driven by a mixture of inorganic and organic bases and acids, from neutral to alkaline pH, and is thought to be dominated by the carbonate species (CO_3^{2-} and HCO_3^-) (Tishchenko et al., 2006; Williams et al., 2009).

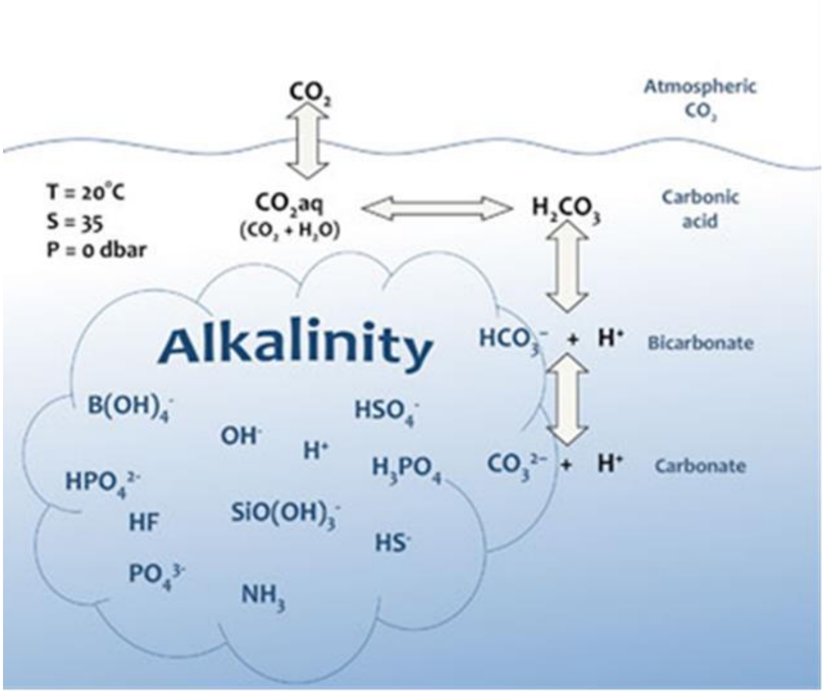


Figure 1-3 Carbonate and non-carbonate species present in seawater, the carbon cycle and carbon exchange with the atmosphere are shown. The total alkalinity is driven by the assemblage of carbonate and non-carbonate species (taken from http://www.whoi.edu/OCB-OA/).

In that sense, TA is fundamentally described by the expression (Wolf-Gladrow et al., 2007):

$$[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \tag{1}$$

It is than possible to define alkalinity as the sum weighted sums of proton acceptors: 2 $[CO_3^{2-}] + [HCO_3^-] + [OH^-]$ and donors: $[H^+]$ (Wolf-Gladrow et al., 2007). It is important to note that the sum of the concentrations above describe the alkalinity where (or when) there are no significant concentrations of other weak acids and bases in solution, such as in standard seawater (the oligotrophic open ocean seawater). In coastal areas or other water bodies, where above-trace amounts of these other solutes exist (non-carbonate alkalinity), alkalinity is described as follows:

$$TA = HCO_3^- + 2CO_3^{2-} + B(OH)_4^- + OH^- + HPO_4^{2-} + 2PO_4^{3-} + H_3SiO_4^- + 2H_2SiO_4^{2-} + HS^- + 2S^- + NH_3 + Org^- - H^+ - H_3PO_4 \tag{2}$$

In this expression, Org^- is a collective term representing anions of organic acids (Hunt et al., 2011). Furthermore, Hunt et al., (2011) suggested that, in the absence of information on organic matter quality and quantity (very common, as organic matter may comprise several hundred different compounds in natural waters) and the typology and concentration of non-carbonate inorganic other species that can contribute to the alkalinity, it is possible to simplify the expression representing the TA as:

$$TA= \text{C-Alkalinity} + \text{NC-Alkalinity} + OH^{-} - H^{+} \tag{3}$$

Where C-Alkalinity is the sum of carbonate and bicarbonate and NC-Alkalinity is the net contribution of non-carbonate species to the alkalinity of the solution. The magnitude of NC-Alkalinity is repeatedly assumed to be small compared to carbonate alkalinity, but this assumption is often based on the notion that the study refers to the ocean water (or standard sea water), where the ionic species relevant to NC-Alkalinity are diluted to trace and sub-trace levels. It is not the same in coastal waters, though, where inputs from land and mineralization of organic matter in sediments introduce significant amounts of non-carbonate alkalinity, including boron, phosphorus, nitrogen and silicon dissolved species, amongst others, and enhancing concentration of Dissolved Organic Carbon (DOC), Dissolved Organic Nitrogen (DON). Unfortunately, concentrations of these species are sometimes only roughly estimated or simply ignored when using TA to calculate pCO_2 or other carbonate system parameters in coastal areas.

It is important to know how to measure and calculate the TA in coastal areas and the influence of the other ions that contribute to the non-carbonate total alkalinity. A few studies are focused on TA on coastal areas, however there are authors that have identified the importance of non-carbonate alkalinity in systems like estuaries and coastal water ecosystems (Hernández-Ayon et al., 2007; Kuliński et al., 2014).

TA generally shows a conservative behaviour in the ocean's surface water (Key et al., 2006);

- it stays constant with varying temperature and pressure;
- it is not affected by CO_2 exchange with the atmosphere;
- ionic concentrations are generally governed by factors that affect salinity, such as precipitation and evaporation (Key et al., 2006; Millero et al., 2008).

The explicit conservative expression for TA (named as TA_{ec}) suggested in (Wolf-Gladrow et al., 2007), contains concentration of conservative ions only. In such expression of TA_{ec} the most important ions (in terms of concentration) in oxic seawater are the following:

$TA_{ec}= [NA^{+}] + 2[Mg^{2+}] + 2 [Ca^{2+}] + [K^{+}] + [Sr^{2+}] +…-[Cl^{-}]-[Br^{-}]-NO_3^{-}]-…TPO_4 + TNH_3 -2TSO_4- THF-THNO_2$

(4)

where:

TPO_4 is the total phosphate: $[H_3PO_4] + [H_2PO_4^{-}] +[HPO_4^{2-}] +[PO_4^{3-}]$, TPO_4 concentration stays constant even when the concentrations of various phosphate species change with temperature and pressure;

TNH_3 is the total ammonia: $[NH_3] +[NH_4^{+}]$;

TSO4 is the total sulphate: $[SO_4^{2-}] +[HSO_4^{-}]$ (the contribution of H_2SO_4 to total sulphate can be neglected);

THF is the fluoride: $[F^{-}]+ [HF]$;

$THNO_2$ is the nitrite: $[NO_2^{-}] + [HNO_2]$;

In the open ocean, the changes of TA are due to salinity (changes in the concentration of Na^{+} and Cl^{-} etc.,(Friis, 2003)): additional changes are attributable to other biogeochemical processes that are discussed throughout the thesis. TA decreases with $CaCO_3$ formation, while it increases with the dissolution of $CaCO_3$, with a slight increase with photosynthesis due to the uptake of protons with nitrate by phytoplankton (Wolf-Gladrow et al., 2007; Zeebe, 2012).

The formation or dissolution of calcium carbonate is expressed as:

$CaCO_3 = Ca^{2+} + CO_3^{2-}$

(5)

The $CaCO_3$ saturation state of seawater (Ω) is determined from:

$\Omega = [Ca^{2+}]_{SW} \times [CO_3^{2-}]_{SW} / K_{SP}$

(6)

where $[Ca^{2+}]_{SW}$ is the concentration of calcium and $[CO_3^{2-}]_{SW}$ is the concentration of carbonate in seawater, and K_{SP} is the solubility product (constant) at in situ conditions of temperature, salinity and pressure. The Ω greater than 1 indicates that the seawater is supersaturated with respect to calcium carbonate, and this would predict $CaCO_3$ precipitation, while Ω less than 1 indicates undersaturation, meaning that $CaCO_3$ tends to dissolve. Ca^{2+} is a major constituent of seawater and concentrations vary only slightly in the open ocean (Feely et al., 2004), therefore, the $CaCO_3$ saturation state is mainly determined by the carbonate ion concentration (Zeebe, 2012). Several carbonate minerals polymorphs exist in the marine environment, aragonite and calcite are naturally occurring polymorphs of calcium carbonate in seawater (Morse et al., 2007). The K_{SP} for the two minerals have different values, i.e. different solubilities, due to differing crystal lattice structures; aragonite stoichiometric solubility product in sea water is 6.65×10^{-7} mol^2 kg^{-2} is about 1.5 times more soluble than calcite, 4.39×10^{-7} mol^2 kg^{-2} (Morse and Muccr, 1980) at 25 °C (Dickson et al., 2007).

1.1.3 pH and pCO_2

The pH is a measure of the hydrogen ion concentration of a solution. Solutions with a high concentration of hydrogen ions have a low pH and solutions with a low concentration of H^+ ions have a high pH. pH can be defined by the following equation:

$$pH = -\log[H^+] \tag{7}$$

which means the pH is equal to minus the log of the H^+ concentration. In ocean related studies in order to predict the evolution of carbonate systems, an accurate value of pH is important (Floquet et al., 2012). Small errors in pH measurement will have significant effects on the computed dissolved CO_2 concentration. In the studies regarding the open ocean it was observed small variation of pH during the years with the increasing of CO_2 in the atmosphere and decreasing of buffer capacity (Riebesell, 2004). In the coastal area these variations are more significant due to the contribution coming from external input (e.g., freshwater derived inputs).

The International Union of Pure and Applied Chemistry defined the National Bureau of Standards (NBS) pH scale as a series of standard buffer solutions across a range of pH values. These buffer solutions have very low ionic strength (~0.1) while seawater has a relatively high ionic strength (~0.7). For what concerns the pH measured in seawater it is necessary to convert the pH values from NBS scale to Total pH scale, knowing that the conversions depend on temperature, salinity and pressure. At 20 °C, 35 salinity and 1 atm, pH values on the total scale are about: 0.09 lower than those on free scale, 0.01 higher than those on the seawater scale and 0.13 lower than those on the NBS scale (Lewis and Wallace, 1998). For the seawater analysis the following scales can be used: pH total scale (pHT), pH in seawater (pH_{SWS}) and pH free scale (pH_F). These three scales can be described by the following equation:

$$pH_F = -\log [H^+]_F \tag{8}$$

$$pHT = -\log ([H^+]_F + [HSO_4^-]) \tag{9}$$

$$pH_{SWS} = -\log ([H^+]_F + [HSO_4^-] + [HF]) \tag{10}$$

The free scale is the free hydrogen ion concentration, including hydrated forms. Due to the protonation of sulphate ions in seawater, the stability constant of HSO_4^-, K_S, has to be determined. The total scale includes the effect of sulphate ion and therefore avoids the difficult task of determining the K_S. On the total pH scale the standard buffers to measure pH use artificial seawater, therefore reducing electric potential difference between the buffer and the sample due to similar ionic strength between the two solutions. If the sample solution also contains fluoride ions, the protonation of F^- ($HF \leftrightarrow H^+ + F^-$) should also be considered, which defines the seawater scale. The difference between the total and seawater scale is however small because the concentration of HSO_4^- in seawater is much larger than the concentration of HF (Zeebe and Wolf-Gladrow, 2001). The total scale (total hydrogen ion concentration scale) is used in this thesis as it is recommended by (Dickson et al., 2007) to best describe the pH of seawater.

The partial pressure of carbon dioxide, in a seawater sample, is the pCO_2 in the gas phase that is in equilibrium with that seawater. The net difference of pCO_2 between the ocean and atmosphere indicates the direction and magnitude of air-sea gas exchange, and when in equilibrium, the net exchange is zero. pCO_2 is temperature dependent, with higher pCO_2 found in warmer waters. The fugacity of carbon dioxide, fCO_2, accounts for the non-ideal behaviour of CO_2 and includes the dimension of pressure; it is therefore used instead of pCO_2 in the equilibrium constant definition. The pCO_2 is generally determined from DIC and TA, and the first and second dissociation constants of carbonic acid (Lueker et al., 2000).

pH measurement techniques

pH measurements have been widely used to measure of the acidity of fluids, there are two methods for measuring pH: colorimetric methods using indicator solutions or papers, and the electrochemical methods using electrodes and a millivoltmeter (pH meter) (Webster, 2003). To improve the accuracy and precision of measurements of other inorganic carbon system parameters (Sharp and Byrne, 2019), generally spectrophotometric indicators have been used (Wang et al., 2007; Sharp and Byrne, 2019) including TA, (Yao and Byrne, 1998) pCO_2, (Wang et al., 2003) and DIC (Byrne and Mcneal, 2002).

To measure the oceanic seawater that has a pH range between 7.2 and 8.2, the use of Meta-cresol purple (mCP) is advised. Following the work of Yao and Byrne, (1998) who described the effect of indicator impurities on spectrophotometric pH measurements, Liu et al., (2011) demonstrated that purified mCP could be used to accurately and precisely determine seawater pH on the total hydrogen ion concentration scale over a wide range of temperature ($5\ °C \leq T \leq 35\ °C$) and salinity ($20 \leq S \leq 40$) (Easley and Byrne, 2012). However, there are also other methods that have showed a high accuracy ± 0.01, for instance using glass electrode. In the coastal areas studies a high precision pH meter and a combination pH electrode Orion 8102BN thermos Scientific (Huang et al., 2012) are often used. The use of electrodes is convenient also for the TA analysis to apply the open cell titration methods, recommended also by Dickson et al., (2007).

1.2 Ocean acidification

After the industrial revolution and the consequent intense burning of fossil fuels, the amount of CO_2 released in the atmosphere increased exponentially (Doney, 2010), and, as a consequence, the ocean buffer capacity slightly decreased (Riebesell, 2004). The CO_2 in the atmosphere reacts with the water, forming H_2CO_3 that is then dissociated in HCO_3^- and H^+ (Figure 1-4). The increase of CO_2 that has to be absorbed by the ocean implies also an increase of H^+ ions dissolved in the water, decreasing then the pH. This process has been named as ocean acidification.

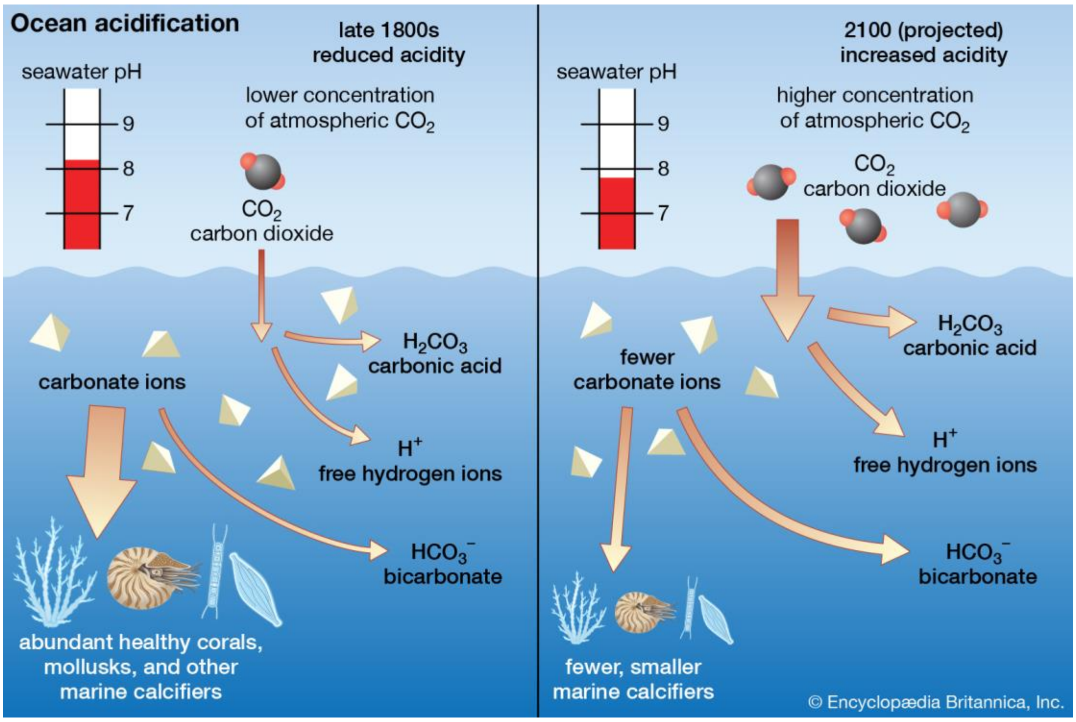


Figure 1-4 Conceptual diagram where the state of carbonates in the ocean is compared before the industrial revolution on the left and a projected forecast built on the current emissions rate on the right https://www.britannica.com/science/ocean-acidification.

Between 1750 and 2000, the oceans have absorbed one-third of the total CO_2 emitted by human activities. At the moment the pH decrease in the open ocean is about 0.1 units, from ~8.2 to ~8.1 (Doney et al., 2009). It is important to consider that pH is measured in logarithmic scale, which means that each decreasing unit makes a large difference in H^+ concentration (Bopp et al., 2013). Surface ocean pH was probably never below 8.1 during the past 2 million years (Raven, Caldera, et al. 2005; Zeebe and Wolf-Gladrow, 2001). What is concerning the scientific community in the last decades, is that, according to the current figures, the pH will continue to decrease and could be about 0.7 units less by the year 2300

(Fabry et al., 2005). This is a likely scenario in case CO_2 emissions and the use of fossil fuels are not mitigated. In the Figure 1-5, it is described the rate of increase in atmospheric CO_2 from the industrialization period to 2015.

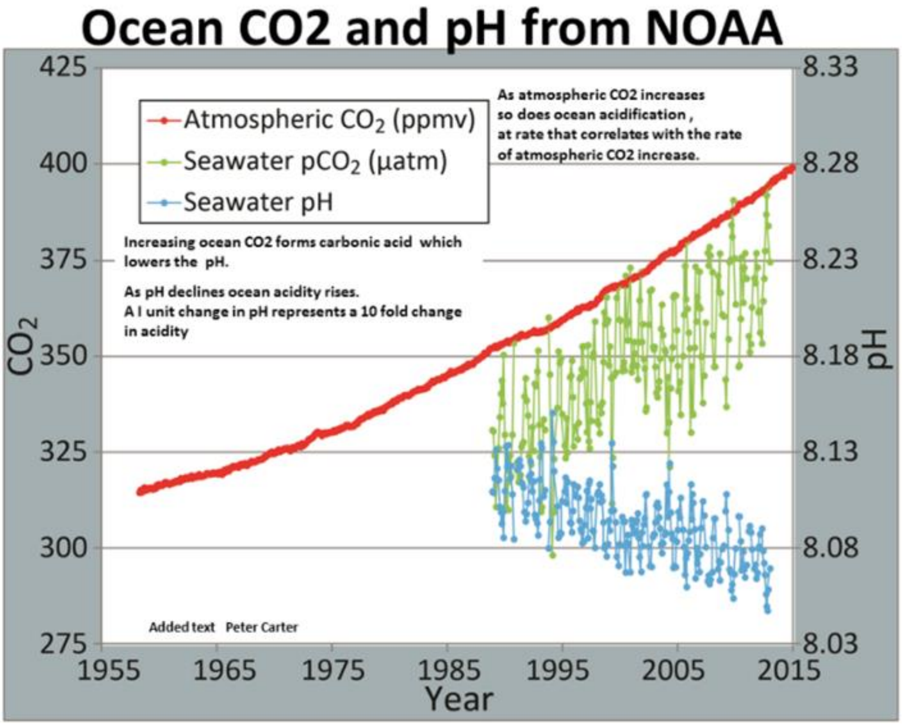


Figure 1-5 In this figure it is shown the increase of atmospheric CO_2 and the consequent pH decreasing (NOAA, PMEL graph).

1.2.1 Effects of ocean acidification on marine organisms

OA has a direct effect on the food web structure since there are calcifying organisms that have an external structure made of $CaCO_3$. Since the H^+ ions are increasing, following protonation mechanisms with the free CO_3^{2-}, they are forming HCO_3^- (Baird and Cann, 2012). As a consequence, the availability of CO_3^{2-} is decreasing and this leads to the dissolution of the $CaCO_3$ mineral structures of marine organisms (Zeebe and Wolf-Gladrow, 2001).

In addition, with the exchange with the atmosphere, there are several reactions that might increase the amount of CO_2 in the water column, for instance sulphate reduction by anaerobic bacteria that convert organic matter in carbon dioxide:

$$2SO_4^{2-}+ 3CH_2O+4H \rightarrow 2S+3CO_2+5H_2O \qquad (11)$$

This reaction is particularly important in sea water where the sulphate ion is more abundant than in freshwater systems (Baird and Cann, 2012). Furthermore, land-derived inputs can act as an additional source of inorganic carbon to the coastal areas that could intensify ocean acidification processes (Borges and Gypens, 2010; Cai et al., 2011; Hunter et al., 2011).

These changes affect different marine organisms, from phytoplankton to fish, and their responses could lead to profound ecological shifts in marine ecosystems (Doney et al., 2009).

In a near future the ocean chemistry could see the saturation of aragonite and calcite that support biogenic calcification and this could drive the net dissolution of carbonate structures leading to malformed structures (Hofmann et al., 2010; Kelly and Hofmann, 2013) see Figure 1-6.

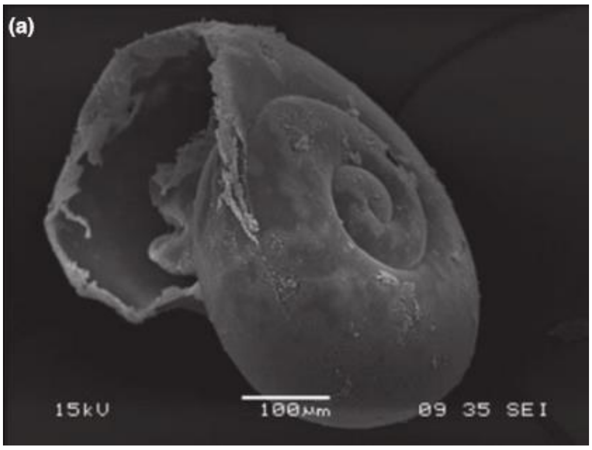


Figure 1-6 Example of surface shell dissolution in a Pteropods species after CO_2 enrichment in the water to simulate the OA's effects (Bednaršek et al., 2012).

The calcifying organisms are more sensitive to ocean acidification than others, and among them organisms with more soluble mineral forms of $CaCO_3$ in their structure (e.g., aragonite) are more sensitive than organisms with less soluble mineral forms (e.g., calcite) (Kroeker et al., 2010). To prevent the $CaCO_3$ dissolution, seawater should be supersaturated with Ca^{2+} and CO_3^{2-} ions. On the contrary, dissolved CO_2 reacting with seawater increases the amount of H^+ and HCO_3^- with a concurrent decrease in the concentration of CO_3^{2-} (Kelly and Hofmann, 2013) that, instead, encourages the $CaCO_3$ dissolution.

As shown in Figure 1-5, the increase of CO_2 in the atmosphere is correlated to the decreasing pH. Lower pH reduces the carbonate saturation of the seawater, aragonite saturation state (Ω_{Ar}) decreases as a function of decreasing pH, see equation (6), making calcification more difficult and, consequently, weakening any structures that have been formed. Although calcite is less soluble than aragonite, making it less susceptible to pH changes, the incorporation of magnesium into the two forms increases the solubility of the structures (Smith and Buddemeier, 1992; Raven et al., 2005; Gazeau et al., 2007).

For these reasons ocean acidification it is one the major threats to marine ecosystems, in particular for corals, foraminifera and coccolithophores (Gattuso et al., 1998; Kleypas et al., 1999; Barker and Elderfield, 2002; De Moel et al., 2009; Schlüter et al., 2014). Coccolithophores' calcification mechanism can be affected by several factors: temperature, salinity, nutrients (Zondervan, 2007; Feng et al., 2008) and light intensity (Gao et al., 2018). Therefore, for what is known in the literature, under the current conditions of increased CO_2, the entire marine calcifying communities seem likely to be affected in the future. However, there are species like *Emiliania huxleyi*, that show high calcification mechanisms despite the higher amount of CO_2 dissolved in the water (Beaufort et al., 2011).

Some studies indicated that OA may either enhance photosynthesis and growth in phytoplankton (Zimmerman et al., 1997; Palacios and Zimmerman, 2007; Riebesell, 2011) or have no significant effect (Tortell et al., 2000; Kim et al., 2006; Gao et al., 2018) or may even decrease productivity of the ecosystem by enhancing mitochondrial respiration and photorespiration (Wu et al., 2010; Gao et al., 2012; Mackey et al., 2015). To predict the responses of the whole calcifying organisms community will not be straightforward (Beaufort et al., 2011).

Changes in carbonate chemistry will also impact the early stages of organisms. However, highly mobile organisms with high metabolic rates may be more capable to compensate carbonate chemistry than sessile organisms, as well autotrophs with less efficient or absent carbon-concentrating mechanisms (CCMs) will be more responsive than those with efficient CCMs (Kroeker et al., 2010). The CCMs is an environmental adaptation where the organisms actively transport and accumulate inorganic carbon into their chloroplast (Ghoshal and Goyal, 2001). Studies on marine autotrophs in which CCMs are common, are showing that they do not look affected by the current seawater carbonate chemistry

(Raven and Beardall, 2003). The marine phytoplankton have adapted CCMs to support photosynthetic carbon fixation at the concentrations of CO_2 present in ocean surface waters. The efficiency of CCMs vary from species to species, coccolithophores for instance showed less efficiency compared to diatoms (Reinfelder, 2011). Even if phytoplankton share certain traits and perform similar biogeochemical functions, they are phylogenetically highly diverse (Mackey et al., 2015).

Also, some algae have developed their own CCMs but, being strongly dependent on the availability of forms of external energy (i.e., the solar radiation), these mechanisms can be hardly activated in those regions where these forms of energy are not available. Therefore, limitations of light and nutrients could be a reason why the phytoplankton does not entirely rely on the uptake of inorganic carbon even if the HCO_3^- pool is abundant (Riebesell, 2004). Because of the high variability throughout taxa, the scientific community suggested to focus the future research on the effects of multiple stressors, or the potential evolutionary outcomes of long-term growth under ocean acidification (Mackey et al., 2015).

Ocean acidification effects on organisms living in coastal areas

In addition to the general effect of ocean acidification on the calcifying organisms, the scientific community focused the attention on mussels and oysters since they are organisms living in coastal environments. They play a critical role in the community structure of coastal ecosystems and are also important economic resources for the fishery and aquaculture industries (Han et al., 2017; Lowe et al., 2019). For this reason, it is important to understand the effects of ocean acidification on them (Zhao et al., 2016, 2017) and, particularly, if some physiological adaptation mechanisms are in progress (Kelly and Hofmann 2013; Melzner et al., 2013). Several experiments were focused on commercially valuable species like the blue mussel (*Mytilus edulis*), the Pacific oyster (*Megallana gigas*) (Dubois et al., 2007; Riba et al., 2016; Doney et al., 2009) because of their importance for aquaculture, especially in northern hemisphere coastal waters. Studies of these organisms have shown a strong decline in their metabolic activities, as a consequence of decreasing pH, increasing pCO_2 and decreasing CO_3^{2-}. Differently from mussels, oysters are less susceptible to dissolution processes of their shell structure, and of delay in their metabolic activities. This can be explained by the different mineralogy of the shell (Gazeau et al., 2007). In fact the oyster *Megallana gigas* (Stenzel et al., 1963) is mainly constituted by calcite while the mussel *Mytilus edulis* contains up to 83% of aragonite (Hubbard et al., 1981).

Mussels are trying to maintain their internal pH by decreasing their metabolic activity and/or dissolving their shell (Gattuso et al., 1998; Gazeau et al., 2007). When mussels are exposed to high CO_2 levels, the increased Ca^{2+} concentration in the haemolymph causes shell dissolution (Bibby et al., 2008). The shell dissolution in calcifying organisms is therefore a way to react to the environmental stress imposed by raising levels of pCO_2 or lowering pH. Since the mussels have to spend more metabolic energy to react to the environmental stress, the growth and the reproduction are muted and the immune system becomes weaker (Bibby et al., 2008). Some species are able to maintain their calcified structures under an acidifying water column, but this requires more energy. If nutrients are abundant, some of these species can keep constant the calcification rate by increasing feeding rate and food intake (Melzner et al., 2013; Thomsen et al., 2013). Even so, the shell can become thinner and weaker following higher rates of dissolution (Talmage and Gobler, 2010; Kwiatkowski et al., 2016). The fact that these organisms evidence some recovery strategies under laboratory experimental conditions does not mean that under the field conditions populations of these species are not ultimately vulnerable (Widdicombe and Spicer, 2008). The resulting changes in marine chemistry are even more complex in coastal ecosystems due to a multitude of drivers influencing pH, including nutrient input from the land, watershed processes and tidal exchange (Duarte et al., 2013). In addition, marine animals are exposed to many other anthropogenic stressors including decreasing salinity, hypoxia and nutrient enrichment (Przeslawski et al., 2015). The change of the water chemistry might be faster than what was experimentally tested on laboratory bases. Some studies combined the effects of changing temperature and simultaneous changing pH, because the combining effects of multiple stressors are greater compared with the individual effect of one only stressor (Przeslawski et al., 2015; Gunderson et al., 2016). Research focusing on multiple stressors is required to represent real field scenarios (Munday et al., 2013; Przeslawski et al., 2015), which should also include the increase of organisms' vulnerability to be predated (Zeebe, 2012).

1.3 Climate change and future actions

The ocean acidification and the consequences for the marine environment, are just one of the aspects of a wider issue known as “climate change”. The increase of CO_2 in the atmosphere due to human activities has in fact other consequences, because it intensified the natural greenhouse effect. This resulted in an increase of the Earth ‘s global temperature of 0.74°C ±0.18°C between 1906 and 2006 (Solomon, 2007). This phenomenon is known as global warming. The effects of global warming are many and are impacting the whole ecosystem, including biodiversity assemblage (Habiba et al., 2002; Lovejoy, 2008), physical processes, such as rainfall, flooding (Tarhule, 2005; Guhathakurta et al., 2011; Smith et al., 2011; Zhang et al., 2018) which can significantly increase the organic and inorganic carbon transport to the coast (Bauer et al., 2013).

The current climate change scenario could be mitigated by actions and collaboration between science and politics. The following picture shows a future projection of the interrelation between pH, carbon dioxide and carbonate ions under the hypothesis that the current emissions will not be reduced.

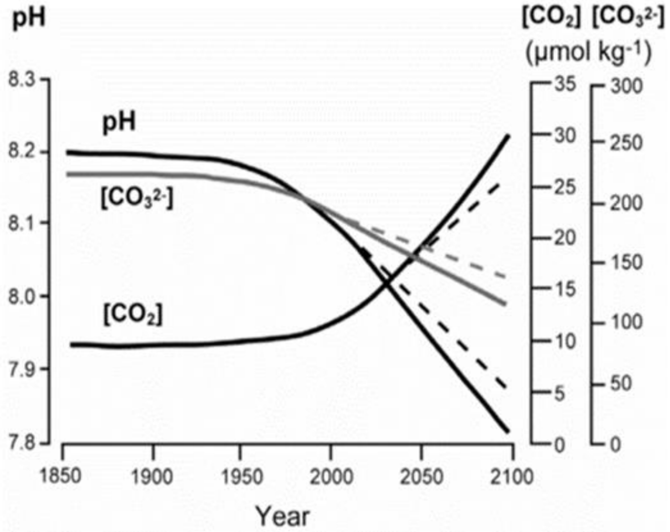


Figure 1-7 Seawater pH and the dissolved carbon dioxide (CO_2) and carbonate ion (CO_3^{2-}) concentrations in the surface layer of the ocean assuming a “business as usual” (IS92a) anthropogenic CO_2 emission scenario. Dashed lines represent the predicted changes in carbonate chemistry if CO_2 emissions are reduced according to the Kyoto Protocol (Riebesell 2004).

In 2015 there was the United Nations Climate Change Conference in Paris also known as COP21, during which 197 countries agreed to reduce the carbon emissions, in particular the attending countries. The long-term target was established to keep the increase of global temperature below 2°C above the pre-industrial levels struggling to limit this increase within 1.5°C. The identified strategies were an immediate reduction of emissions that will presumably take longer for the developing countries to achieve a balance between emissions and removals in the second half of the century. Additionally, the countries involved in the agreement set a long-term goal for adaptation, which includes the ability to adapt the societies to adverse conditions due to climate change, to foster climate resilience and to pursue low greenhouse gas emissions policies, in order to protect the food production. The finance flow should be consistent with a pathway towards low greenhouse gas emissions and climate-resilient development (https://unfccc.int/process-and-meetings/the-paris-agreement/the-parisagreement/nationally-determined-contributions-ndcs). In Figure 1-8 a prediction of the future trends following the adopted policies is represented.

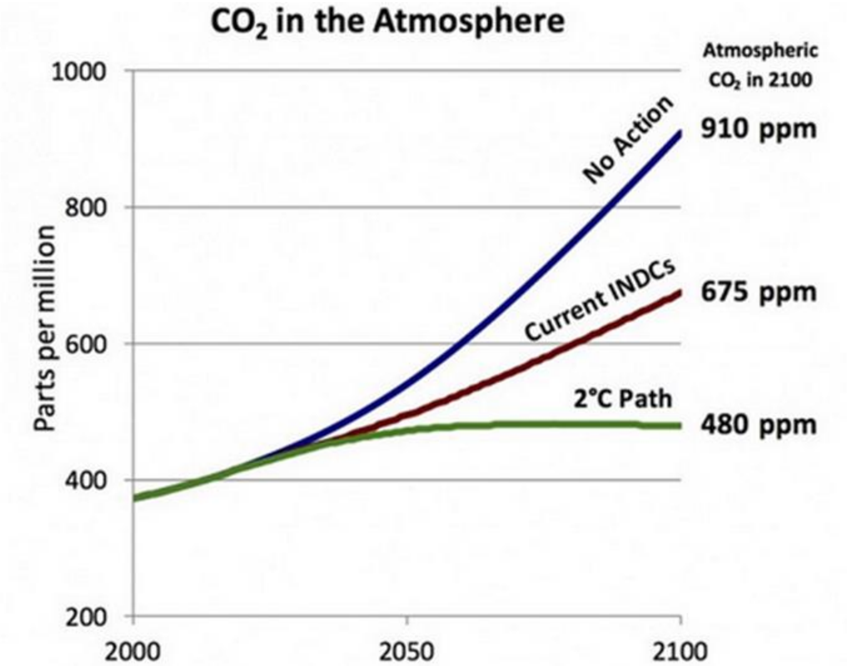


Figure 1-8 Three different pathways of CO_2 increase in the next years according to the action plan approach. The blue curve represents the case of no action, where the CO_2 will continue to grow in the next years. The red curve, the Intended Nationally Determined Contributions (INDCs), represents the country ambition to reduce the current CO_2 level as long-term goal (a commitment to a 40% reduction in emission by 2030 compared to 1990) and the green curve represents the achievement of each country.(https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement/nationally-determined-contributions-ndcs).

1.4 Watershed inputs and coastal biogeochemical processes

In addition to the CO_2 source from the atmosphere, coastal areas have additional sources of carbon, organic and inorganic materials that could interfere with biogeochemical cycles (Duarte et al., 2013), leading to buffer or to intensify the current ocean acidification. Drivers of acidification in coastal areas exist that are independent of fossil-fuel contributions and have operated over evolutionary timescales, but all are now influenced by human activities (Hofmann et al., 2010). By following there is a list of these possible drivers:

- Deposition of reactive nitrogen and sulphur from fossil-fuel combustion and agriculture, that can reduce alkalinity in coastal waters (Doney, 2007).
- Inputs of river water, which typically are more acidic than receiving waters, that further reduce alkalinity, as well as the interactions with bottom sediments (Waldbusser and Salisbury, 2014).
- Oxidation of organic matter from upland areas that can reduce pH and influence carbonate system variables (Gattuso et al., 1998).

1.4.1 Rivers

The watershed inputs should be considered in the studies related to the coastal areas, because additional nutrients and organic matter accumulated in the catchment area are delivered to the river stream (Young and Huryn, 1999). For this reason, the land use can affect the rate of primary production due to the increase of nutrients availability (Field et al. 1998; Fuß et al., 2017; O'Boyle et al., 2013; Pellerin et al., 2012). The supply of organic carbon from land makes the fluvial ecosystem mostly heterotrophic, and they are sinks of organic carbon (Duarte and Prairie 2005; Battin et al., 2009). Because of the additional delivery of nutrients to the coast, rivers contribute to the coastal biogeochemical cycles and sometimes to eutrophication processes (Borges and Gypens, 2010). The consequences of eutrophication are: increasing harmful algal blooms and a decrease of water quality, effects that are particularly visible in coastal areas since they are more compromised by human activities on land, industrialization and climate change effects (Rabalais et al., 2009).

1.4.2 Submarine groundwater discharge, SGD

SGD includes any kind of water flow to the continental margins coming from the seabed. All water flows are considered SGD independently on the composition or origin of the water

(Burnett et al., 2003). The scientific community recognized the importance of the study of groundwater as a source of new chemicals to the coastal sea, first of all because SGD has been estimated to be 3-4 times greater than the freshwater flow into the oceans from rivers (Kwon, 2014), and secondly, because it is a source of nutrients and carbonates that may have significant effects on the quality of surface water bodies (Moore, 1999; Burnett et al., 2003; Hwang et al., 2005; Lee and Kim 2007; Niencheski et al., 2007; Lee et al., 2009; McCoy and Corbett, 2009; Moore 2010; Santos et al., 2014). The higher concentration of nutrients present in groundwater by comparison to surface waters leads to a significant impact of SGD to coastal waters in terms of eutrophication processes (Valiela et al., 1990). For example, the increase of algal blooms in the coastal water (e.g., brown tides) is in some cases due to a high nitrate level dissolved in groundwater (Moore, 1999), as for instance observed in Long Island by Laroche et al., (1997).

SGD can alter the salinity, temperature and chemistry of seawater, introducing anthropogenic substances from land including pathogens, toxins and other pollutants, and supports aquatic plants and algae by providing nutrients (Burnett et al., 2006; Paytan et al., 2006). It has been well documented that SGD affects the biogeochemical cycling of nutrients (Liu et al., 2014; Rocha et al., 2015), acting as a source of DIC and TA to the ocean, as observed in several studies (Charette et al., 2013; Cyronak et al., 2013; Cyronak et al., 2014; Jeffrey et al., 2016; Liu et al., 2012; Liu et al., 2014; Cyronak et al., 2018). It is estimated that SGD delivery of carbon into the coastal system is 27% of the total riverine carbon flux on a global scale (Cole et al., 2007).

The direct flow of groundwater into the ocean and the chemical reactions of meteoric and sea water mixtures within coastal aquifers are processes that have been largely ignored in estimating material exchange between the land and the sea (Moore, 2010). Based on the definition of SGD it is possible to recognise the presence of different kinds of driving forces:

- the hydraulic gradient from the land;
- the advective flow of recirculated seawater through sediments (Burnett et al., 2003).

The advantage of defining groundwater discharge as a flow of water from the seabed to the marine environment (including fresh, saline and brackish SGD) comes from considering discharges of both terrestrial groundwater and recirculated seawater. It is obvious that in the coastal ecosystem the seawater intrusions into the sediment are a common process (Massel, 2005).

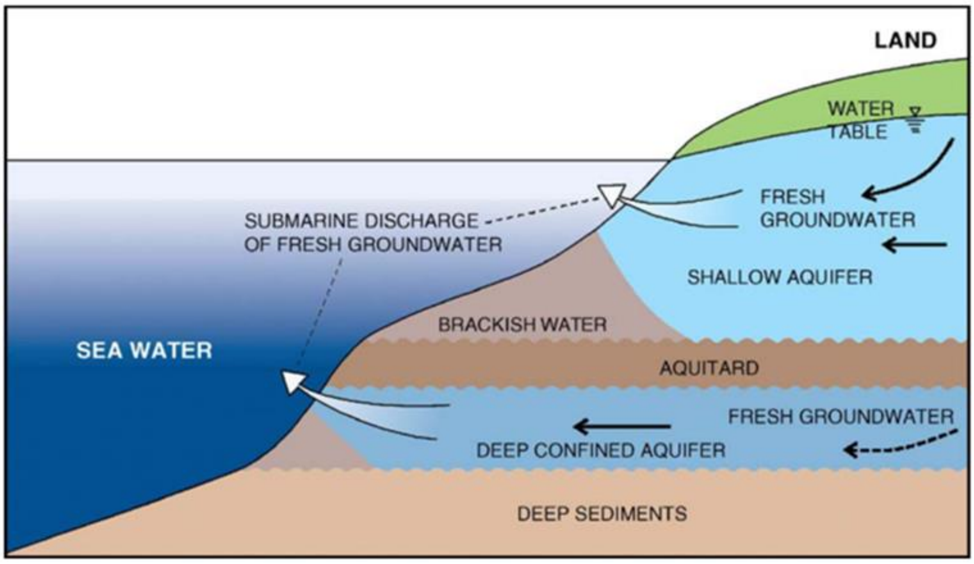


Figure 1-9 General scheme of SGD. Groundwater located in the shallow, unconfined aquifer can discharge directly to the coastal ocean or can mix with seawater already in the sediment and be discharged as brackish water. SGD is determined by both terrestrial and marine forces (Burnett et al., 2006).

1.5 Coastal carbonate chemistry and Net community production

The understanding of carbonate cycle in coastal areas is more complex than open ocean because of the land use modification, nutrient inputs, wetland degradation in addition to the climate change that adds further complexity to understand if the changes in coastal carbonate chemistry have natural or anthropogenic origin (Bauer et al., 2013) .

Bauer et al., (2013) reconstructed the carbon system in the pre-industrial continental shelf (heterotrophic): the ocean has been identified as a source of CO_2 to the atmosphere, Figure 1-10, where the pCO_2 was 280 ppm. After the changes in the twentieth century due to the increasing atmospheric pCO_2, which reached 380 ppm, the coastal ocean became a CO_2 sink (autotrophic). The increase of pCO_2 in coastal areas is due to the CO_2 uptake from the atmosphere and to the external supply of inorganic carbon, which includes the DIC transport from rivers (Raymond et al., 1997; Cai and Wang, 1998; Mackenzie et al., 2004; Laruelle et al., 2010; Cai et al., 2011) and/or SGD (Cai et al., 2003). The increase of DIC in the coastal area would therefore lead to an increased DIC inventory in the open ocean (Laruelle et al., 2018). However, Bauer et al. (2013) (Figure 1-10) proposed an alternative mechanism which did not require changes in the shelf NCP, but only increased the physical uptake of atmospheric CO_2. The reason why the author Bauer et al., (2013) suggested this, is because the atmospheric levels of CO_2 have risen to a much greater rate than those on the shelf, and it could provide a first understanding about why the ocean shifts from source to sink of CO_2. However, as previously said the inputs from rivers, estuaries and wetlands add levels of complexity to predict future changes in the organic and inorganic carbon fluxes in the coastal areas (Cai et al., 2011; Cai, 2011).

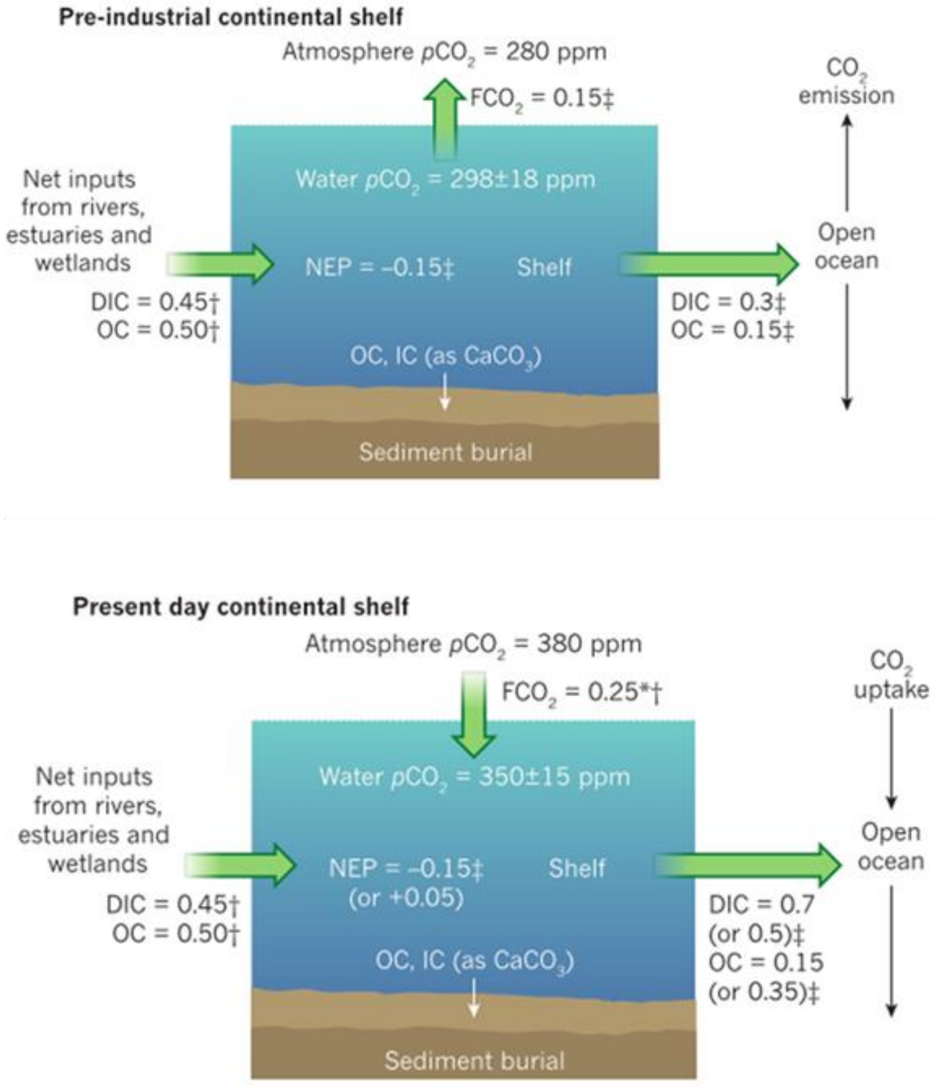


Figure 1-10 The pCO_2 levels, net ecosystem production and organic and inorganic carbon fluxes in pre-industrial and current continental shelves, all carbon fluxes showed, including Net Ecosystem Production indicated as NEP have units of Pg C yr^{-1} (Bauer et al., 2013).

Net Community Production (NCP), or NEP as indicated in Figure 1-10, is defined as the difference between Primary Production (PP) and Respiration (R) (Kempe and Pegler, 1991; Staehr et al., 2010) and represents the organic carbon cycle; these two variables offer important insights into the carbon cycle (Stanley et al., 2010). The Net Community

Calcification (NCC) represents the difference between calcification and dissolution, therefore represents the inorganic carbon cycle. The NCP is positive, net autotrophic system, when production exceeds respiration, and negative, net heterotrophic system, (as it likely was, during the pre-industrial period (Bauer et al., 2013)) when respiration exceeds production (Caffrey 2004). The positive value of NCC implies that carbonate preservation and calcification are greater than carbonate dissolution.

NCP is an important factor to be measured in coastal and estuarine environments because it allows to understand whether such environments are sources or sinks of carbon (Smith et al., 1991; Hollinbaugh, 1997; Gattuso et al., 1998). However, NCP responds to seasonal drivers and is spatially variable depending on the location and magnitude of marine organic inputs (Kempe and Pegler, 1991; Hollinbaugh, 1997).

In coastal areas studies, the TA:DIC relation has been used to understand how the inorganic NCC (calcification/dissolution) is related to organic NCP (photosynthesis/respiration): these two parameters describe the whole system metabolism (Richardson et al., 2017). TA:DIC relation in coastal areas allows to understand if the system accelerates acidification or increases the buffer capacity, especially in areas where there are additional sources of carbonates. Basically, if the ratio between TA:DIC is lower than 1, the DIC concentration in the water column is higher than TA. Under these circumstances the increase of DIC might be due to a decrease of photosynthesis efficiency and as a consequence, the acidification processes are accelerated. Reversely, if TA:DIC relation is greater than 1, the decrease of DIC over TA is due to the uptake of CO_2 during photosynthesis and the system buffer capacity increases . The changes in TA:DIC slope leads to different acidification scenarios: these changes can have spatial and temporal variations affecting the calcifying organisms and the benthic community (Tribble et al., 1990; Shamberger et al., 2014; Shaw et al., 2015).

A few authors studied the TA :DIC relation in a coral reef community (Lantz et al., 2014; Cyronak et al., 2018). In the following Figure 1-11, TA versus DIC is plotted and the relative proportion of NCP and NCC is shown. According to the relative contribution from different metabolic processes, the resulting change in TA and DIC influences seawater pH differently (Cyronak et al., 2018). Photosynthesis and $CaCO_3$ dissolution increase seawater pH while respiration and $CaCO_3$ precipitation decrease pH. When NCP and NCC are closely balanced (i.e., TA-DIC slope ~1), there is a little change in seawater pH, as observed in the open ocean (Hofmann et al., 2011). Conversely, with the change of TA-DIC slope, the pH can be altered. In the Figure 1-11 the pH calculation at each TA and DIC value is made assuming constant temperature (25˚C) and salinity (35). In the figure, the net $CaCO_3$ precipitation and the net autotrophy (+NCP) are represented in the green area +NCC, the net dissolution (-NCC) and net heterotrophy (-NCP), are represented in pink/red area. With the increase of DIC the TA-DIC slope will decrease as well, with a consequent decrease of coral reef pH (pHr) compared to the ocean pH (pHo) (under constant salinity and temperature conditions) (Cyronak et al., 2018).

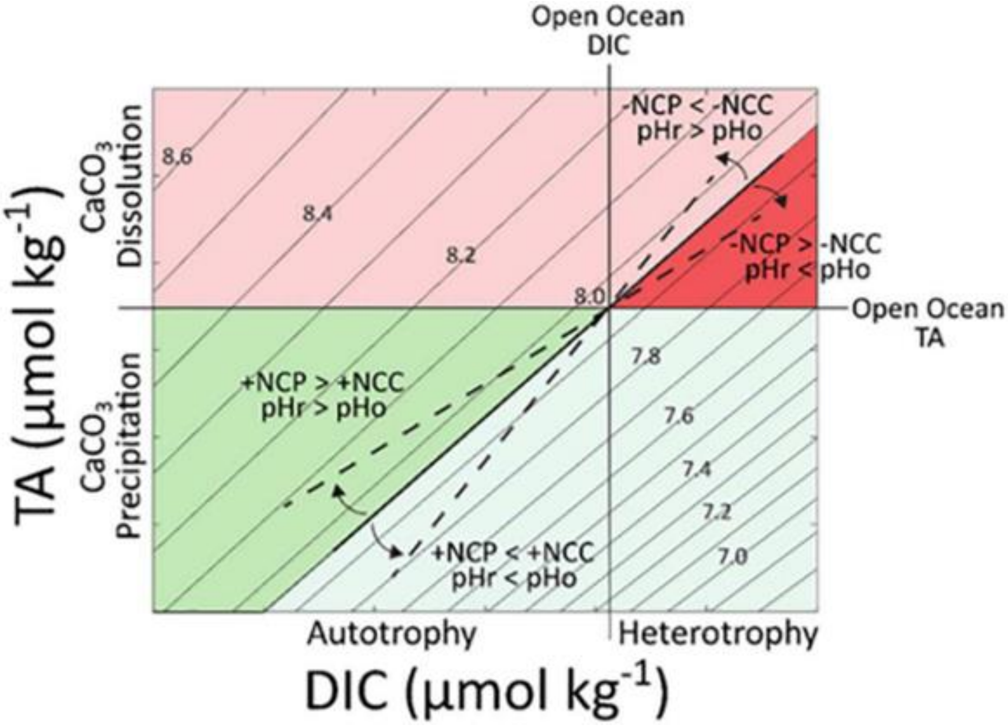


Figure 1-11 TA versus DIC are plotted, the different slopes representing the balance between organic and inorganic metabolism NCP:NCC graph from (Cyronak et al., 2018).

1.5.1 Net community production quantification

The TA-DIC slope is then used in the aquatic ecosystem to understand the balance between organic and inorganic metabolism. To quantify the NCP, the measurements of diel dissolved oxygen (DO) are widely used (Cole et al., 2000; Staehr and Sand-jensen 2007; Hanson et al., 2008; Staehr et al., 2010; Karakaya 2011; Hu et al., 2015). The diel DO provides a representative evaluation of NCP, showing the spatial and temporal variability of this parameter (Caffrey, 2003, 2004; Bogert et al., 2007; Hu et al., 2015). The ecosystem metabolism is influenced by different physical, chemical, and biological features, such as temperature, irradiance, wind speed, pH, DOC, Dissolved Inorganic Nitrogen (DIN), Total Phosphorus (TP), chlorophyll-a, and phytoplankton, etc. (Hu et al., 2015; Cole et al., 2007; Giorgio 1994; Hanson et al., 2003; Caffrey, 2004) that can vary according to the characteristics of the study areas and the time of the year. In addition to carbon, also nutrients delivered to the coast play a role in the coastal biogeochemical cycles: nitrogen, phosphorus and silicate are limiting factors for the primary productivity in coastal ecosystems (Prasad, 2012). In the open ocean the balance between carbon, nitrogen, phosphorus and silicate is described by the Redfield's ratio C:Si:N:P 106:15:16:1 (Redfield, 1958; Brzezinski, 1985). The increase in the molar ratio between these limiting nutrients might lead to an increase of NCP and possible eutrophication processes (Howarth and Marino, 2006). The enrichment of coastal waters with these nutrients, (particularly the nitrogen) can alter the macroalgae community composition by progressive selection for fast-growing algae (phytoplankton, microphytobenthos and macroalgae) (Borum, 1996; Cohen and Fong 2006). Indeed, nitrogen delivery to the coast is considered one of the main drivers of eutrophication in marine systems (Breitburg et al., 2009). Coastal carbonate chemistry is expected to be strongly regulated by changes in biological activity related to the increase of anthropogenic nutrient delivery by rivers, groundwater, and atmosphere (Borges and Gypens, 2010). The molar concentration of nitrogen in the SGD normally exceed Redfield's ratio (McGarrigle et al., 2010).

Land ocean interactions and the different factors that can regulate the coastal metabolism should be considered in order to evaluate the NCP. Land-Ocean Interactions in the Coastal Zone (LOICZ) project has led to the development of a modelling approach to estimate the NCP and biogeochemical functions of coastal aquatic systems (Gordon et al., 1996). The model is based on the budget model of non-conservative materials: DIN and Dissolved Inorganic Phosphate (DIP) (or Soluble Reactive Phosphate SRP). Deviations of budgets/concentrations (DIP and DIN) from predicted values are assumed to depend upon non-conservative processes or internal transformations, and basically represent the net difference between nutrient sources and sinks (Giordani et al., 2008).

1.6 Synopsis

From what has been explored in the literature, the importance of understanding how biogeochemical cycles are working in coastal areas arose, and specifically for what concerns coastal carbonate chemistry, the need to understand the role of freshwater discharge on coastal carbonate chemistry. The carbonate chemistry and the ocean buffer capacity are governed by the reactions occurring in the water-atmosphere interface, therefore the CO_2 concentration in the atmosphere can be recognised as the main driver in changing carbonate chemistry in the open ocean. Conversely, the coastal area receives freshwater input that can be derived from rivers, streams or SGD. Studying the composition of these waters is fundamentally important to understand their impact to the coast, and how this impact can affect the carbonate biogeochemistry and net community production.

Ocean acidification is a topic that is extensively discussed nowadays, mainly for the effects that decreasing pH has on calcifying organisms and the relative impacts (e.g., delay in growth, reproduction, and vulnerability to predation) that could have on the entire food chain. Several authors predicted the decrease of pH in the open ocean according to an increase of CO_2 in the atmosphere in case the burning of fossil fuels will not decrease by 2100. In the coast the situations are more complex and multiple drivers can act simultaneously changing the coastal ocean buffer capacity. Watershed input is considered an important driver of coastal areas biogeochemistry, since it is a supply of nutrients, organic and inorganic carbon that cannot be overlooked. The human activities on land, grazing and agriculture can further intensify the delivery of nutrients Figure 1-12. The supply of TA and DIC from the freshwater discharge might change their ratio in the coastal areas, affecting NCP. The coast can potentially act as a source of DIC towards the open ocean intensifying current ocean acidification. Therefore, the coastal carbonate chemistry and the role of freshwater input is a topic that needs to be explored.

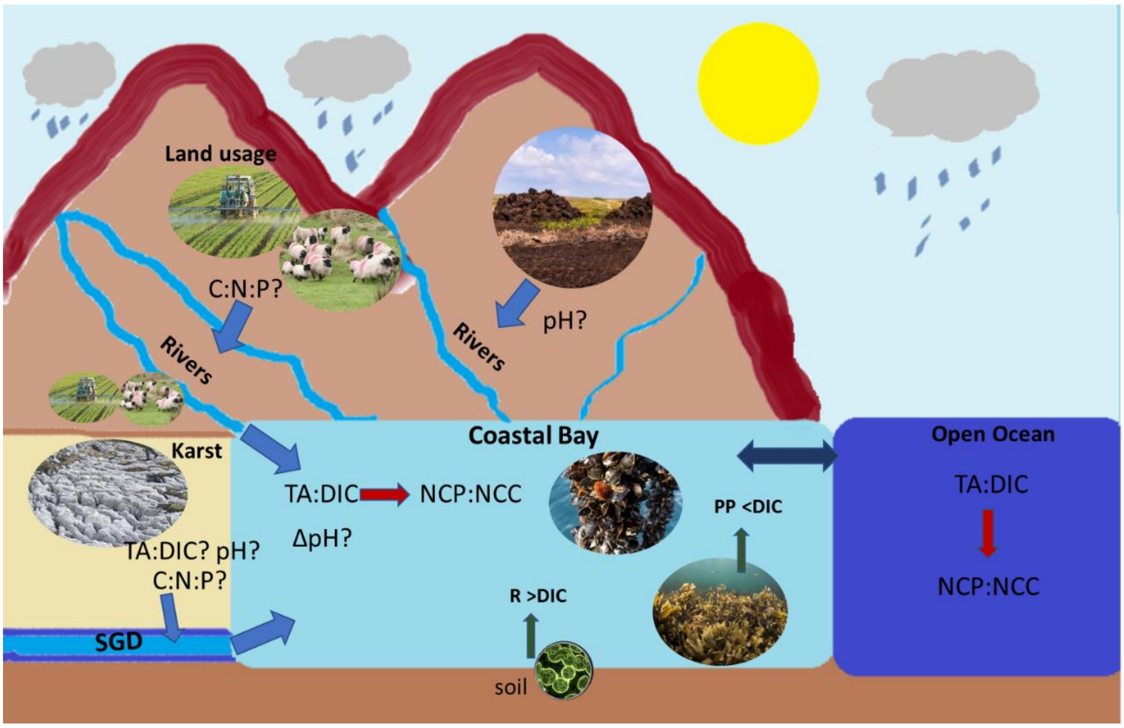


Figure 1-12 Coastal bay is represented schematically. Rivers and SGD are carrying nutrients and/or TA and DIC, potentially affecting TA:DIC ratio and in turn NCP. The land usage might add further nutrients to the rivers that will be then discharged on the coastal areas. The water coming from subterranean estuaries in the karstic areas might be enriched in TA due to the rocks weathering; this phenomenon might be exacerbated because of climate change and possible flooding events. The coastal areas might have different responses to the land derived inputs. Freshwater inputs can drive the changes in the coastal carbonate chemistry and community production (Primary Production PP and Respiration R).

2 Materials and Methods

In the general introduction chapter, the importance of freshwater input as an additional source of nutrients and alkalinity to the coast has been explained. The freshwater inputs can be in the form of surface runoff or SGD. The organic and inorganic composition of the freshwater inputs depend on the watershed geology and/ or human activities that could affect the water components. The aim of this research is to understand the role of SGD in coastal carbonate biogeochemistry. To do this, a comparison approach of areas with contrasting watershed inputs was considered appropriate to understand their effect on the coastal areas. The concentrations of nutrients delivered by SGD may differ from that delivered by a surface estuary of similar salinity and the same initial inland nitrate, phosphate and carbon concentrations. In surface estuaries the nutrients are assimilated from the primary producers (Paerl, 2009), and the CO_2 dissolved in the water will be equilibrated with the CO_2 in the atmosphere. Differently in the subterranean estuary the nutrients are not consumed, and the CO_2 is accumulated.

The selected study sites are Kinvarra Bay and Killary Harbour in Western Ireland. The research questions arisen from the analysis of the literature are presented in the next paragraph, followed by the study areas description.

2.1 Research questions

- ***Which are the main drivers of carbonate chemistry along the Irish coastal sea?***

From the literature studies it has been observed that different types of freshwater input can lead to different water chemical compositions compared to the open ocean (e.g., high nutrients level or high alkalinity). The human activities on the land can have a significant role in the coastal water composition and eutrophication, therefore, the first question that arises is which freshwater typology are present in the Irish coastlines and how they can drive the changes in coastal carbonate chemistry. The hypotheses that have to be tested are the following (the subscript H_0 refers to the null hypothesis; the subscript H_1 refers to the alternative hypothesis):

H_1: The carbonate system variability of TA-DIC and pH is related to the type of freshwater input and watershed geology.

H_0: TA-DIC and pH are varying according with local biological processes not correlated with the type of freshwater discharge.

- ***What are the pH dynamics in coastal areas characterized by a contrasting origin of freshwater inputs?***

Kinvarra Bay and Killary Harbour are characterized by different types of freshwater discharge. The first one is dominated by SGD and the second one by surface runoff, in the form of a river and several seasonal streams. We accept that: a) open exchange of CO_2 with the atmosphere occurs with river water and that the freshwater flux into the bay varies with precipitation on a seasonal basis; b) conversely, groundwater accumulates CO_2 produced by soil mineralization processes during percolation, and the exchange of CO_2 with the atmosphere is limited while it travels seaward. Furthermore, SGD into the bay, being controlled by the tide, varies in tidal as well as seasonal timescales. Comparison of these two systems therefore allows the testing of the following hypothesis:

H_1: The timescale of pH variability in lower salinity areas of a marine system is controlled by freshwater input dynamics.

H_0: The timescale of pH variability is similar in both the sites, suggesting that this is independent of freshwater input dynamics.

- ***What is the TA:DIC relation in estuarine areas characterized by contrasting types of freshwater input?***

Differential controls on the amount of DIC transported by freshwater sources into marine areas will be imposed by exposure time of the water to the atmosphere, which controls CO_2 exchange, while on the other hand, the TA will depend on exposure time with bedrock and its mineral composition. The mineral reactions that could affect the TA are for instance calcite dissolution occurring in limestone areas:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \tag{12}$$

Or the hydrolysis of rocks that contain feldspars minerals: an example might be the albite hydrolysis (which requires CO_2) (Suchet et al., 2003):

$$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 2Na^+ + 4H_4SiO_4$$

(13)

Freshwater delivered through a groundwater system will therefore have a different carbonate system composition because it has spent more time in contact with bedrock with limited interaction with the atmosphere. It follows that we can test the following hypothesis:

H_1: The TA:DIC relationship at the low salinity areas of the two sites will be significantly different, and directly linked to freshwater composition, indicating the dominant control exerted by type of freshwater input over the dynamics of local carbonate system. Watershed input composition becomes a dominant driver of TA:DIC portioning in marine systems.

H_0: If TA:DIC relationship is driven by other factors, including processes occurring in the marine domain, the TA:DIC ratio will not be correlated with freshwater composition, and could be causally and statistically indistinguishable.

- ***How do SGD and rivers influence the TA and DIC relation in the water column over diurnal and seasonal timescales?***

The TA:DIC relation within marine areas of restricted exchange with the open sea will provide information regarding the status of the coastal carbonate system and how it evolves over the time. If the water column chemical composition is controlled primarily by biological drivers (NCP or net community production, driven by the balance between PP and R) the systems will exhibit similar scales of carbonate system variability and these will be related to the NCP variations. Conversely if physical processes (e.g. hydrology, tidal excursion and mixing) are the primary control over water column carbonate chemistry the TA:DIC relationship will be unrelated to NCP and quite different in the two systems. The following hypothesis have to be tested:

H_1: The carbonate system in coastal areas as described by the TA:DIC relation is under biological control, i.e, causally co-varies with NCP.

H_0: The carbonate system in coastal areas as described by the TA:DIC relation is controlled by fresh-water sea-water mixing.

2.2 Study areas

2.2.1 Kinvarra Bay

Kinvarra Bay (53° 09' N, 8° 56' W) is elongated in the NNW-SSE direction and connects to the southern edge of Galway Bay, which opens to the Atlantic Ocean. The bay is inserted into a karstic area, and as it can be observed from Figure 2-1, it is characterized by limestone geology. The bay can be considered small: the maximum submerged areas during high tide is 5.97 km^2 (approximately 4.5 km long), with a volume of approximately $21 \times 10^6\ m^3$ (with an average depth of 4.2 meters) as determined by the analysis of LANDSAT imageries by Rocha et al., (2015). Freshwater springs have been identified in previous studies as the principal freshwater sources feeding the area (Cave and Henry 2011). The water discharging into Kinvarra Bay is coming from the Gort-Kinvara aquifer (Cave and Henry, 2011; Gill et al., 2013). The water discharge in Kinvarra Bay is mainly through the subterranean estuary (the SGD springs) and part in the form of runoff. The whole drainage zone has an area of 483.41 km^2 (EPA, 2011). There is one main spring that has been identified by (Rocha et al., 2015; Schubert et al., 2015) and has been called Kinvarra Castle spring. Periodically, there may be shallow rivulets entering the bay during periods of high discharge.

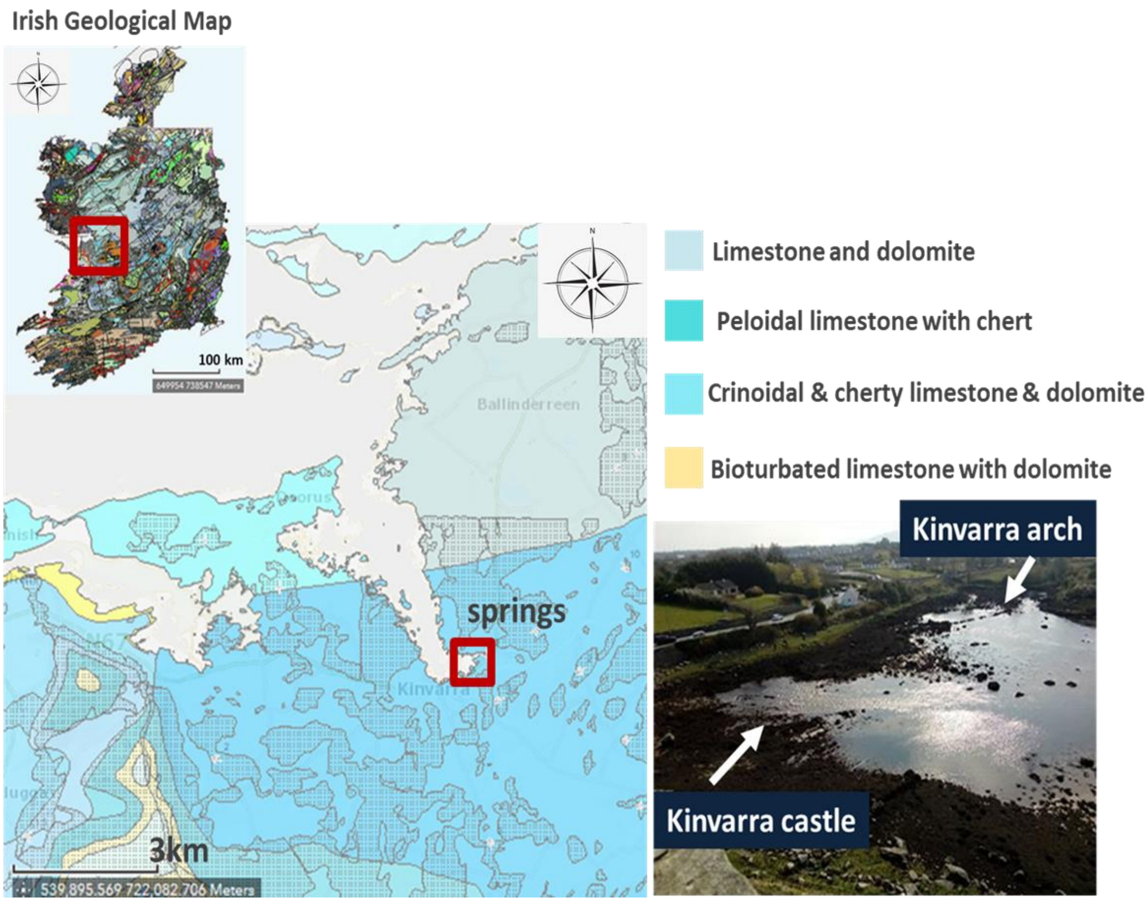


Figure 2-1 Kinvarra Bay geological map. The main geological feature is the limestone. On the right side of the graph the principal springs in Kinvarra Bay are indicated.

Previous literature studies

Kinvarra Bay was largely studied in the last years because it is characterized by several SGD springs and is a fascinating area for its complex karst system. Kinvarra Bay is an important aquaculture hotspot: following the Bord Iascaigh Mhara annual reports, the average annual shellfish production in the last ten years was about 120 tonnes. *Mytilus edulis* and the pacific oyster *Megallana gigas* are cultivated. Wells and groundwater springs are constantly monitored by the Environmental Protection Agency (EPA). The west Ireland population relies on water coming from the ground, for cattle's and their sustainment, therefore, monitoring programmes are necessary.

Kinvarra's hydrogeology has been studied by several authors in the past years and a few hydrogeological models were made in order to quantify the SGD amount into the bay (McCormack et al., 2014; 2017, Gill et al., 2013). Furthermore, due to the complexity of this area, a few authors approached the study of this karst system using tracer methods to understand the connections between the main springs of the area and the boreholes located around (Schubert et al., 2014; 2015). As previously discussed, SGD could be a huge source of TA, DIC and nutrients to the coastal areas, therefore, a few studies were focused on the compositions of this water and on the daily fluctuation of these parameters (Rocha et al., 2015; 2016; Kelly, 2018). In the study of McCormack et al., (2014) the two springs feeding Kinvarra were analysed and Kinvarra west showed a low bicarbonate water with mean alkalinity of 156 mg/l $CaCO_3$ whereas Kinvarra East, or Kinvarra Castle exhibited higher alkalinity concentrations (mean: 260 mg/l $CaCO_3$) due to its autogenic, bicarbonate rich recharge. However, since in the study of (Schubert et al., 2015) Kinvarra castle has been identified as the main freshwater source into the bay, this site has been selected for this study.

2.2.2 Killary Harbour

Killary Harbour (53° 36' N, 9° 47' W) is a fjord-like inlet, at the boundary between counties Galway and Mayo on the west coast of Ireland. Running in a south-easterly direction and flanked by the Mweelrea mountains to the north and the Maumturk mountains to the south, it is 13 km long and is approximately 700 m wide with a surface area of approximately 9.1 Km^2 (Nunes et al., 2011). It has a mean depth of 15 m; the harbour is deepest (42 m) just inside the mouth and immediately outside (Keegan and Mercer, 1986). The geology is characterized by shale, sandstone and conglomerates (Keegan and Mercer, 1986). Freshwater input to the bay is dominated by river flow, draining a catchment of approximately 260 km^2 (Mcmahon and Patching, 1984). The main rivers feeding the harbour are the Erriff and Bundorragha: their catchment areas are 176 km^2 and 51 km^2, and respectively deliver ~ 63% and ~ 19% of total freshwater flow to the system, respectively (Anon, 1958; Keegan and Mercer, 1986; Donohue, 2012). The rest of the discharge to the bay comes from streams draining small catchment areas, some of them seasonal (Keegan and Mercer, 1986; Costelloe et al., 1995).

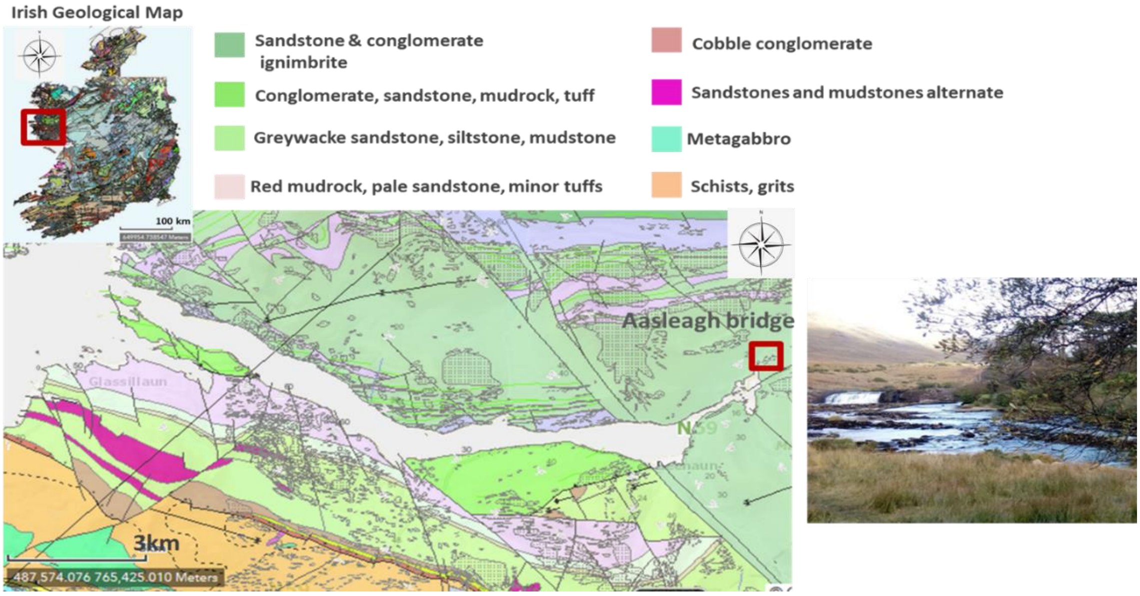


Figure 2-2 Killary Harbour geological map. The main geological feature is sandstone conglomerates and schists. On the right side of the figure Erriff River, the principal river that feeds Killary is shown.

Killary Harbour is an important area for the Irish aquaculture, in fact both mussel’s and salmon’s aquacultures are present. From the monitor program of the Bord Iascaigh Mhara, the shellfish aquaculture in Killary (*Mytilus edulis* is cultivated) produce an annual average of 800 t/y, based on data over ten years’ time. Due to its geographical location the hydrography off the west coast of Ireland provides unique salmon producing conditions: the fish are grown in exposed marine sites, experiencing stronger tidal currents and higher wave energy (BIM, 2019).

Figure 2-3 Aquaculture ropes along Killary Harbour. Mussels are grown on longlines from which 8 m long dropper ropes are suspended (Nunes et al., 2011).

Previous literature studies

In the 1980's a few literature studies focused on the nutrients and carbon fluxes from the freshwater input in Killary Harbour (Mcmahon and Patching, 1984; Roden and Burnell, 1984). These surveys took place in 1974, before the aquaculture began (Nunes et al., 2011). Salinity and temperature analysis of Killary Harbour were measured in the study of Keegan (1986) and the results showed a clear stratification. In the upper layer of the fjord there is a removal of saline water which is compensated by a net inflow of saline water into the lower layer at the mouth (Keegan, 1986). Keegan (1986) described Killary as "a partially mixed estuary with large variations in water structure that depend on river run-off and local wind".

Recently, there were a few studies analysing Killary ecological status, that was defined as an eutrophication status moderate low by (Nunes et al., 2011) and a few studies were focused on the physiological status and growth of the benthic organisms and phytoplankton growth (Rodhouse et al., 1987; Rodhouse and Roden, 2007).

2.3 Sampling and laboratory analysis

Coastal carbonate chemistry is a topic that was not deeply investigated yet. The sampling strategy adopted in this thesis can be considered innovative since it provides information about the status of the carbonate chemistry in two areas with contrasting watershed input. Furthermore, because the sampling was **conducted in different discharge conditions (including the exceptional dry season July 2018**), it follows that the **data acquired are unique**. Each survey was conducted on both: the coastal embayment and in their freshwater end-member, **the variations were analysed accordingly**. The recent work of McGrath et al., 2019 also analysed and compared contrasting Irish coastline, however the sampling were conducted during winter period and during productive season, not necessarily according to discharge conditions. This is the first work that aims to identify specifically the role of SGD and its contribution to coastal acidification.

For what concerns data analysis, the scientific community emphasizes the importance of using approved and updated standard methods for the ocean studies. In 2021 it was conducted a workshop to discuss about the standard methods used in the ocean community and the development of methods into community-wide best practices. As marine biologist and biogeochemist I co-lead the surface radiation workshop session (Cronin, Riihimaki, Guerra et al., 2021). The debate on the surface radiation topic is still open and to build ocean best practices is important to consider the needs of the whole ocean scientists included biogeochemists. In the present thesis work, the ocean best practices guidelines have been used for the analysis of carbonate system.

The data acquired during this project about coastal carbonate chemistry will be made available on Trinity's Access to Research Archive (TARA) the open access repository in TCD.

2.3.1 Sampling strategy

In order to address the research questions, it was necessary to obtain spatial and temporal variability of the carbonate system in the two selected study areas.

The spatial variability was addressed collecting samples in a transect from a boat. This samples' collection covered the areas from the head to the mouth of the bays, including fresh and ocean end-members. This strategy is useful to understand the mixing processes between the ocean and the freshwater end-members, identifying the main drivers of the system variability, according to the magnitude of freshwater discharge.

The freshwater discharge depends on meteorological conditions, e.g., rainfall; and its chemical composition could change according to the increase of weathering and land usage. Therefore, to capture the temporal variability of the system, it is important to sample in different periods of the year, which implies different magnitudes of freshwater discharge and different water chemical composition (e.g., loading of alkalinity and nutrients). The temporal variability of the system might be also due to other factors; such as temperature, irradiance, wind speed, rainfall etc. (Hu et al., 2015; Cole et al., 2007; Giorgio 1994; Hanson et al., 2003; Caffrey, 2004). These factors show variations over the year.

Five sampling surveys have been carried out in Killary Harbour, respectively on: February, July and October 2018, January, April and September 2019; and five in Kinvarra Bay on: July and October 2018 and January, April and August 2019.

2.3.2 Transects strategy

During each collection campaign the areas were covered with six sampling locations inside the bay, each of them called "station", with the addition of the ocean end-member and freshwater end member (SGD or rivers accordingly): an example of the adopted sampling strategy is illustrated in Figure 2-4 and Figure 2-5. The campaigns were conducted during the spring tide in order to have the maximum water mixing conditions and the samples were collected during the ebb tide, when it was possible, according to logistics and weather, with the scope to emphasize the freshwater discharge effects.

Kinvarra Bay is a shallow bay and has an average depth of 4 meters (see study area description), therefore, only one water sample, one meter below the surface, was collected at each station.

Killary Harbour is a fjord, a long narrow inlet, and stratification was observed in previous literature studies (see study area description): for this reason, water samples at one meter of depth below the surface and at one meter above the bottom water column were collected. Samples from two different depths allow to understand if there is stratification in the water column, capturing different salinity, temperature, nutrients etc.

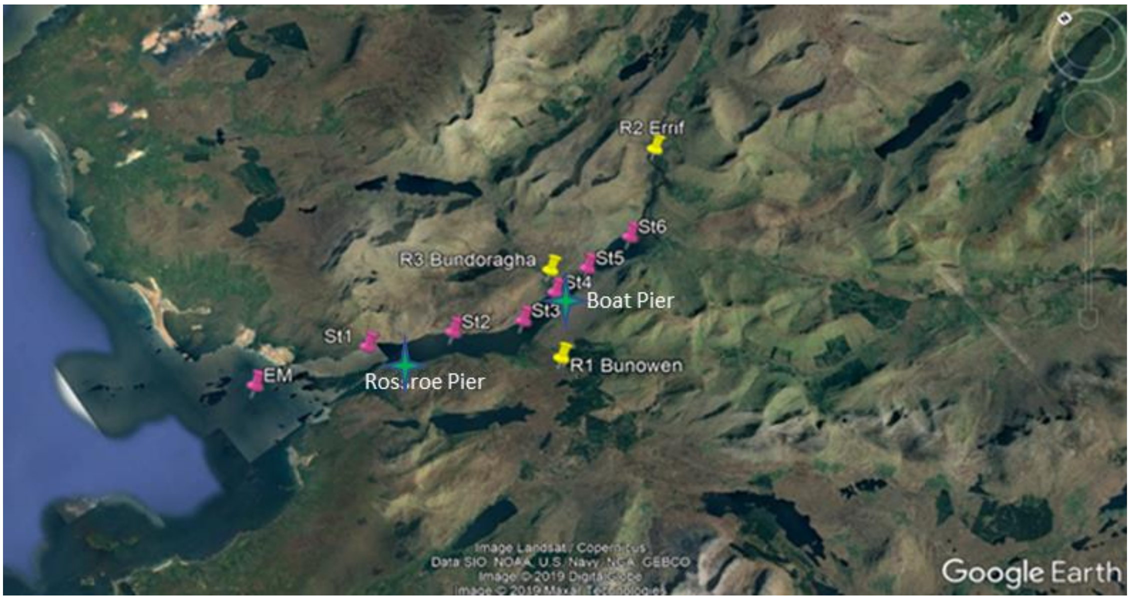


Figure 2-4 Example of Killary Harbour transect sampling strategy from the head to the mouth of the bay, rivers and ocean end-member samples collected at all campaigns. Boat Pier diel sampling carried out in February 2018 and April 2019 and in Rossroe Pier in July 2018 and January 2019.

Figure 2-5 Example of Kinvarra Bay transect sampling strategy from the head to the mouth of the bay, rivers and ocean end-member samples collected at all campaigns. Tarrea Pier diel sampling carried out in July and October 2018, and in Parkmore Pier in January and April 2019.

At each station, a few parameters were measured using a multi-parameter probe (Aqua-read AP 1000). This probe provided the following parameters: Electrical Conductivity (EC), Dissolved Oxygen saturation state (DO%), Total dissolved solids mg/l, Oxide reduction potential mV, temperature, Turbidity, Salinity as Practical Salinity Unit (PSU) equivalent as per thousand ‰, pH.

The water was collected using 5 L Niskin bottle, then dispensed in the different vials and bottles. Collection, preservation and analysis followed standard methods for the seawater acidification studies and for general seawater studies (Millero et al., 1993; Dickson and Goyet, 1994; Dickson et al., 2007; Grasshoff, Kremling and Ehrhardt, 2009).

Samples for pH, TA and DIC were collected using 500 ml borosilicate glass bottles. After collection, the sample was immediately poisoned using 0.05% of the total volume of mercuric chloride $HgCl_2$, following the ocean best practices for the ocean carbonate system (Dickson et al., 2007).

In addition to the carbonate system parameters also samples for other parameters were collected: DOC, DIN as a sum of NH_4^+, NO_3^-, NO_2^-, and SRP. The DOC samples were collected in 12 ml amber glass vials and were acidified with two drops of HCl to get them ready for the analysis (allowing the degassing of DIC, keeping the pH below 3 to avoid biological activity that can change the chemistry). Filtration of DOC and SRP samples was carried out using GF/F filters recommended in the literature for the marine water (Dickson et al., 2007; Wolf-Gladrow et al., 2007; Bockmon and Dickson, 2015) to remove the organic matter. Samples for DIN determinations were collected following the procedure outlined by Jiang, et al., (2017): aliquots of water were transferred into vacutainers using a Rhizon Soil Moisture Sampler (Rhizosphere, The Netherlands) and following the precautions suggested by Ibánhez and Rocha (2014) to avoid the effect of the sorption capacity of the sampler on the filtrate composition.

2.3.3 Short-term, diel fluctuations in the bays

To understand short term variability that includes tidal cycle effects and day/night metabolism, 24h sampling was conducted in two locations of Killary Harbour and Kinvarra Bay. Collection of samples every 3h was carried out in the outlet of Kinvarra Bay (Parkmore Pier) and Killary Harbour (Rossroe Pier) and in the middle of the two Bays, Tarrea Pier (Kinvarra) and Boats Pier (Killary) (see Figure 2-4 and Figure 2-5). During the 24h samples for TA and pH were collected, additionally the multi-parameter probe (Aqua-read AP 1000) was used to record the other previously listed parameters.

The aim of 24h sampling was as first to understand the diel salinity fluctuations to calculate the freshwater discharge in Kinvarra Bay using a tidal prism approach. Furthermore, to catch the fluctuations of TA and pH over diel timescale and understanding if they were correlated with the freshwater discharge. Afterwards, the analysis of short-term (diel) variation at high resolution scale (instead of every 3 hours) it was considered more appropriate to better understand the carbonate system dynamics at the freshwater end-member.

2.3.4 Short-term, diel fluctuations in the freshwater end-members

In order to quantify the NCP at the freshwater end-member locations and to understand the main drivers of diel TA:DIC variations, short-term variability was addressed in the main freshwater source in Kinvarra Bay, (Kinvarra Castle Spring (Rocha et al., 2015; Schubert et al., 2015), and in Killary Harbour (Erriff River (Rodhouse et al., 1987)). The samples were collected covering two tidal cycles in a period of 24h, sampling at high resolution (every 30 minutes). In addition to the carbonate system parameters, TA and pH, the electrical conductivity was measured with a portable conductivity meter CTD (WFW-profilLine cond 197i). The CTD diver was submerged into the sediment for the 24h, to record the conductivity, temperature and pressure of the water every 30 minutes. Eventually, the multi-parameter probe (Aqua-read AP 1000) was used to record the other parameters previously listed. In particular, the DO% variations and temperature were essential to measure the NCP using diel dissolved oxygen dynamics.

2.3.5 Total Alkalinity: Open cell titration

The measurement of collected marine TA samples was based on the ocean best practices guidelines for CO_2 outlined by Dickson et al., (2007). The samples were analysed at 25 °C constant temperature. Each sample was weighed on a balance with accuracy of 0.01 gr and the weight of 60 gr for each sample was chosen. Each sample was analysed three times in order to have triplicates and to measure the error of the procedure within the samples. To stabilize the temperature, a thermostat bath was used. A jacketed beaker kept the sample at the same temperature during the titration (Figure 2-6).

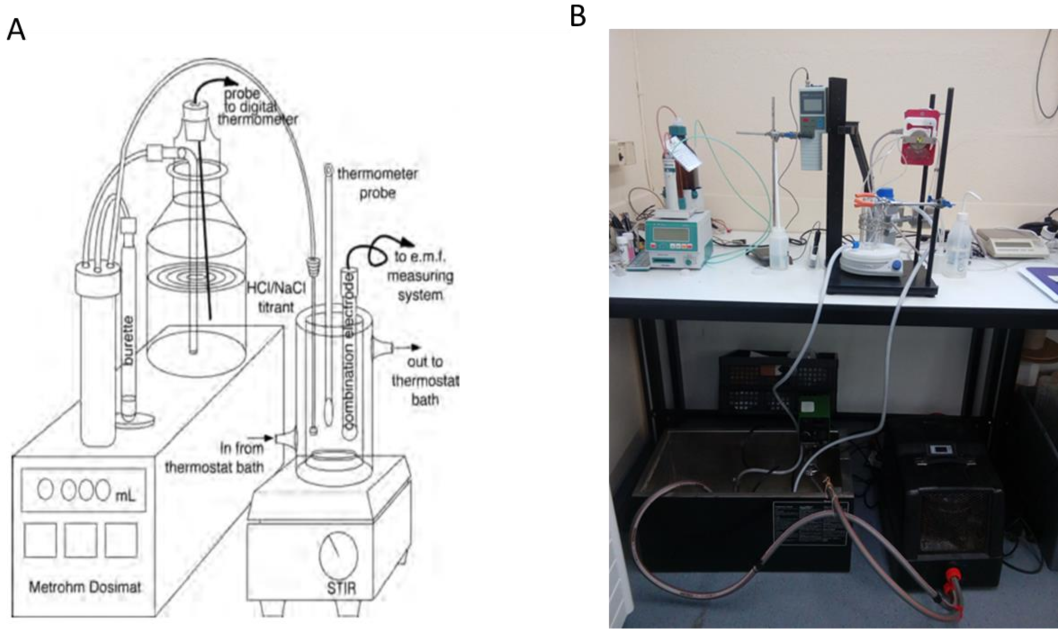


Figure 2-6 Open-cell alkalinity measurement set-up. Figure B shows the machine set-up in Biogeochemistry lab, with a thermostat bath on the ground that, with a circular water pumping and mixing system, kept the samples at 25 °C. Biogeochemistry research laboratory is located in Museum Building, Trinity College, Dublin.

The titrant solution was made by dissolution of 0.1 mol kg^{-1} HCl and 0.6 mol kg^{-1} NaCl in 1 kg of water (Dickson, 2007). This procedure was designed for the open ocean studies, therefore the 0.6 mol kg^{-1} of NaCl corresponds to 35 gr of NaCl dissolved in the water to obtain the normal sea water salinity and to titrate the ocean samples with a titrant of same salinity. To account for the range of salinities encountered at both sites, 4 different 0.1 Molal HCl titrant solutions were prepared in artificial seawater with different NaCl concentration. The titrant solution was made by dissolution of 0.1 mol kg^{-1} HCl and 0.6 mol kg^{-1} NaCl in 1 kg of water (Dickson, 2007). The other three titrants had been made using 0.43 mol kg^{-1}, 0.18 mol kg^{-1} of NaCl, and to titrate the freshwater samples, a titrant solution with 0.1 mol kg^{-1} HCl without salt addiction was made. Finally, these three different titrant solutions have been standardized against Certified Reference Materials (CRMs) titrant solution provided by Pr. A. Dickson (SIO, Univ. California, USA).

To titrate the samples a Titrino Methrom, model 785, was used to mix the acid into the sample: the instrument had an accuracy of ±0.001 ml. The Titrino was calibrated before the analysis and the manual option was used for the acid handling. For the open cell titration, the sample was titrated with low stirring, dispensing HCl to take the sample to pH just above 3.5. Then, increasing the stirring rate and turning on air flow through the solution allowed the CO_2 degassing. After that, the titration continued until pH 3 was reached, using an increment of 0.05 ml.

The TA endpoint was then obtained from linear regression of the change in pH against the volume of added acid, according to the Gran transformation:

$$\mathrm{GF} = \frac{(\mathrm{v}+\mathrm{V}_0)}{\mathrm{V}_0 * 10^{-\mathrm{pH}}} \tag{14}$$

where GF is the resulting Gran Function, v is the volume of acid added to the sample, V_0 is the original sample volume, and pH is the pH value measured after each successive addition of volume v (Hunt et al., 2011). An example of how the Gran Function was calculated can be found in the appendix. The measurement system was calibrated with CRMs provided by Pr. A. Dickson (SIO, Univ. California, USA) (Figure 2-7). The precision of the system, evaluated from the analysis of CRMs, was ±10 µmol kg^{-1}. The reproducibility of the measurements, based on the analysis of replicate samples, was better than 10 µmol kg^{-1} for both TA and DIC.

Figure 2-7 Certified Reference Materials from Pr. A. Dickson (SIO, Univ. California, USA). On the right the TRIS Buffer Solution in Synthetic Seawater and on the left the Reference Material for Oceanic CO_2 Measurements. Several Batches were provided by Dickson: the information related to each batch can be found in the following website: https://www.ncei.noaa.gov/access/ocean-carbon-data-system/oceans/Dickson_CRM/batches.html.

2.3.6 Total Alkalinity and Dissolved Inorganic Carbon: close cell titration

A second set of duplicate samples of TA and DIC were sent to a marine laboratory station SNAPOCO2-LOCEAN in La Sorbonne University in Paris, where the analysis by closed cell potentiometric titration was conducted. The automated system used for the simultaneous determination of TA and DIC in seawater was based on the potentiometric method introduced by Edmond in 1970 (dosage of sea water by a strong acid in a variable volume air-tight cell during dosing). It consists essentially of a burette, a pH meter, an automated 'home-made' titration cell and a computer to conduct the analysis (Figure 2-8 and Figure 2-9). A continuous flow of thermostatic water kept the ensemble (cell, burette, acid reservoir) at a constant temperature. The analysis was controlled using a LabView based program that commands the burette delivering HCl (Titrant solution made of 0.1M HCl (CAS n ° 7647-01-0) and 0.6 mol kg^{-1} of NaCl). The LabVIEW program enabled to check each step of the analysis (real-time visualization, Figure 2-10), and to process the data at the end of the analysis. A non-linear method was used to determine the equivalent points (following recommendation at the international level (Dickson and Goyet, 1994)). The measurement system was calibrated with CRMs. The precision of the system, evaluated from the analysis of CRMs, was ±3 µmol kg^{-1} for both TA and DIC. The reproducibility of measurements, based on the analysis of replicate samples, was better than 5 µmol kg^{-1} for both TA and DIC.

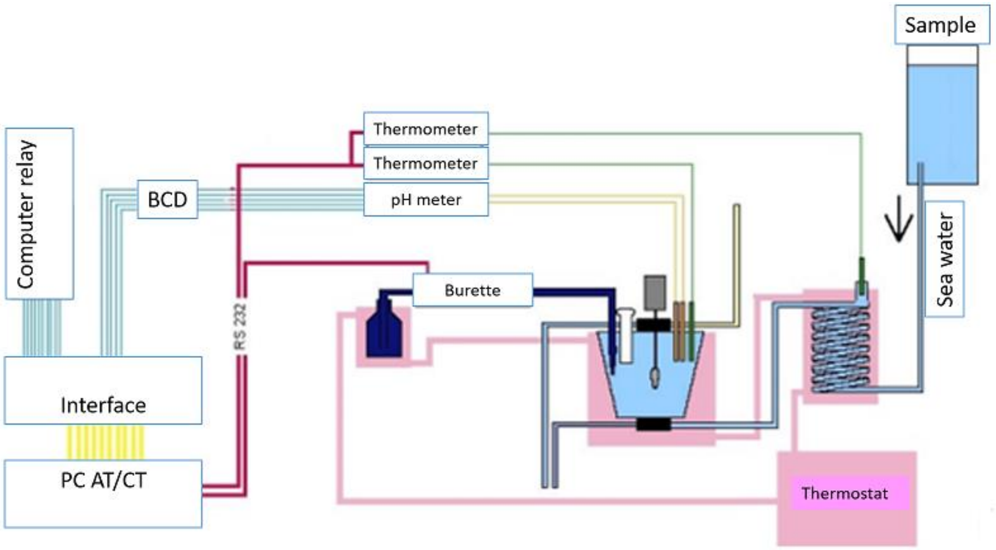


Figure 2-8 Schematic representation of the Edmond's method.

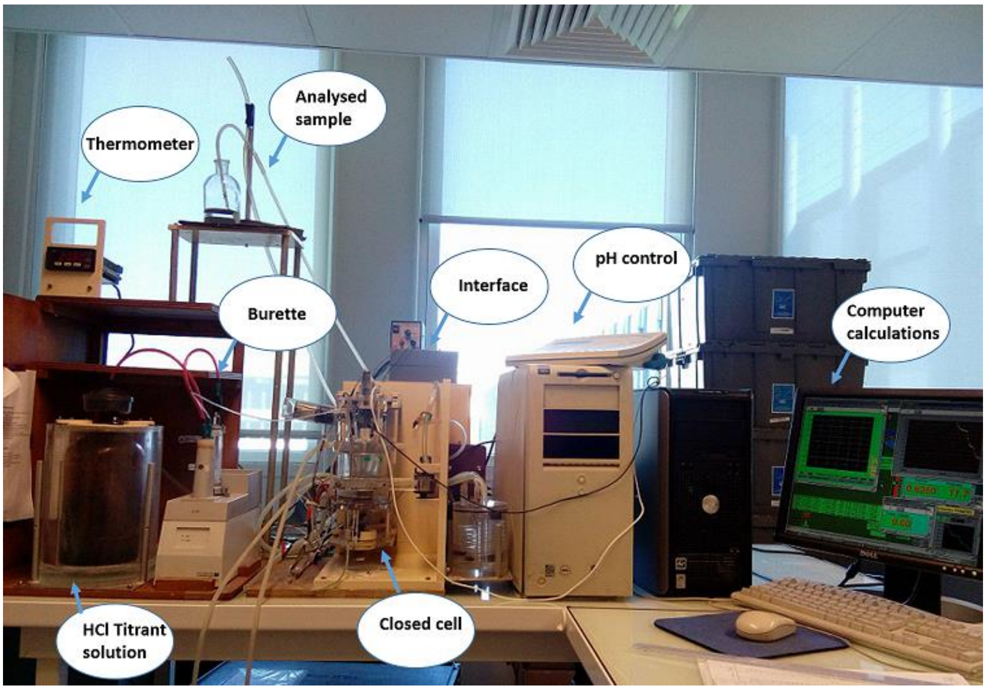


Figure 2-9 Picture of TA and DIC measurement system used at the SNAPOCO2.

Sigma potentiel 0.07

#Pt 33

Ymin -230.00

Volume 4.928

Potentiel -210.3

Temp. Cellule 21.59

Pour modifier ces valeurs, cliquer sur le bouton bleu (Modifier ces valeurs)

Durée Impulsion (msec) 1000

Durée Attente (msec) 5000

Figure 2-10 Visualization of the potential decrease with the addition of HCl.

2.3.7 pH measurements

The pH measurement was particularly important in the open cell titration method since the whole process was based on the pH value displayed on the pH meter during the procedure. The pH recorded at the beginning of each TA titration was then considered as a representative value of the water sample. As explained earlier the TA water samples were all poisoned with $HgCl_2$: therefore, the biological activity was stopped as well as the possible pH changes.

Water pH (expressed in the total hydrogen ion concentration scale) was measured to an accuracy of ± 0.01 at 25 °C with a Thermo Scientific Orion 8102BN Ross combination pH electrode (Figure 2-11), calibrated against Orion NBS standards (for freshwater samples) and against certified reference materials (CRMs) supplied by Prof. A. Dickson (SIO, Univ. California, USA), i.e., 2-amino-2-methyl-1,3-propanodiol (Tris) buffer in synthetic seawater (Figure 2-7)(Nemzer and Dickson, 2005). The conversions to Total pH scale were made knowing that the conversions depend on temperature, salinity and pressure, and to convert the pH from NBS scale to the Total Scale, the CO2SYS software was used (Lewis and Wallace, 1998).

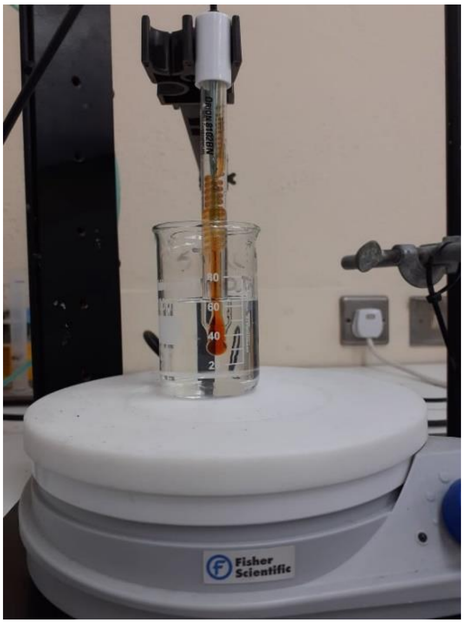


Figure 2-11 Orion 8102BN Ross combination pH Electrode, Biogeochemistry research laboratory Museum Building Trinity College Dublin.

2.3.8 CO2SYS

The CO2SYS software performs calculations of carbonate system parameters in seawater and freshwater. The program uses two of the four measurable parameters of the carbonate system TA, DIC, pH, and either fugacity (fCO_2) or partial pressure of CO_2 (pCO_2), to calculate the other two parameters at a set of input conditions: temperature pressure, Total Silicate and Total Phosphate which are optional and at a set of output conditions chosen by the user (Lewis and Wallace, 1998; Pierrot et al., 2016). The total pH scale (pHT) was used (Dickson 1984). The used dissociation constants for carbonic acid (K1 and K2) in the marine water samples were taken from Mehrbach et al. (1973); Dickson, (1987), along with Dickson's dissociation constant for HSO_4 (KSO_4) (Dickson, 1990). For the freshwater samples the used dissociation constants for carbonic acid (K1 and K2) was taken from Millero, (1979). CO2SYS program also provides other parameters that are calculated from the input conditions: Revelle Factor, aragonite and calcite saturation states. The Revelle factor, or homogeneous buffer, is the percent change in fCO_2 (or pCO_2) caused by a 1% change DIC, at constant alkalinity. This value is dependent on temperature, salinity, TA and DIC (or any combination of two of the CO_2 system parameters) of the sample. In seawater the Revelle factor ranges between 8 and 20. Additionally, the program provides the saturation states for both calcite and aragonite, the saturation states are given in terms of the solubility ratio, Omega Ω, see equation (6). Thus, values of Ω 1 represent conditions of oversaturation. The concentration of calcium, [Ca^{2+}], is assumed to be proportional to the salinity, and the carbonate concentration, [CO_3^{2-}], is calculated from DIC, pH and the values of K_1 and K_2 for carbonic acid. The constants used in this work are from Mehrbach et al., (1973); Dickson, (1987). The calcium concentration used is from Riley and Tongudai, (1967). The values of K_{sp} for calcite and aragonite are from Mucci, (1983). The pressure correction for K_{sp} for calcite is from Ingle, (1975) and that for aragonite is from Millero, (1979).

It is important to highlight the fact that this program has been developed following the sea-water open ocean carbonate chemistry and uses the open ocean equilibrium constants. The software can be used as a support to calculate any carbonate system parameters having two of them, but it is highly recommended to have three parameters of the carbonate system in coastal areas in order to obtain more reliable values for the other data.

2.3.9 PHREEQC

PHREEQC stands for PH REdox Equilibrium, is a geochemical modelling software, it can be used to calculate saturation indices, the distribution of aqueous species, and the density and specific conductance of a specified solution composition (Parkhurst and Appelo, 1999; Parkhurst and Appelo, 2013). The program utilizes input conditions: the ions present in the solution, minerals in equilibrium (if any), solids added to solutions, temperature, pressure, surface conditions (if needed). Solution compositions can be specified with a variety of concentration units (Parkhurst and Appelo, 1999; Parkhurst and Appelo, 2013). In this thesis work CO2SYS was used for most of the calculation since it is generally used for ocean carbonate chemistry studies. However, for freshwater environments such as groundwater systems and boreholes, PHREEQC is used for simulating chemical reactions and transport processes in natural or polluted water. The program is based on equilibrium chemistry of aqueous solutions interacting with minerals. In this thesis the aragonite and calcite saturation indices were estimated in the freshwater systems using PHREEQC. The geochemical database used to assess the potential loss of solutes through precipitation in the groundwater spring samples was WATEQ4F. Since Kinvarra catchment area is characterized by limestone geology, calcite mineral was added using the equilibrium phase function, to let the aqueous solution to equilibrate with respect to calcite. This procedure allowed to have the aragonite and calcite saturation indices output conditions.

2.3.10 Dissolved Organic Carbon

The DOC was measured in the selected study areas to determine the inputs and outputs from freshwater towards the open ocean and to understand the organic carbon dynamics in the analysed coastal areas. DOC concentration in the samples were determined using an Elementar Vario TOC Cube at 680°C. TOC-JS method (Elementar, 2016) was used for this analysis. This instrument works correctly with freshwater samples: for this reason, the analysis of salty samples was carried out carefully. The instrument makes 4 injections of 0.5 ml from each sample; the first result is generally excluded and at least 3 values are used for statistics. At first the blanks and the quality control (QCs) samples have been run, then the standards with respectively 1.000, 2.000, 4.000, 10.000, 20.000 TOC mg/l. After another run of blanks and QCs, the samples analysis started. Rivers and end-member samples were run before the others because they were from freshwater and then all the other marine samples were analysed in a random order. Blanks and QCs were run every 10-12 samples. The analytical uncertainty was better than 0.1 mg/l.

2.3.11 Dissolved Inorganic Nitrogen

The DIN concentration, that is NO_3^-, NO_2^- and NH_4^+, for all the water samples were determined with a LACHAT Quickchem 8500 Flow Injection Analysis system following standard colorimetric methods (Grasshoff K. and Kremling K., 1999). Instructions to determine NO_3^-, NO_2^- in brackish and seawater using flow injection, standards and reagents procedure are described by Smith and Bogren, (2001). For the NH_4^+ the procedures are taken from Liao, (2002). The samples were run in triplicates. Blank samples were run every 10-12 samples to account for the instrumental shift and the experimental error. The analytical uncertainty was better than 0.4 µmol/l.

2.3.12 Soluble Reactive Phosphate

After the samples were filtered, as explained previously, they were analysed within 48h.

Phosphate ions (PO_4^{3-}) react with sodium molybdate and antimony potassium tartrate; the resulting compound is reduced by ascorbic acid to "molybdenum blue" which is determined spectrophotometrically. The stock solution for the Phosphate analysis includes antimony, molybdate, sulfuric acid and ascorbic acid.

The mixed reagent was prepared in the following way:

- 2.3 ml of sulfuric acid into a 100 ml volumetric flask;
- addition of 25 ml of antimony and other 25 ml of molybdate;
- addition of 0.2 gr of ascorbic acid;
- addition of distilled water until 100 ml of solution was reached.

The procedure for the analysis required the following step:

- 5 ml pipette samples and standards into the test tube;
- addition of 1 ml of mixing reagent and strong mixing;
- reading of the absorbance at 882 nm using a HACH DR5000.

The absorbance values obtained were then converted using a calculator programme based on the Beers Law:

$$C = \frac{A}{\varepsilon\, l} \tag{15}$$

where C is the molar concentration (L mol^{-1} cm^{-1}), A is the absorbance (nm), ε is the molar absorptivity coefficient (M^{-1} cm^{-1}), and l measures the path length of the test tube (5 cm). QCs were run for every batch to ensure the accuracy of results. Three replicates of each sample were measured in order to reduce the error. The analytical uncertainty was better than 0.07 µmol/l.

2.4 Freshwater discharge quantification

2.4.1 Freshwater discharge in Kinvarra Bay

To determine freshwater discharge to Kinvarra bay (groundwater + surface drainage), it was used a salinity based equation previously applied for this system (equation 2 in Cave and Henry, (2011)), based, with several important modifications, on principles similar to the equation originally developed by Ketchum (1951). The equation used in this study is defined as (Cave and Henry 2011):

$$\mathrm{Q} = \text{Seawater salinity} \times \text{Tidal prism} \tag{16}$$

or, explicitly:

$$\mathrm{Q} = \frac{(\mathrm{SHW} - \mathrm{SLW})}{\mathrm{Max\ Flood\ salinity}} \times (\mathrm{HHW} - \mathrm{LHW}) \times \mathrm{Surface\ area} \tag{17}$$

where Q is the discharge, SHW and SLW are respectively the maximum and the minimum salinity (kg m^{-3}) measured during ebb and flood that are divided by the maximum salinity recorded during the flood period, HHW and LHW are respectively the tidal height at high and low tide time, and the Surface area refers to the estuary at mean tide (m^2). The data used to apply this equation were collected during a period of 24h in Parkmore Pier and Tarrea Pier. Therefore, the data of maximum and minimum salinity recorded are related to a period of 24h (two tidal cycles).

2.4.2 Freshwater discharge in Killary Harbour

On the Environment Protection Agency website, under the Hydronet session, it is possible to find flow rate continuous measurements at Bundorragha River, which is one of the rivers feeding Killary Harbour. In previous studies the contribution of each river to the system was estimated knowing the sub-catchment limits (Anon, 1958; Keegan and Mercer ,1986; Donohue, 2012). Therefore, the contribution of each river to the total freshwater flow coming from the catchment was estimated assuming catchment size-dependent flow rates. Following the estimation made by Donohue, (2012), the Bundorragha River contributes for about 19% of the total water volume flowing into Killary Harbour. The flow rates observed in Bundorragha River were divided by the proportion of the catchment occupied by the river sub catchment (19%), to determine the total flow rate from the catchment for any given time. The flow rate considered for the computation was an average value of the flow rate recorded in Bundorragha River over the previous 10 days of each campaign.

2.5 Budgeting approach Land-ocean interactions in the coastal zones (LOICZ)

The LOICZ budget model has been described in detail in Gordon et al., (1996). This methodology is applicable to different types of coastal marine ecosystems and it is therefore a useful approach to compare their metabolisms and to compare materials fluxes. Based on the information obtained from LOICZ, it is also possible to classify the typology of the ecosystem (e.g., source or sink of carbon, autotrophic/heterotrophic). In order to apply the model some general information are required: average water depth and area, the water fluxes coming into the system in the form of precipitation, river discharge or groundwater discharge, salinity and nutrients concentration into the system and on the adjacent water body (what has been defined as an ocean end member).

The LOICZ biogeochemical model is based on mass balances, which describes the rates with which a material reaches (input), leaves (output) and changes its presence (storage) within a system (Padedda et al., 2010; Giordani et al., 2008; Swaney and Giordani 2007).

Some substances are subjected to internal transformations leading to net releases or accumulations in the system. Therefore, the system will be defined as a source or sink of the substance. The behaviour of the materials that are affected by these transformations are defined as non- conservative (such as carbon, nitrogen and phosphorus). The substances that do not undergo these transformations are defined conservative (water and salt) (Padedda et al., 2010; Giordani et al., 2008; Swaney and Giordani, 2007).

There are some assumptions behind the use of this approach:

- the system must be considered in a steady state;
- the water and salt mass balance are used to estimate water flows and exchanges;
- the non-conservative behaviour of the substance is used to estimate biogeochemical flows of the ecosystem.

The non-conservative flow of DIP is considered to be proportional to NCP. The net nitrogen budget is derived by the differences between the observed DIN and the DIN expected from the DIP, and the C:N:P ratio of the main primary producers (Giordani, 2002). In the analysis paragraph the phosphorous was measured as SRP, the fraction of SRP is mainly composed by orthophosphate (Calvo-López et al., 2021). The main form of Phosphorus that can be found in natural water is the orthophosphate, this one provides a good estimation of the amount of phosphorus available for algae and plant growth (Wetzel, 2001). This is the form of phosphorus that is most readily utilized by biota, (Calvo-López et al., 2021; Wetzel, 2001): therefore, SRP was used as representative of DIP.

2.5.1 One-layer box model

Water Budget

The first step is to establish a budget of freshwater inflows (such as runoff, precipitation and groundwater) and evaporative outflow. There must be compensating outflow to balance the water volume in the system.

$$\Sigma(\text{input}) + \Sigma(\text{output}) = 0 \tag{18}$$

$$V_Q+V_P+V_G+V_O-V_E+V_R = 0 \tag{19}$$

In the previous equation, the following inputs terms are included: V_Q, the water coming from the rivers and the surface discharge; V_G, the freshwater input from subterranean estuary (e.g., SGD); V_0, any other freshwater input and V_P, the precipitation. The outputs are the V_E, the evaporation and V_R, the residual flux of water towards the sea. The residual flow (V_R) is the net water flow that balances the inputs and outputs, is direct from the system to the sea or vice versa. A seawater flow coming into the lagoon/bay is observable in cases where evaporation is very intense and fresh water supplies are negligible. This parameter is usually difficult to measure and therefore the mass balance of the water is used to obtain an estimate of V_R, equation (20). V_R is negative when a net outflow from the estuarine system to the adjacent sea takes place, and positive when a net inflow from the sea to the estuarine system occurs.

$$V_R = (-V_Q-V_P-V_G) +V_E \tag{20}$$

To estimate the water loss from the bay by evaporation V_E (mm day^{-1}), the method described in Rocha et al., (2015) was used: the Meyer's formula (Meyer, 1915) was corrected for the water molar fraction for saline waters (Kokya and Kokya, 2008) as following:

$$Qe =K\ f\ (u)\ (XH_20)\ (e_S -e_A) \tag{21}$$

where f (u) is the evaporation coefficient as a function of wind speed (u, in kmh^{-1}) taken as f (u) = (1 + v/ 16); e_S is the saturation vapour pressure (mmHg) of the water; e_A is the vapour pressure of the water in the air (mmHg) and XH_2O the water molar fraction for seawater at a salinity of 30 (~0.98). Average air temperature (°C), relative humidity (%) and wind speed (kmh^{-1}) for the duration of the surveys were taken from Met Éireann records at Athenry station, 25 km from Kinvarra Bay and 95 km from Killary Harbour.

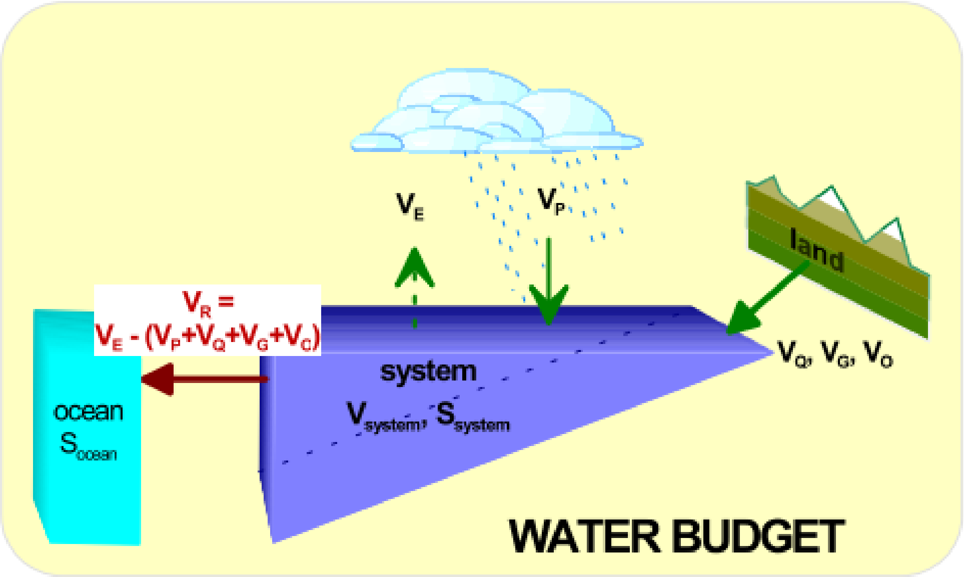


Figure 2-12 Water budget from (Giordani, 2002).

Salt Budget

Among the movements of water masses in a coastal ecosystem, in addition to the ones indicated in the previous paragraph, there is the exchange flow (V_X). This is the volume of water in the lagoon/bay which is constantly being replaced by an equal volume of sea water. This flow does not lead to significant changes in volume and therefore is not counted in the mass balance of the water, but it is very important for nutrient flows since a nutrient-rich lagoon water mass is replaced by an equal mass of nutrient-poor sea water. This leads to a net loss of nutrients for the system. The mass balance of the salt is used to quantify V_X, which has a conservative behaviour and can be used to estimate the movements of the water masses (Giordani, 2002; Swaney and Giordani, 2007).

$$V_X = \frac{1}{(Socean - Ssys)} V_R S_R \tag{22}$$

where S_{OCEAN} and S_{sys} are, respectively, the salinity of the marine end-member and the average salinity of the estuarine area; S_R is the average salinity between the system and the marine end-member: it follows that V_RS_R, is the volume of the residual flow multiplied by the S_R.

In Figure 2-13, the salt budget is represented. V_ES_E and V_PS_E are represent the salinity input and output from evaporation and precipitation. V_QS_Q, V_GS_G, V_0S_0 are represent the salinity inputs from the rivers, SGD and any other freshwater source. V_{system} S_{system} is the average salinity in the analysed system. V_RS_R is the salinity of the water associated with the residual flow. V_X represents the exchange flow, and S_{OCEAN}, the salinity in the ocean end-member. All salinity values are expressed as ‰.

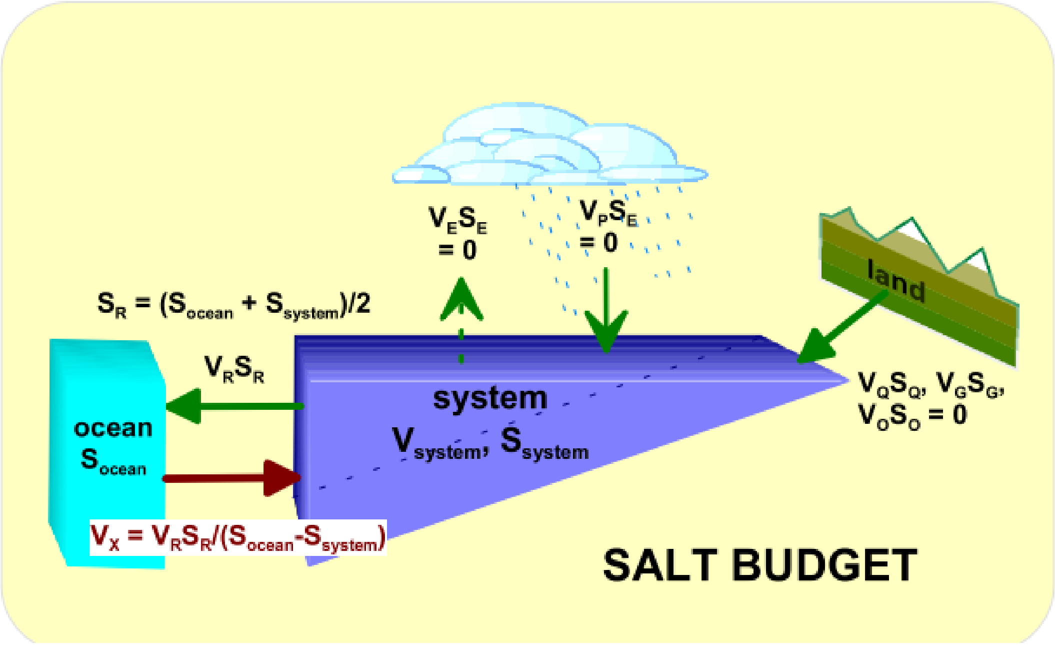


Figure 2-13 Salt balance from Giordani, (2002).

Non-conservative material budgets

As a third step, the budget of non-conservative materials can be calculated between the system (bay) and the adjacent system (ocean) according to the water budget and salt budget (Gordon et al., 1996). The retention flux of TA, DIC, DOC, DIN and DIP can be calculated applying the non-conservative materials budget.

Inorganic nutrients have a classic non-conservative behaviour as they undergo transformations within the system that lead to their lower availability (sink) or to their mobilization (source). Among these transformations the most important are the organization or mineralization of nutrients in the tissues of the primary producers and the adsorption-desorption in the sediment (Gordon et al., 1996).

The balance of non-conservative material is calculated from (Y is the generic parameter among the ones of interest):

$$\Delta Y = -(V_QY_Q+V_PY_P+V_GY_G+V_0Y_0+V_EY_E+V_RY_R+V_X(Y_{ocean}-Y_{sys})) \tag{23}$$

where V_QY_Q and V_GY_G are the loadings of the non-conservative substance from rivers and SGD respectively; V_PY_P is the loading from precipitation; V_0Y_0 is any other possible freshwater inputs to the system (e.g., streams, rivulets); V_EY_E is the evaporation; V_RY_R is the volume associated with the residual flow, and V_X is the mixing flow with the open ocean. When ΔY is positive, a net export from the bay to the open ocean occurs.

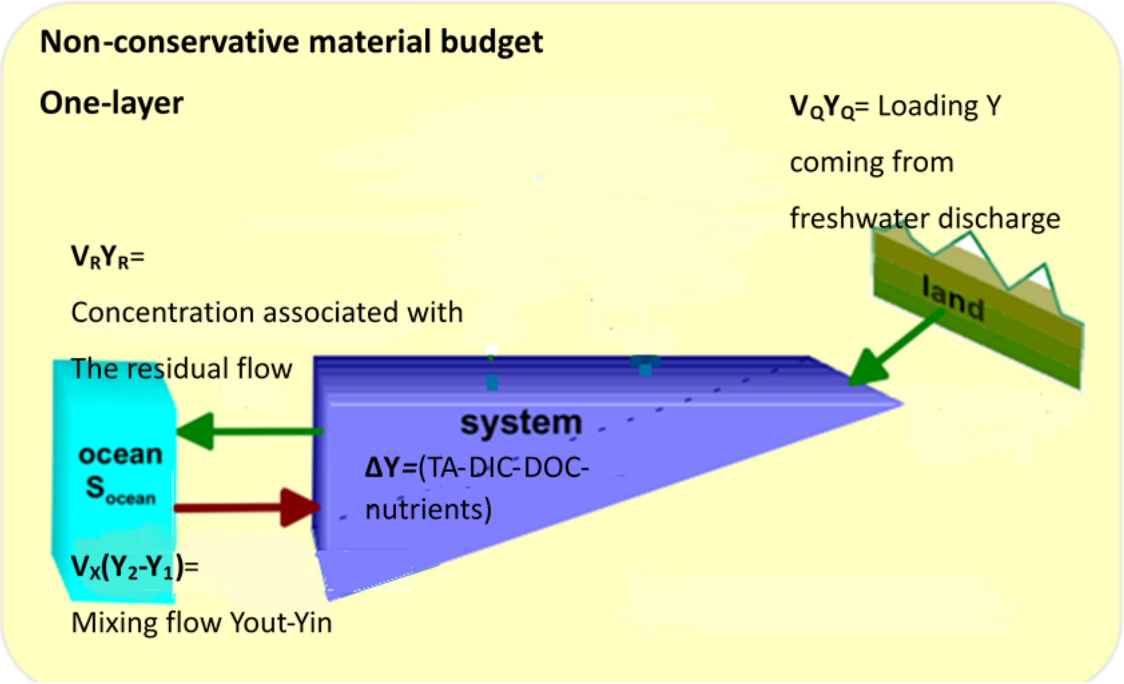


Figure 2-14 Non-conservative materials budget model one-layer. ΔY is the non-conservative flux of the analysed constituent, Y_R is the constituent concentration associated with the residual flux (i.e. the average value of Yout and Yin). If ΔY = 0, it implies that constituents in ecosystem are in conservative behaviour. For what concerns the nutrients, in case of non-conservative behaviour, they are utilized for biological productivity; ΔY will have a non-zero value. A positive value of ΔY imply a net mobilization since the outputs are greater than the inputs, therefore the system will be a source. Reversely if ΔY is negative means that inputs are greater than outputs and the system acts as a sink. Figure modified from (Giordani, 2002).

2.5.2 Two-layers box model

In a stratified system, the two layers budget can be applied (Giordani, 2002), assuming as before, a box model with a single compartment. This type of budget can be applied in Killary Harbour area, since as shown by previous literature studies in the general introduction chapter, Killary Harbour is a narrow inlet characterized by a stratified structure.

Water budget

Terrestrial and atmospheric terms remain the same and are considered to enter or leave from the surface layer, though groundwater flows can conceivably be a source to both layers. However, the nature of classic estuarine circulation is based on stratified flow: water in the surface layer is assumed to be less saline because it is influenced by the freshwater inputs compared to the deep layer (Swaney and Giordani, 2007). The outflow from the system to the open ocean will occur in the surface layer, and this one will be compensated by the inflow from the open ocean that will occur in the bottom layer. The exchange term (V_X) with no net flow is now effectively isolated into an outflow term from the surface layer balanced by an inflow term from the bottom layer, which also carries salt and nutrient from the bottom layer to the surface (Giordani et al., 2008; Swaney and Giordani, 2007). The resulting flows are defined as:

V_{deep} – Deep inflow volume: the advective inflow from the ocean to the bottom layer (which also continues from the bottom to the surface layer). It will take values greater than or equal to zero. Actually, V_{deep} in a two-layer model represents the volume of water inflow from the sea into the bottom layer and the equivalent outflow in the surface layer.

V_SY_S – Surface outflow volume: it is the outflow from the surface layer to the ocean or adjacent downstream compartment. It is the sum of V_R (as defined for the single compartment case, above, with the addition of a flow equal and opposite in sign to any deep groundwater flow, V_{Gd}). As an outflow, it will take a negative or zero value.

V_{ent} – Vertical entrainment flow volume: it is the advective flow of water from the deep to the surface layer. It is equal in magnitude to the sum of V_{deep} and any deep groundwater sources to the bottom layer, V_{Gd}. Its sign is negative with respect to the deep layer and positive with respect to the surface layer.

V_Z – Vertical exchange volume: in two-layer systems, this is the vertical mixing between the surface and deep boxes. Like V_X, V_Z is always zero or positive, and represents the absolute value of a mixing flow transporting salinity and nutrients between the bottom and the surface layers with no net change in volume.

The water budget equations for surface and deep layers will be written as follows:

Surface layer:

$$0 = V_E + V_Q + V_G + V_P + V_O + V_S + V_{ent} = V_Q + V_S = V_Q + V_R + V_{deep} \tag{24}$$

Bottom layer:

$$0 = V_{Gd} - |V_{ent}| + V_{deep} \tag{25}$$

Salt budget

In the two layers the salt fluxes are defined in relation to the water fluxes and exchange terms similar to the ones of the single compartment model. The V_{deep} component carries salt into the bottom compartment at the salinity of the local ocean at the same depth, and Vs carries salinity from the surface layer to the local ocean surface layer. V_{ent} transfers salinity from the bottom layer to the surface layer. V_Z carries salinity from the two layers in proportion of the difference in salinity between them (Giordani et al., 2008). The equations can be rearranged for V_{deep} and V_Z as follows:

$$V_{deep} = \frac{V_R\, \mathrm{Ss} + V_{Gd}\, S_{Gd}}{S_{sys} - S_{oceandeep}} \tag{26}$$

$$V_Z = \frac{V_{Gd}\left(S_{Gd} - S_{deep}\right) + V_{deep}\left(S_{oceandeep} - S_{sysdeep}\right)}{S_{sysdeep} - S_{syssurf}} \tag{27}$$

Non-conservative materials budget

Eventually, the budget for non-conservative materials in two layers system can be written as follows:

$$\Delta Y_{surf} = -[V_Q Y_Q + V_P Y_P + V_G Y_G + V_0 Y_0 + V_{ent} Y_{deep} + Vz\,(Y_{deep} - Y_{surf}) + V_S\, Y_S] \tag{28}$$

$$\Delta Y_{deep} = -[(V_{deep}\, Y_{ocndeep} + V_{Gd}\, Y_{Gd} + V_Z\,(Y_{surf} - Y_{deep})) - V_{ent}\, Y_{deep}] \tag{29}$$

where: $V_Q Y_Q$, $V_G Y_G$, $V_0 Y_0$ and $V_P Y_P$ are respectively the loading coming from river discharge, SGD, other inputs and precipitation; $V_{ent}\, Y_{deep}$ is the vertical entertainment flow volume multiplied by the average concentration of the substance in the deep layer of the system; $V_Z\,(Y_{surf} - Y_{deep})$ is the vertical exchange volume multiplied by the difference in concentration of the nutrient in the surface and deep layer; $V_S Y_S$ is the concentration of the substance in the outflow volume. $V_{deep}\, Y_{oceandeep}$ is the volume of inflow from the sea multiplied by the concentration of the substance in the ocean end-member.

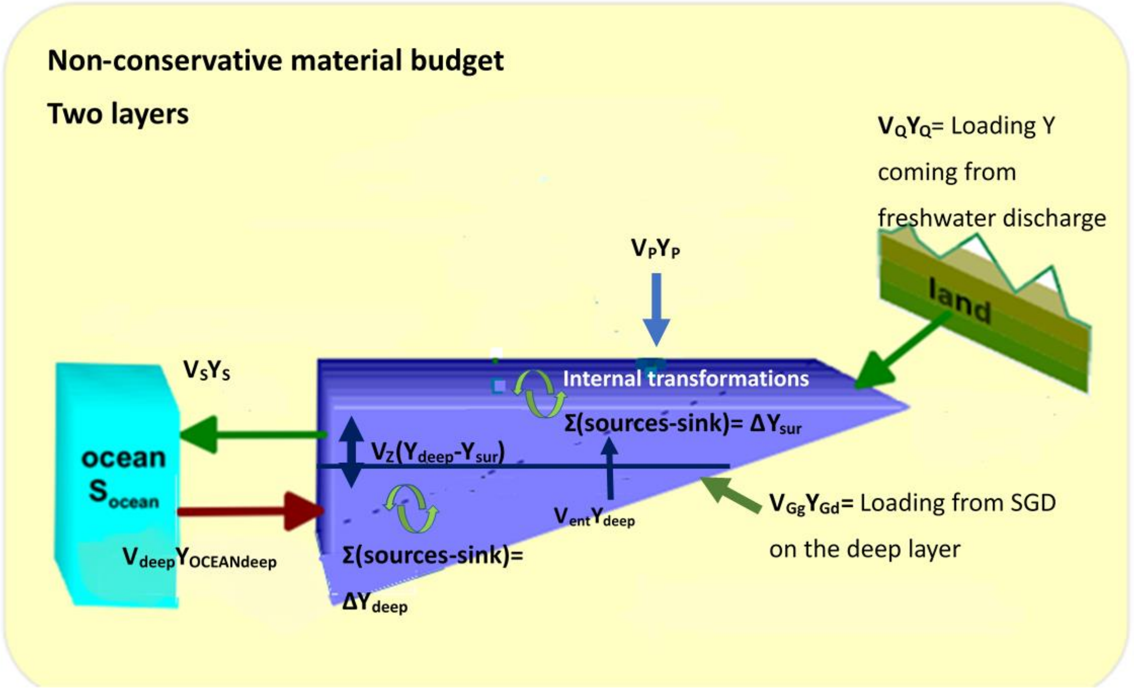


Figure 2-15 Non-conservative materials budget two layers: two separate values of ΔY will be obtained from the surface and deep layer. The average values between them will be the ΔY representative of the system. For what concerns the ΔDIP, the average between surface and deep layer was used to estimate the NCP. Figure modified from (Giordani, 2002).

2.6 Net community production estimation

To estimate the NCP, it is possible to use the ΔDIP in the system knowing the molar ratio C: N: P of the main primary producers. A direct estimate of this ratio is always preferable but, in absence of this, Redfield's 106: 16: 1 ratio is suitable for environments dominated by phytoplankton; for other primary producers it is possible to obtain information in (Atkinson and Smith, 1983; Duarte, 1992). The negative value of ΔDIP indicates a net loss of DIP and therefore a prevalence of carbon production processes that lead to a consumption of phosphate. The relative proportions of carbon and phosphate follow the given C: P ratio from the primary producers which indicates how these two cycles are linked together. To calculate NCP, that is (PP - R), the following equation is applied:

$$NCP = (PP - R) = -\Delta DIP\ (C{:}P) \tag{30}$$

2.6.1 Nitrogen fixation and denitrification

Nitrogen fixation and denitrification are biogeochemical processes affecting the nitrogen biogeochemical cycle in many coastal waters (Swaney and Giordani 2007). The LOICZ budget methodology provides a way to quantify them. To quantify the expected amount of Nitrogen as ΔDIN_{exp} it is possible to apply the equation (31) as follows:

$$\Delta DIN_{exp} = \Delta DIP\ \left(\frac{N}{P}\right) \tag{31}$$

where ΔDIN_{exp} is equal to the ΔDIP value found applying the non-conservative material budget, multiplied by the N:P ratio.

To understand if the net nitrogen fixation (N_{fix}) is lower or greater than denitrification (N_{denit}) the following equation can be applied:

$$(N_{fix} - N_{denit}) = \Delta DIN_{obs} - \Delta DIN_{exp} \tag{32}$$

where ΔDIN_{obs} is the net internal nitrogen flux (that can be obtained by balancing the LOICZ nitrogen budget in equation (23) in one layer system or as the average ΔY value of surface and deep layer equations (28) and (29) in a two layers system). The expected amount of nitrogen previously calculated, $\Delta DIN_{exp,}$ will be subtracted to ΔDIN_{obs} to obtain (N_{fix}-N_{denit}).

2.7 Net Community Production quantification using Dissolved Oxygen dynamics

To calculate the NCP of the two freshwater end-member (SGD in Kinvarra Bay and Erriff river in Killary Harbour), DO% have been used in order to apply the governing equation of Odum, 1956 :

$$\frac{\Delta O_2}{\Delta t} = \text{GPP} - \text{R} - \text{F} - \text{A} \tag{33}$$

where GPP is Gross Primary Production; R is respiration; F is the physical gas flux and A represents all the other processes that could change DO% concentration. The basic and generally accepted assumption behind this approach is that diel changes in DO% in the water column are an integrated response to the metabolism of the entire ecosystem (all autotrophs and heterotrophs). The work from Staehr et al., (2010), describes in detail the equations to calculate a lake metabolism using the diel oxygen dynamic technique. Their methodology was followed in this work: however, since the present activities are conducted at sea level, the altitude was not considered in the equation.

The NCP was calculated for each time interval following the equations from (34) to (40)

(Cole et al., 2000).

$$\text{NCP}_{hr} = \Delta O_2 \; \frac{-F}{Z_{mixing}} \tag{34}$$

The NCP_{hr}, expressed in g O_2 $m^{-3}hr^{-1}$ is equal to the ΔO_2 expressed as g m^{-3} hr^{-1}, multiplied by -F , which is the physical gas flux, expressed as (g O_2 m^{-2} h^{-1}), and divided by Z_{mixing} which is the mixing depth.

F can be calculated as following:

$$F = k\ (O_{2mean} - O_{2sat})$$

(35)

where k is the piston velocity expressed as m h^{-1}; the O_{2sat} expressed as mg L^{-1} is calculated as a function of temperature and salinity; the O_{2mean} expressed as mg L^{-1} is the conversion of O_2% to O_2 concentration. The piston velocity k was determined using the equations described in Jähne et al., (1987), Cole and Caraco, (1998).

The piston velocity is commonly estimated as a function of wind speed at 10 m above the bay surface. The wind speed considered comes from the hourly variation data of the Athenry Met Éireann (the Irish meteorological service) records. The Z_{mixing} was added as a factor related to the tidal excursion when the equation was applied in Kinvarra Castle Spring (the freshwater end-member monitored in Kinvarra Bay location).

$$NCP_{daytime} = \text{average } (NCP_{hr} \text{ during daylight}) \times \text{dayfraction} \times 24$$

(36)

The $NCP_{daytime}$ expressed as g O_2 m^{-3} during the daytime was then calculated using the equation (36), and this NCP includes the photosynthesis occurring during the daylight multiplied by the dayfraction (which is the proportion of a 24-h period when there is solar light).

Following the method of Staehr et al., (2010) there are assumptions to determine Respiration (R):

- there is no photosynthesis occurring during the night;
- therefore, the respiration during the night is equal to the NCP quantified in the night hours.

It follows that the hourly respiration R_{hr}, expressed as g O_2 m^{-3} h^{-1}, is equal to the average NCP_{hr} calculated in darkness (equation (37)).

$$R_{hr} = \text{average } (NCP_{hr} \text{ (during darkness)})$$

(37)

The night respiration is therefore equal to the daytime respiration ($R_{daytime}$): the $R_{daytime}$ expressed in g O_2 m^{-3}, can be calculated as follows:

$$R_{daytime} = R_{hr} \times 24h \times dayfraction \tag{38}$$

The day length was checked at each survey in the Met Éireann website.

The diel respiration (R_{diel}) is equal to R_{hr} multiplied by 24 hours:

$$R_{diel} = R_{hr} \times 24h \tag{39}$$

Eventually, the GPP and NCP expressed as g O_2 m^3 d^{-1} were then calculated as a sum of $NCP_{daytime}$ and $R_{daytime}$, in equation (40), and the NCP as the difference between GPP and R_{diel}, in equation (40)

$$GPP = NCP_{daytime} + R_{daytime} \tag{40}$$

$$NCP = GPP - R_{diel} \tag{41}$$

Uncertainty is common in many current methodologies to calculate NCP which are attributable to under-sampling or natural variability (Staehr et al., 2012). In the current approach, the uncertainty of each parameter of the equation was considered, the error propagation rules were taken into account (Taylor, 1997) leading to an uncertainty of ~20%.

Results

3 Carbonate chemistry along Irish coastal seas: chemical data overview and geology of coastal areas

Abstract

Open ocean carbonate chemistry is altered by the dissolution of atmospheric CO_2 in seawater. Up to 40% of anthropogenic CO_2 emissions have been dissolved in the surface ocean, thus mitigating anthropogenic CO_2 impact on the global climate system. However, this CO_2 dissolution is driving changes in the marine carbonate system and promoting ocean acidification. Thus, research efforts are paid to monitor the carbonate system parameters in the global ocean to understand and predict the consequences of these changes on the marine food web structure. In the open ocean TA shows strong correlation with salinity and temperature due to the conservative nature of its constituents there. However, in coastal areas the interaction with the continent makes these relations much more complex. Freshwater inputs can provide an additional source of TA and DIC to the coast or lower them through dilution. The aim of this part of the research was to understand the impact of land-ocean interactions over the coastal carbonate system and therefore, over local ocean acidification processes. The Marine Institute has provided a large dataset with several surveys along the Irish coastline, from 2009 to 2018, measuring TA, DIC and nutrients (nitrate NO_3^-, nitrite NO_2^- , phosphate PO_4^{3-} and silicate SiO_4^-). In order to understand whether the watershed geology or the land-usage can influence the coastal chemistry, the original dataset was at first reduced to have a set of variables comparable in different locations. Principal Component Analysis (PCA) was then performed, and the results showed a large positive correlation in the first principal component between DIC, TA and nutrients while the second component evidenced a large negative correlation between TA and salinity. In the western coast, TA and DIC were higher compared to other locations: this coastal area actually receives freshwater from the land draining karstic watersheds. Conversely, data from Northern Ireland showed lower values of TA and DIC (at comparable salinity values) compared to mean Atlantic open ocean values. This suggested that freshwater sourced from basaltic catchment areas did not supply carbonate to the adjacent sea. Therefore, contrasting continental influence over the coastal carbonate system was observed, which was related to the geology of the catchment area. Furthermore, in the southern Ireland DIC was particularly high, which might be explainable

by enhanced respiration processes driven by the riverine delivery of organic matter into the sea. Thus, salinity and temperature cannot be used to predict carbonate system parameters in Irish coastal waters. Elucidating how land-ocean interactions affect the coastal carbonate system would help to understand coastal resilience to ocean acidification and thus support better management of coastal resources.

3.1 Introduction

After the industrial revolution there was an increase of CO_2 in the atmosphere that has been absorbed by the ocean (Feely et al., 2004). The rising of CO_2 affects ocean buffer capacity, which now we are aware has been slightly depressed (Doney et al., 2009). This phenomenon, known as ocean acidification, leads to changes of the carbonate chemistry of surface waters altering the rates of primary production and calcification of numerous marine organisms and communities (Doney et al., 2009; Kleypas and Langdon, 2006). Scientific community has focused the research on the open ocean with the aim to reconstruct the carbonate system, using empirical relations between temperature, salinity and oxygen based on multiple linear regressions (Alin et al., 2012). Empirical models provide robust prediction for decadal time scale, however for longer predictions it is necessary to readjust the values according to the human CO_2 emissions (Alin et al., 2012). In the open ocean, salinity and TA are parameters are highly correlated, because the main freshwater sources are rainfall and ice melting (Key et al., 2006). In coastal areas, the prediction of changes in carbonate chemistry is more complex and needs the understanding of other drivers, like watershed inputs. The watershed input is a source of organic carbon, inorganic carbon and nutrients to the coast; the loading of them can vary from surface inputs, rivers or streams and SGD.

The alkalinity loading from the rivers depends on the catchment area geology: it will be high in calcareous areas or low in siliceous areas (Hannigan and Kelly-Quinn, 2013). The central part of Ireland is mainly characterized by limestone (Sanders, 2008): therefore, in coastal areas most of the freshwater discharge is a source of TA. In the west coast of Ireland, the SGD is the main source of discharge. The type of freshwater discharge depends on the geology of the catchment area, however, also the land usage and human activities can contribute as a source of nutrients that are accumulated in the soil, transported from the rivers or SGD (Valiela et al., 1990; Cole et al., 2007). For instance in the south and southeast of Ireland, the agriculture is particularly developed as well as the use of fertilizers, that leads to discharge of nutrients, nitrogen and sulphate in particular, which are higher compared to the rest of the country (O’Boyle et al., 2010; 2015; 2016; 2019). It is known from the literature that nutrients discharge can intensify eutrophication processes (Cai et al., 2011; O’Boyle et al., 2019). In estuarine areas characterized by high discharge of nutrients, it has been observed that during algal bloom events, the TA:DIC relationship changes, and the DIC is drastically consumed (Dai et al., 2008). A general figure says that rivers are responsible for 40% of the DIC content of the coast (Ludwig et al., 1996). The dissolution of carbonate rocks along the river basin, or the biogenic CO_2 resulting from bacterial respiration of marine terrestrial organic matter, can all contribute to DIC pool in coastal areas influenced by the river discharge (Brunet et al., 2009; Vargas et al., 2016). Human activities could positively or adversely modify the coastal carbonate chemistry and its response to ocean acidification (Borges and Gypens, 2010). Increases in the delivery of inorganic carbon to coastal areas can alter the coastal biogeochemical cycles (Campeau et al., 2017). To explore the coastal carbonate chemistry the consideration of the following factors is necessary:

- the role of freshwater input in terms of organic and inorganic carbon;
- the nutrients inputs which can stimulate biological productivity (Cao et al., 2011).

This chapter aims to be a general description of the carbonate geochemistry of Irish coastal seas, and of the main drivers of carbonate chemistry along the Irish coastal sea. The scope of this investigation in the general frame of this thesis work is to understand which role has SGD in the coastal carbonate biogeochemistry of the Irish coast and which weight SGD has respect to the other drivers such as coastal biological processes. The tested hypotheses are:

H_1: the carbonate system variability relates to the type of freshwater input and watershed geology.

H_0: the carbonate system variability relates to local biological processes not correlated with the type of freshwater discharge.

To test these hypotheses, data from the Marine Institute (MI) were used. MI owned a large dataset with surveys from 2000 to 2018. Part of this dataset, which covers the carbonate system parameters and nutrients, was used to address the scope. Further data of TA and DIC collected during an oceanographic cruise with MI Celtic Voyage in October 2017, were integrated to the MI database with additional data from Galway Bay, Shannon Plume and Dingle Bay. The final dataset covered a large part of Irish coast and the data were mainly available for winter campaigns. Statistical analysis was performed in order to understand the geochemical variations along the coast and the principal drivers affecting the coastal carbonate chemistry in winter.

3.2 Methods

3.2.1 Oceanographic cruise- Carbonate system variation in the west of Ireland

In the month of October 2017, an oceanographic cruise with the MI's Celtic Voyager (CV) vessel was attended by the researcher involved in the present investigation. The aim of this oceanographic cruise was to collect a dataset that could describe the coastal carbonate chemistry variation in the west of Ireland. Water samples were collected from Galway bay, Dingle bay and Shannon Plume area (in Figure 3-1 it is possible to see the selected sampling locations). The sampling strategy, a transect methodology, aimed to highlight the impact of freshwater input typology, i.e., the manner and nature of fresh watershed flows from land, on local carbonate system parameters. The stations in Galway Bay and Dingle Bay covered the area from the head to the mouth. During this survey, samples suitable for TA-DIC and pH analyses were collected with 500 ml borosilicate glass bottles and immediately poisoned with 0.05% of $HgCl_2$, as suggested in ocean best practices (Dickson et al., 2007). The measurement of TA, DIC and pH were based on the methods described in paragraphs 2.3.5; 2.3.6; 2.3.7. The CTD rosette of the CV recorded the parameters at each station (see appendix chapter 3).

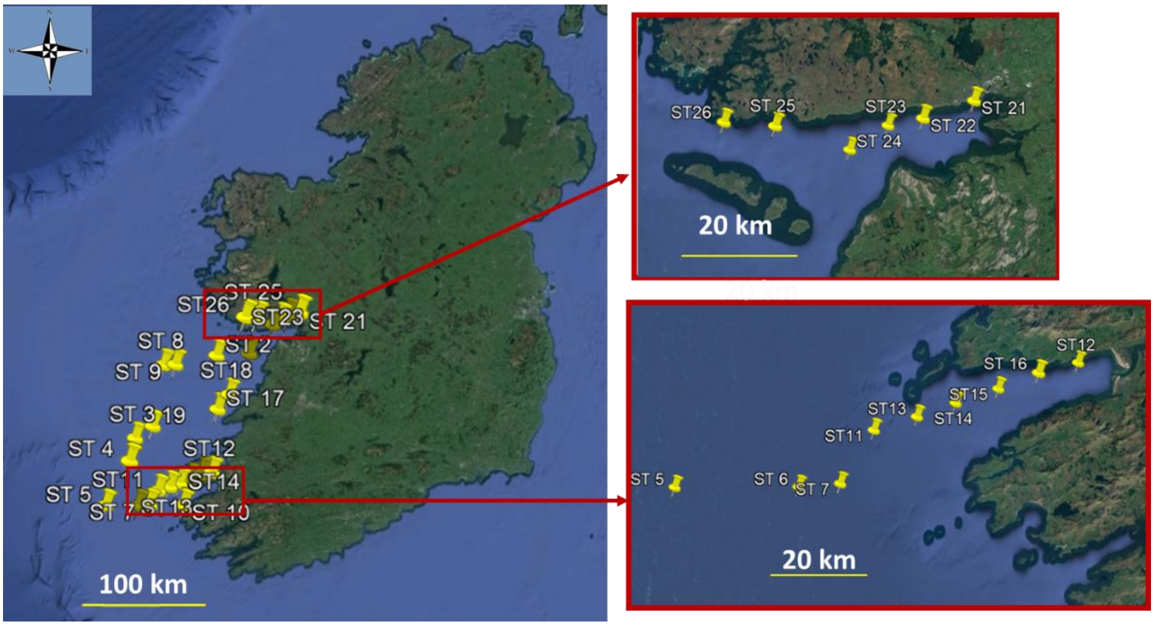


Figure 3-1 Sampling stations selected during the Celtic Voyage oceanographic cruise in October 2017: a few samples were collected along the coast, in the area identified also in the MI database as Shannon Plume area, then transect methodology from the head to the mouth of the bay was applied in Galway Bay and Dingle Bay areas. Transect detail is showed.

3.2.2 Marine Institute database: Carbonate system and nutrients variations along Irish coastal seas

The MI data used for this work, is part of a large dataset that includes coastal and open ocean locations around Ireland from 2000 to 2018 (Figure 3-2). In order to visualise the carbonate system parameters and nutrients variation along the Irish coastal area, Ocean data View (ODV) software was used. Initially, among all the parameters included in the dataset, only the ones of interest for this study (TA-DIC-nutrients and temperature) were considered. Most of the MI surveys were conducted during wintertime, and January and February are the months where TA-DIC and nutrients data are available for the same location. The reason why in winter there are more available data is because the nutrients and in particular the levels of DIN, reach their seasonal maximum values, due to the decrease of plants and algal growth (Hogan, 2019). Furthermore, because winter is also the rainfall season, the intense weathering from rocks increases TA (McGrath et al., 2019).

To perform the PCA and to understand if the freshwater input can influence the coastal carbonate chemistry, only the samples included in the first 10 meters depth were selected. The final dataset included 7 locations with 113 sampling stations. The matrix had the following parameters as variables: temperature°C, salinity ‰, TA, DIC, NO_3^-, NO_2^- , PO_4^{3-} and SiO_4^- µmol/l.

Additionally, thanks to the availability of these data, it was possible to calculate pH, Aragonite saturation state (Ω_{Ar}) and REVELLE factor (Takahashi et al., 1993; Revelle and Suess, 1957), which is often used to quantify the buffer capacity of the seawater inorganic carbon system, and its capacity to take up CO_2, which decreases under high pCO_2 conditions (Thomas et al., 2007). REVELLE factor is ratio of the relative change of CO_2 to the relative change of DIC, and typically ranges between 8 and 15 (Zeebe et al., 2003). These parameters were calculated using the CO2SYS software (see 2.3.8).

The locations represented in the final database are the following: Ards Penninsula, North Channel (the samples considered belong to a transect performed from Torr to Southend area) Dublin Bay, Cork Harbour, Dundalk bay, Galway Bay and Waterford Harbour. These locations represent five different catchment geological areas: Shale/sandstone (Ards Penninsula and Dundalk Bay), Basalt (North Channel), limestone (Galway Bay and Dublin Bay), volcanic rocks interconnected with shale and Sandstone (Waterford Harbour), Sandstone and limestone (Cork Harbour).

In Figure 3-2 the MI full database stations are shown, as well as the locations selected in this work. The data analysed during the oceanographic cruise in 2017 were added to the MI dataset for the initial viewing. The Galway Bay transect conducted during the oceanographic cruise in October 2017, was then compared to the transect conducted in February 2016 by the MI of Galway, to see the effects of the seasonal variations.

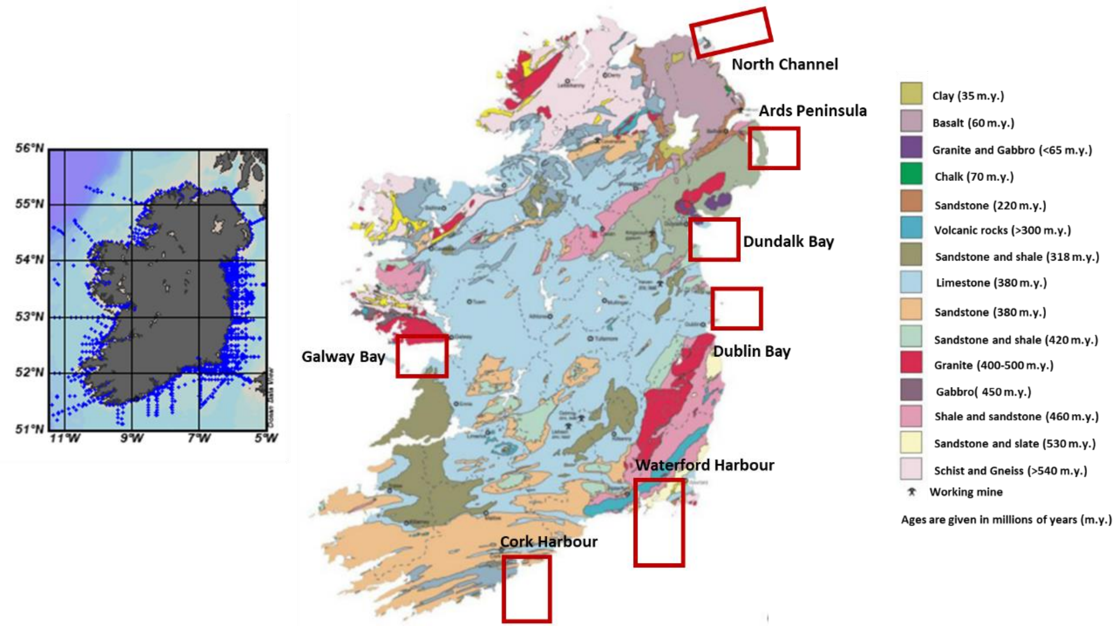


Figure 3-2 On the left the locations of all stations from the MI database are represented. Geological map of Ireland is represented in the middle, and geological periods are listed on the right. The selected locations are those ones where the carbonate system parameters (TA and DIC) and nutrients were available. The red squares indicate the areas selected from the MI database for the comparison and the statistical analysis.

3.2.3 Chemical composition in rivers and SGD feeding the Irish coastal seas

The selected locations on the coast (Figure 3-2) are fed by rivers and/or SGD. To discuss the variation of coastal chemistry and to relate this to the watershed geology and freshwater composition, published literature studies were used. The technical literature taken into account was about watershed geology, as well as the chemical composition of most rivers and SGD. Knowing the chemistry of the freshwater feeding an area allows to understand how this can affect the bays, and consequently, the surrounding coastal bodies. For some areas (Northern Ireland) a few published papers were found. Additional information were requested to the Northern Ireland Environmental Agency (NIEA), which provided water chemistry data on the mouth of the following rivers: Bush, Glenshesk, Dunseverick, Glendun, Glenarm, Lagan and Enler (Figure 3-3). The NIEA dataset covers the period 2009-2017, including the following available data: TA, NO_3^-, NO_2^-, pH, temperature, and salinity.

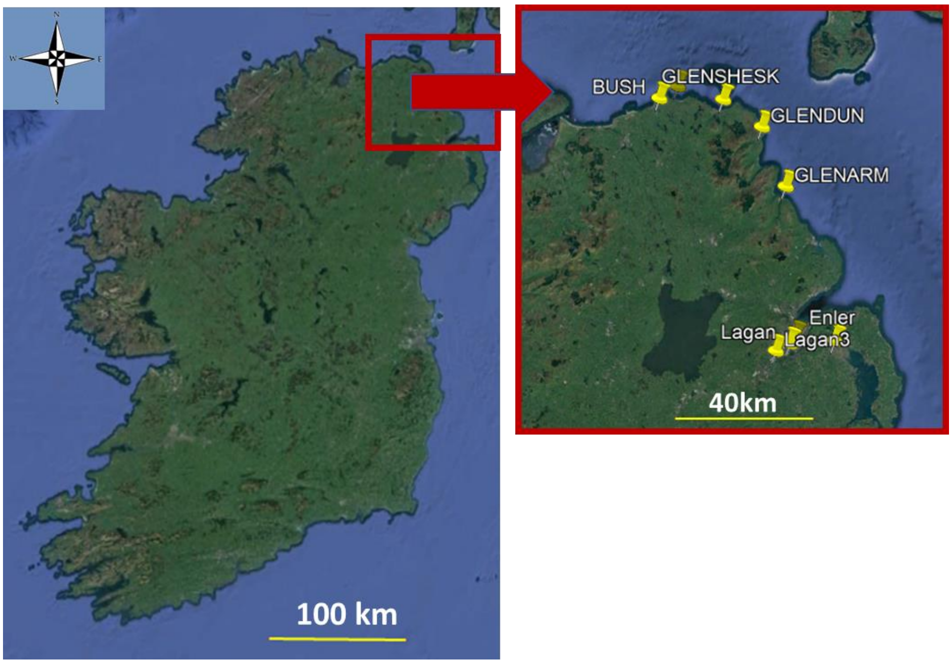


Figure 3-3 TA and nutrients measured at the mouth of the rivers: Bush, Glenshesk, Dunseverick, Glendun, Glenarm, Lagan, Enler by the NIEA, data from 2009-2017.

3.3 Data analysis

The null hypothesis tested was:

H_0: the carbonate system variability relates to local biological processes not correlated with the type of freshwater discharge.

To understand the main correlations between the parameters of carbonate system, salinity and the nutrient data, and to understand if there is geographical significant difference between the water chemistry in the different locations, a number of steps were taken. The matrix was treated as environmental data; the scaling was important since it gives all the variables an equal weight (Zitko, 1994): therefore, the matrix was transformed using the square root function and the values were normalized. The PCA was used as exploratory technique and it was hypothesized that some variables were correlated with freshwater input, therefore with salinity values. The PCA was performed using the normalised matrix, and the Principal Coordinates (PCOs) were obtained using the resemblance matrix. These methods are based on an unconstrained ordination and are both based on Euclidean distance.

On the analysed matrix, the Permutational multivariate analysis of variance (PERMANOVA) test was performed (Anderson, 2017), to determine if there were significant differences between the variables and the selected factors (locations and geology) (McArdle and Anderson, 2001; Zhang et al., 2014). PERMANOVA is a geometric partitioning of variation across a multivariate data cloud, defined explicitly in the space of a chosen dissimilarity measure, in response to one or more factors in an analysis of variance design (Anderson, 2017). The PERMANOVA design was created using one factor (once locations and once geology) and the test was performed. Since Euclidean distance was used, the sum of the squares in PERMANOVA were equal to the sum of the classical univariate sums of squares across the original variables. The F statistic indicates if there are significant differences between the groups. The pseudo F, on Euclidean distances is the same as the F statistic used in classical redundancy analysis (Anderson, 2017). PERMANOVA on one response variable, using Euclidean distance, yields the classical univariate F statistic (Fisher, 1924; Anderson, 2017). PERMANOVA can also be used to do univariate ANOVA, but where p-values are obtained by permutation (Anderson and Millar, 2004), thus avoiding the assumption of normality. The p-value was obtained using 999 permutations, a value >0.05 indicates if there are significant differences between locations or geology. PERMANOVA was applied in this study because it can find differences in the data cloud that are not evident in a two-dimensional ordination.

An unconstrained ordination like the PCA may be useful to visualize overall patterns of dispersion. However, the differences between the clusters might be masked in the PCA and could be uncovered using instead the canonical approach (Anderson and Willis, 2003). Therefore, to further emphasize the significant differences between the factors, the Canonical Analysis of Principal Components (CAP) was also performed after the PCA. The CAP method allows to do a constrained ordination based on any distance or dissimilarity measure (Anderson and Willis, 2003).

The Pearson's correlation coefficient was also calculated between the variables to better understand the correlations between the factors, whether the differences are dependent on catchment geology or locally driven by other human activities on land.

3.4 Results

3.4.1 Ocean Data View and descriptive statistics

As explained in the methods, because the large dataset, in order to have a first overview of the data, the software ODV was used to observe the variations of carbonate system parameters (TA and DIC) along the Irish Coastal sea, as well as nutrients (PO_4^{3-}, SiO_4^-, Total oxidised Nitrogen (ToxN) which is the sum of NO_3^- + NO_2^-) and salinity. This first observation indicated whether the watershed inputs can act as a source of nutrients, TA and DIC to the coastal seas. In the Figure 3-4 and Figure 3-5 it is possible to observe the TA, DIC, nutrients and salinity variability along the Irish coast in the whole dataset acquired between 2000 and 2018 and all the seasons (Dingle Bay and Galway Bay data collected during the October 2017 oceanographic cruise were added to the MI database).

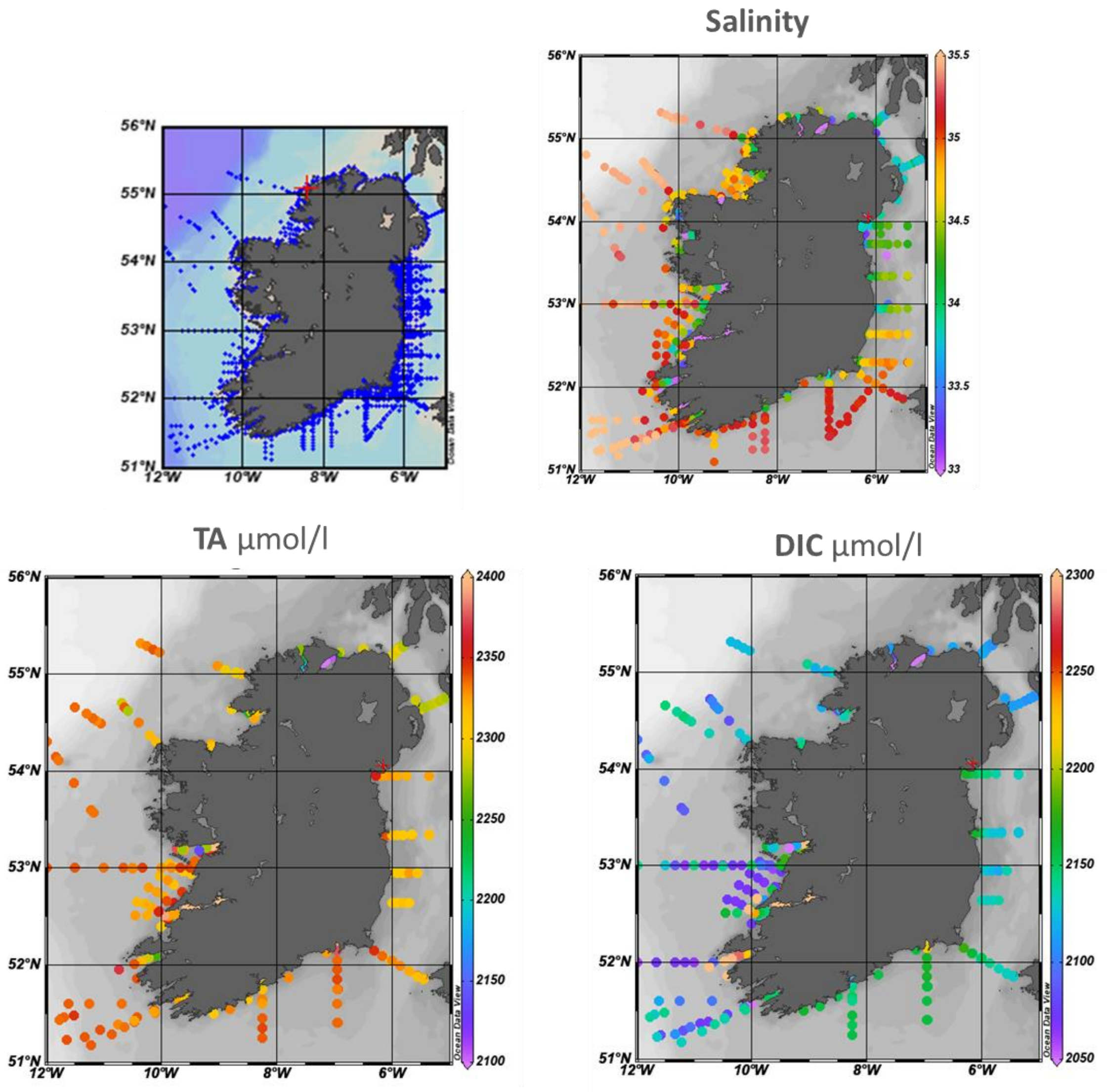


Figure 3-4 TA-DIC and Salinity are represented in all the stations collected by Marine Institute from 2000 until 2018. Further data in Galway Bay, Shannon plume and Dingle Bay were added coming from the Oceanographic cruise of October 2017 (for the data see Appendix chapter 3). Because Ards Peninsula and North Channel are situated in county Antrim, a basaltic area, TA and DIC are directly correlated with salinity. On the western coast, particularly the karstic catchment area shows an inverse correlation between TA and DIC versus salinity, showing the evident source of TA and DIC coming from the land.

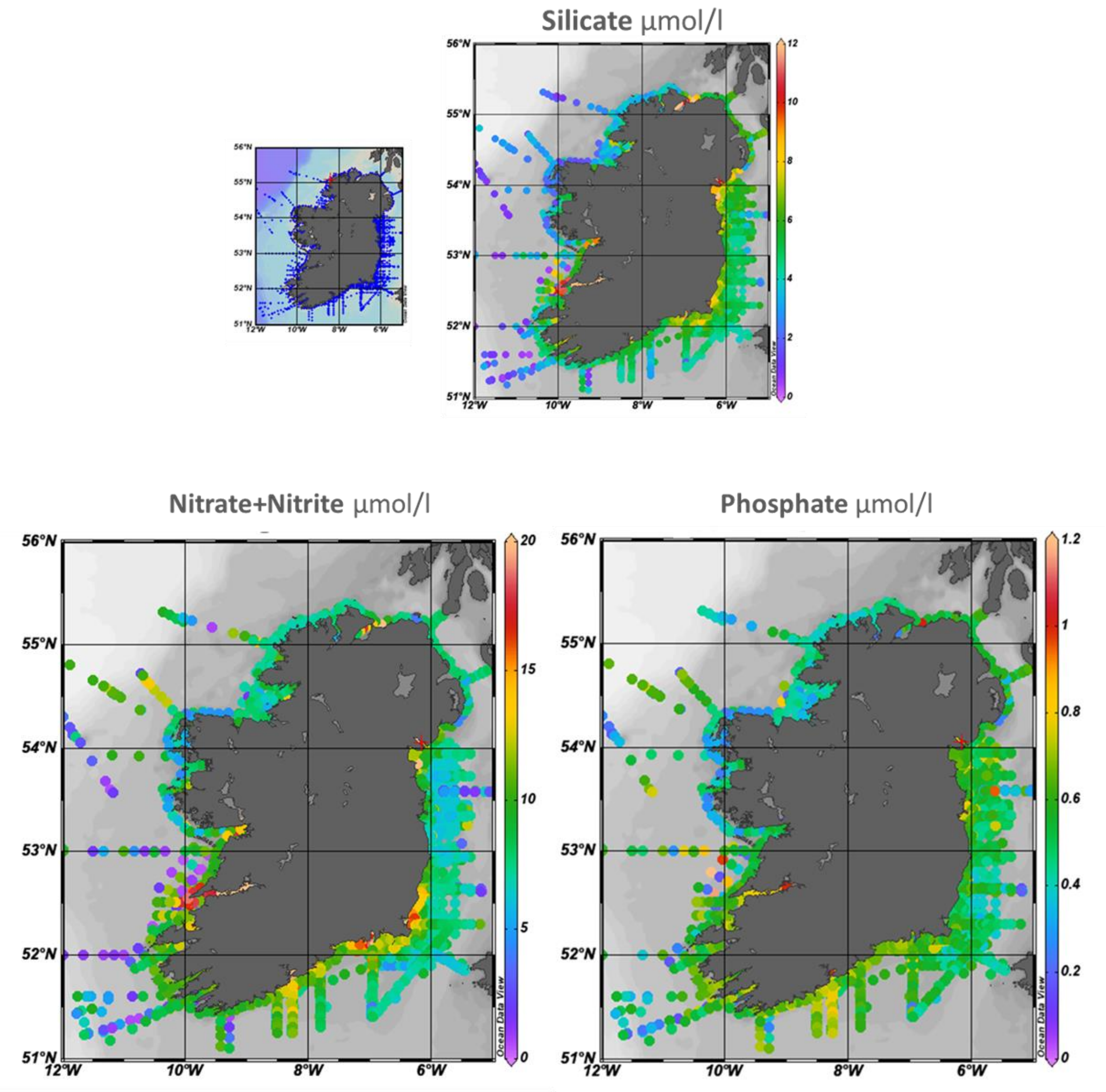


Figure 3-5 NO_3^-+NO_2^-, PO_4^{3-} and SiO_4^- expressed as µmol/l, along Irish coastal sea is represented. The data are from 2000-2018 and come from both surface and deep-water samples.

The descriptive statistics in the Table 3-1, show the mean, minimum and maximum values of each variable in the different locations selected in this work, Figure 3-2. Galway Bay showed the higher range of variability for salinity values.

The locations with higher TA, DIC were Dublin Bay and Galway Bay, which are inserted into a karstic catchment.

ToxN had high values in most of the locations with the exception of Northern Ireland. SiO_4^- showed higher values in Dundalk, Dublin and Galway Bay.

Table 3-1 Descriptive statistics of TA, DIC, ToxN, PO_4^{3-}, SiO_4^-, expressed in µmol/l, salinity ‰ and temperature °C in the selected locations

Variable	Locations	Mean	Minimum	Maximum
TA	Ards Penninsula	2285	2277	2295
	Cork Harbour	2316	2294	2342
	Dublin Bay	2320	2298	2413
	Dundalk Bay	2326	2305	2353
	Galway Bay	2385	2315	2490
	North Channel	2292	2282	2327
	Waterford Harbour	2340	2325	2394
DIC	Ards Penninsula	2113	2105	2139
	Cork Harbour	2136	2132	2141
	Dublin Bay	2140	2104	2219
	Dundalk Bay	2153	2122	2185
	Galway Bay	2233	2131	2383
	North Channel	2115	2106	2125
	Waterford Harbour	2158	2130	2232
ToxN	Ards Penninsula	7.8	6.8	8.5
	Cork Harbour	12.4	8.5	17.8
	Dublin Bay	8.4	6	15.6
	Dundalk Bay	12.1	6.2	21.5
	Galway Bay	13.1	6.1	31.8
	North Channel	7.0	4.2	9.0
	Waterford Harbour	11.6	7.2	23.6
PO_4^{3-}	Ards Penninsula	0.6	0.6	0.7
	Cork Harbour	0.7	0.5	0.8
	Dublin Bay	0.6	0.4	1.4
	Dundalk Bay	0.6	0.5	0.8
	Galway Bay	0.4	0.2	0.5
	North Channel	0.6	0.5	0.6
	Waterford Harbour	0.7	0.5	0.9
SiO_4^-	Ards Penninsula	6.4	5.7	7.0
	Cork Harbour	4.9	2.5	6.8
	Dublin Bay	6.2	4.2	13.4
	Dundalk Bay	9.1	5.4	16.8
	Galway Bay	8.3	4.2	23.5
	North Channel	5.3	3.4	6.7
	Waterford Harbour	5.4	3.7	9.8

Variable	Locations	Mean	Minimum	Maximum
salinity	Ards Penninsula	33.8	33.7	34.0
	Cork Harbour	35.0	34.3	35.6
	Dublin Bay	34.3	31.9	35.2
	Dundalk Bay	33.7	32.5	34.4
	Galway Bay	29.4	12.3	34.2
	North Channel	34.2	33.7	35.1
	Waterford Harbour	34.9	33.8	35.2
temperature	Ards Penninsula	8.7	8.6	9.1
	Cork Harbour	9.5	8.0	11.1
	Dublin Bay	8.2	5.4	9.6
	Dundalk Bay	7.8	6.0	9.3
	Galway Bay	7.5	6.5	9.0
	North Channel	8.8	8.5	9.3
	Waterford Harbour	9.6	8.3	10.6

In Figure 3-6 TA and DIC are plotted against salinity: the focus is on the locations selected for the statistical analysis. In Figure 3-4 the TA and DIC were represented all around Ireland and some positive and negative correlations are recognisable. In Figure 3-6 the positive and negative correlations between the TA and salinity are made clearer. North Channel and Ards Penninsula clearly showed lower TA and DIC values at the same salinity level compared to the other coastal locations. Galway Bay showed lower salinity compared to the other coastal areas and also higher TA and DIC values, which suggested that freshwater input has a high impact on this coastal embayment. The different TA and DIC values at the same salinity suggested that the type of freshwater composition can change the TA and DIC accordingly.

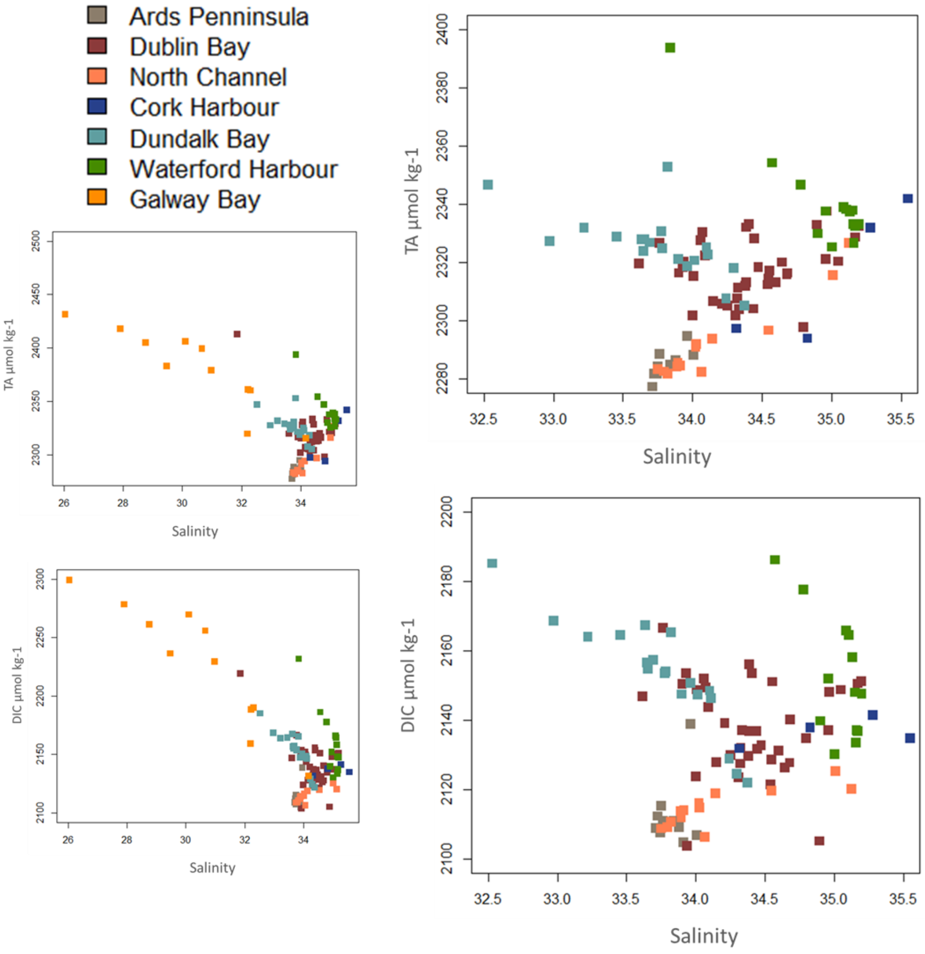


Figure 3-6 TA and DIC versus salinity are plotted in the 7 locations selected for this study: Ards Penninsula, Dublin Bay, North Channel, Cork Harbour, Dundalk Bay, Waterford Harbour and Galway Bay. On the left side all locations are plotted. On the right side there is a zoom on areas with salinity in the range of values between 32 and 36. From the graphs on the right it is possible to observe that the North Channel and Ards Penninsula are showing lower TA and DIC compared to Dundalk Bay, Dublin Bay and Cork Harbour.

3.4.2 Statistical analysis

To understand the correlations between the selected variables and to observe if there were significant differences between the investigated locations or related to the geology, the PCA analysis was performed.

The PCA is a diagram representation that should help to understand the main patterns and correlations between the chosen variables. There are two types of graphical plots, the plots of loadings, which indicate relations among the variables, and the plots of scores, which give the positions of the samples in the coordinates of the principal components (Zitko, 1994). Using Primer™ statistical programme, it was possible to obtain a combination of both graphical representations.

As a second step, the PCO between the variables was performed, using a resemblance matrix with Euclidean distance. Since the PCA implicitly uses Euclidean distance, there was no difference between the two ways of representation, therefore the PCA vectors were plotted on PCO graph and the results are shown in Figure 3-7: positives and negatives correlations between the variables can be observed. Looking at the PCO biplot, the lines pointing in the same direction indicate that the corresponding variables are correlated with each other (Zuur et al., 2007). The more acute angles between lines indicate a greater degree of correlation e.g., SiO_4^- with the ToxN are extremely correlated, but also TA with DIC, TA and pH, and DIC with the SiO_4^- and the ToxN. The lines pointing in opposite directions, indicate negative correlation. For example, the large angle (close to 180°) shows negative correlation between TA and DIC with salinity: the null hypothesis should be rejected, since the carbonate system variability in the Irish coastal seas is correlated with the freshwater discharge. Most of the locations showed this trend indeed, as it is possible to observe with the ODV graphical representation, which also suggests that only in the Northern Ireland (Ards Peninsula and North Channel) the trend is different, and the freshwater source is not an additional source of TA and DIC to the coast (see Figure 3-4).

Another angle of 180° is visible for SiO_4^- and ToxN with temperature. The negative correlation between temperature and nutrients can be explained with seasonal variation: with the increase of primary production and temperature in spring and summer, nutrients are consumed, reversely with the decrease of primary production and temperature in autumn and winter, with the increase of discharge due to the higher precipitation which stimulate the weathering processes, nutrients availability in the water column is increased (Bai et al., 2017).

The lines pointing in opposite directions but with more obtuse angles between lines are indicating a greater degree of negative correlation (Zuur et al., 2007) as it is possible to observe between pH and PO_4^{3-}. Lines with an angle of -90° are uncorrelated (Zuur et al., 2007), e.g. pH with Ω_{Ar} and temperature or temperature with PO_4^{3-}.

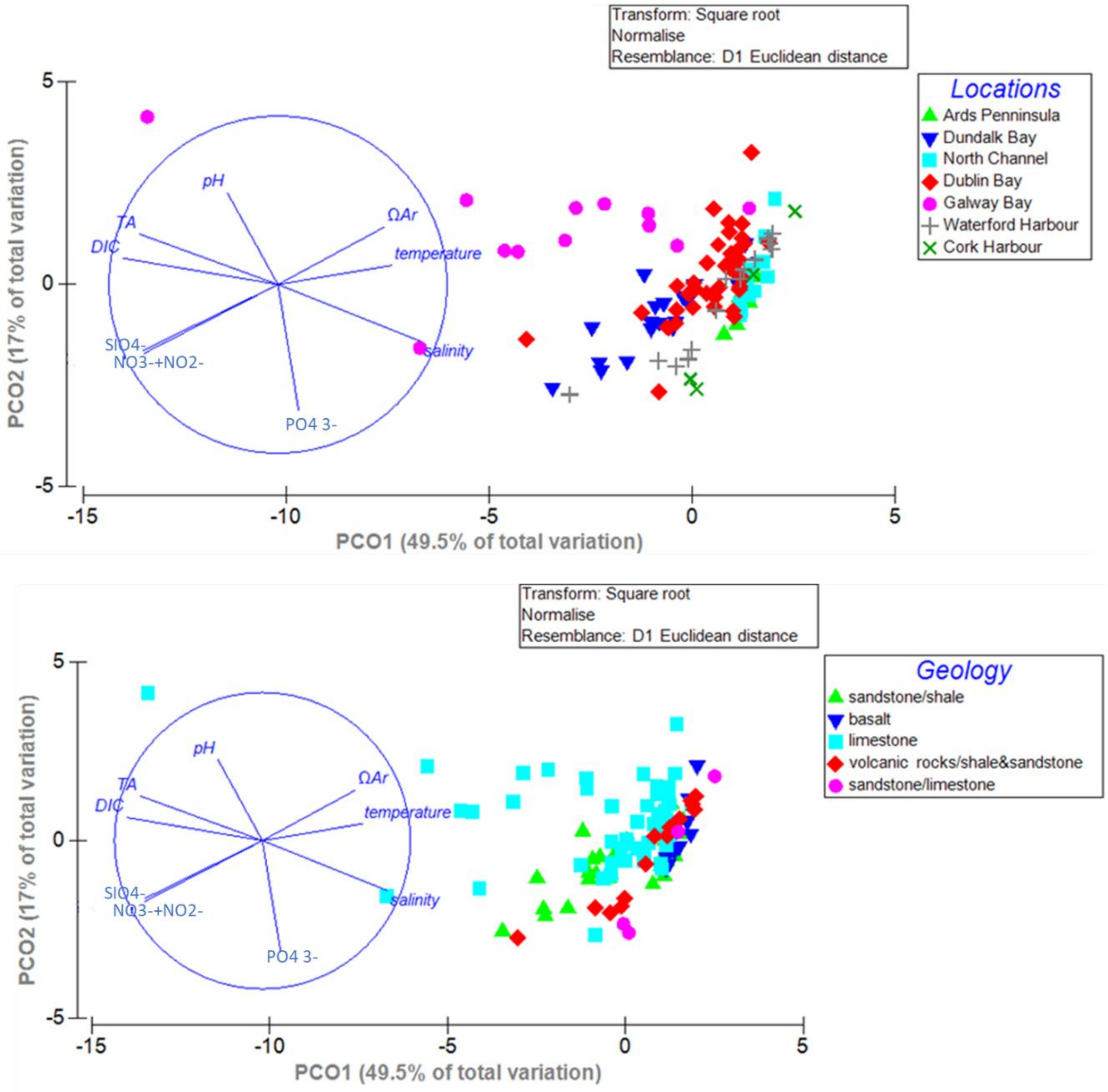


Figure 3-7 The PCOs is represented: the samples have been divided in 7 locations along the Irish coastal sea (on the top) and in areas with 5 different geological characteristics (on the bottom).

The PCO analysis extracts nine components, but only the first two components, which together represent 66.5% of the total variances, are represented. The PCO1 corresponds to the TA and represented the 49.5% of the total variation, and the PCO2, which corresponds to the DIC, represented the 17% of the total variation. Most of the locations showed negative correlation between TA and salinity. However, this trend is not true in all the locations. Therefore, the 49.5% of the variation can be attributable to the differences between the factors (locations and/or geology). The negative correlation between TA and salinity, indicated that some coastal areas are a source of alkalinity to the open ocean, therefore, the linear relation between TA and salinity cannot be applied to the coast. The PCO2 represents the 17% of the variations, and this can be explained because the DIC variation can be in part correlated to the increase of TA for some locations, or alternatively correlated to the increase of nutrients in other locations. Indeed, the DIC and the nutrients are correlated each other as previously observed from the small angle.

As said early, the graphical representation used in this work, Figure 3-7, shows also the position of the samples. It is difficult to distinguish the differences between the clusters on the Y axes. The differences are more visible on the X axes, where, in the PCO1, Galway Bay cluster is distant from the others (less visible where the data were classified by geology). In order to verify if there is significant difference between the groups, PERMANOVA design with one factor (locations and geology separately) was created and the PERMANOVA test was performed (Table 3-2).

Table 3-2 PERMANOVA test performed with 1 factor (Locations and Geology separately).

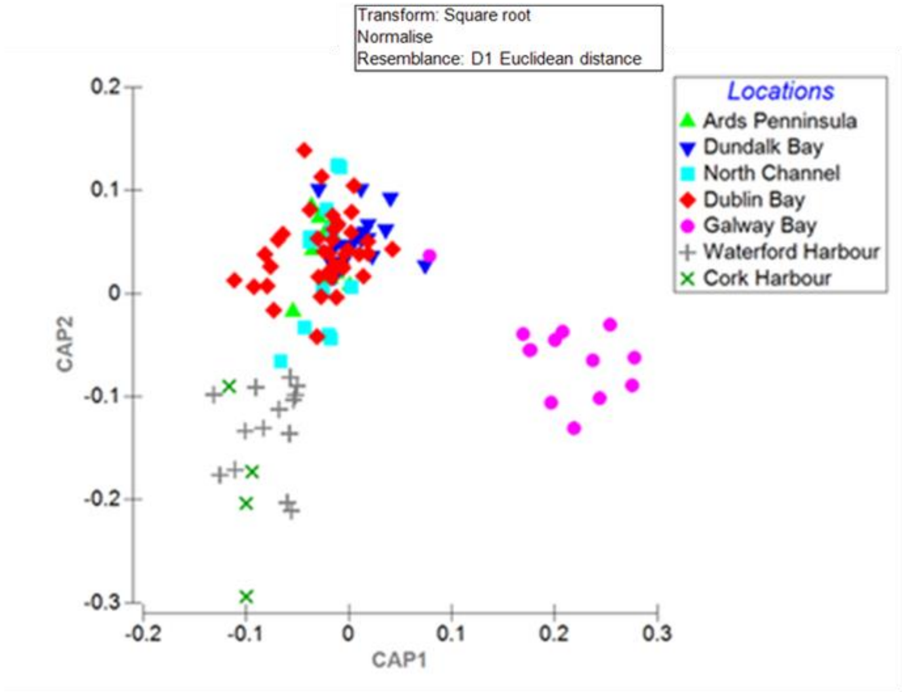
PERMANOVA table of results

Source	df	SS	MS	Pseudo-F	P-perm	Unique Perms
Locations	6	422.67	70.445	10.708	0.001	998
Residuals	106	697.33	6.5786			
Total	112	1120				

Source	df	SS	MS	Pseudo-F	P-perm	Unique Perms
Geology	4	160.39	40.099	4.5129	0.001	999
Residuals	108	959.61	8.8852			
Total	112	1120				

The p-value was less than 0.05 and a value of 0.001 was found on both PERMANOVA test. This means that there is a significant difference between the factors, even if it was not particularly evident in the PCO. In this case, another representation can be used to better understand the clusters, which is the main reason why the CAP was performed. The CAP considers the design and the structure of the data.

From Figure 3-8 it is possible to observe that clusters are more defined. Differently from the PCO representation, where only Galway Bay area was clearly distinguishable from the other locations, following the CAP analyses, also Waterford Harbour and Cork Harbour formed a clearly distinct cluster. The Figure 3-8 showed some patterns related to the geology, however some clusters were still not clearly defined. Cork Harbour and Waterford Harbour positions suggested that the water chemistry was more correlated with the locations than with the geology. From the bottom representation of Figure 3-8, it is possible to observe that Cork and Waterford Harbours are characterized by different catchment geology, however, the fact that they are forming a cluster might suggest that similar freshwater typology is influencing these locations. In Dublin Bay and Galway Bay the watershed geology might be a common factor to distinguish the coastal water chemistry. However, when the CAP was performed using location factor (Figure 3-8), Galway Bay clearly formed a different cluster, suggesting that even if the geology factor is grouping these locations (Dublin Bay and Galway Bay) there is a different driver in the two locations that make them distinguishable. It is known indeed that Galway Bay area is mainly fed by SGD which can likely discharge water with high TA, DIC and nutrients (EPA, 2011; Kelly, 2018), conversely in Dublin Bay area, the main freshwater input is in the form of river discharge, where the Liffey River is the main source of nutrients (O'Higgins and Wilson, 2005) and alkalinity, due to the erosion of limestone bedrock (McGrath et al., 2016).



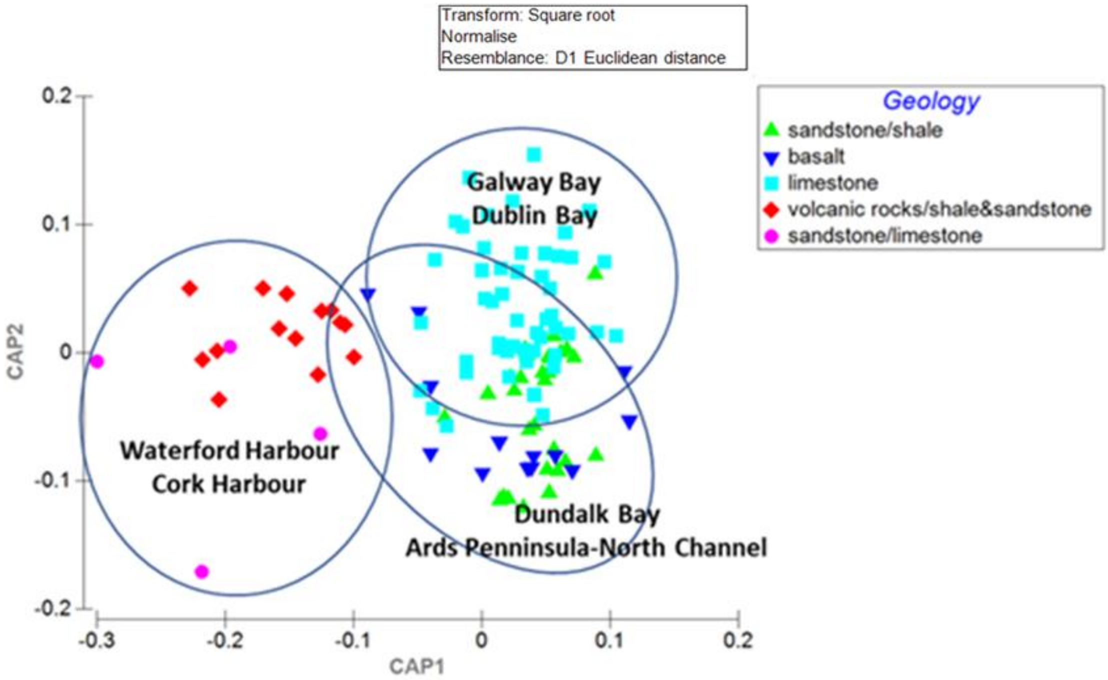


Figure 3-8 CAP was performed using the resemblance matrix using Euclidean distance. On the top the graphical representation was made using the PERMANOVA design for the factor “Locations”, Galway Bay area location and Waterford and Cork Harbours are clearly forming two different clusters, while the other locations look grouped together but still overlapping each other. On the bottom the graphical representation was made using the PERMANOVA design for the factor “Geology”. There are some similitudes, the Waterford Harbour and Cork Harbour are still forming a cluster, the limestone area Dublin Bay and Galway Bay look as a cluster, and the Northern Ireland locations are forming a group but still overlapping.

Pearson's correlation coefficient was calculated between the different variables in the different locations. Galway Bay and Waterford Harbour-Cork Harbour were considered as two different groups since two defined clusters were evident from the CAP performed with the geology factor. Even if the other groups were visible from the CAP, they were not clearly distinguishable, and more details can be observed looking at the specific correlations between the variables.

TA and DIC are not equally distributed along the Irish coastal sea and are not always correlated with salinity (Table 3-3). It is known that changes in coastal carbonate chemistry are due to the freshwater input that could change the carbonate chemistry on the coast (Borges and Gypens, 2010; Pain et al., 2020). From Table 3-3, it is possible to observe some significant positive and negative correlations between carbonate system parameters (TA, DIC and pH) with salinity, as well as some interesting correlations between nutrients with DIC or salinity. Even in locations with similar watershed geology, the correlations between the variables are different (e.g., TA and salinity are positively correlated in the Ards Penninsula, characterized by sandstone and shale, negatively correlated in Dundalk Bay that has a similar geology). ToxN shows positive correlation with DIC, which suggests that the nitrogen source is stimulated by the respiration of organic matter.

The REVELLE factor (Revelle and Suess, 1957; Takahashi et al., 1993) which is the ratio of the relative change of CO_2 to the relative change of DIC, typically ranges between 8 and 15 (Wolf-Gladrow, 2003) and is often used to quantify the buffer capacity of the seawater inorganic carbon system. In the current study this was calculated with CO2SYS as explained in the methods' section. It is possible to observe that REVELLE factor was negatively correlated with salinity in almost all the coastal areas, increasing at low salinity areas and decreasing where the salinity is high. The REVELLE values calculated in the analysed areas were between 12 and 14, with the highest values in Galway Bay area. Furthermore, the $CO_{2(g)}$ saturation index (SI) was calculated using PHREEQC (see methods). In Table 3-4 the Revelle factor, aragonite and calcite and $CO_{2(g)}$ saturation indices are shown from different representative water samples of Irish coastline. It is possible to observe that Revelle factor and $CO_{2(g)}$ SI are inversely correlated. Indeed, with the increase of the Revelle factor the capability of water to absorb atmospheric CO_2 will be reduced.

Table 3-3 In the following table the Pearson's Correlation Coefficient was calculated between the variables in the different locations. In same locations it is shown high positive or negative correlation: the regression analysis was performed and a p-value < 0.05 was found for the correlation > 0.50, which indicates that the correlations are statistically significant. The correlations between the different parameters are partially related with the geological characteristics of the areas. The geology is indicated as following: 1* = sandstone and shale, 2* = basalt, 3* = limestone, 4* = volcanic rocks/shale and sandstone, 5* = sandstone and limestone.

Pearson's Correlation Coefficient r (x,y)

Groups	Locations	Geology	r (TA,salinity)	r (DIC,salinity)	r (pH,salinity)	r (ΩAr,salinity)	r (REVELLE, salinity)	r(PO$_4^{3-}$,salinity)	r(ToxN ,salinity)	r(SiO$_4^-$, salinity)	r (ToxN ,DIC)
Northern-east Ireland	Ards Penninsula	1*	0.72	0.25	-0.03	0.20	-0.10	-0.12	-0.90	-0.23	-0.21
	North Channel	2*	0.96	0.81	0.79	0.89	-0.90	-0.74	0.17	-0.90	0.23
East Ireland	Dundalk Bay	1*	-0.55	-0.69	0.71	0.71	-0.84	-0.70	-0.77	-0.73	0.68
	Dublin Bay	3*	-0.52	-0.57	-0.38	0.01	-0.24	-0.81	-0.73	-0.83	0.63
West Ireland	Galway Bay	3*	-0.88	-0.88	-0.78	0.75	-0.97	0.27	-0.69	-0.71	0.73
South Ireland	Waterford Harbour	4*	-0.32	-0.67	0.60	0.69	-0.79	-0.73	-0.83	-0.90	0.77
	Cork Harbour	5*									

Table 3-4 In the following table a representative sample of each listed location was used to obtain the following output conditions: REVELLE factor, aragonite and calcite saturation state, were obtained using CO2SYS, CO$_2$(g) saturation index was obtained using PHREEQC.

Locations	REVELLE factor	Aragonite saturation state (CO2SYS)	Calcite saturation state (CO2SYS)	SI CO$_2$(g)
Galway Bay	15.07	1.76	2.83	-2.97
North Channel	13.19	1.90	3.01	-2.98
Cork Harbour	14.18	1.67	2.65	-2.97
Dublin Bay	12.96	1.97	3.12	-2.99
Dundalk Bay	12.77	2.13	3.36	-3.01

3.4.3 Comparison of TA and DIC in two different surveys: Galway Bay

Galway Bay area, compared to the other locations, showed higher TA and DIC values, Figure 3-6. The main loading of TA and DIC in this location it can be recognised in the SGD and a comparison between surveys conducted in different period of the year might help to understand the SGD impact on the TA and DIC in the adjacent coastal area. The transect methodology was then applied in order to understand the carbonate system dynamics occurring between the freshwater and the marine end-member.

The two transects' investigations conducted in Galway Bay in February 2016 and October 2017, were compared.

TA and DIC versus salinity regression analysis is represented in Figure 3-9. TA and DIC, as confirmed by the previous data, showed high negative correlation with salinity. The R^2 measured with the linear regression lines showed high negative correlation between TA and salinity and DIC and salinity at both the transects. As it is possible to observe from Figure 3-9, samples collected in the inner Galway Bay during the two different surveys, have similar latitude and longitude. However, TA and DIC showed higher values at comparable salinity in October 2017, suggesting that the freshwater source, which is a source of TA and DIC, might have different TA and DIC composition compared to February 2016, having as a consequence, a greater influence on the carbonate system dynamics in Galway Bay.

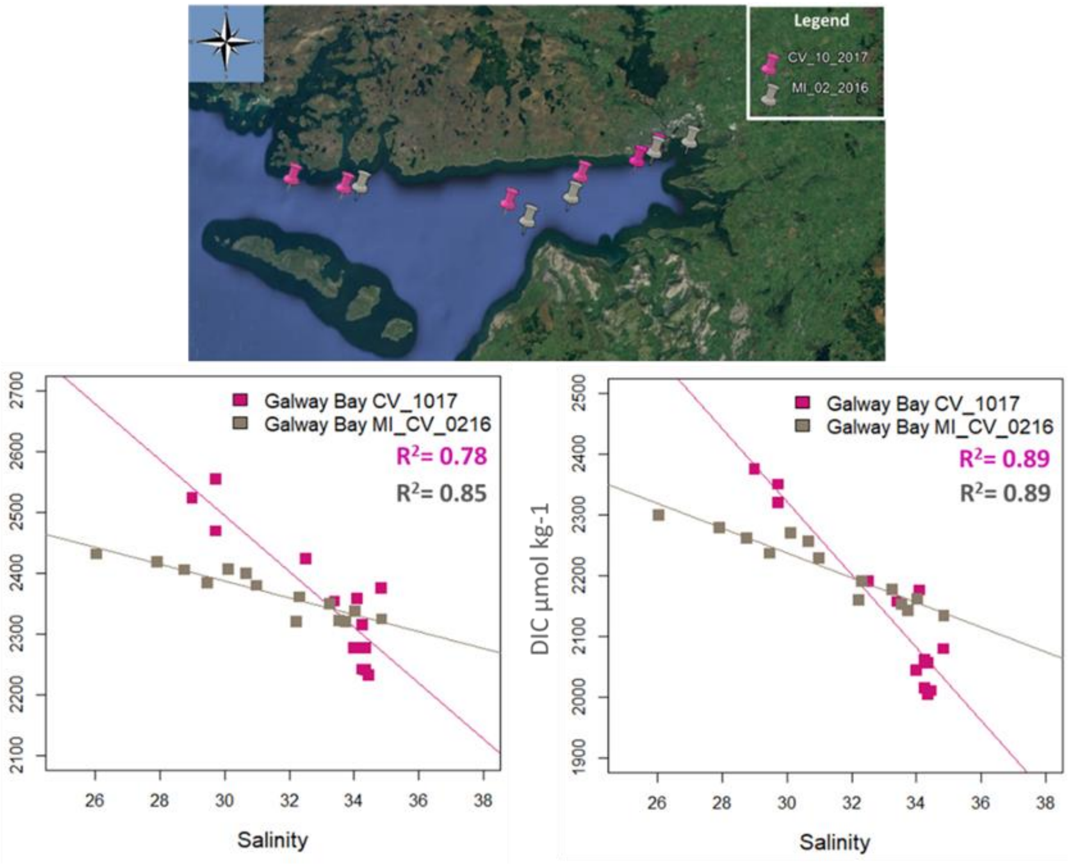


Figure 3-9 On the top, the selected sampling locations for the two surveys conducted in Galway Bay are showed. TA and DIC versus salinity are represented with the respective repression lines. In pink, transect from CV October 2017 is represented, and in grey transect from CV in February 2016 is represented. (For Galway Bay transect CV October 2018 see Appendix chapter 3)

TA and DIC relations in Galway Bay are represented in Figure 3-10 from both the oceanographic cruises. It can be observed that the TA-DIC slopes were different in the two surveys. The slope measured in October 2017 was 0.78±0.06, and in February 2016 was 0.69±0.02. The difference in the slopes might be related with the loading of TA and DIC coming from the freshwater input. This result indicates that the delivery of TA over DIC was higher in October 2017. Furthermore, the average REVELLE factor within the transect, calculated in October 2017 was 12 and in February 2016 was 14.2. This confirms that in October 2017 the buffer capacity of Galway Bay was higher.

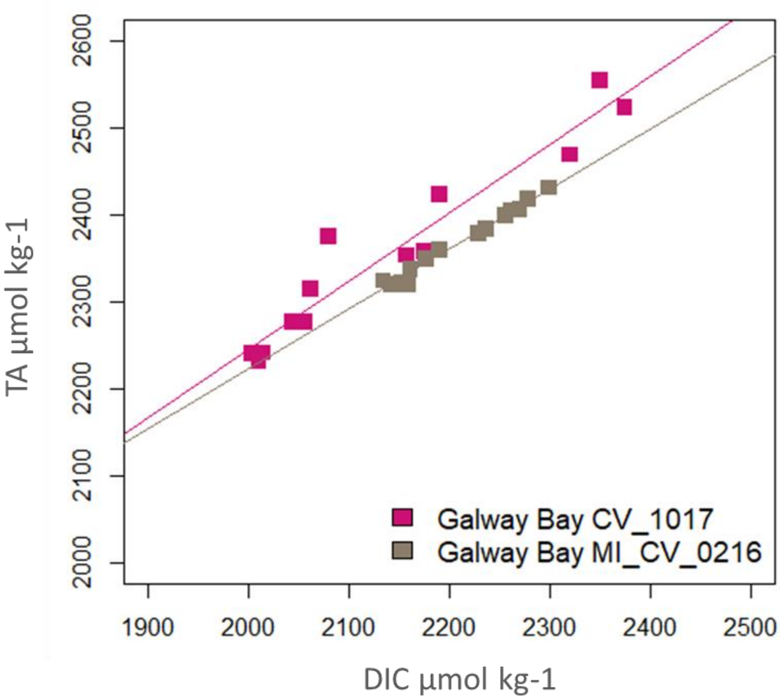


Figure 3-10 TA and DIC relation in Galway Bay. Pink dots represent the transect conducted with the CV in the oceanographic cruise of October 2017. Grey dots represent the transect conducted with the CV in the oceanographic cruise of February 2016.

3.5 Discussions

3.5.1 Nutrients distribution along Irish coastline

Knowing the delivery of nutrients to the coast is important to understand the coastal biogeochemistry. Nitrogen is generally considered the primary limiting nutrient in coastal ecosystems, meaning that the concentration of this nutrient can limit the growth of algae and aquatic plants (Kant et al., 2011). During summer, the increases in nitrogen can lead to elevated growth of phytoplankton and/or macroalgae, leading to eutrophication processes. In winter the DIN is monitored, because the levels are expected to be at their seasonal maximum (Hogan, 2019). The delivery of nutrients is often associated with the delivery of Dissolver Organic Matter (DOM), and Particulate Organic Matter (POM) which can stimulate the respiration processes (Sandberg et al., 2004; Nydahl, Panigrahi and Wikner, 2013; Soares and Berggren, 2019; Nakamoto et al., 2020). It is likely that in areas with high loading of nutrients during winter, and/or DOM and POM, also the DIC increases as a consequence. Unfortunately, DOM and POM data for the Irish coastline were not available.

Another effect of the nutrients enrichment to the coast is their role in promoting ocean acidification (Wallace et al., 2014; Cai et al., 2011; O'Boyle et al., 2019). It follows that because organic processes depend on nutrient availability, then the latter can have an effect on TA and DIC, through the net ecosystem production.

The high negative correlation between nutrients and salinity in most of the analysed coastal areas in Ireland, confirmed that the freshwater is a source of nutrients. The areas with higher nitrogen inputs towards the coast are the west of Ireland (likely due to the SGD) and the south and southeast probably due to the intense agriculture and use of fertilizers (O'Boyle et al., 2016; 2019).

Nutrients Regulation

Land usage and the effects of human discharge on the water bodies is a topic that is under the attention of the scientific community because it needs to be regulated by institutions. The delivery of nutrients in the south and southeast of the country is still high despite the current management actions (Ireland's River Basin Management Plan 2018-2021) (O'Boyle et al., 2019). The Water Framework Directive (WFD) has the aim to protect and restore waterbodies, even though to set the target and to respect them have always been difficult. In Table 3-5 it is possible to observe the current status of different water bodies in Ireland, their level of satisfaction and the relative change since 2015. *The good ecological status of a river water body depends on different physico-chemical parameters that are assessed against annual mean and 95%ile standards which have been set for each* (EPA 2012). Since 2015 there was a net decline of the water quality in 128 river bodies, which are corresponding to the 5.5% of the total waterbodies of Ireland.

Table 3-5 Data related with satisfactory status of the water in Ireland from the EPA Water Quality Report (O'Boyle et al., 2019)

Water body type	Satisfactory % (high or good)	Change since 2015
Rivers	53%	5.5.% decline
Lakes	50%	4.3% improvement
Estuaries	38%	Stable
Coastal	80%	Stable
Groundwater	92%	1% improvement
Canals	87%	Stable

From the Table 3-5 it is possible to observe that groundwater and coastal waters are in good ecological status. However, the river bodies' conditions are still critical. The main reason is attributable to the decrease of ecological status (O'Boyle et al., 2019), which relates to agriculture and wastewater. The increase of nitrogen emission is usually due to cattle and/or nitrogen used for fertilizers. However, it is not only about the increase of agriculture but also the national population in Ireland that increased by a quarter of a million since 2013, which led to more wastewater. From the data analysed in this study, it was observed that the coastal areas with the highest discharge of nitrogen are the south and southeast of the country. The enrichment of nutrients is common in many estuarine waters. However, the eutrophication occurs in certain conditions, when there is insufficient retention time or inadequate light availability (O'Boyle et al., 2015). The major reduction of nutrients loading (mainly phosphate and ammonia) was observed in the Celtic Sea and Irish Sea (O'Boyle, Quinn et al., 2016). However, the disproportion of reducing phosphate over nitrogen creates an imbalance of the N:P ratio, especially in down streams and coastal waters (O'Boyle, Quinn et al., 2016). In the study of O'Boyle et al., (2015), phytoplankton data from EPA have been analysed, a strong correlation between dissolved oxygen supersaturation and phytoplankton growth was found in the south west of the country. This suggested there are not external inputs of organic matter (allochthonous inputs) but instead in situ phytoplankton growth. With the decrease of light availability, during winter time, the oxygen decreases as well, with the increase of respiration over primary production the system can move into heterotrophic conditions (O'Boyle et al., 2015).

- *Northern Ireland*

From the Pearson correlation it was observed a negative correlation of PO_4^{3-} and SiO_4^- with salinity in the North Channel, and a positive correlation of the ToxN with salinity in the Ards Penninsula.

From the NIEA database the selected rivers in the Northern Ireland showed an average of 12 µmol/l of ToxN; the highest values were between 30 and 40 µmol/l, in Bush River. From the NIEA website most of the rivers in the Northern Ireland were classified between good and moderate status in terms of water quality, following WFD 2018. The upper Belfast Harbour was classified in moderate status, which means that the nitrogen loading can be further reduced to reach the good status. From the available sampling stations in Lagan River, it was observed an average value for ToxN of 48 µmol/l, with values higher than 100 µmol/l recorded in the cooler months (from October to March) probably due to the decrease of consumption from primary producers. This might explain the positive correlation found in the Ards Penninsula between ToxN and salinity. The freshwater composition of Lagan River in Belfast could affect the nitrogen level in the adjacent seas, as shown for Ards Penninsula transect.

- *East coast*

In the east coast of Ireland, the two areas considered for this study, Dundalk Bay and Dublin Bay were also showing high nitrogen loading. Dundalk Bay area is influenced by waste water treatment plants discharging to tidal waters (EPA, 2012). Castletown Estuary, located in Dundalk, is currently classified as potentially eutrophic with elevated nutrients loading in summer and winter and elevated phytoplankton growth (Devaney et al., 2013). Inner Dundalk Bay was previously classified as eutrophic but is now showing an intermediate status. Latest results indicate that the winter DIN levels are decreasing, chlorophyll concentrations and oxygen conditions are increasing in this waterbody (Devaney et al., 2013). Dublin Bay is constantly monitored for what concerns Nitrogen and Phosphate delivery from River Liffey which is affected by urban water discharge. Knowing that Nitrogen and Phosphate are limiting factors, they are constantly monitored. The DIN concentration has remained stable between 2007 and 2016, and decreased in the last years (Hogan, 2019).

- *South and south west*

From Pearson's correlation it was observed high negative correlation between nutrients (PO_4^{3-}, ToxN and SiO_4^-) and salinity, which clearly indicated that the freshwater feeding these coastal embayments is a source of nutrients. The south coast of Ireland is enriched by nutrients derived from human activities on land and nitrogen enrichment is particularly evident because of the disproportionate reduction of phosphorus relative to it (O'Boyle et al., 2015). Additionally, during the summer, due to the nutrients enrichment from the rivers discharge, harmful algae blooms (HAB) often occurred. The respiration processes of some species e.g. *Karenia mikimotoi* cells, and bacterial respiration associated with the breakdown of the bloom and decaying macro-organisms increases biochemical oxygen demand (BOD) (O'Boyle et al., 2016). These events are common in coastal areas and bays and could be exacerbated if there is stratification due to the freshwater input and seasonal increase of surface water temperature (O'Boyle et al., 2016). The results show high negative correlation between temperature and SiO_4^- and between temperature and ToxN. Assuming that nutrients loading is also associated with DOM-POM (Sandberg et al., 2004; Nydahl, Panigrahi and Wikner, 2013; Soares and Berggren, 2019; Nakamoto et al., 2020), during the summer, with the increase of temperature, the BOD might increase because of the biological demand.

To summarize, the delivery of nutrients in the south coast of Ireland leads to HAB in summer. Contrastingly, during winter it is likely that because of the decrease of primary production, the delivery of: nitrogen, phosphates, organic carbon, dissolved and particulate organic matter, lead to an increase of DIC in estuarine and coastal waters (Nydahl, Panigrahi and Wikner, 2013; Soares and Berggren, 2019), creating an imbalance to TA:DIC ratio, eventually affecting the coastal carbonate chemistry.

- *West coast*

Galway Bay area is the only one selected on the west coast. A large negative Pearson's correlation between nitrogen and silicate with salinity values is shown. The salinity level into Galway Bay is controlled by the freshwater in the form of SGD coming from the small bays (Kinvarra and Aughinish and Bell Harbour) inserted into Galway Bay, which dilute its water (Gregory et al., 2020). The ToxN discharged into the bay from the SGD has been measured in several studies and high levels of nitrogen species have been recorded (Cave and Henry, 2011; Smith and Cave, 2012; McCormack et al., 2014; Rocha et al., 2015). It follows that because of the high correlation between ToxN and salinity, it is likely that, especially during the winter period when the nutrients consumption decreases, these can be exported from the bays fed by SGD towards Galway Bay. However, the nutrients source into the Galway Bay area might not only originate from the SGD. The Corrib river is known to be a source for the bay (EPA 2013; Donnelly, 2018). Phosphate and Nitrogen loading from the Corrib river mainly originates from pasture (Mockler et al., 2017).

- *North west*

The used database did not offer enough data about the North West Irish coastal seas. What is known regarding its geology is that it is largely characterized by shale and sandstone. Donegal area is mainly characterized by granite and Precambrian Dalradian rocks, as well as County Mayo area with Dalradian rocks and Ordovician basaltic area. However, Lower Carboniferous limestone is still present. The whole North West Ireland did not show large delivery of: NO_3^-, NO_2^-, SiO_4^- and PO_4^-, probably because the area is not significantly affected by the pasture and the use of fertilizers. The rivers feeding the area are almost oligotrophic (AQUAFACT, 2013; EPA, 2018), and considering shale/sandstone and basalt catchment geology characterize them, the TA and DIC could be probably low. However, there is no available literature on this.

3.5.2 TA and DIC distribution along Irish coastline

The chemical erosion of inorganic materials originated by rocks weathering leads to an increase of TA delivery to the coastal zone. The type of weathering reaction is related with the bedrock geology (Hannigan and Kelly-Quinn, 2013). The chemical reactions require CO_2 and release bicarbonate, as can be seen, for example, in the equation (12) for calcite dissolution or (13) for albite hydrolysis (Suchet et al., 2003). The ocean alkalinity naturally increases because of these reactions and transport from rivers (Renforth and Henderson, 2017). Therefore, the TA values observed along the coast can be explained looking at the watershed geology and the main freshwater source feeding the areas.

Previous literature studies tried to understand the relation between carbonate coastal systems and watershed geology, like the study of McGrath et al., (2019) where areas with different watershed geology have been analysed: Kinvarra Bay, Bantry Bay, Slaney estuary (Wexford Harbour) and Suir (Waterford Harbour). McGrath et al., 2019 showed that spatial differences in TA and DIC between these coastal systems are largely correlated to the high DIC and TA freshwater inputs to the bays in limestone areas, compared with the much lower inputs in granitic/sandstone bedrock catchments (McGrath, et al., 2016). The differences in the TA and DIC composition along the analysed coastal areas in the present work can be therefore highly correlated with the type of catchment geology.

- *Northern Ireland*

The Northern Ireland geology is mainly characterized by Paleogene basalt lavas up to the coast. A typical example of Northern Ireland geology is Giant's Causeway area, characterized by natural polygonal basalt columns situated on the coastline, 60 million years old formations (Wyse Jackson et al., 2010). The water carbonate composition in the coastal areas could be correlated with the geology, in fact both rivers and subterranean waters in basaltic areas generally show lower TA values compared with the open ocean. The data of TA provided by NIEA in the rivers in Northern Ireland (Figure 3-3), showed TA values that ranges from 60 to 1000 µmol/l, except for the Dunseverick River that showed values from 1000 to 1800 µmol/l. In Lagan River, which feeds Belfast Harbour, dataset coming from three different sampling stations were provided by NIEA: there, the TA varies from 600 to 1600 µmol/l as well as in Enler River that feeds Strangford Lough. The alkalinity contribution coming from rivers in this geographical area can be explained looking at the geology. Indeed the basalts weathering leads to the dissolution of elements, such as silicates, calcium, magnesium, sodium, potassium and sulphates (Dessert et al., 2003). The dissolution processes are known to consume acidity, to absorb CO_2 from the atmosphere (the rivers become CO_2 important sinks (Dessert et al. 2003; Li et al., 2016)) and to increase the water alkalinity (Tole and Lasaga, 1984; Brady, 1991; Sherlock et al., 1995). Basalt weathering is also temperature dependent, therefore will change in the different periods of the year (Li et al., 2016). Furthermore, in climate change perspective, the basalt weathering in this area might change due to the relations between the increase of runoff and temperature (Dessert et al., 2003).

- *East coast*

Two different bays have been studied representing the east coast of the country: Dundalk Bay, inserted into a shale and sandstone catchment area, and Dublin Bay inserted into a limestone area. Both areas are mainly fed by river discharge and showed negative correlation between both TA and DIC with salinity. The areas fed by rivers with calcareous limestone geology are likely to show high TA values (Hannigan and Kelly-Quinn, 2013) because the weathering processes lead to the dissolution of calcium carbonates e.g., River Liffey feeding Dublin Bay. The rivers coming from a mixed geology show moderate TA values (Hannigan and Kelly-Quinn, 2013) e.g., Creggan River and Flurry River feeding Dundalk Bay. Even if the Dublin Bay area has a similar catchment geology to Galway Bay (west of Ireland), the TA and DIC delivery to the coast was found lower. Differently from the groundwater systems where the water can accumulate CO_2 because there is no interaction with the atmosphere, the river's CO_2 equilibrates with the atmosphere. Therefore, the delivery of DIC from a river basin, even if in this area showed higher values compare to the Northern Ireland, is still lower compared to the DIC delivered from groundwater.

- *South and south west*

It is known from the literature that River Lee feeding Cork Harbour is characterized by high DOM with reduced oxygen concentration because of the oxygen consumption of polluting organic matter. River Lee was found with less than 50% of oxygen saturation (O'Boyle et al., 2019), which suggests that respiration processes might stimulate the increase of DIC in the system. The Pearson's correlation coefficient for DIC and salinity was -0.67, therefore, the rivers are a source of DIC to the coast. The Cork Harbour survey considered in this work was in February, wintertime. Therefore, it is reasonable to hypothesize that the DIC increased as a result of bacterial respiration and reduced autotrophic carbon fixation in the cold months.

Suir Estuary, which feeds Waterford Harbour has a large input of pCO_2 and has a carbonate bedrock. The river Barrow passing through the County Laois is inserted into a Lower Carboniferous limestone area, which can explain the high values of TA recorded along the Waterford Harbour trajectory (Figure 3-4). The weathering of HCO_3^- from the river bedrock is increased by intense rainfall and river discharge (McGrath et al., 2019). These events might intensify in the near future, due to climate change and the increase of flooding events. The increase of HCO_3^- delivered to the coast, might increase the ocean buffer capacity, since leads to a removal of CO_2 from the atmosphere (Renforth and Henderson, 2017).

From the satellite imagery study conducted by (Wilson and Rocha, 2012), temperature anomaly along the west and south of Ireland was observed and linked with SGD plumes. The imagery data were integrated also with radon-222 and salinity tracer techniques, and several SGD hotspots were found, also in the area of Cork and Waterford Harbour. The high TA and DIC values in the south part of the country might derive from additional SGD sources and not only from the rivers. However, water carbonate chemistry assessment must be done in the localized freshwater springs to quantify their TA and DIC contribution to the coast. Furthermore, as suggested by Wilson and Rocha, (2012) additional data and quantitative estimation of SGD are necessary.

- *West coast*

The data presented in this study showed the TA and DIC distribution in two areas of the west coast of Ireland: Galway Bay and Dingle Bay. The Dingle Bay data were collected during the oceanographic cruise in October 2017, and because no winter data were available, this location was not considered for the PCA analysis. However, a few observations can be made looking at the TA and DIC distribution from the head to the mouth of the bay. Dingle Bay is chiefly fed by river discharge and River Maine is the main source. The valleys of the Rivers Maine are underlain by a thick cover of Quaternary deposits resting on Carboniferous limestones (Pracht, 1997). In the River Main basin five main limestone formations have been identified, two of which are of a clean, massive mud-bank type and the other three are well-bedded, more argillaceous and chertier (Pracht, 1997). From ODV Figure 3-4, it was possible to observe an increase of TA from the head to the mouth and a decrease of DIC from the head to the mouth of Dingle Bay, with the increase of salinities, which indicated that the freshwater source in this part of Ireland might be a source of DIC to the coast. However, no previous data were available for the carbonate system parameters in this area. It is important to consider that the oceanographic cruise was conducted immediately after the Ophelia Hurricane passed through the west coast of the country. Floods in the area were likely (Guisado-Pintado and Jackson, 2019, 2018), as well as the influence from other rivers which might dilute the TA. Further data should be collected in this bay to better understand the drivers of carbonate chemistry and possibly seasonal variations.

The data analysed from the MI dataset covered the area of Galway Bay for what concern the west coast of Ireland. Galway Bay catchment geology is characterized by limestone. The area mostly fed by SGD showed higher TA and DIC compared to the other locations.

3.5.3 The Galway Bay case

The Galway Bay area is widely studied because a large part of it is inserted into a karstic catchment, carboniferous limestone. A few rivers are draining into Galway Bay in the north site characterized by granite and Ordovician igneous volcanic rocks, e.g., Corrib River. However, a granite riverbed has low TA and DIC values. Most of TA and DIC sources into Galway Bay area come from the numerous small bays feeding the area, e.g. Kinvarra Bay, Aughinish Bay, Bell Harbour which are in turn fed by water coming from subterranean estuaries: several SGD springs were identified (Drew, 2008).

The transects of Galway Bay shown in this study are peculiar: the TA and DIC show linear relations with salinity in both surveys. However, TA-salinity and DIC-salinity slope is steeper in the survey of October 2017. In a few literature studies the SGD composition in Kinvarra Bay was characterised (McCormack et al., 2017; Kelly, 2018), and it is also monitored from the EPA: TA and DIC values are higher than in the open ocean. In the PhD thesis of Kelly, (2018) TA and DIC were measured in Kinvarra Castle Spring, one of the main spring feeding the area (Schubert et al., 2015), and the average TA and DIC values were 4700 $\mu mol/L^{-1}$ and 4500 $\mu mol/L^{-1}$ respectively. The SGD was quantified in previous studies (Schubert et al., 2015; Rocha et al., 2015) and estimated using models (Gill et al., 2013). The estimated water flux in Kinvarra Bay was 8.7 $m^3\ s^{-1}$ by McCormack et al., (2014), and, using radon, a value of 10.4 ± 6.3 x $10^4\ m^3\ d^{-1}$ (Rocha et al., 2015) was found in summer. The SGD in Kinvarra Bay might be even higher during winter and autumn. Considering the freshwater TA and DIC composition in the SGD and the amount of freshwater discharge, it follows that it is likely that this source can be a potential driver of carbonate chemistry composition in Galway Bay.

The TA-DIC slope in February 2016 was 0.69±0.02 and in October 2017 was 0.78±0.06. Just a few days before the survey conducted in October 2017, Ophelia hurricane impacted the western coast of Ireland: floods were consistent in the Galway Bay area (Guisado-Pintado and Jackson, 2019, 2018). Because Galway is a karstic area, HCO_3^- dissolution might have increased the TA delivery to the coast, and this could explain the increase in the TA:DIC ratio in October 2017.

In the areas where the salinity ranges between 33-34, it is interesting to observe higher TA and DIC values in February 2016 than October 2017. February 2016 has been identified as a month of high discharge in Ireland, the SGD measured in Bell Harbour (one of the small bay inserted in Galway Bay area) was around 3 m^3/s (Schuler et al., 2018) which was an extraordinary peak for the location. Considering that SGD in Kinvarra Bay is generally 3 times greater than Bell Harbour, (McCormack et al., 2014; Schuler et al., 2018, 2020) it is likely that the SGD from the other sources was higher as well. Groundwater flooding and associated storage of water was significantly higher than October 2017 (Schuler et al., 2018). The results obtained from the comparison TA and DIC in two different season in Galway Bay, legitimate the hypothesis that SGD can change TA:DIC ratio, hypothesis that also arose from previous studies (Hall and Tank, 2005; Johnson and Wiegner, 2014). Further analyses about the role of SGD as a driver of coastal carbonate chemistry in different discharge conditions are necessary.

3.6 Conclusions

The results presented in this chapter illustrate the carbonate chemistry along the Irish coasts with a particular focus on the Galway Bay. The null hypothesis H_0 formulated for this study is rejected. The variability of the carbonate system relates to both the type of freshwater input (rivers or SGD, human activities on land that can change the supply of nutrients to the coast) and watershed geology (higher and lower TA dependent on the type of catchment areas).

TA and DIC distribution along the Irish coastline show different correlations with salinity values, and for a large part of the country an opposite correlation, which makes impossible to predict TA through salinity values, as usually done for the open ocean. The coastal areas can act not only as a source of nutrients, that could enhance eutrophication, but also as a source of alkalinity and inorganic carbon that could change the coastal metabolism and accelerate acidification processes. From the available data it might be hypothesized that an increase of nutrients delivery to the coast can further stimulate the benthic metabolism and accelerate microbial respiration, with the increase of DIC during the winter.

The novel aspects that can be identified in this part of the research based mostly on existing data with the only exception of the oceanographic cruise are listed by following:

- from the performed analyses, it can be concluded the importance of introducing TA and DIC in all coastal monitoring programme for a better comprehension of the coastal carbonate chemistry and its variability, and consequently the effects on the coastal aquaculture areas;
- it is needed to expand the research on a seasonal time scale. In fact, with the increase of temperature and day-length, the phytoplankton and plants consume more nutrients and increase the primary production, which might reflect in a decrease of DIC as observed in the south and west of Ireland;
- it is showed the increase of REVELLE factor in the Galway Bay, during wintertime, which led to a decrease of ocean buffer capacity;
- TA:DIC relation can diverge in areas fed by rivers or SGD. The role of SGD, its spatial and temporal variability in the loading of TA, DIC and nutrients must be understood in order to apply a correct management approach of the human activities on the land.

In the next chapters a comparison will be made between two Irish coastal bays: Killary Harbour, located in the northwest of Ireland, where there is a lack of information in terms of coastal carbonate chemistry, and Kinvarra Bay which is an area largely studied in the last years because of its dominance of freshwater input in the form of SGD. It is well known that Killary Harbour catchment area is less impacted by human activities compared to the south and southeast of the country. Therefore, because the rivers feeding Killary Harbour are oligotrophic, and because the catchment area is almost characterized by shale, sandstone and conglomerates, like in the northeast of Ireland, the alkalinity and inorganic carbon contribution from the freshwater discharge found in Killary could be similar to the ones in the northeast. Killary Harbour and Kinvarra Bay can be considered as contrasting watershed inputs where the coastal carbonate chemistry can be compared and further understood.

4 Freshwater input drives the spatial and temporal variability of the carbonate system in two Irish embayments

This chapter forms the basis of a peer-review paper that is currently in the peer-review process in the Estuarine Coastal and Shelf Science Journal ECSS. I am first author of this work and my contribution is: Conceptualization in terms of planning and sampling strategy; methodology in terms of fieldwork, sampling, laboratory analysis; formal analysis; data curation; writing—original draft preparation; writing—review and editing.

I modified the content of the manuscript to embed this into the dissertation for examine purposes:

- I reduced the introduction to avoid repetitions with the general introduction chapter,
- I recalled the methods Chapter 2 in the methods sections. I then followed the same structure throughout the thesis.

Abstract

The spatial and temporal variability of Total Alkalinity (TA), pH and Dissolved Inorganic Carbon (DIC) were studied in two coastal bays in Ireland. Kinvarra Bay is mainly fed by submarine groundwater discharge (SGD) derived from a karst catchment, whereas freshwater inputs in Killary Harbour mainly derive from surface runoff from a sandstone catchment. Rivers flowing into Killary Harbour transported low TA (~20 - 450 µmol kg^{-1}), whilst SGD was a large source of TA (3111 - 4793 µmol kg^{-1}) and DIC (3241 - 4983 µmol kg^{-1}) into Kinvarra Bay. Both freshwater sources have low pH (6.01< pH < 7.70). Salinity-normalized TA-DIC slopes were compared, with reference to the open ocean. Freshwater inputs drove both systems into distinct metabolic (net autotrophy vs net heterotrophy) and biogeochemical (net $CaCO_3$ precipitation vs net $CaCO_3$ dissolution) states. The balance between organic and inorganic drivers of the TA:DIC ratio did not change in Killary Harbour with freshwater discharge or time of the year but did change in Kinvarra Bay. The work shows that both magnitude and origin (i.e., surface, underground) of freshwater inputs distinctively affect the metabolic state of coastal systems. In groundwater-dependent systems, soil use might shift the TA:DIC compositional ratio in SGD and contribute to the catalysation of coastal acidification.

4.1 Introduction

Coastal areas are complex systems as they are strongly linked to rivers/inland waters, groundwater, coastal wetlands, shelfs/marine environments and the atmosphere (Serafy et al., 1997; Gillanders and Kingsford, 2002). Awareness of the importance of watershed inputs in near-shore carbon metabolism has accelerated efforts to better understand the drivers of carbonate chemistry in coastal seas (Caffrey, 2003). Freshwater flows into the ocean, often with lower pH than seawater, drive seasonally variable carbon inputs to coastal areas (Cai et al., 2017; Joesoef et al., 2017). Also, and in addition to surface runoff, several studies have underlined the importance of submarine groundwater discharge (SGD) as a source of inorganic carbon to coastal seas (De Weys et al., 2011; Santos et al., 2011, 2014; Cyronak et al., 2013; Luijendijk et al., 2020), but its impact on coastal carbon biogeochemistry is largely unknown. It follows that predicting future changes to coastal carbonate chemistry can only be done if the effects of type, discharge magnitude and composition of freshwater flowing into coastal areas on local carbonate systems are understood. The drivers of composition and magnitude of these freshwater fluxes may yet be one of the key factors in successfully predicting the future of the aquaculture of calcifying organisms such as mussels and oysters in coastal areas, particularly sensitive to current and projected Ocean Acidification (OA) processes (McGrath et al., 2019; Caldeira and Wickett 2005).

The aim of this study is to evaluate the effects of the magnitude and composition of freshwater discharge on pH and carbonate system dynamics in Irish coastal seas. To achieve this aim, two coastal basins in the western coast of Ireland with contrasting catchment areas were studied: Kinvarra Bay, a small coastal bay fed essentially by SGD (McCormack et al., 2014; Rocha et al., 2016) ensuing from the Gort karst aquifer, and Killary Harbour, a fjord embayment further north chiefly fed by surface drainage from a largely sandstone hinterland. Both coastal systems host important aquaculture activity, comprising raft cultivation of *Mytilus edulis*, with production averaging 800 t/y and 150 t/y respectively, over the last ten years. In addition to *Mytilus edulis*, *Magallana gigas* is also cultivated in Kinvarra Bay (BIM, 2019). Three of the four parameters characterizing the marine carbonate system: Total Alkalinity (TA), DIC and pH were measured.

The balance between organic and inorganic carbon metabolism, represented by the relationship between Net Community Production (NCP) and Net Community Calcification

(NCC), also affects pH in coastal areas, and may provide insights into whether or not particular systems have inbuilt resilience to ocean acidification pressure (Cyronak et al., 2018). A positive value of NCP implies that Primary Production (PP) is greater than Respiration (R), and a positive NCC implies that carbonate preservation and calcification are greater than carbonate dissolution. To evaluate the metabolic state of the selected study areas, i.e., the state of the balance between the organic and inorganic whole-system carbon metabolism (Cyronak et al., 2018; Raymond et al., 2008) the relation between TA and DIC was used. TA and DIC relation and its dependence on type and seasonality of freshwater inputs was also evaluated.

4.2 Materials and Methods

4.2.1 Study areas

Study areas were previously described in Chapter 2 paragraph 2.2. In the Figure 4-1 the study areas and the sampling strategy adopted are represented.

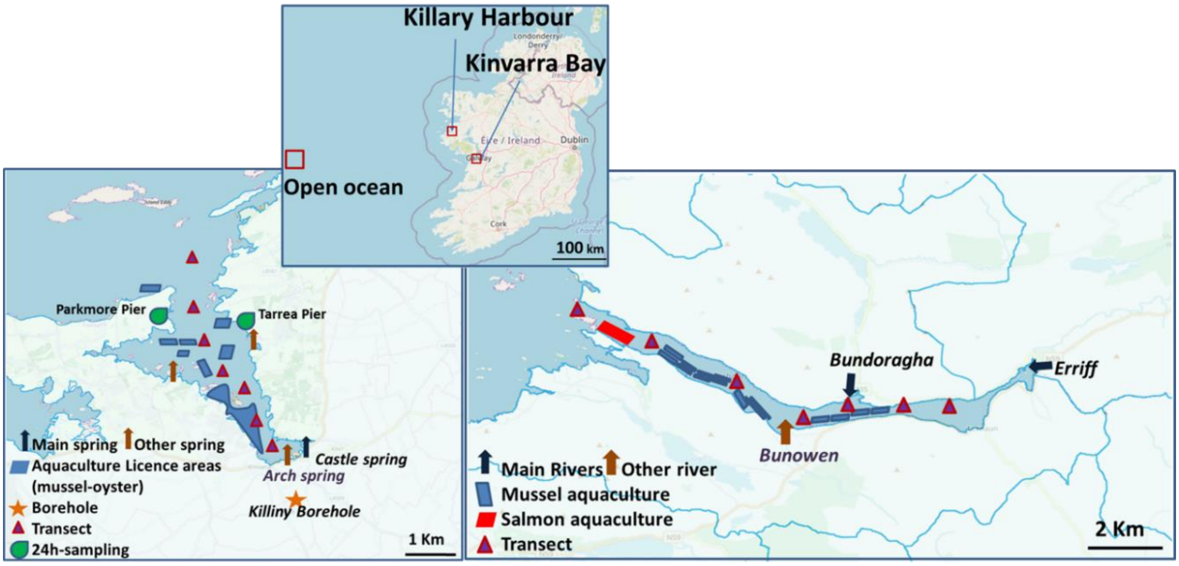


Figure 4-1: Kinvarra Bay and Killary Harbour bay sub-catchment areas from http://www.gis.epa.ie water framework directive units maps, together with major springs and rivers represented following Environmental Protection Agency reports (EPA 2011; Mara and Connolly 2016) are shown. Surface water sampling stations are marked with triangles. The areas where 24h fixed-point surveys were carried out in Kinvarra are also shown. The data collected in these two locations were used to build the tidal prism and to estimate the freshwater discharge. Aquaculture sites data were obtained from the Ireland's Marine Atlas at http://atlas.marine.ie/ on the 03/04/2020. The location of the open ocean data obtained from the Marine Institute (Galway) is represented in the central map.

4.2.2 Sampling strategy

Sampling was carried to capture annual variance in freshwater discharge (i.e. high and low flow conditions), temperature and light availability. Five surveys were carried out in the two studied inlets. Sampling in Killary Harbour was performed during February, July and October 2018, January and April 2019. In Kinvarra Bay, surveys were carried out during July and October 2018, January, April and August 2019. All surveys were performed during spring tide periods. For Killary Harbour, the EPA provides hourly flow rate data from a gauge station located in Bundorragha River. These were studied prior to sampling to cover a wide range of freshwater discharge conditions. In Kinvarra Bay, flow data for Kinvarra Springs are not available, but groundwater level is monitored by the EPA in Killiny borehole (Figure 4-1) located at (53° 7'N, 8°56'W) which is hydraulically connected to the castle spring as shown by tracer tests in the catchment (Drew, 2003) and stable water isotope fingerprinting (Schubert et al., 2015). This was used as an indicator of the potential magnitude of SGD before sampling surveys were planned.

The spatial variability of carbonate system parameters was captured by sampling a longitudinal transect from the head to the mouth of each bay during ebb tide. Six points were sampled on each transect, in addition to a marine end-member just outside the mouth of the bay. Freshwater end-members, including rivers, SGD springs and a borehole were also sampled in order to understand compositional variability of freshwater input sources. Temperature, pH, salinity, electrical conductivity, and dissolved oxygen were measured at each station using a multi-parameter probe (Aqua-read AP 1000). Electrical conductivity was measured independently with a portable conductivity meter (WFW-profilLine cond 197i). Water samples for analysis of TA, DIC and pH in the laboratory were taken using a 5-liter Niskin bottle deployed at each station of the transect. Collection, preservation and analysis followed standard methods in ocean acidification studies (Dickson et al., 2007). Briefly, water samples were carefully transferred into borosilicate glass bottles on-board and immediately poisoned with 0.05% $HgCl_2$, following standard protocols (Dickson et al., 2007). In Killary Harbour, samples were taken from approximately 1 m below the surface and from 2-3 m above the bay floor to capture the vertical variability due to stratification that occurs in the bay (Keegan and Mercer, 1986). Since Kinvarra Bay is relatively shallow (average depth of 4 meters), the relative effect of the freshwater inflow to the tidal flow, following the definition of Schultz and Simmons, (1957), is less than 0.1 during spring tides for the annual range of fresh water flow into the bay. Kinvarra Bay is therefore likely to be vertically mixed during spring tides (Gregory et al., 2020) and samples collected approximately one meter below the surface were considered representative of the vertical water column (Keegan and Mercer, 1986).

In addition to the spatial surveys, fixed-point, 24-hour time-series were performed in two different piers in Kinvarra Bay: in Tarrea Pier in July and October 2018 and in Parkmore Pier in January and April 2019 (see Figure 4-1 for the locations). At each location, temperature, pH, salinity and dissolved oxygen were measured every 3 hours using a multi parameter probe (Aqua-read AP 1000).

4.2.3 Analysis

The analysis of carbonate system parameters, TA, pH and DIC were conducted as described in paragraphs: 2.3.5; 2.3.6; 2.3.7.

The DIC was measured only in the LOCEAN lab in France, and for some batches the analyses were not carried out. For some surveys where DIC values were not available, this one was calculated with the CO2SYS software (Lewis and Wallace, 1998; Pierrot et al., 2016) (see paragraph 2.3.8). To calculate DIC using CO2SYS the propagation of uncertainties associated to TA and pH was applied (Orr et al., 2018) leading to an uncertainty associated with calculated DIC of ± 10 μmol kg^{-1}. Ω_{Ar} was calculated using the CO2SYS software as well, from TA and pH and from DIC and pH when the three parameters were available, to account for any differences related to the choice of the parameter. When DIC was not available, Ω_{Ar} was calculated pairing TA and pH. In the current study, the error associated with Ω_{Ar} estimation is ± 0.08. A comparison between DIC measured at LOCEAN and that calculated with the CO2SYS software showed that the latter underestimated DIC by comparison to the measured DIC in Kinvarra Bay, and overestimated DIC by comparison to measured samples for Killary Harbour. To assess if these differences could have a statistically significant impact on the results, the slopes between measured TA and calculated DIC on the one hand and measured TA and DIC on the other were compared, and a 5% systematic error between both was found. To evaluate the statistical significance of this difference, the slopes of the regression lines were compared following the method described by Andrade and Estévez-Pérez (2014). The F-test showed a critical value higher than the F value with 95% confidence interval (CI), for both Kinvarra Bay and Killary Harbour, meaning the null hypothesis could not be rejected, and the two variances were similar. Therefore, the effects of calculating DIC from measured pH and TA did not significantly affect the slopes of the TA-DIC plots and had no impact on the results and discussion presented. Additional data from the adjacent open ocean (53° N, 15° W; Figure 4-1) were used as reference values; TA, DIC, temperature and salinity were determined on surface waters of the selected oceanic area by the Ireland's Marine Institute (Foras na Mara) in February 2009.

4.2.4 Freshwater discharge magnitudes

See Methods Chapter 2, paragraph 2.4.

4.2.5 Metabolic state in the selected study areas

To evaluate the metabolic state of the study areas, the relative percent influence of NCP on changes in DIC was calculated based on the equation built for coral reef environment by (Suzuki and Kawahata, 2003) and later rearranged by (Koweek et al., 2015; Takeshita et al., 2018; Cyronak et al., 2018) as follows:

$$\% \text{ NCP} = (1 - \text{mTA-DIC} / 2) * 100 \tag{42}$$

where mTA-DIC is the slope of the TA-DIC vector Figure 4-4. During photosynthesis and respiration processes, TA does not change, the change of DIC is ±1, mTA-DIC is close to 0 and the system is dominated by organic metabolism (%NCP=100). During the calcification and dissolution processes, the change of TA is ±2, the change of DIC is ±1, mTA-DIC is close to 2, and the system is dominated by inorganic metabolism (%NCP=0). This equation, that was previously applied by Cyronak et al., (2018) to understand the metabolic state of coral reefs, considered TA as carbonate alkalinity. The TA-DIC vectors can provide insights into the metabolic state of aquatic systems, including an understanding of acting drivers of the local carbon cycle, pH variability and regional carbonate buffering capacity (Joesoef et al., 2017). In this study the relative influence of net community metabolism on changes to the DIC pool (expressed as a percentage) was assessed from the algebraic ratio between TA and DIC in equilibrium, taken as the oceanic reference (Deffeyees, 1965).

The TA measured included carbonate and non-carbonate ions. Previous literature studies have identified the importance of non-carbonate alkalinity (Hunt et al., 2011; Lukawska-matuszewska et al., 2018) particularly in systems like estuaries and coastal water ecosystems (Hernández-Ayon et al., 2007; Kuliński et al., 2014). Solute inputs from land and benthic mineralization of organic matter can introduce significant amounts of non-carbonate alkalinity to coastal waters, including boron, phosphorus, nitrogen and silicon dissolved species, amongst others, and increasing the concentration of Dissolved Organic

Carbon (DOC) and Dissolved Organic Nitrogen (DON). Previous literature studies have shown the importance of non-carbonate alkalinity particularly in coastal systems (Hernández-Ayon et al., 2007; Kuliński et al., 2014). It follows that because of the importance of non-carbonate alkalinity, to estimate its contribution in the selected study areas it can provide important information to the biogeochemical linkage between organic and inorganic carbon cycling particularly in water enriched by organic carbon (Song et al., 2020). The contribution of non-carbonate alkalinity (e.g., organic acids) was addressed as following: adding to the determinations of TA and pH performed, DIC was analysed in selected replicates (n=8 in Kinvarra Bay and n=20 in Killary Harbour). The CO2SYS software was used to calculate the carbonate alkalinity (CA), using as before the dissociation constants for carbonic acid (K1 and K2) of Mehrbach et al., (1973) refit by Dickson and Millero (1987), from pH and DIC. The results provided the HCO_3^- and CO_3^{2-}, the carbonate alkalinity was then calculated as:

$$CA = [HCO_3^-] + 2[CO_3^{2-}] \tag{43}$$

The CA was then compared to the measured TA to evaluate the contribution of non-carbonate alkalinity in the studied bays (Hunt et al., 2011).

4.3 Results

4.3.1 Freshwater sources: carbonate chemistry and TA:DIC ratios

Table 4-1: Characteristics of catchment inputs into Kinvarra Bay (groundwater end-member) and Killary Harbour (Erriff (*) and Bundorragha (, italics) rivers). TA:DIC represents the TA to DIC molal ratio within the freshwater end-member. The pH range measured within both systems is also shown as well as the temperature indicated with T °C. The TA, DIC and pH mean value recorded in the freshwater end-member is represented together with the analytical error. The standard error between the replicates was ± 4 for the measured TA, and ± 10 for the calculated DIC. The standard error for the measured pH was less than the analytical error. To have a clear comparison between the areas, only the periods where both inlets were sampled (July, October, January and April) were included.**

Location	Year	Period	Freshwater input	TA	DIC	TA:DIC	pH	T	Range of pH in the bay
			(m^{3}d^{-1}×10^5)	µmol kg^{-1} (±10)	µmol kg^{-1} (±10)		(±0.01)	°C	
Kinvarra Bay	2018	July	4.8	4793	4895	0.97	7.66	17.9	7.97-8.01
		October	8.5	3502	3820	0.91	7.25	12.5	7.76-8.04
	2019	January	14	3111	3241	0.95	7.45	10.2	7.32-7.81
		April	21	4502	4658	0.96	7.70	11.9	7.76-8.00
Killary Harbour	2018	July	1.4	272*	310	0.87	7.02	19.9	7.95-8.07
				*380***	*458*	*0.82*	*6.83*	*19.1*	
		October	14	89*	113	0.78	6.78	12.1	7.82-7.94
				*16***	*22*	*0.72*	*6.65*	*12.3*	
	2019	January	20	42*	104	0.40	6.12	9.1	7.26-7.90
				*32***	*91*	*0.35*	*6.01*	*10.1*	
		April	9.3	148*	255	0.58	6.44	14.2	7.90-8.02

Calculated freshwater discharge into the studied systems ranged from 4.8 to 21×10^5 m^{3}d^{-1} and from 1.4 to 36×10^5 m^{3}d^{-1} in Kinvarra Bay and Killary Harbour, respectively (Table 4-1). The lowest discharge rates, i.e., 1.4×10^5 m^{3}d^{-1} for Killary Harbour and 4.8×10^5 m^{3}d^{-1} for Kinvarra Bay in July 2018 Table 4-1 coincide with drought conditions; Met Éireann (the Irish meteorological service) recorded an average of 0.28 mm per day in the month prior to the sampling period, from 24st June to 25th July, at its Athenry station, located 20 km NE of Kinvarra Bay, and at Leenane station located in Killary Harbour. The historical data for the period June-July in the last 10 years showed an average value in that month between 1.8 and 3.5 mm per day, indicating that summer 2018 was particularly dry compared to the previous decade. April 2019 was also somewhat atypical, coinciding with the coolest period in which our surveys were conducted - the mountains surrounding the fjord were covered by snow. Precipitation that would usually feed the rivers that drain into Killary Harbour might instead have been stored as snow and ice in the surrounding uplands, leading to relatively low surface runoff into the bay for this period.

“Kinvarra Castle” spring (Figure 4-1) was previously identified as the main SGD spring and the dominant nutrient source into Kinvarra Bay (Schubert et al., 2015; Rocha et al., 2015). The water from this spring is characterized by high TA and DIC (Table 4-1) and TA:DIC ratios < 1 (Table 4-1). TA and DIC in water collected at the chosen freshwater end-member (Killiny borehole) were similarly high, ranging between ~3000 to ~5000 µmol kg^{-1}, with DIC > TA. In contrast, Killary Harbour showed opposite values of TA and DIC compared to Kinvarra Bay. In Killary Harbour the TA and DIC in the sampled rivers varied seasonally from ~ 20 to ~ 450 µmol kg^{-1}, with higher values recorded during drought periods (see Table 4-1). In both end member locations, rivers and SGD spring, the increase of temperature correlates with the increase of pH and alkalinity.

4.3.2 TA and DIC variability in the two coastal embayments

The concentrations of TA and DIC in the sampled freshwater end-member of Kinvarra Bay are higher than in the nearby ocean. Contrastingly, the sampled rivers in Killary Harbour showed TA and DIC concentrations lower than in the nearby ocean. As a consequence, the two sites show DIC-salinity relations and TA-salinity relations with slopes of opposite sign (Figure 4-2). This observation highlights the effect of coastal bedrock geology and hydraulic pathway followed by freshwater in transit to sea on the mixing patterns of TA and DIC observed in coastal areas influenced by large watershed inputs: the freshwater typology affects the mixing gradient, regulating the TA and DIC content of mixed coastal waters. Killary Harbour shows the typical behaviour of a river dominated system (Cai et al., 2010) with low riverine TA and DIC.

In Kinvarra Bay, TA and DIC in October 2018 and January 2019 showed an apparent conservative distribution along the salinity gradient (Figure 4-3). Different results are shown for July 2018, April and August 2019: TA and DIC deviate from the linear mixing pattern between fresh and marine end-member, showing an upward deviation, which suggests an increase of photosynthesis and carbonate dissolution (Miyajima et al., 2009) (see Figure 4-3). In July 2018 TA and DIC in the bay look very similar to those in the nearby ocean, suggesting that the latter is the main driver of these constituents in the bay, likely due to the low freshwater discharge conditions. In April 2019 TA and DIC values are lower than what can be expected from the conservative mixing, suggesting that other drivers (e.g., bay metabolism) take precedence. Also, in August 2019 TA and DIC deviated from conservative mixing, suggesting production and consumption according to the location. TA and DIC carried into the system by SGD are very high compared to the marine concentrations. Therefore, the magnitude of freshwater flow has a significant effect on the distribution of TA and DIC in the system, i.e., the mixing gradient, unlike what is observed in Killary Harbour.

In Killary Harbour, some data also deviate from the linear model in February 2018, when river discharge to the bay was the highest and the water column was highly stratified (Keegan and Mercer, 1986; Donohue, 2012). The ocean is the main source of TA and DIC, regardless of the magnitude of freshwater discharge. In particular, in July 2018, during a period of drought, the river discharge was very low and the marine DIC and TA dominated the inorganic carbon system in Killary Harbour (Figure 4-2).

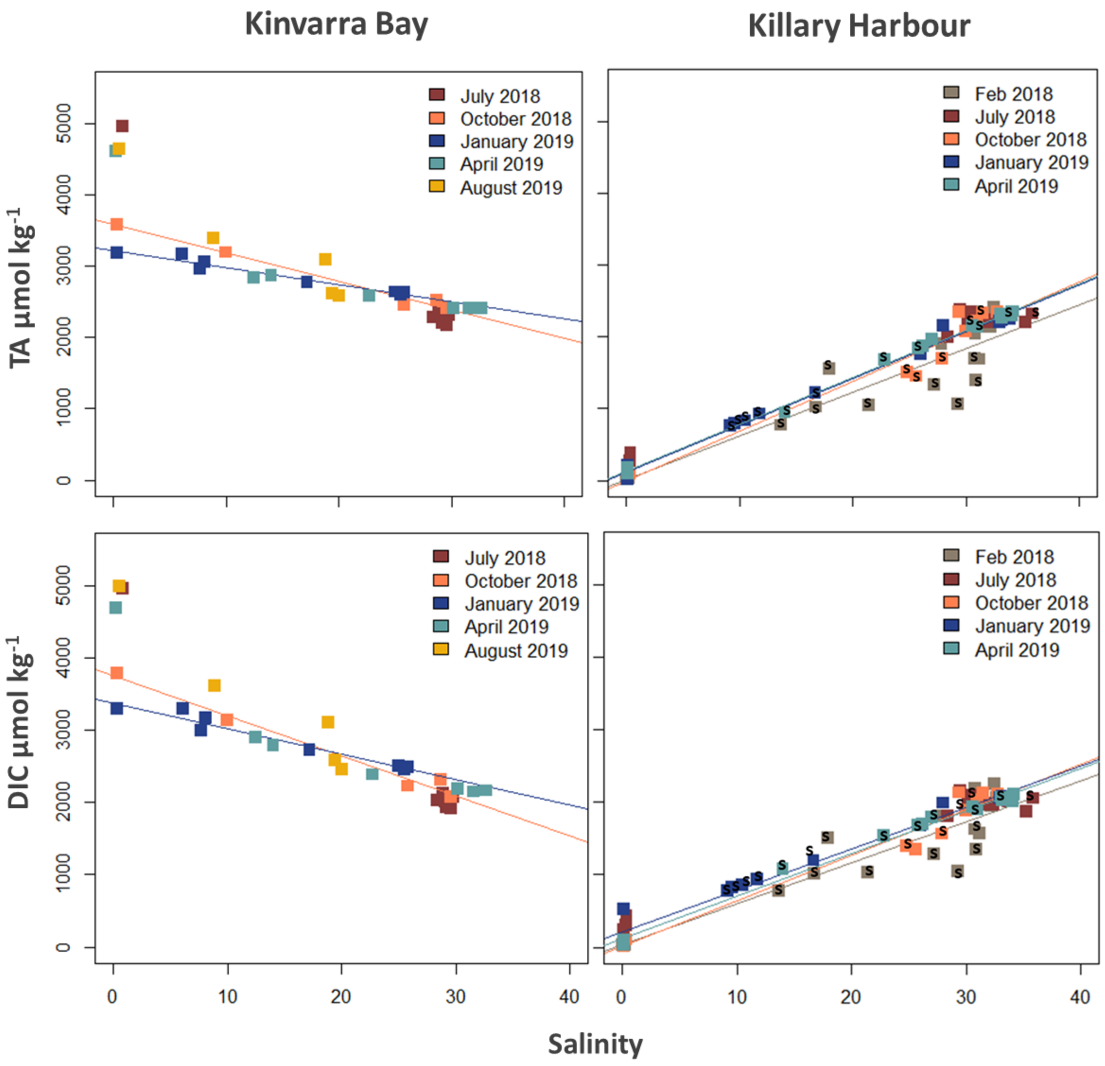


Figure 4-2: TA (µmol kg^{-1}), DIC (µmol kg^{-1}) and salinity linear regression figures for Kinvarra Bay (July 2018-August 2019) and Killary Harbour (February 2018 – April 2019). Killary Harbour transects include surface and deep-water samples, with the "s" in the graph indicating surface water. Kinvarra Bay shows a linear regression only in October 2018 and January 2019.

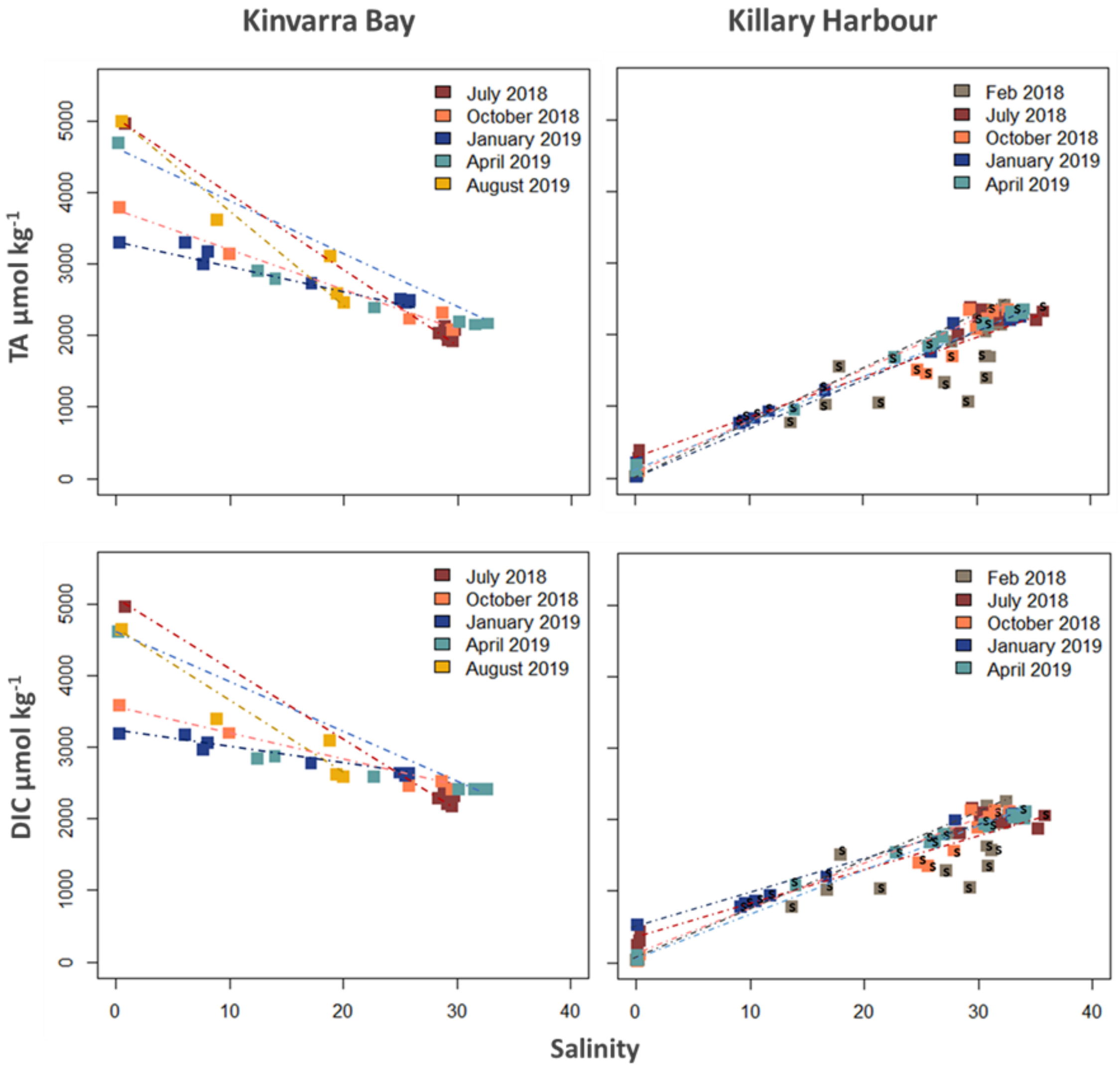


Figure 4-3: TA (µmol kg^{-1}), DIC (µmol kg^{-1}) and salinity mixing lines for Kinvarra Bay (July 2018-August 2019) and Killary Harbour (February 2018 – April 2019) are represented in the figure. As previous figure, Killary Harbour transects include surface and deep-water samples, with the "s" in the graph indicating surface water. Kinvarra Bay showed conservative mixing in October 2018 and January 2019, in the other surveys the TA and DIC values are lower compared to the freshwater end-member. In Killary Harbour the mixing lines showed almost conservative behaviour of TA with salinity. In February 2018 Killary Harbour shows lower TA and DIC values compared to what can be expected looking at the conservative mixing dashed line.

4.3.3 Freshwater discharge effects on the spatial variability of pH and aragonite saturation state

While the ground- and surface freshwater sources described above have different composition in terms of carbonates, both are characterized by lower pH and Ω_{Ar} than the open ocean. The freshwater end-member pH varies seasonally between 7.25 and 7.70 in Kinvarra Bay and between 6.01 and 7.02 in Killary Harbour (Table 4-1). For both systems, the input of low pH freshwaters affects the pH distribution on the bays (Figure 4-4).

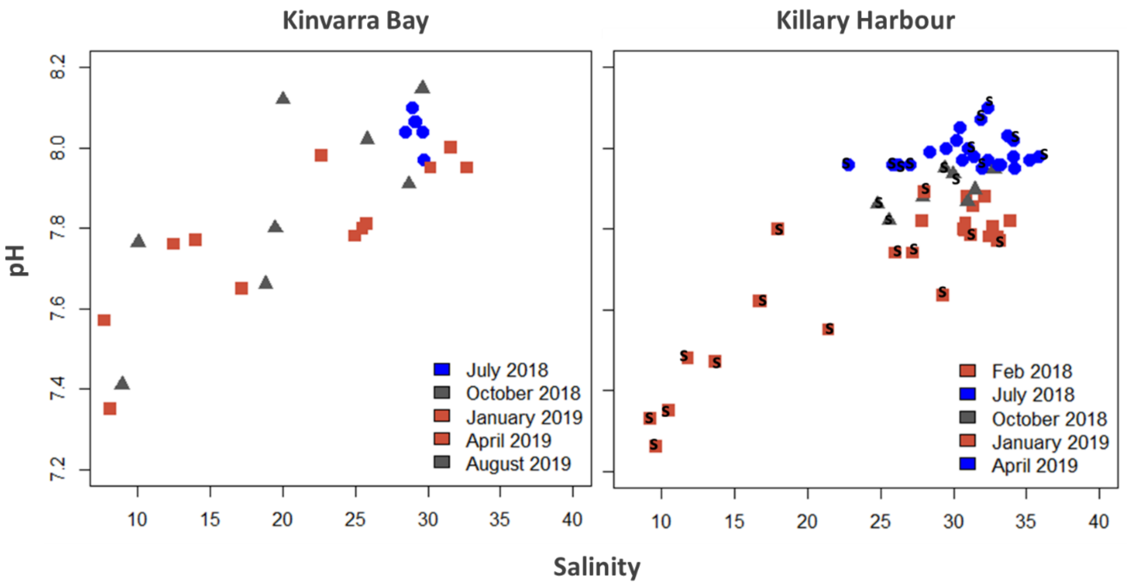


Figure 4-4: Longitudinal variation of pH for Kinvarra Bay and Killary Harbour. The Killary Harbour transect includes surface and deep-water samples, with "s" in the graph indicating the surface waters. The blue dots indicate the months on which the estimated freshwater discharge was low (July 2018 in Kinvarra Bay, July 2018 and April 2019 in Killary Harbour). The red squares indicate the months on which high discharge was estimated (January and April 2019 in Kinvarra Bay, February 2018 and January 2019 in Killary Harbour). The grey triangles indicate intermediate discharge (October 2018 and August 2019 in Kinvarra Bay, October 2018 in Killary Harbour). The discharge data are reported in Table 4-1.

The magnitude of freshwater discharge seems to be an important driver of the spatial variation of pH within the studied bays. During high discharge periods, pH and salinity are correlated in both study areas (Figure 4-4). There, pH showed an almost linear mixing along the salinity gradient. Conversely, during the months where low freshwater discharge occurred (blue dots in Figure 4-4), no clear correlation of pH with salinity is observed.

In Killary Harbour the pH of surface water differs from deep-water. Stratification of the water column was exacerbated in February 2018 and January 2019 when the highest freshwater discharge into the bay was recorded; this resulted in a steep increase of pH from the head to the mouth of the bay in the surface water samples, but smaller variations of pH levels in the deep water (0.01 to 0.03 units) were not correlated with salinity.

In Killary Harbour the calculated aragonite saturation state (Ω_{Ar}) was between 0.8 and 1.6 at the bay head, where the impact of the riverine discharge is more notorious (Figure 4-5). Only in July 2018, when the freshwater discharge was exceptionally low, i.e., 1.4×10^5 m^3 d^{-1}, the Ω_{Ar} was higher than 2 even at the bay head. During April 2019, with a freshwater discharge of 9.3×10^5 m^3 d^{-1}, the Ω_{Ar} remained higher than 1, whereas the remaining surveys showed zones with Ω_{Ar} below 1.

In Kinvarra Bay the pH increased from the head to the mouth of the bay except for July 2018, the month with the lowest discharge recorded. There, the Ω_{Ar} was below 1 only in the upper part of the bay, where the salinity values were between 16 and 24. During the spring tides water residence time in Kinvarra Bay is lower than in Killary Harbour (Gregory et al., 2020). This can explain why, even during high discharge periods, the freshwater composition affected the pH and Ω_{Ar} mostly in the upper part of the bay. In periods of low discharge, the Ω_{Ar} was greater than 2 all along the transect (Figure 4-5), with low spatial variations. The Ω_{Ar} showed values lower than 1 only in January 2019, at high discharge conditions (14 × 10^5 m^3 d^{-1}).

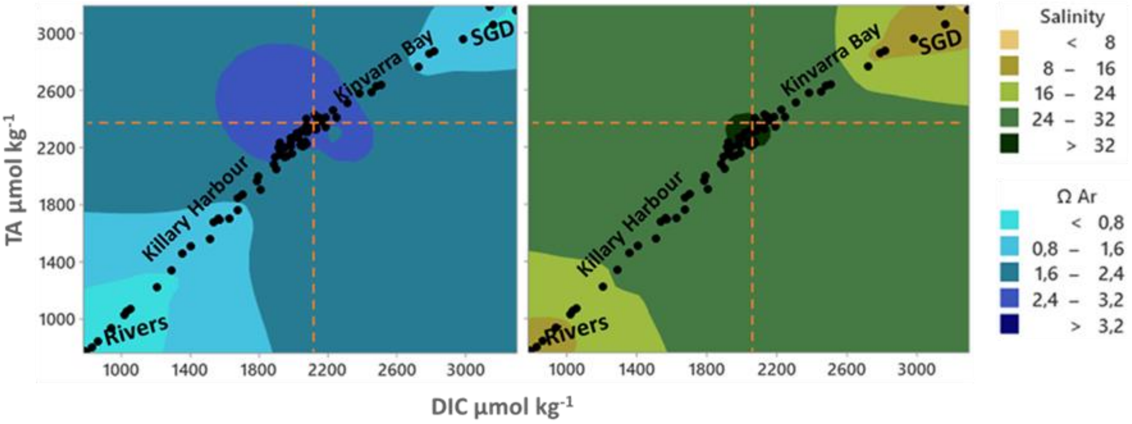


Figure 4-5: Distribution of aragonite saturation state (Ω_{Ar}) and salinity in Kinvarra Bay and Killary Harbour, as a function of TA and DIC. The figures represent the spatial variations of TA-DIC-Salinity and Ω_{Ar} at all surveys in both study areas. It is possible to observe that even if both freshwater sources are characterized by low pH and low Ω_{Ar}, the TA and DIC components are contrasting. The effect of freshwater inputs on the decreasing aragonite saturation level is visible in the low salinity areas. The central point of the dashed lines represents TA, DIC, salinity and Ω_{Ar} in the open ocean. The Ω_{Ar} was calculated with the CO2SYS software using the three parameters of carbonate system TA-DIC and pH when they were all available and only from TA and pH when they were not.

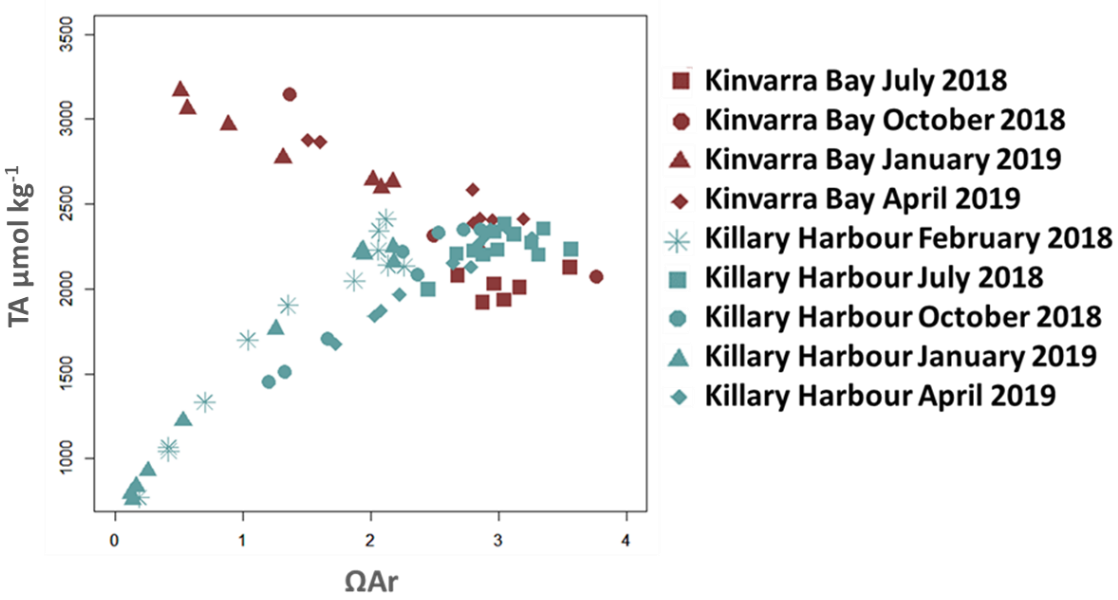


Figure 4-6: At high discharge conditions the Ω_{Ar} decreases since the carbonate system is more influenced by the freshwater composition. TA shows high and low values depending on the end member type (river or SGD).

4.3.4 TA-DIC slopes and NCP:NCC relation

The metabolic characterization of Killary Harbour and Kinvarra Bay is shown in Table 4-2 and graphically represented in Figure 4-7. In the Figure 4-7 TA versus DIC is plotted. The centre of the graph represents the TA and DIC composition found in the open ocean, where the system NCP and NCC are balancing each other as well as dissolution and calcification processes. However, coastal areas might show different trends and according to the changes of TA over DIC, the system might shift more in autotrophic or heterotrophic conditions with the consequential change of pH in respect to the open ocean pH (Figure 4-7). In the graph the dashed lines show weather the two systems (Killary and Kinvarra) moved towards positive NCP (ecosystem production and DIC assimilation is greater than respiration) and a positive NCC (where carbonate preservation and calcification are greater than carbonate dissolution) or vice versa with negative NCP and NCC. Additionally, the dashed lines show when photosynthesis and $CaCO_3$ dissolution lead to the increase of seawater pH, or when respiration and $CaCO_3$ precipitation lead to the decrease of pH. In the analysed transects in Kinvarra Bay and Killary Harbour, it is possible to observe a decrease of pH values relative to the open ocean (pHo). The slopes represented in Figure 4-7 are based on TA and DIC normalized to a salinity of 35 following Friis (2003), and indicated as nTA:nDIC in Table 4-2. The adjusted values showed independence from salinity, with Pearson r = -0.12 with a p-value of 0.54 for Kinvarra Bay and an r = 0.08 with p-value of 0.53 for Killary Harbour. Following the same procedure as for Killary Harbour and Kinvarra Bay data, the selected open ocean TA-DIC data have been normalized using the freshwater end-members (SGD and river). Open ocean nTA-nDIC curves presented a slope of 1.00 ±0.12 regardless the freshwater end-member used for normalization. This slope shows an equilibrium between inorganic and organic drivers of carbon cycling in the open ocean where NCP and NCC are balanced (Cyronak et al., 2018) and is used as reference line in Figure 4-7. The deviations caused by non-carbonate alkalinity from the carbonate alkalinity in the studied areas was between 16 and 145 µmol kg^{-1} in the samples analysed in Kinvarra Bay and between 18 and 110 µmol kg^{-1} in the samples analysed in Killary Harbour. These results showed that the average contribution of non-carbonate alkalinity was ~2.5% in Kinvarra Bay and 2.3% in Killary Harbour. Therefore, it is possible to assume that the influence of non-carbonate alkalinity to the observed TA-DIC slopes and the balance between NCP:NCC is minor.

Killary Harbour shows TA-DIC and nTA- nDIC slopes larger than one in all surveys (see Table 4-2), underscoring the smaller relative influence of the organic carbon metabolism on the local carbonate system. No significant difference between the slopes arising from different surveys was found regardless of the changes in freshwater discharge magnitude, supporting the hypothesis that freshwater discharge variability does not lead to shifts in the carbonate system state in Killary Harbour. Indeed, even if the ratio between TA and DIC delivered by the inflowing rivers (Table 4-1) into Killary Harbour is always lower than that observed in the open ocean, freshwater mixing does not change the relationship between the two within the bay (TA:DIC is always greater than 1). The TA:DIC relations, and the balance between organic and inorganic carbon metabolism (NCP:NCC) within Killary Harbour is regulated by ocean chemistry. Kinvarra Bay deviates from this pattern, depending on the period of the year. The F test showed no significant differences between the non-normalized and normalized TA vs DIC slopes in October 2018 and January 2019, but a significant difference between the normalized and non-normalized TA vs DIC slopes in April 2019 and August 2019 (Table 4-2), indicating processes other than mixing are actively shifting the balance between the effects of inorganic and organic metabolism on the freshwater end-member composition in the bay during spring and summer time.

Table 4-2: Whole system metabolic characterization of Kinvarra Bay and Killary Harbour derived from the linear relationships between TA and DIC within the water column, normalized and not normalized to salinity. Open ocean data normalized with the river and SGD freshwater end-members is also shown. The calculated standard error is represented in the table.

Location	Year	Period	Slope TA=f(DIC)	%NCP	Data normalized to S=35	
					Slope nTA=f(nDIC)	%NCP
Kinvarra Bay	2018	July	1.19 ±0.12	40.5±4.1	0.98 ±0.15	51.2±6.1
		October	0.76 ±0.04	62±3.7	0.77 ±0.04	61.4±3.1
	2019	January	0.67 ±0.01	66.5±1.3	0.60 ±0.02	70.2±2.8
		April	0.71 ±0.04	64.5±2.6	1.09 ±0.04	45.7±1.8
		August	0.73 ±0.05	63.5±3.2	0.95 ±0.13	52.3±7.3
Killary Harbour	2018	February	1.13 ±0.01	43.5±0.6	1.13 ±0.03	43.5±1.3
		July	1.1 ±0.12	45±4.9	1.08 ±0.11	46±5.0
		October	1.14 ±0.02	43±0.9	1.10 ±0.06	45.1±2.7
	2019	January	1.13 ± 0.01	43.5±0.6	1.18 ±0.12	41.1±4.5
		April	1.2 ± 0.01	40±0.6	1.17 ±0.09	41.6±3.3
Open Ocean	2009	February	1.00± 0.12	50±6.5	1.00 ±0.12	50±6

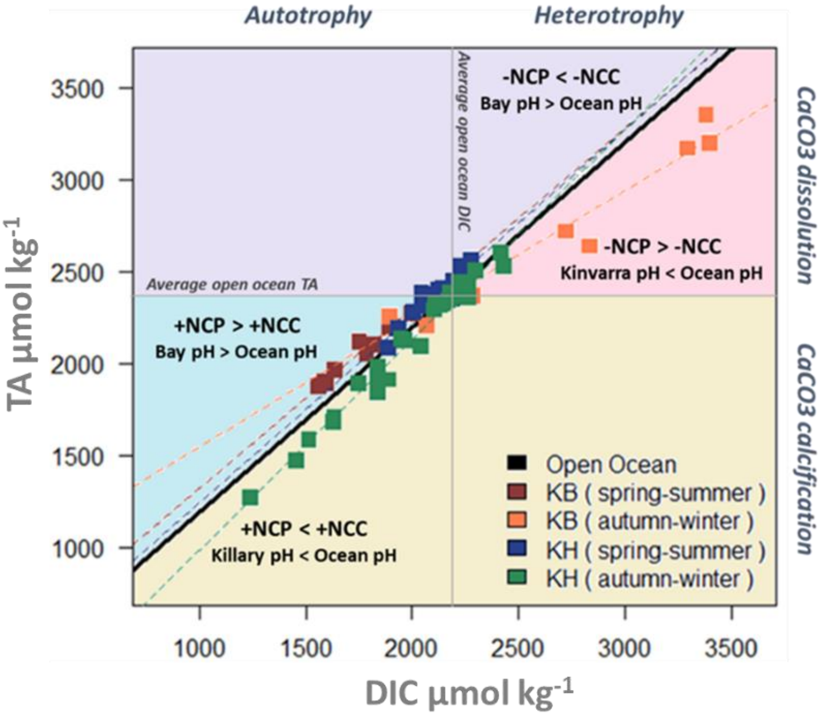


Figure 4-7: Metabolic drivers of TA and DIC for Kinvarra Bay (KB) and Killary Harbour (KH), situated against the adjacent Atlantic TA, DIC mean values and TA:DIC slope. With the brown KB (spring and summer) and blue KH (spring and summer) the surveys carried out in July 2018, April 2019 and (also August 2019 for KB) are represented. With the orange KB (autumn and winter) and green KH (autumn and winter) the surveys carried out in October 2018 and January 2019 are represented. Slopes close to one, as in the open ocean, reveal a balance between organic and inorganic drivers of the local carbon cycle. Imbalance is revealed by slopes differing significantly from ~1, which results in changes of pH of the system relative to the ocean. For example, the slope of the TA:DIC vector for Kinvarra Bay in winter/autumn (orange points) is significantly lower than one (see Table 4-2), implying from the position of the data on the graph that NCP is negative within the system (Heterotrophy), respiration rates increase DIC content in bay water more rapidly than net carbonate dissolution can buffer (-NCP>-NCC) and consequently pH decreases significantly within the system with reference to the open ocean.

The highest relative contributions of organic metabolism to the balance between TA and DIC in Kinvarra Bay occur in October 2018 and January 2019, when TA and DIC are also relatively lower (Table 4-2). Conversely, the lower contribution of net community production to the balance between TA and DIC in the bay occurs in April, when discharge is highest (Table 4-1) and freshwater levels of TA and DIC are comparable to July 2018 and August 2019. It can be suggested that in January and August 2019 because of similar discharge conditions the TA-DIC slope, is driven by this. In Killary Harbour, regardless the magnitude of freshwater inputs, there is not a significant change in the TA-DIC slopes, and the small variations recorded between the different surveys may be related to other factors such as the seasonality in the bay's metabolism or nutrients availability. In Kinvarra Bay, a specific relationship between TA-DIC slopes and freshwater discharge magnitude was not observed (see appendix Chapter 4). However, during the cooler months, the TA-DIC slopes are lower than 1.

4.4 Discussion

4.4.1 Seasonal variation of total alkalinity at the end member location: influence of temperature, pH and organics.

In both freshwater end members, a relation between the increase of alkalinity, temperature and pH was observed. As already discussed in the previous chapter the type of weathering reactions occurring on land drives the alkalinity delivered on the coastal areas. The areas characterized by calcite bedrock geology show higher alkalinity values due to the dissolution of calcium carbonate in the water. Indeed, 80% of calcium and 60% of magnesium reaching the sea every year are derived from limestone and dolostone weathering (Gaillardet et al., 2019). From literature studies, the relation between carbonate weathering and temperature is shown: the maximum dissolution rate observed is between 10 and 15 °C (Gaillardet et al., 2019).

In Kinvarra spring a higher alkalinity was observed with temperature greater than 15 °C, like for instance in summer 2018. Since the summer was a drought-period, probably the water spent more time in the ground, accumulating calcium carbonate ions. Reversely, in October 2018 and January 2019 despite the temperature was lower (between 10 and 12 °C) and higher calcium carbonate dissolution rate would be expected, lower alkalinity was recorded. A possible explanation of the observed trend can be found in the increase of precipitation during winter, leading to an increase of runoff infiltration into the groundwater system. To understand and to predict the carbonate dissolution and the alkalinity values in the karstic area is necessary to consider both: dissolution processes and runoff dilution (Romero-Mujalli, Hartmann, and Börker 2019). In April 2019 it is possible to observe higher alkalinity value with low temperature; the calcium carbonate dissolution is higher; additionally slurry applied from Irish farmers in the area might contribute to the increase of organic alkalinity (Regueiro, Coutinho, and Fangueiro 2016). It is known from the literature, that carbonate weathering can be enhanced by reacting with sulfuric acid, (Romero-Mujalli, Hartmann, and Börker 2019) that may be produced naturally by the oxidation of sulphide minerals, or driven by anthropogenic sources (Godderis et al., 2012; Li et al., 2008;. Wang et al., 2015). The organic alkalinity was considered in the current study and minimal contribution was detected, however further research on this topic is necessary to better understand the organic alkalinity variation in different conditions: freshwater discharge, temperature, and human activities on land.

The freshwater end member in Killary Harbour are the rivers. These shown alkalinity values much lower than those recorded in the SGD, due to the catchment geology-type. However, some seasonal variations in the alkalinity and pH are observed. The decrease of TA and pH during the wet season (October and January) might be correlated with the precipitation which dilutes TA and decreases pH values. Additionally, the drainage of peatland that surrounds Killary catchment area, might lead to decrease of pH and alkalinity, due to the presence of organic acids which increases H^+ ions (Hemond, 1980; Mcknight et al., 1985; Mclaughlin and Webster, 2010). It is interesting to observe that in April 2019 the alkalinity values were similar to July 2018 (drought-season): it is possible to explain this with the precipitation type. Indeed, in April, precipitation was mostly in the form of snow and the effect of runoff had probably less impact. This explanation is also aligned with the decrease of the estimated freshwater input.

Even if the temperature is a driver of mineral dissolution, in a multi-variables system the changes in the carbonate chemistry derive from the combination of different factors leading to different results. In Table 4-3 the factors discussed in this paragraph and their effects on TA and pH are summarized.

Table 4-3 In the following table the variables affecting TA and pH changes in Kinvarra Bay and Killary Harbour are shown. In the last column it is explained how the combinations of the variables affect the areas of study.

Location	Geology	Variables	Effects	How
Kinvarra Bay	Karst	$CaCO_3$ dissolution (that is maximum in the temperature range 10- 15 °C) (Gaillardet et al., 2019)	increases TA and pH	During wintertime, lower temperature is recorded, and higher dissolution rate is likely. However, the increase of precipitation that leads to an increase of runoff infiltration into the groundwater system, decreases TA and pH (Romero-Mujalli, Hartmann, and Börker 2019).
		Rainfall	decreases TA and pH	
		Agricultural slurry	increases TA and pH	The oxidation of organic matter, derived from use of fertilizers enhances sulphate reduction, which produces alkalinity (Romero-Mujalli, Hartmann, and Börker 2019)
Killary Harbour	Shale, conglomerate	Silicate minerals dissolution correlated with increase of temperature (Li et al., 2016; Williams et al., 2010)	increases TA and pH	With the increase of temperature and decrease of precipitations, TA and pH increase.
		Rainfall	decreases TA and pH	During winter period, with low temperature, the increase of precipitation would increase the weathering of catchment geology. The peat-bogs surrounding the area decrease TA leading to more acid water, decreasing pH.
		Peat-bogs	decreases TA and pH	

4.4.2 TA and DIC distributions in the estuary: drivers of TA-DIC slopes and metabolic state

Kinvarra Bay

In the present study, TA and DIC were plotted against salinity values and both linear regressions and conservative mixing lines were shown.

In Kinvarra Bay different patterns were shown. In July 2018, April and August 2019 there was no conservative mixing, suggesting that the system might become a sink of TA and DIC. Rather than implying that TA and DIC were not mixed conservatively within the system, this observation might be caused by large diel variation in the freshwater end-member carbonate system composition during the warmer months, which would distort the expected linear distribution at the very low salinity region of the mixing plot (Loder and Reichard, 1981).

The estimated SGD expressed in $m^3d^{-1}\times10^5$ in January and August 2019 showed high values (Table 4-1), however, the SGD composition in TA and DIC are very different, and this in turn affect the TA-DIC slope as well as on the relative role of organic metabolism that vary from 70% in January to ~ 50% in August. This can be due to a) an increase in the preservation of CO_2 from soil respiration in percolating recharge during fall winter given higher soil humidity and lower temperatures, combined with b) the timing of the application of farmyard manure and slurry to agricultural land in Ireland. Close to half the annual amount of manure is applied to soils in Ireland during fall (August to November) while 50% of the annual slurry applied to Irish farms is done so early in the growing season, starting in January and on to early April (Hennessy et al., 2011). The combination would contribute to enhance microbial respiration, CO_2 production and preservation in soils (Li et al., 1994; Paustian et al., 2000). Hence it is not only the freshwater magnitude that conditions carbonate balance, soil use and soil use change on land may also affect the state of the coastal carbonate system by shifting the balance between organic and inorganic metabolism in regulating the TA:DIC compositional ratio in SGD. Even if both sites are acidified compared to the open ocean, in Kinvarra Bay the increased CO_2 production in soil would contribute to accelerate coastal acidification in the colder months of the year. The metabolic state of the studied systems is also influenced by the water residence time inside the bays.

Gregory et al., (2020) observed that water retention into Kinvarra Bay is larger during neap tides than during spring tides. In fact, the drifter velocities at neap tide found in Gregory work were 0.10, 0.06 and 0.05 m s^{-1} in the outer, middle and inner bay respectively and during spring tide were 0.79, 0.51 and 0.13 m s^{-1}. Furthermore, in the Savatier's thesis (2021) water residence times was calculated in Kinvarra Bay from Ra isotopic ratios measured during the surveys presented here. These were around 3-4 days during July, October 2018 and January 2019 and around 5-6 days during April 2019. In Rocha et al. (2015) the survey was conducted during summer, the water residence time was around 7 days. These results might explain why, even at high discharge conditions, in April 2019 the TA-DIC slope was similar to July 2018, where the loading of TA and DIC was at the minimum value. For a small bay like Kinvarra, the flushing time might be more important than freshwater discharge (Gregory et al., 2020), considering that the SGD spring is also a huge source of nutrients (Rocha et al., 2015; Schubert et al., 2015), with the increase of permanence of water into the bay (particularly during warmer periods) these will stimulate the metabolic activity of the system, which in turn would affect the TA and DIC compositional ratio.

Killary Harbour

In Killary Harbour the conservative mixing lines were very similar, suggesting these properties were nearly conservative within the bay. Nevertheless, during February 2018, TA and DIC along the salinity gradient showed lower values compared to the expected conservative mixing of fresh and saline end-members. This might be explained looking at the freshwater discharge estimated for this survey, the bay was highly stratified (Savatier et al., 2021). In Savatier et al., (2021), it has been observed that, in the survey of February 2019, the water residence time was the lowest between the analysed surveys (2-3 days). The non-conservative downward deviation (February 2018) can be attributable to the addition of isotopically light respiratory CO_2 to the DIC pool, as suggested by Miyajima et al., (2009). Thus, the large freshwater discharge together with the limited mixing within the bay due to the strong stratification might enhance the impact of the local rivers over the carbonate system of surface waters. Conversely, during July 2018 and April 2019, the freshwater discharge was lower, the bay was less stratified (Savatier et al., 2021), and the carbonate system of the bay was dominated by the oceanic end-member signature. The bay showed conservative mixing along the salinity gradient, suggesting a balance between production and consumption. For what concerns the TA-DIC slopes in the different surveys, no significant change was observed, the area can be classified as autotrophic during all surveys, regardless the impact of freshwater discharge. In Killary Harbour, the biological components might have the major role controlling the TA:DIC compositional ratio, e.g., the rate of carbon dioxide assimilation through the photosynthetic process (see equation (44) could be the main driving factor of DIC concentration over TA in the bay.

$$6CO_2 + 6H_20 \rightarrow (C_6H_{12}O_6) + 6H_2O \tag{44}$$

The equation (44) shows the reagents and products of photosynthesis, this reaction occurs during daylight period and is facilitated when the light period is protracted.

Moreover, small changes of TA can be also related to other biogeochemical reactions; marine autotrophs can use nitrate, nitrite, ammonia or molecular nitrogen as nitrogen source (Wolf-Gladrow et al., 2007). According to the predominant reaction, TA can increase by 1 mole per mole of nitrate converted (denitrification) according to the following reaction:

$$5CH_2O + 4H^+ + 4NO_3^- \rightarrow 2N_2 + 5CO_2 + 7H_20 \tag{45}$$

Or decrease by 2 mole per mole of nitrate formed (nitrification):

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + H_2O + 2H^+ \tag{46}$$

Furthermore, assimilation and remineralization processes are also occurring in algae and the uptake of phosphate can also affect TA. However since the marine plankton follows the Redfield ratio according to the proportion 106:16:1 (for C, N, and P respectively)(Redfield, 1958) the effects on TA are small compared to the nitrate uptake (Wolf-Gladrow et al., 2007).

4.4.3 Drivers of pH and aragonite saturation state in the estuarine areas: spatial variation

In surface waters, the correlation of pH with salinity may suggest that mixing is the main process explaining pH distribution in both systems. During periods of very low discharge, longitudinal pH distributions are not correlated with salinity for both sites, however, spatial fluctuation of pH (0.1 to 0.2 pH units) is still apparent though, suggesting that second order processes (balance between photosynthesis and respiration) affect the water pH (Vargas et al., 2017; Narváez et al., 2019; Saavedra et al., 2020) in both systems even when the marine end-member dominates the carbonate system composition. Indeed, water retention is spatially variable even in small bays and the phytoplankton community composition is always patchy (Gregory et al., 2020), which would lead to small scale pH variability due to local metabolism.

Kinvarra Bay

Kinvarra Bay is characterized by waters with low pH values compared to the nearby ocean, influenced by the high TA:DIC compositional ratio in the SGD end-member. However, two different results can be observed. In July 2018 the pH and Ω_{Ar} were higher and closer to the nearby ocean probably due to the low discharge conditions and the larger influence of oceanic waters inside the bay. In April 2019 TA-DIC slope falls into autotrophic conditions, even if the pH and Ω_{Ar} were lower in the SGD. During this period of the year, metabolic processes predominate in the bay. Several factors influence the carbonate chemistry variability in the coast. It might be worth focussing on short term variability to identify the main drivers of the variations, particularly in the aquaculture areas (Saavedra et al., 2020).

Killary Harbour

During high-stratified conditions in Killary Harbour, the high pH of the deeper water column suggests a significant impact of benthic processes over the overlying water composition. The high stratified conditions in Killary Harbour correspond to high discharge (Savatier et al., 2021), and in such conditions, low pH and low Ω_{Ar} were observed near the river mouth at the surface. The Ω_{Ar} is affected by changes in the carbonate chemistry due to both NCP and NCC (McMahon et al., 2013). The freshwater inputs characterized by low TA are reducing the Ω_{Ar} (Ruesink et al., 2018), since it is known that carbonate dissolution processes are favoured when Ω_{Ar} is < 1 (Cubillas et al., 2005), the net $CaCO_3$ formed per mussel will be reduced (Morris and Humphreys, 2019). It is then possible to hypothesize that the rope mussel's located in the low salinity areas might have to adapt to more stressful conditions. Even if coastal areas are characterized by a really dynamic environments and stressful conditions for calcifiers might have always occurred in the estuarine areas (Ruesink et al., 2018), this might have an impact on *Mytilus edulis* aquaculture species particularly in the early life stages (Medaković 2000; Gazeau et al., 2010).

To summarize, land use and land use change, as well as freshwater discharge and local metabolism, have an important bearing on the variability of the carbon parameters in the bay. At both study sites, local food webs including cultured bivalve species experience large temporal and spatial pH fluctuations, and in most cases pH values are much lower than those predicted for the end of the century in the open ocean under the worst case scenarios (Fabry et al., 2008; Byrne et al., 2010; Caldeira and Wickett, 2003; Orr et al., 2005). These findings reinforce the shortcomings of studies that rely on open ocean carbonate system drivers to forecast the extent of acidification pressure on aquaculture, rather than recognizing the coastal carbonate system exceptionality and the fact that most aquaculture takes place in coastal regions (Blackford and Gilbert, 2007; Ferreira et al., 2014; FAO, 2018). Even if local adaptations may be occurring (Kelly and Hofmann, 2013; Hofmann et al., 2010; Barillé et al., 2020), long term effects of exposure are still unidentified. Even if both sites are acidified compared to the open ocean, in Kinvarra Bay the increased dissolved inorganic carbon accumulated in the groundwater and released into the bay at the Kinvarra Castle spring, would contribute to accelerate coastal acidification in the colder months of the year.

4.5 Conclusions

In addition to the physical drivers that primarily govern the carbonate system of the open ocean, coastal acidification processes are influenced by land-ocean interactions and the local balance between inorganic and organic metabolism. The combined effect of these drivers on the coastal carbonate system are highlighted by studying two contrasting Irish embayments. In the present study, areas with different watershed geology were compared. Surface runoff and SGD contribute to different freshwater end-member composition prior to discharge and affect the TA and DIC content along the coastal salinity gradient. When surface runoff dominates freshwater inputs, such as in Killary Harbour, a typical river-dominated distribution develops within the coastal embayment, with low TA and DIC. In contrast, freshwater sources into Kinvarra Bay are characterized by high TA and DIC associated with karst-borne submarine groundwater discharge. The freshwater sources of both systems are more acid compared to the open ocean, this can be also correlated with the presence of organic acids that might affect mineral weathering decreasing pH. The contribution of non-carbonate alkalinity estimated in this study was minor. However, this might be subject of further investigation and comparison between the two analysed systems. The results showed that surface and groundwater inputs drive the pH distribution along the salinity gradient that commonly falls below levels predicted for the open ocean by end of the century.

Nevertheless, local carbon metabolism also affects the pH distribution in both systems and this effect is in turn shaped by the local freshwater discharge magnitude and typology. The TA-DIC slopes, and therefore the balance between organic and inorganic carbon metabolism, showed no seasonal differences in the river-dominated Killary Harbour despite variations in the amount of freshwater entering the embayment. Thus, carbon metabolism within the embayment is primarily governed by ocean chemistry. In Kinvarra Bay, the freshwater composition likely influenced by the karstic catchment geology and by the soil use over the year, can in turn affect the TA and DIC compositional ratio and local metabolism.

This promotes a seasonal shift in the relative dominance of organic and inorganic carbon metabolism in the embayment, causing an acceleration of coastal acidification in the colder months of the year. Thus, land-ocean interactions can be dominant drivers of coastal acidification, driving the system away from open ocean trends. These results highlight the idiosyncrasy of the coastal carbonate system and the need for specific approaches to understand and to predict coastal ocean acidification processes.

5 Short term variability of carbonate system parameters and metabolism in two different coastal freshwater sources.

Abstract

Kinvarra Bay and Killary Harbour are both important aquaculture hotspots, characterized by contrasting watershed inputs. The aim of this part of the research work is to understand the main drivers of the short-term fluctuations of the carbonate system parameters in their freshwater end-member locations. The second aim is to quantify the NCP in these freshwater end-member location and how it might be related to the TA and DIC changes. The analysed freshwater sources were: Erriff River (Aasleagh Bridge location) which is the main river feeding Killary Harbour and Kinvarra Castle Spring which is the main freshwater source to Kinvarra Bay.

The river and the freshwater spring locations were sampled over a period of 24h at high resolution (every 30 minutes). The NCP was calculated following the dissolved oxygen dynamics. The diel variation of TA and DIC in the Erriff River were in the range of ~ 130 µmol kg^{-1} and pH changed by about 0.47 units. In Kinvarra Castle Spring diel fluctuations of TA and DIC were ~1200 µmol kg^{-1} and ~1800 µmol kg^{-1} respectively; the pH fluctuation was about 0.85 units. Statistical analysis of the carbonate system parameters showed high positive correlation of TA with pH in the Erriff River and negative correlations of TA with pH in Kinvarra Castle Spring. The diel variation of TA and pH was correlated with the tidal excursion. The time-series analysis showed non-stationarity. Kinvarra Castle Spring showed time-series seasonality; therefore, to have a complete understanding of the diel carbonate system fluctuation, the trend analysis was combined with statistical decomposition to evaluate the principal drivers of the diel change. The trend analysis in Kinvarra Bay confirmed that the main driver of the diel carbonate system fluctuations in the freshwater-seawater mixing control by the tidal excursion. Time-series in Erriff River showed a random pattern. The NCP at Aasleagh Bridge was 0.270±0.054 g m^2 d^{-1} and in Kinvarra Spring NCP was negative -0.037±0.006 g C m^2 d^{-1}. The result confirmed that Erriff River is an autotrophic and oligotrophic system as known from other literature studies. Kinvarra Castle Spring, conversely, has been identified as a heterotrophic system, since the dissolved oxygen dynamics during the day showed that the respiration processes exceeded the rate of

photosynthesis. The TA diel fluctuations at the SGD end-member location were used to understand the conservative mixing with samples collected in the bay area, the results showed that the large fluctuations occurring on the spring end-member might affect the conservative or non-conservative mixing of TA and salinity, particularly in the low salinity areas.

5.1 Introduction

A river system receives input from land, i.e. nutrients and organic matter accumulated in the catchment area are delivered to the river stream (Young and Huryn, 1999) and then, they are consumed or transported to the coast. As remarked in the previous chapter, land use can affect the rate of coastal primary production due to the potential to increase availability of nutrients (Fuß et al., 2017; O'Boyle et al., 2013; Pellerin et al., 2012). Each coastal habitat can be structurally and functionally diverse, because they can be differentiated by morphology, climatology, freshwater influx, productivity, or human pressure (Baumann and Smith, 2018). The supply of organic carbon from land makes fluvial ecosystems mostly heterotrophic, and they are usually sinks of organic carbon (Duarte and Prairie, 2005; Battin et al., 2009). However, there are areas less influenced by the human activities where the level of nutrients carried from the river towards the open ocean is not particularly high (as discussed in the chapter 3 of the present thesis). In the literature there are few studies focused on diel carbonate variations occurring in the freshwater systems, (Escoffier et al., 2018; Reiman and Xu, 2018; Parker et al., 2007). A few studies were focused on the diel fluctuations occurring in the coastal bays in order to understand the diurnal cycle in the carbonate system parameters and their effects on the coastal areas and ecosystem functions (Halley et al., 2006; Chou et al., 2020; Zablocki et al., 2011). In order to understand drivers of coastal carbonate system variability expressed as a change in pH and alkalinity at sea, it is important to analyse the diel change of temperature, dissolved oxygen, primary production and respiration (Parker et al., 2007).

This chapter reports the short-term variability of the carbonate system occurring in the freshwater end-members under investigation. Considering the importance of the freshwater source, the diel dynamics of the freshwater end-member might be illustrative of possible dynamics occurring on the coastal embayment to which they are connected (de Montety et al., 2011; Parker et al., 2007). In rivers, a substantial increase of pH and dissolved oxygen has been usually observed during the day and is followed by a decrease during the night in response to the aquatic metabolism, photosynthesis and respiration (Parker et al., 2005). In the SGD spring connected to coastal areas the diel change of dissolved oxygen might be more correlated with freshwater sea water mixing rather than diel metabolic changes. The groundwater system would be dominated by inorganic carbon biogeochemistry, while the river, since it is opening up to light the diel metabolism might change.

This part of the research aims to understand the driver of NCP in two contrasting freshwater sources (SGD and river) over a short time scale (diel), then to discuss the implications that these diel changes in the selected freshwater sources might have on the adjacent coastal embayments. The following hypotheses have been tested:

- *H_1: the carbonate system in the freshwater source, described by the TA:DIC relation, is driven by biological factors, i.e, causally co-varies with NCP.*
- *H_2: The carbonate system in the freshwater source, described by the TA:DIC relation, is driven by physical processes (e.g. weathering).*
- *H_3: the carbonate system in the freshwater source, described by the TA:DIC relation is controlled by freshwater-seawater mixing.*

The hypotheses were tested in two contrasting freshwater typologies, in order to observe if different dynamics were occurring. The two areas selected for the comparison were: Erriff River, which is the main freshwater source (Donohue, 2012; Rodhouse et al., 1987) feeding Killary Harbour, and Kinvarra Castle Spring, which has been identified as the major freshwater source (Rocha et al., 2015; Schubert et al., 2015) feeding Kinvarra Bay. The short-term variability of the carbonate system was addressed with a 24 h sampling strategy: measures of TA and pH were performed every 30 minutes, together with other environmental variables (temperature, DO etc.). The DO dynamics were used to quantify the NCP at the freshwater end-member location. The high-resolution sampling strategy adopted allowed to assess time-series analysis: trend analysis and forecast of the carbonate system parameters (TA, pH) were carried out based on the diel carbonate fluctuations.

As shown in Chapter 4, SGD was characterized by high TA and DIC values (Kinvarra Bay), particularly during summer and spring, in such condition the conservative mixing line between TA and salinity (between freshwater and marine end-member) showed non conservative behaviour (Chapter 4). Analysing the short-term variability of the constituents in the freshwater sources allows to understand:

- how carbonate system parameters at the point of entry (the mouth of the bay) are driven by carbon biogeochemistry in the up-system (end-member location);

- how in turn variability of parameters of the carbonate system at the end-member might create a non-conservative behaviour in the receptor system, in this case the adjacent bay area.

5.2 Methods

5.2.1 Study areas

Erriff and Bundorragha rivers are the main rivers feeding Killary Harbour and they have a catchment area of 176 km^2 and 51 km^2, respectively (Anon, 1958). Erriff river is part of a shale, sandstone and conglomerate catchment area (Rodhouse et al., 1987). Mcmahon and Patching (1984) found that Erriff River provides 10 times the amount of particulate organic carbon (POC) compared to Bundorragha River. Mcmahon and Patching (1984) explained this difference by the fact that the Bundorragha catchment is steep and provides relatively short contact time periods for land runoff, whereas the catchment of the Erriff River provides a greater opportunity for the erosion of POC from the soil. There are a few recent studies on this area of Ireland, however for what is known from recent ecological surveys, land use did not change massively in the last 30 years and it is still an area with a not intense pasture and grazing (AQUAFACT, 2013; EPA, 2018). The diel sampling location selected was the Erriff River because it was recognized as the main water source to the bay (Rodhouse et al., 1987; Anon, 1958).

Kinvarra Bay has been selected because is mainly fed by SGD. In Figure 5-1, it is represented the karstic catchment area related to the freshwater spring considered for this study. The Gort lowlands catchment covers an area of approximately 500 km^2 in south County Galway on the western coast of Ireland (Gill et al., 2013; Morrissey et al., 2020). Small rivers are present, and they drain into the catchment from the border of the Burren limestone. Several springs discharge into Kinvarra Bay. The reason why Kinvarra Castle Spring was selected to analyse the diel variabilities in the carbonate system, is because was identified from previous studies as the main spring in terms of volume of water that feeds the bay (Rocha et al., 2015; Schubert et al., 2015).

Because the SGD not always showed a conservative with the marine end-member in Kinvarra Bay (Chapter 4), in order to understand the mixing processes occurring in the transect, additional sampling stations were added there. The four locations on land are represented in Figure 5-1. This sampling strategy allowed to understand if TA has a conservative or non-conservative behaviour related to the diel changes of freshwater source.

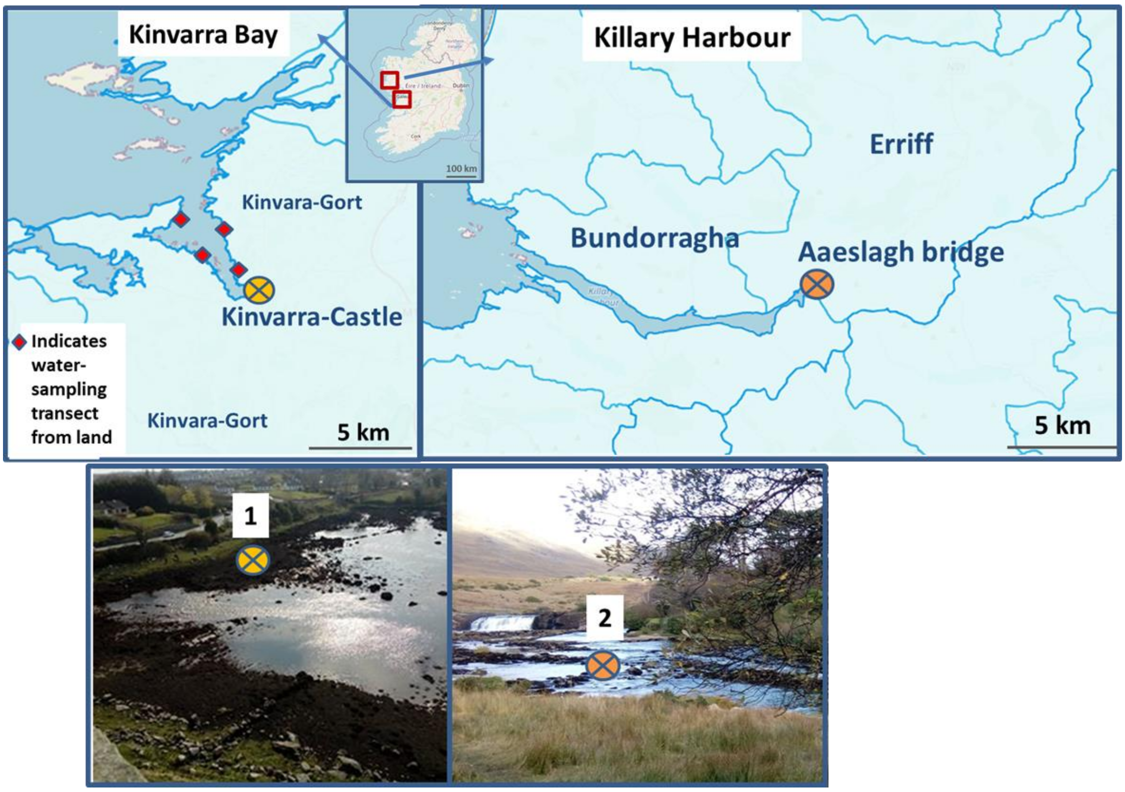


Figure 5-1 Kinvarra Bay and Killary Harbour areas sub-catchment areas are represented. 1* indicates the freshwater end-member selected in Kinvarra Bay, named "Kinvarra castle" 2* indicates the freshwater end-member selected in Killary Harbour, specifically the samples have been collected at Aasleagh Bridge. The four-sampling locations selected in Kinvarra Bay are also represented.

5.2.2 Sampling strategy

The samples were collected at the end of the summer/ beginning of autumn (on the 30th August 2019 in Kinvarra Bay and on the 21st September 2019 in Killary Harbour) every 30 minutes for a period of 24 h. In Kinvarra Castle Spring (Figure 5-1) the samples started on the 30th August at 13:15 and finished on the 31st August at 12:45: the sunrise was at 6:41 and the sunset at 20:30 (Met Éireann website). In the Erriff River (see image 2 Figure 5-1) the samples started on the 21st September at 12:20 and finished on the 22nd September at 11:50: the sunrise was at 7:22 and the sunset at 19:40 (Met Éireann website).

To understand the TA diel conservative mixing with salinity between freshwater end-member and nearby ocean, a transect from the land was carried out during the low tide, when the submerged area was about 2.47 km^2. At low tide the access to the water from land is complicated by the sandy mud sediment in the intertidal (Rocha et al., 2015), which makes the area not easily accessible, therefore the four additional selected points are the only points in which it was logistically possible to sample.

Field measurements of pH, temperature, salinity, electrical conductivity, and DO were performed using a multi-parameter probe, Aqua-read AP 1000. The electrical conductivity was also measured with a portable conductivity meter WFW-profilLine cond 197i which was submerged on the sediment in the freshwater locations and set to record data every 30 minutes. The conductivity data were then transformed to salinity using online converter with algorithm based on (UNESCO, 1983), and compared with the salinity recorded with the aqua-read probe. pH was also measured in the lab with a pH meter and Ross Orion electrode (see paragraph 2.3.7). The samples for TA were collected using High Density Polythylene (HDPE) bottles and were immediately poisoned with mercuric Chloride ($HgCl_2$) following the standard procedure for marine water (Grasshoff and Kremling, 1999; Dickson et al., 2007). HDPE bottles were used for TA measurements in other literature studies previously (Gray et al., 2008; Huang et al., 2012) and the analyses were conducted after a few days from the sampling. Carbonate system parameters were measured as described in paragraphs 2.3.5; 2.3.7; 2.3.8. These samples were analysed in the TCD lab, and no DIC analysis in LOCEAN lab were carried out. The DIC values were calculated using CO2SYS, as described in paragraphs 2.3.8; 4.2.3. Therefore, the DIC values showed in this study might be an underestimation of the actual values, the contribution or organic alkalinity might be significant in freshwater systems. In previous studies the importance of non-carbonate alkalinity was actually evaluated and in the river freshwater might vary from 30% to 80%, (Hunt et al., 2011; Lukawska-matuszewska, 2016). It follows that the DIC values calculated, if on one hand were useful qualitative indicators for this part of the research, on the other hand, were not used for the time series representation.

5.2.3 Statistical analysis

The high-resolution sampling strategy provided time-series of TA, pH, DO and salinity that were subsequently statistically analysed. The first step was to understand if the data had a stationary or non-stationary behaviour (Hamilton, 1990). Afterwards, the understanding of time-series' typology was carried out. Based on the findings of these first two steps of the research, a forecast was formulated. The trend-analysis approach is generally used for data representing months or years' time-series in order to forecast climate e.g. rainfall variations, climate change (Mudelsee and Wegener 2010). Human activities have altered the atmosphere chemical composition e.g. the CO_2 emissions, therefore, the changes in the ocean chemistry are studied, like for instance to forecast the pH changes and the consequences for ocean acidification (Kleypas and Langdon, 2006). In this study the analysis of the time-series is applied on 24 hours' time-series data, which already has in built physiological determinants of the variabilities. However, to apply the trend analysis in this context can be considered a useful tool to better understand the drivers of the variations. Particularly the scope of the study is to understand the drivers of carbonate system parameters over a diel time scale. Therefore here, the trend analysis was not made with the purpose to predict behaviors of carbonate system parameters, on which it would be necessary to have several daily cycles, but rather to understand the main trends of the time-series which will then be in turn identified by the forecast.

The trend analysis can be applied on a time-series where some patterns can be observed, with the aim to describe the trend and to make a forecast (Hamilton, 1990). It cannot be applied a trend analysis on a random walk time-series (Brockwell and Davis, 1997).

The trend analysis is not able to define cycle trends, therefore trend analysis itself cannot define the exact trend of the time-series where cycle pattern is present. In the case of cyclic time-series, it is possible to combine the decomposition model with the trend analysis. The decomposition was used in the present study to separate the linear components from the seasonal/cyclic components (Zarnowitz and Ozyildirim, 2006). The results from the two analyses allowed to obtain a more reliable forecast that considered the cyclic components of the time-series.

For the time-series analysis and to forecast the trend, the methods described are following Hamilton, (1990). Additionally, the Chapter 6 of Brockwell and Davis, (1997) was consulted for what specifically concerned nonstationary and seasonal time-series models. The method applied can be described as following:

Minitab 17 was the software used for the analysis. Trend analysis in Minitab 17 allows to fit the experimental data into the following models: linear, quadratic, exponential growth and S-curve (pearl-reed logistic). The quadratic model was applied, and 24 points forecasting was made (that according to the data collected corresponds to a 12 hours prediction). Afterwards, it was observed that the residuals of the trend analysis showed fluctuations. The fluctuations in the residuals were originated from the fluctuations of the actual values due to the seasonality of the time-series. A second step, using the decomposition, was then necessary. The decomposition was applied on the residuals of the trend analysis, to create a model that considered the seasonality of the time-series.

Eventually, to have a correct forecast that considered both linear and seasonal trends of the time-series, a “newfit” and a “newforecast” were created. The newfit can be described as the sum of the fit1 from the trend analysis and fit2 from the decomposition made on the residual of the trend analysis. At the same way, the newforecast can be described as the sum of the forecast1 (trend analysis) and forecast2 (decomposition). The new fit and the new forecast considered both the linear and the cyclic components of the time-series (Zarnowitz and Ozyildirim, 2006). The final graphical representation included: the original time-series, the newfit and the newforecast.

5.2.4 Organic metabolism calculation using dissolved oxygen dynamics

To calculate the NCP of the two analysed systems, the dissolved oxygen measured as dissolved oxygen saturation state (DO%) was used in order to apply the governing equation of Odum, 1956 (see paragraph 2.7).

5.3 Results

5.3.1 Differences in the end-member diel dynamics: Kinvarra Castle Spring and Erriff River (Aasleagh Bridge)

The main difference between the two sampling locations is:

Erriff River is a surface runoff and it is exposed to the atmosphere and light, which imply equilibrium between atmospheric CO_2 and dissolved CO_2 in the river. The river system is dominated by the organic metabolism due to the effect of light i.e., autotrophic metabolism.

Kinvarra Castle Spring water comes from a groundwater system, the CO_2 will not be equilibrated with the atmosphere before coming out of the spring, and the inorganic processes dominate. Once the water comes out of the spring, it will be mixed with the bay water during the high tide. Therefore, in this location the tidal range will have an effect on the measured carbonate system parameters. In the Table 5-1 and Table 5-2, the parameters considered for this study and measured in the two freshwater location are represented. The DIC has been calculated as explained in the methods.

Table 5-1 TA, temperature, pH, salinity, dissolved oxygen and tidal excursion measured in Kinvarra Castle Spring. The DIC data were calculated using CO2SYS software. The first two columns indicate the time of each samples and the name of the sample. The last column indicates the TA:DIC ratio at each sampling time.

Time	sample	TA	T	pH	Salinity	DO	DO	DIC	Tide	TA:DIC
		µmol kg^{-1}	°C		‰	%	µmol kg^{-1}	µmol kg^{-1}	m	
13:15	T1	5254	15.6	7.16	0.41	66.4	106	6194	1.19	0.85
13:45	T2	5255	14.6	7.13	0.41	57.2	91	6283	1.60	0.84
14:15	T3	5220	14.0	7.20	0.41	69.2	110	6098	2.10	0.86
14:45	T4	5248	16.6	7.15	0.40	67.0	107	6192	2.64	0.85
15:15	T5	5291	15.5	7.20	0.40	72.6	115	6156	3.19	0.86
15:45	T6	5407	15.5	7.30	0.40	80.2	128	6108	3.75	0.89
16:15	T7	5326	15.8	7.37	0.40	96.8	154	5909	4.30	0.90
16:45	T8	4898	18.2	7.47	0.40	94.9	151	5303	4.83	0.92
17:15	T9	4588	16.3	7.36	0.46	90.2	143	5097	5.32	0.90
17:45	T10	4911	16.9	7.61	1.42	94.8	151	5208	5.73	0.94
18:15	T11	4621	16.6	7.60	3.32	90.0	143	4909	6.00	0.94
18:45	T12	4298	16.0	7.53	4.52	87.2	139	4619	6.08	0.93
19:15	T13	4603	15.3	7.49	3.01	80.7	128	4985	5.96	0.92
19:45	T14	4747	15.0	7.45	0.70	70.3	112	5183	5.64	0.92
20:15	T15	4530	14.5	7.53	0.45	71.1	113	4878	5.18	0.93
20:45	T16	5348	13.4	7.07	0.42	63.2	100	6579	4.64	0.81
21:15	T17	5394	13.2	7.15	0.42	63.8	101	6430	4.05	0.84
21:45	T18	5291	13.3	7.16	0.42	59.8	95	6282	3.43	0.84
22:15	T19	5422	13.3	7.14	0.40	64.3	102	6486	2.78	0.84
22:45	T20	5351	12.9	7.20	0.41	58.7	93	6272	2.11	0.85
23:15	T21	5362	13.2	7.16	0.41	64.2	102	6368	1.49	0.84
23:45	T22	5334	13.1	7.16	0.41	59.5	95	6336	0.97	0.84
00:15	T23	5387	12.9	7.14	0.41	57.8	92	6452	0.63	0.83
00:45	T24	5415	13.0	7.10	0.41	58.7	93	6587	0.52	0.82
01:15	T25	5408	13.3	7.10	0.41	66.9	106	6572	0.62	0.82
01:45	T26	5394	13.1	7.10	0.41	67.2	107	6559	0.91	0.82
02:15	T27	5423	13.0	7.10	0.41	66.3	105	6596	1.33	0.82
02:45	T28	5366	13.0	7.14	0.41	62.8	100	6424	1.82	0.84
03:15	T29	5423	13.0	7.08	0.42	66.5	106	6652	2.36	0.82
03:45	T30	5408	13.3	7.07	0.42	60.2	96	6656	2.91	0.81
04:15	T31	5465	13.0	7.07	0.42	66.1	105	6733	3.49	0.81
04:45	T32	5465	12.8	7.10	0.41	60.5	96	6653	4.06	0.82
05:15	T33	5494	12.6	7.20	0.41	63.8	101	6444	4.63	0.85
05:45	T34	5468	12.6	7.24	0.76	64.0	102	6331	5.15	0.86
06:15	T35	5596	12.4	7.30	0.58	67.3	107	6367	5.59	0.88
06:45	T36	5201	12.6	7.30	1.44	74.2	118	5914	5.87	0.88
07:15	T37	4972	18.8	7.30	1.95	75.8	121	5579	5.95	0.89
07:45	T38	4914	12.7	7.30	2.88	76.0	121	5587	5.81	0.88
08:15	T39	4937	12.8	7.30	3.60	76.3	121	5612	5.47	0.88
08:45	T40	5284	13.3	7.40	2.13	78.4	125	5849	5.00	0.90
09:15	T41	5468	13.6	7.31	1.08	77.2	123	6187	4.46	0.88
09:45	T42	5539	13.8	7.24	1.04	77.2	123	6392	3.88	0.87
10:15	T43	5511	13.7	7.27	0.29	65.3	104	6573	3.28	0.84
10:45	T44	5497	13.5	7.20	0.29	67.6	107	6431	2.66	0.85
11:15	T45	5368	14.0	7.15	0.28	65.6	104	6382	2.04	0.84
11:45	T46	5396	13.7	7.09	0.28	68.0	108	6575	1.47	0.82
12:15	T47	5440	14.0	7.18	0.28	73.9	118	6399	1.04	0.85
12:45	T48	5397	14.0	7.20	0.28	70.0	111	6306	0.80	0.86

Table 5-2 TA, temperature, pH, salinity, dissolved oxygen measured in Aasleagh Bridge. The DIC data were calculated using CO2SYS software. The first two columns indicate the time of each samples and the name of the sample. The last column indicates the TA:DIC ratio at each sampling time.

Time	sample	TA	T	pH	Salinity	DO%	DO	DIC	TA:DIC
		µmol kg^{-1}	°C		‰	%	µmol kg^{-1}	µmol kg^{-1}	
12:20	T1	166	16.60	6.64	0.03	103.5	164	263	0.63
12:50	T2	155	16.20	6.50	0.02	104.5	165	281	0.55
13:20	T3	164	16.20	6.54	0.20	104.4	165	286	0.57
13:50	T4	164	16.60	6.56	0.02	108.7	172	279	0.59
14:20	T5	148	16.30	6.58	0.02	103.6	164	248	0.60
14:50	T6	164	16.40	6.68	0.02	107.1	169	252	0.65
15:20	T7	164	16.60	6.63	0.02	109.0	172	262	0.63
15:50	T8	99	16.10	6.63	0.02	106.9	169	159	0.62
16:20	T9	66	16.40	6.56	0.02	107.0	169	114	0.58
16:50	T10	83	16.50	6.26	0.04	108.0	171	200	0.41
17:20	T11	89	16.30	6.28	0.02	106.9	169	210	0.42
17:50	T12	99	16.20	6.30	0.02	108.0	171	227	0.43
18:20	T13	125	16.90	6.57	0.02	105.4	167	211	0.59
18:50	T14	118	16.30	6.56	0.02	104.4	165	202	0.58
19:20	T15	177	16.20	6.55	0.02	104.2	165	305	0.58
19:50	T16	193	16.00	6.65	0.02	101.9	161	305	0.63
20:20	T17	193	16.00	6.70	0.02	102.0	161	293	0.66
20:50	T18	154	15.70	6.56	0.02	100.7	159	265	0.58
21:20	T19	180	16.00	6.60	0.02	101.0	160	297	0.61
21:50	T20	170	16.10	6.64	0.02	100.0	158	271	0.63
22:20	T21	167	16.00	6.56	0.02	101.0	160	286	0.58
22:50	T22	170	16.10	6.54	0.02	100.3	158	297	0.57
23:20	T23	174	15.90	6.54	0.02	100.1	158	303	0.57
23:50	T24	167	19.90	6.54	0.02	102.0	161	284	0.59
00:20	T25	167	15.90	6.56	0.02	100.0	158	286	0.58
00:50	T26	148	15.90	6.42	0.02	100.0	158	293	0.50
01:20	T27	167	15.90	6.54	0.02	101.0	160	292	0.57
01:50	T28	144	15.80	6.54	0.02	102.0	161	253	0.57
02:20	T29	141	16.00	6.52	0.02	106.0	167	252	0.56
02:50	T30	131	16.20	6.51	0.02	110.0	174	236	0.56
03:20	T31	140	16.10	6.50	0.02	111.0	175	254	0.55
03:50	T32	148	16.20	6.56	0.02	113.9	180	253	0.58
04:20	T33	131	15.80	6.51	0.02	113.6	179	237	0.55
04:50	T34	128	15.80	6.50	0.01	114.3	181	234	0.55
05:20	T35	128	15.60	6.52	0.02	113.6	179	229	0.56
05:50	T36	148	15.60	6.58	0.01	113.8	180	249	0.59
06:20	T37	135	15.60	6.48	0.01	113.6	179	251	0.54
06:50	T38	131	15.60	6.40	0.01	114.0	180	268	0.49
07:20	T39	123	15.40	6.40	0.01	114.6	181	252	0.49
07:50	T40	125	15.60	6.44	0.01	115.0	182	243	0.51
08:20	T41	125	15.60	6.40	0.01	115.1	182	255	0.49
08:50	T42	131	15.80	6.30	0.01	116.0	183	303	0.43
09:20	T43	131	15.80	6.32	0.01	115.8	183	295	0.45
09:50	T44	131	16.00	6.30	0.01	116.0	183	302	0.43
10:20	T45	112	16.10	6.26	0.01	116.2	184	272	0.41
10:50	T46	99	16.00	6.23	0.01	116.4	184	251	0.39
11:20	T47	99	16.20	6.25	0.01	116.1	183	243	0.41
11:50	T48	99	16.20	6.28	0.01	116.0	183	233	0.42

Kinvarra Castle Spring was covered twice a day by the bay-water because of the tidal excursion. The freshwater composition was characterized by high TA and low pH. During the sampling period (Table 5-3), TA values reached 5596 µmol kg^{-1} at low tide with a pH value of 7.07 and decreased until 4298 µmol kg^{-1} with a pH value of 7.60 at high tide. The dissolved oxygen showed large variation along the sampling period, from 57.2% during the low tide (day-time 13:45) until 96.8% during the high tide (day-time 16:15). The salinity values fluctuated in the range between 0.28 and 4.52 between low and high tide. From these preliminary observations it is suggested that the mixing between the freshwater end-member and the water coming from the bay (which is mixed with the ocean end-member) reduces the TA and increases pH, DO% and salinity. TA and pH showed negative correlation, with Pearson coefficient of -0.77 and p-value <0.001. TA and salinity were also negatively correlated -0.66 as well as TA and DO% -0.59, both with p-value < 0.001.

The Aasleagh Bridge, that is located 16 meters above the sea level, is not influenced by seawater and tidal range does not affect the sampling location. This has been confirmed by the data collected with the CTD diver which did not detect any salinity changes during the sampling period: the minimum and maximum salinity values recorded were between 0.01 and 0.20 respectively. Differently from Kinvarra Castle Spring, where the fluctuations were probably chiefly driven by the mix between the freshwater and the bay-water during the high and low tide, these results in Aasleagh Bridge suggested that the observed fluctuations of TA and pH might be correlated to other factors. The TA was found variable during the 24 h from 66 to 193 µmol kg^{-1}; pH changed from 6.23 to 6.70. Moreover, the Pearson correlation coefficient between pH and DO% was -0.62 with a p-value < 0.001. The pH values in this location are quite low compared to Kinvarra Castle Spring, and this might be due to the peat characteristic of the catchment area on which the water interacts with (Rostk and Schmidt, 2017). TA and pH showed a Pearson coefficient of 0.68 with a p value < 0.001. A Pearson coefficient of -0.58 was found for TA and DO% with a p value < 0.001. Moreover, the Pearson correlation coefficient between pH and DO% was -0.62 with a p-value < 0.001.

Table 5-3 Descriptive statistics of TA expressed as µmol kg^{-1}, pH, salinity, DO%, and calculated DIC expressed as µmol kg^{-1} in Kinvarra Castle Spring and Aasleagh Bridge at Erriff River on the 48 collected samples.

Descriptive Statistics

Kinvarra Castle Spring

Variable	Mean	StDev	Minimum	Maximum
TA	5236	307	4298	5596
T °C	13.86	2.36	1.70	18.80
pH	7.24	0.15	7.07	7.61
Salinity	0.87	1.00	0.28	4.52
DO%	70.74	10.27	57.20	96.80
DIC	6098	562	4619	6733
Tide	3.4	1.83	0.52	6.08

Erriff River, Aasleagh Bridge

Variable	Mean	StDev	Minimum	Maximum
TA	140	29	66	193
T °C	16.13	0.64	15.40	19.90
pH	6.49	0.13	6.23	6.70
Salinity	0.02	0.03	0.01	0.20
DO %	108.01	5.87	100.00	116.40
DIC	257	38	114	305

5.3.2 Time-series representation

In the Figure 5-2 and Figure 5-3 time-series data are represented: TA, pH, salinity and DO% for Kinvarra Castle Spring, TA pH and DO% for Aasleagh Bridge are reported. As previously observed in Table 5-2 and Table 5-3, the salinity in Aasleagh Bridge did not show significant changes over the 24 h therefore it was not represented in the time-series.

Kinvarra Castle Spring is strongly influenced by the tidal excursion, and Figure 5-2 emphasizes the correlation between the fluctuations of the analysed variables with the tidal curve.

The aim of this work was to understand the main drivers of carbonate system parameters in the freshwater end-members over diel timescale. In this case the samples parameters of the carbonate system are: TA-pH. As a first step the time-series was plotted to observe the trend of the different variables. Kinvarra Castle Spring, as said before, showed evident presence of cyclic components. Following the definition of stationary data, time-series should respect the following criteria (Manuca and Savit, 1996; Witt et al., 1998):

- The mean of time-series is constant
- The standard deviation of the time-series is constant
- There is no seasonality

Kinvarra Castle Spring 24 hours' time-series showed a clear seasonal behaviour, and in Aasleagh Bridge the mean and the standard deviation over the 24 hours sampling was not constant. Therefore, both time-series showed a non-stationary behaviour. In the case of non-stationary data, the autocorrelation function quickly drops to zero, without showing significant autocorrelation values. The non-stationary trends showed random walks (see graphs appendix Chapter 5). In Kinvarra Castle Spring (Figure 5-2) it is possible to observe that all the variables clearly followed the cyclic movement of the tide. Trend analysis and forecast can be therefore applied on this location.

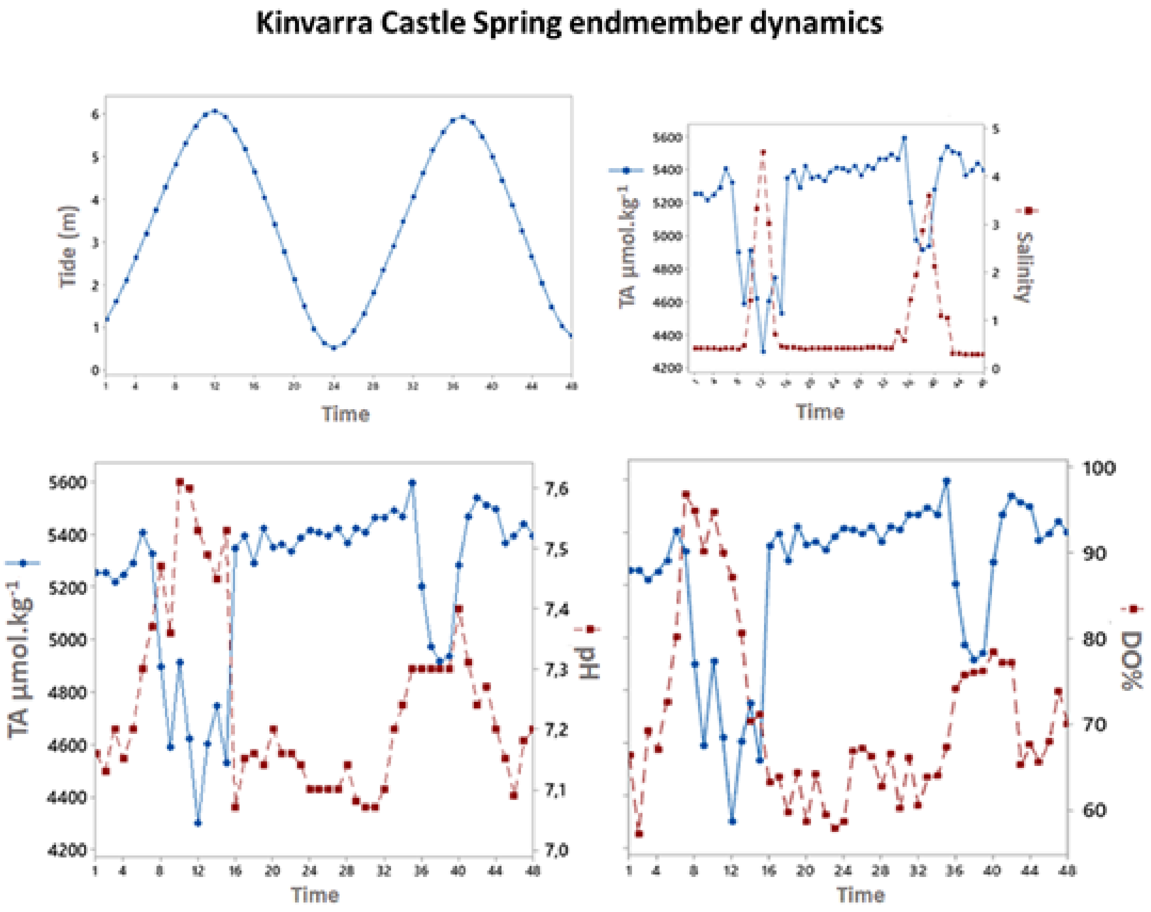

Kinvarra Castle Spring endmember dynamics

Figure 5-2 The fluctuation of salinity, pH, TA and DO% are represented in the graphs over a period of 24h. The time on x axis represents a sample value collected every 30 minutes. As it is possible to observe the main driver of the diel variation is the tidal excursion. During high tide the spring water is mixed with the bay water characterized by low alkalinity, higher pH and DO%.

In Aasleagh Bridge (Erriff river) it was not possible to observe a clear trend of TA and pH over the day, which can be defined as a random walk. The DO% decreased during the night and increased again during the day, which suggested a periodic trend was occurring for the metabolism, with an increase of PP after the sample number 30, (corresponding to time 02:50). The high negative correlation previously observed between pH and DO% suggests that the diel change of DO% can be the driver of the large pH fluctuations observed in this location. However, the sampling strategy should be extended to 48-72 hours to acquire more confidence in the data analysis and to better understand these fluctuations and their meaning, as well as to test if the metabolism affects the TA:DIC ratio. The TA showed a drop after 5 hours from the beginning of sampling (from 15:20 to 16:50 Table 5-2, Figure 5-3) which was likely correlated to the increase of precipitation during the sampling period, rain is assumed to have zero alkalinity and zero salinity (Park, 1968) and this might dilute the river alkalinity (Figure 5-3). Additionally, also a decrease of pH value was observed, this might be due to the lower pH value of the rain. To observe how the ionic speciation changed during the time, the sample collected at 15.20 was compared, using PHREEQC software with the samples collected at the following times, where the decrease of alkalinity and pH were observed. Indeed, the cation H^+ activity at time 15:20 was 2.34×10^{-7} leading to a pH of 6.64 and the H^+ activity at time 16:50 increased until 5.50×10^{-7} leading to a pH of 6.26. Knowing that bogs characterize the catchment geology around Killary, it can be hypothesized that decreasing pH values might be related with the increase of land drainage that acidifies the water.

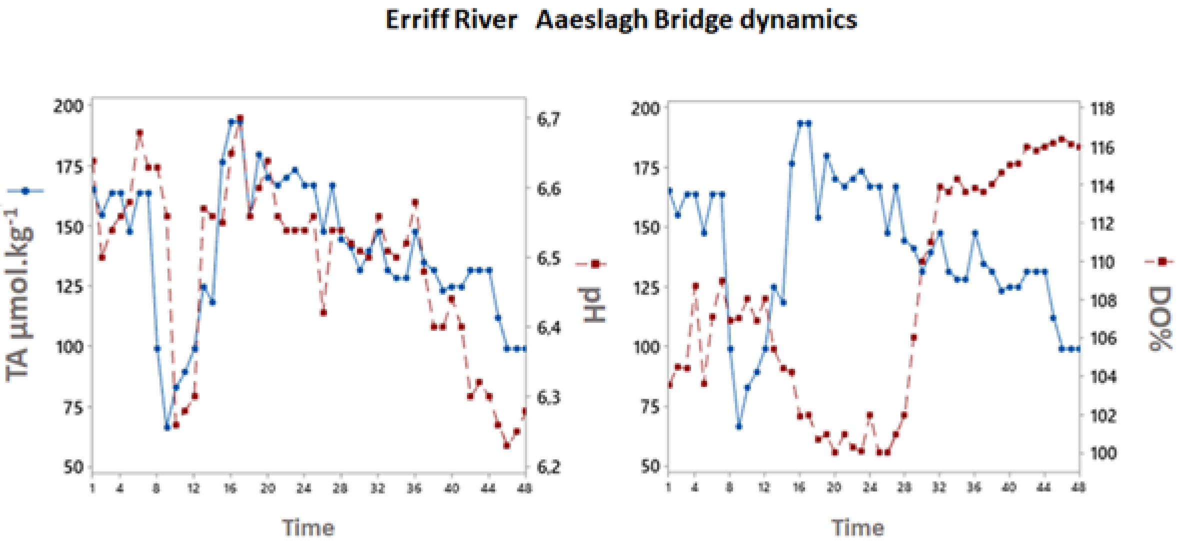


Figure 5-3 The diel fluctuations of TA and pH, and TA and DO% are represented. The time on x axis represents a sample value collected every 30 minutes. The salinity was close to zero and no fluctuations occur. pH and TA are highly correlated, and TA is inversely correlated with DO%.

5.3.3 Time-series forecast: Kinvarra Castle Spring

In Kinvarra Castle Spring a seasonal time-series has been observed. Short-term variability in the freshwater end-member was mainly dependent on the tidal fluctuation. Considering that the samples were collected every 30 minutes, the 48 samples are representative of the 24h. To make a prediction of the next 12 hours and to get an estimation of the fluctuations driven by the next tidal excursion, 24 points have been forecasted. In Figure 5-4 the original time-series of TA, pH, DO% and salinity, the newfit and the forecast are shown. The forecast was calculated as explained in the methods. The original trend analysis and decomposition graphs can be consulted in the appendix for result Chapter 5.

TA showed two different trends:

- linear increase during the sampling period
- Diel fluctuation related with the tidal excursion.

Therefore, the 24 points of forecast (Figure 5-4) are obtained considering both the identified trends. The reason why the forecast method has been applied on this time-series data is to test if one of the three hypotheses listed in this introduction chapter might be true to understand the diel dynamic occurring in Kinvarra castle spring. For what concerns the linear increasing of TA values, it should be considered that in nature different drivers are acting at the same time, therefore, it is likely that, natural readjustment of TA forecasted values occurs. In this study the forecast was made for the following 24 points, corresponding to the 12 hours in order to observe the next tidal excursion in Kinvarra Castle Spring. However, this can be considered as a forced prediction, given the dataset of 48 samples. Therefore, it is important to consider possible errors made from the forecast (Brockwell and Davis, 1997).

The two-samples standard deviation between the original TA, pH, salinity dissolved oxygen time-series and the newfit of TA, pH, salinity dissolved oxygen has been calculated to test the hypothesis that:

the standard deviation of sample 1 (TA, pH, salinity dissolved oxygen) differs from standard deviation of sample 2 (TA, pH, salinity, dissolved oxygen newfit).

For the TA the results showed a p-value equal to 0.39, which indicates that there is not enough evidence that the standard deviation of the two samples differs.

Similarly, for pH and salinity the main driver of the fluctuations can be attributable to the tide. The same hypothesis has been tested for pH and salinity and a p-value of 0.22 and 0.68 was found (see appendix for Chapter 5 for further info).

The dissolved oxygen showed different results, even if the tidal excursion is an important driver of the diel fluctuations, tide is not the only driver of dissolved oxygen fluctuations. Indeed, it is possible to observe that during the first high tide, the recorded DO% values were higher compared to the second-high tide. The first high tide was at 16:15 and the DO% was 96.8, the second high tide was at 7.15 and the DO% was 75.8 (Table 5-1). Considering that the samples were collected at different times of the day, the light intensity and the rate of photosynthesis was likely different, this might suggest the possible importance of the biological component affecting the amount of DO% during the day.

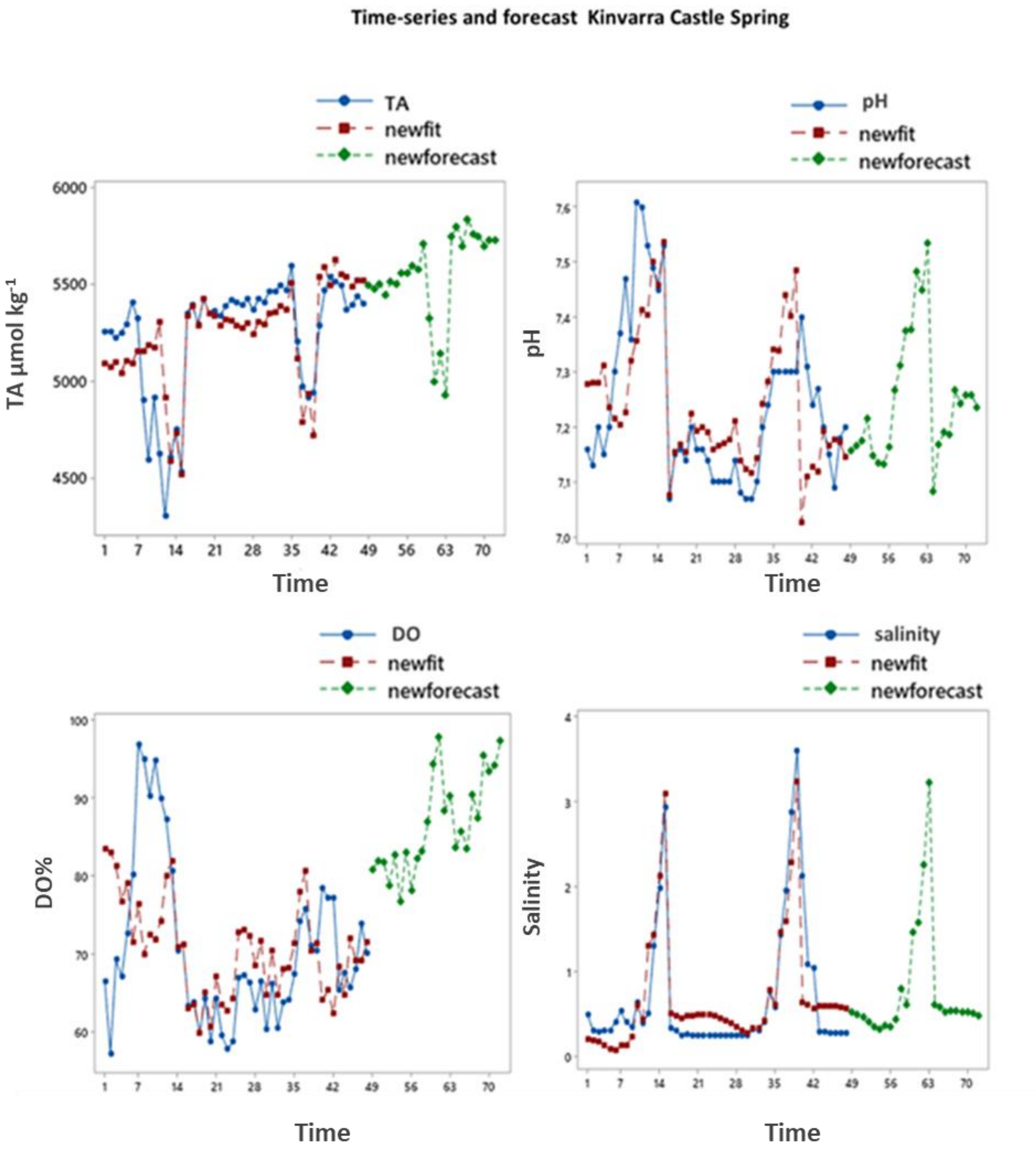


Figure 5-4 Time-series analysis: original values, newfit and new forecast predicted using trend analysis and decomposition. The forecast is made for the two measured parameters of the carbonate system: TA and pH, and for DO% and salinity measured at Kinvarra Castle spring. On the x axis the 70 points that indicate the time are: 48 points representative of 24 hours samples collected every 30 minutes, plus the 24 forecasted values, which are representative of 12 hours.

5.3.4 NCP quantification using dissolved oxygen dynamics

The results of NCP obtained using the DO dynamics were in g O_2 m^3 d^{-1}. To convert O_2 to C the Photosynthetic Coefficient (PQ) of 1.2 was selected (Mcmahon and Patching, 1984). See paragraph 2.7 for details.

Kinvarra Castle Spring

The groundwater system is likely to induce heterotrophy on the nearshore water because of the high delivery of TA and DIC, (promoted by dissolution of calcareous rocks and decomposition of organic matter) (Wang et al., 2018), furthermore, because no photosynthetic processes occurring in the groundwater, the dissolved oxygen is usually low.

As it is possible to observe from the Figure 5-2, during the low tide the water sampled at the Castle Spring location was characterized by high TA, low pH and low DO%. During the high tide the water coming from the spring was mixed with the bay, which then increased the TA:DIC relation that reached values close to 1 (Table 5-1). TA:DIC ratio can also increase because of the greater efficiency of photosynthesis due to the presence of vegetation (plants and macroalgae) surrounding the area. Indeed, at high tide DO% reached 96.8.

However, even if photosynthetic processes were occurring during the high tide, they were limited to a short temporal scale when the bay-water was covering the intertidal area. In fact, with the exception of the high tide when the chemical composition was highly affected by mixing, and/or metabolic processes, during the ebb the DO% decreased again because of the freshwater coming from the groundwater.

An overall negative value of NCP was found equal to -0.037±0.006 g C m^2 d^{-1}.

Because of the increase of TA:DIC ratio during the high tide, NCP was calculated during this period. The Primary Production (PP) and respiration (R) were calculated only using the samples collected when the whole spring was covered by the bay-water.

Knowing the sunrise and sunset times (see method), the samples considered for the light period were the ones collected from 17:15 to 20:15 of the 30th August and from 6:45 to 9:45 am of 31st August. The samples representative for the night-time were the ones collected from 20:45 to 21:15 pm and from 5:15 to 6:15. The NCP during high tide was positive and equal to 0.170 ±0.030 g C m^{-2} d^{-1}.

Erriff River

In the Erriff River the carbonate system parameters were not fluctuating as much as in Kinvarra Spring. As can be observed from Table 5-2, Table 5-3, the DO% reached the minimum value of 100% during the night and increased during the day until 108%. Using the dissolved oxygen dynamics, the calculated NCP was 0.270±0.54 g C m^{-2} d^{-1} or 98±20 g C m^{-2} y^{-1}. Erriff River can be therefore defined as an autotrophic and oligotrophic system.

5.3.5 Total alkalinity versus salinity conservative mixing in Kinvarra Bay, using different freshwater end-member values

In Figure 5-5, TA vs salinity is plotted and the transect values are represented. Five conservative mixing lines (dashed lines) built between the freshwater end-member and the sample collected at the higher salinity value (in this case the sample collected in Parkmore Pier that showed salinity 20) are shown. Each line was built with a different value of TA recorded in the spring, four conservative lines are overlapped since the TA end-member values did not show large changes. The selected values are from high and low tide sampling, however, since the tidal values represent the value at the bay entrance and because some delays from the entrance to the bay mouth occurred, to visualize the large fluctuations of TA the samples with lower and higher salinity values were selected. Therefore, the following samples were selected: T1, T12, T24, T39, T48 (see Table 5-1). This criteria to select the samples allowed to observe the maximum fluctuations of TA occurring at the freshwater end-member (Officer and Lynch 1981; Loder and Reichard 1981).

The water coming from the freshwater end-member has TA values that are largely different from the TA coming from the open ocean (that should be around 2300-2400 µmol kg^{-1} in Galway Bay area, see result Chapter 3).

The sample location could be more or less influenced by the mixing processes occurring between the ocean end-member and the freshwater end-member. In the freshwater end-member the samples named T1, T24, T39 and T48 showed almost a conservative mixing with the samples collected within the transect (blue squares Figure 5-5). Reversely, the sample named T12, which corresponds to one of the high tide end-member, did not show conservative mixing with the samples collected in the transect and an upward deviation is visible. Even if both the samples T12 and T39 are representative of high tide, according to the salinity data (Table 5-1), they showed different TA values: 4298 µmol kg^{-1} and 4937 µmol kg^{-1} respectively. The TA at T39 sample was particularly high and this can be related with the different effects of freshwater-seawater mixing, in fact T12 and T39 showed different salinity values 4.52 and 3.70 respectively.

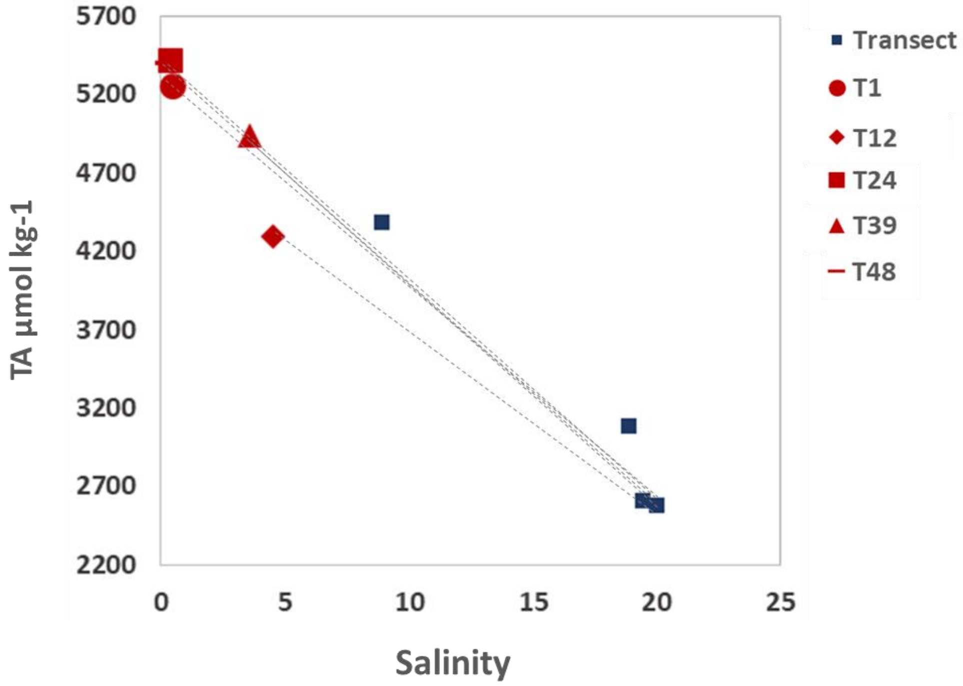


Figure 5-5 In this figure the blue squares represent the 4 sampling stations collected at the edge of Kinvarra Bay, along the salinity gradient. The red samples T1, T12, T24, T39 and T48 are representing the maximum fluctuations in the TA and salinity occurring in Kinvarra Castle Spring. The dashed lines represent the conservative mixing between freshwater end-member and the sample collected at Parkmore Pier.

5.4 Discussion

5.4.1 Drivers of diel fluctuations of the carbonate system

Kinvarra Castle Spring

The diel variations of the carbonate system parameters in Kinvarra Castle Spring are attributable to two different factors:

- the tidal excursion that led to cyclic behaviour in the measured parameters;
- the chemical reactions occurring in the groundwater system that might be enhanced during the freshwater-seawater mixing at the low tide (O'Connor et al., 2018) and land use (Buss et al., 2006; Einsiedl, 2012), that presumably led to the observed increasing of TA during the sampling period.

During the high tide, the bay water mixes with the freshwater spring, with the consequential increase of salinity and alteration of the carbonate system parameters. High-resolution sampling was applied in previous studies present in the literature, where radon measurements were also carried out to estimate water residence time and to quantify the discharge: the freshwater discharge was minimal during the high tide (Richardson et al., 2017). The intermittency of the freshwater discharge from the spring was also previously observed, since the tidal force into the subterranean estuary can lead to an attenuation of the discharge (Robinson et al., 2007). Specifically in Kinvarra Bay the pulsing effect modulated by the tide was shown in Rocha et al., (2015). This effect was also confirmed by a hydrogeological model where the temporal variation of discharge at the springs and how this discharge is affected by the tidal cycle was shown in McCormack et al., (2017). In the presented results during the two observed high tide, the salinity first reached 4.52 with a TA value of 4298 µmol kg^{-1} and during the second high tide the salinity was 3.60 with TA value of 4937 µmol kg^{-1}. This might suggest that in the analysed sampling condition the freshwater discharge was not minimal during the high tide, even though, a different freshwater pulsing effect is possible.

However, not only the mixing processes and tidal excursions are responsible for the diel carbonate system fluctuations, also the reactions occurring in the groundwater system could play a role (Moore, 1999; Charette and Sholkovitz, 2006).

TA values in the freshwater end-member were not stable: a linear increase of TA within the diel sampling period was observed and between the two low tides, a difference of about 200 µmol kg^{-1} was recorded. The decrease of temperature can lead to an increase of $CaCO_3$ dissolution processes (Coto et al., 2012; Krumins et al., 2013; Wolf-Gladrow et al., 2007; Weyl, 1959) and because the spring is located in a karstic catchment area this option can be considered likely at longer time scale. However, even if a decrease of temperature was observed, at diel time scale, specifically here a few hours, cannot affect carbonate dissolution since weathering processes are slow. In this thesis work the carbonate system calculations, including the estimation of aragonite and calcite saturation states, were made using CO2SYS. In this case of study, since the maximum salinity value recorded during the sampling period was 4.5, PHREEQC, that is the more common tool for freshwater environments analyses such as rivers or groundwater (Hunt et al., 2011), was used. The values of alkalinity, temperature and pH were used as input. Additionally, since Kinvarra catchment area is characterized by limestone geology, calcite mineral was added using the equilibrium phase function, to let the aqueous solution to equilibrate with respect to calcite. PHREEQC provided aragonite and calcite saturation states of -0.15 and 0 respectively for all the samples. This result suggested that carbonate dissolution does not change during the diel sampling period. However, the acquisition of additional elements such as: Chloride, Nitrogen, Sulphate, Calcium, Potassium, Magnesium and Sodium, would help to better understand if the diel fluctuations are correlated with reactions occurring in the groundwater system or if they are only driven by tidal excursions. Indeed, the observed increase of 200 $\mu mol\ kg^{-1}$ in Kinvarra Castle spring might be the result of the balance between biotic (e.g., denitrification, Fe-oxide reduction and sulphate reduction) and abiotic (e.g., carbonate and silicate dissolution) processes (Chaillou et al., 2014).

Another possible interpretation of the increase of TA is the effect of human activities on land, such as the increase of organic matter originated by the use of fertilizers (Oh et al., 2003). It is known that TA production is dominated by the oxidation of organic matter during sulphate reduction, which is the major diagenetic pathway in nearshore sediments:

$$2CH_2O + SO_4^{2-} = 2HCO_3^- + HS^- + H^+ \tag{47}$$

where CH_2O refers to hydrolysed marine organic matter with a Redfield stoichiometry $(CH_2O)106(NH_3)16(H_3PO_4)$ (Chaillou et al., 2014; Krumins et al., 2013; Wolf-Gladrow et al., 2007). In a system not open to CO_2 gas exchange, continued oxidation of organic matter can stimulate the increase of alkalinity (Stuyfzand, 1999). This conclusion might be reasonable considering that the flow rate in the area (determined with tracing techniques) ranges between 5 to 250 m/h (Drew, 2008). Water that enters the conduit system is transported relatively rapidly down-stream towards Kinvarra Bay (McCormack et al., 2014) (the flow velocities within this conduit network have been estimated between 60 and 1000 m/h) (Drew and Daly, 2003). However, expanding the sampling strategy and comparing more than one diel variation in the carbonate system parameters, as made in other literature studies (Cyronak et al., 2018), might help to understand if the linear increase observed in this time-series is occasional or is due to other chemical reasons not identified in the present study. Diel changes in the groundwater system, dissolution rate and flow rate are all elements that must be considered in order to understand the causes of TA increase within a short-time frame (Flower et al., 2017; Menning et al., 2015).

Erriff River (Aasleagh Bridge)

The Erriff River showed different results compared to Kinvarra Castle Spring. The observed pH fluctuations were from 6.29 to 6.70. The TA and dissolved oxygen fluctuations occurring within the diel sampling period did not show large amplitude. The TA and pH time-series did not show a clear trend within the 24h, and the time-series could be defined as a random walk, therefore the variability is random. To better understand the driver of the fluctuations of these two parameters, an extension of the sampling strategy might be necessary. In the meanwhile, some hypothesis can be formulated. The drop of TA and pH after a few hours from the beginning of the sampling period, might be due to the strong increase of precipitation (17.5 mm/h recorded in Leenane station from Met Eireann meteorological station) that also led to an increase of the riverbed. The rain has an alkalinity value close to zero (Durand et al., 1992; Copin-montgut, 1993), and, considering that the samples were collected on the surface and the water depth of the River in the sample location was around 1 meter, (see detail of sampling location Appendix Chapter 5) the water TA likely decreased because of the influence of rainfall (Edwards 1973; Diamond and Cohen 2018). At the time 16, corresponding to 8.45 pm, an increase of DIC can be observed, and this might be related to the decrease of biological productivity (increase of respiration >DIC) (Parker et al., 2005). The increase of TA might be promoted by the increase of flow rate stimulated by the rain, which increased the rocks weathering on the upper part of the river (Chen, 2002). The start of the decrease of DO% at 18:50, and the drop off at 19:50 just after the sunset (19:40), might suggest a diurnal change of this parameter in the night and day period. In the case that photosynthesis and respiration are the only processes occurring in the water column a ratio close to 1:1 on the diel δ (amplitude of diel variability) of DIC and DO change can be expected based on the following equation (Zablocki et al., 2011):

$$CO_2 + H_2O \leftrightarrow CH_2O + O_2 \tag{48}$$

In Aasleagh Bridge the diel δ DIC: diel δ DO ratio found is 7.4:1, which confirms that in this location the fluctuations of carbonate parameters in a diel time-scale are not related to photosynthetic processes. In Aasleagh Bridge location physical factors, rainfall variations and weathering products transported from the upstream can potentially drive the carbonate system parameters. However, to verify this hypothesis it would be necessary to extend the sampling strategy or to compare different diel time-series.

5.4.2 Freshwater end-member metabolism

The Photosynthetic Coefficient (PQ) of phytoplankton varies under different environmental conditions (Burris, 1981; Raine, 1983). In systems dominated by seagrasses the PQ can vary from 1.03 to 1.3 (Duarte et al., 2010). Specifically for this study the PQ considered converting g O_2 to g C was 1.2, which have been also selected in previous studies in Killary Harbour area (Mcmahon and Patching, 1984). The PQ of 1.2 was used also for Kinvarra Bay, however, because the spring discharges into a rocky area and macroalgae are a dominant group in the local ecological assemblage (e.g. *Fucus serratus, Fucus Ceranoides)* (Field, 2006; Foley, 2014; Perry and Budd, 2016), the PQ selected might be lower than the effective PQ value suitable for a macroalgae dominated system. The NCP can be therefore underestimated for Kinvarra Castle Spring.

Kinvarra Castle Spring metabolism

Kinvarra Castle Spring showed a negative NCP, which can define the freshwater spring end-member as heterotrophic system. These results correspond to what has been found in the literature: even if the SGD is recognised as a source of nitrogen and phosphate that leads to an increase of primary production, they do not compensate the delivery of inorganic carbon, leading to an increase of respiration, decreasing NCP (Richardson et al., 2017; Wang et al., 2018). Kinvarra Castle Spring is dominated by water with low dissolved oxygen saturation and DIC values greater than TA. It is known that no photosynthetic processes are occurring in the groundwater system. However, at the spring location, the high-resolution sampling and the availability of the dissolved oxygen data made possible to calculate the NCP during the high tide, where a positive value was found.

In Kinvarra castle spring positive NCP during the high tide was measured and this might be related to a combination of factors:

- the effect of seawater mixing that enriches in oxygen in the spring area
- the efficiency of the primary production rate.

Observing the dissolved oxygen time-series data, it can be noticed that the fluctuations of this parameter were not strictly related to the tidal fluctuations. The increase of photosynthesis during the day might be another driver of the diel dissolved oxygen increase. A possible reason of the primary production increase over respiration it concerns the specific sampling conditions, i.e., light availability: the 31st August the day length was ~14 hours. The algae (especially *Fucus ceranoides* (Foley, 2014)) surrounding the intertidal area of Kinvarra (as it is possible to observe from Figure 5-1 and from the appendix Chapter 5) were likely playing an important role consuming the DIC and nutrients (that are also load from the spring (Rocha et al., 2015; Schubert et al., 2015; Kelly, 2005)) and increasing the dissolved oxygen.

It might be possible to test the hypothesis that only during the high tide δ DIC: diel δ DO ratio, might be governed by photosynthesis and respiration processes. However, even considering the δ DIC: diel δ DO ratio only at high tide, the ratio between them is too large. Even if the photosynthesis might play a role during the high tide, this cannot be confirmed, nevertheless, it is possible to say that the tidally mixing waters appears to drive the high diel δ DIC-to diel δ DO ratio (Zablocki et al., 2011).

Erriff River metabolism

Aasleagh Bridge location in Erriff River looks not affected by the tidal excursion: therefore, the fluctuations observed in the analysed parameters were not due to the mixing of different masses of water. The DO% was high during all sampling periods probably due to day length (12 hours) that had a role in the photosynthetic efficiency. In this study the measured NCP was positive, 0.270±0.054 g C m^2 d^{-1}. Assuming this value as representative of the average system conditions, less than 100 g C m^2 y^{-1} , classifies this location as oligotrophic (Nixon, 1995). The presence of the aquatic angiosperm *Najas flexilis* along the river (Roden and Murphy, 2014), was associated in previous studies with the high water quality, which means low eutrophication status and low nutrients level (Rostk and Schmidt, 2017; Connor, 2013), which confirms Erriff River to be an autotrophic and oligotrophic system.

These results are different from what was expected in the literature, where rivers and streams are often heterotrophic systems, due to the high delivery of allochthonous organic matter from human activities on the land (Abril and Frankignoulle, 2001; Abril et al., 2003; Brett et al., 2017; Hellings et al., 2001; Maher and Eyre, 2012; Wang et al., 2018) which fuels microbial respiration (Hopkinson and Smith,2005; Maher and Eyre, 2012).

Conversely, Killary Harbour catchment area is not affected by intensive agriculture usage and human discharges are limited in this area. It is known that farming is a common activity within the Connemara region, with mountains grazed by sheep; however, most of the land around Killary Harbour is privately owned and this provides some protection from overgrazing (AQUAFACT, 2013).

Erriff River catchment area is affected by the drainage of peatland for peat-cutting and this leads to darkening of the water colour characteristic of this area, associated with low pH value (Rostk and Schmidt, 2017). Even if TA and pH dynamics observed in this location did not show a clear trend, DO showed a clear decrease during the night. A strong relation between pH and DO fluctuation was previously observed, and it was previously documented in other literature studies (Melzner et al., 2012; O'Boyle et al., 2013; Baumann et al., 2014; Wallace et al., 2014). Short-term variations of DO might be attributable to the metabolic processes (Duarte et al., 2013). The pH and DO coupled conditions have been observed also in Aasleagh Bridge.

The pH and TA fluctuations might be correlated not only to metabolic processes but also to physical ones. The catchment area of Killary Harbour consists mainly of peat bog (Mcmahon and Patching 1984), that receive most of their water through precipitation (Glaser et al., 1997). The decrease of TA and pH within a few hours after the start of the sampling might be related to the isolated rainfall event, particular weathering processes occurring at the specific sampling time. Indeed, the bogs acidify surface water through the production of hydrogen ions dissociated from mineral acids and organic acids (Hemond 1980; Mcknight et al. 1985; Mclaughlin and Webster 2010). However, since the time-series did not show a clear TA and pH behaviour over 24 h, it follows that, in order to understand the diel variability of carbonate system parameters in the Erriff River, longer sampling strategy would be necessary.

5.4.3 Mixing processes: conservative and non-conservative behaviour of TA in a bay dominated by SGD

In Kinvarra Castle Spring a wide diel fluctuation of the carbonate system parameters was found. In the previous chapter it was observed that the mixing processes between the freshwater and marine end-member sometimes did not lead to a conservative behaviour of TA. Several factors could affect the mixing processes and the conservative mixing curve, according to the time on which each sample is collected and according to the tidal curve. The conservative mixing curve built between the freshwater end-member T12 compared to the others (T1, T24, T39 and T48) showed a broadening effect, however it can be observed a decrease toward the mouth of the estuary (Loder and Reichard 1981; Officer and Lynch 1981). The fluctuations occurring at the SGD locations are large, however, previous studies observed these fluctuations at the river end-member location. The point at which the curve broadening is a conservative mixing can be again identified (e.g., T12 from salinity 15) is a function of the eddy diffusivity coefficient and the frequency of the input variability relative to the flushing time (Loder and Reichard, 1981). This point occurs at lower salinities as mixing increases (i.e., high eddy diffusivity coefficient) and at higher salinities as the frequency of the input variability decreases (Loder and Reichard, 1981). Literature studies showed that TA can have a non-conservative behaviour in the upper estuaries with salinity less than 5 which can be attributable to changes in the physico-chemical conditions driven by biogeochemical processes (Mora, 1983; Hoppema, 1990; Howland et al., 2000 Abril et al., 2003). This non-conservative behaviour has been confirmed in Kinvarra Bay in the low salinity area. Moving away from the main freshwater source a nearly-conservative behaviour of TA and DIC can be explained by the counterbalance between sources and consumption of TA and DIC along the salinity gradient (Oliveira et al., 2017). The samples with salinity greater than 15, showed a conservative behaviour. Even if the pH values in the SGD are higher compared to the river, the mixing between freshwater with TA and DIC composition contrastingly different from the adjacent coastal sea, led to large fluctuations of the carbonate system parameters that are not limited on Kinvarra Castle Spring location but affect large part of the bay area. The large diel fluctuations occurring in the low salinity area might affect the calcifiers.

5.5 Conclusions

Kinvarra Castle Spring is heterotrophic and the DIC was higher than TA. However, during the high tide the TA:DIC ratio increased, and a positive NCP was found. The increase of NCP is likely related to the freshwater seawater mixing, which is the main driver of the diel fluctuations of the TA:DIC ratio in the freshwater spring, as also confirmed by the time-series analysis. However, because of the presence of algae surrounding the area, and because of the light availability during the sampling period, local biological factors might be relevant in this period of the year. The photosynthesis effect potentially increases its role in spring and summer over the bay area, however, the δ DIC: diel δ DO ratio showed that mixing processes are the main driver of the carbonate system variability.

The H_3 hypothesis that has been proposed in this chapter can be accepted for Kinvarra Castle Spring, since the main driver of the fluctuation in the spring is the freshwater seawater. The mixing processes occurring between the freshwater and marine end-member with the changes in the conservative mixing lines emphasized the importance of freshwater-seawater mixing as a possible driver of the carbonate chemistry in this coastal embayment. These findings must be considered in the studies related to calcifiers and their adaptations mechanisms in such dynamic environment.

In the Erriff River, NCP was positive, and freshwater system analysed can be defined as autotrophic and oligotrophic. For what concerns the diel fluctuations of carbonate system parameters, they did not follow a specific trend within the day and, therefore, the fluctuations of the time-series were defined as random walk. The H_2 hypothesis may be the most likely for this location and probably the carbonate system variability is driven by physical processes. However, because the variables observed during the diel sampling did not show a pattern that can be identified with a specific process, it might be necessary to compare different time-series, to understand the main driver of the diel fluctuation.

6 Net Metabolism in two contrasting coastal system in Ireland

Abstract

In order to understand TA, DIC and DOC storage in two coastal embayments and to estimate NCP, LOICZ budgeting methodology was applied. Killary Harbour showed negative ΔTA and ΔDIC for all surveys and positive NCP, with an average value of ~ 14 mmol C m^2 d^{-1} (equivalent to 61 g C m^2 y^{-1}). Killary Harbour could be thus considered as an autotrophic system. On the other hand, Kinvarra Bay showed positive ΔTA and ΔDIC during the autumn and winter surveys implying a net export of TA and DIC to the open ocean, and a negative NCP. NCP in Kinvarra Bay was positive for the surveys taken during the other periods of the year, giving an average annual NCP of ~37 g C m^2 y^{-1}. These results suggest that freshwater inputs into Kinvarra Bay could seasonally drive the system into heterotrophy, intensifying ocean acidification trends. On an annual scale both areas can be considered autotrophic, although the net export of ΔTA and ΔDIC associated with negative NCP during the cold months in Kinvarra Bay moves the system into heterotrophy, intensifying ocean acidification.

6.1 Introduction

The open ocean's metabolic state is under control of the marine carbon cycle (Karl et al., 2003; Ducklow and Doney, 2013). The heterotrophic or autotrophic conditions in the surface ocean determine when it becomes a source or a sink of carbon dioxide (CO_2) relative to the atmosphere (Letscher and Moore, 2017). Coastal areas are heterogeneous and coastal acidification studies are still limited (Teeter et al., 2018). Multiple environmental variables act in coastal areas, which leads to added complexity compared to the open ocean. The organic and inorganic metabolisms of coastal areas are impacted by human activities on land (Smith and Hollibaugh, 1993), as it has been discussed in the previous chapters (e.g. increase of nutrients inputs from the production and use of chemical fertilizers, human and animal wastes) (Hu et al., 2006; Kim and Lee, 2009; McCoy and Corbett, 2009).

The delivery of nitrogen, phosphates and carbon compounds could affect the metabolism of coastal areas, changing the Net Community Production (NCP). As previously observed, different watershed geology can lead to different freshwater typology that could affect the coastal carbonate chemistry (Kempe and Pegler, 1991; Lauerwald et al., 2013). The rate and the type of alteration of carbonate chemistry can vary from region to region and depending on the types of watershed (Waldbusser and Salisbury, 2014) leading to different water chemical compositions and consequences for the biogeochemical cycles.

Coral reef, salt marshes, seagrasses and in general coastal areas are considered the most productive ecosystems on earth (Harrison et al., 1987; Costanza et al., 1998; Botsford et al., 2006; Hales et al., 2006; Gazeau et al., 2007; Bopp et al., 2013), hence the understanding of coastal areas resilience to ocean acidification is even more important. The knowledge of their present ecological state and of their functioning is extremely important, also in the light of the current climate change issues (e.g. increase of rainfall and flooding) (Bevacqua et al., 2019).

The aim of this part of the research is to understand the role of the watershed inputs on the coastal carbonate chemistry, and to verify the following hypotheses:

H_0: The carbonate system in coastal areas as described by the TA:DIC relation is under biological control, i.e, causally co-varies with NCP.

H_1: The carbonate system in coastal areas as described by the TA:DIC relation is controlled by fresh-water sea-water mixing.

To address this scope, the temporal variation in areas with contrasting watershed input was considered important to understand the variability of carbonate system and/or NCP. The surveys were then conducted at different discharge conditions. LOICZ biogeochemical modelling approach was applied (Gordon et al., 1996; Swaney and Giordani, 2007; Giordani et al., 2008), to evaluate the whole system metabolism. LOICZ provides a reasonable evaluation of the functioning of aquatic ecosystems, based on conservative and non-conservative material flux balances (Padedda et al., 2010).

SGD has been identified in the last years as a large source of TA and DIC and DOC in the coastal area (Burnett and Dulaiova 2003; Moore, 2000). Specifically in the Kinvarra Bay spring, high values of TA (McCormack et al., 2014; Kelly, 2005) DIC and DOC (Kelly, 2005) were recorded. Some authors hypothesized a role of SGD in altering the coastal metabolism (Hall and Tank, 2005; Johnson and Wiegner, 2014). The relation between TA and DIC in coastal systems has been suggested to identify whether areas can be considered as a sink or a source of carbon in a few studies focused on the health monitoring of coral reefs (Albright et al., 2013; Andersson and Gledhill, 2013; Cyronak, et al., 2018). Indeed, the ratio between them provides a valuable indication of the balance between NCP and NCC (Takeshita et al. 2016) as it was observed in Chapter 4. It is known that NCP varies with the flow conditions (Russell et al., 2006) and between different catchment areas. This is the reason why in the present research the NCP was estimated from different surveys (considering different flow conditions) in the two considered catchment areas (Kinvarra Bay and Killary Harbour). The non-conservative material budget was applied to quantify the inputs and outputs of TA, DIC and DOC in order to quantify the export of these constituents towards the open ocean.

6.2 Materials and Methods

6.2.1 Study areas

Study areas are described in Chapter 2 paragraph 2.2. In the following figure the study areas and sampling locations are Figure 6-1.

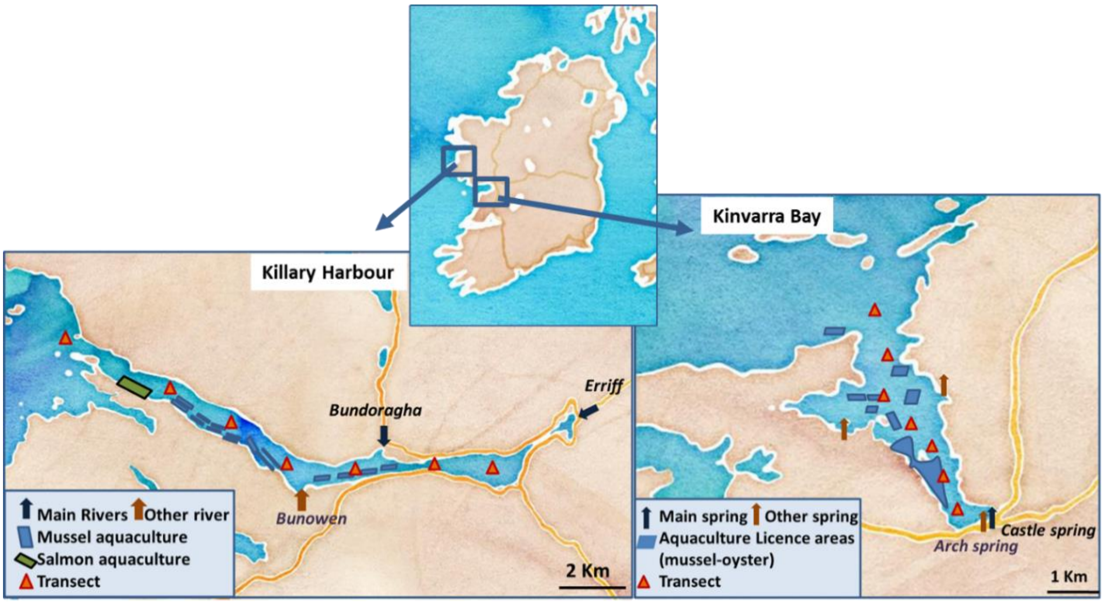


Figure 6-1 Kinvarra Bay and Killary Harbour maps from http://www.gis.epa.ie water framework directive (WFD) units map, major spring site is represented following EPA reports (Mara and Connolly 2016; EPA 2011). The stations represented in the transect provide a rough idea about the chosen locations in the different surveys, with the aim of having a homogenous spatial covering of the area. The aquaculture licensed area from https://atlas.marine.ie are represented.

6.2.2 Sampling strategy

The sampling strategy adopted in this chapter was already described in Chapter 4 paragraph 4.2.2. To understand the water composition and the consequences for coastal metabolism, inputs and outputs of materials from the freshwater sources to the open ocean, the parameters considered in the study are:

- TA, DIC, and pH as carbonate system parameters;
- additionally, DOC was measured, in order to determine the loading and the export of organic carbon from the two study areas;
- DIN was measured as a sum of NH_4^+, NO_3^- and NO_2^- . DIN was used in this study to quantify nitrification-denitrification rate;
- SRP was used as representative of Dissolved Inorganic Phosphate (DIP) and it was used to estimate NCP;

- field measurements of pH, temperature, salinity, electrical conductivity, and dissolved oxygen were performed using a multi-parameter probe (Aqua-read AP 1000). Additionally, pH was measured in the lab with a pH meter and a Ross Orion electrode, calibrated with both a freshwater Orion standard and CRMs Tris-buffer in synthetic sea water, with an error of ± 0.01.

6.2.3 Analysis

For the determination of the parameters listed in the previous paragraph see paragraph 2.3.

6.2.4 Freshwater input estimation

The freshwater input was estimated in both the bays and the procedure was described in paragraph 2.4. The results were used for the LOICZ budget.

6.2.5 Biogeochemical budgeting approach

The LOICZ non-conservative biogeochemical modelling approach was applied to evaluate the ecosystem status of the selected study areas (Gordon et al., 1996; Giordani, 2002; 2008; Padedda et al., 2010). The LOICZ biogeochemical model is based on mass balances, which describe the rates with which a material reaches (input), leaves (output) and changes its presence (storage) within a system. Some substances are subject to internal transformations leading to net releases or accumulations in the system. Therefore, the system can be defined as a source or sink of the substance (Gordon et al., 1996; Giordani et al., 2008). The behaviour of the materials that are affected by these transformations is defined as non-conservative (such as carbon, nitrogen and phosphorus). The substances that do not undergo these transformations are defined conservative (usually water and salt) (Giordani, 2002). The model is applied with the assumption that the system is under steady-state conditions (Gordon et al., 1996; Giordani et al., 2008; Padedda et al., 2010).

A one-layer budget model was applied in Kinvarra Bay, following the assumption that the bay was well mixed during the survey. A two-layer budget model was applied for Killary Harbour, since the bay is a narrow inlet with an average depth of 15 meters. In previous literature studies stratification was observed, therefore, the two layers budget approach results are more appropriate for this study area (Swaney and Giordani, 2007). Both the budgets are considered the bay as a unique box that connects freshwater input to the open ocean. This approach can be applied even with a few data availability and allows an immediate comparison between different sites (Padedda et al., 2010). For further details regarding the applied equations see paragraph 2.4**.** Note that for Killary Harbour freshwater inputs were assumed to originate only from surface runoff while by contrast in Kinvarra they were taken as sourced entirely from SGD. The freshwater input was considered only to affect the surface layer in Killary Harbour.

6.2.6 NCP estimation, nitrification and denitrification processes

The net community production and the nitrification and denitrification processes were determined as described in the methods Chapter 2 paragraphs 2.6; 2.6.1.

6.2.7 Total Alkalinity, Organic and Inorganic Carbon fluxes

Total Alkalinity is generally assumed to be a conservative property in aquatic systems with high buffering capacity (Kempe, 1990). However, in systems that receive high inputs of organic matter and nutrients, the assumption of conservative behaviour for TA is no longer applicable because of the linkage between proton and electron transfers associated with redox reactions (Bianchi, 2006). It is likely that in a system with multiple end-members, non-conservative modification of TA concentrations can be exacerbated (Hydes et al.,2010), the accumulation of organic carbon, denitrification and carbonate mineral precipitation and dissolution might affect non-conservative perturbation of TA (Cross et al., 2013). Numerous reactions like nitrogen assimilation and remineralization, nitrification and denitrification lead to increase or decrease of TA (Wolf-Gladrow et al. 2007). The ΔTA in the system can be assigned to sulphate reduction or calcification (Gordon et al., 1996).

The budget of non-conservative material was applied also on TA, organic and inorganic carbon in the studied bays (ΔTA, ΔDIC, ΔDOC) with the scope to quantify the export of them from the coast to the open ocean.

6.3 Results

6.3.1 Water and salt budgets

In Table 6-1 it is possible to see a summary of water fluxes in the year 2018-2019 in the different surveys in the two selected study areas. The river and groundwater discharge were evaluated in Chapter 4.

The largest volume of evaporation was detected during the spring and summer period, 24 × 10^3 m^3 d^{-1} in July 2018 and 21.7 × 10^3 m^3 d^{-1} in April 2019 in Killary Harbour, and 9.8 × 10^3

m^3 d^{-1} in July 2018 and 8.7 × 10^3 m^3 d^{-1} in April 2019 in Kinvarra Bay (evaporation was calculated as explained in Chapter 2).

The average precipitation was calculated using the historical data of Met Éireann (the Irish meteorological service) at the Athenry station, located 20 km NE of Kinvarra Bay, and at the Leenane station located in Killary Harbour. The highest rate of precipitation occurred in February 2018 and April 2019 in Killary Harbour, respectively 35 × 10^3 m^3 d^{-1} and 31 × 10^3 m^3 d^{-1}. The lowest precipitation was recorded in July 2018 for both areas: 0.5 × 10^3 m^3 d^{-1} in Killary Harbour and 0.2 × 10^3 m^3 d^{-1} in Kinvarra Bay.

Table 6-1 Kinvarra Bay and Killary Harbour water fluxes (in 10^3 m^3 d^{-1}).

In Kinvarra Bay: groundwater (V_G), precipitation (V_P), evaporation (V_E), residual flow (V_R), mixing flow (V_X). In Killary Harbour: river discharge (V_Q), precipitation (V_P), evaporation (V_E), water coming from the deep layer (V_{DEEP}) and mixing between the two layers without exchange of volume (V_Z).

Kinvarra Bay water fluxes 10^3 m^3 d^{-1}

Months	V_Q	V_E	V_P	V_R	V_X
Jul-18	480	9.8	0.2	-470	17467
Oct-18	965	3.7	10.4	-971.7	4573
Jan-19	1408	0.7	0.5	-1407	2567
Apr-19	2109	8.7	12.4	-2112	7935

Killary Harbour water fluxes 10^3 m^3 d^{-1}

Months	V_Q	V_E	V_P	V_S	V_{DEEP}	V_Z
Feb-18	3600	6	35	-3629	3600	185
Jul-18	140	24	0.5	-116	140	3681
Oct-18	1400	9.2	25.9	-1416.7	1400	250
Jan-19	2000	1.7	12.2	-2010	2000	616
Apr-19	930	21.7	31	-939	930	80

*Vent is not presented in the table, this parameter is equal to the sum of V_{DEEP} and V_G (as explained in Chapter 2 of this thesis work): in Killary Harbour, because the groundwater flow was assumed equal to zero (as confirmed by another research carried in the same Biogeochemistry Group), V_{ent} is equal to V_{DEEP}. V_{ent} assumes positive value for the surface layer and negative for the deep layer.

Salinity detected in the rivers in Killary Harbour between February 2018 and April 2019 was always low, between 0.1 and 0.3 (Table 6-2).

In Kinvarra Bay the salinity detected at low tide in the freshwater spring was between 0.35 and 0.54, except for July 2018 when a value of 1.50 was measured. Precipitation in July 2018 was low, the groundwater flow was the lowest recorded, and therefore, seawater intrusion into the karst was likely. The salinity in the bays was highly influenced by the freshwater input and showed the lowest values in the months where high freshwater discharge was recorded.

In Killary Harbour it is possible to observe that deep water salinity was always higher than on the surface, suggesting that the freshwater discharge predominantly affects the surface water of the bay, which is then stratified. In July 2018 the survey with the lowest discharge of freshwater was carried out. One of the consequences of such circumstances is that there is less difference in salinity between surface and deep water following the low contribution of freshwater. The Vz (mixing between the two layers without exchange of volume) shown in Table 6-1 is higher compared to other surveys, which means that there was a higher exchange of salinity and nutrients between the two layers.

Table 6-2 Salinity (in ‰) measured: in the river (S_Q), groundwater (S_G), bay (Ssys), ocean (S_{OCEAN}), and mean salinity of net flux to the sea (S_R). In Killary Harbour the Ssys and S_{OCEAN} on both surface (sur) and deep (deep) layer.

Killary Harbour salinity (in ‰)

Months	S_Q	S_{SYS}(sur)	S_{SYS}(deep)	S_{OCEAN}(sur)	S_{OCEAN} (deep)
Feb-18	0.1	21.67	31.60	30.90	31.40
Jul-18	0.3	31.40	32.40	31.90	32.00
Oct-18	0.1	27.50	31.70	29.40	32.80
Jan-19	0.1	13.90	33.27	28.00	33.90
Apr-19	0.1	27.20	33.65	34.10	34.20

Kinvarra Bay salinity (in ‰)

Months	S_G	S_{SYS}	S_{OCEAN}	S_R
Jul-18	1.50	29.00	29.75	29.38
Oct-18	0.54	23.53	29.00	26.27
Jan-19	0.55	14.93	25.80	20.37
Apr-19	0.35	23.95	31.20	27.58

6.3.2 Non-conservative material budget of TA, DIC and DOC

One-layer-Kinvarra Bay

The one-layer budget used for Kinvarra Bay is represented in Figure 6-2. In the previous paragraph the input of freshwater discharge is shown: since the TA and DIC measured in the SGD are always high, between ~3200 and ~5000 µmol kg^{-1}, the daily loading of these parameters varied from 24 to 96 × 10^5 mol d^{-1} for the TA and from 24 to 99 × 10^5 mol d^{-1} for the DIC. The LOICZ budget provided positive ΔTA and ΔDIC values in October 2018 and

January 2019, respectively 19 and 47 mmol m^{-2} d^{-1} in October and 6 and 29 mmol m^{-2} d^{-1} in January, (Table 6-3). In autumn and winter Kinvarra Bay becomes a net TA and DIC source towards the open ocean**.** Through the budget it was possible to quantify the export of DIC which was on average 38 mmol m^{-2} d^{-1}, or 26.8 t d^{-1} during the autumn and winter period. Also, the TA export was quantified, and an average value of 12.5 mmol m^{-2} d^{-1} or 10.5 t d^{-1} was found for the autumn and winter period. The loading of DOC coming from the SGD was also high at all the surveys, from 0.9 × 10^5 mol d^{-1} in July 2018 to 9.5 × 10^5 mol d^{-1} in April 2019, with an average value of 5.7 × 10^5 mol d^{-1}, (Figure 6-2). ΔDOC was positive at all the surveys, Table 6-3: a positive value of ΔDOC implies a net mobilization, therefore the system is a source towards the open ocean.

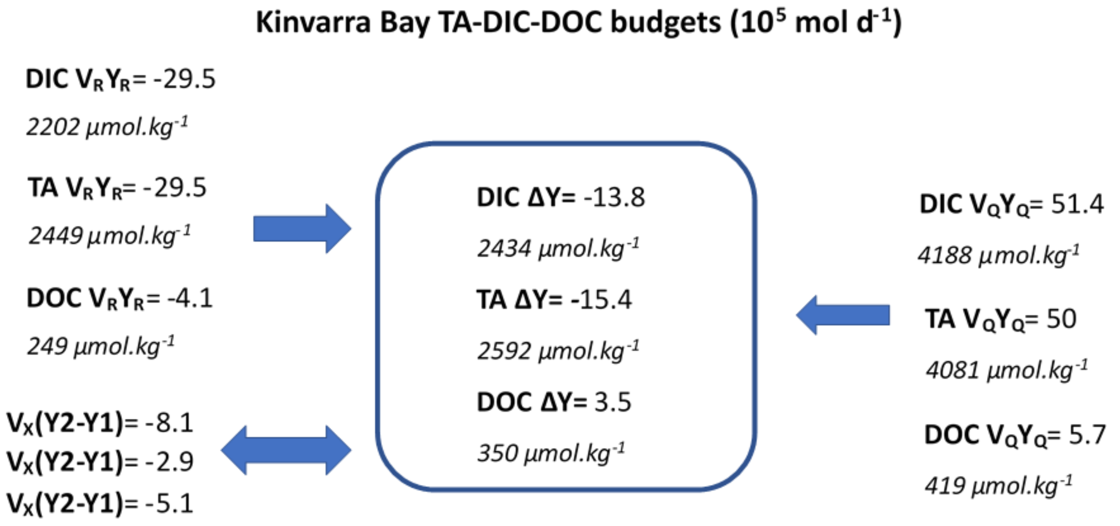


Figure 6-2 Kinvarra Bay non-conservative materials annual budget for TA-DIC and DOC. An average annual value for each parameter is represented, the ΔY for each survey is represented in Table 6-3. Positive ΔY value indicates a net export from the coastal embayment to the open ocean.

Table 6-3 Kinvarra Bay ΔTA, ΔDIC, ΔDOC are represented in the following table.

Location	Survey	ΔTA	ΔDIC	ΔDOC	ΔTA	ΔDIC	ΔDOC
			mol d^{-1}			mmol m^{-2} d^{-1}	
Kinvarra Bay	Jul-18	-3.20E+06	-2.77E+06	4.35E+05	-759	-656	103
	Oct-18	8.02E+04	1.98E+05	4.01E+05	19	47	95
	Jan-19	2.53E+04	1.22E+05	2.87E+05	6	29	68
	Apr-19	-2.82E+06	-2.78E+06	2.36E+05	-669	-658	56

Table 6-4 In the previous table a positive export of TA and DIC in October 2018 and January 2019 was found, therefore the export of these constituent towards the open ocean is converted in tonnes per year (t y^{-1}).

Survey	ΔTA	ΔDIC	ΔTA	ΔDIC
	mmol m^{-2} d^{-1}		t d^{-1}	
Oct-18	19	47	16	33
Jan-19	6	29	5	20

Two layers-Killary Harbour

Killary Harbour's two-layers budget is represented in Figure 6-3. The river freshwater end member did not act as a significant source of TA and DIC to the system. Indeed, the surface layer showed negative outflow volume, 29 × 10^5 mol d^{-1} of TA and 27 × 10^5 mol d^{-1} of DIC, which indicates that the bay does not act as an additional source of TA and DIC towards the open ocean. However, from the deep layer the ocean added to the bay 33 × 10^5 mol d^{-1} TA and 31.4 × 10^5 mol d^{-1} DIC. It is possible to observe a negative ΔY for TA and DIC in all the surveys in the surface layer, Table 6-5, and, because the system ΔTA and ΔDIC can be calculated summing the surface and deep layer values (Swaney and Giordani, 2007), the bay did not export these properties to the open ocean. The loading from the freshwater discharge of TA and DIC, that could be called "flux in", even in the presence of an intense amount of discharge, was always low at all the surveys when compared to the TA and DIC volume coming from the ocean. The DOC loading from the river's end-member showed an average annual value of 4.4 × 10^5 mol d^{-1} Figure 6-3. However, the ΔDOC was negative in all the surveys meaning that no net export of DOC towards the open ocean occurred.

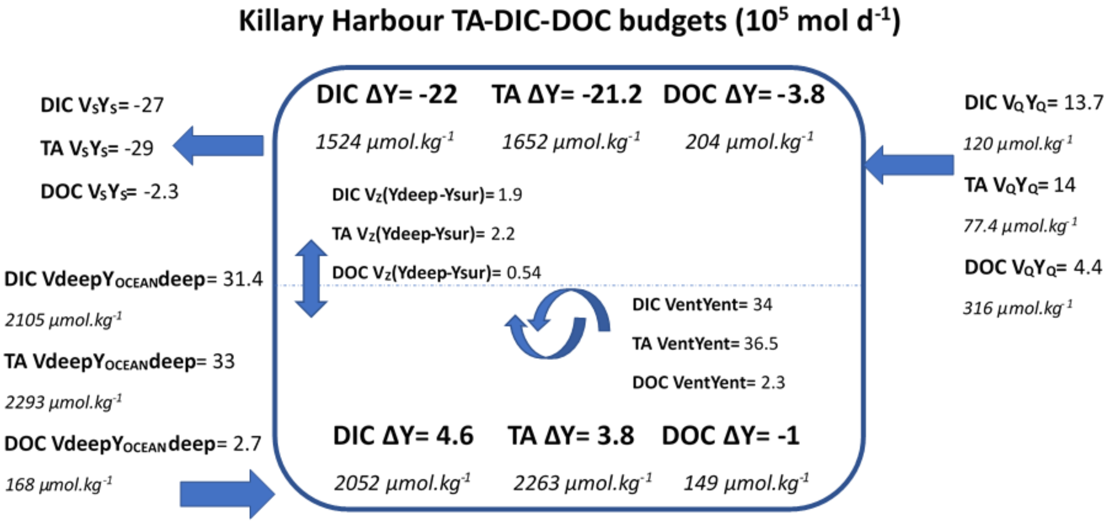


Figure 6-3 Killary Harbour Non-conservative materials annual budget two layers for TA-DIC and DOC. An average annual value for each parameter is represented. The ΔY showed on surface and deep layer are an average value found in the different surveys (all ΔY values are showed in Table 6-5), since a negative value is shown for DIC, TA and DOC systems can be considered as a sink of inorganic and organic carbon.

Table 6-5 Killary Harbour ΔTA, ΔDIC, ΔDOC in the different surveys on surface and deep layer are represented in the following table.

Location	Survey	ΔTA	ΔDIC	ΔDOC	ΔTA	ΔDIC	ΔDOC
			mol d^{-1}			mmol m^{-2} d^{-1}	
Killary Harbour	Feb-18	-3.67E+05	-3.70E+06	-6.47E+05	-3	-352	-6
		-1.60E+04	-3.95E+03	-6.81E+04	0	0	-1
	Jul-18	-3.14E+06	-2.80E+06	-7.77E+05	-30	-266	-7
		6.79E+05	6.22E+05	-3.74E+04	6	59	0
	Oct-18	-1.09E+06	-9.83E+05	-2.36E+05	-10	-94	-2
		8.53E+04	1.04E+05	-5.92E+04	1	10	-1
	Jan-19	-3.18E+05	-3.18E+05	1.41E+05	-3	-30	1
		4.56E+04	-1.21E+05	-1.82E+05	0	-11	-2
	Apr-19	-6.65E+06	-6.48E+06	-3.86E+05	-63	-617	-4
		1.72E+06	1.21E+06	-1.37E+05	16	115	-1

6.3.3 Non conservative-materials budget DIN and DIP

Kinvarra Bay

The DIP and DIN concentration in the different water sources was measured during the different surveys. In Table 6-6 the concentration of DIN and DIP is expressed in mmol m^{-3}. In Kinvarra Bay the SGD showed always high level of DIN, which is expressed as DIN$_G$, ranging from 45.6 mmol m^{-3} in April 2019 to 84.2 mmol m^{-3} in January 2019. The DIN level in the system was high in October 2018, January and April 2019.

In July 2018 the DIN loading was lower, probably due to a combination of factors: the low SGD discharge leading to lower DIN$_G$ loading compared to other surveys (30 × 10^3 mol d^{-1}

Table 6-7), and the consumption from primary producers within the system. Also, in the sea compartment the DIN varied from 1.17 mmol m^{-3} in July 2018 to 28.90 mmol m^{-3} in January 2019. The DIP variation in concentration in the SGD (DIP_G) was not aligned to the Redfield's ratio, ranging from 0.16 to 0.54 mmol m^{-3}, with the highest value in October 2018 (Table 6-6).

Table 6-6 Kinvarra Bay DIP and DIN concentration measured in the different water sources, expressed in mmol m^{-3}.

Kinvarra Bay DIP-DIN mmol m^{-3}

Months	**DIP_G**	**DIN_G**	**DIPsys**	**DINsys**	**DIPocean**	**DINocean**
Jul-18	0.30	63	0.49	1.04	0.51	1.17
Oct-18	0.54	68	0.29	21.00	0.22	3.20
Jan-19	0.16	84.2	0.23	62.00	0.28	28.90
Apr-19	0.43	45.6	0.21	21.00	0.23	10.00

The loading of DIN from the freshwater end-member was high in Kinvarra Bay, where a minimum value of 30 × 10^3 mol d^{-1} was recorded in July 2018, and a maximum value in January 2019 of 119 × 10^3 mol d^{-1}. The loading of DIP in Kinvarra Bay varied from 206 mol d^{-1} in July 2018 to 907 mol d^{-1} in April 2019.

Table 6-7 Calculated loading of DIN and DIP from the river freshwater end-member in Kinvarra Bay.

Months	**loading DIN**	**loading DIP**
	10^3 mol d^{-1}	**mol d^{-1}**
Jul-18	30	206
Oct-18	66	521
Jan-19	120	225
Apr-19	96	907

Killary Harbour

In Killary Harbour the rivers showed DIN concentration that varied from 3.66 mmol m^{-3} in February 2018 to 7.92 mmol m^{-3} in January 2019. The lowest average concentration within the system was recorded in July 2018: 0.29 mmol m^{-3} (Table 6-8). A possible explanation of this value can be found in the freshwater discharge, which was low in summer 2018 (see Table 6-1). Furthermore, in July 2018 the water column was less stratified (Vz value found was the highest recorded, suggesting large flux of materials between the two layers, Table 6-1) leading to a consumption along the water column, further stimulated by the higher temperature and light availability during summer period.

The average deep-water DIN concentration was higher than the surface, especially in February 2018 and January 2019. Because in the winter months high discharge was recorded (Table 6-1), it is possible to say, observing salinity and Vz values, (Table 6-1), that the bay was likely stratified, therefore, the sediment can act as an additional source of DIN. The DIP concentration in the rivers showed variations between 0.03 mmol m^{-3} in February 2018 to 0.14 mmol m^{-3} in October 2018 (Table 6-8). In the deep-water samples collected along the harbour, slightly higher concentration of DIP was detected, which varied from 0.28 mmol m^{-3} in April 2018 to 0.94 mmol m^{-3} in February 2018, suggesting that sediments are also acting as a source of DIP to the water column. Similarly to what has been observed for the DIN, the difference between surface DIP and deep DIP was more pronounced in February 2018 and January 2019, the months with higher discharge and higher stratification.

Table 6-8 DIN and DIP concentration in the different water sources, expressed in mmol m^{-3}.

Killary Harbour DIN mmol m^{-3}

Months	DINQ	DINsys(surface)	DINsys(deep)	DINocean(surface)	DINocean(deep)
Feb-18	3.66	5.11	5.00	7.44	5.50
Jul-18	5.34	0.29	0.33	0.25	0.38
Oct-18	4.00	1.56	2.40	2.00	0.76
Jan-19	7.92	7.62	8.85	9.00	10.70
Apr-19	5.43	3.69	5.87	1.78	6.16

Killary Harbour DIP mmol m^{-3}

Months	DIPQ	DIPsys(surface)	DIPsys(deep)	DIPocean(surface)	DIPocean(deep)
Feb-18	0.03	0.16	0.94	0.34	0.38
Jul-18	0.05	0.18	0.24	0.14	0.28
Oct-18	0.14	0.26	0.35	0.32	0.33
Jan-19	0.11	0.23	0.48	0.36	0.40
Apr-19	0.09	0.18	0.28	0.35	0.39

The loading of DIN was lower compared to Kinvarra Bay, which ranged from 1 × 10^3 mol d^{-1} in July 2018 to 19 × 10^3 mol d^{-1} in January 2019 (Table 6-9). The loading of DIP ranged from 7 mol d^{-1} in July 2018 to 200 mol d^{-1} in January 2019. Freshwater discharge, especially in February 2018 and January 2019, added more DIP and DIN to the bay compared to the other surveys (Table 6-9).

Table 6-9 Calculated loading of DIN and DIP from the river freshwater end-member in Killary Harbour

Months	loading DIN	loading DIP
	10^3 mol d^{-1}	mol d^{-1}
Feb-18	13	108
Jul-18	1	7
Oct-18	6	196
Jan-19	19	200
Apr-19	5	84

6.3.4 Net Community Production (NCP) estimation

Both study areas are not only dominated by phytoplankton, but also sea weeds, macroalgae and seagrasses play an important role in the Irish coastal areas (Morrissey et al., 2001; Kelly, 2010; O'Boyle and Silke, 2010; Monagail and Morrison, 2020). To calculate NCP from ΔDIP, was used the C:P characteristic of primary producer 106:1, similar to the environment dominated by phytoplankton. However, it is known in the literature that this stoichiometry might change according to the dominant species present in the selected study areas. An average C:P, similar to a dominant presence of macroalgae and seagrasses of 550:1 was found in the literature (Atkinson and Smith, 1983). It follows that the estimated NCP in this work can be an underestimation of the actual NCP value, particularly in spring and summer where the role of macroalgae increases. Furthermore, it is known in the literature that the water coming from the SGD is characterized by a different Redfield's compositional ratio (McGarrigle et al., 2010), which might lead to an underestimation of the NCP values in Kinvarra Bay.

Kinvarra Bay NCP

In Kinvarra Bay the NCP was negative in October 2018 and January 2019 and positive in July 2018 and April 2019 (Table 6-10). Hence, the average annual NCP was about 37 g C m^2 y^{-1}. The difference between nitrification and denitrification was positive in October 2018 and January 2019, and April 2019 suggesting that oxidative reactions were dominant in the area. October 2018 and January 2019 were months characterized also by net export of ΔDIN, which can be explained due to the loading of nitrogen species coming from SGD (from 66×10^3 mol d^{-1} in October 2018 to 120×10^3 mol d^{-1} in January 2019 Table 6-7). In April 2019 the ΔDIN was positive as well, which implies that despite the NCP being positive, the nitrogen is not entirely utilized with the system and the export towards the open ocean still occurs. In July 2018, the denitrification processes had become prevalent: NO_3^- was the dominant form of DIN and the bay was a net sink of DIN.

Killary Harbour NCP

NCP in Killary Harbour was estimated to be 61 g C m^2 y^{-1} which is obtained summing the values of the two layers (Swaney and Giordani, 2007). The minimum value was measured in July 2018 with 0.005 g C m^2 d^{-1}. The maximum NCP was estimated in February 2018 and January 2019 with values of 0.15 g C m^2 d^{-1} and 0.57 g C m^2 d^{-1} respectively. The results obtained suggest that the freshwater discharge might have an effect on the NCP. To understand if the changes of NCP might be correlated with the freshwater input, the regression analysis was done between NCP and freshwater inputs. However, since the regression analysis considered five surveys, the R^2 was 0.45 and the Pearson correlation coefficient equal to 0.66, with p-value of 0.2 was found (greater than 0.05). In the previous paragraph, from the non-conservative material budget of TA, DIC and DIN, it was observed that the ocean is the main source of these constituents to the bay. It follows that NCP in Killary Harbour is likely driven by the variations of NCP occurring in the open ocean which are driven by biological factors (e.g., nutrients, light intensity, temperature). NCP was always positive in the different survey periods (Table 6-10) which confirms that even if the freshwater discharge magnitude differs throughoutthe year, the system maintains autotrophic conditions. Except for April 2019, denitrification outweighs nitrogen fixation, so that the estuary appears to be a net sink of nitrogen in the upper layer. In the Table 6-11, the DIP concentrations were compared, higher DIP values were found in the deep layer, following the budget result and the positive value of ΔDIP in the deep layer in February, July and October, it can be confirmed that the deep layer is a source of DIP for the surface layer.

Table 6-10 Net community production calculated in the different surveys in Kinvarra Bay. The NCP was quantified assuming C:P stoichiometric relation is 106:1, similar to phytoplankton. ΔDIN, ΔDIN_{exp} and N_{fix}-N_{denit} which is the nitrification minus denitrification are shown.

Location	Survey	ΔDIN_{obs}	ΔDIN_{exp}	N_{fix}-N_{denit}	ΔDIP	NCP			
			mmol m^{-2} d^{-1}		mol d^{-1}	mmol m^{-2} d^{-1}	g m^{-2} d^{-1}	g m^{-2} y^{-1}	g m^{-2} y^{-1}
Kinvarra Bay	Jul-18	-7.04	-3.07	-3.97	-811	20	0.24	89.3	37
	Oct-18	7.2	0.05	7.15	13	0	0.00	-1.3	
	Jan-19	6.53	0.19	6.34	52	-1	-0.02	-5.6	
	Apr-19	5.65	-2.27	7.92	-601	15	0.18	66.1	

Table 6-11 Net community production calculated in the different surveys in Killary Harbour. The NCP was quantified assuming C:N stoichiometric relation is 106:1, similar to phytoplankton. ΔDIN and N_{fix}-N_{denit} and N_{fix}-N_{denit} which is the nitrification minus denitrification are shown.

Location	survey	depth	ΔDIN_{obs}	ΔDIN_{exp}	N_{fix}-N_{denit}	N_{fix}-N_{denit}	ΔDIP	NCP			
				mmol m^{-2} d^{-1}			mol d^{-1}	mmol m^{-2} d^{-1}	g m^{-2} d^{-1}	g m^{-2} y^{-1}	g m^{-2} y^{-1}
Killary Harbour	Feb-18	s	-6.8	-0.79	-6.01	-5.87	-1369	14	0.17	54	61
		d	-0.01	-0.15	0.14		145	-2	-0.02		
	Jul-18	s	-47.3	-5.66	-41.64	-38.51	-262	3	0.03	2	
		d	0.01	-3.12	3.13		233	-2	-0.03		
	Oct-18	s	-10.9	-0.56	-10.34	-10.25	-346	4	0.04	16	
		d	0.01	-0.08	0.09		50	-1	-0.01		
	Jan-19	s	-0.7	-0.43	-0.27	0.22	-3711	38	0.45	164	
		d	0.01	-0.48	0.49		-1048	10	0.12		
	Apr-19	s	-60	-2.09	-57.91	-61.33	-517	5	0.06	22	
		d	-0.1	3.32	-3.42		-101	1	0.01		

6.4 Discussion

6.4.1 Kinvarra Bay: DOC flux from the SGD

The SGD flux of DOC in coastal areas and its export to the open ocean has been observed in several studies (Oh et al., 2017; Kim et al., 2012). The increase of allochthonous organic materials to the coast is principally due to the erosion of agricultural lands (Howarth, 1991). In Kinvarra Bay high loading of DOC was observed at all surveys, as well as a net export of DOC towards the open ocean. It is known that in coastal water characterized by elevated DOC concentrations can lead to an increase of respiration (Navarro et al., 2004). The open question is if the allochthonous DOC that is delivered from the SGD is readily metabolized by the system and therefore leading to an increase of respiration or if is a material that passes through the system without being respired (Howarth et al., 1992). It was not observed a clear relation between the sign of ΔDOC and the autotrophic or heterotrophic conditions of Kinvarra Bay. In summer 2018 the ΔDOC export was higher compared to the other surveys, and this can be explained because, even if the discharge was lower compared to the other campaigns, the low level of water in the subterranean estuary leads to an increase of recirculated SGD. The water in the bay is then enriched of DOC from both freshwater and recirculated seawater (Dorsett et al., 2011).

In bays system fed by rivers it was observed that, during the periods of heterotrophic conditions, there was a net consumption of DOC within the system, as observed in the study of Navarro et al., (2004). However, the loading of DOC coming from a groundwater system can be higher than rivers and specifically, from these comparative studies the loading of DOC from SGD in Kinvarra Bay was higher than in Killary Harbour (5.7×10^5 mol d^{-1} from the SGD spring and 4.4×10^5 mol d^{-1} from the rivers). Therefore, in Kinvarra Bay because of the high loading of DOC from the SGD, even if this one can be partially consumed within the system in heterotrophic conditions (e.g., October 2018 and January 2019), part of it was still exported towards the open ocean.

Moreover, it is known that residence time of DOC is equal to residence time of water (Raymond and Bauer, 2001). Therefore, in October 2018 and January 2019, because of the higher freshwater discharge, and because the samples were collected during the spring tide, the flushing time of DOC in the bay was low (Gregory et al., 2020). The metabolism of terrestrial organic matter might occur primarily on the shelf, rather than within the estuary (Canuel et al., 2012), leading to an increase of ΔDOC.

During the transport through rivers and estuarine areas the DOC is enriched in ^{13}C and depleted in ^{14}C (Raymond and Bauer, 2001) . Therefore, the study of isotopic signature can help in the understanding of the DOC autochthonous production and/or removals from heterotrophic bacteria, leading to a more robust interpretation of the system as a source or sink of this parameter (Raymond and Bauer, 2001).

As a consequence of climate change, the loading of both nutrients and organic carbon from land are altered. Particularly the increase of allochthonous carbon and the consequent respiration, (e.g. as has been observed the increase of DIC over TA within the system) can potentially exacerbate hypoxia (Canuel et al., 2012). The hypoxia in coastal areas could lead to change in the food-web structure and system function (e.g., habitat loss, changes in the organisms life cycles and reproduction) (Zhang et al., 2010; Rabalais et al. 2009).

6.4.2 Kinvarra Bay: SGD as a source of nutrients towards the open ocean

The SGD spring loading of DIN was high at all the surveys, from 25 to 170 $\times 10^3$ mol d^{-1}, or from 430 to 2700 kg d^{-1}, values that are comparable with 273 kg d^{-1} measured during summer 2010 in Rocha et al., (2015) and also of the same order of magnitude of the hydrogeological model of McCormack et al., (2014) 190-1920 kg d^{-1}. The dominant form of DIN was NO_3^- and a net export towards the open ocean was observed in October 2018, January 2019 and April 2019. The positive ΔDIN can be explained with the decrease of photosynthetic rate during cooler months, therefore, not utilized within the system and exported to the open ocean. From the budget results it is possible to observe positive N_{fix}-N_{denit} values, which suggest that N-fixation prevailed over denitrification (Padedda et al., 2010). The remineralization of particulate organic matter changes TA, depending on the form of reactive nitrogen produced (Wolf-Gladrow et al., 2007). In an aerobic environment ammonia is oxidised to nitrate (see nitrification equation (45)) ΔTA consequently decreases by 2 moles per mole of NO_3^- formed (Schlesinger, 1997).

A negative value of N_{fix}-N_{denit} is shown in July 2018. In summer, the high loading of NO_3^- could lead to an increase of denitrification (Pelegrí and Blackburn, 1994), (see equation (46)) which leads to an increase of TA by 1 mole per mole of nitrate converted (Wolf-

Gladrow et al., 2007).. The macrofauna can stimulate the overall denitrification (Cornwell et al., 1999), and, additionally, the submersed macrophytes might increase the denitrification rate (Caffrey and Kemp, 1990). The denitrification represents an important nitrogen sink and this result explains why the nitrogen is not exported in July 2018. This excess of DIN loading from the SGD can lead to eutrophication especially during the neap tide where the water is more stagnant at the bay head (Gregory et al., 2020).

The nutrients loading from the SGD spring was always high even during the cooler months (October 2018, January 2019), and this could suggest a positive value of NCP. However, because multiple drivers are playing at the same time, like temperature and light availability, they decelerate the photosynthesis rate. After all, the light availability has been recognized as the most important limiting factor in an urbanized estuary, as well as the availability of nutrients does not drive the ecosystem into eutrophic conditions if the primary producers do not utilize them (Yoshiyama and Sharp, 2006). Moreover, Sugimoto et al., (2017) suggested that in some cases, despite the high delivery of nutrients coming from SGD, they are not used by phytoplankton because of low residence times. Specifically, in Kinvarra Bay the residence time in the same surveys was calculated (Savatier, 2021 thesis work) and a value of 3-4 days was found for July 2018, October 2018 and January 2019. Therefore, particularly in winter periods, these nutrients loading were passing through the system without being consumed and were, hence, moved towards the open ocean compartment. In April 2019 a value of 5-6 days was found, with the increase of time that water spend into the bay, might increase the nutrients as well assimilated by phytoplankton.

6.4.3 Kinvarra Bay: SGD as a source of TA and DIC, impact on NCP

The NCP, estimated with the LOICZ budgeting modelling approach, provided a positive value on an annual time-scale, 38 g m^2 y^{-1}, classifying Kinvarra Bay as oligotrophic, following the definition of Nixon, (1995). During summer 2018, and spring 2019 the NCP increased with a value of 0.24 g C m^2 d^{-1} and 0.18 g C m^2 d^{-1}, which provides 0.9 × 10^5 mol C day^{-1} and 0.6 × 10^5 mol C day^{-1}. The increase of NCP during spring and summer, can be explained by the high loading of nutrients, and higher light availability, which in turn increases the consumption from photosynthetic organisms. The estimated NCP during spring and summer was lower than the NCP calculated through the dissolved organic nitrogen mass balance in the study of Rocha et al., (2015), which was 3.01×10^5 mol C day^{-1}, classifying the bay as eutrophic (Nixon, 1995). However, as mentioned earlier, to calculate the NCP using the SRP value and assuming that the stoichiometric relation of C:P follows the Redfield ratio 106:1 (generally used in environments dominated by phytoplankton), can lead to NCP underestimation. Particularly in bays fed by SGD, because it is a source of carbon and nutrients is known to modify their ratio (Slomp and Van Cappellen, 2004; Santos et al., 2013). Furthermore, it is important to recall that summer 2018 was particularly dry and the nutrients loading from the SGD was lower compared to what was measured in previous studies conducted during the summer period.

Therefore, without considering exceptional events, the loading of DIN was always high, and this can lead the bay into eutrophication during the summer. Although, the water circulation in Kinvarra Bay was recently studied, the retention areas stimulates the phytoplankton growth because of the high availability of nutrients (particularly at the inner part of the bay) (Gregory et al., 2020). The high nitrogen loading and the increase of primary production might support the occurrence of harmful algal blooms during the summer period (Rocha et al., 2015; Gregory et al., 2020).

The increase of primary production in Kinvarra Bay can also derive from the increase of photosynthetic rate from algae and sea grasses. Some species common along the Irish coastal seas (e.g. Zostera spp.), Kelps *Laminaria hyperborea* and *Laminaria saccharina,* and the brown algae *Fucus serratus*, or *Fucus ceranoides* living in the Kinvarra Bay intertidal area (Field 2006; Foley 2014; Perry and Budd, 2016) are increasing their role as important primary producers. Sea grasses assimilate inorganic carbon either via diffusion (CO_2) or active uptake of HCO_3^- by carbon concentration mechanisms which results in the increase of seawater pH and drop in seawater CO_2 partial pressure (Han et al., 2017). These species can induce shift in DIC system according with the following reaction:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \tag{49}$$

which then has an impact on the DIC buffering capacity of seawater (Han et al., 2017; Rubio et al., 2017). During autumn and winter period, TA and DIC delivery from the SGD increases and due to the reduced assimilation of carbon from the sea grasses might leads to the increase of H^+ ions dissolved in the water, decreasing pH and accelerating further dissolution processes (Ω_{Ar} less than 2 in October 2018 and January 2019 see chapter 4). From the results expressed in this chapter, it is shown that in autumn and winter ΔTA and ΔDIC have positive value and indicate the export of them from the bay to the open ocean. The nitrification processes during winter are predominant, this led to a decrease of TA over DIC. Furthermore, DIC and nitrate are not assimilated as shown by the negative NCP values estimated during this period of the year. The freshwater input composition affects the metabolic activity in the system. It follows that the null hypothesis H_0 tested should be rejected for the autumn and winter in Kinvarra Bay, the alternative hypothesis H_1 can be instead accepted, since NCP was controlled by freshwater-seawater mixing. A net export of ΔTA and ΔDIC was estimated using the LOICZ budget model, 10.5 and 26.8 t d^{-1}, respectively. Kinvarra Bay is an important source of CO_2 to the open ocean which intensifies the acidification processes currently occurring due to the increase of CO_2 in the atmosphere.

In April 2019 the discharge was high, however the NCP was positive, which indicates that in spite of the loading of DIC from the SGD the metabolism is able to consume it, limiting the export of inorganic carbon to the open ocean. This result is also aligned with the negative ΔTA and ΔDIC values found with the LOICZ budget, which indicates that TA and DIC inputs are greater than outputs and the system acts as a sink of these properties (Giordani, 2002).Indeed, during spring and summer, with the increase of the light availability and temperature, primary production increases as well, and this can explains the positive TA:DIC relation, with the decrease of DIC over TA. These findings suggest that TA:DIC ratio and NCP are under biological control and the null hypothesis H_0 can be accepted.

6.4.4 Killary Harbour: DOC source from the rivers

Rodhouse et al., (1987), found an annual loading of particulate organic carbon from the river of 1907 C t y^{-1}: in this study the average annual DOC loading from the rivers was 1932 C t y^{-1}. Mcmahon and Patching, (1984) showed that 1531 C t y^{-1} were metabolised, including phytoplankton respiration, microzooplankton and bacterial respiration and around 62 t y^{-1} of C were available for sedimentation. Their studies have been done before aquaculture started: the first rope mussel production started in 1989. The increase of aquaculture licensed areas might be responsible for an increase of DOC uptake from mussel (Roditi et al., 2000; Pan and Wang, 2004). However, from the study of Pan and Wang, 2004, where the DOC uptake from mussel was quantified, it was observed that DOC contributes only 0.8% to the mussels' total organic carbon acquisition. The loading of DOC from rivers can be also absorbed through abiotic processes occurring in the water column (McKnight et al., 2002). The DOC that is not metabolised within the system can be exported to the open ocean, as it was previously observed in Kinvarra Bay and in several heterotrophic estuarine areas (Cauwet et al., 1990; Raymond et al. 2007; Raymond et al., 2008; Raymond and Bauer 2000; Fichot and Benner, 2014). However, because of the high residence time of the water in Killary Harbour which can be up to 60 days (Hartnett et al., 2011), the DOC might be partially consumed or moved into the lower layer or can be available for sedimentation. This could explain why, even with high loading of DOC from the rivers, on an annual time scale no net export of DOC occurred.

6.4.5 Killary Harbour: NCP and carbonate system dynamics

The primary production estimated by Mcmahon and Patching, (1984), (not recent studies have been found for the specific area) was 179 g C m^2 y^{-1}: this value is comparable with NCP of 61 g C m^2 y^{-1} estimated here. Killary Harbour eutrophication status was classified as *moderate low with a future trend of no change* by AQUAFACT International Services Ltd, (2013). After all, because a system that produces < 100 g C m^2 y^{-1} can be considered oligotrophic (Nixon, 1995) the results from the present work confirms this. Killary Harbour eutrophication status is oligotrophic during all surveys. Additionally, Killary Harbour results in an autotrophic system, following the definition of Caffrey, (2003).

In Killary Harbour, the river input of TA, DIC and nutrients to the bay is lower compared to the input from the open ocean. The TA and DIC are driven by the ocean which is the main source of these compounds into the bay. This result is aligned to the result of (Nunes et al., 2011) where the source of nutrients into the bay is mainly coming from the deep layer, and it is the same for TA and DIC.

The null hypothesis H_0 that has been tested in this chapter, whether or not the TA: DIC relation is under biological control and co-varies with NCP, can be accepted, since the freshwater input can only dilute the TA:DIC ratio and decrease the nutrients availability in the upper part of the bay. The NCP was always positive during the year despite the variation in the freshwater discharge magnitude.

Nunes et al., (2011) showed that the upper part of the bay is more affected by the freshwater composition and does not receive the influence of ocean carbonate chemistry. Indeed, freshwater discharge from rivers can modify the carbonate chemistry and the biogeochemical characteristics of habitats proximal to the river mouth (Borges and Gypens, 2010; Aufdenkampe et al., 2011; Duarte et al., 2013; Salisbury et al., 2008; Pérez et al., 2015). These conditions suggest that aquaculture sites located in the upper part of the bay could experience stressful physiological conditions due to the effect of freshwater carbonate chemistry. In a recent study with the *Perumytilus purpuratus* mussel, Pérez et al. (2016) compared the physiological response of this organism under two different field conditions: in the open ocean and in a riverine influenced habitat. Pérez et al., (2016) results did not show significant effects of riverine influence on the growth and calcification rates of *Perumytilus purpuratus* in comparison with the open ocean results. The river discharge often cause acidification, due to the composition of the freshwater that affect the water chemistry, decreasing pH and Ω_{Ar}, however, the increase of POC which is often associated with food supply can counterbalance acidification stress (Wood et al., 2008; Melzner et al. 2011; Gazeau et al., 2013; Pérez et al., 2016; Lassoued et al., 2019). However, their study was focused only on one species. Nevertheless, several studies emphasized the importance of food availability as an essential parameter for mussel growth (Thomsen and Melzner, 2010; Thomsen et al., 2010; Lassoued et al., 2019). In this regard, Lassoued et al., (2019) suggested that *Mytilus galloprovincialis* are resilient to ocean acidification when the food availability is also high, and decreases under a suboptimal diet. Similar results were also reported by Thomsen et al., (2013) for *Mytilus edulis*. From the analysis of nutrients in Killary Harbour, low loading from the freshwater input was found in this area (Savatier et al., 2021), therefore, from these results it would be legitimate to suppose that aquaculture ropes located in the upper part of the bay could be less productive. The situation might be different for the aquaculture ropes located closer to Killary Harbour mouth, since there, the nutrients level can increase thanks to the salmon aquaculture (Figure 6-1). Multi trophic aquaculture can be used to reduce the impacts of nutrients emission from fish farms (Chopin, 2006; Ridler et al., 2007; Barrington et al., 2009; Troell et al., 2009; Maar et al., 2020). In the case of Killary Harbour, the nutrients coming from the salmon aquaculture might be also useful to promote physiological adaptation to contrast the low pH and low aragonite saturation state (Thomsen et al., 2013).

6.5 Conclusions

The budgets of the two analysed bays with contrasting watershed input showed different loading of nutrients. Alkalinity and inorganic carbon from the freshwater sources have different chemical concentrations and also different mixing processes take place in the coastal bays.

The NCP in Kinvarra Bay was positive during summer and spring periods which confirmed that even with high loading of TA and DIC from the SGD, the latter did not change the NCP. Even if the SGD delivers DIC that might drive the system towards heterotrophic conditions, the greater effects of primary producers consuming nitrogen, phosphates and inorganic carbon during photosynthetic processes are able to counterbalance the effect of SGD water composition. The null hypothesis H_0 can be accepted for the spring and summer period, where the TA:DIC ratio was under biological control, i.e., causally co-varies with NCP.

However, because during autumn and winter the production rate decreased, NCP showed negative values; the chemical composition of the freshwater spring suggested that freshwater seawater mixing was the main driver. From these results the null hypothesis should be rejected for the Kinvarra Bay during cooler months, since the system turns into heterotrophy. The TA and DIC budget showed a net export of these constituents towards the open ocean, 10.5 and 26.8 t d^{-1} respectively. These results demonstrated that this coastal area fed by SGD can act, under specific conditions, as an additional source of inorganic carbon to the open ocean, potentially increasing ocean acidification. The contribution of SGD is an important factor that must be included in the carbon budgets for the coastal areas, since it might affect current ocean acidification. The awareness of the role of freshwater input as a driver of coastal metabolism might help in the management of current regulation to forecast the consequences of land usage and climate change, in order to protect coastal productivity.

In Killary Harbour the loading of TA, DIC and DIN was not particularly high compared to the open ocean even if the loading of DOC was quite important ~440 × 10^3 mol d^{-1}. Further biological studies which take into account field conditions might be suggested in the future, in order to understand if the freshwater composition and variation, (particularly in the low salinity areas) could negatively impact the mussel aquaculture or if there are some physiological adaptations occurring.

The aim of this study was to have an immediate and effective comparison in areas with contrasting watershed input, and this is the reason why one compartment box model approach was used. However, multi-boxes models (Rodhouse and Roden, 1987; Gordon et al., 1996) can be more appropriate to understand the system variability and the effects of freshwater discharge in the different areas where rope mussel is present.

7 General conclusions

7.1 How the results chapters answered to the research questions

This thesis work has been structured in four research questions. The Chapters 3, 4, 5 and 6 were focused on those questions and the formulated hypothesis (see Chapter 2) have been verified.

The first research question was:

- **Which are the main drivers of carbonate chemistry along the Irish coastal sea?**

To answer this question available data were used and an oceanographic cruise organised by MI was carried out. The sampling strategy adopted during the cruise provided a dataset which described the carbonate system parameters in the west coast of Ireland. Two different coastal embayments were sampled: Galway Bay and Dingle Bay. These two coastal areas showed different TA and DIC trends versus salinity, suggesting that the type of freshwater inputs could affect the coastal carbonate chemistry. Secondly, a dataset owned by the MI was used to compare coastal areas characterized by different freshwater typology and catchment geology. The results from the analysis showed that the carbonate chemistry along Irish coastal seas is driven by the type of freshwater input. The chemical composition of the freshwater input is affected by the geological interactions with the watershed, as previously mentioned in the literature. Furthermore, human activities on land are affecting the amount of nutrients in the rivers, leading to an increase of loading of them on their surrounding coastal areas. These increases of nutrients can in turn affect the coastal metabolism with consequences for eutrophication and acidification. Additionally, in Galway Bay area, which is highly influenced by freshwater discharge as SGD, two different surveys carried out in different seasons were compared. The SGD was identified as a driver of TA:DIC relation, making reasonable the need to better understand its role in the coastal areas.

The second and third research questions were:

- **What are the pH dynamics in coastal areas characterized by contrasting origin of freshwater inputs?**
- **What is the TA:DIC relationship in estuarine areas characterized by contrasting types of freshwater input?**

To answer these research questions, it was necessary to adopt a sampling strategy that covered different periods of the year. In facts in different months different discharge conditions can occur, leading to a certain loading of nutrients and carbonate to the coast. Areas with contrasting watershed inputs have been identified in order to compare their effects on the coast. The pH, TA and DIC were therefore measured, and spatial and temporal variability was assessed. In Chapter 4 the differences between SGD and rivers composition were shown. The two selected coastal areas are fed by different freshwater typology. However, both areas showed pH values lower than the open ocean and an intense spatial variation of pH in relation to the volume of freshwater discharge. In Killary Harbour particularly low pH was recorded in the upper part of the bay. The rivers are diluting the TA and DIC compared to the ocean end-member; however, they are not able to modify their ratio which remains constant regardless of the change in the freshwater input. Contrastingly the SGD was a higher source of TA and DIC compared to the open ocean. The SGD was able to drive the TA:DIC ratio in Kinvarra Bay during the cooler months, possibly affecting the NCP, and driving the system into heterotrophic conditions.

- **How do SGD and rivers influence the TA and DIC relationship in the water column over diurnal and seasonal timescales?**

To answer this question the SGD and the rivers have been analysed at diurnal time scale (Chapter 5) and at seasonal time scale (Chapter 6). The carbonate system parameters were measured, and the NCP was quantified.

The diurnal fluctuations in the carbonate system parameters in Kinvarra Castle Spring, which was the main freshwater source identified for Kinvarra Bay, were prevalently driven by freshwater/seawater mixing. The tidal fluctuations have been identified from the time-series analysis as the main reason for the diel changes of pH and TA.

The Erriff River in Killary Harbour area, conversely, did not show defined trends for pH and TA. The diel changes of these parameters can be related with physical process occurring in the specific sampling conditions. Possible decrease of dissolved oxygen during the night was observed, suggesting a possible seasonality of the time-series (day/night) that might be proved elongating the sampling period.

Ultimately, in Chapter 6, using the sampling strategy adopted in Chapter 4, a budget methodology was applied to first quantify the NCP in the two selected coastal areas and secondly to understand the TA and DIC dynamics, and to establish if the systems might be a source or a sink of these properties. The export of TA and DIC in Kinvarra Bay was quantified and a positive value was found in the cooler months. These results are important to understand the current and future acidification processes occurring in coastal areas. As was observed through the literature review the ocean acidification in the open ocean was widely studied in the last decades as well as the effects of ocean acidification scenarios to calcifiers. For what concerns the coastal areas, the freshwater input and human activities on land are possible drivers of ocean acidification and, therefore, are important factors to be considered for the coastal management. Furthermore, the quantification of TA and DIC coming from SGD and its export towards the open ocean should not be overlooked in the coastal carbon budgets.

7.2 What this thesis added to the state of art and suggested future research

Coastal carbonate chemistry is a topic that has been under the spotlight in the last decades. Most of the scientific community has focused attention on the open ocean carbonate chemistry and the effects of atmospheric CO_2 on the ocean buffering capacity. Furthermore, calcifying organisms' response to open ocean carbonate chemistry has been extensively discussed in the introduction.

From the results presented in this thesis work, the need to consider the coastal carbonate chemistry and the effects of freshwater discharge as possible driver of ocean acidification, has been remarked. Both SGD and rivers are characterized by pH values lower compared to the open ocean. Most of the literature studies related with mussel physiology and adaptations mechanisms were based on laboratory experiments in mesocosms, and often built using the knowledge acquired from the open ocean data. However, a more complex scenario represents the coastal dynamics and more drivers should be considered in order to simulate the coastal variations and the field conditions. Short-term variability for instance, showed large fluctuations of carbonate system parameters occurring at the low salinity areas. The aquaculture areas close to the river’s mouth are affected by: freshwater input with low pH, tidal excursion, mixing processes, which leads to create a dynamic environment.

The mussel's adaptations mechanisms to diel changes might be a significant aspect in order to integrate the present knowledge and to adopt the best measures to manage the aquaculture licensed areas. Additionally, in situ experiments can be considered in order to apply a comparison approach and to monitor the spatial adaptations mechanisms. As previously discussed, some species could show higher adaptations mechanism when food availability is high. Considering the contrasting nutrients loading in the selected study areas, further research on the biological and physiological response of *Mytilus edulis*, oysters and other aquaculture species should be considered. Killary Harbour, for instance, did not receive a large amount of nutrients, and the loading of DOC and DOM was high. It follows that some further research questions can be formulated, e.g.,

- **Is *Mytilus edulis* showing adaptation mechanisms to pH and Ω_{Ar} fluctuations in Killary Harbour's low salinity area?**
- **DOM and DOC loading can compensate the effects of low pH and Ω_{Ar}?**

Considering that most of the available literature studies in Killary Harbour have been carried out before development of the aquaculture, the carbonate chemistry outcomes of this thesis can be utilized to explore biological adaptation mechanisms occurring in the area.

Another aspect that should be better analysed is how the groundwater carbonate system varies on short (diel) and long (season) timescale. In chapter 5 the carbonate system short-term variability was observed in Kinvarra spring location, and some data interpretation was made. However, to have a deeper understanding and to build some models, in the light of climate change issues, further analyses are necessary. The ions analysis should be added, it might provide better interpretation about the reactions occurring in the groundwater (e.g., effects of freshwater-seawater mixing, effect of anthropogenic pollutants, on carbonate precipitation). Possibly, the sampling should be planned in different seasons, to get the anthropogenic inputs from the slurry and to understand how they drive chemical reactions. Previous literature studies had foreseen the role of SGD as a driver of TA:DIC relation. From the results presented in this thesis work the SGD role as driver of coastal carbonate chemistry was identified (Chapter 4). Additionally, with the application of LOICZ, the net export of TA and DIC was also quantified. The spatial and temporal variabilities of the SGD and the loading of TA and DIC is an important factor to be considered for what concerns the coastal carbon budgets.

From the explored literature and from the results of this thesis, the TA and DIC ratio as an informative tool of coastal metabolic conditions is proven. The present knowledge of the rivers and groundwater from EPA monitors and the geological characterization of the catchment areas, can be used as indicators to select sites of interest for coastal acidification studies.

From what is known from the EPA reports, the main pressure on water quality comes from agriculture as pollution of nutrients and pesticides. At European level the MSFD has the goal to achieve a target water quality (surface water and groundwater) in the water bodies by 2027. To address the goals, the cooperation between agriculture and water authorities is fundamentally important. The case of Ireland is peculiar, since the authorities have been positively working together. However, in other European States this is still a big challenge. There are still long-standing problems related to agriculture: hydromorphology, persistent chemicals, correlated with uneven implementation and monitoring, in addition to new problems related to water quality such as pharmaceutical, micro-plastics and climate change. The MSFD progress for 2027 is slower than expected and to achieve the goals established for 2027, additional efforts are necessary on both to implement the research and to implement the communication and cooperative behaviour for management actions.

The Irish Centre for Research in Applied Geosciences (iCRAG) that funded this research project, responded to the Public Consultation on the Draft National Marine Planning Framework for Ireland. In particular, this thesis work contributed also to the comments related to the water quality. In the MSFD document it is quoted that “Ocean acidity has increased significantly in sub-surface and deep ocean offshore waters around Ireland between 1991 and 2010”. What has been emphasized, due to more recent literature data and the research finding of this thesis, is the role of freshwater input and land ocean interactions, as a driver and, in some cases, acceleration of coastal acidification processes (iCRAG, p.47-50, 2020). Similarly, with regard to the issue of nutrient enrichment, there seems to be a lack of sufficient data on baseline nutrient status in Irish coastal waters. Nutrient sampling, as it was observed from the MI database analysed in Chapter 3, should be carried out during winter months, where phytoplankton depletion of nutrients does not affect the results. However, this can be difficult for the extremely severe weather conditions particularly at sea. Additionally, the higher input of nitrogen observed in the Irish sea compared with the Celtic Sea and Atlantic, with the highest proportion originating from sewage rather than industrial source, again shows the need to encourage further research and regulations.

For what concerns the methodology applied in this thesis work, the TA open cell titration and the use of standard methods for the open ocean were extended to the coastal areas. The standards utilized (from Dickson Marine laboratory in the USA as explained in the methods) and the procedure were built for studies of carbonate chemistry with salinity greater than 34. However, because the coastal area that is characterized by a wide range of salinity from the freshwater end-member to the marine end-member, was the principal environment analysed in this thesis, the gradient of salinity was considered for the standardization. Different titrants at different salinity have been used in order to avoid the ions addition on the sample analysed. Each titrant was made with different % of $NaCl_2$, then they were standardized against Dickson's CRMs titrant batch. For what concerns the pH standard solution, two different batches were used for fresh and for marine water. The development of a protocol for coastal waters accepted by the scientific community operating in the field of the coastal areas carbonate chemistry might be necessary for future studies.

Currently the scientific community is aware about the need to collaborate and to find common agreements. For this reason, a new programme “coast-predict” is now focused on the prediction of Global Coastal Ocean, concept defined by Robinson, (2005). The improvement of multidisciplinary and extended range predictive capabilities for the coastal zone is one of the objectives. The biogeochemistry of coastal areas will be considered as an important integrative subject, together with marine biology and chemistry. The key of the coast-predict programme is to create a common scientific approach to study the different coastal areas. The propositional direction on which the scientific community is moving on, offers some positive hopes about the future and prosperity of our Global Coastal Ocean.

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Appendix: Chapter 2 Materials and Methods

Table 8-1 In the following table is showed an example of how the manual calculation of Total Alkalinity was made. As first the sample is titrated until pH 3.5 in the example 1.716 ml of HCl were added. After 10 minutes stirring and degassing of the sample, is then titrate until pH 3, adding at each step 0.05 ml of HCl.

Sample Name	pH measured	Sample weight	Volume of HCl added
marine EM	8.02	60	1.716

Density of water g/cm³	volume added after pH3.5 ml
1.02337	0.05

TOT weight	Vol of Titrant added (mL)	Mass of titrant added (g)	Measured pH	[H+] ($10^{-(pH)}$) mol/dm3	Mass of titrant added (g)	Gran Function (g*mol/dm3)
61.76	1.806	1.76	3.5	0.0003162	1.76	0.0003160
61.81	1.856	1.81	3.43	0.0003715	1.81	0.0003715
61.86	1.906	1.86	3.38	0.0004169	1.86	0.0004172
61.91	1.956	1.91	3.33	0.0004677	1.91	0.0004685
61.96	2.006	1.96	3.29	0.0005129	1.96	0.0005141
62.01	2.056	2.01	3.24	0.0005754	2.01	0.0005773
62.06	2.106	2.06	3.21	0.0006166	2.06	0.0006190
62.11	2.156	2.11	3.18	0.0006607	2.11	0.0006638
62.16	2.206	2.16	3.15	0.0007079	2.16	0.0007119
62.20	2.256	2.20	3.12	0.0007586	2.20	0.0007634
62.25	2.306	2.25	3.09	0.0008128	2.25	0.0008186
62.30	2.356	2.30	3.07	0.0008511	2.30	0.0008579
62.35	2.406	2.35	3.04	0.0009120	2.35	0.0009199
62.40	2.456	2.40	3.02	0.0009550	2.40	0.0009641

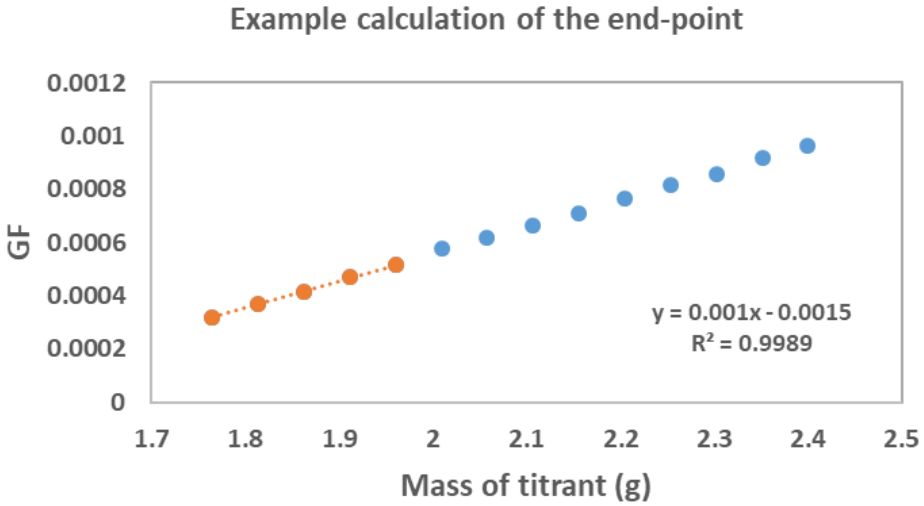


Figure 8-1 The Gran Function has been plotted versus the mass of the titrant and the slope and intercept at the maximum R2 value are showed. The Total Alkalinity is calculated using the x axis intercept value -intercept/slope.

Appendix: Chapter 3

Table 8-2 Data collected during the Oceanographic Cruise carried with the Celtic Voyage from the 17/10/2017 to the 23/10/2017.

Date	Station Number	Latitude (decimal degree)	Longitude (decimal degree)	Depth	Salinity	TA	DIC	LOCEAN TA	LOCEAN DIC	pH	T
				(m)	‰	µmol kg^{-1} (±10)	µmol kg^{-1} (±10)	µmol kg-1 (±10)	µmol kg-1 (±10)	±0.01	°C
17/10/2017	1	52.951481	-9.678168	3	34.96	2165	-	-	-	7.96	13.8
				70	35.1	2377	-	-	-	0.01	13.2
17/10/2017	2	52.931167	-10.067667	3	34.97	2269	-	-	-	7.97	13.9
				96	35.09	2257	-	-	-	7.99	10.4
18/10/2017	3	52.323333	-11.020833	3	35.18	2243	-	-	-	7.95	13.3
				121	35.37	2390	-	-	-	8.03	10.5
18/10/2017	4	52.148167	-11.085000	3	35.19	2178	-	-	-	7.98	13.5
				129	35.4	2324	-	-	-	8.01	10.7
18/10/2017	5	51.832333	-11.351333	3	35.18	-	-	-	-	-	13.9
				195	35.45	-	-	-	-	-	11.0
18/10/2017	6	51.841000	-10.962833	3	34.8	-	-	-	-	-	13.8
				146	35.4	-	-	-	-	-	10.9
18/10/2017	7	51.850000	-10.833500	3	35.34	-	-	-	-	-	13.5
				131	35.44	-	-	-	-	-	10.8
18/10/2017	8	52.854833	-10.701333	3	35.11	-	-	-	-	-	13.2
				100	35.32	-	-	-	-	-	11.3
18/10/2017	9	52.860833	-10.561833	3	35.09	-	-	-	-	-	12.5
				91	35.23	-	-	-	-	-	11.9
18/10/2017	10	51.855500	-10.433000	3	34.96	2331	2145	2330.8	2144.9	7.74	13.2
				68	35.04	-	-	-	-	-	12.6

Date	Station Number	Latitude (decimal degree)	Longitude (decimal degree)	Depth	Salinity	TA	DIC	LOCEAN TA	LOCEAN DIC	pH	T
				(m)	‰	µmol.kg^{-1} (±10)	µmol.kg^{-1} (±10)	µmol.kg-1 (±10)	µmol.kg-1 (±10)	±0.01	°C
18/10/2017	11	51.954833	-10.733000	2	35.16	2333	2149	2332.7	2149.3	7.69	12.8
				114	35.3	-	-	-	-		11.0
19/10/2017	12	52.094167	-10.099333	3	33.01	2275	2062	2223.3	2061.9	7.58	13.1
				14	34.7	2345	-	-	-	8	13.2
19/10/2017	13	51.983000	-10.599333	3	35	-	-	-	-	-	12.7
				80	35.28	-	-	-	-	-	11.0
19/10/2017	14	52.011333	-10.479667	3	35.02	2569	-	2329.5	2147	7.67	12.6
				65	35.1	2276	-			8	12.4
19/10/2017	15	52.040833	-10.346833	3	34.34	2488	-	2296.2	2125	7.66	13.1
				45	34.97	2333	-			7.98	12.8
19/10/2017	16	52.071000	-10.223000	3	33.91	2725	-	2282.5	2129.5	7.61	13.1
				23	34.96		-				13.1
20/10/2017	17	52.548500	-10.044667	3	34.28	2348	-	2347.5	2156.3	7.71	13.1
				65	35.1	2345	-			8.02	13.2
20/10/2017	18	52.655167	-9.910667	3	34.47	2346	-	2345.8	2155.9	7.65	12.7
				69	35.15	-	-	-	-	-	13.1
20/10/2017	19	52.801371	-9.697281	3	34.27	-	-	-	-	-	12.6
				46	34.8	-	-	-	-	-	13.8

Date	Station Number	Latitude (decimal degree)	Longitude (decimal degree)	Depth	Salinity	TA	DIC	LOCEAN TA	LOCEAN DIC	pH	T
				(m)	‰	µmol kg^{-1} (±10)	µmol kg^{-1} (±10)	µmol kg-1 (±10)	µmol kg-1 (±10)	±0.01	°C
20/10/2017	20	52.256726	-10.453982	3	32.52	2423	-	-	-	7.93	11.9
				24	34.27	2241	-	-	-	7.92	13.9
23/10/2017	21	53.240200	-9.082300	3	29	2625	2375	2522.8	2374.5	7.68	13.0
				12	26.70	2707	-	-	-	7.88	12.9
23/10/2017	22	53.226500	-9.114500	3	29.74	2887	2320	2469	2320.1	7.67	12.5
				15	29.74	2554	-	-	-	7.89	13.0
23/10/2017	23	53.208667	-9.216333	4	33.4	2621	2157	2353.2	2156.6	7.58	13.2
				23	34.00	2277	-	-	-	7.93	13.4
23/10/2017	24	53.177585	-9.346088	3	34.11	2363	-	2358	2175.5	7.73	13.4
				31	34.46	2137	-	-	-	7.91	13.5
23/10/2017	25	53.199167	-9.737833	3	34.36	2093	-	-	-	7.91	13.4
				56	34.85	2375	-	-	-	8.02	13.9
23/10/2017	26	53.190833	-9.642167	4	34.26	2169	-	-	-	7.93	13.4
				48	34.36	2277	-	-	-	7.90	13.4

Appendix: Chapters 4 and 6

Table 8-3 Row data detail of salinity, TA, DIC (measured and calculated) pH, temperature and dissolved oxygen for the transects carried out in Kinvarra Bay (KB) and Killary Harbour (KH)

Location	Date sampled	Station number	Latitude (decimal degree)	Longitude (decimal degree)	Salinity	TA	DIC CO2Sys	LOCEAN TA	LOCEAN DIC	pH	T	Dissolved oxygen
					‰	µmol kg^{-1} (±10)	µmol kg^{-1} (±10)	µmol kg^{-1} (±5)	µmol kg^{-1} (±5)	±0.01	°C	(% saturation)
KB	13/07/2018	EM0718	53.1762500	-8.9602170	29.75	2307	2080	-	-	7.97	18.3	102.6
KB	13/07/2018	ST10718	53.1622830	-8.9616830	29.15	2197	1934	-	-	8.07	19.9	104.4
KB	13/07/2018	ST40718	53.1647330	-8.9421290	29.61	2172	1920	-	-	8.04	18.8	103.7
KB	13/07/2018	ST50718	53.1631000	-8.9541000	28.90	2426	2125	-	-	8.10	18.8	104.6
KB	13/07/2018	ST30718	53.1554170	-8.9482330	28.42	2279	2028	-	-	8.04	19.1	104.1
KB	13/07/2018	ST20718	53.1454500	-8.9397170	29.08	2277	2008	-	-	8.07	20.2	64.0
KBspring	12/07/2018	spr0718	53.1414880	-8.9265930	1.54	5627	5944	-	-	7.28	17.9	57.4
KB_borehole	12/07/2018	KINVBHAM0718	53.1287320	-8.9287360	7.42	4951	4953	-	-	7.66	15.3	21.8
KB	21/10/2018	ST41018	53.1721630	-8.9683680	29.61	2405	2072	2453	2177	8.15	13.0	106.4
KB	21/10/2018	ST21018	53.1446900	-8.9305070	10.01	3192	3141	3179	3264	7.76	14.8	97.4
KB	21/10/2018	ST31018	53.1538570	-8.9528480	25.82	2461	2226	-	-	8.02	14.0	102.0
KB	21/10/2018	ST11018	53.1661020	-8.9430770	28.70	2514	2310	2491	2304	7.91	14.3	98.8
KBspring	20/10/2018	Spr10am1018	53.1414880	-8.9265930	0.53	4422	4922	-	-	7.03	12.5	54.2
KB_borehole	20/10/2018	KINVBHAM1018	53.1287320	-8.9287360	0.34	3582	3781	-	-	7.30	12.1	42.1
KB	28/01/2019	EM0119	53.1809160	-8.9636310	25.80	2629	2483	2693	2606	7.81	11.1	-
KB	28/01/2019	St60119	53.1714810	-8.9627710	25.50	2592	2453	2625	2517	7.80	10.6	-
KB	28/01/2019	St50119	53.1654890	-8.9548840	25.00	2639	2509	-	-	7.78	10.8	-
KB	28/01/2019	St40119	53.1585520	-8.9478290	17.20	2769	2724	2851	2861	7.65	10.6	-
KB	28/01/2019	St30119	53.1510730	-8.9411010	7.70	2964	2989	-	-	7.57	11.0	-
KB	28/01/2019	St20119	53.1455400	-8.9380770	6.10	3165	3297	3217	3457	7.32	10.7	-

Location	Date sampled	Station number	Latitude (decimal degree)	Longitude (decimal degree)	Salinity	TA	DIC CO2Sys	LOCEAN TA	LOCEAN DIC	pH	T	Dissolved oxygen
					‰	µmol kg^{-1} (±10)	µmol kg^{-1} (±10)	µmol kg^{-1} (±5)	µmol kg^{-1} (±5)	±0.01	°C	(% saturation)
KH	17/02/2018	K17-1D0218	53.6301490	-9.8778230	30.77	2344	2188	-	-	7.80	8.2	100.7
KH	17/02/2018	K17-1S0218	53.6301490	-9.8778230	27.85	1903	-	1887	1806	7.82	6.2	97.0
KH	17/02/2018	K17-2D0218	53.6205010	-9.8570460	30.83	2048	1898	-	-	7.82	7.3	100.3
KH	17/02/2018	K17-2S0218	53.6205010	-9.8570460	27.19	1333	-	1325	1285	7.74	6.4	96.5
KH	17/02/2018	K17-3S0218	53.6102160	-9.8124390	16.76	1023	-	1027	1015	7.62	5.5	98.3
KH	17/02/2018	K17-4D0218	53.6013500	-9.7582910	31.17	1690	1565	-	-	7.79	7.5	96.6
KH	17/02/2018	K17-4S0218	53.6013500	-9.7582910	17.97	1558	-	1555	1509	7.80	5.4	98.9
Bunowen	18/02/2018	R1 - 0218	53.5835830	-9.7782070	0.23	31	84	-	-	6.01	9.2	100.7
Erriff	18/02/2018	R2 -0218	53.6158190	-9.6706020	0.06	42	100	-	-	6.11	8.2	100.1
Bundoragha	18/02/2018	R3 - 0218	53.6069670	-9.7531550	0.05	25	52	-	-	6.21	8.6	99.8
KH	16/07/2018	EM0718	53.6006260	-9.7216920	31.88	2200	1913	-	-	8.07	14.9	104.0
KH	16/07/2018	1D0718	53.6223830	-9.8565680	31.39	2336	2090	-	-	7.98	13.8	93.9
KH	16/07/2018	1S0718	53.6223830	-9.8565680	30.41	2351	2073	-	-	8.05	15.1	102.0
KH	16/07/2018	2D0718	53.6132330	-9.8202830	33.68	2269	1985	-	-	8.03	14.8	94.7
KH	16/07/2018	2S0718	53.6132330	-9.8202830	35.88	2321	2045	-	-	7.98	16.2	101.4
KH	16/07/2018	3D0718	53.6045330	-9.7944170	35.23	2201	1945	-	-	7.97	15.0	94.4
KH	16/07/2018	3S0718	53.6045330	-9.7944170	32.35	2233	1922	-	-	8.10	15.2	102.1
KH	16/07/2018	4D0718	53.5997000	-9.7828920	30.19	2230	1980	-	-	8.02	14.8	95.8
KH	16/07/2018	4S0718	53.5997000	-9.7828920	29.47	2380	2134	-	-	8.00	15.1	100.4
KH	16/07/2018	5D0718	53.6007830	-9.7573330	32.34	2221	1983	-	-	7.97	15.0	96.8

Location	Date sampled	Station number	Latitude (decimal degree)	Longitude (decimal degree)	Salinity	TA	DIC CO2Sys	LOCEAN TA	LOCEAN DIC	pH	T	Dissolved oxygen
					‰	µmol kg^{-1} (±10)	µmol kg^{-1} (±10)	µmol kg^{-1} (±5)	µmol kg^{-1} (±5)	±0.01	°C	(% saturation)
KH	16/07/2018	6S0718	53.6010330	-9.7239500	31.97	2207	1982	-	-	7.95	16.4	98.7
Bunowen	16/07/2018	R1 -0718	53.5835830	-9.7782070	0.28	272	307	-	-	6.98	16.9	100.5
Erriff	15/07/2018	R2 - 0718	53.6158190	-9.6706020	0.36	380	424	-	-	7.02	19.9	99.6
Bundoragha	15/07/2018	R3 - 0718	53.6069670	-9.7531550	0.15	204	241	-	-	6.83	19.1	100.5
KH	25/10/2018	EM1018	53.6316200	-9.8818910	29.39	2345	2128	-	-	7.95	13.4	91.9
KH	25/10/2018	1D1018	53.6145070	-9.8252830	32.77	2345	2106	2349	2148	7.95	12.9	91.1
KH	25/10/2018	1S1018	53.6145070	-9.8252830	29.98	2079	1883	1811	1704	7.94	12.6	91.7
KH	25/10/2018	2D1018	53.6010920	-9.7893320	31.46	2331	2127	-	-	7.90	12.9	86.3
KH	25/10/2018	2S1018	53.6010920	-9.7893320	27.89	1701	1560	-	-	7.88	12.0	92.3
KH	25/10/2018	3D1018	53.6005820	-9.7595520	30.96	2217	2036	-	-	7.87	12.9	83.8
KH	25/10/2018	3S1018	53.6005820	-9.7595520	24.79	1510	1399	1557	1477	7.86	12.1	91.7
KH	25/10/2018	4S1018	53.6009440	-9.7223910	25.59	1452	1351	1543	1435	7.82	12.0	92.2
Bunowen	24/10/2018	R1 - 1018	53.5835830	-9.7782070	0.33	89	107	-	-	6.78	12.8	95.5
Erriff	24/10/2018	R2 - 1018	53.6158190	-9.6706020	0.12	16	21	-	-	6.65	12.1	96.3
Bundoragha	24/10/2018	R3 - 1018	53.6069670	-9.7531550	0.10	44	62	-	-	6.48	12.3	95.5
KH	23/01/2019	EM0119	53.6316200	-9.881891	28.00	2159	1988	2247	2159	7.89	9.0	90.7
KH	23/01/2019	1S0119	53.6122330	-9.817082	26.00	1762	1671	1779	1701	7.74	7.8	90.5
KH	23/01/2019	1D0119	53.6122330	-9.817082	33.90	2245	2067	2282	2144	7.82	8.2	90.6
KH	23/01/2019	2S0119	53.5998330	-9.778845	16.70	1222	1199	1171	1169	7.62	7.0	90.5
KH	23/01/2019	2D0119	53.5998330	-9.778845	33.00	2206	2051	2250	2116	7.78	8.9	91.5

Location	Date sampled	Station number	Latitude (decimal degree)	Longitude (decimal degree)	Salinity	TA	DIC CO2Sys	LOCEAN TA	LOCEAN DIC	pH	T	Dissolved oxygen
					‰	µmol kg^{-1} (±10)	µmol kg^{-1} (±10)	µmol kg^{-1} (±5)	µmol kg^{-1} (±5)	±0.01	°C	(% saturation)
KH	23/01/2019	3D0119	53.6004830	-9.758313	33.21	2228	2075	2261	2127	7.77	9.0	86.8
KH	23/01/2019	4S0119	53.6009330	-9.742187	10.50	834	855	787	822	7.35	6.9	91.4
KH	23/01/2019	4D0119	53.6009330	-9.742187	33.00	2218	2066	2255	2136	7.77	9.1	89.7
KH	23/01/2019	5S0119	53.6009500	-9.73033	9.20	761	784	675	718	7.33	6.9	90.5
KH	23/01/2019	6S0119	53.6010580	-9.715354	9.60	792	824	703	765	7.26	6.4	91.7
Bunowen	24/01/2019	R1 - 0119	53.5835830	-9.778207	0.15	36	73	-	-	6.12	10.0	92.7
Erriff	24/01/2019	R2 - 0119	53.6158190	-9.670602	0.13	31	73	-	-	6.01	9.1	96.1
Bundoragha	23/01/2019	R3 - 0119	53.6069670	-9.753155	0.10	18	35	-	-	6.16	7.9	94.5
KH	04/04/2019	EM0419	53.6316200	-9.881891	34.10	2301	2016	2249	2114	8.02	7.4	103.3
KH	04/04/2019	1S0419	53.6122330	-9.817082	31.00	2130	1893	2119	1959	8.00	7.2	101.9
KH	04/04/2019	1D0419	53.6122330	-9.817082	34.10	2341	2075	2308	2126	7.98	8.3	101.6
KH	04/04/2019	2S0419	53.5998330	-9.778845	30.60	2150	1929	2084	1928	7.97	8.0	102.0
KH	04/04/2019	2D0419	53.5998330	-9.778845	34.20	2352	2102	2285	2131	7.95	8.3	101.9
KH	04/04/2019	3S0419	53.6004830	-9.758313	27.00	1967	1786	1853	1731	7.96	8.5	101.6
KH	04/04/2019	3D0419	53.6004830	-9.758313	33.10	2311	2066	2255	2120	7.96	8.7	102.0
KH	04/04/2019	4S0419	53.6009330	-9.742187	25.80	1841	1674	1599	1508	7.96	7.9	102.0
KH	04/04/2019	4D0419	53.6009330	-9.742187	33.20	2267	2024	2283	2099	7.96	12.9	100.0
KH	04/04/2019	5S0419	53.6009500	-9.73033	26.20	1872	1701	-	-	7.96	8.2	102.0
KH	04/04/2019	6S0419	53.6010580	-9.715354	22.80	1675	1535	-	-	7.96	8.2	101.0
Bunowen	03/04/2019	R1 -0419	53.5835830	-9.778207	0.12	63	93	-	-	6.44	6.0	100.0
Erriff	03/04/2019	R2 -0419	53.6158190	-9.670602	0.14	80	102	-	-	6.65	7.8	99.9
Bundoragha	04/04/2019	R3 - 0419	53.6069670	-9.753155	0.09	16	29	-	-	6.26	8.1	101.7

Table 8-4 Data collected during a period of 24h in Tarrea Pier and Parkmore Pier in the different surveys: July 2018, October 2019, January 2019 and April 2019. The samples have been collected every 3 hours. The salinity values have been used for the tidal prism method applied in Kinvarra Bay, to quantify the freshwater input.

Location	Date sampled	Station number	Time (Local)	Salinity	TA	DIC CO2Sys	pH	T	Dissolved oxygen
Kinvarra Bay				‰	µmol kg^{-1} (±10)	µmol kg^{-1} (±10)	±0.01	°C	(% saturation)
24hTarrea pier	13/07/2018	T10718	07:00:00	26.34	2389.61	2338.10	7.56	17.8	76.5
24hTarrea pier	13/07/2018	T20718	09:00:00	31.66	2412.39	2136.69	8.02	18.8	129.3
24hTarrea pier	13/07/2018	T30718	11:00:00	27.24	2580.09	2336.26	8.00	18.7	112.2
24hTarrea pier	13/07/2018	T40718	13:00:00	22.61	2868.20	2712.69	7.86	19.1	102.3
24hTarrea pier	13/07/2018	T50718	15:00:00	36.21	2795.13	2369.90	8.13	18.8	104.6
24hTarrea pier	13/07/2018	T60718	16:00:00	34.88	2531.18	2051.39	8.26	22	131.6
24hTarrea pier	13/07/2018	T70718	19:00:00	36.80	2404.47	2096.60	8.01	20	101.7
24hTarrea pier	13/07/2018	T80718	21:00:00	37.23	2480.11	2198.92	7.95	19.2	93.6
24hTarrea pier	13/07/2018	T90718	23:00:00	31.03	2333.27	2291.45	7.48	18.3	85.3
24hTarrea pier	14/07/2018	T100718	01:00:00	20.24	2905.88	2774.99	7.83	17.3	98
24hTarrea pier	14/07/2018	T110718	03:00:00	21.20	2772.95	2613.43	7.90	17.3	96.1
24hTarrea pier	14/07/2018	T120718	05:00:00	26.16	2532.70	2320.91	7.96	16.5	88.7
24hTarrea pier	14/07/2018	T130718	07:00:00	29.94	2408.54	2157.17	8.00	17	95.9
24hTarrea pier	22/10/2018	T11018	10:00:00	29.66	2710.94	2551.81	7.78	12	70.5
24hTarrea pier	22/10/2018	T21018	13:00:00	27.73	2663.90	2426.69	7.97	12.5	109.9
24hTarrea pier	22/10/2018	T31018	16:00:00	27.76	2559.03	2333.71	7.96	13.2	104.8
24hTarrea pier	22/10/2018	T41018	19:00:00	28.65	2558.52	2348.82	7.92	12.9	92.2

Location	Date sampled	Station number	Time (Local)	Salinity	TA	DIC CO2Sys	pH	T	Dissolved oxygen
Kinvarra Bay				‰	µmol kg^{-1} (±10)	µmol kg^{-1} (±10)	±0.01	°C	(% saturation)
24hTarrea pier	22/10/2018	T51018	22:00:00	27.46	2810.71	2695.79	7.70	13.5	82.3
24hTarrea pier	23/10/2018	T61018	01:00:00	25.68	2909.56	2816.88	7.66	12.5	83.1
24hTarrea pier	23/10/2018	T71018	04:00:00	26.24	2627.19	2621.57	7.42	12	91.2
24hTarrea pier	23/10/2018	T81018	07:00:00	27.52	2575.25	2519.47	7.55	12.2	89.6
24hTarrea pier	23/10/2018	T91018	10:00:00	27.29	2724.09	2578.15	7.78	12.3	90.1
24hParkmorepier	25/01/2019	T10119	17:00:00	27.60	2672.49	2522.56	7.79	9	91.4
24hParkmorepier	25/01/2019	T20119	20:00:00	28.50	2498.21	2341.87	7.81	10.7	87.9
24hParkmorepier	25/01/2019	T30119	23:00:00	28.50	2517.60	2381.59	7.76	9.6	87.7
24hParkmorepier	26/01/2019	T40119	02:00:00	27.76	2659.58	2534.78	7.73	9.6	88.9
24hParkmorepier	26/01/2019	T50119	05:00:00	25.95	2475.57	2338.77	7.80	9.7	90.2
24hParkmorepier	26/01/2019	T60119	08:00:00	28.50	2510.16	2353.23	7.81	9.6	90.5
24hParkmorepier	26/01/2019	T70119	11:00:00	26.80	2462.01	2316.97	7.81	9.9	96.2
24hParkmorepier	26/01/2019	T80119	14:00:00	26.87	2512.39	2343.30	7.86	9.9	99
24hParkmorepier	26/01/2019	T90119	17:00:00	27.30	2487.21	2342.35	7.80	9.3	91
24hParkmorepier	07/04/2019	T10419	12:50:00	18.00	2736.41	2479.87	8.15	11.5	120.3
24hParkmorepier	07/04/2019	T20419	16:00:00	29.00	2644.73	2316.08	8.11	12.6	121
24hParkmorepier	07/04/2019	T30419	19:00:00	29.30	2579.85	2273.39	8.08	13	107.9
24hParkmorepier	07/04/2019	T40419	22:00:00	30.20	2426.24	2263.28	7.81	10.7	100.2
24hParkmorepier	08/04/2019	T50419	01:00:00	27.90	2824.09	2675.45	7.77	10.9	94.7
24hParkmorepier	08/04/2019	T60419	04:00:00	27.80	3598.30	3563.20	7.48	9.3	101.4
24hParkmorepier	08/04/2019	T70419	07:00:00	29.00	2494.29	2387.98	7.68	9.1	86
24hParkmorepier	08/04/2019	T80419	10:00:00	28.30	2624.41	2374.94	7.99	10.3	122.3
24hParkmorepier	08/04/2019	T90419	13:00:00	26.50	2698.19	2418.08	8.06	11.8	134

In the following figure the TA-DIC slopes versus Q was explored in the two selected study areas:

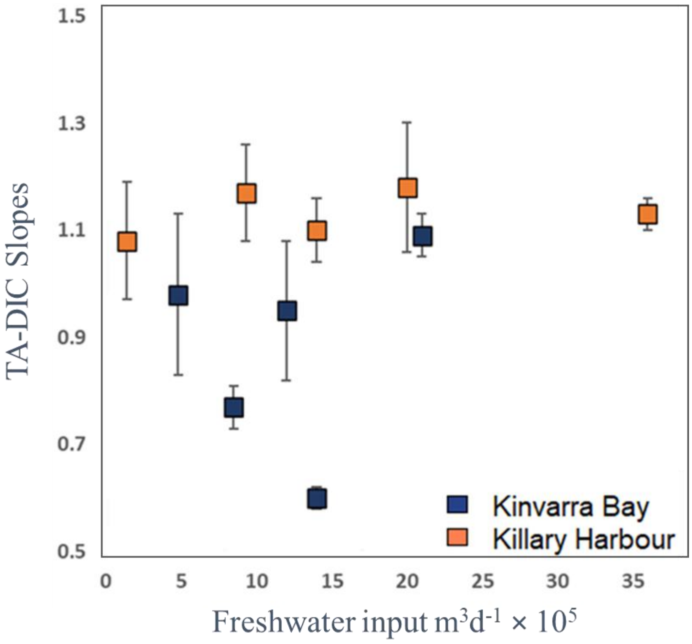


Figure 8-2 In this figure the TA-DIC slopes, both normalized to a 35 salinity, were plotted against the freshwater discharge. It is possible to observe that in Killary Harbour regardless the magnitude of freshwater inputs there is not a significant change in the TA-DIC slopes. The observed small variations recorded between the different surveys may be related to other secondary processes such as seasonal metabolic changes, nutrients availability, etc. In Kinvarra Bay there is not a clear relationship between freshwater discharge and TA-DIC slopes. During April and August 2019, with contrasting freshwater discharge magnitudes, the TA-DIC slopes are closed to 1. This was discussed in the paper and the possible factors explaining the observed distribution discussed (e.g. freshwater end-member compositional ratio, metabolic rates in the bay, water residence time).

Appendix: Chapter 5

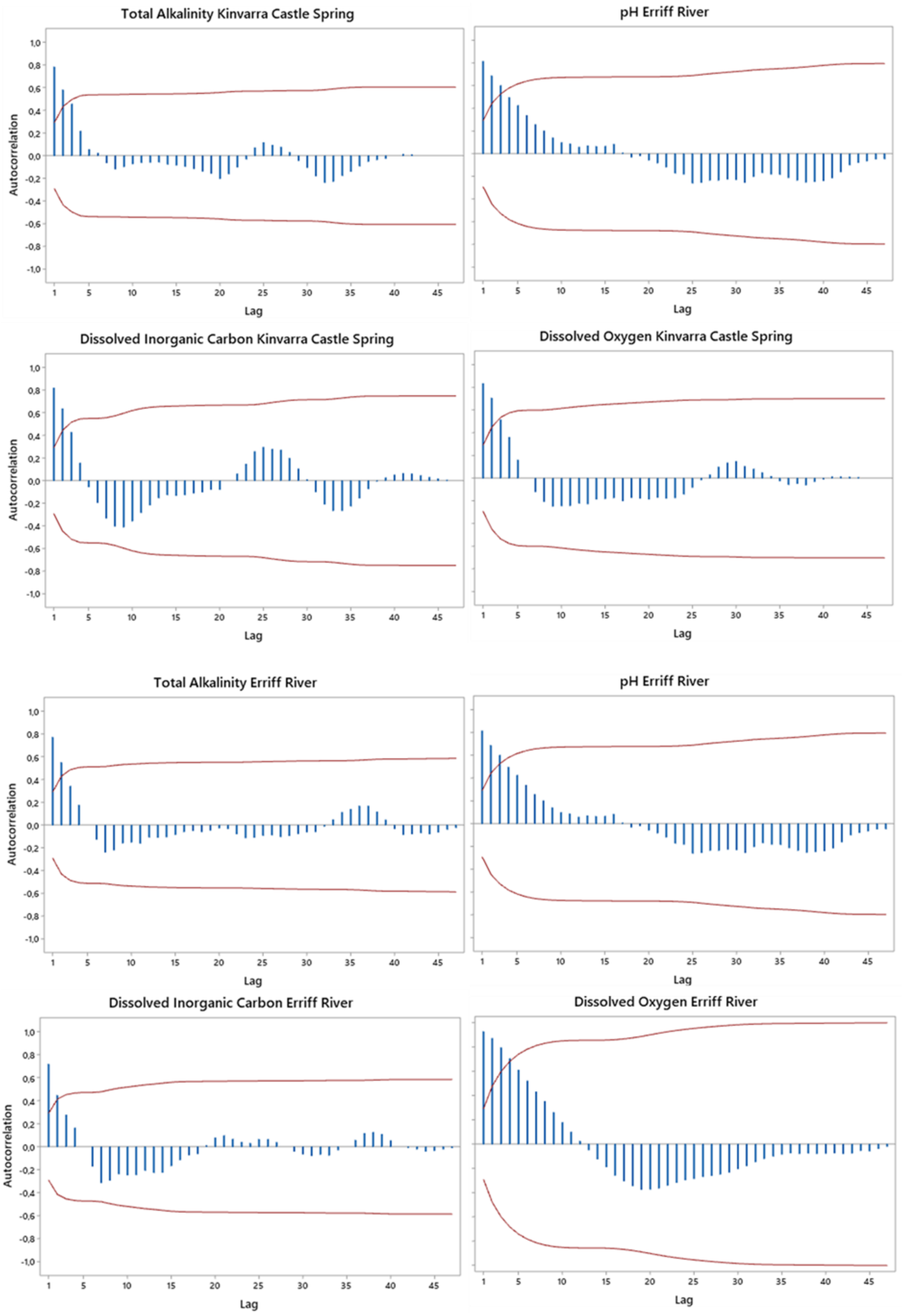


Figure 8-3 Autocorrelation function (ACF) is shown for TA, pH, DIC and DO in the two end-member locations. On the Y axis the correlation coefficient is represent and in the x axis the number of Lag. 47 Lag are expressed since the samples have been collected every 30 minutes and each lag represent the time delay from the previous half hour. Therefore, 24h cycle is represented.

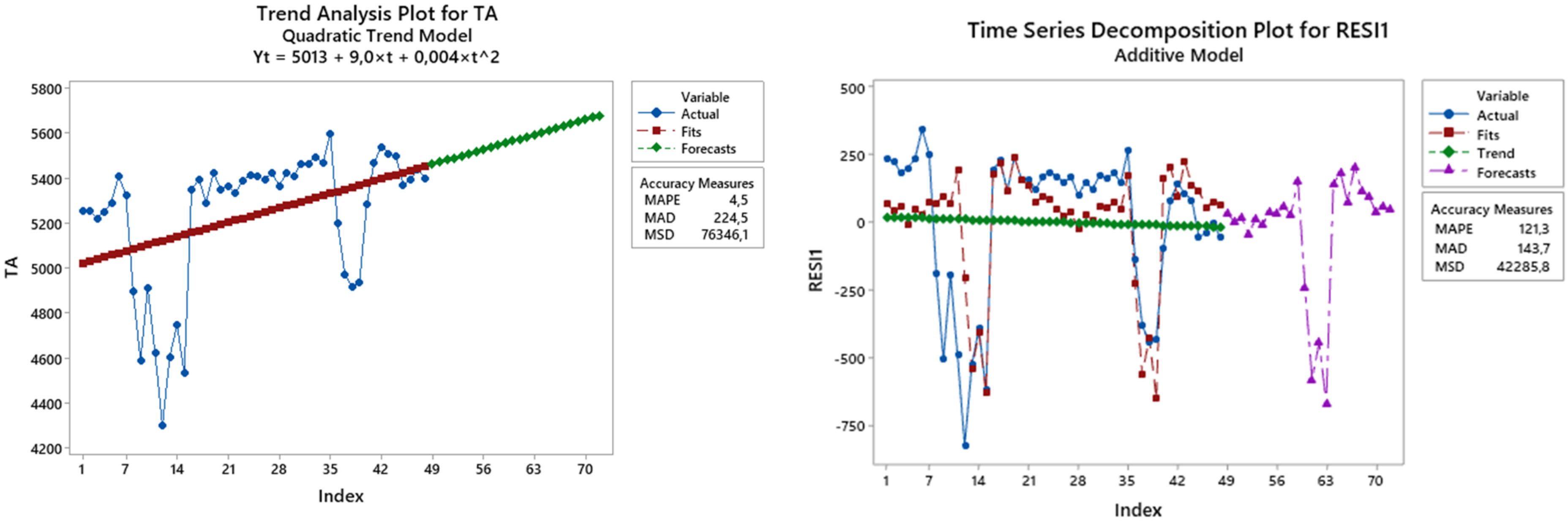


Figure 8-4 TA trend analysis and decomposition of diel time-series in Kinvarra Castle Spring. On the right the quadratic trend model is applied on the original data, the trend analysis does not consider the seasonality of the time series. The decomposition is applied on the residual of the trend analysis and the decomposition is showed on the right graph.

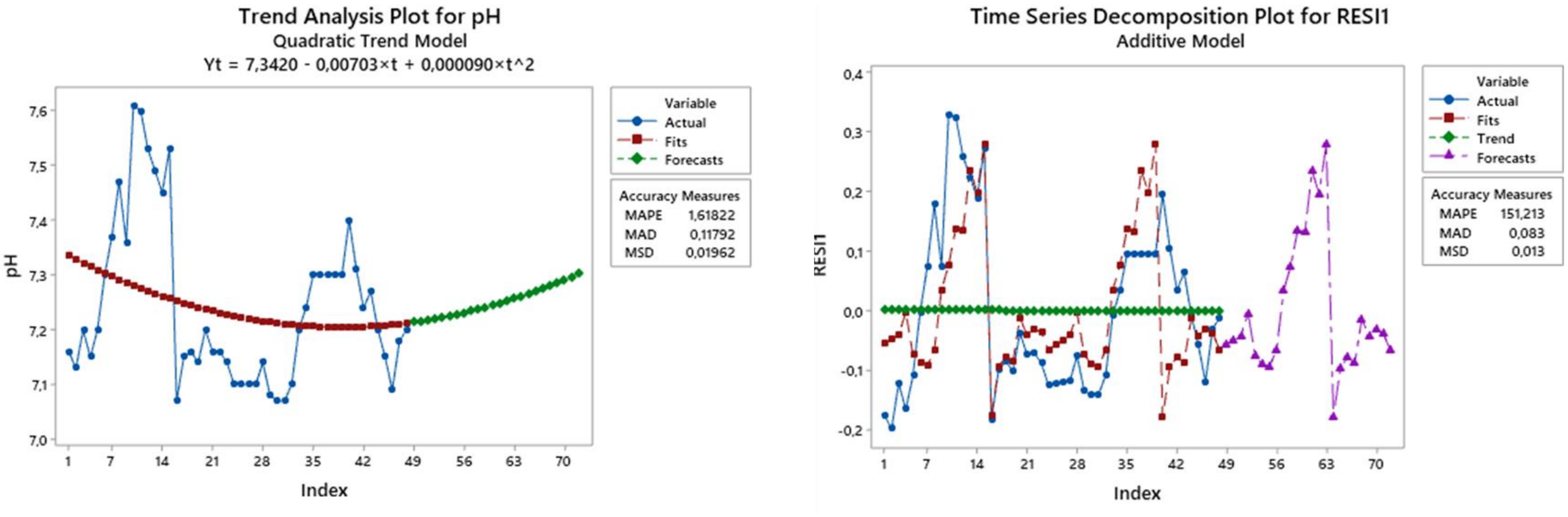


Figure 8-5 pH trend analysis and decomposition of diel time-series in Kinvarra Castle Spring. On the right the quadratic trend model is applied on the original data, the trend analysis does not consider the seasonality of the time series. The decomposition is applied on the residual of the trend analysis and the decomposition is showed on the right graph.

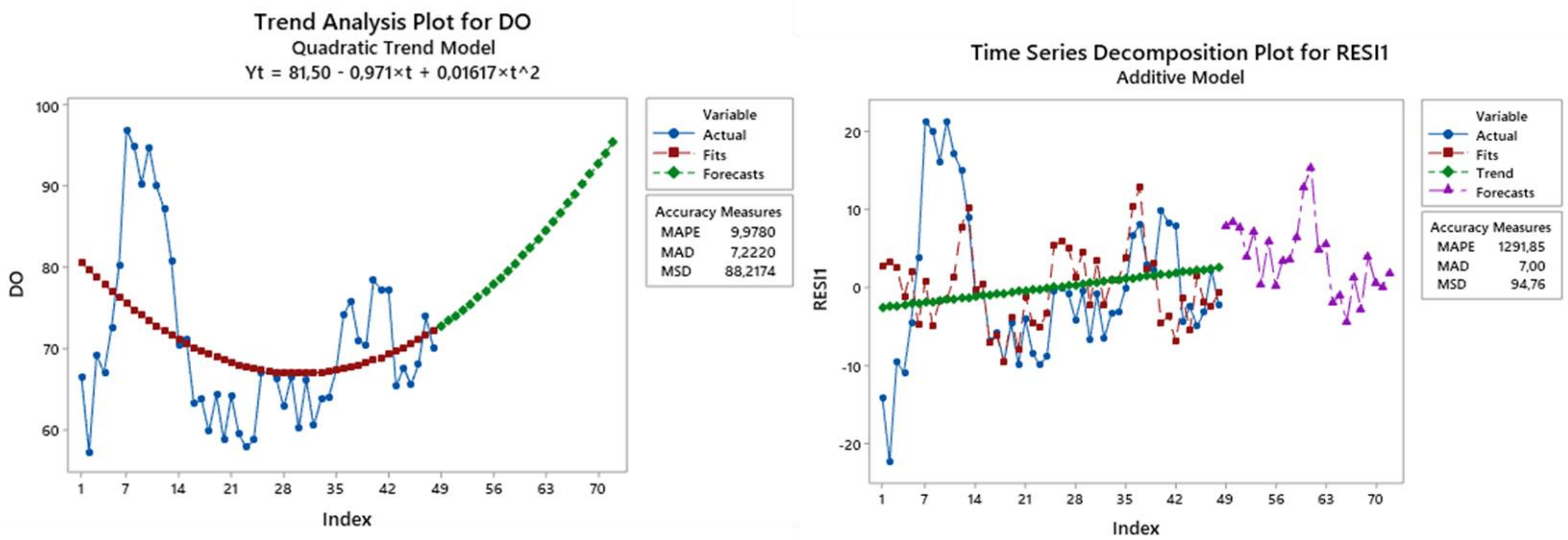


Figure 8-6 DO trend analysis and decomposition of diel time-series in Kinvarra Castle Spring. On the right the quadratic trend model is applied on the original data, the trend analysis does not consider the seasonality of the time series. The decomposition is applied on the residual of the trend analysis and the decomposition is showed on the right graph.

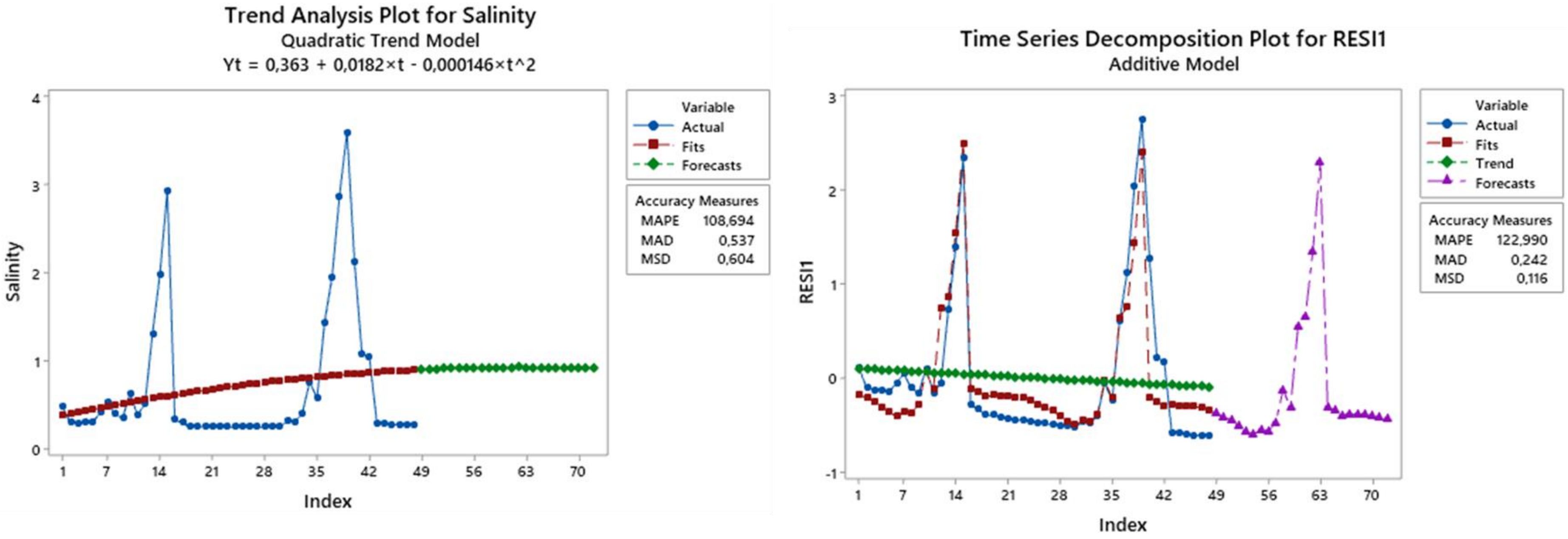
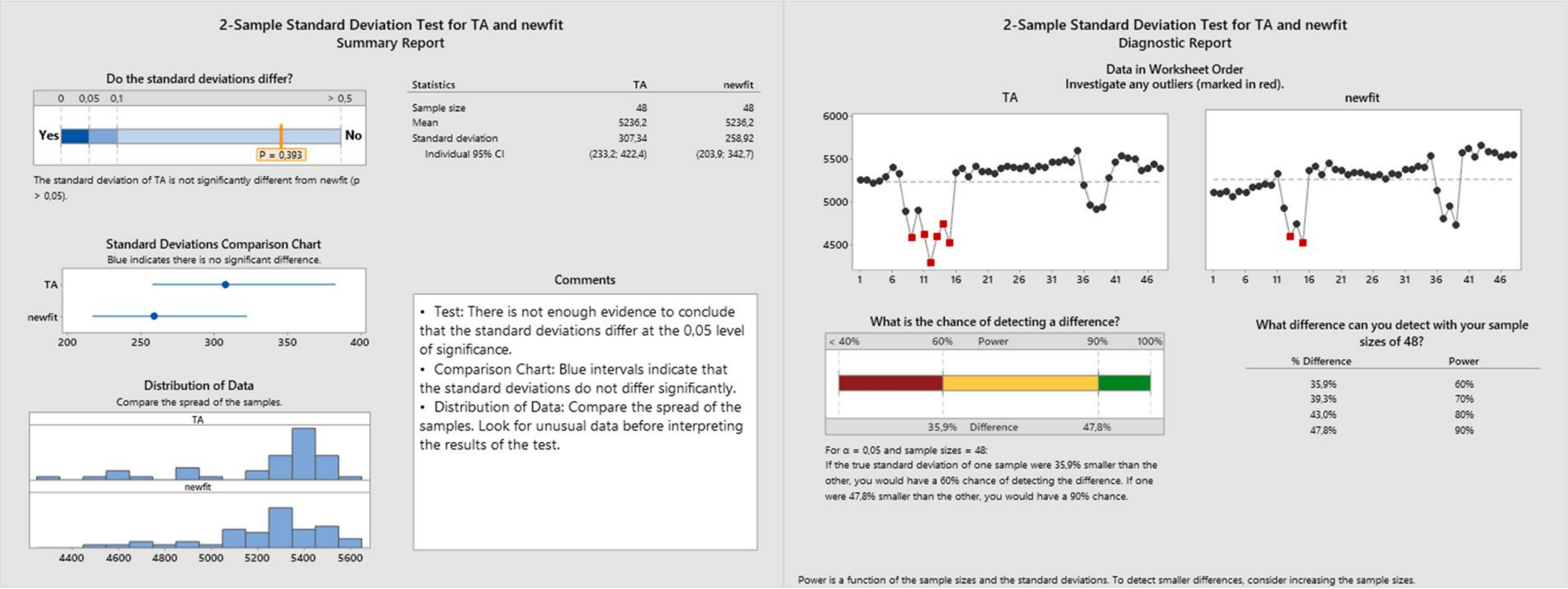


Figure 8-7 Salinity trend analysis and decomposition of diel time-series in Kinvarra Castle Spring. On the right the quadratic trend model is applied on the original data, the trend analysis does not consider the seasonality of the time series. The decomposition is applied on the residual of the trend analysis and the decomposition is showed on the right graph.



2-Sample Standard Deviation Test for TA and newfit
Summary Report

Do the standard deviations differ?

The standard deviation of TA is not significantly different from newfit (p > 0,05).

Statistics	TA	newfit
Sample size	48	48
Mean	5236,2	5236,2
Standard deviation	307,34	258,92
Individual 95% CI	(233,2; 422,4)	(203,9; 342,7)

Standard Deviations Comparison Chart
Blue indicates there is no significant difference.

Distribution of Data
Compare the spread of the samples.

Comments

- Test: There is not enough evidence to conclude that the standard deviations differ at the 0,05 level of significance.
- Comparison Chart: Blue intervals indicate that the standard deviations do not differ significantly.
- Distribution of Data: Compare the spread of the samples. Look for unusual data before interpreting the results of the test.

2-Sample Standard Deviation Test for TA and newfit
Diagnostic Report

Data in Worksheet Order
Investigate any outliers (marked in red).

What is the chance of detecting a difference?

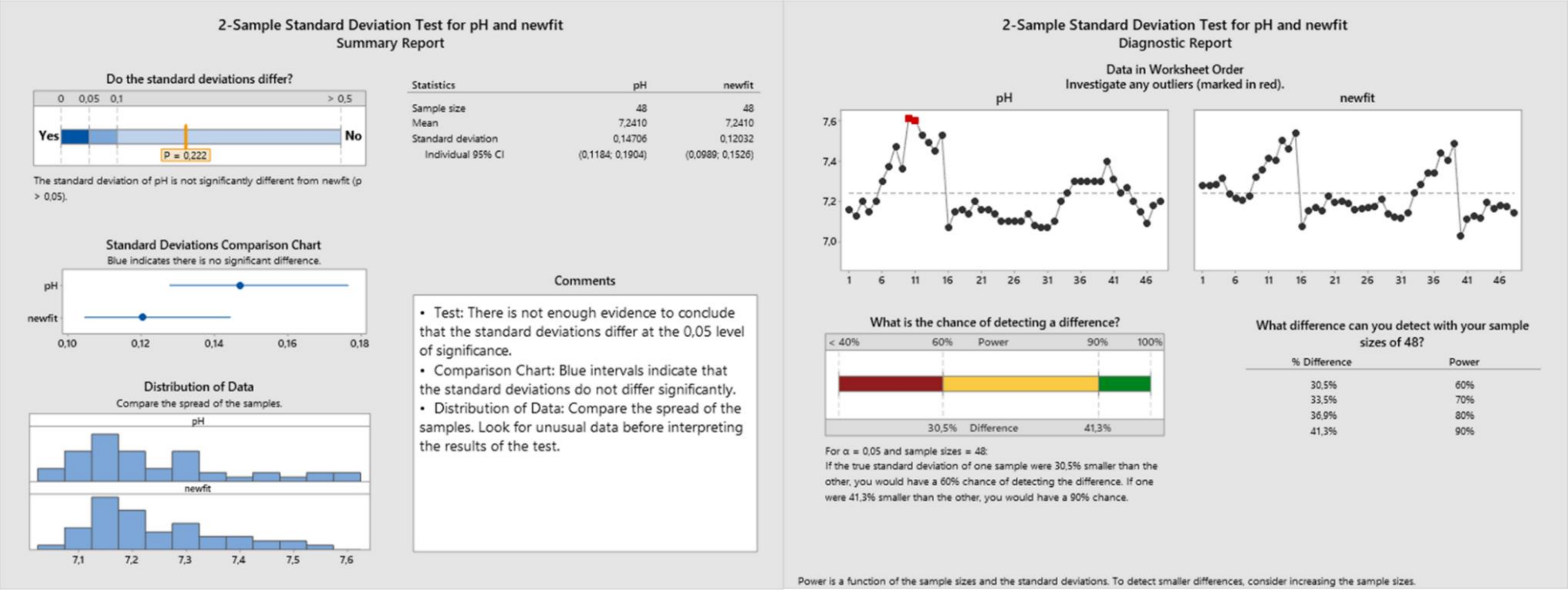
For α = 0,05 and sample sizes = 48:
If the true standard deviation of one sample were 35,9% smaller than the other, you would have a 60% chance of detecting the difference. If one were 47,8% smaller than the other, you would have a 90% chance.

What difference can you detect with your sample sizes of 48?

% Difference	Power
35,9%	60%
39,3%	70%
43,0%	80%
47,8%	90%

Power is a function of the sample sizes and the standard deviations. To detect smaller differences, consider increasing the sample sizes.

Figure 8-8 Two-samples standard deviation tested for TA and TA newfit.



2-Sample Standard Deviation Test for pH and newfit
Summary Report

Do the standard deviations differ?

The standard deviation of pH is not significantly different from newfit (p > 0,05).

Statistics	pH	newfit
Sample size	48	48
Mean	7,2410	7,2410
Standard deviation	0,14706	0,12032
Individual 95% CI	(0,1184; 0,1904)	(0,0989; 0,1526)

Standard Deviations Comparison Chart
Blue indicates there is no significant difference.

Distribution of Data
Compare the spread of the samples.

Comments

- Test: There is not enough evidence to conclude that the standard deviations differ at the 0,05 level of significance.
- Comparison Chart: Blue intervals indicate that the standard deviations do not differ significantly.
- Distribution of Data: Compare the spread of the samples. Look for unusual data before interpreting the results of the test.

2-Sample Standard Deviation Test for pH and newfit
Diagnostic Report

Data in Worksheet Order
Investigate any outliers (marked in red).

What is the chance of detecting a difference?

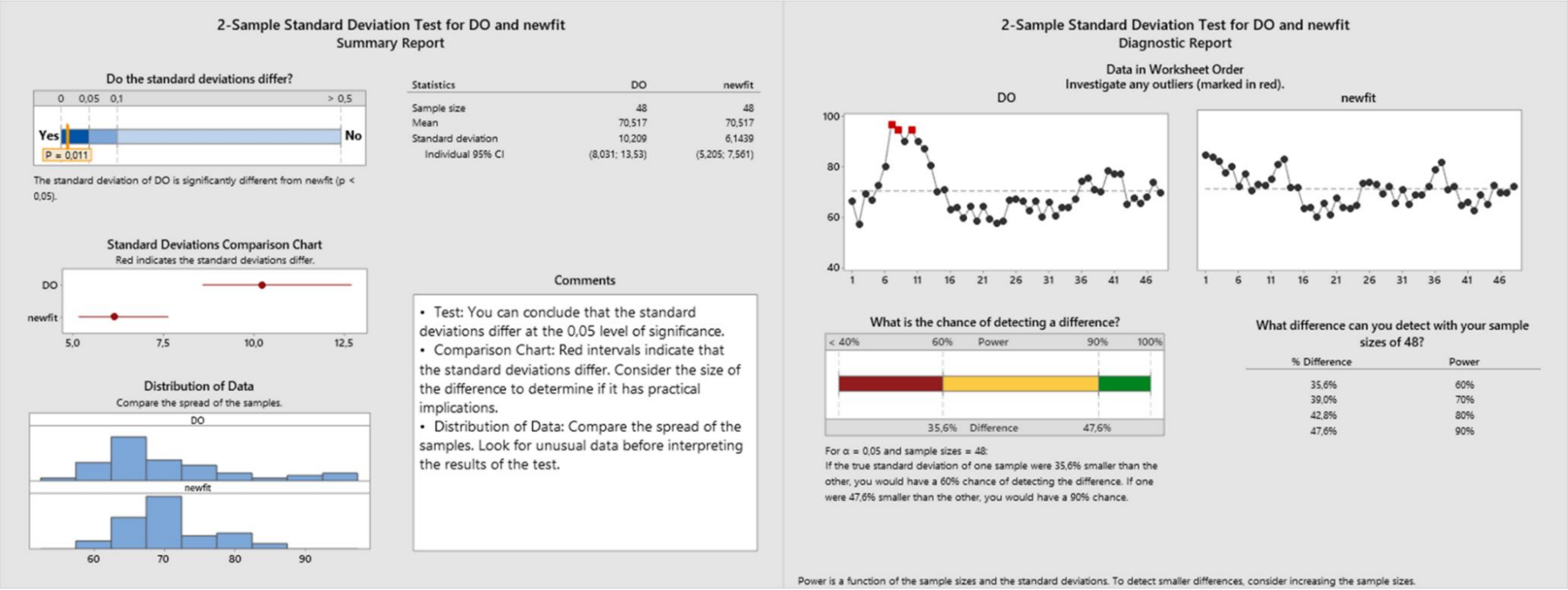
For α = 0,05 and sample sizes = 48:
If the true standard deviation of one sample were 30,5% smaller than the other, you would have a 60% chance of detecting the difference. If one were 41,3% smaller than the other, you would have a 90% chance.

What difference can you detect with your sample sizes of 48?

% Difference	Power
30,5%	60%
33,5%	70%
36,9%	80%
41,3%	90%

Power is a function of the sample sizes and the standard deviations. To detect smaller differences, consider increasing the sample sizes.

Figure 8-9 Two-samples standard deviation tested for pH and pH newfit.



2-Sample Standard Deviation Test for DO and newfit
Summary Report

Do the standard deviations differ?

The standard deviation of DO is significantly different from newfit (p < 0,05).

Statistics	DO	newfit
Sample size	48	48
Mean	70,517	70,517
Standard deviation	10,209	6,1439
Individual 95% CI	(8,031; 13,53)	(5,205; 7,561)

Standard Deviations Comparison Chart
Red indicates the standard deviations differ.

Distribution of Data
Compare the spread of the samples.

Comments

- Test: You can conclude that the standard deviations differ at the 0,05 level of significance.
- Comparison Chart: Red intervals indicate that the standard deviations differ. Consider the size of the difference to determine if it has practical implications.
- Distribution of Data: Compare the spread of the samples. Look for unusual data before interpreting the results of the test.

2-Sample Standard Deviation Test for DO and newfit
Diagnostic Report

Data in Worksheet Order
Investigate any outliers (marked in red).

What is the chance of detecting a difference?

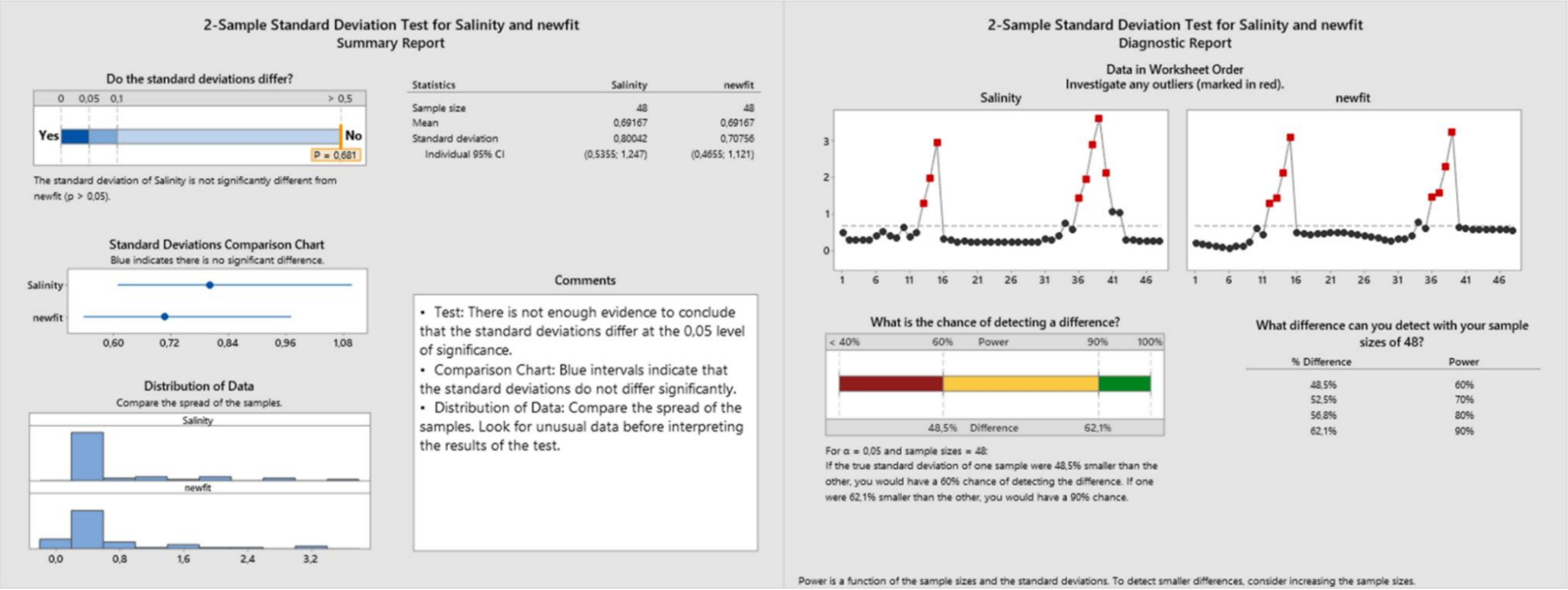
For α = 0,05 and sample sizes = 48:
If the true standard deviation of one sample were 35,6% smaller than the other, you would have a 60% chance of detecting the difference. If one were 47,6% smaller than the other, you would have a 90% chance.

What difference can you detect with your sample sizes of 48?

% Difference	Power
35,6%	60%
39,0%	70%
42,8%	80%
47,6%	90%

Power is a function of the sample sizes and the standard deviations. To detect smaller differences, consider increasing the sample sizes.

Figure 8-10 Two-samples standard deviation tested for DO and DO newfit.



2-Sample Standard Deviation Test for Salinity and newfit
Summary Report

The standard deviation of Salinity is not significantly different from newfit (p > 0,05).

Statistics	Salinity	newfit
Sample size	48	48
Mean	0,69167	0,69167
Standard deviation	0,80042	0,70756
Individual 95% CI	(0,5355; 1,247)	(0,4655; 1,121)

Comments

- Test: There is not enough evidence to conclude that the standard deviations differ at the 0,05 level of significance.
- Comparison Chart: Blue intervals indicate that the standard deviations do not differ significantly.
- Distribution of Data: Compare the spread of the samples. Look for unusual data before interpreting the results of the test.

2-Sample Standard Deviation Test for Salinity and newfit
Diagnostic Report

For α = 0,05 and sample sizes = 48:
If the true standard deviation of one sample were 48,5% smaller than the other, you would have a 60% chance of detecting the difference. If one were 62,1% smaller than the other, you would have a 90% chance.

What difference can you detect with your sample sizes of 48?

% Difference	Power
48,5%	60%
52,5%	70%
56,8%	80%
62,1%	90%

Power is a function of the sample sizes and the standard deviations. To detect smaller differences, consider increasing the sample sizes.

Figure 8-11 Two-samples standard deviation tested for salinity and salinity newfit.

Sampling location Kinvarra Castle Spring

Figure 8-12 Kinvarra Castle Spring location during the low tide. On the right there is a picture of the typical plants living in the intertidal area.

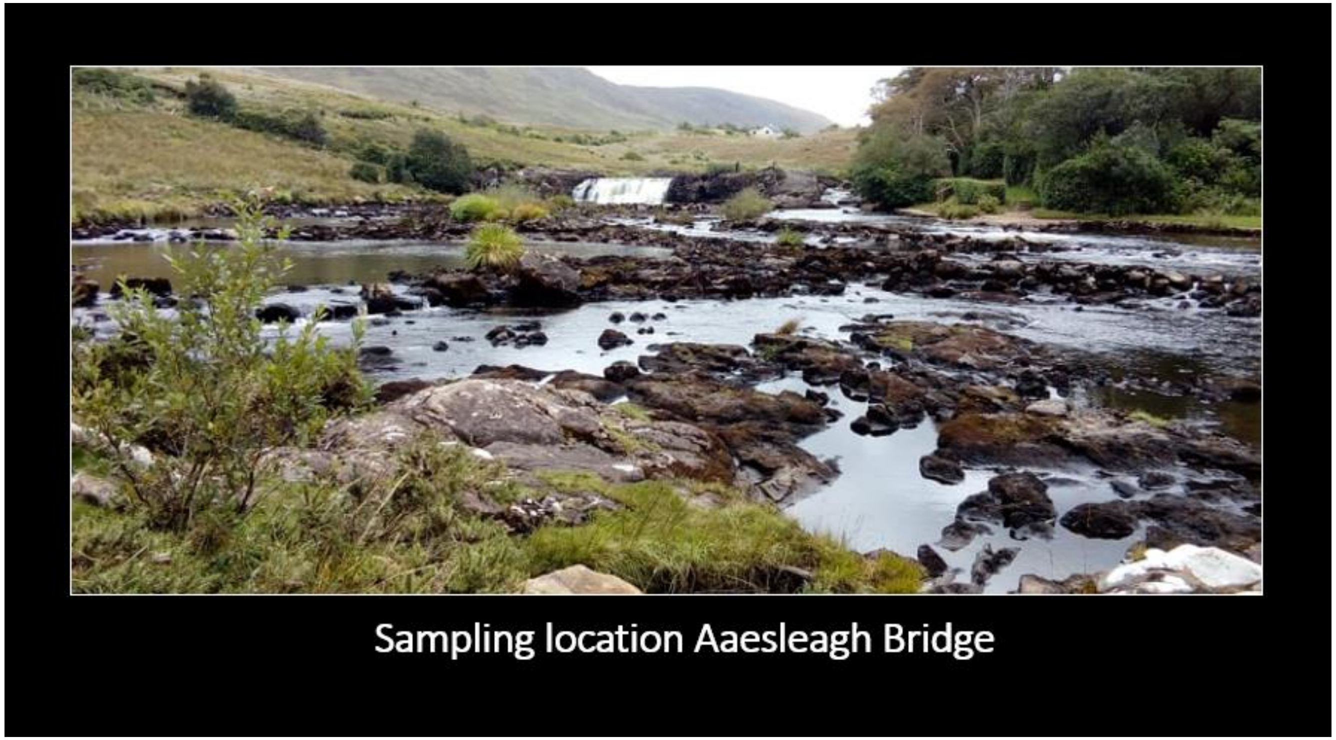


Figure 8-13 Aaeslagh Bridge location, thanks to the rocks, the morphology of the area and the absence of tidal excursion it was possible to sample from the rocks on the middle of the area, avoiding the puddles of standing water.