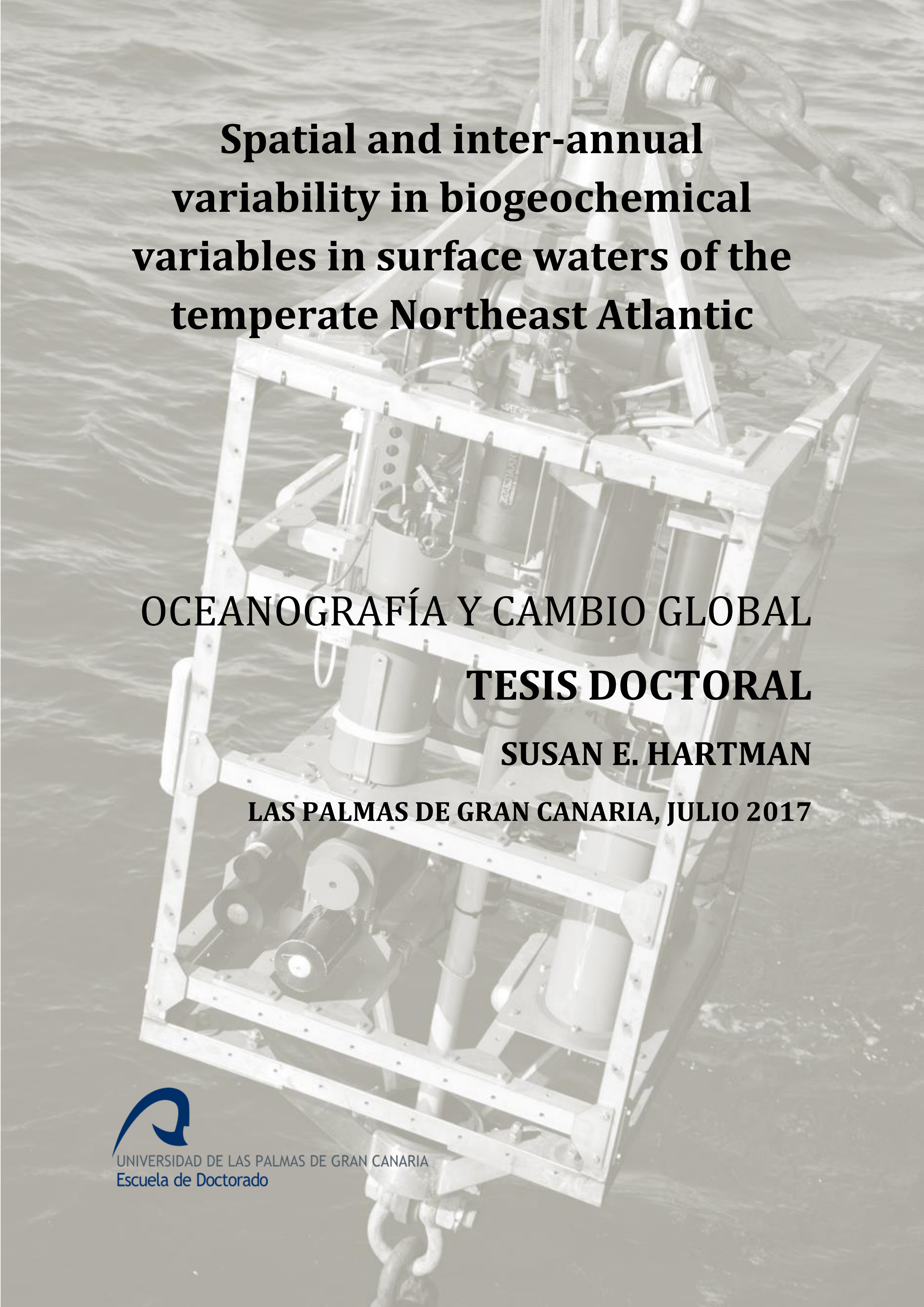

Spatial and inter-annual variability in biogeochemical variables in surface waters of the temperate Northeast Atlantic

OCEANOGRAFÍA Y CAMBIO GLOBAL

TESIS DOCTORAL

SUSAN E. HARTMAN

LAS PALMAS DE GRAN CANARIA, JULIO 2017

UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA
Escuela de Doctorado

UNIVERSIDAD DE LAS PALMAS
DE GRAN CANARIA

D SANTIAGO HERNÁNDEZ LEÓN COORDINADOR DEL PROGRAMA DE DOCTORADO EN OCEANOGRAFIA Y CAMBIO GLOBAL DE LA UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA,

INFORMA,

Que la Comisión Académica del Programa de Doctorado, en su sesión de fecha .... tomó el acuerdo de dar el consentimiento para su tramitación, a la tesis doctoral titulada " **Spatial and inter-annual variability in biogeochemical variables in surface waters of the temperate Northeast Atlantic**" presentada por la doctoranda Dª SUSAN E. HARTMAN y dirigida por el Doctor ALEX POULTON.
Asimismo, dicha Comisión tomó el acuerdo de aprobar su Mención Internacional al cumplir con todos los requisitos establecidos en la normativa vigente.

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UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA
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SUSAN E. HARTMAN

LAS PALMAS DE GRAN CANARIA

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Contents

Contenido en Español

Abbreviations

BATS	Bermuda Atlantic Time-series Study
Bbay	Bay of Biscay
C:N	Carbon to nitrate ratio
CO_2	Carbon dioxide
CO_3	Carbonate
CTD	conductivity, temperature and depth sensors
DCM	Deep Chlorophyll Maxima
DIC	Dissolved Inorganic Carbon (also Carbon Total - CT; Sum of CO_2)
ENACW	Eastern North Atlantic Central Water
ESTOC	European Station for Time-Series in the Ocean at the Canary Islands
GLODAP	Global Ocean Data Analysis Project
HCO_3	Bicarbonate
ISFET	ion-sensitive field-effect transistors
JGOFS	Joint Global Ocean Flux Study
MLD	Mixed Layer Depth
NAC	North Atlantic Current
NAO	North Atlantic Oscillation
NAS	Nutrient analyser
NCEP	National Centre for Environmental Prediction
NCP	net community production
NDIR	Non-dispersive infrared absorption
NERC	Natural Environment Research Council
NHF	Net Heat Flux
NO_3	Nitrate (also NO_2+NO_3, nitrite + nitrate; or HNO_3)
NP	New Production
O_2	Oxygen (also as DO, dissolved oxygen)
OWSM	Ocean Weather Station Mike
PAP-SO	Abyssal Plain sustained observatory
pH	defined as the negative log of the hydrogen ion concentration, H^+
PO_4	Phosphate, also as H_3PO_4
PP	Primary Production
Pro-C	Pro-oceanus CO_2 sensor
SOCAT	Surface Ocean CO_2 Atlas
SOO	ship of opportunity
SPG	Sub Polar Gyre
SST	Sea Surface Temperature
STG	Sub Tropical Gyre
TA	Total Alkalinity (also as AT, TALK)
UV	Ultraviolet
VOS	Voluntary observing ship

Abreviaturas

BATS	Estación de series temporales en Bermuda
Bbay	Bahía de Vizcaya
C:N	Relación Carbono a nitrato
CO_2	Dióxido de carbono
CO_3	Carbonato
CTD	Sensor de conductividad, temperatura y profundidad
DCM	Máximo profundo de clorofila
DIC	Carbono inorgánico disuelto (También carbono total - CT; Suma de CO_2)
ENACW	Agua central del Noratlántico este
ESTOC	Estación europea de series temporales en las Islas Canarias
GLODAP	Proyecto de análisis de datos globales oceánicos
HCO_3	Bicarbonato
ISFET	Transistores de efecto de campo sensible a iones
JGOFS	Estudio de flujos globales oceánicos combinados
MLD	Profundidad de la capa de mezcla
NAC	Corriente Noratlantica
NAO	Índice de oscilación del Atlántico Norte
NAS	Analizador de nutrientes
NCEP	Centro Nacional de Predicción Medioambiental
NCP	Producción neta comunitaria
NDIR	Radiación infrarroja no dispersiva
NERC	Consejo de investigación del Medioambiente natural
NHF	Flujo de calor neto
NO_3	Nitrato (también NO_2+NO_3, nitrito + nitrato; o HNO_3)
NP	Producción nueva
O_2	Oxígeno (también DO, oxígeno disuelto)
OWSM	Estación oceánica-meteorológica Mike
PAP-SO	Observatorio mantenido en la cuenca abisal de Porcupine
pH	Definido como el logaritmo negativo de la concentración de iones hidronio, H^+
PO_4	Fosfato, también H_3PO_4
PP	Producción Primaria
Pro-C	Sensor de CO_2 Pro-oceanus
SOCAT	Atlas Superficial oceánico de CO_2
SOO	Barco de oportunidad
SPG	Giro Subpolar
SST	Temperatura del agua superficial
STG	Giro Subtropical
TA	Alcalinidad total (también AT, TALK)
UV	Ultravioleta
VOS	Barco voluntario de observación

Resumen

Comprender el papel de los océanos en el ciclo global del carbono es esencial para poder realizar predicciones futuras de los efectos del cambio climático. Las medidas de alta frecuencia de series temporales mantenidas todo el año permiten aumentar el conocimiento de la variabilidad biogeoquímica en los océanos. De esta manera, el objetivo general de este estudio es caracterizar la variabilidad en la biogeoquímica del Atlántico noreste. Se han identificado las variables clave de las variaciones estacionales e interanuales en el contenido de nutrientes, carbono y producción primaria en la estación fija abisal Porcupine (PAP-SO), localizada a 49°N, 16.5°W en el Atlántico Noreste. Otras series temporales, tales como barcos de oportunidades entre el Reino Unido (UK) y España junto con muestreos intensos en la plataforma Europea Noroeste, muestran también la variabilidad regional y estacional en la biogeoquímica del Atlántico Noreste.

En primer lugar, se revisa el contexto histórico y los componentes de la estación PAP-SO. Al centrarnos en la biogeoquímica del océano superficial, comenzamos con la lista de los sensores utilizados en el estudio global. En la sección resumen se muestra la información de los sensores y la validación de los mismos con una revisión crítica de cómo se obtienen los datos y cómo se validan. A continuación, se presentan los resultados, mostrando la variación en nitratos superficiales en el Atlántico Noreste en la localización de PAP-SO. El objetivo era estudiar la variación estacional e interanual del suministro de nitratos, la mezcla y la productividad del área. En un futuro de calentamiento climático, la productividad puede disminuir debido a un aumento en la estratificación de la columna de agua. A lo largo de los tres primeros años de estudio de la serie, se observó una disminución tanto en el suministro de nutrientes como en la productividad en PAP-SO. En parte, la disminución en nitrato puede estar relacionado con la advección lateral de agua subtropical. Estos resultados soportan la hipótesis de que la advección lateral es importante en la región. La variación año tras año en el periodo del florecimiento primaveral se ha relacionado con la estabilidad de la capa superficial a través del cálculo de flujo de calor neto.

Posteriormente, se ha considerado una escala más larga, una década, en la serie de datos en PAP-SO. Para ello se ha considerado también datos de un barco de oportunidades que cruza esa parte del Atlántico Noreste. El objetivo era observar la variación interanual en la biogeoquímica que se produce en PAP-SO, en particular en el Sistema del carbonato. Se ha observado un aumento claro en la presión parcial del dióxido de carbono (CO_2) en las aguas superficiales de PAP-SO, consistente con el aumento de CO_2 en la atmósfera. Se ha confirmado que la región es un sumidero persistente de CO_2. La hipótesis de que el flujo de CO_2 hacia el océano cambiará con los años no ha podido ser confirmado dado que ha existido muy poca variabilidad en los índices climáticos y en la profundidad de la capa de mezcla a lo largo del periodo de estudio en PAP-SO. El estudio sí que ha mostrado variación en la relación de carbono inorgánico disuelto a nitrato (C:N) a lo largo del año, lo cual es importante ya que este ratio suele ser considerado constante en los modelos oceánicos.

Las observaciones hidrográficas, biogeoquímicas y los datos de trampas de sedimentos en PAP-SO, se utilizaron también para profundizar en la relación C:N. El objetivo era mirar la incorporación biológica de carbono y nitrato en la superficie y su transferencia hacia las aguas más profundas. Se calculó la productividad a partir de la disminución tanto de carbono como nitrato en la superficie y la comparación de las relaciones de exportación derivadas de estas dos estimaciones de la productividad superficial. La localización de la fuente de material exportado se investigó además utilizando técnicas de seguimiento de partículas. Se ha mostrado la relación entre la productividad superficial, el flujo profundo de carbono y la eficiencia con la que el material exportado se transfiere hacia aguas más profundas.

Al objeto de considerar la variación biogeoquímica en una región Atlántica más amplia, se utilizó 8 años de datos de series temporales obtenidos con un barco de oportunidad. Estos datos mostraban la variación estacional e interanual en el contenido de nutrientes superficiales entre UK y España. Se asociaron los inviernos más cálidos con menores profundidades de la capa de mezcla y menores concentraciones de nutrientes. Se calculó la productividad haciendo uso de datos de oxígeno mientras que la progresión del florecimiento se siguió viendo su evolución desde aguas fuera de la plataforma hacia los sitios más costeros. Por último y utilizando datos entre 2014 y 2015, se caracterizó la variabilidad biogeoquímica a lo largo de la plataforma europea noroeste. La variabilidad estacional en la hidrografía y en la biogeoquímica a lo largo de la plataforma se estudió en relación con la observada en PAP-SO y en el Atlántico Noroeste. Se ha mostrado, además, la influencia de la temperatura en la pCO_2, así como la variación regional en el flujo de CO_2 a lo largo de la plataforma continental.

La región del Atlántico Noreste es un área estudiada de forma frecuente; sin embargo, la importancia de considerar una estación de series temporales capaz de obtener tanto datos de alta resolución como medidas en invierno, hace especial este estudio. Se presenta una revisión crítica de los métodos utilizados para caracterizar los ciclos del carbono y del nitrato en el Atlántico Noreste. Se han utilizado, además, datos de barcos de oportunidad, de satélite y Argo para complementar los datos de series temporales y poder estudiar la variabilidad en la región del giro en el Atlántico Noreste. Estudios realizados utilizando gliders en PAP-SO, confirman que los sensores de la serie temporal se sitúan en la zona del máximo profundo de clorofila (DCM), que es una zona altamente productiva en los océanos y que no puede ser observada por los satélites. La combinación de datos hidrográficos y biogeoquímicos mostrados en esta tesis pueden ser utilizados para definir la variabilidad estacional e interanual en los procesos superficiales y su relación con la incorporación de carbono en aguas más profundas.

Summary

To make future predictions of the effects of climate change it is vital that the role of the ocean in the global carbon cycle is well understood. Year round, high frequency time-series measurements increase understanding of biogeochemical variability in the oceans. The aim of this study is to assess variability in the biogeochemistry in the northeast Atlantic. At the Porcupine Abyssal Plain sustained observatory (PAP-SO), at 49°N, 16.5°W in the Northeast Atlantic key drivers of both the seasonal and inter-annual variations in nutrients, carbon and productivity are identified. Other time-series, including a ship of opportunity running between the United Kingdom (UK) and Spain plus shelf wide sampling on the Northwest European shelf, show the regional and seasonal variation in biogeochemistry in the wider Northeast Atlantic.

Initially we review the historical context and the components of the PAP-SO. As we focus on the upper ocean biogeochemistry the list of sensors presented is pertinent to the whole study. Information on sensor choice and validation is updated in the synthesis section with a critical review of how data are obtained and validated. We then look at the results, showing the variation in nitrate in the surface waters of the Northeast Atlantic at the PAP-SO. The aim was to look at seasonal and inter-annual variations in nitrate supply, mixing and productivity. In a future warming climate productivity may decrease due to increased stratification of the water column. Over the first 3 years of this time-series a decrease in both nitrate supply and productivity was seen at the PAP-SO. In part the decrease in nitrate may be linked to the lateral advection of low nitrate sub-tropical waters. The results support the hypotheses that lateral advection is important in this region. The year to year variation in the timing of the spring bloom was linked to the stability of the surface layer through net heat flux calculations.

We then consider the longer, one decade, time-series at the PAP-SO. Supplementary data came from a ship of opportunity that crosses this part of the Northeast Atlantic. The aim was to look at year to year variations in the biogeochemistry at the PAP-SO and in particular the carbonate system. A clear increase in the partial pressure of carbon dioxide (CO_2) was seen in the surface waters at the PAP-SO, consistent with increasing CO_2 in the atmosphere. The region is confirmed as a perennial sink for CO_2. The hypothesis that CO_2 flux into the ocean would change from year to year could not be confirmed as there was little variability in the climate indices and mixed layer depths over this time period at the PAP-SO. This study showed variations in the dissolved inorganic carbon to nitrate (C:N) ratio through the year, which is important as this ratio is often taken as a constant in modelling studies.

Hydrographic, biogeochemical and sediment trap observations from the PAP-SO were then used to further investigate the C:N ratio. The aim was to look at the biological uptake of carbon and nitrate at the surface, and its transfer into deeper waters. Productivity was calculated from the drawdown of both carbon and nitrate at the surface and export ratios derived from a comparison of these two estimates of surface productivity. The source location of exported material was also investigated using particle tracking techniques. We showed the link between surface productivity, deep ocean carbon flux and the efficiency with which exported material is transferred to depth.

To consider biogeochemical variations in the wider Atlantic an 8-year time-series of ship of opportunity data was used. It showed the seasonal and inter-annual variation in surface nutrient data between the UK and Spain. The warmest winters were associated with the lowest mixed layer depths and winter nutrient concentrations. Productivity was calculated from oxygen data and bloom progression was followed from off shelf to the on-shelf sites. Finally more recent data, from 2014 to 2015, was used to look at biogeochemical variability around the Northwest European shelf. The seasonal variation in hydrography and biogeochemistry around the shelf is shown in contrast to the PAP-SO and the North Atlantic western approaches.

We showed the influence of temperature on pCO_2 and regional variations in CO_2 flux around the shelf.

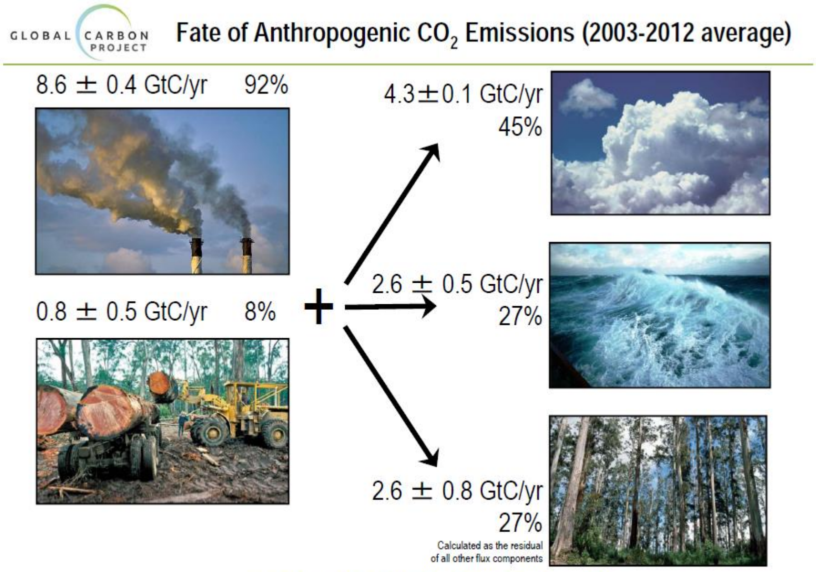
The Northeast Atlantic is a frequently studied region; however the strength of a time-series is in obtaining both high resolution data and the relatively rare winter measurements. We present a critical review of the methods used to look at the carbon and nitrate cycles in the Northeast Atlantic. Supplementary datasets from ships-of opportunity, satellites and Argo float data have been used which are complementary to the time-series data to study variability in this inter gyre region of the Northeast Atlantic. Recent studies using gliders at the PAP-SO confirm that the time-series sensors there are within the deep chlorophyll maxima (DCM), which is a potentially productive layer in the ocean that cannot be assessed by satellites. The combined hydrographic and biogeochemical data set presented here can be used to assess seasonal and inter-annual variability in surface processes and the linkages with carbon uptake at depth.

General Introduction

Background

Carbon dioxide (CO_2) is the second largest greenhouse gas after water vapour. CO_2 absorbs long wave radiation, enhancing radiative forcing and warming the surface of the Earth. Atmospheric CO_2 concentrations have increased by over 40% since pre industrial times, primarily from fossil fuel emissions and secondarily from changes in land use (Quéré et al., 2015). In 2014 atmospheric concentrations at Mauna Loa reached over 400ppm (co2now.org) and levels are predicted to reach 490 ppm by the end of the 21st century.

The ocean is a significant carbon store, absorbing more than one quarter of anthropogenic CO_2 emissions each year (Quéré et al., 2015 and Figure 1). The oceans absorb about 2 Pg C yr^{-1} (Wanninkhof et al., 2013), which will moderate the change in CO_2 in the atmosphere.



Source: Le Quéré et al 2013; CDIAC Data; Global Carbon Project 2013

Figure 1: The fate of Anthropogenic CO_2 Emissions (from Le Quéré et al., 2013)

The amount of CO_2 dissolved in seawater is often described by the equilibrium of CO_2 between the air and water. CO_2 in seawater is measured and reported as the partial pressure of CO_2 at the sea surface (more precisely expressed as fugacity or fCO_2). The exchange or flux of CO_2 between the air and surface seawater can be calculated from the air-sea CO_2 difference along with measurements of sea surface temperature, salinity and wind speed. The flux is modified by physical and biogeochemical processes that vary both temporally and spatially. As well as local variations in temperature and wind, the flux of CO_2 can be influenced by advection and large-scale thermohaline circulation in the ocean. The flux of CO_2 is further modified by biological uptake driven by nutrient availability and light.

In effect there are three main mechanisms that influence the uptake of CO_2 in the ocean: the physical or solubility pump; the biological or organic carbon pump and the carbonate counter pump (Heinze et al., 1991). The influence of these varies temporally and spatially across the ocean so that the globally estimated CO_2 flux map (Figure 2) shows regions with a larger and smaller annual uptake of CO_2. For example the productive North Atlantic has a particularly strong annual uptake of CO_2.

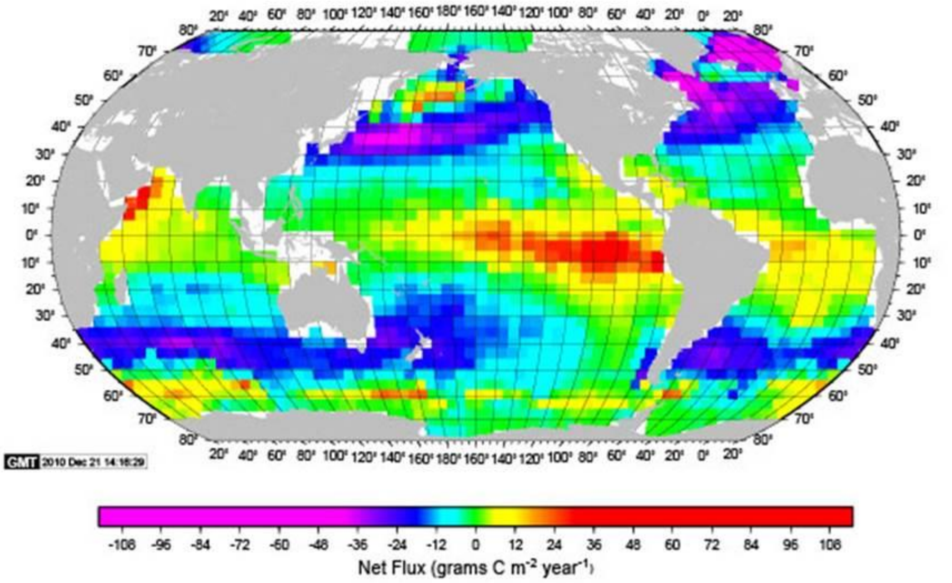


Figure 2: Climatological mean values of CO_2 flux in 4° Latitude by 5° Longitude box areas. Originally published in: Takahashi, et al., (2009)

The physical or solubility pump describes the physical processes influencing the amount of CO_2 dissolved in the water column, which is more soluble at lower temperatures. The thermodynamic flux of CO_2 into or out of the sea surface (Figure 2) is driven by the difference between the water and atmosphere pCO_2. It is influenced by the transfer coefficient 'k', which is based on wind speed-dependent formulations (eg: Nightingale et al., 2000) scaled to the temperature-dependent Schmidt number (eg: Wanninkhof, 1992 and later revision Wanninkhof, 2014).

The organic carbon pump is the rapid removal of CO_2 from the water by primary production (PP), which is the synthesis of organic compounds from carbon dioxide and nutrients through photosynthesis. This is followed by a slower compensating CO_2 flux into the ocean. The organic carbon pump has a profound impact on the marine carbon cycle as it favours CO_2 drawdown from the atmosphere turning it into organic matter (McGillicuddy et al., 1998). The drawdown of carbon and nutrients in the ocean is illustrated in the following equation (Anderson et al., 1995) of photosynthesis and the reverse process of remineralisation. The atomic ratio (or stoichiometry) of carbon, nitrogen, phosphorus and oxygen is derived from this. Known as the 'Redfield Ratio' (Redfield et al., 1963) this stoichiometry is broadly found in phytoplankton and throughout the deep oceans.

$$106\ CO_2 + 16\ HNO_3^- + H_3PO_4 + 78\ H_20 = C_{106}H_{175}O_{42}N_{16}P + 150\ O_2$$

carbon dioxide + nitrate + phosphate + water = carbohydrate + oxygen

PP results in depletion of surface CO_2 and nutrients and it occurs largely in the euphotic surface ocean, (where light attenuation ranges from ~1 up to ~10% of that at the surface; Mackey et al., 1995). The CO_2 and nutrients are taken up into organic matter and a proportion of this sinks to be exported out of the euphotic layer. The organic matter is remineralised in deeper water resulting in increasing nutrients and Dissolved Inorganic

Carbon (DIC) with depth. A fraction of the nutrients and DIC return to the surface through mixing and upwelling, fuelling further production. DIC is the sum of all the inorganic carbon species and is about 90% bicarbonate and 8% carbonate.

CO_2 is a very soluble gas (compared with oxygen), it also reacts with the seawater to form carbonic acid (Figure 3), which rapidly dissociates to form bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydrogen ions (H^+). The reactions of CO_2 in seawater are illustrated in Figure 3.

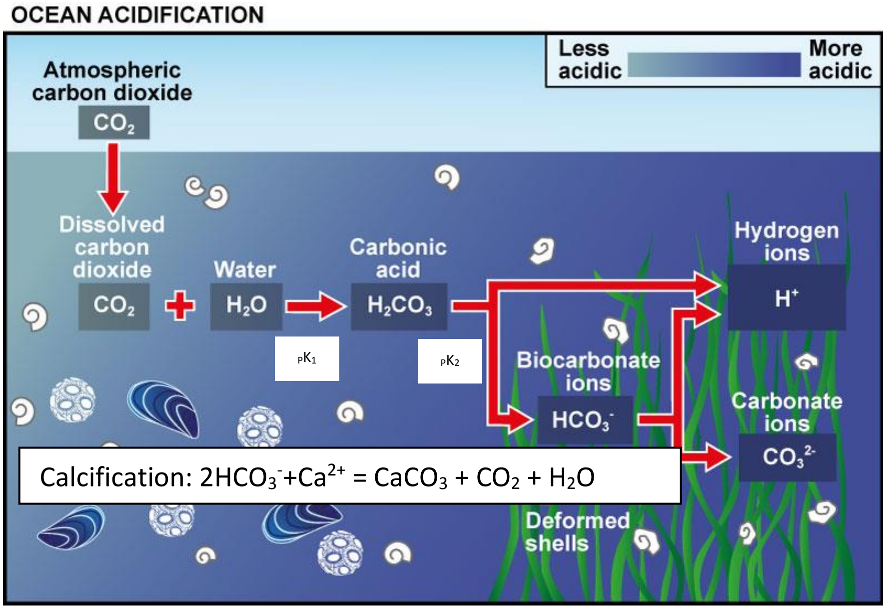


Figure 3: A schematic illustration of the carbonate system in the ocean including reversible reactions and dissociation constants leading to ocean acidification (adapted from a graphic by the University of Maryland, taken from www.oceanacidification.org.uk) with an equation for calcification overlaid on this.

The increase in seawater CO_2 tracks the increase in atmospheric CO_2 concentrations causing a shift in the carbonate system equilibrium balance (Figure 3). Calcification releases CO_2 so this pump has the opposite effect on CO_2 to the organic carbon pump and is known as the 'carbonate counter pump'. Calcification is driven by the uptake of bicarbonate by coccolithophores and other groups of organisms that create calcium carbonate shells. The equations for calcification have been overlaid onto Figure 3.

The oceans are presently mildly alkaline (~pH 8.1, where pH is defined as the negative log of the hydrogen ion concentration) but the increase in CO_2 uptake and in the hydrogen ions in seawater is driving a decrease in the oceanic pH, which is known as ocean acidification (OA). Many studies are looking at the potential impact of OA such as detrimental effects on calcification (eg: Riebesell et al., 2011; Smith et al., 2012; Schermer et al., 2016).

Trends in pH (and CO_2) have been detected in oceanic time-series sites such as ALOHA near Hawaii (http://aco-ssds.soest.hawaii.edu/ALOHA). Data from the ALOHA site (Figure 4) shows a large seawater CO_2 increase and associated pH decrease over a 20 year time period. There is also a large seasonal variation, which makes measurement throughout the year necessary. The predicted global trend is a 0.002 pH decrease per year and a decrease of up to 0.5 pH units by the end of the 21st century (Bates et al., 2014). The Bates et al., (2014) study included trends for the North Atlantic time-series stations at Bermuda (BATS) and the Canary Islands (the European Station for

Time-Series in the Ocean at the Canary Islands, ESTOC).

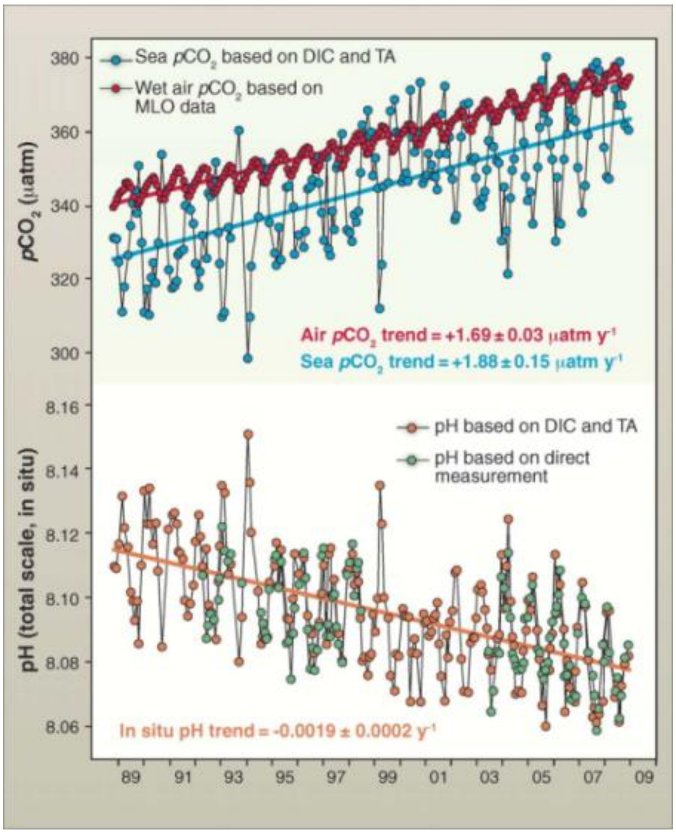


Figure 4: Data from the ALOHA time-series, showing increased CO_2 in both the atmosphere and seawater, with a corresponding decrease in seawater pH.

Changes in pH may not be directly proportional to the increase in CO_2 as there are other water mass characteristics to take into consideration such as the alkalinity. Alkalinity is the ability of the water to neutralise protons (H^+), so provides a 'buffering capacity' to changes in pH. 'Total alkalinity' (TA) is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids) over proton donors in 1kg of sample. TA is related to the bicarbonate and carbonate concentrations in the seawater, with contributions from other proton acceptors including boron, phosphate and silicate. The amount of alkalinity will determine the potential pH change by CO_2; so if DIC rises faster than the TA then pH will decrease**.** The process of calcification removes the surface DIC and increases it at depth (Heinze et al., 1991) then dissolution of the calcium carbonate in deep waters resupplies alkalinity to the system. Global surface ocean alkalinity maps (Carter et al., 2014; Fry et al., 2015) reveal a pole-ward increase of alkalinity. The distribution of alkalinity is influenced by physical and biogeochemical processes but is independent of CO_2 dissolution.

The competing processes of calcification and carbonate dissolution; CO_2 uptake and release; photosynthesis and respiration and their effect on DIC, TA and pH are all summarised in Figure 5.

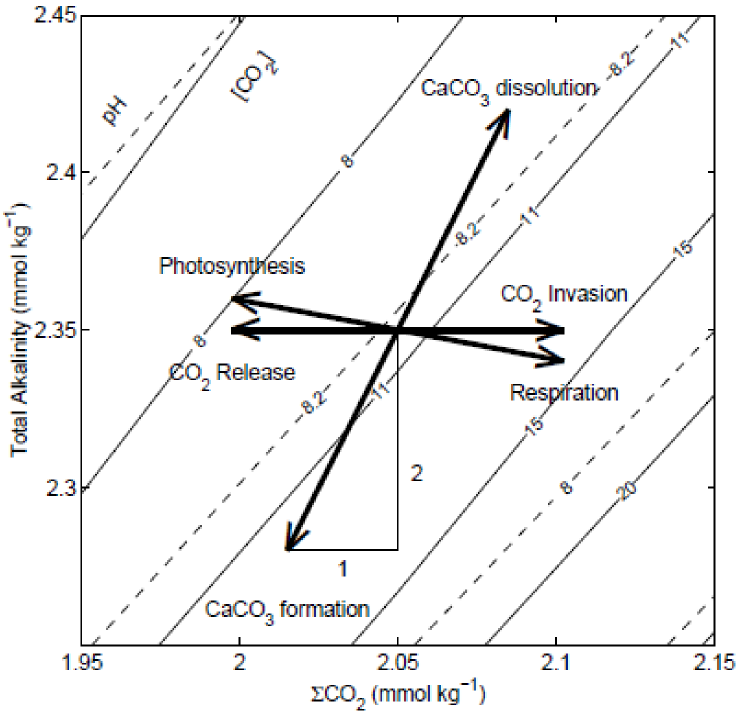


Figure 5: Schematic of total alkalinity and sum of carbonate species (DIC, ΣCO_2), with contours of CO_2 (solid lines) and pH (dashed lines), showing the competing processes acting on these four variables (after Zeebe & Wolf-Gladrow, 2001).

Some of the CO_2 taken up by the ocean and into organic matter is recycled in the water column. In turn some of the organic material sinks in the water column and so carbon is sequestered to depth. The North Atlantic is an important region to study the uptake of CO_2 by the ocean because it is the largest store of anthropogenic carbon (Khatiwala et al., 2013). Some 38% of the anthropogenic carbon is stored in the North Atlantic (Sabine et al., 2004). These high inventories are seen in the map in Figure 6 and are largely a consequence of deep water formation in the North Atlantic.

Despite the enormous increase in observations, temporal and regional variability in surface carbonate parameters (and knowledge of their physical and biogeochemical controls) are still quite poor (Steinberg et al., 2001; Wanninkhof et al., 2013). There is a need to measure the biogeochemical variability in the oceans and to understand the links between different parts of the carbon and nutrient cycles to make any future predictions on potential CO_2 uptake.

This thesis includes an introduction to the carbon and nutrient cycles and why these measurements are important. Four of the chapters focus on a long running time-series site in the North Atlantic, the Porcupine Abyssal Plain Sustained Observatory (PAP-SO). The first presents the measurements made at the PAP-SO, focusing on the background and context, plus the methods employed. The next two present results for measurements of the seasonal and inter-annual variability in surface biogeochemistry. The fourth chapter looks at the influence of the surface processes deeper in the water column critical for long term storage. The PAP-SO data are supplemented with other data sources that are described here. The results are synthesised, summarising the main findings and placing the work into the wider global context. With regional comparisons in mind a fifth chapter considers on and off shelf biogeochemical data from a ship of opportunity time-series between the UK and Spain. The final chapter considers the PAP-SO data in relation to biogeochemical data from the Northwest European Shelf.

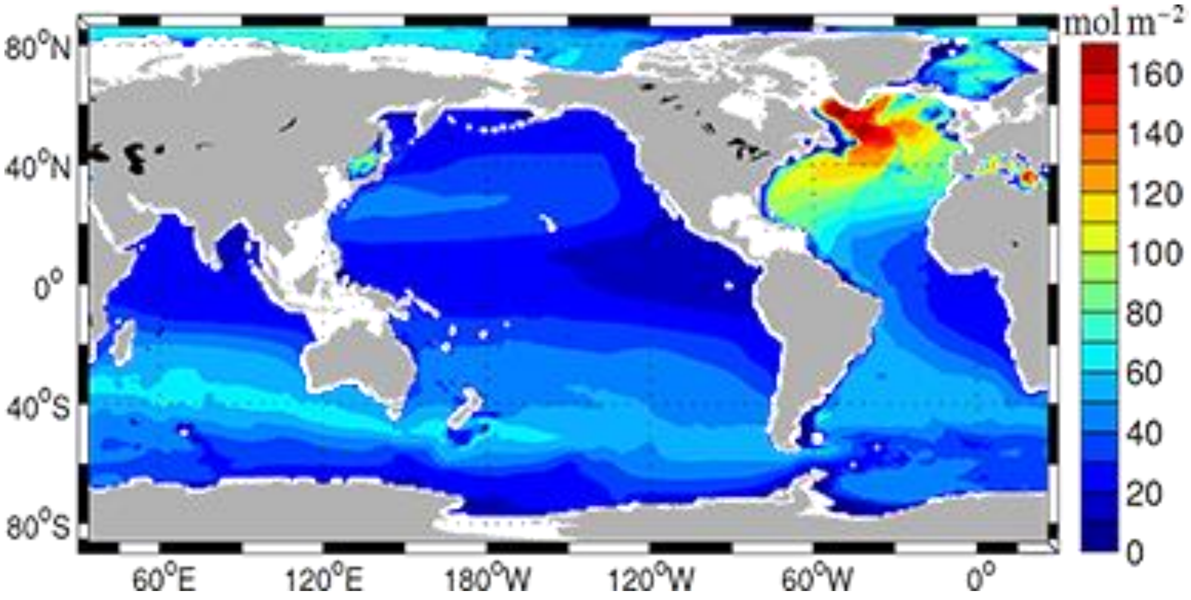


Figure 6: Column inventories of anthropogenic carbon in the ocean shows the importance of the North Atlantic Ocean to CO_2 uptake. (Source: Khatiwala et al., 2013).

Oceanic carbon and nutrient cycles in the North Atlantic

Primary Production (PP) depends on light, nutrients and grazing at the temperate latitudes considered in this study. Light is limiting in the winter (and with depth) so light and temperature will control the seasonal and daily CO_2 cycle and drawdown through photosynthesis. The classical hypothesis of bloom development in the North Atlantic (Sverdrup, 1953) is that heat input in spring results in stratification of the water column. A bloom develops in the stratified water when there is sufficient light and nutrients. The spring bloom occurs when the mixed layer depth decreases to a point that production is greater than respiration. As productivity proceeds the decreasing nutrients start to limit growth until they are again mixed back to the surface in autumn. The Critical Depth is the limit of the productive zone resulting from the balance between vertical light penetration and vertical mixing, first quantified by Sverdrup (1953), reformulated by Nelson & Smith (1991). There are many other hypothesis of bloom formation as blooms may occur before or in the absence of stratification (Townsend et al., 1992). For example the critical turbulence hypothesis (Huisman et al., 1999) suggests that blooms can occur when convective mixing has reduced sufficiently. Another example is Behrenfeld (2010), who suggested that the decoupling of phytoplankton and micro-zooplankton after winter will result in net phytoplankton growth through a reduction on grazing.

As the spring bloom continues nutrients are used up and become limiting, although they can be replenished through storm events (Rumyantseva et al., 2015). Of the inorganic macro-nutrients nitrate (NO_3) is one of the most widely measured as it is limiting to phytoplankton growth in many regions of the surface ocean. Globally up to 75% of the surface ocean is nitrate limited (Duce at al., 2008). Nitrate limitation has also been shown in experiments (Moore et al., 2013). The growth of some species may be enhanced by increased CO_2 (Riebesell et al., 2011), but carbon is not generally limiting to the growth of photosynthetic organisms.

Primary production can be estimated from remote sensing satellites (Falkowski et al., 1998). However after the initial bloom period a maximum in the concentration of chlorophyll below the surface develops, generally between the thermocline and nutricline at around the 1% light level. This seasonal subsurface maxima occurs in temperate regions and is known as the Deep Chlorophyll Maxima (DCM). The timing, location and causes of the DCM varies widely (Cullen, 1982). The occurrence of the DCM means that remote sensing may not detect all of chlorophyll so in order to get an accurate estimate of productivity below the surface *in situ* subsurface measurements are required.

From the view point of the oceanic carbon cycle the measurement of productivity that can best be related to the carbonate system is the net community production (NCP). NCP is the sum of new and regenerated production where new production is estimated by considering changes in the concentration of nitrate (Dugdale & Goering, 1967). New production is supported by the input of nitrate into the euphotic zone through upwelling and horizontal mixing, and also by processes such as atmospheric deposition and nitrogen fixation (Gruber, 2009; Sarmiento & Gruber, 2006). The growth of autotrophs or productivity can be inferred from the net uptake of nutrients or DIC (Bargeron et al., 2005) or by an increase in dissolved oxygen (Ostle et al., 2015) in the euphotic zone. NCP represents the organic carbon (both particulate and dissolved) available for export out of the euphotic zone or to be utilised by higher trophic levels. On an annual basis, assuming the system is in steady state, export production is considered to be equivalent to new production (Eppley & Peterson, 1979).

To calculate new production from the net annual flux of nitrate (Eppley & Peterson, 1979; Henson et al., 2003) there must be a conversion to carbon units. The conversion to carbon units is done on the basis of the Redfield ratio (Redfield et al., 1963), which is a key variable of marine biogeochemistry (Falkowski et al., 2000). In particular the Redfield C:N is an important constant in many models relating the capacity to take up carbon to a unit of nitrogen in the ocean. Many recent studies suggest however that the Redfield ratio is not constant, although there is a consensus view that it is relatively fixed on a global scale (Sterner et al., 2008). In the open ocean an averaged C:N of 6.6 is often assumed (Redfield et al., 1963) in the calculation of new production.

In detail the Redfield Ratio appears to vary with region and depth (Sterner et al., 2008). Changes in the C:N can result from many factors such as nutrient status, light intensity and species composition. These factors may be controllable in laboratory studies but in the natural world there is a heterogeneous mix and several studies report a C:N greater than the Redfield ratio in the inorganic fraction. For example C:N ratio can vary with light levels and this may result in the increase in C:N seen from spring to summer at northern latitudes (Bates at al., 2005). High C:N may be due to an increased drawdown of DIC over nutrients or preferential mineralisation of carbon rich organic material and is known as carbon overconsumption (Sambrotto et al., 1993). Coastal systems tend to release CO_2 to the atmosphere because of the contrasting elemental C:N stoichiometry of terrestrial organic matter decomposition and aquatic primary production. Organic material carried to the coast by rivers typically has a high C:N (30:1) whereas organic matter produced by phytoplankton in coastal systems has C:N near 7:1 (Bauer et al., 2013).

The Northeast Atlantic

The general ocean circulation in the Northeast Atlantic is dominated by the north-eastward extension of the Gulf Stream, known as the North Atlantic Current (NAC). The NAC is an important pathway for the advection and transport of relatively warm, nutrient and oxygen-rich surface water towards the European coasts (Williams et al., 2011). The NAC also marks the boundary between the Sub Polar Gyre (SPG) and the Sub Tropical Gyre (STG) around 40°N. The position of the NAC varies from year to year in the temperate North Atlantic. The approximate position of the NAC is shown on the map in Figure 7.

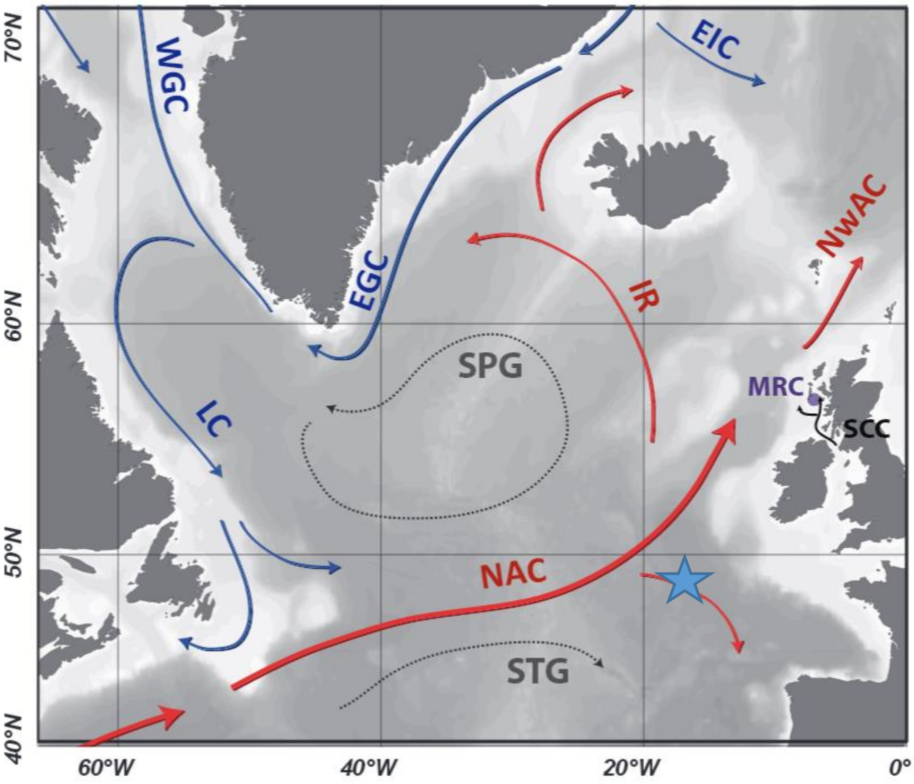


Figure 7: Major surface circulation features of the North Atlantic showing how sub-polar and sub-tropical (SPG and STG) waters meet, mix, and feed into the North Atlantic Current (NAC). Red arrows show main branches of the warmer more saline North Atlantic Current (NAC). Blue arrows show the main cooler fresher East Greenland Current (EGC) and Labrador Current (LC). The blue star shows the position of the PAP-SO. Adapted from Dourarin et al., 2016 who used the map to illustrate the MRC (Mingulay Reef Complex) and SCC (Scottish Coastal Current) on the Northwest European shelf, that are not discussed further

The seasonal variation in seawater pCO_2 differs between locations in the Atlantic (Bates et al., 2014) as the warming and cooling of seawater alters CO_2 solubility. Warming surface water has a reduced capacity to dissolve CO_2 while cooling elevates the CO_2 solubility and more CO_2 is absorbed. The extent of biological uptake, air-sea gas exchange, and the amount of CO_2 supplied by upwelling and mixing from the deeper waters will interact with these processes (Takahashi et al., 2014).

In the oligotrophic Sub Tropical Gyre (STG) the upper water column is permanently stratified so annual productivity is lower and less seasonally variable. Nutrients and DIC are supplied to the productive surface waters through eddy pumping and convection processes. Winter convection is important in the east of the STG; whereas eddy pumping is a more important source of nitrate to the surface in the western STG (Cianca et al., 2007). The seasonal cycle of seawater pCO_2 in the STG is dominated by temperature, with a single summer maximum and a single winter minimum (Bates et al., 1996; González-Dávila et al., 2003). The STG is a small carbon sink or possibly a CO_2 source region (McKinley et al., 2016).

In the SPG the seasonal cycles of nutrients and carbon are controlled by a strong seasonal cycle of deep winter mixing and primary production. Convection leads to an increase in nutrient and DIC supply to the surface in winter, then there is a decrease in the spring due to the development of the spring bloom. The SPG is productive for about 7 months of the year (Ostle et al., 2015) and CO_2 is taken up through photosynthesis in the production of organic matter.

There is a high solubility of CO_2 in the SPG due to the lower sea surface temperature (SST) and the stronger intensity of winter mixing. The dominant control in regulating spatial DIC patterns is sea surface temperature, but nitrate also plays an important role due to its relationship with biological uptake and upwelling. DIC and nutrients tend to co-vary, and show a predictable seasonal pattern, so relationships between SST and nitrate can be used to describe the global distribution of surface DIC (Lee et al., 2000).

The Northeast Atlantic region is important in the global carbon cycle and is a substantial sink of CO_2 with anthropogenic carbon accumulation at depth. In particular the sub-polar Northeast Atlantic is currently a strong sink for the CO_2 although the amount of CO_2 taken up by the ocean would be expected to vary from year to year, due to variations in mixing and productivity (Schuster & Watson, 2007). It is essential that processes that may cause variations in the capacity of the ocean to uptake CO_2 in the future are studied.

Importance of climate change

Changes in the amount of CO_2 absorbed into the ocean have implications for the global carbon cycle and importance of the oceans as a carbon sink in the future. There are various feedbacks on the carbon system that make future changes difficult to predict. For example increased stratification of the water column would be expected in a warming ocean and this could influence future carbon uptake in the surface ocean. Increased stratification in a warming climate would also potentially decrease nitrate supply to the surface; decreasing PP and consequent CO_2 uptake (Duce et al., 2008; Behrenfeld et al., 2010). Changes in CO_2 uptake would influence future trends in acidification. Likewise the transfer of CO_2 into organic matter and into the deeper water column would potentially decrease with increased stratification. As the extent of the STG is expanding (Henson et al., 2009) a future scenario for the Northeast Atlantic may be decreased productivity in this region. Variations in productivity will influence zooplankton distribution and ultimately relate to fish stock dynamics (Henson et al., 2009).

The North Atlantic Oscillation (NAO) is the dominant mode of the atmospheric pressure variation over the North Atlantic (Marshall et al., 2001). The NAO is used as an indicator of atmospheric variability in the northern hemisphere (Osborn et al., 1999) and is strongly expressed in the atmosphere in winter. The NAO is an indicator of year to year variability in the North Atlantic as it impacts surface hydrography (Schuster & Watson, 2007) and has been linked to changes in nutrient supply to the surface ocean (Cianca et al., 2007). A high NAO results in warmer, wetter conditions in northern Europe and drier condition in the south and in the sub-polar gyre a deeper mixed layer depth (Cullen et al., 2001; Jiang et al., 2013). It has been suggested that there is a decreasing trend in NAO over the next century (Osborn et al., 1999). Decreased winter mixing (low NAO) would imply more stratification and a barrier to nutrient exchange and consequent decreases in productivity.

The NAO is also an important indicator of inter-annual variability in CO_2 flux. A shift from negative to positive NAO was associated with a decrease in surface pCO_2 in the sub-tropical gyre (Watson et al., 2009). Detecting the influence of the NAO has to take into account that there is often a lag time in seeing the effects due to the time taken for water mass advection and this is dependent on where the measurements are made. For example at the ESTOC site the oceanic response is delayed by 3 years relative to the shifts in the NAO and may be more directly related to another climatic indicator, the East Atlantic pattern (González-Dávila et al., 2007; Santana-Casiano et al., 2007).

Henson et al., (2009) showed decadal variability in bloom timing in the Northeast Atlantic from 1959 to 2004. However there was no trend in productivity that could be related to climate change. Henson et al., (2009) identified a transition zone between the SPG and STG where there was a large variability in the timing of the spring bloom (see Figure 8). A positive NAO phase was associated with expansion of the SPG, when the transition zone shifted south resulting in later bloom timing. In a negative NAO phase the transition zone was shifted north and the spring bloom started earlier. A shift in the transition zone would have consequences for the timing of CO_2 drawdown within this part of the Northeast Atlantic.

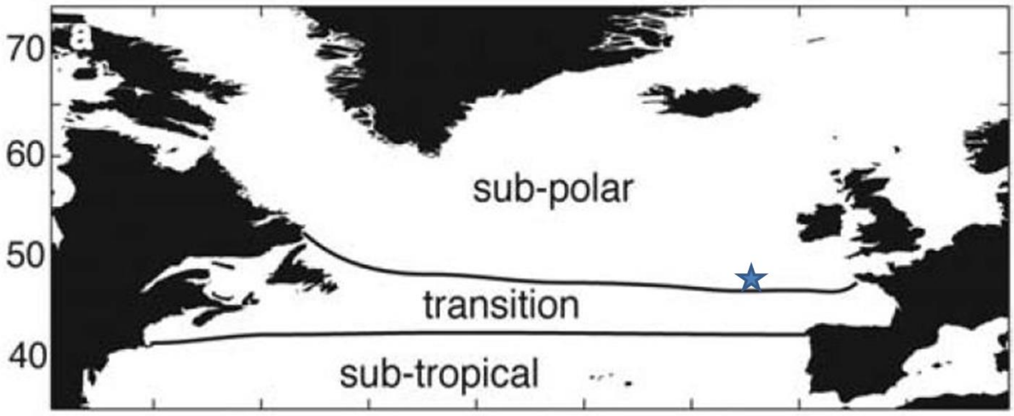


Figure 8: The position of the PAP-SO (shown as a star) relative to the mean conditions for the position of the SPG, STG and transition zone (after Henson et al., 2009).

Measurement techniques

Predicting the effects of anthropogenic pressures and climate change requires knowledge of the role of the ocean in the global carbon cycle (Steinberg et al., 2001). Studies looking at the physical and biological controls on CO_2 *in situ* are particularly important in the natural environment. This requires long term, high resolution nutrient and carbon observations to assess natural variability and quantify perturbations and trends that may be due to climate change.

Some of the most common oceanographic measurements made after salinity and temperature are dissolved oxygen and inorganic nutrients. Dissolved Oxygen (DO) is the amount of oxygen a volume of water holds and is dependent on temperature and the balance between primary production and respiration. Oxygen enters the surface of the ocean through diffusion from the atmosphere or is produced *in situ* by photosynthetic organisms (photosynthesis) and is removed by respiration. Oxygen in seawater can be measured in the laboratory using the Winkler technique (Dickson, 1994) or using *in situ* sensors (eg: Hydes et al., 2009).

The inorganic macro nutrients measured are nitrite and nitrate (NO_2^- and NO_3^-, together referred to as nitrate), phosphate and silicate. The nutrients are measured on an auto-analyser in the laboratory using colorimetric techniques (eg: Grasshoff, 1976). Miniaturised auto-analysers and sensors for measuring nutrients *in situ* have been developed (eg: Johnson et al., 2009).

There are four variables of the carbonate system that can be measured: DIC, total alkalinity (TA), pH and CO_2. The carbonate system can be characterised from the measurement of any two of these variables using the CO_2SYS toolbox (Lewis et al., 1998). The CO_2SYS toolbox must be used with appropriate dissociation constants (Dickson & Millero, 1987; Dickson, 1990). Any measurement errors and uncertainty in dissociation constants will propagate through the calculations and increase uncertainty in the output. Although there are acknowledged errors in calculations (Lee et al., 1997) some carbonate pairs have lower errors associated with them (Ribas-Ribas et al., 2014). Ancillary data for salinity, temperature and the inorganic macro-nutrients is vital to these calculations.

Dissolved inorganic carbon (DIC, C_T) is the sum of the concentrations of dissolved CO_2, bicarbonate (HCO_3) and carbonate (CO_3). DIC tracks changes in carbon and is independent of temperature and pressure.

Total Alkalinity (TA, TALK, AT) is defined as 'the number of moles of H^+ equivalent to the excess of proton acceptors in 1 kg of sample' and indicates the ability of seawater to neutralise protons (H^+) 'buffer capacity'. In the open ocean alkalinity is considered to be a quasi-conservative parameter as it is influenced in a similar way to salinity through evaporation, precipitation and mixing (Lee et al., 2006), although alkalinity is also influenced by photosynthesis and remineralisation. Open ocean salinity can be used to predict TA using the linear relationship between TA and salinity, which is regionally defined (Lee et al., 2006).

pH is a measure of the acidity or basicity of a solution and is defined as 'the negative of base 10 logarithm of the hydrogen ion concentration of a solution'. pH has been expressed on a number of different scales valid in seawater such as the total proton scale, the seawater scale and the free scale (Schuster et al., 2009). pH is not independent of temperature and pressure changes.

Carbon dioxide (CO_2) dissolves in the ocean to form carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) as shown in Figure 3. The concentration of CO_2 in seawater is expressed as the partial pressure (pCO_2) which will change with temperature and pressure changes. pCO_2 measurements do not take into account the non-ideal behaviour of CO_2 in sea water at atmospheric pressure so carbon dioxide may also be recorded as the fugacity (fCO_2). fCO_2 is the partial pressure of CO_2 (pCO_2) corrected for non-ideal behaviour of the gas (Bakker et al., 2013; Pfeil et al., 2012).

Currently DIC and TA measurements are made in the laboratory (Mintrop, 2010), whereas pH and CO_2 can be measured using sensors (Johnson et al., 2009; Fiedler et al., 2013).

Platforms for measurements

Long term monitoring programs are needed to detect the trends in these variables however *in situ* biogeochemical sensing in the marine environment is challenging. The environment is hostile (e.g. remote, dark, corrosive) and characterised by a large range in temperature and pressure. Additionally high levels of precision coupled to long-term stability are required (Mowlem et al., 2008).

Remote sensing by satellites can provide estimates over a wide area for many variables, such as sea surface temperature, salinity and primary production. The measurements rely on algorithms derived from *in situ* measurements and many variables cannot as yet be directly estimated from satellite measurements.

There is little restriction on the types of variables that can be measured at sea on-board ships or analysed in laboratories ashore following *in situ* sample collection. Process studies from research vessels can focus on regional and basin scales and there are many examples of studies that show the temporal and spatial variation of CO_2 (eg: Sabine et al., 2002; Bates et al., 2006; Clargo et al., 2015). Large data synthesis efforts collate many decades of full depth surveys within projects such as Carina (CARbon dioxide IN the Atlantic Ocean) and GLODAP (Global Ocean Data Analysis Project) (eg: Key et al. 2004 and 2010). Repeat transect surveys offer the possibility to create time-series on a basin wide scale. Annual occupation of the Ellett Line for example in the Northeast Atlantic has provided eight years of full depth carbonate measurements and calculations of anthropogenic carbon uptake (Humphreys et al., 2016).

Ships of opportunity (SOOs) or Voluntary Observing Ships (VOS) are particularly effective for providing surface measurements especially if they are on repeatable, year-round, trans-basin repeat routes (Hydes et al., 2003). When the SOO is a ferry the sensor package on-board is referred to as a 'Ferry-Box'. An example was the UK to Spain route on the *Pride of Bilbao* (P&O ferries) that had a Ferry-Box on-board for 8 years (Jiang et al., 2013). The *in situ* measurements on a SOO can be compared with on-board standards and sampling to assure quality. There has been a substantial effort to get carbon dioxide data from VOS into large quality controlled data bases such as SOCAT (Surface Ocean CO_2 Atlas; Bakker et al. 2014; Pfeil et al. 2012). For example a UK to Caribbean route transects the Atlantic on a monthly turn around and frequent samples are taken on this route to validate the measurements made underway (Hartman et al., 2010a). Results from the route have identified year to year variations in carbon uptake in the North Atlantic (Schuster & Watson et al., 2007).

Argo floats cover large regions of the world's oceans and have the advantage of providing depth profiles. Biogeochemical measurements from floats (eg: Johnson et al., 2009; Fiedler et al., 2013; Hemsley et al., 2015) are still relatively rare compared with hydrographic measurements, especially where sensors are large or have high power requirements (Henson et al., 2016).

Open Ocean moorings provide high resolution data at a single point in the ocean. They can be built into large networks. Neptune Canada is a good example of this where the moorings are cabled to provide power and so there is no restriction on sensor size or power usage (Barnes et al., 2008). In Europe the FixO3 initiative (Lampitt et al. 2014; www.fix03.eu) incorporates existing time-series sites into a network of open ocean deep water moorings. The FixO3 network includes biogeochemical measurements and aims to standardise procedures used to collect data. On a global scale 'Oceansites' (Send et al., 2010; www.oceansites.org) is a worldwide network of ocean moorings. Taking into account the 'footprint' of each site (for each biogeochemical variable) then this network is representative of between 9% and 15% of the global surface ocean (Henson et al., 2016). The map in Figure 9 shows the Oceansites observatories that have (or plan to have) biogeochemical measurements.

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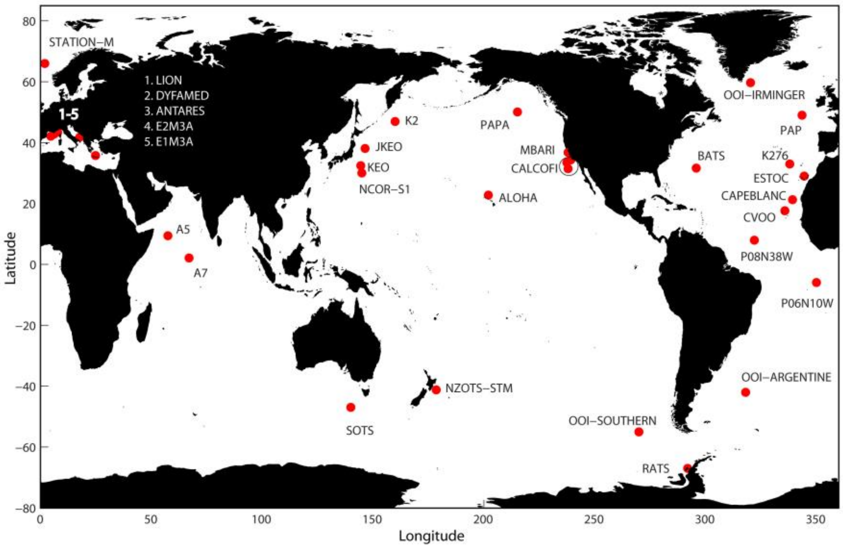

Figure 9. Locations of the Oceansites observatories with a biogeochemical component, including currently operational and planned stations (from Henson et al., 2016).

The Porcupine Abyssal Plain time-series site

The work of this thesis focuses on the Porcupine Abyssal Plain sustained observatory (PAP-SO). The PAP-SO is a time-series site in the temperate Northeast Atlantic and is part of both the ‘Oceansites’ and European FixO3 networks. The PAP–SO is a multidisciplinary open-ocean time-series site in the sub-polar Northeast Atlantic (49°N, 16.5°W) at a water depth of 4800 m, where *in situ* measurements have been made since the late 1980s. The PAP-SO site is a single point location set up to study connections between the surface and deep-ocean. The PAP-SO provides *in situ* time-series data of climatically and environmentally relevant variables from the water column and the seafloor beneath. Prior to 2003, biogeochemical measurements were made from samples taken on research vessels at both the PAP site and the nearby JGOFS station at 47°N, 20°W (Lochte et al., 1993; Lampitt et al., 2010). A fixed-point mooring has been in place since 2002, with a surface buoy being added in 2007. In 2010, collaboration between the UK’s Natural Environment Research Council (NERC) and Meteorological Office led to a redesigned infrastructure, first deployed on 1 June 2010.

The location of the PAP-SO (Figure 10) is considered remote from the complexities of the continental slope and the mid-Atlantic ridge. As shown in Figure 8 the PAP-SO site is in the inter gyre region between the seasonally stratified SPG and the permanently stratified STG (McKinley et al., 2016), where there is an influence of both polar and tropical water masses (Waniek, 2003; Henson et al., 2009).

The multidisciplinary set of sensors on the mooring have produced *in situ* time-series datasets since 2002, including subsurface (~25-30 m depth) measurements of temperature, salinity, chlorophyll-*a* fluorescence, pH, nitrate, light, oxygen and pCO_2. Since 2012 additional shallower biogeochemical measurements have been made (on the keel of the buoy at 1m depth). Also on the buoy meteorological sensors record wave height, wind speed and direction and air temperature.

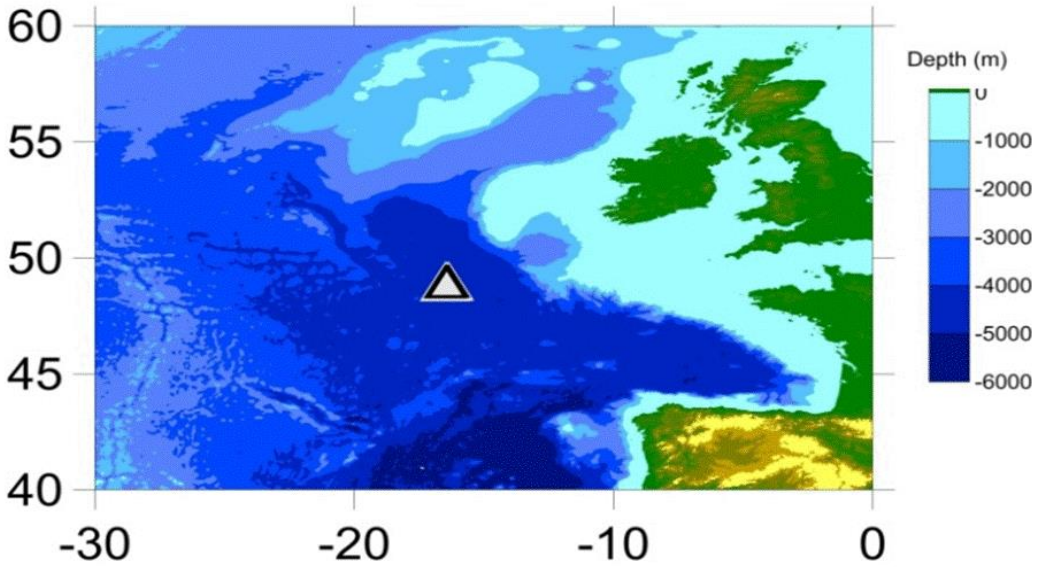

Figure 10: The northeast Atlantic showing the position of the Porcupine Abyssal Plain sustained observatory (PAP-SO) at 49°N, 16.5°W, and water depth (m)

Data are sent through Iridium telemetry to the National Oceanography Centre (NOC), UK. All PAP-SO datasets are open access through websites and as quality-controlled datasets for a range of remote users using ftp sites and uploaded daily to MyOcean and the global telecommunications system for use in modelling activities.

In the temperate north Atlantic the growth of phytoplankton is light limited in the winter and a bloom occurs in spring following stratification of the water column (Sverdrup, 1953). With the increase in productivity the nutrients are depleted and the bloom stops until deep overturning starts in the autumn and resupplies nutrients to the surface throughout winter. The expected seasonal cycle at the PAP-SO is a peak in winter nutrients and DIC, coinciding with the deepest mixing and lowest surface temperature (Körtzinger et al., 2008). Lampitt et al., (2010) showed that the extent of deep mixing at the PAP-SO varies from year to year, reaching 400m in some years. The winter nutrient and DIC concentrations would be expected to vary accordingly. Likewise the timing of the spring bloom, its duration and magnitude would vary from year to year.

A persistent feature of the North Atlantic is under saturation of CO_2 in surface waters throughout the year. The continuous under saturation is characteristic of the entire sub-polar North Atlantic, resulting from the general cooling of surface waters during their passage from low to high latitudes. The under saturation of CO_2 suggests that this are will be a perennial CO_2 sink and a net annual oceanic uptake has been calculated as 3 mol m^{-2} a^{-1} at the PAP-SO (Körtzinger et al., 2008). The region is a relatively large sink region for CO_2, especially in comparison with sub-tropical sites such as ESTOC where the uptake is about 0.05 mol m^{-2} a^{-1} (González-Dávila et al., 2003), so it is of great importance in measuring the global carbon cycle.

Aims and outline

The main goal of this thesis is to identify the drivers of seasonal and inter-annual variations in biogeochemistry in the northeast Atlantic. This study builds on extensive biogeochemistry data sets including over 10 years of biogeochemical data collected at the Porcupine Abyssal Plain sustained observatory (PAP-SO); an 8 year time-series from a ship of opportunity (SOO) running between the UK and Spain, and two years of biogeochemical sampling around the Northwest European shelf. The aims are:

- To consider how biogeochemical data can be obtained and validated using autonomous instruments. Winter measurements from ship based surveys are still relatively rare so sensors were used to collect year round data. The aim is to combine these measurements with complementary data from Argo floats, satellites, ship based process studies and ships of opportunity.
- To capture events that occur on different time scales, as short term trends and variability will contribute to longer climate-driven trends. For example looking at seasonal changes in carbon chemistry, nutrient supply, and productivity will lead to an understanding of seawater pCO_2 and processes controlling its variability.
- To understand year to year changes in carbon chemistry, nutrient supply, and productivity in the Northeast Atlantic by considering the extent to which winter nitrate concentrations are influenced by deep winter mixing and how the deep mixing is calculated. The lateral advection of low nutrient waters to the PAP-SO may also contribute to inter-annual variability and this process has previously been neglected in studies at this site.
- To investigate year to year variation in nitrate with respect to carbon at the PAP-SO. The ratio of carbon to nitrate is used in the calculation of productivity and has previously been taken as a constant in many studies.
- To investigate year to year variation in CO_2 flux at the PAP-SO. The PAP-SO area is a net sink of CO_2, however in a changing climate the capacity of the ocean to take up CO_2 may change.
- To look at episodic events (e.g. spring-bloom events) using high frequency sensor data from the PAP-SO. The aim is to see how the variation in winter nitrate links to productivity the following spring and to look at year to year variation in the timing of the spring bloom using calculations of net heat flux.
- To consider the links between surface productivity and deep ocean carbon flux as measured by the sediment traps. To consider the region of influence on the flux of material from the surface to depth using lateral advection output.
- To expand the findings at the PAP-SO to the wider Atlantic looking at the seasonal and inter-annual variation in nutrients in relation to mixing and productivity in the Bay of Biscay, using SOO data.
- To look at the timing of increases in nutrient concentrations (due to winter mixing) and decreases (from the spring bloom) on and off shelf using SOO data.
- To consider the PAP-SO as part of the Atlantic approaches to the Northwest European shelf, comparing biogeochemical variations at the site with on-shelf seasonal variations.

This study is based on work presented in the following chapters that are each based on published (and one submitted) papers.

Chapter 1: The Porcupine Abyssal Plain fixed-point sustained observatory (PAP-SO): Variations and trends from the Northeast Atlantic fixed-point time-series

In this chapter (Hartman et al., 2012) we describe the PAP-SO site and the sensors that have been in place since 2002. The PAP-SO in the Northeast Atlantic (49°N, 16.5°W; 4800 m) produces high-resolution datasets, integrating environmental and ecologically relevant variables from the surface to the seabed. Since 2002, a full-depth mooring has been in place with autonomous sensors measuring temperature, salinity, chlorophyll-*a* fluorescence, nitrate, and pCO_2. These complement on-going mesopelagic and seabed observations on downward particle flux and benthic ecosystem structure and function. The chapter considers how sensors are selected and how their use has evolved over time. In the synthesis section different sensor options and data validation are discussed.

Chapter 2: Seasonal and inter-annual biogeochemical variations in the Porcupine Abyssal Plain 2003-2005 associated with winter mixing and surface circulation

In this chapter (Hartman et al., 2010) we used high-resolution year-round autonomous measurements including temperature, salinity, chlorophyll-*a* (derived from *in situ* chlorophyll-fluorescence) and inorganic nitrate. This chapter considers the first three years of autonomous measurements (2003-2005) at the PAP-SO, made from a mooring frame with a nominal depth of 30m below the sea surface. Here *in situ* time-series data are compared with: 1) satellite derived chlorophyll-*a* data, 2) regionally adjacent data from a ship of opportunity, 3) measurements of mixed layer depth derived from profiling Argo floats and 4) estimates of lateral advection derived from satellite altimetry measurements. This combined and substantial dataset was used to interpret seasonal and inter-annual variability in hydrography and nitrate concentrations at the PAP-SO. The hypothesis is that lateral advection is important at the PAP-SO site. The influence of convective mixing and lateral advection on the supply of nitrate to the surface is discussed as this influences productivity the following spring. High resolution chlorophyll-fluorescence data and calculations of net heat flux are then used to look at controls on bloom timing at the PAP-SO site.

Chapter 3: Biogeochemical variations at the Porcupine Abyssal Plain Sustained Observatory in the Northeast Atlantic Ocean, from weekly to inter-annual time scales

In this chapter (Hartman et al., 2015) high-resolution autonomous measurements of carbon dioxide partial pressure (pCO_2) taken *in situ* at the PAP-SO are presented. There is a comparison of newer data (2010-2012) with the earlier datasets (2003-2005). Measurements of pCO_2 made at 30m depth on the sensor frame were compared with other autonomous biogeochemical measurements at that depth (including chlorophyll-*a* fluorescence and nitrate concentration). Comparisons were also made with *in situ* regional time-series data from a ship of opportunity and mixed layer depth (MLD) measurements from profiling Argo floats. The year to year variability in pCO_2 and in CO_2 flux was investigated confirming that the region is a perennial sink for CO_2. Controls on pCO_2 flux in this inter-gyre region of the North Atlantic were investigated. The hypothesis was that the CO_2 flux will change from year to year, driven by changes in productivity controlled by winter nutrient concentrations.

Chapter 4: Links between surface productivity and deep ocean particle flux at the Porcupine Abyssal Plain sustained observatory

In this chapter (Frigstad et al., 2015) hydrographic and biogeochemical data are used, collected from the PAP-SO between 2003 and 2012, along with sediment trap observations. The time-series is unique in the Northeast Atlantic as it allows for investigation of the link between surface productivity and deep ocean carbon flux. Chapter 4 quantified and compared NCP and new production calculations from the average monthly drawdown of DIC and NO_3, respectively. Export ratios were calculated by comparison with satellite derived productivity estimates and published values of shallow particulate organic carbon flux at the PAP-SO. Secondly the link between production at the surface and particle flux at 3000 m depth was investigated. The carbon transfer efficiency between the surface and deep-ocean was calculated. The source location of exported material was also described, using particle tracking techniques.

Chapter 5: Seasonal and inter-annual variability in nutrient supply in relation to mixing in the Bay of Biscay

In this chapter (Hartman et al., 2014) high resolution, autonomous measurements from a Ferry-Box running between the UK and Spain are presented. An 8 year time-series of hydrographic data from the Ferry-Box (2002-2010) are supplemented with samples collected on a monthly basis and analysed for dissolved inorganic nutrients. In this chapter we quantify the year to year variability in nutrient concentrations in relation to the winter mixing processes and the NAO index. Productivity was calculated from the Ferry-Box oxygen data and was used to look at timing of the spring bloom both on and off shelf.

Chapter 6: Seasonality and spatial heterogeneity of the surface water carbonate system on the Northwest European shelf

In this chapter (Hartman et al., 2017, submitted) a large coordinated study of carbonate parameters around the Northwest European shelf is presented. Daily surface samples were collected between 2014 and 2015. The discrete samples were analysed for nutrients, DIC and TA and these measurements were used to calculate pH and pCO_2. The PAP-SO is considered here as part of the western Atlantic approaches to the shelf. Seasonal hydrographic and biogeochemical variations around the shelf are presented. The shelf was divided into 9 ecohydrodynamic regions and seasonal time averages were determined for all measured and derived parameters in each region.

Chapter 1

The Porcupine Abyssal Plain fixed-point sustained observatory (PAP-SO); variations and trends from the Northeast Atlantic fixed-point time-series

Hartman, S.E., Lampitt, R.S., Larkin, K.E., Pagnani, M., Campbell, J., Gkritzalis, T., Jiang, Z.P., Pebody, C.A., Ruhl, H.A., Gooday, A.J. and Bett, B.J., 2012. *ICES Journal of Marine Science: Journal du Conseil*, p.fss077

Abstract

The Porcupine Abyssal Plain sustained observatory (PAP-SO) in the Northeast Atlantic (49°N 16.5°W; 4800 m) is the longest running open-ocean multidisciplinary observatory in the oceans around Europe. The site has produced high-resolution datasets integrating environmental and ecologically relevant variables from the surface to the seabed for > 20 years. Since 2002, a full-depth mooring has been in place with autonomous sensors measuring temperature, salinity, chlorophyll-*a* fluorescence, nitrate, and pCO_2. These complement ongoing mesopelagic and seabed observations on downward particle flux and benthic ecosystem structure and function. With national and European funding, the observatory infrastructure has been advanced steadily, with the latest development in 2010 involving collaboration between the UK's Meteorological Office and Natural Environment Research Council. This resulted in the first simultaneous atmospheric and ocean datasets at the site. All PAP-SO datasets are open access in near real time through websites and as quality-controlled datasets for a range of remote users using ftp sites and uploaded daily to MyOcean and the global telecommunications system for use in modelling activities. The combined datasets capture short-term variation (daily–seasonal), longer term trends (climate-driven), and episodic events (e.g. spring-bloom events), and the data contribute to the Europe-wide move towards good environmental status of our seas, driven by the EU's Marine Strategy Framework Directive (http://ec.europa.eu/ environment/ water/marine)

The Porcupine Abyssal Plain sustained observatory

The Porcupine Abyssal Plain sustained observatory (PAP-SO) is situated in the subpolar Northeast Atlantic (49°N 16.5°W) at a water depth of 4800 m (Figure 1). This location is considered remote from the complexities of the continental slope and the Mid-Atlantic Ridge. It is the longest running multidisciplinary open-ocean time-series observatory in Europe and one of the longest in the world. Since 1989, it has produced high-resolution *in situ* time-series data of climatically and environmentally relevant variables from the entire water column and the seabed beneath.

Historically, the measurements have been sampled from a research vessel. However, a fixed-point mooring has been in place since 2002, with a surface buoy being added in 2007. In 2010, collaboration between the UK's Natural Environment Research Council (NERC) and the Meteorological Office led to a redesigned infrastructure, deployed on 1 June 2010, and the first simultaneous monitoring of *in situ* meteorological and ocean variables at the PAP-SO (Table 1).

The multidisciplinary set of sensors on the mooring (Figure 2) have produced high-resolution *in situ* time-series datasets, including subsurface (30 m depth) measurements of temperature, salinity, chlorophyll-*a* fluorescence, nitrate, and pCO_2.

Recent enhancements to the mixed layer variables include oxygen and irradiance, and a water sampler has been added to the sensor frame. A full list of the variables is provided in Table 1. Data are sent in near real time from the upper 1000 m through Iridium telemetry to the UK National Oceanography Centre (NOC). This full-depth observatory has allowed the analysis of trends in seasonal and interannual processes, and forms an integrated system from the euphotic zone to the benthic boundary layer and seabed.

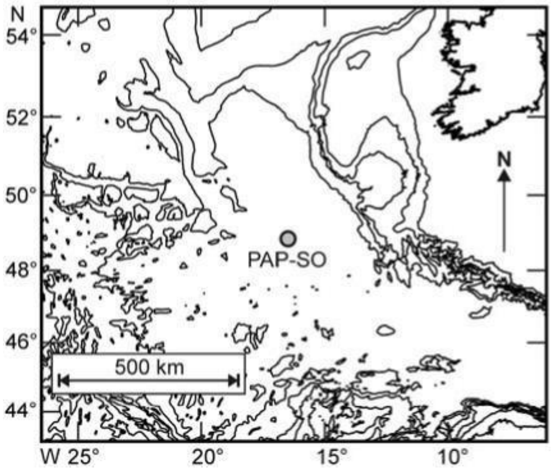

Figure 1. Location map of the Porcupine Abyssal Plain Sustained Observatory (PAP-SO). The depth contours shown are 200, 1000, 2000, 3000, and 4000 m.

Research to date at the PAP-SO site has focused on understanding surface processes (e.g. Hartman *et al*., 2010) and the link between upper ocean physical and biogeochemical processes, the supply of particulate organic carbon (POC) to the deep ocean (e.g. Lampitt *et al*., 2010a), and the response (in terms of biodiversity and ecosystem functioning) of the benthic fauna below (e.g. Billett *et al*., 2001, 2010; Wigham *et al*., 2003; Gooday *et al*., 2010; Kalogeropoulou *et al*., 2010; Soto *et al*., 2010). In some cases, community changes have been attributed to longer-term climate-driven changes (Ruhl *et al*., 2008). More details on the benthic biological observations and time-series from the PAP-SO site can be found in Glover *et al*. (2010), Lampitt *et al*. (2010b), and Larkin *et al*. (2010).

Upper ocean biogeochemistry

A three-year time-series (2003–2005) of physical and biogeo-chemical data was analysed for both seasonal and interannual variation (Hartman *et al*., 2010).

Results from that analysis showed evidence of increased temperature and salinity signals in surface waters from 2003 to 2005, with increased stratification, decreased nitrate concentration (Figure 3) and consequent decline in productivity, and delay in the spring bloom (Hartman *et al*., 2010). In addition, indications of changes in surface circulation and mode waters supplying the region suggested that eddy activity and lateral advection cannot be ignored at the site (Hartman *et al*., 2010).

The variation in open ocean *in situ* data, of increasing temperature and salinity over a three-year period, confirms other observations including UK coastal *in situ* observations, e.g. the L4 buoy in the western English Channel (Smyth *et al*., 2010). Results from the PAP-SO also align with the trend documented from remote (satellite) observations of chlorophyll-*a* fluorescence across the North Atlantic, showing a progressive decline in primary production in the open ocean from 1999 to 2004 (Gregg *et al*., 2003; Behrenfeld *et al*., 2006).

Progressive warming at the PAP-SO site from winter 2003 to winter 2005 was observed in both the National Centre for Environmental Prediction (NCEP) sea surface temperature (SST) and subsurface (30 m) temperature records from the PAP-SO mooring Associated decreases in nitrate concentrations and productivity (Behrenfeld *et al*., 2006) may be attributable to a combination of shallower convective mixing, changes in surface circulation, and mode waters supplying the region (Hartman et al., 2010). These variations in the physical and biogeochemical processes in the Northeast Atlantic will have a notable impact on the pelagic (and benthic) ecosystems. This will cause a variability in zooplankton distribution and population size that ultimately relates to fish stock dynamics

Table 1. Sensor types, variables measured, and measurement frequency at the PAP-SO.

Depth	Parameters/variables	Sensor	Frequency
Atmospheric (UK Meteorological Office buoy)			
3.5 m above surface	Windspeed and direction	Gill acoustic sensor and magnetic compass	Hourly (10 min mean)
2 m above surface	Relative humidity	Rotronic Hygroclip R/S sensor	Hourly (instantaneous reading)
2 m above surface	Air temperature	Electrical resistance thermometer (ERT)	Hourly (10 s mean)
1 m (subsurface)	Sea temperature	Electrical resistance thermometer (ERT)	Hourly (10 s mean)
1.75 m above Surface	Atmospheric pressure	Druck RPT350 pressure sensor	Hourly (20 s mean)
Surface	Significant wave height	Datawell heave sensor	Hourly (17.5 min)
Surface ocean (fixed frame)			
30 m	CTD	Seabird MicroCAT	10 min
30 m	CTD, dissolved oxygen	Seabird MicroCAT IDO	30 min
30 m	Nitrate and nitrite (chemistry)	NAS	4 h
30 m	Nitrate and nitrite (UV absorption)	Satlantic ISUS	1 h
30 m	Chlorophyll	WETlabs FLNTUSB and Cyclops	6 h, 1 h
30 m	Dissolved oxygen	Aanderaa optode on Seaguard	1 h
30 m	Currents	DCS	1 h
30 m	CO_2 (IR absorbance after eqm)	PRO-OCEANUS	12 h
30 m	Dissolved gases (GTD)	PRO-OCEANUS	12 h
30 m	Radiance Lu upwelling	7-channel Satlantic OCR	1 h
30 m	Irradiance Ed, Eu downwelling irradiance	7-channel Satlantic OCR radiometer	1h
30 m	Irradiance Es total irradiance	7-channel Satlantic OCR	1 h
30 m	Zooplankton sampler	McLane zooplankton sampler	Every 2 d
Deep ocean (subsurface mooring)			
25–1 000 m	CTD	Seabird MicroCAT	10 min
3000 m	Particle flux (sediment traps)	McLane sediment trap	Variable (d)
3000 m	Currents	Aanderaa RCM9	4 h
3050 m	Particle flux (sediment traps)	McLane sediment trap	Variable (d)
100 m above seabed	Particle flux (sediment traps)	McLane sediment trap	Variable (d)
100 m above	Currents	Aanderaa RCM9	4 h
Seabed (lander)			
Seabed (4 800 m)	Time-lapse photos	Imenco AS (SDS 12100) stills camera	8 h

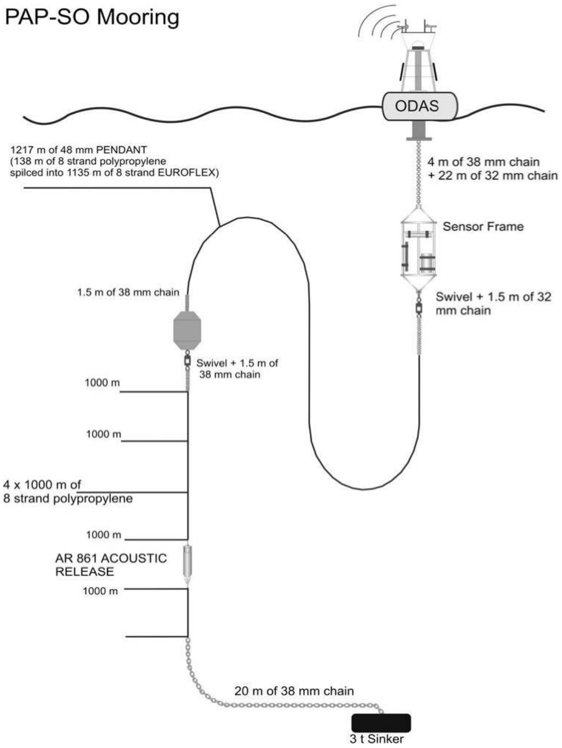

Figure 2. The PAP-SO full depth mooring design and Ocean Data Acquisition System (ODAS) surface buoy.

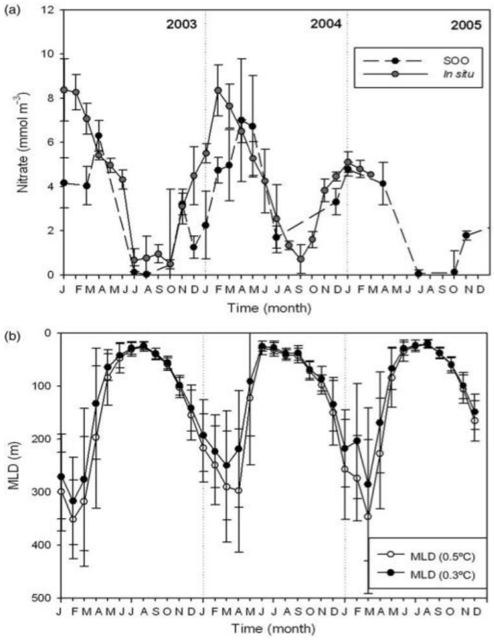

Figure 3. Nitrate concentrations and mixed layer depth (MLD) estimates at the PAP-SO site from 2003 to 2005 showing: (a) *in situ* monthly mean (±1 s.d.) nitrate concentrations (grey circles), compared with discrete samples taken from a ship of opportunity (black circles); and (b) monthly mean (±1 s.d.) MLD from Argo float profiles (across 45–52°N 26.08–8.92°W) calculated using a temperature difference criterion of 0.5°C (open circles), compared with a 0.3°C criterion (black circles). Tick marks indicate the start of the month (from Hartman *et al*., 2010).

A persistent feature of the North Atlantic is undersaturation of CO_2 in surface waters throughout the year, which gives rise to a perennial CO_2 sink (Körtzinger *et al*., 2008). This makes the PAP-SO a region of great importance in the global carbon cycle. The continuous undersaturation is characteristic of the entire Subpolar North Atlantic, resulting from the general cooling of surface waters during their passage from low to high latitudes. However, there is evidence for a trend of less CO_2 being absorbed into the oceans for the period 2003/2004 (Körtzinger *et al*., 2008). This demonstrates the need to monitor temporal changes in the ocean in a sustained way on oceanographic and ecologically relevant time-scales. Changes in the amount of CO_2 absorbed into the ocean may have implications for the global carbon cycle and importance of the oceans as a carbon sink in the future. To assist in making these estimates, pCO_2 data are available from the site in near real time (Figure 4).

Deep ocean and benthic studies

The PAP-SO is the only long-term time-series site in the Atlantic to combine sustained water column and benthic biological sampling effort. This dataset is vital for understanding environmental change. For example, carbon sequestration from the upper ocean is monitored through an understanding of the changes in the downward flux of particulate material in the deep-sea environment. At the PAP-SO site, mesopelagic particle flux samples have been collected from the mooring for more than 20 years using sediment traps at depths between 3000 and 4700 m (Figure 5). Results show that the site is characterized by a relatively high level of flux of organic carbon with high seasonal and inter-annual variability (Lampitt *et al*., 2001, 2010a). The causes and trends for this long-term variability of downward particle flux in the region are discussed in Lampitt *et al.* (2010a). These include indications that substantial variation in the date of the spring change in mixing (shoaling) may have a large effect on the biogeo-chemistry of the remainder of the productive season and the resulting carbon sequestration. The PAP-SO site is an important long-term reference site across the global ocean for benthic biological community studies. The benthic macrofauna. Significant differences were observed in some trophic groups (predators, surface deposit-feeders, and burrowers) and in the dominant families (Cirratulidae, Spionidae, and Opheliidae). Studies of benthic for-aminifera have shown a significant increase in total densities from 1996 to 2002 compared to 1989–1994, together with changes in assemblage composition at the species and higher taxa levels (Gooday *et al*., 2010).

Studies carried out at the site are reviewed in Glover *et al.* (2010) and Lampitt *et al.* (2010b), and summarized together with other key benthic biological time-series in Larkin *et al.* (2010). More than 20 years of sampling the abyssal seabed (4800 m) at the PAP-SO site has permitted studies of benthic bio-diversity, rate processes, and ecosystem change in the deep seabed. Often, this impact can be related to food quality and quantity (Wigham *et al*., 2003; Billett *et al*., 2010). In particular, the quality and quantity of the organic matter were shown to influence benthic ecosystem functioning and resulted in radical changes in the density and species diversity of benthic fauna, in particular of large invertebrates (megafauna), as documented in a population explosion of holothurians dominated by the species *Amperima rosea* in 1997 and 2002, in the latter case, following a notable peak in particle flux (Figure 6). Community shifts and population changes were also seen in other size classes.

Community changes at the PAP-SO site have been attributed to climate-driven changes in POC flux quantity and quality. The North Atlantic Oscillation (NAO), for example, was linked to POC fluxes to the seabed with a time-lag of several months, as well as to megafauna community composition (Billett *et al*., 2010).

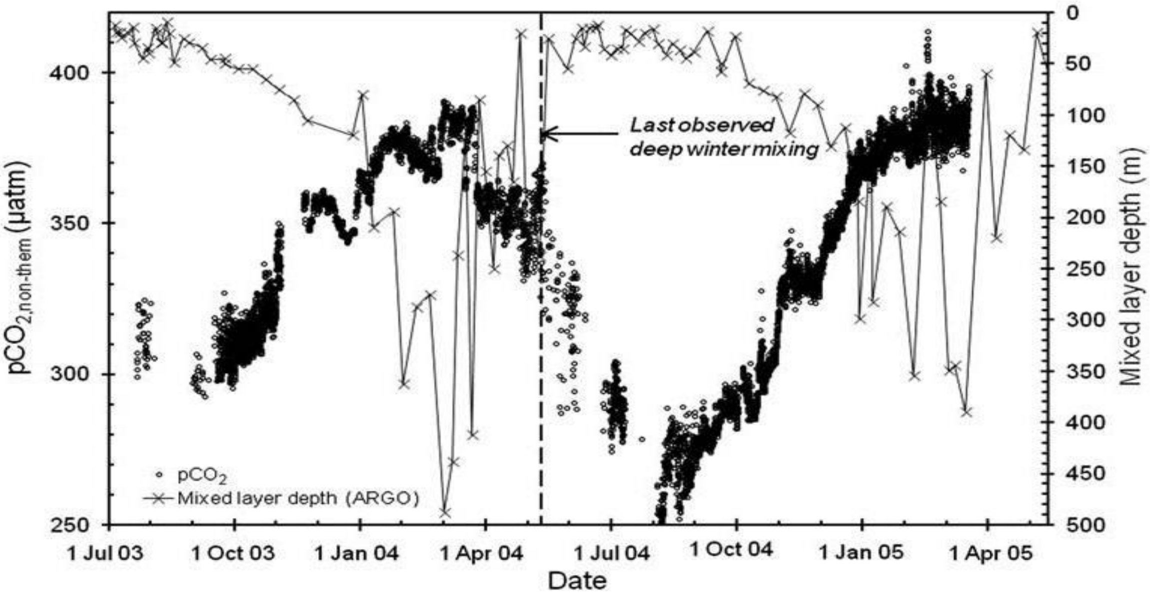

Figure 4. Observed pCO$_2$ corrected to the annual mean SST of 2004 and estimated MLD. Reproduced from Körtzinger *et al*. (2008)

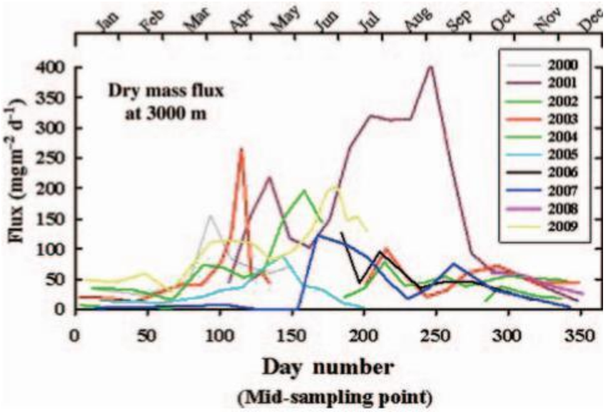

Figure 5. Time-series of particle flux (dry mass), 2000–2009, showing clear interannual seasonal and interannual time-scales, from small meiofauna to larger macro and megafaunal size classes.

Notably, the observed ecosystem changes at the PAP-SO were linked to qualitative variations in the biochemistry of particulate organic matter (Wigham *et al*., 2003) that are believed to be critical to the reproductive and recruitment success of key species such as *A. rosea* (FitzGeorge-Balfour *et al*., 2010)

European and global context

The PAP-SO is funded by the UK National Environment Research Council (NERC) with dedicated webpages (www.noc.soton.ac.uk/pap). In addition, the site has been supported by a number of earlier European projects, including BENGAL, ANIMATE, MERSEA, and MarBEF. Notably, the observed ecosystem changes at the PAP-SO were linked to qualitative variations in the biochemistry of particulate organic matter (Wigham *et al*., 2003) that are believed to be critical to the reproductive and recruitment success of key species such as *A. rosea* (FitzGeorge-Balfour *et al*., 2010),.

Most recently, the PAP-SO has become a key open-ocean time-series site contributing to the EuroSITES network (www.eurosites.info). Within the EuroSITES FP7 Collaborative Project (2008–2011), the PAP-SO was maintained and enhanced with additional sensors, including measurements of carbon dioxide and meteorological variables, thereby increasing its capacity to monitor environmentally and climatically relevant variables (Table 1).

Further maintenance will be supported largely by national funding (NERC) together with support for benthic research by the European project HERMIONE. As a European platform, PAP-SO has been used for science missions and the development and testing of novel sensors. These include the IODA6000 for *in situ* oxygen consumption (developed by CNRS: University of Marseille) and the research and development for enhancing long-term capabilities of a meso-zooplankton sampler. Strong links exist between EuroSITES and other European initiatives, e.g. ESONET (European Sea Observatory Network). For example, ESONET funded a collaboration design study to enhance the seabed observation infrastructure at the PAP-SO site. This utilized the existing water-column mooring to send multidisciplinary data in near real time via an acoustic link from a lander at 4800 m to the surface and to shore. The PAP-SO is also a key site in the European Multidisciplinary Seabed Observatory (EMSO) planning that aims to establish a long-term governance entity for operating observatories in Europe.

PAP-SO ocean and atmospheric data are sent in near real time from the upper 1000 m through Iridium telemetry to NOC (Southampton), acting as the PAP-SO and EuroSITES Data Assembly Centre. Data are available through the EuroSITES website (www.eurosites.info). Internationally, the site contributes to the OceanSITES global array (www.oceansites.org), complementing other *in situ* observing systems (e.g. Argo, CPR, Ships of Opportunity) that monitor the region. In line with other time-series sites within this network, there is an open access policy to data that are available through the CORIOLIS ftp site (ftp://ftp.ifremer.fr/ifremer/oceansites).

Physical datasets (temperature and salinity) are also sent to the global telecommunication system. As a component of EuroSITES and OceanSITES, the PAP-SO is a key data provider to MyOcean (European Marine Core Services). In future, it is envisaged that more near real-time data will be utilized by modelling and reanalysis activities to produce services and products for society. The PAP-SO is located in international waters, but in proximity to four member-state European economic zones. It is also an associated site in (http://www.westernshelfobservatory.org/).

PAP-SO time-series datasets from the open ocean North Atlantic are invaluable as an early warning system for the European shelf and coastal waters at a regional level. Research at the PAP-SO site contributes to the subsea component of GMES (Global Monitoring for Environment and Security) and to the Global Earth Observation System of Systems (GEOSS) through the OceanSITES deep-water reference stations and the Global Ocean Observing System (GOOS).

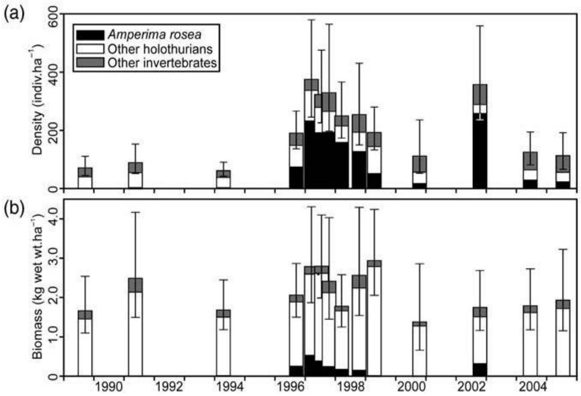

Figure 6. Histograms illustrating temporal variations in the (a) abundance and (b) biomass of selected megafaunal groups at the PAP-SO site (means and 95% confidence intervals). Adapted from Wigham *et al*. (2003)

Many science themes benefit from data supplied by ocean observatories (Ruhl *et al*., 2011), and PAP-SO scientists regularly inform government policy on strategic issues, e.g. marine processes and climate, marine habitats and species (biodiversity in the deep sea), open ocean productivity, ocean governance, geo-engineering, and ocean fertilization. Regular advice is provided to the Royal Society, the Department of Environment, Food and Rural Affairs (Defra), the UN International Seabed Authority, and the European Commission (EC). The PAP-SO is also detailed as an existing *in situ* infrastructure for ocean observation contributing to the Group on Earth Observation (GEO) in Lampitt *et al.* (2010c) and related outputs from the OceanObs'09 conference. The combined datasets obtained enable short-term (daily–seasonal) and longer-term (climate-driven) trends to be captured, contributing to the Europe-wide initiative for good environmental status of our seas by the EU Marine Strategy Framework Directive (http://ec.europa.eu/ environment/water/marine/).

Summary and conclusions

The PAP-SO in the Northeast Atlantic at 49°N 16.5°W is the longest running multidisciplinary open ocean time-series observatory in Europe and has produced a high-resolution *in situ* multidisciplinary time-series dataset of climatically and environmentally relevant variables from the euphotic zone to the seabed beneath (4800 m) for 20 years. More than 225 peer-reviewed papers have been published on the PAP-SO since 1975, including a recent special issue in Deep Sea Research (Volume 57, Issue 15) that details recent water column and seabed studies at the PAP-SO.

Results from the time-series have proven vital for understanding a range of ocean processes at different temporal scales, including an integrated understanding of seasonal and interannual surface processes and how these affect the deep ocean and seabed communities. Results have also highlighted the potential role of deep-sea benthic communities as indicators of climate change. As technology allows the measurement of more variables to be available in near real time from the open and deep ocean, the potential for societal benefit from these datasets, in terms of products and services, is set to increase exponentially. There is therefore a growing need for developing and maintaining longterm time-series sites to provide important *in situ* ocean datasets. However, sustaining these time-series through long-term funding commitments is an ongoing challenge.

Acknowledgements

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Chapter 2

Seasonal and inter-annual biogeochemical variations in the Porcupine Abyssal Plain 2003–2005 associated with winter mixing and surface circulation

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Abstract

We present a 3-year multidisciplinary biogeochemical data set taken *in situ* at the Porcupine Abyssal Plain (PAP) time-series observatory in the Northeast Atlantic (49°N, 16.5°W; water depth >4850 m) for the period 2003 to 2005. The high-resolution year-round autonomous measurements include temperature, salinity, chlorophyll-a (derived from *in situ* chlorophyll-fluorescence) and inorganic nitrate, all at a nominal depth of 30 m on a Eulerian observatory mooring. This study compares these *in situ* time-series data with satellite chlorophyll-a data, regional data from a ship of opportunity, mixed-layer depth measurements from profiling Argo floats and lateral advection estimates from altimetry. This combined and substantial data set is used to analyse seasonal and inter-annual variability in hydrography and nitrate concentrations in relation to convective mixing and lateral advection. The PAP observatory site is in the inter-gyre region of the North Atlantic where convective mixing ranges from 25 m in the summer to over 400 m in winter when nutrients are supplied to the surface. Small inter-annual changes in the winter mixed layer can result in large changes in nitrate supply and productivity. However, the decrease in maximum winter nitrate over the three-year period, from 10 to 7 mmol m $^{-3}$, cannot be fully explained by convective mixing. Trajectories leading to the PAP site, computed from altimetry-derived geostrophic velocities, confirm that lateral advection cannot be ignored at this site and may be an important process along with convective mixing. Over the three years, there is an associated decrease in new production calculated from nitrate assimilation from 85.4 to 40.3±4.3 gCm $^{-2}$ a $^{-1}$. This confirms year-to-year variability in primary production seen in model estimates for the region. The continuous *in situ* dataset also shows inter-annual variation in the timing of the spring bloom due to variations in heat flux; the 2005 bloom occurred earlier than in 2004

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Introduction

In the well-lit, temperate, upper ocean, production and phytoplankton biomass are largely controlled by nitrate supply (Eppley and Peterson, 1979; Williams et al., 2000; Hydes et al., 2001). North of 42°N the vertical transfer of nitrate by winter convective mixing dominates the transport of new nitrate into the euphotic zone (Williams et al., 2000; Cianca et al., 2007) over diapycnal diffusion, eddy transfer and Ekman processes (Oschlies and Garson, 1998; Williams and Follows, 1998; Fernández, et al., 2005). Wind-driven cooling and deep convective mixing lower the surface temperature and supply nutrient-rich water to the euphotic zone to fuel phytoplankton growth, following restratification of the water column in the spring. Many factors influence the timing and the magnitude of the spring bloom, although it tends to be initiated once there is enough light and the convective mixing rate is less than a critical threshold (Sverdrup, 1953; Colebrook, 1982; Esaias et al., 1986; Siegel et al., 2002). Inter-annual variations in convective mixing influence production through variations in nutrient supply (Palter et al., 2005; Levy, 2005; Williams et al., 2006; Cianca et al., 2007). Behrenfeld et al. (2006) suggested that the progressive decline in primary production (Field et al., 1998) seen in the North Atlantic from 1999 to 2004, was due to enhanced stratification forming a barrier to nutrient exchange. Frontal systems and mesoscale variability will also influence production, through changes to surface nutrient supply (McGillicuddy et al., 1995; Waniek, 2003). The net annual flux of nitrate can be used as a proxy for new production in regions where nitrogen fixation is negligible (Eppley and Peterson, 1979; Oschlies and Garson, 1998; Henson et al., 2003). The nitrate assimilation method requires knowledge of seasonal changes in nitrate from the winter maximum to low concentrations at the end of summer (Minas and Codispoti, 1993; Louanchi and Najjar, 2000). However, direct measurements of upper-ocean wintertime nutrient concentrations are rare, even in the extensively surveyed Northeast Atlantic (Waniek, 2003; Koeve, 2006). Examination of the ICES database (http://www.ices. dk/ocean) from 1989 to 2006 for example shows 223 profiles within a 5 by 5-degree box around the Porcupine Abyssal Plain (PAP) observatory site (49°N, 16.5°W); yet none of these represent ‘winter’ sampling (January to March).

Individual projects, such as the Programme Ocean Multidisciplinaire Meso Echelle (POMME) field study south of 45°N during 2001 (Levy et al., 2005b), provide winter nitrate data for individual years but tend to be to the south of the PAP region. Estimates of winter nitrate concentrations in the absence of direct measurements (Glover and Brewer, 1998; Koeve, 2001, 2006) can compound the errors associated with new production estimation, which also include nitrification (Yool et al., 2007) and assumptions regarding the nitrate uptake to carbon fixation ratio (Sambrotto et al., 1993; Koeve, 2006).

Studies of processes regulating nitrate supply to the surface are critical for making year-to-year estimates of productivity (Behrenfeld et al., 2006). This requires accurate, high-resolution, long-term datasets. Such data are available from the Porcupine Abyssal Plain (PAP) observatory site (49°N, 16.5°W; >4850 m water depth). PAP is within the North Atlantic Drift Region (NADR), a biogeographical province (Longhurst, 1998) defined by deep winter convective mixing of up to 600 m (Monterey and Levitus, 1997). We present a three-year time-series (2003–2005) of year-round nitrate, temperature, salinity and chlorophyll-fluorescence (chlorophyll-a) data collected from a mooring at the PAP observatory site. Long-term time-series data from the PAP observatory provide a context for short-term studies in the area such as from research cruises (Painter et al., 2010).

Materials and methods

Study Site

The Porcupine Abyssal Plain (PAP) deep-ocean observatory site at 49°N, 16.5°W is shown in Figure 1 with the larger PAP region, which included the 1989 Joint Global Ocean Flux Study (JGOFS) site for the North Atlantic Bloom Experiment (NABE; DSR Special volume 40:1/2, 1993). JGOFS studies in the 1990’s (Savidge et al., 1992; Koeve, 2002) provided considerable background information on the upper-ocean processes in this region. Lampitt et al. (2001) summarise the hydrography, meteorology and upper mixed layer dynamics in the region. Information on the particle flux (measured and modelled) at the PAP observatory site can be found in Lampitt et al. (1995, 2000, 2010 and Lampitt et al. (2001), respectively.

In situ data

Between 2003 and 2005 instruments on a mooring at the PAP observatory site recorded a suite of biogeochemical parameters from the euphotic zone to the benthic boundary layer. This has produced a unique set of *in situ* time-series data from the Northeast Atlantic including water-column measurements of temperature and salinity over the top 1000 m and biogeochemical sensors measuring nitrate, chlorophyll-fluorescence and pCO_2 on a sensor frame at a nominal depth of 30 m, within the deep chlorophyll maxima. The sensor frame depth varied (from 20 to 225 m), deflecting in response to local currents.

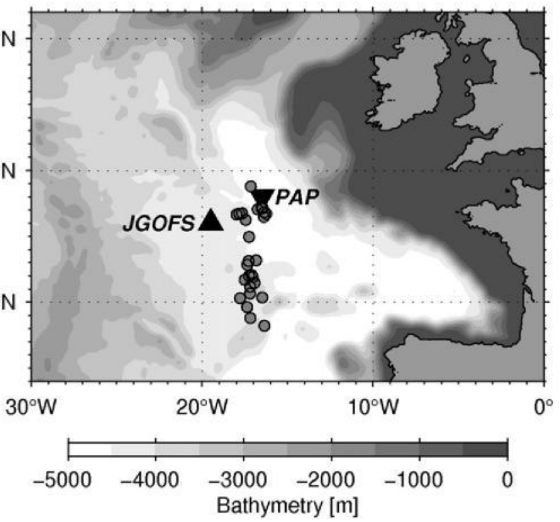

Figure 1: Northeast Atlantic showing the positions of the PAP observatory (inverted triangle), the JGOFS site (upright triangle), and the ship of opportunity programme (SOO, grey circles).

Nitrate measurements were taken using EnviroTech Nitrate Analysers (NAS-2), hereafter referred to as NAS and described in Hydes et al. (2000). Samples were taken twice daily and analysed for nitrate plus nitrite (hereafter referred to as nitrate) following the standard method described in Grasshoff (1983) adapted for the NAS (Boyd, 2003). The NAS was calibrated internally each week during the deployment using onboard 5 and 10 mmol m $^{-3}$ standards, which were used to quality control the data (selected between 20 to 70 m depth). The full nitrate dataset for 2003 to 2005 are shown in Kortzinger et al. (2008). In this paper we present nitrate data as monthly averages (71 standard deviation), calculated from up to 52 data points per month.

The HS-2 (Hobi Labs Inc., Tucson, Arizona, USA) fluorometers on the PAP mooring are self-contained instruments measuring optical backscatter at 2 wavelengths and fluorescence at 676 nm. To calibrate the instruments, fluorescence output was compared with samples collected on hydrographic casts, prior to each deployment. The samples were filtered and frozen onboard, then chlorophyll-a was acetone extracted and analysed on shore using the method of Welschmeyer (1994). Chlorophyll-fluorescence output provides an approximation of chlorophyll-a as the calibration changes throughout the year, due to variations in the phytoplankton species composition. On the mooring, chlorophyll-fluorescence measurements were taken every 2-h over 1-year deployments. Biofouling was significantly reduced using a motorised copper shutter, and instrument drift was corrected for using a second calibration on recovery of the instrument. HS-2 chlorophyll-fluorescence data, selected on depths shallower than 45 m, were available from July 2003 to July 2005.

Temperature and salinity measurements were made using Seabird SBE 37-IM recorders (Sea-Bird Electronics Inc., Bellevue, Washington, USA).

Other observational data sources

To extend the PAP time-series dataset and put it into a regional context, comparisons were carried out between *in situ* chlorophyll-fluorescence and those derived from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) on the OrbView-2 satellite, processed at NASA level 3 (global composites) as 8-day composites of 18 km pixel data.

Other ancillary observational data include Mixed-Layer Depth (MLD) data calculated from vertical temperature and salinity profiles, obtained from Argo profiling floats (http://www.coriolis. eu.org/). To obtain a continuous seasonal description, a large region was selected (45°N to 52°N and 26.08°W to 8.92°W, excluding the shelf area). In this region, the monthly average MLD represents between 12 and 22 profiles. De Boyer Montegut et al. (2004) found that the timing of the seasonal mixed-layer cycle was dependant on the choice of MLD criteria. In the North Atlantic a temperature change of 0.5°C is widely used as the MLD criterion (Monterey and Levitus, 1997; Spall et al., 2000; Cianca et al., 2007). The base of the mixed layer was identified as the first temperature that was 0.5°C lower than the surface Argo data and is directly comparable with that used by Cianca et al. (2007) for time-series studies in the Atlantic. This criterion was therefore used consistently throughout the study, to investigate relative year-to-year variations. For comparison, the MLD was also calculated using a temperature difference of 0.3°C (Dickey et al., 2001) to show how the winter MLD and timing of spring stratification varies with different criteria.

As the subsurface *in situ* nitrate time-series ceased in March 2005 the time-series was extended with surface data from a ship of opportunity (SOO), *Santa Maria* (Schuster and Watson, 2007). Onboard the *Santa Maria*, discrete nutrient samples were collected at 4-h intervals along the route from Portsmouth to the Caribbean. The nominal depth of these samples was 5 m (Hartman et al., 2008), which is shallower than the subsurface samples from the PAP observatory site although both are within the mixed layer. SOO data between 44°N and 50°N, 18°W to 16°W (see Figure 1) were selected, for comparison with the monthly mean *in situ* NAS nitrate data and there were up to three data points available per month within this area.

Satellite-derived near-surface velocities are used to analyze pathways of water advected to the PAP site. The velocities are computed from altimetric sea surface height through the assumptions of geostrophy and are readily available from AVISO (ftp://ftp.cls.fr/pub/oceano/AVISO/).

These velocity fields are integrated backwards in time for a given arrival date at the PAP location, in this case between January and March. Uncertainties in the method include the chaotic nature of the flow field, unresolved space and time scales in the velocity fields, and the lack of sub-gridscale mixing. Despite these limitations the data can be used to qualitatively display inter-annual differences in advection pathways.

Throughout this study new production refers to nitrate uptake calculated using the method shown in Henson et al. (2003). In summary, new production was calculated by multiplying the change in nitrate between months by the mixed-layer depth (calculated from Argo temperature profiles using the 0.5°C temperature criterion) with conversion of units to grams C using a C:N ratio of 6.6 (Redfield et al., 1963). All of the nitrate data for new production calculations were taken within the mixed layer either from the mooring (subsurface) or from the SOO (surface), neither extending to the base of the mixed layer. Monthly mean new production was positive in the productive months (March to August) and these values were summed to obtain the annual productivity. The errors were calculated (Fanning, 1992) from a consideration of the errors both in the monthly averaged MLD and monthly averaged nitrate concentrations.

From satellite data, primary productivity (PP) was calculated using the model described in Smyth et al. (2005). This method uses chlorophyll data from SeaWiFS merged into 8-day composites at a resolution of 18 km; taking into account day length, photosynthetically active radiation (PAR, from SeaWiFS monthly composites) and Sea Surface Temperature (SST, from Pathfinder monthly composites) as basic parameters to generate PP values (g C m^{-2}). The positive values were summed to obtain annual productivity.

Latent and sensible heat flux, solar and longwave radiative flux data were used to calculate daily air-sea Net Heat Flux (NHF). The data were obtained from the National Center for Environmental Prediction (NCEP) for the PAP observatory location (http://ingrid.ldeo.columbia.edu/SOURCES/.NOAA/.NCEP-NCAR/.CDAS-1/. DAILY).

Results and discussion

Three years of nitrate and hydrographic data from the *in situ* mooring at the PAP site are presented and discussed here in relation to changes in convective mixing and circulation. Inter-annual variations in production and in the timing of the spring bloom are also presented and discussed.

Inter-annual variations in hydrography

In situ temperature and salinity measurements from the sensor frame are shown in Figure 2. The main thermocline water mass in the PAP region is the Eastern North Atlantic Central Water (ENACW). This is a mode water that forms from deep winter mixing of subtropical North Atlantic Current (NAC) waters. It is circulated and modified to 300m within the inter-gyre region, between the Northeast Azores and European shelf east of the Azores (Pollard et al., 1996; Gonzalez-Pola et al., 2005; Gonzalez-Pola et al., 2006). The properties of ENACW change along a continuum with a temperature decrease to the north (due to heat loss and strong winds and increased winter convective mixing, Huthnance et al., 2001). Near-surface temperature and salinity profiles show considerable variability reflecting expected day-to-day changes in surface heating (Painter et al., 2010). During the winter period (January to March) three variants of Eastern North Atlantic Central Water (ENACW) can be distinguished (Figure 2). These are a low temperature, low salinity polar variant (ENACWp) and a high temperature and high salinity tropical variant (ENACWt), as identified by Castro et al. (1998). The third variant has intermediate transition characteristics of 12.2°C temperature and 35.66 salinity and was identified as type ‘H’ in the Castro et al. (1998) water mass analysis.

The lowest temperature and salinity water mass associated with the polar ENACWp variant is especially prominent in 2003 (Figure 2). This water mass tends to form north of 42°N and is associated with a higher nitrate signature (Castro et al., 1998). The highest salinity and temperature readings were seen in 2005 and are indicative of tropical ENACWt, which is formed further south near the Azores current around 36°N and is associated with lower nutrient concentrations (Castro et al., 1998). This reflects a trend of warming surface water at the PAP observatory location over three years (2003–2005) as seen in both the NCEP Sea Surface Temperature (SST) data and the *in situ* temperature data from the sub-surface mooring (Figure 3). For the January to March winter period, the surface temperature increased over the three-year period and winter 2005 is associated with warmer surface water (Figure 3). For example the average (±1 standard deviation) *in situ* daily temperature over this 3 month winter period increased from 12.14±0.34°C, (n=90) in 2003 to 12.25±0.23°C (n=91) in 2004 and then to 12.61±0.16 °C (n=90) in 2005.

In the Northeast Atlantic, year-to-year variations in the proportion of polar and tropical variants of ENACW reflect variations in winter convective mixing and advection (Perez et al., 1993; Pollard et al., 1996). This is in contrast to the western North Atlantic where sustained cold periods, associated with deep convective mixing in low NAO (North Atlantic Oscillation, Hoerling et al., 2001) years, can deliver low nutrient Sub Tropical Mode Water (STMW) to surface waters reducing productivity downstream (Palter et al., 2005).

In the region of the PAP observatory site Williams et al. (2000) and Kortzinger et al. (2008) suggest that the seasonal cycles of vertical convective mixing have a greater influence on the mixed-layer temperature than advection.

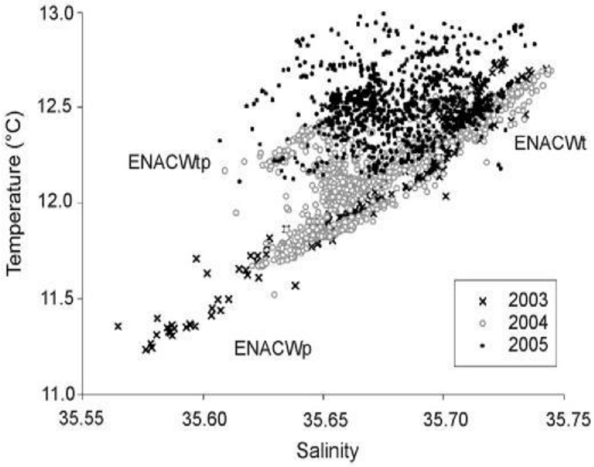

Figure 2: Inter-annual variation in water masses at the PAP time-series observatory site from temperature and salinity characteristics (from 20 to 225 m depth) in the January to March period, showing data from 2003 (crosses), 2004 (open circles) and 2005 (dots). Variants of Eastern North Atlantic Central Water ENACWt, ENACWp and ENACWtp are marked as described in the text.

The progressive warming, at the PAP site from winter 2003 to 2005 (seen in both the NCEP SST and subsurface temperature records in Figure 3), associated with a decrease in nitrate concentrations and productivity (Behrenfeld et al., 2006), may be due to a combination of shallower convective mixing and changes in surface circulation.

Seasonal and inter-annual variation in nutrients and mixed layer depth

Figure 4 shows seasonal and inter-annual variations in nitrate concentrations from 2003 to 2005 compared with MLD variations. Figure 4A compares monthly mean nitrate concentrations calculated from the *in situ* NAS dataset (up until March 2005) and surface nitrate concentrations from the ship of opportunity (SOO) to December 2005.

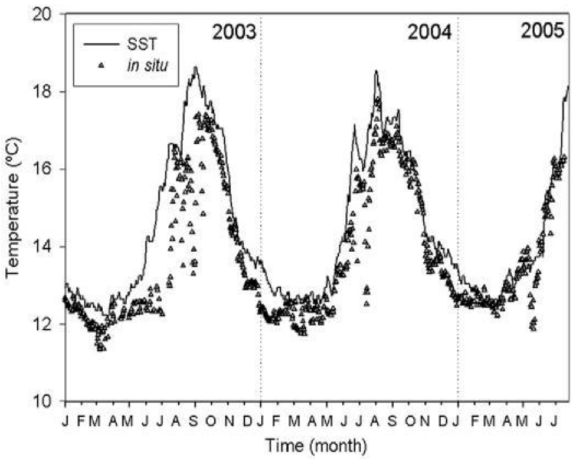

Figure 3:Variation in temperature at the PAP observatory site from 2003 to 2005 comparing *in situ* subsurface mooring based measurements (from 20 to 225 m, triangles) with sea-surface temperature (SST) data from the National Center for Environmental Prediction (NCEP, black line). Tick marks indicate the start of the month.

Overall, the nitrate data show the characteristic increase in concentration during winter months and nitrate depletion, due to phytoplankton growth, in the spring and summer. The winter nitrate concentrations were similar in 2003 and 2004 (Figure 4A) but lower in 2005. Over the three years presented the winter (January to March) surface nitrate concentration decreased from an average (±1 standard deviation) of 8.3±0.2 mmol m^{-3} (n=30) in 2003 to 7.0±1.6 mmol m^{-3} (n=45) in 2004, with a further decrease in 2005 to 4.9±0.4 mmol m^{-3} (n=65). The full *in situ* NAS nitrate data set, from which the monthly mean values were calculated (shown in Kortzinger et al., 2008), shows a decrease in the maximum individual winter nitrate measurements from a concentration of 10 to 7 mmol m^{-3} over the three-year period.

Variations in surface nitrate concentrations between the two datasets arise due to the wide area covered by the SOO sampling sites. These also tend to be south of the PAP observatory site (Figure 1). There is also an associated high spatial variability in the Northeast Atlantic in general (as illustrated by the variation in surface temperature and salinity in Figure 2 and Painter et al., 2010). However, the clear seasonal cycle in the SOO surface nitrate data confirms the general annual pattern seen in the *in situ* data at the PAP observatory site. In addition, the SOO surface nitrate data confirm the relatively low nitrate concentrations seen in the January to March period of 2005, compared with the preceding two years (Figure 4A). From the surface SOO nitrate data-set the monthly mean nitrate concentration in January 2005 was 5.7±0.17 mmol m^{-3} (*n*=7), compared with the *in situ* NAS nitrate concentration of 5.1±0.2 mmol m^{-3} (*n*=30) at the PAP observatory (Figure 4A).

Figure 4B presents seasonal and inter-annual variation in MLD from 2003 to 2005, calculated from Argo float temperature profiles. Monthly averaged MLD (±1 standard deviation) is shown, calculated using a temperature change criterion of 0.5°C (Monterey and Levitus, 1997) and 0.3°C (Dickey et al., 2001). The choice of criteria for calculating the MLD is important as using a lower temperature difference criterion of 0.3°C results in shallower estimates of winter MLD for each year from 2003 to 2005 (Figure 4B). Recent papers suggest that the 0.5°C MLD criterion may over-estimate the MLD (De Boyer Montegut et al., 2004). However, this criterion has been used widely in the North Atlantic and in the comparison of time-series data (Monterey and Levitus, 1997; Spall et al., 2000; Cianca et al., 2007). For each MLD criterion shown (Figure 4B), MLD peaks as expected in March (and as early as February in 2003), coinciding with the high winter nitrate concentrations. If overturning sets the peak surface nitrate concentrations at this latitude the year-to-year variation in winter nitrate may be due to variations in MLD between the years. However, from Figure 4B the MLD in winter 2005 is not any shallower than in other years, although, when a three month winter period (January to March) is considered there is an apparent decrease in MLD in 2005 (compared with 2003). For example using the temperature difference criterion of 0.5°C (Monterey and Levitus, 1997) the average MLD decreases from 322.65±94.1 m (*n*=124) in 2003 to 252±88 m (*n*=69) and 288.84±114.79 m (*n*=47) in 2005.

The variation in MLD is therefore in the order of 40m whereas calculations from nitrate profiles in the region (not shown) suggest a variation in MLD of the order of 150 m would be necessary to obtain the low winter nitrate concentration seen in 2005. Additionally the observed inter-annual variation in maximum MLD is not necessarily significant (note the high standard deviation in Figure 4B) and cannot fully account for the low winter nitrate concentrations in 2005.

Inter-annual variation in the winter mixed layer temperature depends on variations in surface heat flux, and on changes in stratification. This will influence the convective mixing of nutrients to the surface (Tang et al., 2006). At the PAP observatory site, there was a significant surface warming in 2005 seen in both the NCEP sea surface temperature (SST) and in situ observatory data (Figure 3). The average (±1 standard deviation) in situ temperature for the January to March winter period increased from 12.25±0.23°C (*n*=91) in 2004 to 12.61±0.16°C (*n*=90) in 2005. It is clear that this cannot be fully explained by variations in convective mixing.

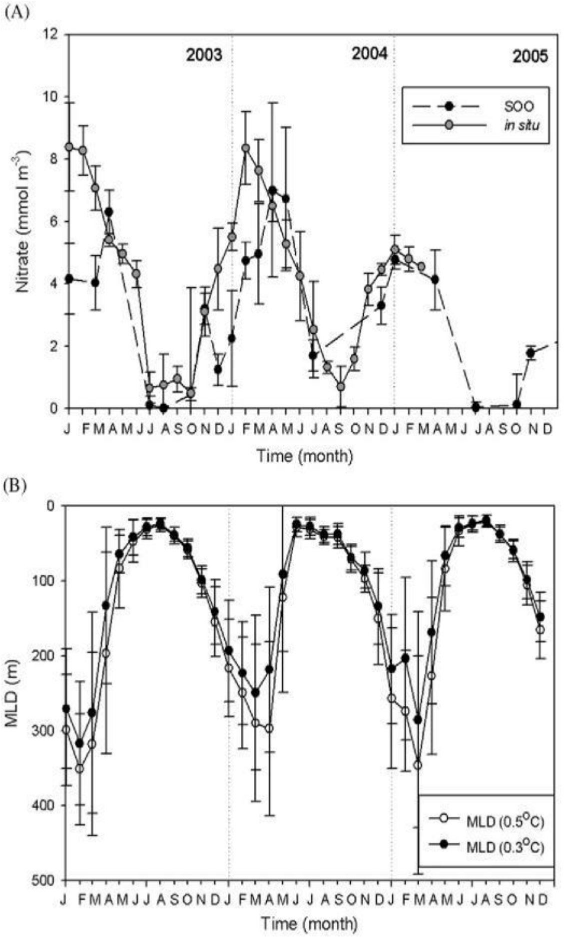

Figure 4. Nitrate concentrations and mixed-layer depth (MLD) estimates at the PAP observatory site from 2003 to 2005 showing: (A) *in situ* monthly mean (±1 standard deviation) NAS nitrate concentrations (grey circles), compared with discrete samples taken from a ship of opportunity (SOO, black circles). (B) monthly mean (±1 standard deviation) MLD from Argo float profiles (across 45°N to 52°N and 26.08°W to 8.92°W) calculated using a temperature difference criterion of 0.5°C (open circles), compared with a 0.3°C criterion (black circles). Tick marks indicate the start of the month.

Inter-annual variation in lateral advection

Figure 5 shows trajectories of 90 days duration ending at the PAP location in three consecutive winters (January to March of 2003, 2004 and 2005), computed from satellite-derived near-surface velocities. For all three years, mesoscale activity dominates the visual appearance of the trajectories (Figure 5). The PAP observatory site is influenced by both the North Atlantic Current (NAC) and a subsurface flow (0.05 m s^{-1}) of ENACW (Huthnance et al., 2001).

In all three years, episodes with direct feed from an eastward meandering NAC branch to PAP can be identified (Figure 5). However, the period in early 2005 differs from its counterparts in 2003 and 2004 in that there is no evidence for flow from the European shelf to the PAP site. In particular, the shelf break off Porcupine Bank (location shown in Figure 5a) seems to be a source region for waters arriving at PAP in the winters of 2003 and 2004, but not in 2005. The shapes of the trajectories (Figure 5) suggest that eddy activity is important for transporting the water from the shelf region to the PAP site.

The observed changes in hydrography and nutrient concentrations at the PAP site between the winters of 2003, 2004 and 2005, coincide with a latitudinal shift of where the NAC crosses the Mid-Atlantic Ridge and enters the eastern basins as published by Bower and von Appen (2008): they identify a shift from a "southern mode"to a more northerly crossing between early 2003 and late 2004. The southern mode would seem to bring the NAC closer to the PAP site, while the northern location may leave the PAP site more exposed to subtropical conditions and less influenced by NAC-related eddy activity. This hypothesis is in agreement with the inter-annual changes of properties observed at the PAP site, namely the higher temperature and salinity signal, with lower nutrient concentrations seen in 2005.

Kortzinger et al. (2008) largely ignored circulation at the PAP site, assuming convective mixing is a dominant process influencing mixed-layer temperature and nitrate concentration in the region (Williams et al., 2000). However, fixed-point time-series observations are influenced by spatial variability passing the point of observation (McGillicuddy et al., 1998; Painter et al., 2010). On short time-scales sub-mesoscale (Levy et al., 2001) and mesoscale eddy events may increase nutrient availability (McGillicuddy et al., 1998). For example, connections between upper ocean mesoscale variability and biological signals of the spring bloom in the Northeast Atlantic were revealed at the JGOFS NABE site (Robinson et al., 1993) and in the POMME project (Levy et al., 2005a). Variations in nutrient concentration and phytoplankton activity have been reported within an eddy at 60°N in the Atlantic over 12 days in June (Rees et al., 2001). Painter et al. (2010) suggests that eddy capping may prevent surface expression of higher nitrate concentrations affecting surface signals. However, Wilson and Adamec (2002) and Palter et al. (2005) suggest that once the seasonal signal has been removed there is insufficient correlation between sea level anomalies and surface chlorophyll to generate the surface chlorophyll fields they observed. In conclusion, it is clear that lateral advection cannot be ignored and may significantly influence the surface temperature and nitrate concentrations in the region of the PAP site.

Seasonal and inter-annual variation in production

Figure 6 presents new production and total primary production estimates for the PAP region and the results suggest a decrease in productivity from 2003 to 2005. New production was estimated from nitrate assimilation using nitrate concentrations (shown in Figure 4A) and MLD data (Figure 4B, calculated using the 0.5°C temperature change criterion) following the method in Henson et al. (2003).

The values obtained were summed to show the annual new production over the productive period (from March to August). The results show that there was a decrease in new production from 85.4±4.3 gC m^{-2} a^{-1} in 2003 to 78.5±6 gC m^{-2} a^{-1} in 2004, with a further decrease to 40.3±4.3 gC in 20 m^{-2} a^{-1} in 2005.

The trend towards lower production over the three-year period was also reflected in independent calculations of total Primary Production (PP) using the SeaWiFS data. Variations in primary production (calculated from methods by Smyth et al., 2005) are shown in Figure 6 (as an average ±1 standard deviation). The primary production presented here may represent the lower limit as it is biased toward the surface mixed layer. These satellite productivity calculations also assume a constant chlorophyll concentration with depth, which may also be a source of error in the primary production calculations through the year. The integrated annual primary production was calculated from satellite data and is higher than new production, as expected. It also decreases from 143±17 gC m^{-2} a^{-1} in 2003, to 141±19 gC m^{-2} a^{-1} in 2004 with the lowest productivity in 2005 at 116±17 gC m^{-2} a^{-1}. Therefore, both independently calculated productivity data sets (new and primary production) show a similar trend of decreasing production over the three-year period from 2003 to 2005, at the PAP observatory site.

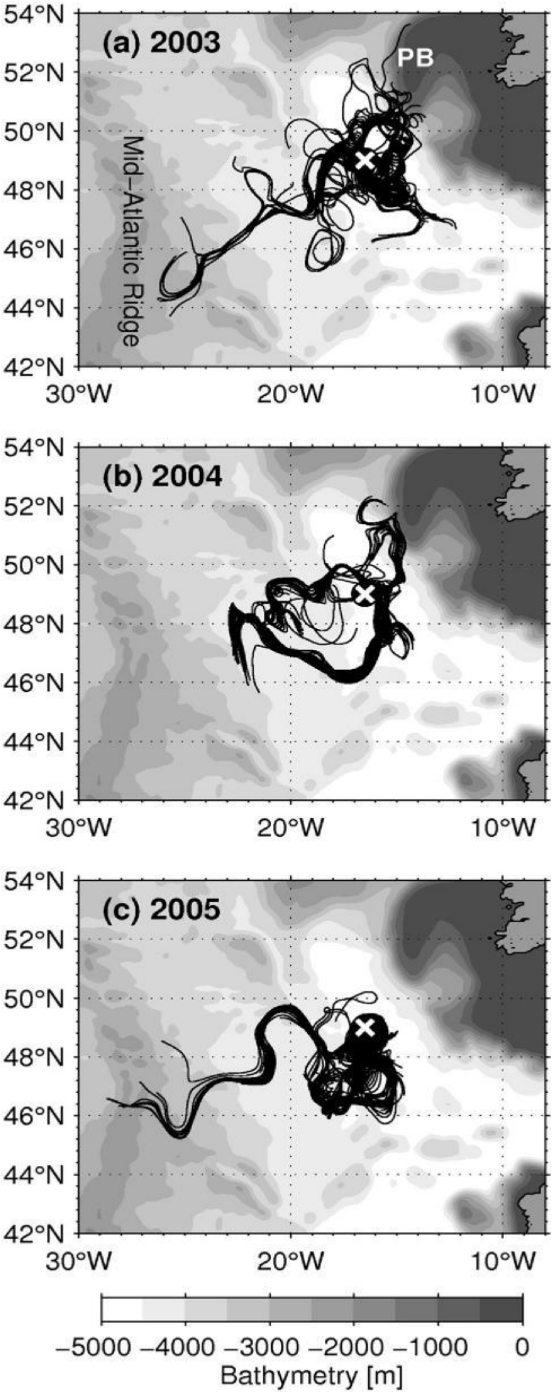

Figure 5. Trajectories leading to PAP site computed from altimetry-derived geostrophic velocities. Each trajectory begins at the "open" side, lasts for 90 days, and ends at the PAP site (white cross) in the period January to March of the indicated years. In Figure 5a PB indicates the Porcupine Bank and the Mid-Atlantic Ridge is also highlighted.

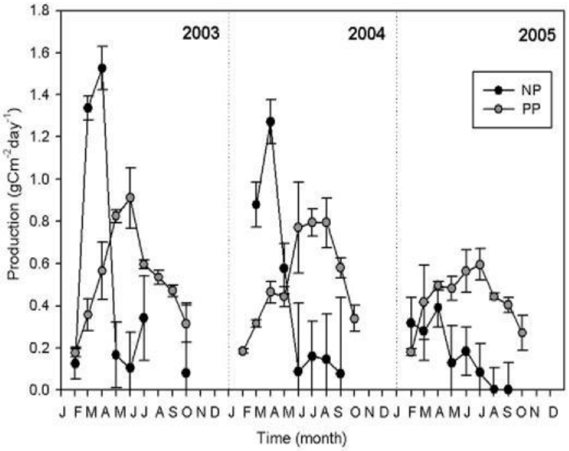

Figure 6. New production (NP) with 1 standard deviation error bars (calculated from a consideration of the errors in MLD and nitrate data) at the PAP observatory site from 2003 to 2005 (black circles), compared with primary production (PP), calculated from SeaWiFS chlorophyll data within 200 km radius of the PAP observatory site (grey circles). Tick marks indicate the start of the month.

New production estimates show the potential production based on nitrate convectively mixed to the surface during winter; whether or not the bloom occurs will depend on many other factors. The upward flux of nitrate has been routinely used to estimate production (Minas and Codispoti, 1993; Emerson et al., 1993; Koeve, 2001; Henson et al., 2003). However, the nitrate assimilation method may be biased to low or high estimates between post and pre-stratification events (Kortzinger et al., 2008). Overestimation of new production estimated solely with nitrate data can arise when other sources of biologically available nitrate, such as nitrate regenerated from ammonium nitrification, are ignored (Dugdale and Goering, 1967; Yool et al., 2007). Nitrification can be important within the euphotic layer, and may sustain a variable fraction of photoautotrophic production (Yool et al., 2007). It is acknowledged that these methods do not take regenerated nitrate into consideration (Waniek et al., 2005).

New production estimates are heavily dependent on the choice of MLD. For example, using a temperature difference criterion of 0.3°C (Dickey et al., 2001) decreases the calculated new production over the productive period, to 68.7 ± 4.4 m^{-2} a^{-1} (for 2003), compared with 85.4 ± 4.3 gC m^{-1} a^{-1} calculated using the 0.5°C criterion (Monterey and Levitus, 1997). However irrespective of the temperature difference criteria for MLD calculation new production estimates decrease from 2003 to 2005. The nitrate assimilation method may underestimate the bio-available nitrate especially when the euphotic depth is deeper than the mixed-layer depth in summer. It also makes assumptions on the C:N ratio (Kortzinger et al., 2001). However, the calculation of new production from nitrate uptake is still common practice in biogeochemical studies (Koeve, 2001; Henson et al., 2003; Waniek et al., 2005). In having a year-round *in situ* dataset some of the assumptions can be minimised. For example, there is no need to calculate wintertime nitrate with the associated errors (Glover and Brewer, 1998; Koeve, 2001) and there is no need to make assumptions on the length of the productive cycle (Waniek et al., 2005).

The method provides a simple illustration of year-to-year variations in nitrate uptake at the PAP observatory site with low production corresponding to low winter nitrate concentrations and warmer surface water in 2005, compared with the previous two years. One possible reason for the decrease in productivity observed in 2005 is increased stratification, which forms a barrier to nutrient exchange, although the advection of low nutrient water to the region will also decrease the productivity seen. Despite the limitations associated with the calculation of new production, it indicates year-to-year variations in productivity within the context of large-scale changes in annual production derived from satellite data. A 6.7% decrease in production in the North Atlantic has been seen since the 1980's as shown by Gregg et al. (2003), from a comparison of the Coastal Zone Color Scanner (CZCS, 1979–1986) and Sea-viewing Wide Field-of-view Sensor (SeaWiFS, 1979–2003) datasets. Gregg et al. (2003) found a corresponding increase in sea-surface temperature in the high-latitude North Atlantic. Likewise, Behrenfeld et al. (2006) shows a general trend of decreased convective mixing, increased stratification and consequent decrease in production in the Northeast Atlantic since 1999.

Overall, the estimates of new production presented here provide a useful, if simplistic, indication of new production. Independent calculations of total primary production (using the Smyth et al., 2005 productivity model based on SeaWiFS data) confirm the trend of decreasing productivity from 2003 to 2005.

Comparison of in situ and satellite chlorophyll estimates

Figure 7 shows a comparison of weekly averaged *in situ* chlorophyll-fluorescence data with near surface SeaWiFS chlorophyll over one year (2004). In general, there is good agreement between *in situ* and satellite data in the winter as the water column is well mixed and chlorophyll is constant with depth. The data presented in Figure 7 show increases in chlorophyll to a maximum value (with large variation) in April, indicating the spring bloom. There is also a clear summer bloom at the PAP observatory site seen in both the remote sensing and *in situ* datasets. Summer phytoplankton blooms occur when surface heat flux and optical properties are dominant in determining the mixed layer temperature (Tang et al., 2006). The implied chlorophyll concentrations from the *in situ* data tend to be higher than suggested by surface satellite data in the summer (Figure 7) due to the development of a seasonal deep chlorophyll maximum (Cullen, 1982). Once the mixed-layer depth shoals (to 25 m) the surface layer becomes decoupled from the seasonal deep chlorophyll maximum. The euphotic depth (48 m, Martin et al., 2010) is deeper than the MLD in the summer and is beyond the reach of satellite measurements (Joint and Groom, 2000).

It should be noted that chlorophyll-fluorescence measurements are a qualitative tool for the estimation of relative changes in biomass (Aiken, 1981) and *in situ* measurements of chlorophyll- fluorescence are subject to considerable uncertainties due to changes in taxa, size and physiological state of the organisms being observed and photo-quenching due to changes in the ambient light field. However, chlorophyll measurements derived from satellite data are also subject to uncertainties, as a result of generic pigment retrieval algorithms being used (Fuentes-Yaco et al., 2005) and the naturally varying optical characteristics of phytoplankton dependent on the seasonally changing dominance in phytoplankton assemblages.

The larger fluctuations seen in the *in situ* chlorophyll-fluorescence data may be attributable to changes in the depth of the sensor frame, although the sensor was at a fairly consistent depth (with an average depth ± 1 standard deviation of 37.5 ± 14.82 m) throughout the year. The PAP observatory provides point measurements (in space), whereas satellite measurements are averaged in the vertical and horizontal, which may remove some of the patchy nature of the system. Overall the high-resolution *in situ* dataset can resolve short-term variability in bloom timing, which may not be adequately resolved with 1-week composites of satellite data (Levy et al., 2005b). Data from 2003 are not shown, as the in situ measurements did not start until later in the year. In 2004 the spring bloom chlorophyll-florescence peaks at 1.5 mg m^{-3} on 29 April whereas in 2005 the spring bloom peaks earlier, on 11 April (Figure 8), indicating year-to-year variations in the timing of the spring bloom at the PAP site. Inter-annual variations in spring bloom timing are linked to changes in sea-surface temperature as winter meteorological conditions affect the depth of the winter mixed layer and end of winter nitrate concentrations (Waniek, 2003; Behrenfeld et al., 2006).

Inter-annual variation in bloom initiation and Net Heat Flux

Year-to-year variation in the timing of the spring bloom can be seen in Figure 8, which shows a comparison between Net Heat Flux (NHF), calculated from NCEP data, with in situ chlorophyll-fluorescence (chlorophyll-a) data, between January and May in 2004 and 2005.

At the PAP observatory site production is intimately coupled to MLD (Kortzinger et al., 2008), although it is clear from this study that lateral advection may also influence production at the PAP observatory site.

Phytoplankton growth can be related to heat flux (across the atmosphere-ocean boundary) as it controls the actual state of convective mixing at a given location and a negative heat flux indicates increased convective mixing (Waniek, 2003; Levy et al., 2005b). The bloom is initiated following periods of near zero Net Heat Flux (NHF) during transient conditions in winter and early spring (Waniek, 2003) and then ceases when NHF is negative. Overall, there were large variations in NHF in 2004 with few periods of sustained positive NHF until April (Figure 8).

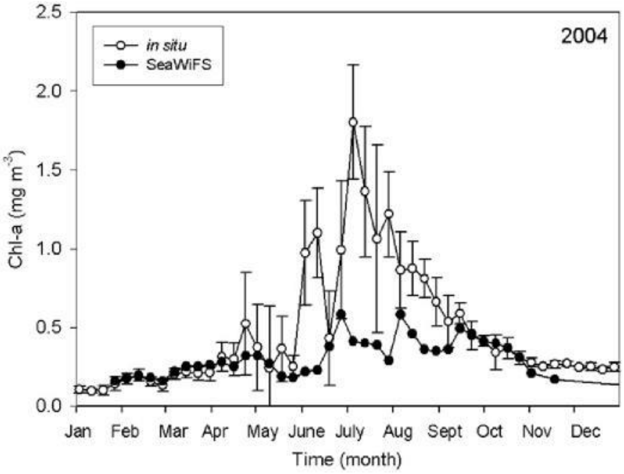

Figure 7. Weekly mean (±1 standard deviation) chlorophyll-fluorescence (Chl-a) during 2004 from the *in situ* HS-2 fluorometer located subsurface (at an average ± 1 standard deviation depth of 37.56±14.82 m) on the mooring at the PAP observatory site (open circles) compared with 8-day composites of SeaWiFS chlorophyll data (black circles) within 200 km radius of the PAP observatory site. Tick marks indicate the start of the month

In 2004 there is a suggestion of winter production in the in situ chlorophyll-fluorescence data (Figure 8), with periods of slightly elevated in situ chlorophyll-fluorescence (of up to 0.3 mg m^{-3}) on 23 January, 4 and 10 February 2004 corresponding to positive NHF on the previous day. In the spring periods (eg: April 2004) increasing chlorophyll-fluorescence can be linked to periods of positive NHF (Figure 8), 7 to 9 days prior to initiation of the bloom. The specific dates in 2004 of positive NHF were 31 March and 19 April with respective increases in chlorophyll-fluorescence on 8 and 26 April 2004. Early in 2004 NHF did not remain positive for more than three days at a time (Figure 8) and consequently there were a series of disruptions to bloom development. The first chlorophyll-fluorescence peak in April was followed by a single period of negative NHF, which resulted in two distinct chlorophyll peaks to the spring bloom.

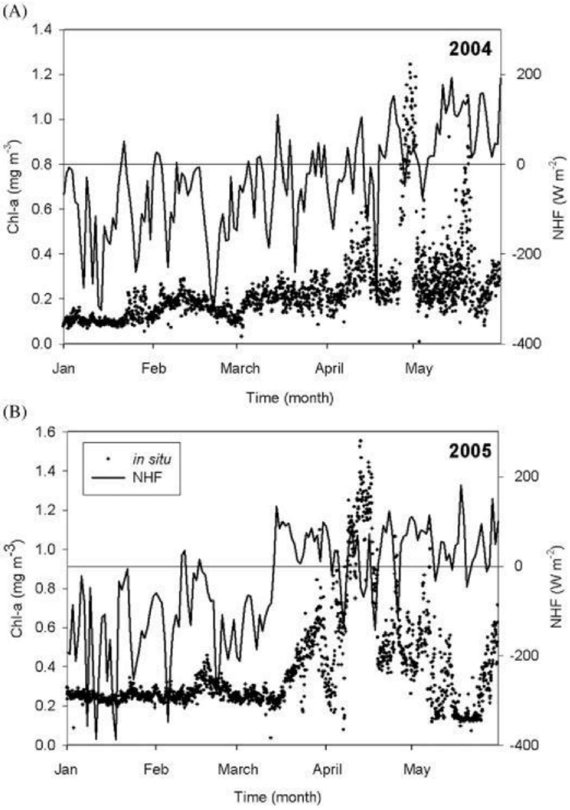

Figure 8. Timing of the spring bloom at the PAP observatory site during the January to May period (tick marks indicate the start of the month) for (A) 2004 and (B) 2005 showing: daily *in situ* HS-2 chlorophyll-fluorescence (Chl-a) from the mooring (black dots); and daily Net Heat Flux (NHF, black line) with an illustration of zero NHF (horizontal line) for reference. NHF was calculated from sensible, latent heat flux, solar and radiative flux data available from NCEP

In 2005, there are two periods of winter phytoplankton growth indicated by an increase in chlorophyll-fluorescence (Figure 8). These occurred on 23 January 2005 and 19 February 2005. Both can be linked to increased NHF (Figure 8), which occurred on 22 January and 10 February respectively, although NHF does not reach positive values at this time this may be due to errors associated in calculating NHF (which are in the order of 10W m^{-2}, S. Josey, pers com).

Previous studies estimate that up to 50% of annual production occurs before the main spring bloom (Garside and Garside, 1993; Koeve, 2001). The brief periods of winter production in January and February at the PAP time-series site suggest short periods of adequate solar radiation to initiate an increase in chlorophyll at that time. Spring shoaling of the mixed layer occurred earlier in the year in 2005 than in 2004, which may have prompted early stabilization and stratification of the water column. Therefore, chlorophyll-fluorescence increased earlier in the year with the main spring bloom increase from mid-March 2005 following a period of positive NHF (Figure 8). Overall in spring 2005, NHF was less variable than in 2004 and there were fewer disruptions to the initial spring bloom development. Spring bloom development was interrupted by a period of negative NHF (Figure 8) from 6 to 8 April, when in situ chlorophyll-fluorescence decreased. Following a turn to positive NHF chlorophyll-fluorescence increased to 1.55 mg m-3 (Figure 8) reaching a peak on 11 April. Overall, there were three springtime peaks in chlorophyll-fluorescence in 2005 (Figure 8) and each of these (on 30th March, 13 April and 7 May) followed a period of negative to positive NHF. The early bloom in 2005 corresponds to warmer surface water seen at the start of the year compared with 2004 (Figure 3).

The results are consistent with Waniek, 2003, who showed delays of up to 12 days between a turn to positive NHF and bloom initiation in the Northeast Atlantic. The timing of the spring bloom at the PAP site is strongly influenced by the shoaling of the local MLD. The dataset suggests increases in chlorophyll-fluorescence following periods of stabilisation, indicated by positive net heat flux between January and March. The dataset also shows a delay in the spring bloom initiation between years. The passage of weather systems will vary in frequency and intensity from year-to-year affecting mixed-layer shoaling in spring (Follows and Dutkiewicz, 2002). Storms can influence primary production in spring and summer through increased vertical convective mixing of nutrients and single storms can double the MLD, increasing euphotic zone nutrients over days rather than months (Huthnance et al., 2001).

The apparent timing of the seasonal cycle of the mixed layer can be influenced by the criteria used to calculate MLD, for example decreasing the temperature difference used in the calculation will shift MLD shoaling to earlier in the year (De Boyer Montegut et al., 2004). It would be difficult to model inter-annual variability in the timing of the spring bloom using a vertically resolved 1D model given the importance of horizontal advection at the PAP site location, although similar observations have been modelled by Waniek (2003) and Levy et al. (2005b). It is also difficult to quantify the exact timing of bloom initiation in relation to a NHF of zero given the spatial variability in the region and errors associated with the calculation of NHF. However, a turn to positive NHF values indicates a bloom (with a delay of 1 to 9 days in the region of the PAP observatory), while negative NHF can be associated with a decrease in chlorophyll-fluorescence as shown by Waniek (2003).

Conclusions and further work

We have presented three years (2003 to 2005) of year-round surface and subsurface time-series data at the PAP time-series observatory. These data provide a biogeochemical dataset of high temporal resolution. These long-term datasets are essential for interpreting shorter term sampling efforts, for example from research cruises (Painter et al., 2010; Smythe-Wright et al., 2010). The data set also provides key winter data absent from many other studies (Koeve, 2006). Although the seasonal cycles are generally well known, the resolution of this dataset provides an opportunity to investigate year-to-year variations in the winter nitrate concentrations in relation to phytoplankton growth and production. Changes in the timing and depth of winter convective mixing with corresponding changes in winter nitrate and production were considered within broader trends in the Northeast Atlantic.

In the winter period, surface waters were evidently warmer at the PAP observatory site in 2005 than in the previous two years (from NCEP SST and *in situ* data). Likewise, the surface nitrate and productivity decreased. Overall year-to-year variations in annual new production and independent primary production estimates from the PAP observatory suggest a decrease in production from 2003 to 2005. The lowest production occurred in 2005 during a warm winter when surface and subsurface nitrate concentrations were lower than in the preceding two years. This is supported by a progressive decline in primary production in the North Atlantic since 1999 (highlighted by Gregg et al., 2003 and Behrenfeld et al., 2006).

To date there has been an assumption that in the Northeast Atlantic, in the region of the PAP observatory site, the main control over inter-annual variability in nitrate supply is convective mixing (as shown by Williams et al., 2000). Although the source of nutrients to the surface and subsurface waters at the PAP observatory site still needs to be fully resolved, it is clear that lateral advection and mesoscale variability (see Painter et al., 2010) are important influences at this site. These processes may explain the year-to-year variability in temperature, productivity and nitrate concentrations in the absence of significant differences in convective mixing.

The frequency of observations made at fixed positions is critical to the interpretation of data (McGillicuddy et al., 1998). Calculating monthly means from the high-resolution (twice-daily) nitrate data has allowed us to identify seasonal trends. In contrast, the high-resolution *in situ* chlorophyll-fluorescence dataset aids resolution of short term (1–8 day) variability in bloom timing, driven by atmospheric forcing, which cannot be adequately resolved with 1-week satellite data (Levy et al., 2005b). We have shown a clear year-to-year variation in the spring bloom timing with increased chlorophyll-fluorescence following periods of positive net heat flux, with a delay of 1–9 days. The spring bloom at the PAP observatory site occurred earlier in 2005 than in 2004 due to variable NHF in 2004, with few periods of sustained positive NHF until April. A thorough modelling investigation would be required to take account of all of the factors influencing bloom initiation and intensity at this site.

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Chapter 3

Biogeochemical variations at the Porcupine Abyssal Plain Sustained Observatory in the northeast Atlantic Ocean, from weekly to inter-annual timescales

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Abstract

We present high-resolution autonomous measurements of carbon dioxide partial pressure p(CO_2) taken in situ at the Porcupine Abyssal Plain sustained Observatory (PAP-SO) in the northeast Atlantic (49° N, 16.5° W; water depth of 4850 m) for the period 2010-2012. Measurements of p(CO_2) made at 30 m depth on a sensor frame are compared with other autonomous biogeochemical measurements at that depth (including chlorophyll-a fluorescence and nitrate concentration data) to analyse weekly to seasonal controls on p(CO_2) flux in the inter-gyre region of the North Atlantic. Comparisons are also made with in situ regional time series data from a ship of opportunity and mixed layer depth (MLD) measurements from profiling Argo floats. There is a persistent under-saturation of CO_2 in surface waters throughout the year which gives rise to a perennial CO_2 sink. Comparison with an earlier data set collected at the site (2003- 2005) confirms seasonal and inter-annual changes in surface seawater chemistry. There is year-to-year variability in the timing of deep winter mixing and the intensity of the spring bloom.

The 2010-2012 period shows an overall increase in p(CO_2) values when compared to the 2003-2005 period as would be expected from increases due to anthropogenic CO_2 emissions. The surface temperature, wind speed and MLD measurements are similar for both periods of time. Future work should incorporate daily CO_2 flux measurements made using CO_2 sensors at 1m depth and the in situ wind speed data now available from the UK Met Office Buoy.

Introduction

A persistent feature of the subpolar North Atlantic is under-saturation of carbon dioxide (CO_2) in surface waters throughout the year, which gives rise to a perennial CO_2 sink (Körtzinger et al., 2008). This makes the north east Atlantic a region of great importance in the global carbon cycle. There is evidence for inter-annual variation in the CO_2 sink (1-3 molm^{-2} a^{-1}) due to changes in wintertime mixing and stratification (Schuster and Watson, 2007). Changes in the amount of CO_2 absorbed by the ocean may have implications for the global carbon cycle now and for the role of the ocean as a carbon sink in the future. Studies of the physical and biological processes regulating surface water p(CO_2) (partial pressure of CO_2) are required to estimate future trends in the ability of the ocean to act as a sink for increasing CO_2 in the atmosphere. Frequent observations from fixed positions are critical to make these calculations (McGillicuddy et al., 1998).

Accurate, high-resolution, long-term data sets are offered by time series studies such as the Porcupine Abyssal Plain sustained Observatory (PAP-SO) in the northeast Atlantic at 49° N, 16.5° W (4850 m water depth) where a fixed-point mooring has been in place since 2002 (Hartman et al., 2012). The PAP-SO is in the North Atlantic Drift Region, a biogeographical province defined by deep winter convective mixing (Longhurst, 2006; Monterey and Levitus, 1997). The surface mixed layer depth can change from 25 m in the summer to over 400 m in winter. A 2-fold decrease in winter nitrate concentration over a 3-year period from 2003 has been attributed to a combination of shallower winter convective mixing and changes in surface circulation (Hartman et al., 2010). The PAP-SO is in an area with relatively high wind speeds, frequently greater than 10 ms^{-1}. High wind speeds have a significant effect on CO_2 flux (Takahashi et al., 2002). The CO_2 flux at the PAP-SO was calculated from $p(CO_2)$, between 2003 and 2005 as a net flux into the ocean of over 3 mol m^{-2} a^{-1} (Körtzinger et al., 2008). This is a significant sink compared with subtropical time series sites such as ES-TOC (near the Canary Islands, 29.17° N, 15.5° W), which is an overall annual CO_2 source region (0.05 mol m^{-2} a^{-1}, González-Dávila et al., 2003).

Recently, the decline in North Atlantic CO_2 uptake from 1994-1995 to 2002-2005 has been linked to a variation in the North Atlantic Oscillation (Schuster and Watson, 2007; Padin et al., 2011). The decreased uptake may be a consequence of declining rates of wintertime mixing and ventilation between surface and subsurface waters due to increasing stratification. Enhanced stratification forms a barrier to nutrient exchange, which may result in a progressive decline in primary production (Field et al., 1998), as was seen in the North Atlantic between 1999 and 2004 (Behrenfeld et al., 2006). The observed decrease in nitrate concentration and productivity in this region (Behrenfeld et al., 2006), may in turn affect the oceanic uptake of $p(CO_2)$.

In this paper, we present recent year round time series data of temperature, salinity, nitrate concentration, chlorophyll-a fluorescence and $p(CO_2)$ collected at 30 m depth from May 2010 to June 2012. The data are compared with an earlier published data set (from July 2003 to July 2005) and additional $p(CO_2)$ measurements made from a ship of opportunity. The in situ data set is considered in relation to convective mixing processes using mixed layer depth (MLD) estimates calculated from profiling Argo floats. The weekly air-sea CO_2 flux at the PAP-SO site was calculated from in situ $p(CO_2)$ measurements and ancillary satellite wind speed data sets. The objective of this study is to examine the biogeochemical variations at the PAP-SO in the northeast Atlantic over different periods from weekly, seasonal to annual.

Materials and methods

Study site

The position of the PAP-SO at 49° N, 16.5° W is shown in Figure 1. Lampitt et al. (2001) has summarised the hydrography, meteorology and upper mixed layer dynamics in the region.

In situ data

The instrumentation of the PAP-SO has been described in detail by Hartman et al., 2012 (see Table 1 and Figure 1 therein) and is briefly summarised here. Since 2002 instruments on a mooring at the PAP-SO (49° N, 16.5° W) have recorded a suite of parameters in the mixed layer. Temperature and salinity measurements were made on a frame at a nominal depth of 30 m, using Seabird SBE 37-IM MicroCAT recorders (Sea-Bird Electronics Inc., Bellevue, Washington, USA). Measurements of nitrate concentration, chlorophyll-a fluorescence and $p(CO_2)$, were also made using biogeo-chemical sensors on the frame, often within the deep chlorophyll maximum. Between 2002 and 2007 the sensor frame depth varied from 20 to 225 m, deflecting in response to local currents. A surface buoy was added in 2007 so that measurements were consistently made at 30 m depth. In 2010, collaboration with the UK Met Office led to a redesigned infrastructure, providing simultaneous surface physical and biogeochemical measurements with surface meteorological data.

p(CO$_2$) data during the two periods of time examined here were collected using different instrumentation. From 2003 to 2005 it was measured using a SAMI (Sunburst Sensors LLC, USA) sensor, which is based on equilibration of a pH indicator solution, contained in a gas-permeable membrane, with ambient p(CO$_2$) and subsequent spectrophotometric determination in the equilibrated solution (DeGrand-pre et al., 1995). Twice daily p(CO$_2$) measurements, from 2010 to 2012, were made using a membrane-based PRO-CO$_2$ sensor (Pro-Oceanus, Canada), which uses an infrared detector and is internally calibrated through an auto-zero calibration function (Jiang et al., 2014). Note that a measurement error of an early version of the PRO-CO2 sensor during the deployment, induced by the fluctuation of detector cell temperature, was identified and corrected (see Jiang et al., 2014 for further details). A pump was used (Seabird Inc.) to improve water flow across the sensor membrane to accelerate attaining equilibrium. The surface in situ p(CO$_2$) time series ceased between 2006 and 2009 due to funding issues.

Although measured by different instruments, the two p(CO$_2$) data sets were calibrated in a way to make them comparable: the sensor outputs were calibrated against p(CO$_2$) values calculated from dissolved inorganic carbon (DIC) and total alkalinity (TA) from discrete samples taken at the mooring site during deployment/recovery cruises; and plausibility checks were made with underway p(CO$_2$) measurements around the PAP site. The 2003-2005 data were previously published (see Körtzinger et al., 2008 for details) with a precision of 1 µatm and accuracy estimated as 6-10 µatm. The 2010-2012 data have a similar precision (1 µatm) and accuracy (6 µatm).

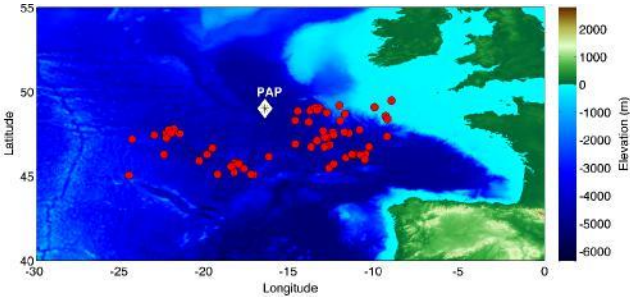

Figure 1: Map of the inter-gyre region of the northeast Atlantic showing the bathymetry around the PAP observatory (white diamond) and the ship of opportunity (SOO) sampling positions (red circles) from 2010 to 2012.

A Hobi Labs Inc., HS-2 fluorometer (Arizona, USA) was used on the PAP-SO mooring to estimate chlorophyll-a concentration until 2005 when an alternative ECO FLNTU (WETlab, USA) fluorometer came into use. The quoted precision for fluorescence measured by these fluorometers is 0.04 %, however as described by Hartman et al. (2010), fluorescence output can only provide an approximation of the chlorophyll-a concentration.

The ratio of fluorescence to chlorophyll-a concentration changes throughout the year, due to variations in the phytoplankton species composition. On the mooring, chlorophyll-a fluorescence measurements were taken every 2 h over the 1 year deployments and biofouling was controlled using motorised copper shutters on each of the fluorometers.

Nitrate concentration measurements were initially made using wet chemical NAS Nitrate Analysers (EnviroTech LLC, USA), precision 0.2 µmol L^{-1}, as described in Hydes et al. (2000), with twice daily sampling frequency and internal calibration as described by Hartman et al. (2010). From 2010 additional higher frequency inorganic nitrate measurements were made using UV detection methods (ISUS, Satlantic), with a precision of 1 µmol L^{-1}.

For each instrument, the manufacturer's calibration was checked at the start of each deployment and a correction for instrument drift was made using a second calibration check on recovery of the instruments. Biogeochemical data from the PAP-SO are available from EuroSITES (2014) and the British Oceanographic Data Centre (BODC). Data presented here cover the period when $p(CO_2)$ measurements are available, July 2003 to the end of June 2005 (with deployments in July 2003, November 2003, June 2004) and the period from May 2010 to June 2012 (with sensor deployment in May 2010, September 2010, July 2011, May 2012). All of the measurements are within the mixed layer although the depth of measurements is closer to the 30m nominal depth after mooring redesign to incorporate a surface float in 2007.

Other observational data sources

Temperature and salinity data were taken from Argo floats (http://www.coriolis.eu.org), extracting (30 ± 5) m depth data. To obtain a continuous seasonal description, a large region around the PAP site was selected (45-52° N and 26.08-8.92° W, excluding the shelf area). The Argo data have a potentially lower accuracy (0.005 °C for temperature and 0.1 for salinity) than the in situ MicroCAT data (0.002 for salinity and 0.002 °C for temperature). However, the Argo data were chosen over the in situ data for all calculations as they have a larger temporal coverage and are internally consistent.

The $p(CO_2)$ time series was compared with surface data from a ship of opportunity (SOO) running from Portsmouth, UK, to the Caribbean (Schuster and Watson, 2007). On-board the SOO continuous $p(CO_2)$ measurements are made using a calibrated system with a showerhead equilibrator (Schuster et al., 2009). Data are available from the Surface Ocean CO_2 Atlas (SOCAT; http://www.socat.info/). Discrete nutrient samples were collected at 4 h intervals along the same route and were analysed ashore (Hartman et al., 2008). This provides an approximately monthly nutrient sample and $p(CO_2)$ data points close to the PAP-SO on the return route of the ship. The nominal depth of these samples is 5 m, which is shallower than the 30 m samples from the PAP-SO. We selected SOO data between 52 and 45° N and 8.92 and 26.08° W, and then took the average $p(CO_2)$ values that were within that area on the same day as the sample from the PAP-SO site.

Through collaboration with the UK Met Office in situ wind speed data are available since 2010. However, for consistency in calculations of CO_2 flux between the two time periods (2003-2005 and 2010-2012) considered here we took wind speed data from weekly satellite data: Fleet Numerical Meteorology and Oceanography Center (FNMOC) 1 ° by 1 °. We calculated a weekly mean from the 6 hourly, 10 m height data; available from http://las.pfeg.noaa.gov/.

The air-sea CO_2 flux (in mmol m^{-2} d^{-1}) was calculated from the air-sea $p(CO_2)$ difference, temperature and salinity (30 m) and wind speed at 10 m height, using the following equation:

$$F(CO_2)=k\times K_0\ [p(CO_{2,sea})-p(CO_{2,air})] \qquad (1)$$

where k is the transfer coefficient based on the wind speed-dependent formulation of Nightingale et al. (2000), scaled to the temperature-dependent Schmidt number according to Wanninkhof (1992), K_0 is the CO_2 solubility at the in situ temperature and salinity after Weiss (1974). While $p(CO_2$, sea) and $p(CO_2$, air) are the CO_2 partial pressures of seawater and average CO_2 dry mole fraction measured in air, respectively. As $p(CO_2)$ was reported throughout this manuscript, we used $p(CO_2)$ for the air-sea flux calculation. Using fugacity for the calculation would generate the same results of flux estimates. The atmospheric $p(CO_2)$ is calculated from monthly averaged $p(CO_2)$ measured at Mace Head (53.33° N, 9.90° W) assuming 100 % water vapour saturation under 1 atm air pressure. Please note that 1 atm - 1.01325 bar. This is an appropriate pressure to use at the PAP-SO as the average (and standard deviation) of the air pressure, measured on the buoy at the PAP-SO between September 2010 and July 2011, was (1.0135 ± 13.14) bar.

Total alkalinity (TA) was calculated from Argo temperature and salinity (30 m), following the relationship for the North Atlantic developed by Lee et al. (2006) with an uncertainty of ±6.4 µmol kg^{-1} (Lee et al., 2006). The DIC concentration was then calculated from TA and $p(CO_2)$ using the “seacarb” package (Lavigne and Gattuso, 2011), with Argo temperature and salinity (30 m) and nutrient concentrations set to zero. The chosen constants were Lueker et al. (2000) for K_2 and K_2, Perez and Fraga (1987) for K_f and the Dickson (1990) constant for K_s, as recommended by Dickson et al. (2007). We followed Körtzinger et al. (2008)’s method to correct the DIC changes driven by air-sea exchange:

$$\Delta DIC_{gas} = F(CO_2)/MLD.$$

Using TA and $p(CO_2)$ to calculate DIC, and taking the various uncertainties in the calculation into account, introduces an error in the order of 7.0 µmol kg^{-1}.

The MLD was calculated from density profiles using global gridded fields of temperature and salinity collected by Argo floats, XBTs, CTDs and moorings. These data are collected and made freely available by the Coriolis project and programmes that contribute to it (http://www.coriolis.eu.org). We used the near real-time mode data as these data sets have been quality control checked. Before deciding on a MLD definition an inter-comparison of many definitions commonly used in the literature was done such as density differences, temperature differences and density gradients (Kara et al., 2000; Thomson and Fine, 2003; Montegut et al., 2004). A subset of the global density profiles calculated from the gridded temperature and salinity fields was used to compare the different methods. The depth of the mixed layer was estimated through visual inspection of over 3000 profiles, following a similar approach used by Fiedler (2010). The Holte and Talley (2009) density difference algorithm gave the closest match with the visually estimated MLD (RMSD 29.38 m). The depth of the mixed layer was defined by a density difference of 0.03 kg m^{-3} from the density at a reference depth (in this case 10 m to avoid diurnal changes in temperature and salinity at the surface). This Holte and Talley (2009) density difference algorithm incorporates linear interpolation to estimate the depth at which the density difference is crossed.

The North Atlantic Oscillation (NAO) index (after Hurrell, 1995) was obtained from the University of East Anglia web site http://www.cru.uea.ac.uk/cru/data/nao/.

Results

Figure 2a-c show the in situ observations from the PAP-SO at 30 m depth, including $p(CO_2)$, chlorophyll-*a* fluorescence and nitrate concentration. Figure 2a shows the range of $p(CO_2)$ from 2003 to 2005, which was also shown in Körtzinger et al. (2008). The range was 74 µatm (300- 374 µatm) and the mean was 339 µatm. In comparison, $p(CO_2)$ between 2010 and 2012 had a 57 µatm range (327 to 384 µatm) with a higher mean of 353 µatm. The $p(CO_2)$ data for the 2010-2012 period are confirmed by SOO data from the Portsmouth to Caribbean route in Figure 2a (see Figure 1 for positions of the SOO samples). Körtzinger et al. (2008) also reported a good comparison with a SOO route from Kiel, to the north of the Portsmouth to Caribbean route, for the 2003- 2005 data. The SOO data fill in the gap in the time series when PAP-SO $p(CO_2)$ data were not available due to failure of the instrument logger. The higher

$p(CO_2)$ values in the 2010-2012 period are confirmed by the SOO data.

In situ chlorophyll data in Figure 2b shows the characteristic chlorophyll-*a* fluorescence increase for this area during the spring bloom. There is large inter-annual variability in both the timing and magnitude of the spring bloom for the two time periods shown. For example, the spring bloom in 2004 started in late May compared with an earlier bloom in 2011 (that started in April). The increase in chlorophyll-*a* fluorescence during the 2011 spring bloom was also larger compared with the other years shown.

Nitrate concentration data in Figure 2c shows the characteristic seasonality, with increased winter nitrate concentrations and depletion following the spring bloom (seen in Figure 2b). The seasonality in the nitrate concentration is similar for the two periods shown (2003-2005 and 2010-2012). SOO nitrate concentration data show a good agreement with the PAP-SO data throughout 2010-2012 and fill in the gaps in early 2011 when nutrient measurements at the PAP-SO are not available. Overall, the in situ data show a characteristic increase in inorganic nitrate concentrations, and $p(CO_2)$, through the winter as fluorescence decreases. However, winter nitrate concentrations are significantly lower in the 2004/05 winter compared with other years as has been discussed in Hartman et al. (2010).

Figure 3a shows the Argo temperature data extracted at 30 m depth and the in situ MicroCAT temperature data at the PAP-SO. Temperature shows opposite seasonal variations to the $p(CO_2)$ and nitrate concentration from in situ data. A comparison of Argo temperature with in situ 30 m MicroCAT data ($n = 112$, comparison not shown) suggests errors of up to 1% for temperature in the Argo data compared with the in situ data (when available). Both data sets show that the temperature variations in these years are very similar, showing a summer-winter difference of 6 °C (Figure 3a).

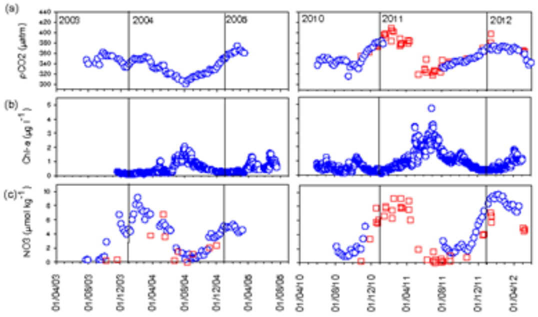

Figure 2: In situ 30 m PAP-SO data (blue circles) from 2003 to 2005 and 2010 to 2012 and 5 m SOO data (red squares) with vertical lines to represent the start of each year showing: **(a)** $p(CO_2)$; **(b)** chlorophyll-a concentration; **(c)** weekly-averaged nitrate concentration.

The seasonality of the in situ data can be put in context when looking at the MLD in Figure 3b. The increase in $p(CO_2)$ and nitrate concentration corresponds to deeper convective mixing in winter. The MLD range varies little over the winters considered here (Figure 3b) and the maximum MLD does not exceed 260 m. However, the timing of the maximum winter mixed layer depth at PAP-SO varies from year to year. For example, the maximum MLD (Figure 3b) for the 2010/11 winter reached 215 m in February 2011 compared with earlier and deeper mixing (to 257 m) in the following 2011/12 winter (December 2011).

The calculated DIC concentrations (Figure 3c) show a closer relationship to the MLD seasonality than nitrate concentration data. Seasonal variation in the concentration of both DIC and nitrate is similar apart from the 2004/05 winter; when low DIC concentrations were not seen at the same time as the low nitrate concentrations (Figure 3c).

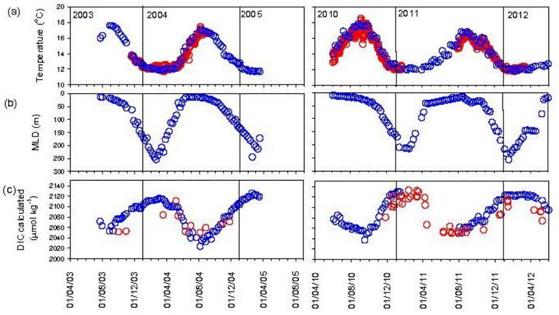

Figure 3: Data from 2003 to 2005 and 2010 to 2012 (blue circles) with vertical lines to represent the start of each year showing: **(a)** Argo temperature data from 30 m depth around the PAP-SO and in situ MicroCAT temperature data at 30 m (red circles); **(b)** calculated mixed layer depth (MLD) data; **(c)** calculations of weekly dissolved inorganic carbon (DIC)

The interrelation between DIC and nitrate concentrations can be considered by comparing the C:N ratios to the Redfield ratio (Redfield, 1958). The 2003-2005 time period has already been considered in Körtzinger et al. (2008) so is not reproduced here. Following Körtzinger et al. (2008) we calculated DIC, corrected for gas exchange. DIC concentrations were plotted against the in situ nitrate concentrations in different seasons for 2010-2012 (Figure 4). The C:N ratio differed from the Redfield ratio of 6.6 with especially high values in spring (14.3).

Figure 5a shows weekly satellite wind speed data used to calculate the CO_2 flux. The wind speeds were similar in the two periods. There is an earlier period of days with high wind speeds towards the end of 2011 that can be compared with the CO_2 data presented. The annual average wind speed was 8.2 ms^{-1} for both time periods. The maximum was 14 ms^{-1}, although in situ winds of up to 20 m s^{-1} were seen from the Met Office data (eurosites.info/pap), this is not seen in the weekly averaged satellite wind speed data presented.

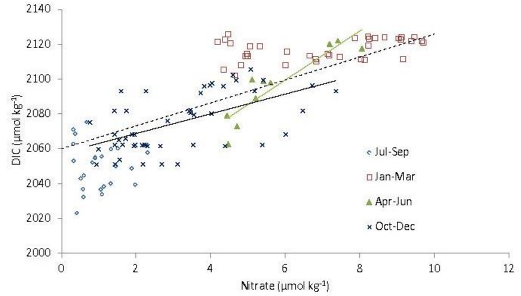

Figure 4: The relationship between concentrations of gas concentrations based on in situ PAP-SO p(CO_2) and salinity-based TA parameterisations (see text for details) with additional DIC calculations based on SOO data (red circles). exchange-corrected DIC and nitrate (2010-2012) at the PAP-SO showing 4 different seasons: winter (January-March, red squares); spring (April-June, green triangles); summer (July-September, blue diamonds); autumn (October-December, dark blue crosses). The green line shows the ratio in spring (14.3) and the blue line is the ratio in autumn (6.4), with the Redfield ratio of 6.6 shown for reference as a dashed line.

Figure 5b shows the sea-to-air CO_2 flux (where a positive flux is defined as from sea to the atmosphere). This was cal¬culated from in situ p(CO_2) data and satellite wind speed data (Figure 5b). The week by week variation in CO_2 flux is shown and an overall average for the two periods of time has been calculated as (-5.7±2.8) mmol m^{-2} d^{-1} for the 2003- 2005 period and (-5.0±2.2) mmol m^{-2} d^{-1} for the 2010- 2012 period. SOO data have been used at the start of 2011 when in situ p(CO_2) data were unavailable. The start and end months of the two periods of time differs, which will contribute to the errors in the flux measurements. However, the errors are comparable for the two periods of time considered and overall the average for the two time periods is similar.

There is little variation in CO_2 flux and MLD between the years shown but for completeness the NAO index is shown in Figure 5c. The 2003/04 winter NAO was near zero and the 2004/05 winter NAO was also low, between -2 to +1. In contrast, there is a large range in the winter NAO in the 2010/11 winter when the NAO changed from -4 to +3. Overall the range in the NAO values was larger for the 2010-2012 time period shown.

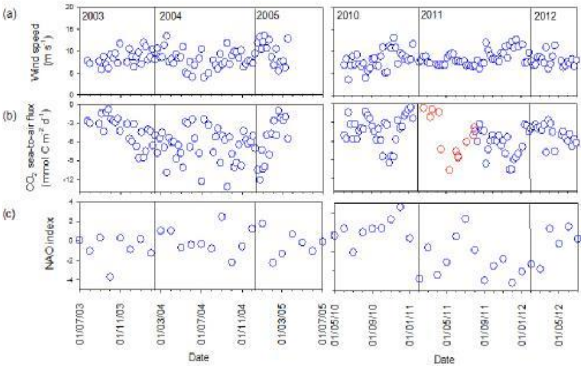

Figure 5: Data from 2003 to 2005 and 2010 to 2012 (blue circles) for **(a)** weekly satellite wind data in the region of the PAP-SO; **(b)** calculations of weekly sea-to-air CO_2 flux (negative: into the ocean) from in situ PAP-SO $p(CO_2)$ data and satellite wind (see text for details) with additional flux calculations from SOO data (red circles); **(c)** the monthly NAO index.

Discussion

PAP-SO seasonal variation

The 2003-2005 and 2010-2013 data sets show very similar seasonal patterns between the years. Concentrations of nitrate and DIC exhibit seasonal variations opposite to temperature. The seasonal variation in nitrate and DIC concentrations is controlled by convective mixing (resulting in the winter maximum) and biological uptake during the spring bloom period (resulting in the summer minimum), which is similar to elsewhere in the North Atlantic (Jiang et al., 2013).

The $p(CO_2)$ distribution pattern at the PAP-SO site is characterised by a single annual peak (high in winter and low in summer), which is similar to that of nutrient and DIC concentrations, but in antiphase to the temperature signal. Jiang et al. (2013) compared seasonal carbon variability between different sites in the North Atlantic and suggested a latitudinal change in $p(CO_2)$ seasonality from the temperature-dominated oligotrophic subtropical gyre to the subpolar region where $p(CO_2)$ is dominated by changing concentrations of DIC.

Our $p(CO_2)$ observations at the PAP-SO site show the subpolar-like seasonal pattern, which is similar to that of the ocean weather station M (Skjelvan et al., 2008). The surface $p(CO_2)$ is mainly governed by the varying DIC concentration while the seasonal cooling and warming have a contrasting effect. The time integrated uptake of DIC and nitrate during the spring bloom is reflected by the slope of the linear regression between them (Figure 4).

The ratio of DIC and nitrate concentrations from 2010 to 2012 shows higher values than the Redfield C:N ratio of 6.6. For example, the spring-time ratio of 14.3 (±5) was considerably higher than the Redfield ratio, in agreement with similar “carbon overconsumption” ratios seen for the North Atlantic (e.g. 14.2, Sambrotto et al., 1993). This value is in agreement with the single C:N ratio reported previously at the PAP-SO of 11.0 (Körtzinger et al., 2008). In both cases the DIC concentrations were calculated and therefore associated with errors in the order of 7.0 µmol kg^{-1}. We have demonstrated seasonal variation in the C: N ratio at the PAP-SO, with an autumn C:N value that is closer to the Redfield ratio and large deviations from the Redfield ratio in winter.

Air-sea CO_2 flux

Wind speeds have an indirect impact on the biogeochemistry, in particular $p(CO_2)$. In the North Atlantic the strength and frequency of wintertime storms is significantly increasing (Donat et al., 2011). Wind speeds are similar for the two time periods considered here. However, there is some suggestion of an earlier increase in winds at the start of the 2011/12 winter (Figure 5a) coinciding with an earlier increase in mixing (Figure 3b). Although the CO_2 flux is not linked linearly to the wind speed there is a corresponding decrease in CO_2 flux into the ocean at this time.

It is well known that the northeast Atlantic is a strong CO_2 sink with large variability. The observations at the PAP-SO provide high frequency data to follow the variability in CO_2 exchange. The largest CO_2 flux shown here was in September 2004, as a combined result of low seawater $p(CO_2)$ (Figure 2a) and high wind speed (Figure 5b). Larger CO_2 flux into the ocean may have occurred in 2011 considering the large, early spring bloom seen in that year but we do not have in situ PAP-SO $p(CO_2)$ data to calculate the flux at that time. However flux calculations from SOO data in early 2011 do not suggest an increase in CO_2 flux. Increases in productivity do not necessarily result in enhanced oceanic CO_2 uptake as the gas exchange is also affected by other factors such as temperature and wind speed (Jiang et al., 2013). The average is similar for the years presented with values of -5.7 mmol m^{-2} d^{-1} in 2003-2005 and -5.0 mmol m^{-2} d^{-1} from 2010 to 2012.

PAP-SO inter-annual variations

It is suggested that NAO plays an important role in modulating the inter-annual variability in the northeast Atlantic region by affecting the intensity of winter convection (Bennington et al., 2009; Jiang et al., 2013). The Gibraltar minus Iceland version of the NAO index is really most applicable to the winter half of the year. During positive NAO periods, the PAP-SO region experiences subpolar-like conditions, with strong wind stress and deep mixed layers (Henson et al., 2012). However, the MLD did not vary significantly at the PAP-SO between the 2003-2005 and 2010-2012 time periods shown here (with a range of only 215-257 m for deepest winter MLD between the years. In previous years such as 2009/10 deep winter mixing of 390 m has been seen with an NAO reaching -3, (not shown). NAO is unlikely to have a large role at the PAP-SO as winter sea surface temperature and MLD were similar in the time periods 2003-2005 and 2010-2012. Data from a winter with deeper mixing would need to be put into the comparison to resolve this.

There was a 2-fold decrease in nitrate concentrations in the 2004-2005 winter despite sea surface temperature and MLD values being close to other years. The low values were confirmed by SOO data, also shown in Hartman et al. (2010). As discussed in Hartman et al. (2010) the lower winter nitrate concentration seen in 2004/05 did not correlate with a decrease in the MLD and this showed the influence of horizontal mixing at the PAP-SO. It was suggested that lateral advection to the site at that time introduced a subtropical water mass with a lower nitrate concentration. Earlier time series studies largely ignored circulation at the PAP-SO site, assuming convective mixing is a dominant process influencing mixed layer temperature and nitrate concentrations in the region (Williams et al., 2000; Körtzinger et al., 2008). However, fixed-point time series observations are influenced by spatial variability passing the point of observation (McGillicuddy et al., 1998; Painter et al., 2010). It is clear from Hartman et al. (2010) that lateral advection may significantly influence the surface temperature and nitrate concentrations in the region of the PAP-SO site.

The observed seawater $p(CO_2)$ increased from (339 ± 17) µatm in 2003-2005 to (353 ±

15) µatm in 2010-2012, which largely agrees with the increasing rate of surface seawater $p(CO_2)$ observed in the North Atlantic basin of (1.84 ± 0.4) µatm a^{-1} (Takahashi et al., 2009). Despite similar maximum winter MLD in 2003-2005 and 2010-2012, the timing and intensity of the spring bloom is quite different and the cause of this requires further investigation.

Conclusions and further work

We have presented recent year-round surface time series bio-geochemical data at the PAP-SO and compared it with previous observations. The surface $p(CO_2)$, and concentrations of DIC and nitrate, at the PAP-SO all show a clear seasonal cycle, which is mainly controlled by winter convective mixing and biological activity in the spring bloom. However, the suggestion that inter-annual variability is dominated by convection (Bennington et al., 2009) is not clear as the MLD did not vary significantly between the winter periods shown. An especially low winter nitrate concentration in 2005 was observed, thought to be due to surface advection and this highlights the need to consider advection when dealing with time series data in the future. Despite the similar winter physical conditions (temperature and MLD), there is a year to year difference in the timing and intensity of the spring blooms, which requires further investigation. At PAP-SO, increasing mean seawater $p(CO_2)$ from (339 ± 17) µatm in 2003 to (353 ± 15) µatm in 2011 was observed. However, the mean air-sea CO_2 flux did not show a significant change. It varied from (-5.7±2.8) mmol m^{-2} d^{-1} in 2003-2005 to (-5.0±2.2) mmol m^{-2} d^{-1} in 2010-2012.

In 2010, between the UK's Natural Environment Research Council (NERC) and Meteorological Office led to the first simultaneous monitoring of in situ meteorological and ocean variables at the PAP-SO (Hartman et al., 2012). From 2013 additional measurements of $p(CO_2)$ will be made at the site, at the shallower depth of 1 m, and should further improve the SOO comparison. The site could be used to investigate the effect of different parameterisations (Prytherch et al., 2010) and wind products on calculations of CO_2 flux, in particular during the high wind conditions seen. Using the contemporaneous atmospheric and ocean data sets we will be able to investigate the effect of storms on CO_2 flux and resolve daily variability.

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Chapter 4: Links between surface productivity and deep ocean particle flux at the Porcupine Abyssal Plain sustained observatory

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Abstract

In this study we present hydrography, biogeo-chemistry and sediment trap observations between 2003 and 2012 at Porcupine Abyssal Plain (PAP) sustained observatory in the Northeast Atlantic. The time series is valuable as it allows for investigation of the link between surface productivity and deep ocean carbon flux. The region is a perennial sink for CO_2, with an average uptake of around 1.5 mmol m^{-2} day^{-1}. The average monthly draw-downs of inorganic carbon and nitrogen were used to quantify the net community production (NCP) and new production. Seasonal NCP and new production were found to be 4.57 ± 0.85 mol C m^{-2} and 0.37 ± 0.14 mol N m^{-2}, respectively. The C:N ratio was high (12) compared to the Redfield ratio (6.6), and the production calculated from carbon was higher than production calculated from nitrogen, which is indicative of carbon overconsumption. The export ratio and transfer efficiency were 16 and 4 %, respectively, and the site thereby showed high flux attenuation. Particle tracking was used to examine the source region of material in the sediment trap, and there was large variation in source regions, both between and within years. There were higher correlations between surface productivity and export flux when using the particle-tracking approach, than by comparing with the mean productivity in a 100 km box around the PAP site. However, the differences in correlation coefficients were not significant, and a longer time series is needed to draw conclusions on applying particle tracking in sediment trap analyses.

Introduction

The Porcupine Abyssal Plain (PAP) sustained observatory is situated in the Northeast Atlantic Ocean (49° N, 16.5° W) in a water depth of 4800 m. It is near the boundary between the sub-polar and sub-tropical gyres of the North Atlantic (Henson et al., 2009). A time series of particle flux measurements at 3000 m depth are available back to the early 1990's (Lampitt et al., 2010), and since 2003 there has also been a multidisciplinary mooring with instruments at approximately 30 m depth recording hydrography, nitrate (NO_3^-), partial pressure of CO_2 (pCO_2) and Chlorophyll-a (Chl a) (Hartman et al., 2012). The simultaneous observations of surface and deep ocean biogeochemistry make this time series ideal to study linkages between surface ocean productivity and deep ocean particle flux. The pathway by which a small fraction (< 1 %; Martin et al., 1987) of the carbon fixed by photosynthesis in the sunlit upper ocean is exported to great depths, thereby constituting a sink for atmospheric CO_2, is referred to as the biological carbon pump.

Carbon sinking to the deep ocean is sequestered on long timescales (100s to 1000s of years), and therefore quantifying the biological carbon pump is key in understanding the global carbon cycle (Falkowski et al., 1998). These factors are currently not fully understood, so it is therefore difficult to predict how they will respond to climate change (e.g. Passow and Carlson, 2012).

Primary production in the surface ocean can be measured by several techniques (broadly separated into vitro incubations or changes in bulk properties; Platt et al., 1989), however, from the perspective of the oceanic carbon cycle the most important rate is the net community production (NCP). NCP is the net primary production (NPP) minus heterotrophic respiration, and represents the sum of the particulate and dissolved organic carbon available for export or utilization by higher trophic levels. NCP is traditionally measured by bottle O_2 incubations (Gaarder and Gran, 1927), but has also been estimated from oxygen or carbon budgets, ^{234}Thorium, sediment traps and O_2 / Ar ratios. It can be challenging to compare between techniques and there is a poor understanding of NCP rates in many regions of the ocean (Quay et al., 2010). In many studies, the steady-state NCP is equated with the export flux at the base of the euphotic zone (Platt et al., 1989; Lee, 2001; Long et al., 2011; Nevison et al., 2012), based on the rationale that NCP is the organic material available for export out of the mixed layer. However, it is not directly comparable to the most common definition of export flux (i.e. the downward flux of POC at a nominal depth) as NCP represents a bulk measurement integrated over the mixed layer and long timescales (and also includes the contribution of DOC to export). The export ratio (i.e. Dugdale and Goering, 1967) is used to quantify the proportion of the organic material produced that is exported below the euphotic zone, and is often calculated as the flux of POC at 100 m divided by the NPP (Henson et al., 2012b). Global estimates of the export ratio range from 10 % (Henson et al., 2011) to 40 % (Eppley and Peterson, 1979), and is well correlated with temperature, and thereby also latitude (Laws et al., 2000).

The new production, Dugdale and Goering (1967), is the production supported by the input of new nitrogen into the euphotic zone through upwelling and horizontal mixing, but also by processes such as atmospheric deposition and nitrogen fixation (Sarmiento and Gruber, 2006; Gruber, 2008). On an annual basis, assuming the system is in a steady state, export production is considered equivalent to new production (Eppley and Peterson, 1979).

From a climate change perspective, the long-term (> 100 years) removal of carbon from the atmosphere is important to quantify, which is often defined as the flux of carbon below 1000 m (Lampitt et al., 2008a), known as the sequestration flux. The sequestration flux is smaller than the export flux out of the euphotic zone or mixed layer, and is ~ 6–25 % of the new production based on sediment trap data (Berelson, 2001; Francois et al., 2002). This large reduction in carbon flux with increasing depth is caused by intensive remineralization of organic material as it sinks through the mesopelagic zone, which is often referred to as flux attenuation (Martin et al., 1987; Steinberg et al., 2008). The ratio of deep POC flux to export flux (POC flux at 2000 m/POC flux at 100 m) is known as the transfer efficiency and has often been used to describe the efficiency of the biological pump (Francois et al., 2002; De La Rocha and Passow, 2012; Henson et al., 2012b). It should be noted that the POC-based metric of calculating export flux and transfer efficiency does not include the contribution from DOC.

In this study we present a time series of surface ocean measurements and particle trap data from the PAP observatory station from 2003 to 2012. Our aim is twofold; firstly, we will quantify NCP and new production from the average monthly drawdown of dissolved inorganic carbon (DIC) and NO_3, respectively. This allows us to compare these two estimates of surface productivity, and derive export ratios by comparison with satellite NPP estimates and published values of shallow POC flux at the PAP observatory. Secondly, we will investigate the link between the production at the surface and particle flux at 3000 m depth, both by investigating the transfer efficiency and by examining the source location of exported material using particle-tracking techniques.

Data and methods

PAP surface mooring

Hydrographical and biogeochemical parameters were measured using data from instruments at a nominal 30 m depth on a mooring at the PAP observatory (49° N, 16.5°

W). The surface mooring was first deployed in July 2003, and more information about the time series can be found in Hartman et al. (2012). Due to problems with damage to the mooring and/or failure of sensors, there is no or little data between 2005 and 2010, however, after May 2010 there is good temporal coverage for all biogeochemical parameters. The data from 2003–2005 have previously been published in Körtzinger et al. (2008) and Hartman et al. (2010). The sensors used after 2005 are described in Table 1 in Hartman et al. (2012). NAS nutrient analysers (Envirotech LLC) were used in the period from 2002 until 2012, which measures NO_3 plus NO_2 (hereafter referred to as NO_3) with a precision of ±0.05 $\mu mol\ L^{-1}$. The NAS was used alongside an optical nitrate sensor from 2009 to 2012, after that time all NO_3 measurements were made with optical sensors (Satlantic ISUS), with a precision of $2 \mu mol\ L^{-1}$.

Sediment trap

The sediment trap mooring at the PAP observatory was deployed in the depth range 3000 to 3200 m, which is around 1800 m above the seabed. The methodology is described in Lampitt et al. (2010). Briefly, a Parflux sediment trap was used with mouth area 0.5 m^2, prefilled with hypersaline buffered formalin, following the JGOFS protocols. The collection period varied between 2 and 8 weeks depending on the time of year and anticipated flux. All fluxes are temporally and spatially integrated, and given in either $ml\ m^{-2}\ d^{-1}$ (volume flux) or $mg\ m^{-2}\ d^{-1}$ (dry weight and Particulate Organic Carbon, POC).

Table 1: Overview of ancillary data.

Parameter	Source
ARGO Temperature and salinity	Temperature and salinity fields: 1° by 1°, monthly temporal resolution. Depth in profiles had resolution of 5 m be-tween 10 and 100 m and 10 m between 100 and 800 m. Available through Coriolis project;http://www.coriolis.eu.org
Atmospheric CO_2	Mace Head land station in Ireland (53.33° N, 9.90° W) from the Cooperative Atmospheric Data Integration Projects (GLOBAL VIEW-CO_2, 2012); http://www.esrl.noaa.gov/gmd/ccgg/globalview/co2/co2_download.html
Sea Level Pressure(SLP)	FNMOC 1° by 1°, 6-hourly; http://coastwatch.pfeg.noaa.gov/erddap/griddap/erdlasFnPres6.html
Wind speed	FNMOC 1° by 1°, 6-hourly at 10m height; http://coastwatch.pfeg.noaa.gov/erddap/griddap/erdlasFnWPr.html
Net primary production (NPP)	Vertically Generalised Production Model; http://www.science.oregonstate.edu/ocean.productivity/ index.php

Ancillary data and calculated parameters

To interpret and expand on the data from the PAP observatory, the following parameters were used from external data sources (see Table 1): temperature and salinity profiles from Argo floats, atmospheric CO_2 concentration, sea level barometric pressure (SLP), wind speed at 10 m height and satellite-derived net primary production (NPP).

Temperature and salinity profiles were extracted from the global fields for the PAP observatory (49° N, 16.5° W), made available by the Coriolis project (http://www.coriolis.

eu.org). The gridded fields use temperature and salinity profiles collected by Argo floats, XBTs, CTD/XCTDs and moorings, and the irregularly sampled data are gridded onto a regularly spaced grid by the statistical objective analysis method (Gaillard et al., 2009). The North Atlantic is the region most frequently sampled by Argo floats and has good coverage in both time and space (Gaillard et al., 2009). Here we use monthly averaged temperature and salinity fields for 2002– 2009 (delayed mode data), however, after 2010 only near-real-time data were available, which has undergone less rigorous quality control than the delayed mode data.

In the calculation of carbon parameters (below) the Argo float temperature and salinity at 30 m were used, because of data gaps in the temperature and salinity data from the PAP sensor (referred to as Argo temperature and salinity in text and Figs. 1 and 2) and the lack of consistent calibration with CTD data. Density profiles were calculated using the recently updated standard for seawater properties (TEOS-10; www.teos-10.org). The mixed layer depth (MLD) was calculated from density profiles using the same global gridded fields used for the temperature and salinity data at 30 m. The depth of the mixed layer was defined by a density difference of 0.03 kg m^{-3} from the density at a reference depth (in this case 10 m to avoid diurnal changes in temperature and salinity at the surface). We followed the algorithm developed by Holte and Talley (2009), which incorporates linear interpolation to estimate the exact depth at which the density difference is crossed.

The atmospheric CO_2 concentration measurements were obtained from the observatory closest to the PAP observatory, the Mace Head land station in Ireland (53.33°N, 9.90°W) from the Cooperative Atmospheric Data Integration Projects (GLOBALVIEW-CO_2, 2012). There were no measurements available after 2010, and so the annual averaged growth rate in atmospheric CO_2 for marine sites from the NOAA ESRL data for 2011 (1.69 µmol mol^{-1}) and 2012 (2.59 µmol mol^{-1}) was added to the seasonal cycle in CO_2 concentrations at the Mace Head station for 2010 (http://www.esrl.noaa.gov/gmd/ccgg/trends/global.html). The atmospheric pCO_2 was calculated using the Mace Head station CO_2 measurements at barometric pressure (6-hourly Sea Level Pressure; Table 1) and equilibrium water vapour pressure (from Argo temperature and salinity at 30 m; Table 1).

The air–sea CO_2 flux (in mmol m^{-2} d^{-1}) was calculated from the air–sea pCO_2 difference, Argo temperature and salinity (30 m) and wind speed at 10 m height, using the following equation:

$$FCO_2 = k \times K0 \times (pCO_2\text{sea} - pCO_2\text{air}), \quad (1)$$

where k is the transfer coefficient based on the wind speed-dependent formulation of Nightingale et al. (2000) scaled to the temperature-dependent Schmidt number according to Wanninkhof (1992), K_0 is the CO_2 solubility at in situ temperature and salinity (Argo temperature and salinity at 30 m) after Weiss (1974), while $pCO_{2\text{sea}}$ and $pCO_{2\text{air}}$ are the CO_2 partial pressures of seawater and air, respectively.

The alkalinity (Alk) was calculated from Argo temperature and salinity (30 m), following the relationship for the North Atlantic developed by Lee et al. (2006). The dissolved inorganic carbon (DIC) was calculated from Alk and measured pCO_2 using the “seacarb” package (Lavigne and Gattuso, 2011), developed for R (R Development Core Team, 2012), using Argo temperature and salinity (30 m) and nutrient concentrations set to zero. The chosen constants were Lueker et al. (2000) for $K1$ and K_2, Perez and Fraga (1987) for Kf and the Dickson (1990) constant for K_s, as recommended by Dickson et al. (2007).

The seasonal drawdown of DIC and NO_3 were used to quantify the NCP and new production, respectively. The gaps in the PAP time series did not allow for examination of the seasonal drawdown on an annual basis (except for the year of 2004, as published by Körtzinger et al. (2008). However, for most months of the year data from at least two to four different years were available, and NCP_{MLD} and $NO_{3\ MLD}$ was estimated two to four times for each of these months. This allowed the quantification of the average seasonal NCP_{MLD} and $NO_{3\ MLD}$ and variability (expressed as one standard deviation; SD) from the PAP time series. With the exception of March and April for $NCP_{MLD,}$ when there was only data for 1 year (2004) and consequently SD could not be calculated (error bars missing in Figure 3).

The monthly changes in Eqs. (3) and (4) (below) were computed in a circular manner, i.e., the change in the 12th month is the difference between January minus December. For $NO_{3\ MLD}$ there was only data for 1 year in December, and consequently the SD could not be calculated. For NCP_{MLD} there was data from 2 different years in December and 3 years in January, however they coincided only for 2004. Therefore, the variability could not be determined for December for both NCP_{MLD} and NO_3 MLD (error bar missing for December in Figure 3). A different source of uncertainty in NCP and new production estimates come from measurement uncertainty, which propagates into calculated values. However, for new production, the variability associated with measurement uncertainty is negligible compared to the natural variability.

The measurement uncertainty for the NO $_3$ sensor given by the manufacturer (Satlantic ISUS V3 sensor) was 2 µmol kg^{-1}. This gives a propagated probable error in the $NO_{3\ MLD}$ estimates of < 0.05 mol N m^{-2} (calculated from the square root of the sum of squared errors), which is considered negligible compared to the uncertainty associated with monthly variation of ±0.14 mol N m^{-2}. Therefore we present the uncertainty related to monthly variation in $NO_{3\ MLD.}$ Conversely, the total uncertainty associated with monthly variations in NCP_{MLD} was ±0.85 mol C m^{-2}, which is smaller than the total error associated with the calculation of DIC from estimated TA and measured fCO$_2$ of ±0.27 mol C m^{-2}. The latter was determined by propagation using the method described in Dickson and Riley (1978), together with the errors in the estimated TA values (± 6.4 µmol kg ^{1}; Lee et al., 2006) and measured pCO$_2$ (±2 µatm; Wanninkhof et al., 2013). We have therefore chosen to present the propagated probable error as a conservative estimate of the uncertainty in our NCP estimates.

The monthly changes in DIC concentrations (ΔDIC_{obs}) can be attributed to changes caused by air–sea gas exchange (ΔDIC_{gas}), physical mixing processes (ΔDIC_{mix}) and biological production (ΔDIC_{BP}). The monthly (ΔDIC_{gas}) (in µmol kg^{-1}) can be estimated from the air–sea CO_2 flux (FCO_2) and MLD by the following formulation:

$$\Delta \text{DIC}_{\text{gas}} = \frac{F_{CO_2}}{MLD} \times \frac{365}{12} \qquad (2)$$

Physical mixing processes, such as vertical entrainment, diffusion and advection, will to some degree contribute to monthly DIC changes, however they are difficult to quantify without information on vertical and horizontal gradients. Following the approach by Körtzinger et al. (2008) we have performed a simplified calculation of seasonal NCP and new production for the summer period when the mixed layer is relatively stable and the biological drawdown in DIC (and NO_3^-) is strong. Therefore, the contribution of ΔDIC_{mix} was assumed negligible, and ΔDIC_{BP} was assumed to be largely determined by NCP (excluding the effect of calcification).

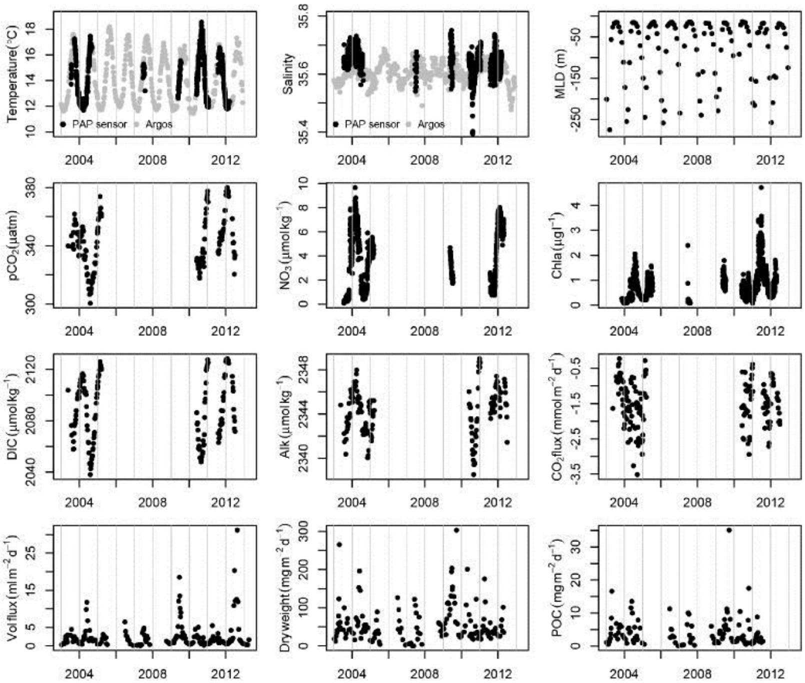

Figure 1: Time series of available data from PAP surface mooring and sediment trap with ±1 SD (vertical bars). Temperature and salinity calculated from the Argo float data (grey dots in first two panels) is also shown, along with derived mixed layer depth estimates. Negative CO_2 flux values indicate flux from the atmosphere to the ocean.

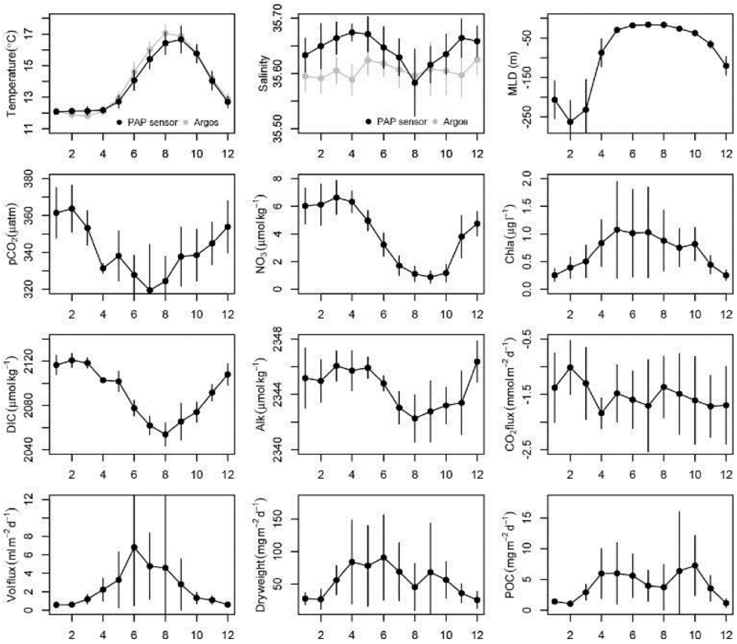

Figure 2: Monthly climatology (black dots) with ±1 SD (vertical bars) of available data from PAP surface mooring (30 m) and sediment trap. Temperature and salinity calculated from the Argo float data (grey dots in first two panels) is also shown, along with derived mixed layer depth estimates.

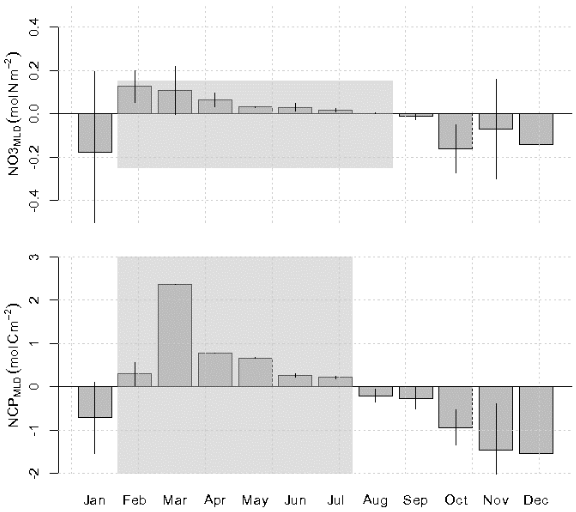

Figure 3: Monthly changes in MLD integrated NO^{3-} (top) and NCP (bottom) with ±1 SD (vertical bars). The shaded grey area indicates the months over which the seasonal new production (0.37 ± 0.14 mol N m^{-2}) and NCP (4.57 ± 0.85 mol C m^{-2}) were calculated. For NCP_{MLD} no SD could be calculated in March and April, and SD is also lacking for December for both NCP_{MLD} and $NO_{3\ MLD}$.

The monthly NCP integrated over the MLD (NCP_{MLD} in mol C m^{-2}) was calculated from the monthly changes in DIC corrected for the effects of air–sea gas exchange ($\Delta DIC^{GasCorr} = \Delta DIC_{obs} + \Delta DIC_{gas}$):

$$\mathrm{NCP_{MLD}} = \left(\Delta \mathrm{DIC}_{m+1}^{\mathrm{GassCorr}} - \Delta \mathrm{DIC}_{m}^{\mathrm{GasCorr}}\right) \times \frac{(\mathrm{MLD}_{m+1} + \mathrm{MLD}_{m})}{2} \quad (3)$$

is the difference in $\Delta DIC^{GasCorr}$ between two consecutive months (m and m+1) and the last term gives the average MLD of the two months. Positive values of NCP_{MLD} represent net autotrophy (i.e. the months where the biological drawdown of DIC exceeds the DIC released by heterotrophic processes), and the seasonal NCP_{MLD} can then be calculated as the sum of months with a positive NCP.

The same rationale can be applied to the monthly changes in NO_3^- concentrations (ΔNO_3), naturally without having to consider the effect of air–sea exchange. The monthly MLD-integrated NO_3^- changes (ΔNO_3 in mol N m^{-2}) were calculated as:

$$NO_{3,MLD} = (\Delta NO_{3,m+1} - \Delta NO_{3,m}) \times (MLD_{m+1} + MLD_{m})/2 \quad (4)$$

Summing up the months with a net drawdown in NO_3^- gives the seasonal new production.

Net primary production (NPP) was estimated from satellite data using the Vertically Generalised Production Model (Behrenfeld and Falkowski, 1997), which requires inputs of chlorophyll concentration, sea surface temperature and photosynthetically available radiation data, here taken from NASA's MODIS Aqua satellite (reprocessing R2012.0). The NPP data were downloaded from the Ocean Productivity website (see Table 1).

Particle tracking and cross-correlations

In addition to estimating the surface origin of particles sinking to the sediment trap using a simple 100 km box around the PAP observatory, we also used modelled velocity fields to determine the likely source region. The velocity field (u and v components) was taken from the NEMO model (Madec, 2008) run at NOC at 5-day, 1/4° resolution for the period 2002–2011. The model has 75 depth levels increasing in thickness with depth, ranging from 1 m near surface to 200 m at 6000 m depth. All particles reaching the PAP sediment trap at 3000 m depth are assumed to have a sinking speed of 100 m day^{-1}, which is chosen because it falls in the middle of the range observed for particle sinking speeds at the PAP observatory of between 60 and 180 m day^{-1} (Riley et al., 2012; Villa-Alfageme et al., 2014). Particles are tracked backwards in time in three dimensions by linear interpolation of the gridded velocity field to the local position of the particle, until they reach the surface (30 days after release).

The cross-correlation between the sediment trap data and either NPP in a 100 km box around the PAP observatory or in source locations identified by particle tracking, were calculated using the ccf function in R (R Development Core Team, 2012). The cross-correlations were performed on monthly anomalies (monthly climatology – observed monthly value), to avoid possible inflation of p values due to auto-correlation. To test for significant differences between the correlation coefficients the Fisher r to z transformation was used (two-tailed test, with two dependent correlations sharing one variable), from the R library "Psych" (Fisher, 1915; Revelle, 2012).

Results

Time series data from 2003 to 2012 from the PAP surface mooring and sediment trap are shown in Figure 1. The temperature and salinity (both PAP sensors and Argo 30 m) varied in the range 12-18 and 35.4-35.8 °C, respectively. The mixed layer depths (MLD) were fairly consistent between years, although the winter mixed layer only extended down to ~100 m in 2010. There was a pronounced seasonal drawdown in $p\mathrm{CO_2}$ (similarly for DIC), with summer values as low as 300 µatm during August 2004 and typical winter values between 360-380 µatm. Corresponding seasonal trends were seen for $\mathrm{NO_3^-}$, with a winter maximum of 10 µmol kg^{-1} in March 2004 and values close to detection limit during summer. The strongest bloom was observed in June 2011 with Chl-a concentrations between 3 and 5 µg L^{-1}, with higher than typical summer values of around 2 µg L^{-1}. The air–sea $\mathrm{CO_2}$ flux was negative (i.e. oceanic uptake of $\mathrm{CO_2}$) throughout the time period, with an average uptake of around 1.5 mmol m^{-2} day^{-1}. There were 3 years with unusually high sediment fluxes, with short bursts of high flux during summer in 2004, 2009 and 2012.

The monthly climatology (or average seasonal cycle) for temperature showed a seasonal warming of around 5 °C, with very good overlap between the temperatures measured by the PAP sensor and the Argo floats at 30 m (see monthly climatologies in Figure 2). There was little seasonal variation in salinity, although the Argo float data are generally around 0.05 lower than the salinity measured by the sensors at the PAP observatory. The summer MLD was around 30 m (usually between May and October), and mixing extended down to 250 m depth in winter. The $p\mathrm{CO_2}$ decreased by around 30 µatm from winter values to the summer minimum in August (reduction of around 35 µmol kg^{-1} for DIC), while $\mathrm{NO_3^-}$ decreased by around 5 µmol kg^{-1} to the summer minimum typically found in September. There was a gradual build-up of Chl-a from February, with highest values typically found between May and July with large standard deviations reflecting the high interannual variability in Figure 1. There was no clear seasonal signal in air–sea $\mathrm{CO_2}$ flux, with high variability throughout the year. The sediment fluxes had high inter-annual variability, however, the highest volume flux was typically found in June, while an autumn peak was often found for dry weight and POC in September or October.

The monthly MLD-integrated $\mathrm{NO_3^-}$ changes ($\mathrm{NO_{3\ MLD}}$) were positive from February to August (Figure 3), which means that during these months there was a net decrease in $\mathrm{NO_3^-}$ concentrations in the mixed layer caused by biological drawdown. Conversely, there were negative $\mathrm{NO_{3\ MLD}}$ from September to February, meaning that during these months the $\mathrm{NO_3^-}$ concentrations increased due to remineralization and entrainment of new nutrients through winter mixing. This corresponds to an MLD-integrated seasonal new production (from February to August) of

0.37 ± 0.14 mol N m^{-2}. Note that all uncertainties given for production estimates in this work are due to interannual variability. The monthly MLD-integrated changes in NCP (NCP$_{MLD}$) showed the same seasonal trend, with a positive NCP$_{MLD}$ (i.e. decrease in DIC concentrations) from February to July. In addition, there was a much higher NCP$_{MLD}$ in March compared to the other spring/summer months. The MLD-integrated seasonal NCP (from February to July) was 4.57 ± 0.85 mol C m^{-2}.

Tracking of the particles arriving at the sediment trap at 3000 m at the PAP observatory, revealed that the source locations of particles could vary substantially between years, and also on an annual timescale (Figure 4). The satellite NPP in these source regions also varied markedly, and the highest NPP of around 210 mmol C m^{-2} day^{-1} was found in 2009.

There was a high cross-correlation between the seasonal anomalies of NPP in source locations identified by the particle tracking and the volume flux in the sediment trap (+0.62; Figure 5) at lag = 0 months. The corresponding cross-correlation for NPP averaged over a 100 km box around the PAP observatory and volume flux was considerably lower (+0.48; Figure 5), however the difference between the two cross-correlations was not significant (Fisher transformation, $n = 111$, $z = 1.58$, $p = 0.11$). The correlation coefficients between either dry weight and POC and the two different NPP estimates were lower, and similarly showed no significant difference between either using the NPP identified by particle tracking or a 100 km box. The highest cross-correlations between NPP and dry weight was found at lag = -1 month (i.e. dry weight lagged NPP by 1 month), while it was at lag = -3 months for NPP and POC. We also tested the cross-correlations using the NPP at the exact latitude and longitude of the PAP observatory (49° N, 16° W) and extending the box to 200 km around the observatory, but there were no significant differences in cross-correlations using these instead of the mean of a 100 km box around the PAP observatory as above (results not shown).

Discussion

Estimates of surface productivity

The seasonal cycles of carbon (pCO$_2$/DIC) and NO_3^- at the PAP observatory are characteristic of highly productive subpolar regions, where cooling, convection and remineralization cause a winter maximum, while drawdown from biological production during spring and summer causes a minimum during late summer (Takahashi et al., 2002). This is true also for pCO$_2$, because the decreasing effect of production is stronger than the opposing effect of warming. The same seasonal effects are seen in the MLD-integrated changes in NO_3^- and DIC concentrations used to calculate new production and NCP (i.e. Figure 3). There were positive monthly changes in NO$_{3\ MLD}$ and NCP$_{MLD}$ during spring/summer, due to decreasing concentrations related to biological production within a shallowing or fairly stable mixed layer. During winter the combined effects of cooling, deep mixing and remineralization caused negative NO$_{3\ MLD}$ and NCP$_{MLD}$ (i.e. increasing NO_3^- and DIC concentrations).

The MLD-integrated seasonal NCP (from February to July) was 4.57 ± 0.85 mol C m^{-2}, which is comparable to, but lower than, the NCP calculated for the PAP observatory by Körtzinger et al. (2008) for 2004 of 6.4 ± 1.1 mol C m^{-2} from March to early August. This is natural given that Körtzinger et al. (2008) integrated over a much deeper fixed mixed layer (238 m) from March until mid-May, while here we used the mean MLD between consecutive months.

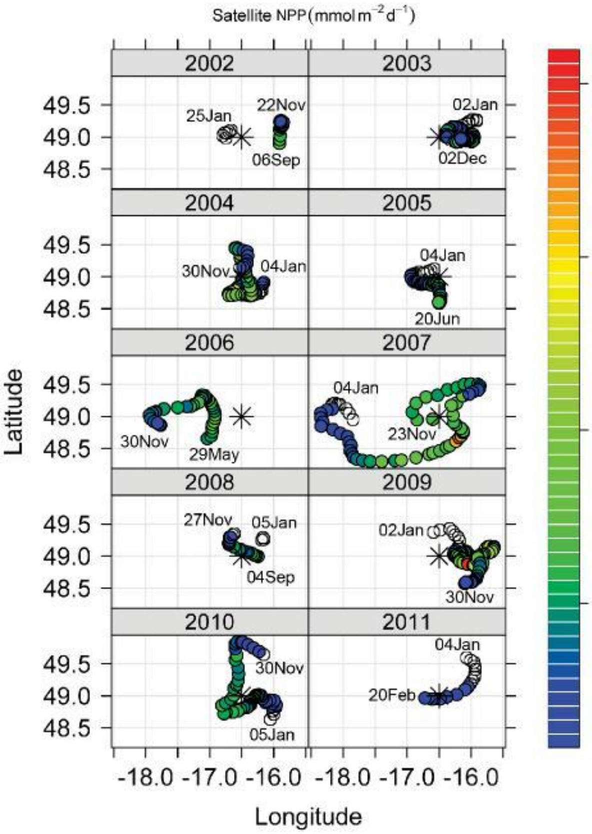

Figure 4: Satellite NPP (mmol C m^{-2} d^{-1}) in the source regions for the sediment trap as identified by particle tracking. The star shows the position of the PAP mooring and unfilled circles indicate that no NPP estimate was available from satellite data (most often during January and February). The start and end dates of the data for each year are indicated in the panels.

As can be seen in Figure 2, the MLD shallows rapidly from around 250 m in March to 50 m in May, and we believe using the actual depth of the mixed layer gives a more realistic estimate of NCP during this period of rapid stratification. From May to August the MLD is slightly shallower than the depth of the sensors at 30 m, which could influence our estimates of NCP and new production. This uncertainty is impossible to quantify without measurements from within the mixed layer, although the effect is believed to be minor. It could potentially overestimate biological production due to more readily available nutrients at 30m than within the mixed layer, or lead to an underestimate due to additional drawdown within the mixed layer.

Consistent with Körtzinger et al. (2008), we find that the strongest NCP occurs before the onset of shallow stratification in summer, with an NCP maximum in March. The MLD-integrated seasonal new production (from February to August) was 0.37 ± 0.14 mol N m^{-2}. This is within the range of new production estimates, using different approaches, from 0.23–1.1 mol N m^{-2} from the Northeast Atlantic Ocean and Icelandic Sea (Fernández I et al., 2005; Hartman et al., 2010; Jeansson et al., 2015). Converting the new production in terms of nitrogen to carbon units using the Redfield ratio of 6.6 (Redfield, 1958), gives a value of 2.5 mol C m^{-2}, which is substantially smaller than the NCP calculated from DIC changes. However, there is not necessarily any basis for assuming that new production and NCP should be equal, even in a steady-state system (cf. Laws, 1991). This would imply that carbon is assimilated and recycled by heterotrophs (as respiration is included in NCP) in the same ratio as nitrogen is assimilated by autotrophs during new production, which need not be the case (i.e. variable stoichiometry, see review by Sterner and Elser, 2002).

The fact that the production calculated from carbon is higher than the production calculated from nitrogen, is referred to as carbon overconsumption (Toggweiler, 1993), and has been demonstrated repeatedly in the North Atlantic (Sambrotto et al., 1993; Körtzinger et al., 2001; Koeve, 2006). It has also been shown specifically for the PAP observatory (Körtzinger et al., 2008; Painter et al., 2010).

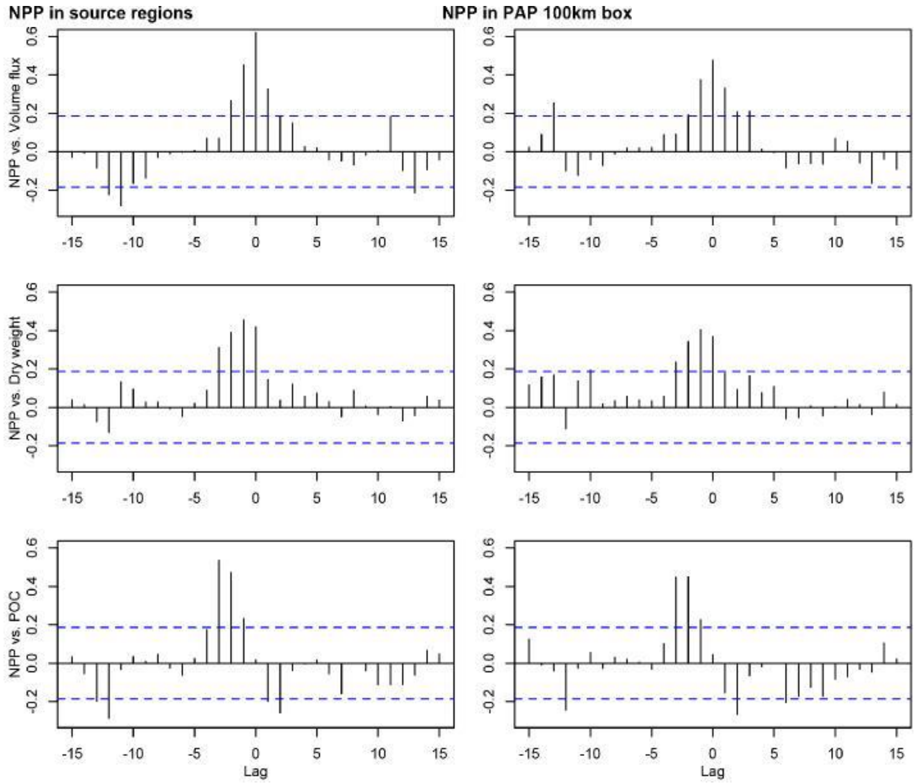

Figure 5: Cross-correlations between sediment trap data (top: volume flux, middle: dry weight, bottom: POC) and NPP in the source regions defined by particle tracking (left) or in a 100 km box around the PAP observatory (right). The dashed lines show the 95 % confidence intervals. The unit of the lags is months

The seasonal C:N ratio for the PAP observatory from this study (i.e. NCP/new production) would be ≈ 12, which is greatly exceeding the Redfield ratio, although within the range of C : N ratios previously found in this region (Koeve, 2006; Körtzinger et al., 2008; Painter et al., 2010).

Studies have found N_2 fixation to be low or zero at latitudes > 40° N (PAP observatory is at 49° N) in the North Atlantic (Moore et al., 2009; Reynolds et al., 2007), therefore N_2 fixation is not thought to be an important factor for C overconsumption. Therefore, the C overconsumption must be sustained by preferential remineralization of nutrients, either in slowly sinking detritus (Sambrotto et al., 1993; Thomas et al., 1999; Körtzinger et al., 2001) or a build-up of C-rich (and N-poor) DOM in the euphotic zone (Williams, 1995; Kähler and Koeve, 2001; Falck and Anderson, 2005). Additionally transparent exopolymer particles (TEP; Alldredge et al., 1993), which have been shown to have high C : N ratios (Engel and Passow, 2001) could represent a route for the C overconsumed in the euphotic zone to reach the deep ocean (Koeve, 2005).

The regenerated nutrients can fuel additional production in the euphotic zone, and consequently estimates of new production based on nitrate might underestimate production rates (Thomas et al., 1999). The degree to which the C overconsumed in the surface waters reaches the deep ocean, and thus is sequestered on long timescales is important, because it represents a potential negative feedback on atmospheric CO_2. Studies have shown an increasing C : N of sinking material due to preferential remineralization of nutrients (Schneider et al., 2003; Lee and Cronin, 1984), and the potential feedback of a depth-dependent C : N ratio may influence atmospheric CO_2 concentrations by about 20 ppm (Schneider et al., 2004). However, the deep ocean remineralization ratio of C : N has been shown to be close to the Redfield ratio (Anderson and Sarmiento, 1994), and if the C overconsumption is mainly during summer (Koeve, 2004; Jiang et al., 2013) and remineralized above the depth of the winter mixed layer, it could be questioned whether the "extra-Redfield" C is sequestered in the deeper ocean, and can therefore influence the oceanic C-budget on longer timescales (Koeve, 2006). However, the deep ocean remineralization rates of Anderson and Sarmiento (1994) did not include the Atlantic Ocean. A study on the remineralization ratios in the North Atlantic Ocean specifically showed higher than Redfield C : nutrient ratios in the remineralized material in the deeper waters, and thereby a higher C drawdown by the biological carbon pump than would be expected from applying Redfield ratios in the formation of organic matter (Thomas, 2002).

The export flux of POC around the PAP observatory has been quantified in several studies using different techniques (see overview in Figure 4 in Riley et al. (2012). The average POC flux in the upper 170 m obtained from PELAGRA drifting sediment trap deployments for short periods of time (3–5 days) between 2003 and 2005 was 72 mg C m^{-2} d^{-1} (Lampitt et al., 2008b). During a cruise in August 2009 the flux was found to be 84 and 146 mg C m^{-2} d^{-1} at 50 m, using PELAGRA and a marine snow catcher, respectively (Riley et al., 2012). Using the ^{234}Th technique the flux of POC at 100 m in the vicinity of the PAP observatory was determined to be in the range between 64 and 207 mg C m^{-2} d^{-1} (based on measurements from a single cruise and long-time trap data; Lampitt et al., 2008b; Thomalla et al., 2008). The export ratio describes the efficiency of nutrient utilization in the euphotic zone, and is often calculated as the POC flux at the base of the euphotic zone or a fixed depth (typically 100 m), divided by the NPP Dugdale and Goering (1967). Using an average of the above values for POC flux out of the surface layer of 115 ± 61 mg C m^{-2} d^{-1} and the March–July average NPP in the 100 km box around the PAP observatory of 772 mg C m^{-2} d^{-1} gives an export ratio of 0.15. This is identical to the estimate by Lampitt et al. (2008b) for the PAP observatory during post-bloom conditions from-2003–2005, and consistent with the estimate by Henson et al. (2011) of between 10 and 30 % for temperate and sub-polar waters, respectively.

Links between surface production and deep ocean flux of POC

Using particle tracking to identify the source location of material arriving in the sediment trap at 3000 m at the PAP observatory showed that the particles could originate up to 140 km away (in 2007; Figure 4). There was large variation in the source location of particles between years, depending on the prevailing current conditions in the given year. There was also large variation within individual years, but the satellite NPP generally increased during spring and decreased during autumn along the trajectory of the particles reflecting the seasonal cycle. Mesoscale variability will also contribute to the variability in source location of particles, both between and within years. The highest NPP was found in 2009 (around 210 mmol C m^{-2} day^{-1}), which corresponds to very high fluxes in both volume flux and dry weight in the sediment trap at the PAP observatory (Figure 1). Interestingly, there was not a strong bloom at the PAP observatory according to the in situ Chl a observations at 30 m depth (sensor data available from May to late July; Figure 1), while the satellite NPP showed high correlations with the volume flux and dry weight in the sediment trap. The correlations were highest between the NPP in source locations as identified by particle tracking, compared to the mean NPP in a fixed 100 km box around the PAP observatory. However, the differences in correlation coefficients were not statistically different, and more observations (n = 111 in present analysis) would be needed to determine if using a particle tracking approach when examining the origin of particles in sediment traps indeed gives higher correlations.

The transfer efficiency is a useful metric to describe the long-term removal of carbon (> 100 years) from the atmosphere (cf. De La Rocha and Passow, 2012). Using the same average POC flux of the surface layer (0–170 m) as in the calculation of the export flux above and the average flux between March and July of POC at 3000 m from the sediment trap at the PAP observatory (5.1 mg C m^{-2} d^{-1}), the transfer efficiency was calculated to be 4 %. This corresponds well with the transfer efficiency between 5 and 10 % found for the 50° N region by Henson et al. (2012b), indicative of regions where the available nitrate is not fully consumed and with strong seasonal mixing. The fairly high export ratio (15 %) and low transfer efficiency (4 %) fits the description of the general trends in high-latitude ecosystems in the above-cited study well. This dichotomy in efficiencies implies that although a large proportion of the primary production is exported below the euphotic zone, this material is relatively labile and is efficiently remineralized in the mesopelagic zone, so that only a very small fraction of the exported organic matter reaches the deep ocean and is stored on long timescales.

The PAP observatory currently sits near the boundary between the sub-polar and sub-tropical gyres of the North Atlantic. Seasonably variable areas, like the sub-polar region, are thought to export a higher fraction of labile material than sub-tropical regions (Lutz et al., 2007). As climate change is predicted to result in the oligotrophic gyres expanding over the next century (Sarmiento et al., 2004), the PAP observatory will likely transition into more sub-tropical conditions. This could result in more refractory material being exported at the PAP observatory, potentially reversing the pattern we report here with a high export ratio and low transfer efficiency. In addition, a more strongly positive NAO index is predicted due to climate change (Gillett, 2003), which is expected to increase diatom abundance at the PAP observatory, and result in reduced organic carbon flux to the deep ocean (Henson et al., 2012a).

Although the precise response of the biological carbon pump to climate change is as yet unclear, transition-zone regions between gyres (such as the PAP observatory), could be among the systems that are most strongly affected by climate change (Henson et al., 2013). lower than the estimate by Körtzinger et al. (2008) for 2004. The MLD-integrated seasonal new production (from February to August) was 0.37 ± 0.14 mol N m^{-2}, which gives a Redfield ratio (NCP/new production) of 12, corroborating other reports of carbon overconsumption for the North Atlantic (Sambrotto et al., 1993; Körtzinger et al., 2001; Ko-eve, 2006) and the PAP observatory specifically (Körtzinger et al., 2008; Painter et al., 2010).

Conclusions

The PAP observatory is characterized by strong interan-nual variability in hydrography, biogeochemistry, and especially sediment fluxes. The seasonal cycles of carbon and nitrogen show a winter maximum and summer minimum, characteristic of highly productive sub-polar regions. The MLD-integrated seasonal NCP (from February to July) was 4.57 ± 0.85 mol C m^{-2}, which is consistent with, but slightly lower than the estimate by Körtzinger et al. (2008) for 2004. The MLD-integrated seasonal new production (from February to August) was 0.37 ± 0.14 mol N m^{-2}, which gives a Redfield ratio (NCP/new production) of 12, corroborating other reports of carbon overconsumption for the North Atlantic (Sambrotto et al., 1993; Körtzinger et al., 2001; Koeve, 2006) and the PAP observatory specifically (Körtzinger et al., 2008; Painter et al., 2010).

The export ratio was 15 %, while the transfer efficiency was 4 %, which is typical of high-latitude ecosystems where, although a large proportion of the primary production is exported out of the euphotic zone, this material is relatively labile and therefore remineralized before it reaches the deep ocean. It is hypothesized that the export regime at the PAP observatory could change with climate change, as the region will probably transition into more sub-tropical conditions over the next century (Sarmiento et al., 2004; Lutz et al., 2007).

Using particle tracking to identify the source regions of material reaching the sediment trap at the PAP observatory, revealed higher correlations between NPP in the identified source regions and export flux than other methods. However, more observations are needed to establish if a particle-tracking approach indeed gives added value in sediment trap analyses.

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Chapter 5

Seasonal and inter-annual variability in nutrient supply in relation to mixing in the Bay of Biscay

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Abstract

A key challenge in oceanography is to capture and quantify processes that happen on short time scales, seasonal changes and inter-annual variations. To address this problem the P&O European Ferries Ltd. Ship *MV Pride of Bilbao* was fitted with a FerryBox from 2002 to 2010 and data returned to NOC in real time providing near continuous measurements between UK (Portsmouth) and Spain (Bilbao) of temperature, salinity, chlorophyll-fluorescence and oxygen. Additional monthly samples were collected on manned crossings. Over 6000 samples were analysed for nitrate (nitrate and nitrite) concentrations. The timing of nitrate concentration increases (with winter mixing) and decreases (with the spring bloom) are different on and off shelf and in autumn nitrate concentrations remain high on the shelf. Off shelf in the Bay of Biscay, the mixed layer depth assessed using Argo floats, was found to vary from 212 m in relatively mild winters (such as 2007/2008) to 476 m in cold winters (2009/2010). Years with deeper mixing were associated with an increase in nitrate concentrations in the surface waters (-3 µmol l^{-1}) and the increased vertical nutrient supply resulted in higher productivity the following spring. Bloom progression could be seen through the increase in oxygen anomaly and decrease in nitrate concentrations off shelf prior to changes further north on the shelf and phytoplankton growth was initiated as shoaling begins. The full dataset demonstrates that ships of opportunity, particularly ferries with consistently repeated routes, can deliver high quality *in situ* measurements over large time and space scales that currently cannot be delivered in any other way.

Introduction

At temperate latitudes nutrient supply to the upper ocean in winter drives phytoplankton productivity and the uptake of carbon dioxide from the atmosphere in the following spring (Eppley and Peterson, 1979; Williams et al., 2000; Hydes et al., 2001). Nutrients can be supplied to the surface through diapycnal diffusion, eddy transfer and Ekman processes (Oschlies and Garson, 1998; Fernández et al., 2005). In the North East Atlantic and the Bay of Biscay winter convective mixing dominates the supply of nutrients (Williams et al., 2000; Puillat et al, 2004; Cianca et al., 2007). Wind-driven cooling and deep convective mixing lower the surface temperature and nutrient rich water is supplied to the euphotic zone from depth to fuel phytoplankton growth, which predominantly occurs in the spring following restratification of the water column (Sverdrup, 1953; Chiswell, 2011). Periods of reduced turbulence and positive heat flux into the ocean prior to the spring restratification results in pulses of phytoplankton growth (Pingree et al., 1976; Garcia-Soto and Pingree, 1998, 2009; Waniek, 2003) and it has been recently hypothesised that these events are significant in calculations of annual productivity (Behrenfeld, 2010).

Behrenfeld et al. (2006) suggested a general trend has occurred of decreased convective mixing, increased stratification and consequent decrease in production in the Northeast Atlantic from 1999 onwards and predicts a decrease in productivity in a warming ocean. There has been a progressive warming of surface waters in the Bay of Biscay over the last 30 years (Garcia-Soto et al., 2002; González-Pola et al., 2005; Somavilla Cabrillo et al., 2011; Holt et al., 2012; Taboada and Anadon, 2012, Garcia-Soto and Pingree, 2012). Winter mixing was studied extensively in Pingree and New (1989). Although there is no direct evidence of progressive changes in productivity or MLD changes in the Bay of Biscay over the last 3 decades studies of the physical processes that regulate nitrate supply to the surface and direct measurements of nutrient concentrations within the mixed layer are critical for making year to-year estimates of productivity and for future model predictions (Waniek, 2003; Behrenfeld et al., 2006).

The change in nitrate or oxygen concentration from the start to the end of the productive period in spring can be used, along with mixed layer depth (MLD), to calculate proxies for phytoplankton growth and net community production (Pingree et al., 1976; Eppley and Peterson, 1979; Oschlies and Garson, 1998; Henson et al., 2003; Bargeron et al., 2006). This requires quantification of change from the high nutrient (low oxygen) winter months to the low nutrient (high oxygen) concentrations at the end of spring (Minas and Codispoti, 1993; Louanchi and Najjar, 2000; Southward et al., 2004). In the past the concentrations of nitrate in winter had to be estimated, as direct wintertime measurements were relatively rare (Glover and Brewer, 1988; Koeve, 2001) or assumptions have had to be made on the length of the productive cycle (Waniek, 2003). Reducing the reliance on estimation requires year round in situ datasets; these can be provided by Ships of Opportunity(SOO) that take consistent repeat routes throughout the year.

In 2002 we initiated year round in situ measurements on a SOO to study the physical and biogeochemical drivers of productivity on and off shelf from the English Channel to the deep water Bay of Biscay. In this study we present an 8 year time-series (2003–2010) of continuous SOO data from in situ FerryBox measurements, with additional nutrient samples from 2003 onwards taken each month over most of the period except for August 2007 to August 2008. MLD estimates, calculated from Argo profiling float temperature profiles (available in increasing resolution from 2004 onwards) were used to look at year to year variations in surface nitrate measurements in relation to convective mixing processes. Measurements of Sea Surface Temperature, PAR irradiance, wind speed and turbulence and phytoplankton concentration for the years 1997–2007 along the same FerryBox line using remote sensing can found in Garcia-Soto and Pingree (2009). We use here the in situ SOO dataset to look at seasonal timescales to investigate periods of mixed layer deepening and if they are associated with increases in nitrate or productivity. The nitrate, oxygen and MLD data are used to estimate net community production (NCP) and this study provides a direct opportunity to study seasonal and inter-annual variations in surface nutrient concentrations and how this may affect phytoplankton production.

Materials and methods

Study site

Surface water data were collected from P & O European Ferries Ltd ship *MV Pride of Bilbao* operating between Portsmouth (UK, 50.8°N, 1.1°W) and Bilbao (Spain, 43.4°N, 3.0°W) (Figure 1). The ship made approximately two crossings weekly between these ports. The FerryBox system ran from

April 2002 to September 2010, operating year-round except for January when the ship was in dry dock for its annual refit. The distance is approximately 1000 km and the journey time is about 35 h each way. This gives a repeat sampling rate of between 4 h and 4 days, depending on location. Over the 8 years the FerryBox measurements cover 0.8 x 10^6 km of ship's track. The map in Figure 1 is reproduced from Bargeron et al (2006) and identifies persistent regional features as identified by Pingree and Griffiths (1978).

In this paper, we focus on the Bay of Biscay section of the ferry route (45–46.5°N, regions 6 and 7 in Figure 1), which is over deep water of up to 4000 m. We contrast this with the on-shelf region 4 (47.5–48.5°N), which remains influenced by strong tides and internal waves. Intermediate to this is the half slope, half stratified shelf region 5, which lies between 46.5 and 47.5°N.

In the deep waters off shelf, the upper water column mixed layer is affected by seasonal cycles of warming and cooling (Pingree et al., 1999; Pingree, 1997). Below this is the main thermocline water mass, the Eastern North Atlantic Central Water (ENACW). Bay of Biscay water properties can be traced back to production on isopycnal surfaces within this mode water (Pingree and Morrison, 1973), which forms from deep winter mixing of North Atlantic Current (NAC) water to the west of the Bay of Biscay and is circulated around the bay down to 400 m (Pingree, 1993; Castro et al., 1998; Pollard et al., 1996; González-Pola et al., 2005, 2006). The properties of the subsurface waters vary from year to year reflecting variations in winter convective mixing and advection (Perez et al., 1993; Pollard et al., 1996).

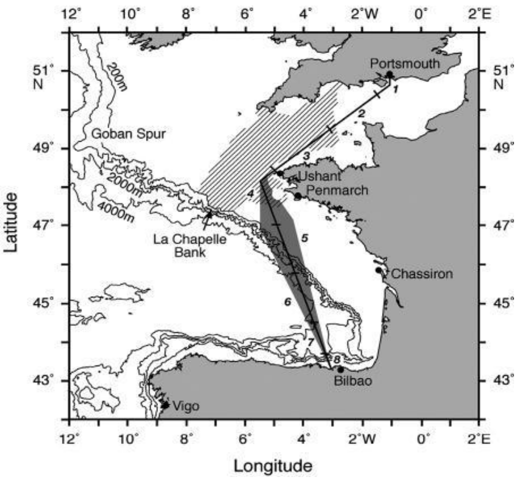

Figure 1: Schematic of the northbound ferry route showing regions 1–8 as identified by Bargeron et al. (2006). Of relevance are regions 4, the western approaches near the French coast at Ushant (30–130 m); the shelf region 5; the slope and adjacent open ocean off-shelf Bay of Biscay regions 6 and 7 (where water depths reach 4000 m). The hatched area shows the extent of the Ushant frontal system (Pingree and Griffiths (1978); see also Pingree et al., 1982).

Ship measurements

Between 2002 and 2010 instruments on the ferry (*MV Pride of Bilbao*) recorded a suite of physical and biogeochemical parameters from within the sea surface mixed layer. Brief details of the sampling and methods are presented here but fuller details can be obtained from various papers (including Hydes et al., 2003; Kelly-Gerreyn et al, 2006) and the full dataset is available from the British Oceanographic Data Centre (BODC).

The sampled water was taken from the ship's cooling water supply at a depth of 5 m. The Ferrybox system consisted of sensors to measure conductivity (precision 0.005 mmho cm^1) to calculate salinity; dissolved oxygen, temperature (precision 0.003°C) and chlorophyll-fluorescence (precision 0.01± 0.01 mg m^3). The flow rate in the Ferrybox system was 15–20 l/m. A comparison between the flow through temperature readings and a hull mounted temperature sensor showed that the flow through temperature readings were 0.5±0.3°C higher than the in situ water (offset ± 1s) from 2005 through August 2008. Subsequent to August 2008 this reduces slightly to 0.3±0.3 °C. These small offsets suggest a low residence time of water in the Ferrybox system. Underway data were logged at a rate of 1 Hz on a NOC (National Oceanography Centre, Southampton) designed logging and control system. Public domain Matlab routines (http://marine. csiro.au/morgan/seawater) provided the calculations for salinity. All sensors were cleaned on an approximately weekly basis to reduce bio-fouling, when the ship was berthed in Portsmouth.

Manned crossings occurred approximately monthly, when water samples were collected from a spur tap near to the sensors. Sample collection was maintained round the clock to calibrate the onboard sensors and to take additional samples for nutrient analysis. Over 6000 samples were taken on the monthly calibration crossings between 2003 and 2010 (except for August 2007 to August 2008) for the measurement of nutrients, including nitrate and nitrite, dissolved reactive phosphate and silicate concentrations. Only nitrate plus nitrite (hereafter referred to as nitrate) data, which was analysed following the standard method described in Grasshoff (1983), is presented here.

The chlorophyll to fluorescence relationship changes due to variations in phytoplankton composition (Falkowski and Kiefer, 1985). Four-fold changes in the chlorophyll to fluorescence ratio have been shown in the productive season in this region with a midday minima (Pingree and Harris, 1988) so the sensor was frequently calibrated to obtain an approximation of chlorophyll-a. Samples for salinity and dissolved oxygen were taken to calibrate the conductivity and dissolved oxygen sensors respectively.

The dissolved oxygen anomaly (DO_{anom}) was calculated as the difference between the measured DO concentration and the saturated value (Benson and Krause, 1984). With the corrections for gas transfer, the changes in the concentrations of DO_{anom} can be attributed to biological activity.

Net community production, integrated over the mixed layer (NCP_{MLD}) was estimated from gas exchange-corrected DOanom ($DO_{anom}^{GasCorr}$) using the methods shown in Jiang et al. (2013). It is expected to be more reliable than using the monthly resolved nitrate data due to the greater frequency of the DO measurements (1–3 days at a given position). It is calculated as follows:

$$NCP_{MLD} = (DO_{anom}^{GasCorr} m + 1 - DO_{anom}{}^{GasCorr}{}_{m})(MLD_{m+1} + MLD_{m}) = 2(C{:}O)NCP$$

where $(MLD_{m+}1+MLD_{m})/2$ is the mean MLD between the two consecutive months. The classical Redfield et al. (1963) ratio for (C:O)NCP of 106:138 was used to convert the changes in oxygen to those of carbon. Monthly mean values were positive in the productive months (March to August) and these values were summed to obtain the annual net community production.

Argo floats (http://www.coriolis.eu.org) provide temperature profiles in the Bay of Biscay for the estimation of the mixed layer depth (MLD). As the thermal gradient of the permanent thermo-cline in the Bay of Biscay is very weak, mixed layer depth estimates based on threshold algorithms may provide biased results. Instead a topology-based algorithm (González-Pola et al., 2006) was used that performs the best-fit of the temperature profiles to a prescribed functional form. The fitting allows a series of parameters to be extracted, that can be identified with properties of the vertical structure of the water column, including the MLD. MLD data are presented for the off-shelf Bay of Biscay region as the Argo float data are only available for water deeper than

1000 m. In the selected region, from 0 to 10°W and 43 to 48°N, over 900 profiles were used in the calculation of MLD. Prior to the 2005/2006 winter there were not sufficient Argo profiles within the Bay of Biscay to calculate MLD. MLD was compared with the North Atlantic Oscillation (NAO) winter index (December–March) assuming this to be the dominant mode of atmospheric pressure variation over the North Atlantic (Visbeck et al., 2003).

Results and discussion

Eight years of monthly resolved nitrate data and continuous in situ hydrographic data from the *MV Pride of Bilbao* are presented and discussed. This is the first time that the full in situ dataset has been presented and it is descriptive at this stage. The high-resolution data were used to resolve regional, seasonal and inter-annual variation in nutrients in the Bay of Biscay, in relation to mixing and productivity.

Regional and inter-annual variations in temperature and nutrients

An overview of 8 years of *in situ* surface temperature measurements from the *MV Pride of Bilbao* (Figure 2) shows the considerable seasonal and regional changes, with lower winter temperatures north of 48°N in the Channel and higher summer temperatures off shelf to the south in the Bay of Biscay. Near identical results were also reported along the Ferry line from SST satellite observations (see Figure 3 in Garcia-Soto and Pingree, 2009).

The regional and inter-annual variation in sea surface temperature is further illustrated in Figure 3. In region 4 strong tides off Ushant mix heat into the 100 m water column and there is a large variation in minimum temperature between years. In the off-shelf Bay of Biscay, regions 5 and 6, there is less variability between years than in other regions. However, the winters of 2007 and 2008 are clearly warmer than in other years and the annual amplitude for the in situ temperature decreased from 9 to 6 °C.

Monthly averaged nitrate data from the Bay of Biscay (Figure 4) shows seasonal and inter-annual variations in nitrate concentrations off-shelf in the Bay of Biscay (regions 5 and 6) in comparison with sea surface temperature changes. Overall the nitrate data show the characteristic increase in concentration during winter months and nitrate depletion due to phytoplankton growth in the spring (and summer). The main differences are in the winter concentrations. Relatively high winter nitrate concentrations were seen in the cold winter of 2005/2006 and low values were associated with the warmer winter of 2006/2007. The warm surface temperatures observed in 2007/2008 were also shown by Garcia-Soto and Pingree (2012).

In the off-shelf Bay of Biscay region (45–47.5°N) the nitrate: temperature relationship is correlated in the winter months (when the temperature is <16 °C) as shown in Figure 5. Linearity in the nitrate: temperature (N:T) signal is widely reported (e.g.: Henson et al, 2003). Although a single line is shown the N:T relationship varies through the autumn and winter months and there will be a range of nitrate concentrations for a given temperature (Garcia-Soto and Pingree, 1998).

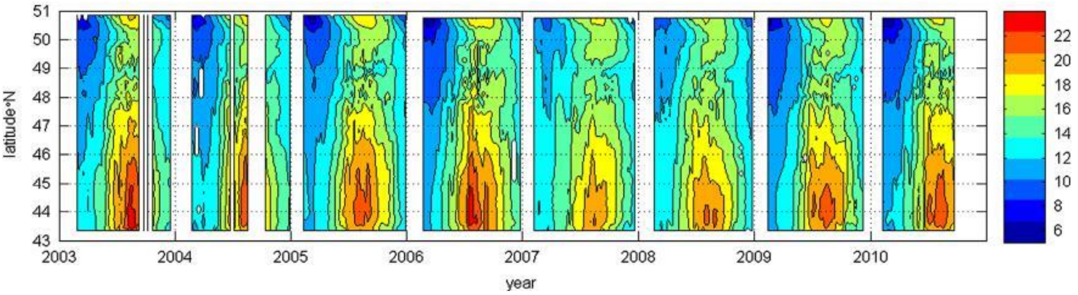

Figure 2: In situ temperature measurements from the FerryBox on route between Portsmouth and Bilbao from 2003 to 2010. The colour bar shows the temperature range encountered (in °C). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article

At temperatures above 16°C, in the summer the relationship no longer holds although small increases in nitrate concentration at may arise due to processes such as for example internal tides, internal waves, eddies and slope current mixing processes (Garcia-Soto and Pingree, 1998).

Variation in nutrients related to mixing

MLD calculated from Argo profiles using the fitting algorithm developed by González-Pola et al. (2007) shows that the *MV Pride of Bilbao* surface nitrate data off-shelf in the Bay of Biscay (Figure 6) is correlated with the MLD as predicted (Glover and Brewer, 1988). A deep MLD is associated with enhanced nutrient supply from strong convection in autumn and winter; shallow MLDs are associated with decreased nutrient supply in spring and summer.

The onset and extent of convective mixing and vertical nutrient supply is influenced by year to year changes in sea surface temperature and consequently density (Tang et al., 2006). Figure 7 shows the inter-annual variation in nitrate due to changes in MLD. MLD information from Argo floats is only available from 2005 and the floats are largely confined to off-shelf regions in the Bay of Biscay.

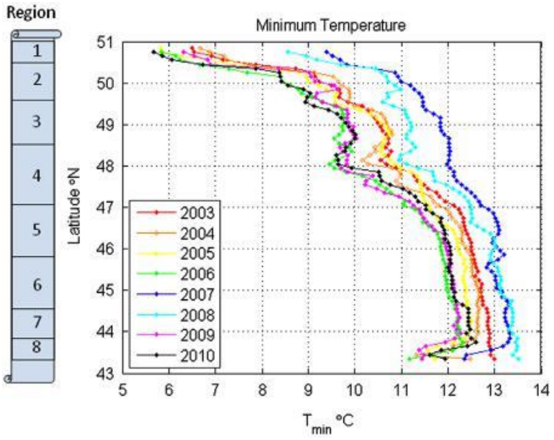

Figure 3: Inter-annual variation in winter sea surface temperature shown as the minimum in-situ temperature identified each year from 2003 to 2010, along the route between Portsmouth and Bilbao

The warmer winter of 2006/2007 is associated with decreased mixing, which lowers the surface nutrient concentrations. Dumousseaud et al. (2010) and Somavilla et al. (2009) showed the hydro-meteorological effects of exceptionally cold winters (2004/2005) and warm summers (2007) on surface nutrient data in the Bay of Biscay. The MV Pride of Bilbao dataset extends the time series to cover 8 years of surface measurements and can resolve the increase in nitrate concentrations in the autumn before the MLD deepens and the nutrients decrease in spring (Figure 7) as discussed in the next section.

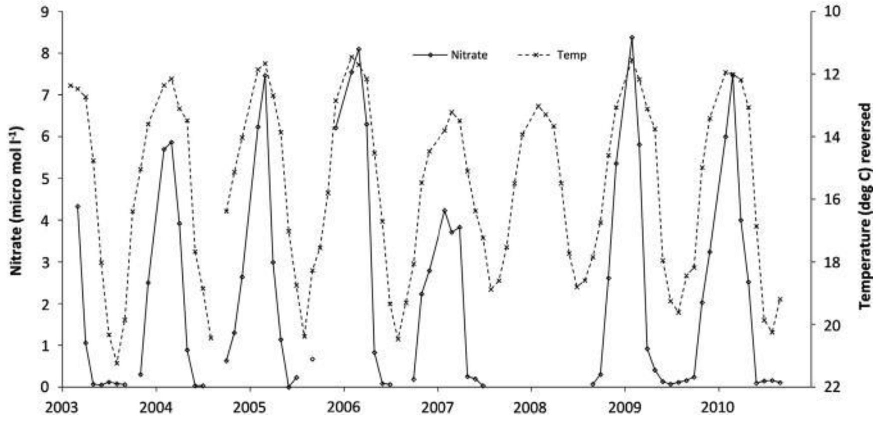

Figure 4: Monthly mean nitrate (solid line) and mean sea surface temperature (reversed scale, dotted line) in the Bay of Biscay (45–47.5°N). Note reversal of the temperature scale in this diagram. The tick marks represent the start of the year.

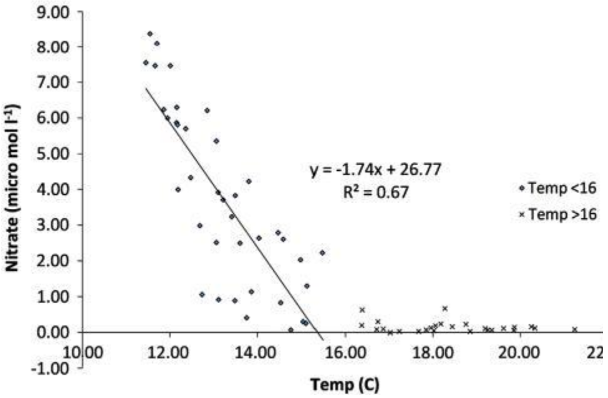

Figure 5: An indication of the relationship between the MV Pride of Bilbao surface nitrate and temperature data 2003–2010, for the off-shelf Bay of Biscay region (46 and 46.5°N), showing the winter relationship (r^2=0.7 at temperatures less than 16 °C).

The position and temperature profiles from all available Argo floats during March (from 2006 to 2009) are shown in Figure 8. Estimates of mixed layer depth based on the temperature profiles confirm that the vertical structure is very different in cold winters (2006 and 2009) compared with warm winters (2007 and 2008).

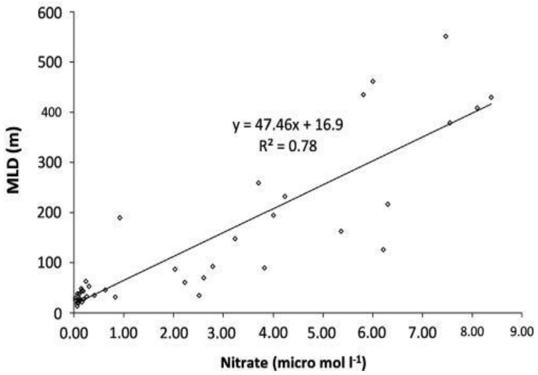

Figure 6: The relationship between the MV Pride of Bilbao surface nitrate and MLD data off-shelf in the Bay of Biscay (46 and 46.5°N) showing a linear relationship (solid line) throughout the year.

The MLD is roughly double in cold winters (approx 170 m vs. 340 m). Despite spatial and temporal variability in the profiles this is a coherent signal across the Bay of Biscay.

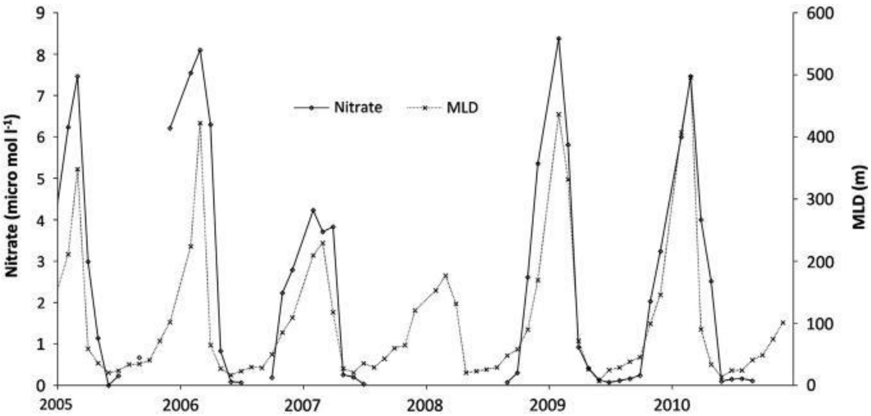

Figure 7: Year to year variations in monthly nitrate data from the MV Pride of Bilbao and monthly MLD data (calculated from Argo float profiles) off-shelf in the Bay of Biscay (46 and 46.5°N).

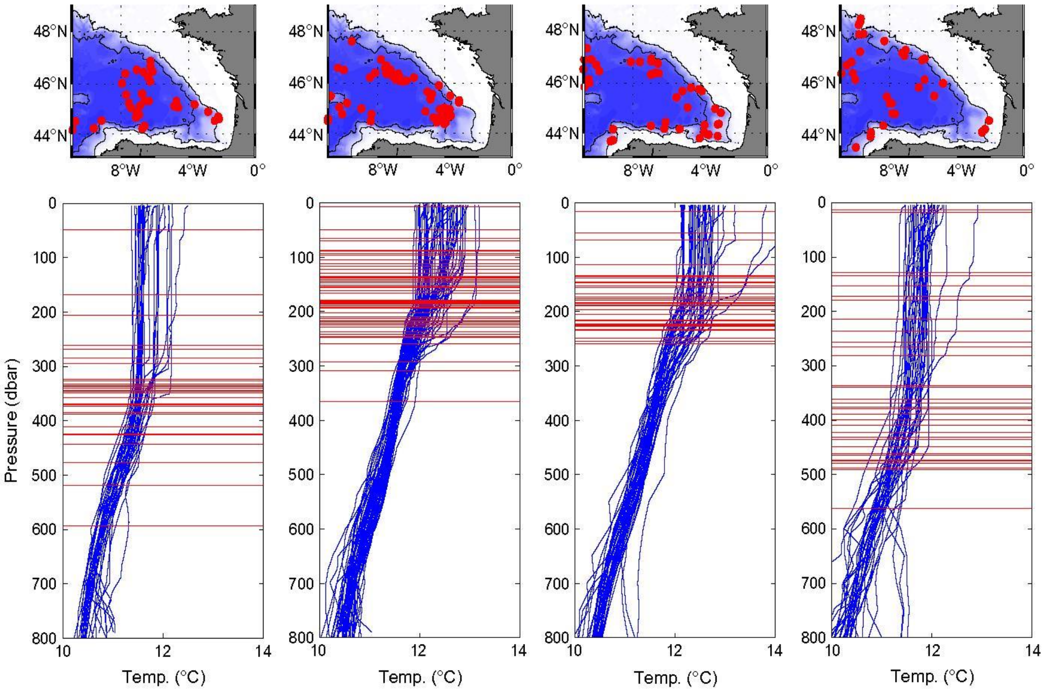

Figure 8. The position of Argo floats, temperature profiles and calculated mixed layer depths in the Bay of Biscay for March 2006 to 2009

Variation in nutrients on and off-shelf

The variation in surface nitrate concentration and salinity along the track at different times of year is illustrated in Figure 9, where selected individual months illustrate the beginning of winter mixing (October), the winter maximum (March) and depleted levels (April). There are clear boundaries to the changes in nitrate and salinity as the ship travels north. These changes were used to define the on-shelf, off-shelf and slope regions shown in Figure 1. In the winter the highest nitrate concentrations are seen off shelf (between 46°N and 46.5°N) where concentrations tend to be greater than 6 μmol l^{-1} (in the March 2005 example shown in Figure 9) peaking near the shelf break (at 46.5°N). Concentrations are lowest around (47.5°N), which can be defined as a half slope, half stratified shelf environment. Slope processes such as internal tides, waves and eddies maintain high nutrient concentrations to the north, on the shelf (Garcia-Soto and Pingree, 1998), as is seen in each of the months shown in Figure 9.

The springtime decline in nitrate is observed to occur over a period of two to three months, occurring earlier in the year to the south, in the off-shelf Bay of Biscay region. The distribution of nitrate in spring (illustrated using April 2005 data in Figure 9) shows nitrate depletion to the south between 45 and 46.5°N due to the spring bloom. Nitrate concentrations in the spring have the expected intermediate concentrations between the winter and autumn values. Nitrate concentrations remain high on the shelf to the north with a transition region of low values in the half slope, half stratified shelf environment. The on-slope nitrate residual is described in Garcia-Soto and Pingree (1998) and reflects the late start to the spring and autumn blooms on the slope.

There is a relatively large change in salinity in autumn, with maximum values at 46.5°N. Salinity decreases through the half slope, half stratified environment (46.5–47.5°N off shelf). Salinity values were lower around 48°N, in October south of Ushant and this is described in Kelly-Gerreyn et al., 2006.

The broad seasonal patterns shown in Figure 9 were seen in each of the 8 years of the study with some year to year variation in the maximum winter nitrate as discussed previously. Off-shelf winter nitrate concentrations reached the highest values (8–10 μmol l^{-1}) in 2005, 2006 and 2009. Some higher on-shelf winter nitrate concentrations were seen particularly in 2004 and 2009 as has been documented previously (eg.: Southward et al., 2004).

Variation in net community production in relation to nutrients and mixing

In Figure 10 seasonal and inter-annual variability in MLD is shown in relation to the monthly oxygen anomaly (DO_{anom}) data from 2005 to 2010, which was used as a measure of productivity (Bargeron et al. 2006). The peak in DO_{anom} indicates the main phytoplankton bloom in spring. In the Bay of Biscay the main spring bloom is dominated by diatoms (Smythe-Wright et al., this issue) and follows a period of sustained positive net heat flux into the ocean (on the scale of 8–10 days, Garcia-Soto and Pingree, 1998; Waniek, 2003).

However, Figure 10 shows that DO_{anom} values increase as soon as the MLD starts to shallow, before the water column in fully stratified and there is some indication of a bloom in the spring of 2008 when the MLD is still relatively deep. The classic view is that phytoplankton blooms develop following high nutrient input due to winter mixing and in conditions of decreased wind, when stratification develops and sea surface temperature increases (Sverdrup, 1953). Results obtained from the *MV Pride of Bilbao* show an increase in phytoplankton growth (with an increase in DOanom) consistent with the Behrenfeld (2010) and Chiswell, 2011 suggestions of pre-spring bloom phytoplankton growth due to a reduction in turbulent mixing, with an upper layer that appears to be still well mixed in terms of temperature and salinity profile data. Comparable results are reported for example by Garcia-Soto-Pingree (1998) in the Bay of Biscay region using CTD and SeaSoar profiles and by Garcia-Soto and Pingree (2009) using remote sensing data, including wind turbulence, along the FerryBox line.

In having a year-round *in situ* dataset some of the assumptions used to calculate NCP can be minimised. For example, there is no need to estimate wintertime nitrate with the associated errors (Glover and Brewer, 1998; Koeve, 2001) and there is no need to make assumptions on the length of the productive cycle (Waniek, 2003). However the calculation of NCP is heavily dependent on the choice of MLD and require assumptions on the C:N ratio (Körtzinger et al., 2001). The relative merit in using chlorophyll-fluorescence or DO_{anom} as an indicator of surface and subsurface phytoplankton growth is beyond the scope of this paper. The high frequency data available from each of these variables could be used to further investigate the timing of the spring bloom in this area although there are numerous studies that have investigated bloom timing in this region using both in situ and remote sensing data (eg: Pingree, 1975; Garcia-Soto and Pingree, 1998, 2009; Garcia-Soto et al., 2002). Table 1 summarises inter-annual variations from 2005 to 2010, highlighting each winter period (December–March) and integrated NCP_{MLD} for the following spring. The winter NAO index, temperature minima, maximum winter MLD; the annual change in dissolved inorganic nitrate and the integrated net community production are shown.

In the Bay of Biscay the MLD (Table 1) was found to vary from 212 m in relatively mild winters (such as 2006/2007) to 476 m in cold winters (2009/2010). Deeper mixing was associated with an increase in nitrate concentrations in the surface waters. Hydes et al. (2001) showed that nutrient concentrations below 300 m remained relatively consistent between cruises and from Hydes et al., 2001 nitrate profiles an increase in mixing from 200 m to 400 m would be expected to increase the surface nutrients by up to 2 μmol l^{-1}. The inter-annual changes seen in the maximum winter nitrate in this study were in the order of 3 μmol l^{-1} (Table 1) which suggests a further source of winter nitrate or a decreased surface advection of low nutrient waters in some years.

The currents were not measured in this study although the water properties reported will reflect changes in the water masses, surface circulation and vertical mixing of depth accumulated nitrate. The slope current and internal tide mixing is particularly important for phytoplank-ton growth and the slope region will experience a continuous injection of nitrate which can enhance productivity (Pingree, 1975; Garcia-Soto and Pingree, 1998). This is a simple illustration of year-to-year variations in winter nitrate in the Bay of Biscay and how productivity is affected the following spring. Our data suggests that low production corresponds to low winter nitrate concentrations and warmer surface water in the 2006/2007 winter, compared with the previous and following years.

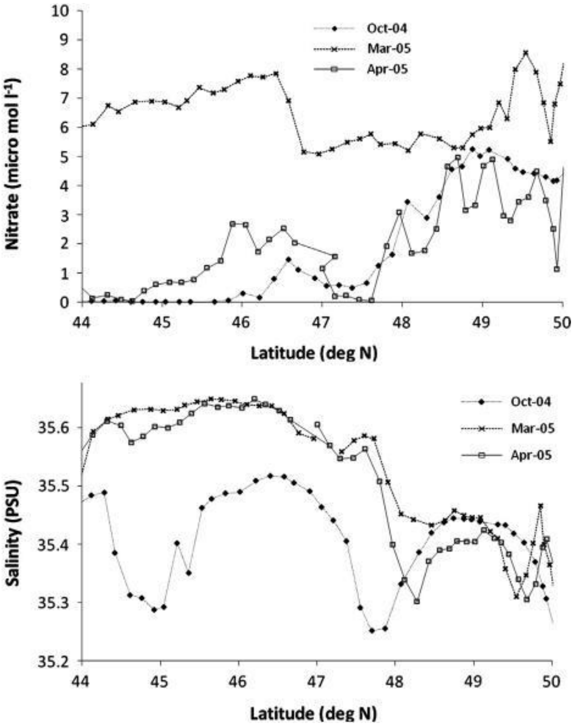

Figure 9: Variation in nitrate concentration and salinity along track from Bilbao in the south to Portsmouth in the north highlighting three months (October 2004, March and April 2005

Overall, the data indicate year to year variation in nutrients and productivity that can be related to changes in sea surface temperature and mixing depth and these changes could be linked to climate indices. A very negative North Atlantic Oscillation index will cool sea surface temperatures from the Azores region to the Bay of Biscay (Pingree, 2005; Garcia-Soto and Pingree, 2012).

Negative winter NAO indices are associated with high seasonal ranges of nitrate concentrations with deep winter mixing (Garcia-Soto and Pingree, 2012). In contrast warm winters, such as 2007 and 2008, correspond to positive winter NAO indices and warmer sea surface temperatures. These positive winter NAO years are associated with shallow winter MLDs, lower seasonal amplitudes of nitrate and winter nutrient concentrations with correspondingly reduced spring time productivity as shown in the dataset (see also Jiang et al., 2013).

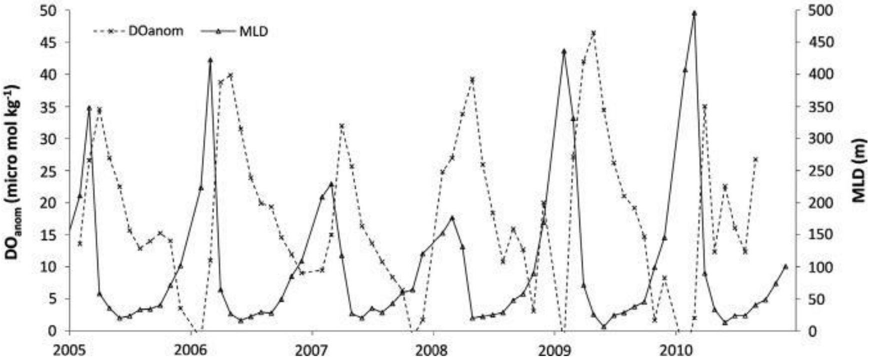

Figure 10: Monthly mean oxygen anomaly (DO$_{anom}$, dashed line) and mixed layer depth (solid line) in the Bay of Biscay (45–46.5°N).

Table 1: Inter annual variation in winter NAO index, temperature minima, mixed layer depth (MLD); annual variation in nitrate concentration; and net community production (NCP) assessed using oxygen data.

Year	NAO index	Temperature minima (°C)	MLD (m)	NO_3 change (μmol l^{-1})	NCP$_{MLD}$ (mol C m^{-2})
2005/2006	-0.24	11.76	469	7.73	20.91
2006/2007	0.63	13.06	212	3.91	10.07
2007/2008	0.51	12.61	265		10.53
2008/2009	0.09	11.89	439	7.41	19.91
2009/2010	-1.48	11.81	476	7.13	16.91

Conclusions

We have presented 8 years (2002 to 2010) of year-round surface time-series data from a SOO in the Bay of Biscay. The data set provided key winter data absent from many other studies (Koeve, 2006). We have shown inter-annual variation in the winter nitrate data, related to changes in the mixed layer depth, specifically in the 2006/2007 winter when the mixed layer depth was shallower reaching 212 m and nitrate concentrations were ~3 μmol l^{-1} less than in years with deeper mixing such as 2009/2010 winter when the mixed layer depth reached 476 m. Although the seasonal cycles are generally well known, the resolution of this dataset provides an opportunity to investigate differences in the cycles between the on and off shelf regions of the Bay of Biscay. In the slope region between these the nitrate concentrations are more consistent throughout the year. Year-to-year variations in the winter nitrate concentrations have also been related to changes in Net Community Production, calculated using high resolution dissolved oxygen data. Deeper winter convective mixing corresponded to colder temperatures and higher winter nitrate but could also be related to an increase in productivity the following spring. A tentative link was made between year to year changes in surface temperature, nitrate and production in relation to climate indices for the Northeast Atlantic.

The full dataset demonstrates that ships of opportunity, particularly ferries with consistently repeated routes, can deliver high quality *in situ* measurements over large time and space scales that currently cannot be delivered in any other way. Hydrographic data are available from the British Oceanographic Data Centre (http://www.bodc.ac.uk).

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Chapter 6

Seasonality and spatial heterogeneity of the surface water carbonate system on the Northwest European shelf.

Hartman, S.E., Humphreys, M., Kivimäe, C., Woodward, M., Kitidis, V., McGrath, T., Mahaffey, C., Greenwood, N., Ostle, C., Pearce, D., Stewart, B., Walsham, P., McGovern, E., Harris, C., Griffiths, A., Smilenova, A., 2017. *Progress in Oceanography (submitted).*

Abstract

To describe seasonal and regional variability in carbonate chemistry around the NW European shelf over 1500 samples were taken for nutrient and carbonate analysis during the 18-month UK Shelf Sea Biogeochemistry research programme field campaign (2014-2015). This is the largest coordinated study to date of carbonate parameters in this area, and involved the cooperation of 10 different institutes and universities, using 8 different vessels. The samples were analysed for carbonate variables and inorganic nutrients, along with the ancillary hydrographic data obtained during the cruises. Carbon dioxide (CO_2) data were obtained from the underway systems on-board three of the research vessels and from the Porcupine Abyssal Plain Sustained Observatory (PAP-SO). Data are considered according to 9 ecohydrodynamic regions, adapted from those used by the EU the Marine Strategy Framework Directive (MSFD) and include Irish waters and the Norwegian Trench. Averages were determined for all measured and derived parameters in each region. Seasonal maps show clear divisions between the low salinity, high nutrient coastal water and high salinity, high DIC waters off-shelf throughout the year. Nutrients remain detectable year-round in the colder waters to the north of Scotland, compared with other regions where they are depleted by the annual spring bloom. Nutrient concentrations recover sooner (in the summer) following the spring bloom in the shallow Irish Sea and Eastern English Channel compared with other regions. For off shelf surface waters, there was a strong inverse relationship between the seawater partial pressure of CO_2 and temperature, especially post-bloom indicating that biological control dominates this relationship. The North-west European shelf is a weak CO_2 sink and we have shown that there is some variation in the capacity to take up CO_2 around the shelf.

Introduction

The partial pressure of seawater CO_2 (pCO_2) is largely controlled by seasonal changes in temperature and phytoplankton productivity (Sarmiento & Gruber, 2006), and additionally by calcium carbonate production and vertical mixing (Laruelle et al, 2014). Where the pCO_2 in the ocean is lower than the atmosphere the ocean will absorb CO_2. The shelf seas comprise only about 5% of area of the global ocean but are important net sinks of CO_2 as primary production and air-sea exchange of CO_2 are in many cases larger in the shelf seas than in the open ocean (Chen & Borges, 2009; Liu et al., 2010). The temperate north East Atlantic is an important CO_2 sink, of about -17 $TgCyr^{-1}$ (Laruelle et al., 2014). There are also important regional differences, e.g. the North Sea is a more significant sink for CO_2 than the English Channel (-1.7mol C m^{-2} yr^{-1} compared with -0.15 mol C m^{-2} yr^{-1}: from Thomas et al., 2004, 2007).

CO_2 uptake by seawater is driving a decline in oceanic pH known as ocean acidification (Caldeira & Wickett, 2003; Riebesell & Tortell, 2011). Ocean acidification in the future could have detrimental effects on organisms that calcify (Feely et al., 2009; Riebesell and Tortell, 2011; Doney et al., 2012). Aragonite is the most soluble form of calcium carbonate in the marine environment and the saturation state of aragonite can give an indication of susceptibility of a region to ocean acidification. As the pH decreases so too does the aragonite saturation state (Feely et al., 2009). There are large regional and seasonal variations in the oceanic pH so there is some inbuilt tolerance to pH changes (Bates et al., 2014; Kitidis et al., 2017), especially in shelf seas (Ostle et al, 2016). The pH range is influenced by the anthropogenic increase in atmospheric CO_2 and changes in temperature but is also influenced by the balance between photosynthesis and respiration; with a pH increase in spring when photosynthesis dominates over respiration and a decrease in summer when respiration becomes more important (Provoust et al., 2010).

Seawater may be able to buffer some of these pH changes through the alkalinity (which is defined as the total concentration of the strongest bases), which can vary seasonally depending on changes in riverine input (Hydes & Hartman, 2012). Monitoring the alkalinity and dissolved inorganic carbon (DIC) of the seawater along with pCO_2 and pH measurements will give an indication of the state of the oceanic carbonate system, and its interactions. As pH is influenced by the balance between photosynthesis and respiration it is also important to measure nutrient concentrations as an indication of potential primary production.

As the seasonal, and inter-annual, variation in pH can be large (Ostle et al., 2016) there is a need for long-term time series measurements (Bates et al., 2014) although over 25 years of consistently measured data are needed to detect pH trends (Henson et al., 2016). ICES studies in the central North Sea (Beare et al., 2013) and southern North Sea (Duarte et al., 2013) have reported decadal changes in pH. A decline in pH (starting in 1990 and 1985 respectively for these two studies) was associated with physical drivers (Salt et al., 2013) and changes in nutrients and eutrophication (Provoost et al., 2010). The DEFRApH project (Hydes et al., 2011; Ostle et al., 2016) looked at time series data on the NW European Shelf; including fixed sampling sites at L4 (Western English Channel) and Stonehaven (off the coast of Scotland). Hydes et al., (2011) showed a trend of decreasing pH around the NW European Shelf of -0.002 to -0.004 pH units per year between 1995 and 2009.

The NW European Shelf is typical of other shelf seas as large areas are stratified in the summer, except where strong tides break up the stratification (Smith et al., 2014). Stratification breaks down in winter so phytoplankton numbers decrease due to low light and turbulence. Nutrients accumulate, reaching maximum concentrations just before the return of stratification when they are consumed by the spring bloom. These general features of the annual cycle of nutrient and plankton levels in the North Sea for example have been established for some time (Cushing, 1973; Johnston, 1973; Brockman et al., 1988; Gerlach, 1988; Nelissen & Stefels, 1988). However, data sets lacked sufficient coherence and breadth of synoptic coverage over an appropriate range of determinands to develop models linking physical and chemical processes to biological production (Huthnance et al., 1993; Radach et al., 1993).

Within the southern North Sea, the NERC North Sea Programme in 1988-89 (NSP) provided the first data set with sufficient information to allow changes in nutrient concentrations and plankton biomass to be investigated quantitatively (Howarth et al., 1994). Prandle et al., (1997) carried out a simple statistical analysis of the data collected at approximately 120 stations on 18 repeated monthly cruises. They provide maps of the spatial distributions of the mean values, the seasonal amplitudes and the percentage variances accounted for by a combination of these mean values and seasonal amplitudes. Correlations between the determinands were calculated; these confirm the similarity in the spatial distributions for the nutrients, especially between nitrate, phosphate and silicate. Maximum concentrations are confined to the coastal regions, except for ammonium and nitrite for which they occurred offshore. Spatial distributions of the anomalous (non-seasonal) components were interpreted to indicate the effect of specific riverine and oceanic exchanges.

The highest pH will coincide with the spring bloom (Kitidis et al., 2012), when CO_2 (and hydrogen ions) decrease in the surface ocean. By the summer there will be an increase in pCO_2 as the solubility of CO_2 decreases at the higher temperatures (Borges & Frankignoulle, 2003). In the autumn pH decreases due to respiration and the return of CO_2 to deeper water as the water column starts to mix again.

These are the broad seasonal trends expected on the NW European shelf. As part of the Shelf Sea Biogeochemistry (SSB) programme we aimed to identify regional variations around the shelf. The SSB programme was established in 2014 (http://www.uk-ssb.org/) to improve the understanding of carbon and nutrient cycling within shelf seas, and its role in global biogeochemical cycles. As part of the 'CANDYFLOSS' (Carbon and nutrient dynamics and fluxes over shelf systems) component of SSB sampling was carried out across the entire UK continental shelf for Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA), inorganic nutrients and Dissolved Organic Matter (DOM). The whole-shelf sampling campaign was a large marine research community effort started in January 2014 and continued onwards for eighteen months, involving the cooperation of 10 institutes and universities and 8 vessels. One of the aims of the shelf wide sampling component was to increase the density and spatial coverage of carbon and nutrient sampling across the entire NW European shelf to compare drivers of seasonal and spatial heterogeneity in the surface waters of the shelf and in adjacent waters and to get a more coherent picture of the overall carbonate system.

It is possible to calculate the entire carbonate system from knowing any two out of TA, DIC, pCO_2 and pH, using equilibrium equations and constants (Park, 1969) and the CO_2SYS program (Lewis et al., 1998). The shelf wide SSB measurements of DIC and TA were used to mathematically calculate pH and CO_2. The calculations can be checked against direct measurements of CO_2 (and pH), which are increasingly being measured by underway systems on-board ships of opportunity, on moorings and on research vessels. During the SSB project underway CO_2 was measured by ships of opportunity, on-board the Cefas and NERC research vessels and at the Porcupine PAP-SO (www.noc.ac.uk/pap).

Calculated and direct measurements from all seasons and regions of the NW European Shelf have been used in this study. The data obtained from the SSB surveys are a valuable resource to extend the time series reported in the 2008-2010 Defra pH project (Hydes et al., 2011) and pH assessments made by Ostle et al. (2016), and to make regional comparisons with other datasets from the NW European Shelf. The data were collected to describe the key processes and how these effect the distribution of biogeochemical variables through the year, and across the shelf.

Description of key regions

Eight ecohydrodynamic regions of the NW European Shelf are defined for reporting under the EU Marine Strategy Framework Directive (MSFD) reporting (Bresnan et al., 2015). They are distinguished by water depth (and seasonal stratification), proximity to the coast, riverine inputs (salinity) and water temperature ranges. These regions have been adapted from those defined in Charting Progress 2 with the addition of the Irish Continental Shelf and the Norwegian Trench (Figure 1). All of these regions were sampled as part of the CANDYFLOSS component of the SSB program (reference to introductory paper).

The North Sea is divided into the seasonally stratified northern North Sea (region 1) and shallower well mixed southern North Sea (region 2) in which the balance of inorganic carbon related processes through the year are different (Thomas et al, 2006; Van Leeuwen et al., 2015). The North Sea is influenced by riverine input (Hydes et al., 1999; Hydes & Hartman, 2012; Bresnan et al., 2015). The balance of inorganic carbon related processes through the year are different. Thomas et al, 2005 & 2006; Van

Leeuwen et al., 2015 have suggested that over the annual cycle water temperature is the dominant control on pCO_2 in the southern North Sea and biological control of the northern North Sea.

The English Channel is divided into the shallower Eastern Channel (region 3) and the more oceanic Western Channel and Celtic Sea (region 4). The Western English Channel and Celtic Sea are characterised by thermal stratification and nitrate depletion in the summer (Smyth et al., 2010). The southern part of the western English Channel is also potentially influenced by the Loire and Gironde river plumes in some years (Kelly-Gerreyn et al., 2006). The carbonate chemistry in this region has been summarised by Kitidis et al, (2012).

The Irish Sea (region 5) and, in particular the Liverpool Bay sub-region are strongly influenced by fresh water inputs. The winter-time distributions of nutrient and carbonate parameters in the whole Irish Sea are described in McGrath et al. (2016), with further summaries of Liverpool Bay carbonate and nutrient cycles in Hydes & Hartman (2012) and Greenwood et al., (2011) respectively. Region 6 are waters west of Scotland and the coastal Minches region. The hydrography of this region is described in Bresnan et al. (2015). Region 6 has the least amount of data covering changes between seasons. The Scottish and Irish continental shelf (region 7) as defined here has a western limit of the 1000m depth contour. It is influenced both by exchanges with the deep waters of the North Atlantic and waters flowing from the south in the shelf edge current (Huthnance, 1995 &1997; Burrows and Thorpe 1999, Hydes et al 2004). The carbonate chemistry on the Scottish continental shelf near the Outer Hebrides (in Region 7) has been discussed by Painter et al. (2016) considering data from a single survey cruise DY017 carried out in autumn-month 2014. That survey data has now been included in the SSB data set. Region 8 is the region deeper than the 1000m contour the open Atlantic and encompasses the north-west approaches, Rockall Trough and the Faeroe/Shetland Channel. Region 9 is the Norwegian Trench. This region is the main outflow path for water leaving the North Sea, and it is permanently stratified (Van Leeuwen et al., 2015).

a)

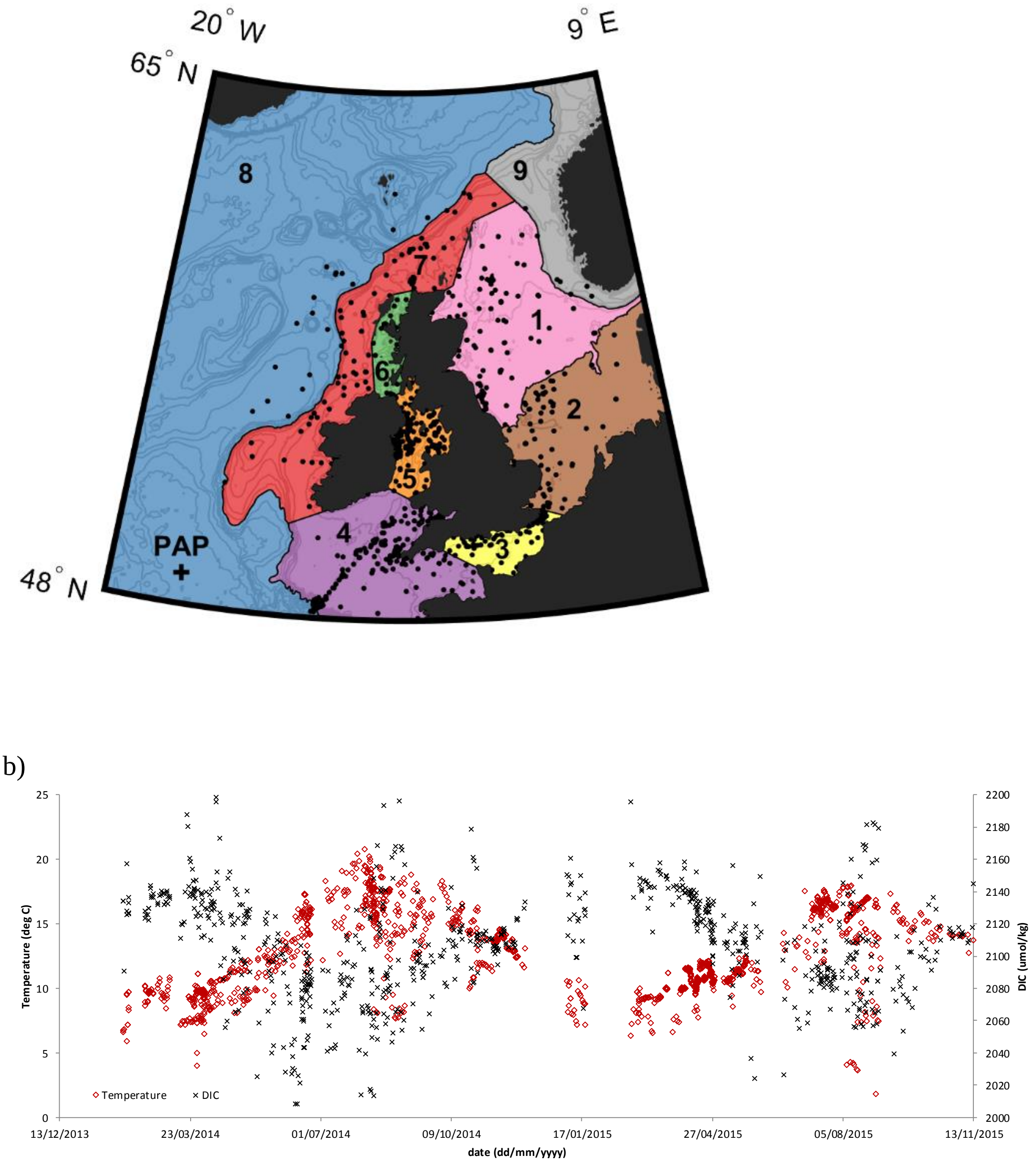


Figure 1: a) Map of the sampling positions (shown as black dots) during SSB Candyfloss (2014-2015) coloured to show the UK ecohydrodynamic regions used for MSFD reporting (adapted from Bresnan et al., 2015 to now include Ireland and the Norwegian Trench) also showing the position of the PAP-SO; b) Temporal coverage of sampling around the shelf showing temperature (red diamonds) and DIC (black crosses) data (2014 and 2015) showing all data from stations in Figure 1a.

Further data included in our comparisons comes from the Porcupine Abyssal Plain sustained observatory (PAP-SO) which is located in the North East Atlantic at 49°N 16.5°W (Hartman et al., 2015). These data are obtained from the instrumented buoy at this site (www.noc.ac.uk/pap), which are supplemented and validated by bottle data from occupations of the site when the buoy is serviced and from a ship of opportunity, which passes the PAP-SO format least once a month on the UK and the Caribbean (Schuster & Watson, 2007; Ostle et al., 2015).

Methods

Between January 2014 to August 2015 approximately 1500 surface water samples were collected at the sites shown in Figure 1a as part of the CANDYFLOSS SSB project. Daily underway samples were taken from the underway seawater supplies on-board. Samples for later DIC and TA analysis were taken into glass bottles and preserved with saturated mercuric chloride (0.05 mL), the dilution effect of adding preservative is negligible (0.02%) due to large sample volume size. Further samples were filtered and frozen for nutrient (and dissolved organic matter analysis although this is not considered further here). Hydrographic properties were measured using in situ underway sensors and results were recorded at the time of sampling, along with time and sample position.

These surface samples were taken daily from the underway water supply whenever the vessels were at sea around the NW European shelf (Figure 1a shows the spatial coverage and 1b the temporal coverage for DIC sampling). The overall sampling programme was a large community effort involving a range of research vessels and organisations. The NERC vessels RRS *Discovery* and RRS *James Cook* (on the 9 SSB cruises DY008, JC105, DY018, 21, 26, 29-30, 33 to DY034); Cefas vessel RV Endeavour (34 cruises CEND03-14 to CEND24-15); Marine Institute cruises on RV Celtic Explorer and RV Celtic Voyager (total 11 cruises including 1412, 14005, 15003); Marine Scotland RV Scotia (7 cruises from 0514 to 0115 and samples from the fixed point Stonehaven site); AFBI vessel RV Corystes (15 cruises). On the UK-Caribbean ship of opportunity nutrients samples are collected and frozen every 4 hours (Hartman et al., 2010).

Analyses

Inorganic nutrients were analysed using a 'Bran and Luebbe AA3' segmented flow colorimetric nutrient auto-analyser. The analytical methods were: Phosphate and Silicate using Kirkwood (1989) and Nitrate with Brewer and Riley (1965). The standard deviation for duplicate measurements was within 2 % and quality was assured through daily use of certified reference materials provided by KANSO (Japan). Sampling protocols and methodologies were carried out where possible according to the GO-SHIP nutrient analytical procedures manual (Hydes et al., 2010).

DIC and TA were measured using the VINDTA 3C (Marianda, Germany) at Southampton University. The analysis of DIC on the VINDTA was by reaction with 10% phosphoric acid. DIC was converted to CO_2 gas, which was carried by nitrogen into the coulometer cell where it reacts with monoethanolamine to form a titratable acid, which causes fading of the blue indicator. Responding to the colour change, an electrical current generates base to remove the acid and restore the indicator to the original colour. The amount of CO_2 can be estimated from the total current required (corrected for blank), and DIC concentration can then be calculated given the sample volume. TA was measured by titration with hydrochloric acid (HCl ~0.10 mol/l) using an open cell procedure, with a pH half-cell electrode (glass bodied Orion 8101SC, Ross, USA) and an Ag/AgCl reference electrode (model 6.0729.100, Metrohm, Switzerland). Then a Gran plot approach was used to calculate TA (Bradshaw et al., 1981). Some measurements were instead carried out using the Apollo SciTech (USA) DIC Analyzer AS-C3 and Total Alkalinity Titrator AS-ALK2. The AS-C3 functions similarly to the VINDTA 3C except that the final CO_2 measurement is by infrared absorbance. Like the VINDTA 3C the AS-ALK2 performs a potentiometrically-monitored titration with 0.1M HCl to determine the TA. In order to standardise the results, Certified Reference Materials (CRM) from A.G. Dickson, Scripps

Institution of Oceanography were analysed as standards to calibrate the instruments at the beginning and end of each day of analysis (Dickson et al., 2003). Repeated measurements on the same batch of seawater (n>=3) in the lab gave consistent results (precision for the whole dataset was estimated as ±2.6 µmol kg^{-1} for DIC and ±2.7 µmol kg^{-1} for TA for VINDTA measurements, and ±4.0 µmol kg^{-1} and ±3.9 µmol kg^{-1} for DIC and TA respectively on the Apollo instruments.

Additional samples were taken using a rosette sampler. This is the case for the Hebrides cruise DY017 (Painter at al., 2016) when the 0-20m samples have been used. Temperature, salinity, pCO_2, nitrate and pH were measured directly using sensors at the PAP-SO site (Hartman et al., 2015 for further details). Samples collected from the UK-Caribbean ship of opportunity near to the PAP-SO were analysed ashore (using an auto-analyser for nutrients, Hartman et al., 2010).

Underway CO_2 was measured using the PML-Dartcom systems (Kitidis et al., 2012), on RRS Discovery and RV Cefas Endeavour. Briefly, the system comprises a vented ‘showerhead’ equilibrator, Peltier cooler for partial drying of the equilibrated gas stream, non-dispersive infrared detection (Licor; LI-840) and associated mechanical/electronic hardware. The system was calibrated against three reference gases (BOC Gases, UK; nominal concentrations 250, 380 and 450 ppmv CO_2 in synthetic air mixtures; changing from 450ppm to 600ppm on the Endeavour from November 2014) which were referenced against primary reference gases (National Oceanic and Atmospheric Administration, 244.9 and 444.4 ppm CO_2). A recent at-sea inter-comparison with a similar but independent system, along with other carbonate observations, found the system was precise to within ±4 µatm (Ribas-Ribas et al., 2014). The underway CO_2 data could therefore be compared directly with the calculated CO_2 data (Figure 2) providing a level of inter-comparison between the data sets.

Calculations

Bottle DIC, TA, temperature, salinity and nutrient data were used to calculate CO_2 and pH, using the CO_2SYS program (Lewis et al., 1998) using the Mehrbach constants (according to Dickson & Millero, 1987). There are documented uncertainties associated with CO_2SYS of ~2µatm in the calculation of pCO_2, (eg: Millero et al., 1993; Hoppe et al., 2012; Salt et al., 2016) arising from inaccuracy in measurements and in determining the dissociation constants.

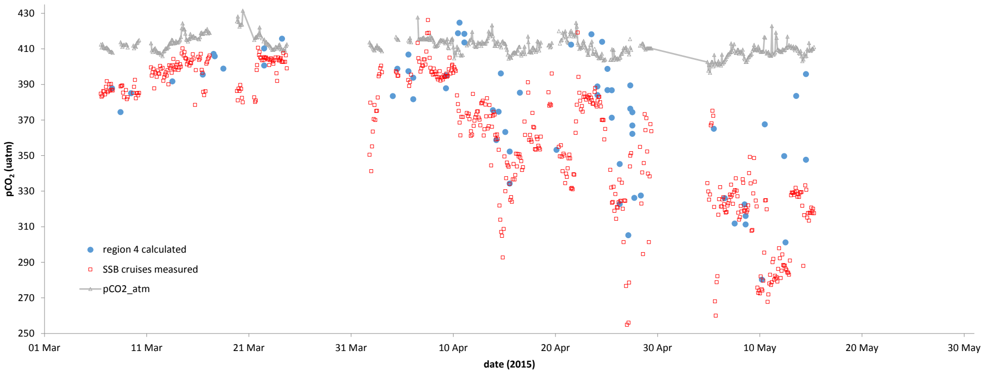


Figure 2: Data from 2 Celtic Sea cruises (DY021 and DY029) in 2015 showing a close agreement between the underway CO_2 data from the Dartcom system (in red) and CO_2 calculated from bottle DIC/TA samples (in blue)

The 2014 and 2015 data were merged and mapped to describe the spatial and seasonal distribution in biogeochemical variables. The data were mapped seasonally where January to March is defined as winter, April-June as spring, July-September as summer and October-December as autumn. The average and standard deviation within each of the 9 ecohydrodynamic regions was tabulated for the winter and summer period (Table 1).

Results and discussion

Hydrographic variability

Temperature

Winter cooling and summer heating dominates the seasonal cycle in sea surface temperature (SST). The maps of sea surface temperature (Figure 3) show an intra annual variation in temperature at the SSB sampling sites of 7-18 °C, with an average surface temperature of 14 °C. The higher temperature readings are nearer to the coast and higher SST persists close to the coast into autumn. From Table 1 the lowest temperature readings were in the North Sea (in both the northern and southern North Sea, regions 1 and 2) in winter. The temperature difference between surface water in the more northerly and more southerly sites was about 3 °C year-round. Ostle et al. (2016) reported that the Stonehaven site (off the East coast of Scotland) remains about 3.1°C colder than at L4 (in the Western Channel) throughout the year.

Salinity

There is little seasonal variability in salinity (Figure 3b) and the average over the whole data set is 35.1 (±0.6). Higher salinities were found to the west of the UK on the continental shelf (region 7) and the Atlantic North West approaches (region 8), showing the Atlantic water influence. There is also a tongue of high salinity water, especially prominent in the summer, in the northern North Sea (region 1) showing the influence of the advection of Atlantic water into this region. The region of highest fresh water influence in the data reported here is Liverpool Bay (region 5) where salinity remains relatively low (34) throughout the year. Relatively low salinities in the Jutland current to the east of the North Sea (region 2) can be identified in the data (Figure3b). This current is the main exit route for fresh water entering the North Sea from the major European continental rivers the Rhine, Elbe and Weser.

Chemical variability

Nutrients

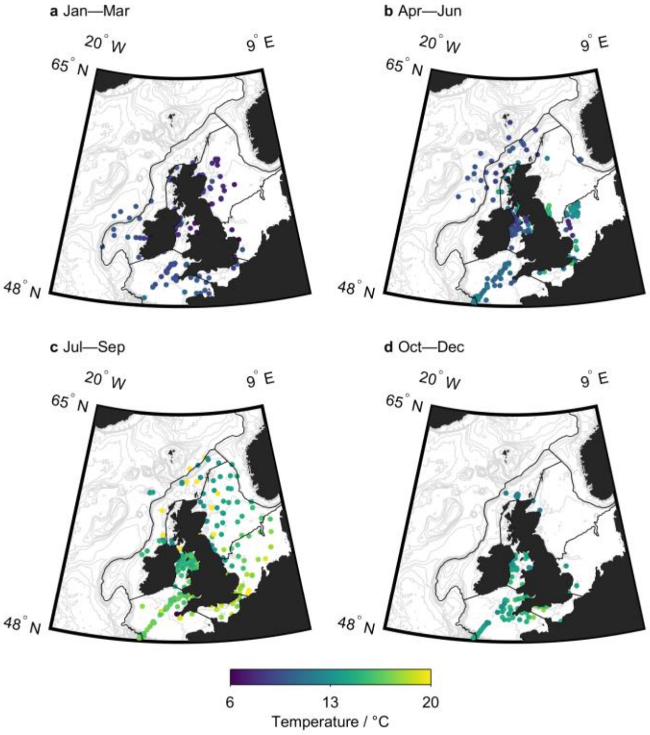
The variation in nutrient concentrations between winter and summer conditions in the 9 regions are summarised in Table 1. From the surface maps in Figure 4 silicate concentrations are highest in the Irish Sea (region 5) and the Eastern Channel (region 3). This illustrates the riverine influence, where rivers from the Irish and UK coasts are adding silicate to the Irish Sea (region 5). Silicate concentrations are about 1umol kg^{-1} lower in the northern North Sea (region 1) and Celtic Sea (region 4).

Scotland where concentrations nutrients detectable in the summer (see Table 1). The largest seasonal change in phosphate (0.5µmol/l) nitrate (8 µmol/l) and silicate (5.4 µmol/l) was seen in Liverpool Bay (in region 5). In this part of the Irish Sea nutrient concentrations start to increase earlier in the year than in the other regions due to riverine inputs (see also Greenwood et al., 2011). In other regions, concentrations of nutrients remain low until autumn storms begin to break down the thermal stratification of the surface waters (see Figure 4)

Table 1: The average (mean and standard deviation) for each variable in winter (Jan-Mar) and summer (Jul-Sep) for each of the 9 ecohydrographic regions. The number of samples used in calculating the winter and summer averages are shown for each region (in brackets). The number of samples remains low in winter compared with other seasons due to the logistics of mounting winter surveys.

Region	Temp (°C)	Salinity	DIC (µmol/kg)	TA (µmol/kg)	pH	pCO_2 (µatm)	NO_3 (umol/kg)	PO_4 (µmol/kg)	SiO_3 (µmo/kg)
1. Northern North Sea (16,87)	7.44 (0.24)-11.96 (3.20)	34.61 (0.49)-34.78 (0.5)	2135.67 (25.3)-2112.19 (56.6)	2317.9 (27)-2302 (19.2)	8.23 (0.2)-8.09 (0.1)	319 (78)-409 (84)	7.5 (1.7)-3.1 (4)	0.5 (0.1)-0.3 (0.3)	3.0 (1.3)-2.2 (1.9)
2. Southern North Sea (10,45)	7.56 (1.44)-17.18 (2.04)	34.01 (1.37)-34.49 (0.39)	2149.9 (37.2)-2113.2 (32.3)	2322.5 (28)-2319 (39)	8.12 (0.02)-8.06 (0.06)	381 (23)-476 (64)	9.5 (9.5)-0.6 (0.9)	0.5 (0.3)-0.2 (0.1)	4.9 (5.9)-2.0 (1.7)
3. Eastern Channel (9,11)	9.44 (0.78)-18.16 (1.02)	34.92 (0.53) - 34.86 (0.3)	2141.4 (24.2)-2093.2 (12.35)	2335 (24)-2316 (13)	8.14 (0.03)-8.09 (0.02)	370 (24)-457 (26)	9.6 (3.6)-1.3 (1.7)	0.5 (0.1)-0.1 (0.1)	5.2 (2.2)-2.3 (1.2)
4. Western Channel Celtic Sea (124,439)	9.56 (0.56)-16.46 (1.90)	35.24 (0.15)-35.24 (0.29)	2139.5 (7.7)-2084.8 (16.7)	2333 (12)-2335 (13)	8.13 (0.02)-8.15 (0.04)	384 (17)-381 (42)	7.8 (2.2)-0.26 (1.5)	0.6 (0.2)-0.1 (0.1)	4.2 (1.0)-0.6 (0.8)
5. Irish Sea (16,51)	8.0 (1.4)-15.37 (1.14)	33.8 (0.78)-34.02 (0.46)	2143.2 (18.3)-2075.5 (26.7)	2298 (27)-2292 (13)	8.07 (0.04)-8.12 (0.06)	435 (41)-410 (58)	9.9 (6.1)-1.0 (1.3)	0.6 (0.2)-0.2 (0.2)	7.5 (3.3)-2.1 (1.2)
6. Minches Western Scotland (4,4)	9.35 (0.39)-11.91 (0.68)	34.45 (0.09)-33.98 (0.45)	2129 (15.2)-2098.1 (10.5)	2287 (11)-2293 (9)	8.06 (0.05)-8.12 (0.02)	453 (62)-397 (17)	6.3 (1)-2.4 (1.5)	0.5 (0.02)-0.3 (0.1)	4.5 (0.3)-1.8 (0.9)
7. Continental Shelf (23,16)	9.77 (1.98)-13.47 (2.5)	34.99 (0.29)-35.18 (0.23)	2068 (5) - 2100.4 (25.8)	2334 (10)-2311 (14)	8.12 (0.06)-8.12 (0.04)	386 (53)-396 (41)	10.0 (6.5)-3.2 (3.9)	0.6 (0.4)-0.2 (0.2)	4.0 (2.3)-1.1 (1.6)
8. PAP-SO and Atlantic Northwest approach (41,14)	9.24 (1.45)-17.3 (1.1)	35.35 (0.1)- 36.2 (0.2)	2126 (5)-2105 (23)	2331 (9)-2343 (12)	8.06 (0.01)-8.13 (0.1)	381 (10)-392 (54)	5.4 (1)--3.6 (5.1)	0.2 (0.1)-0.3 (0.3)	1.7 (0.4)-1.5 (2.3)
9. Norwegian Trench (0,4)	no data-11.43 (3.1)	no data - 35.0 (0.5)	no data - 2109 (56)	no data – 2307 (16)	no data – 8.11 (0.1)	no data – 399 (59)	no data – 7.8 (6.8)	no data - 0.5 (0.6)	no data – 2.8 (3)

3a)



3b)

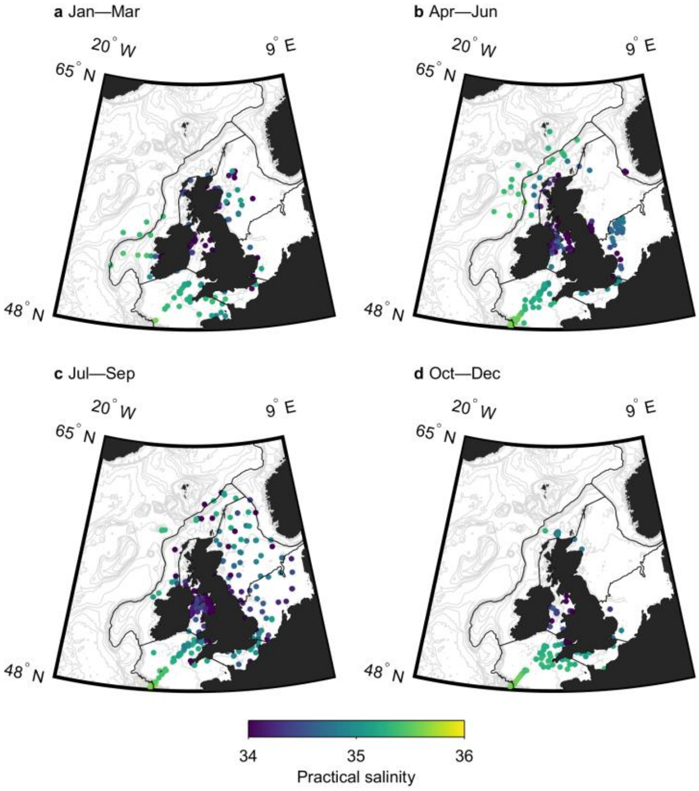
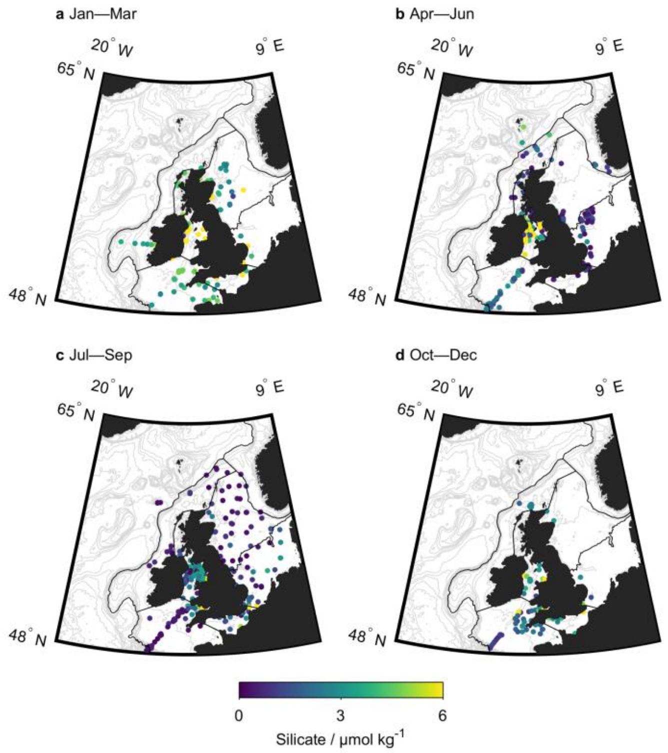


Figure 3: Seasonal SSB maps with winter data (Jan-Mar), spring (Apr-Jun), summer (Jul-Sep) and autumn (Oct-Dec) for 3a) SST and 3b) practical salinity, using sensor data taken at the point of sampling on the SSB surveys.

4a)



4b)

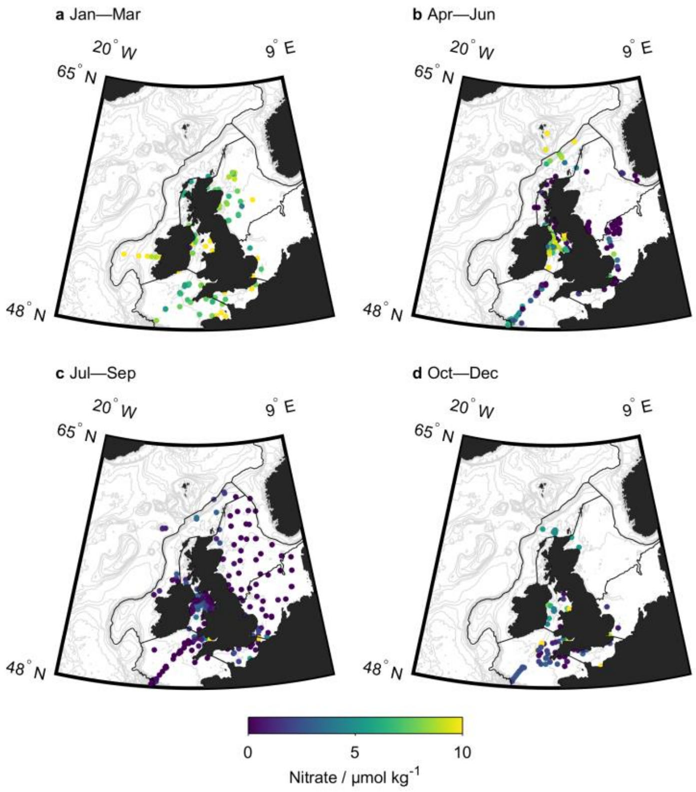


Figure 4: Seasonal SSB maps with winter data (Jan-Mar), spring (Apr-Jun), summer (Jul-Sep) and autumn (Oct-Dec) for 4a) silicate and 4b) nitrate concentrations

All nutrient species are depleted by the spring bloom each year due to the growth of phytoplankton, except in the Scottish continental shelf (region 7) to the northeast of

Low nitrate concentrations are seen in winter off Scottish west coast (region 6) in contrast to waters of similar salinity in the southern North Sea (region 2) and the Eastern Channel (region 3), which show evidence of high nitrate concentrations in the winter, possibly from river input (Figure 4b). Phosphate concentrations were measured but have not been mapped here as they are fairly uniform around the whole of the UK shelf (see Table 1). A comparison of the nitrate and phosphate concentrations in Figure 5 suggests low winter nitrate values (below the Redfield 16:1 relationship) in both the southern North Sea (region 2) and the Irish Sea (region 5). These low ratios have been reported previously (Hydes et al 1999; Gowen et al., 2002) and are probably a result of denitrification in the sediments of these relatively shallow shelf seas (Setzinger and Giblin., 1996). A key feature established in the North Sea Project data (Hydes et al., 1999) is that denitrification reduces on shelf concentrations of dissolved nitrate so the maximum concentration observed in the Central North Sea (Hydes et al., 1999) and in the Irish Sea (Gowen et al., 2002 and 2008) is below that observed in ocean waters adjacent to the shelf (Hydes et al., 2004). Kitidis et al. (accepted), showed that sediment anaerobic ammonium oxidation and denitrification removed 6-9 % of the N in the Celtic Sea over an annual cycle. The process of denitrification to denitrification over muddy sediments, which could lead to increases in pH (Froelich et al., 1979; Provoost et al., 2010).

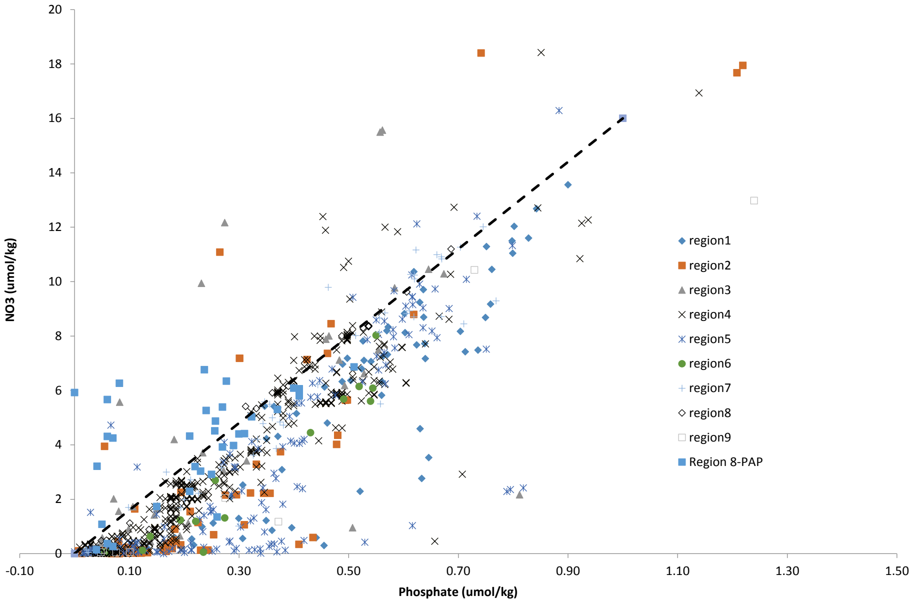


Figure 5: A comparison of the SSB nitrate and phosphate concentrations for each region showing the Redfield et al., (1953) N:P ratio of 16:1.

Alkalinity

The average TA for the whole dataset is 2320 µmol kg^{-1}. (Figure 6). The TA distribution is generally linked to salinity as both are relatively conservative variables, influenced by evaporation, riverine freshwater inputs and precipitation. Like salinity there is a general increase in alkalinity offshore and there are regional variations such as higher alkalinity in the southern North sea (as shown by Salt et al., 2013) not seen in the salinity data. . Previous studies have shown some seasonality in alkalinity, for example Hydes & Hartman (2012) showed higher TA values due to productivity in spring in the Liverpool Bay sub region of the Irish Sea. Additionally alkalinity is influenced by the bedrock of rivers for example the river Liffey (near Dublin) inputs to the Irish Sea (region 5) and has a high TA from limestone bedrock (McGrath et al., 2016). This could have implications for the carbonate system near to the coast, as the alkalinity will buffer the hydrogen ions, resulting in CO_2 under saturation.

A positive TA:S relationship is expected in open ocean waters (Lee et al., 2006). Figure 7 shows that the TA:S is generally a consistent positive linear relationship lying between the Thomas et al (2007) relationship reported for the North Sea and the Lee et al., (2006) relationship reported for the North Atlantic (both also shown in Figure 7). Lines of best fit were calculated for each region; the slope, constant and R^2 for the TA:S relationship in each region are summarized in Table 2.

There is a significant positive correlation in the northern North Sea (region 1) and in the Norwegian trench (region 9) (R^2=0.78). The TA:S relationship is also positive in the Celtic Sea (region 4). Kitidis et al., (2012) reported a similar positive TA:S relationship for the Western Channel (TA = 40.3 x salinity + 911). However both Table 2 and Figure 7 suggests that the TA:S relationship is not conservative in many regions.

Table 2 The slope, constant and R^2 for a linear fit to data for a) the TA:S; b) DIC:NO_3 and c) CO_2:T relationship in each region

Region	TA:S Slope	TA:S c	TA:S r^2	DIC:NO_3 Slope	DIC:NO_3 c	DIC:NO_3 r^2	CO_2:T Slope	CO_2:T c	CO_2:T r^2
1	33.8	1123	0.48	9.38	2072	0.5	-6.1	454	0.05
2	-15.7	2858	0.09	2.89	2111	0.28	9.6	302	0.27
3	-6.5	2553	0.04	1.99	2093	0.39	13.9	190	0.5
4	16.9	1735	0.25	3.76	2099	0.27	1.2	367	0.01
5	20.5	1599	0.35	5.25	2076	0.31	-0.1	397	0.01
6	-5.4	2475	0.03	11.54	2056	0.75	-33.3	759	0.48
7	4.5	2166	0.02	6.38	2076	0.71	3.3	348	0.03
8	47.3	658	0.37	6.01	2081	0.85	-2.6	413	0.07
9	29.5	1278	0.78	8.17	2061	0.98	-13.5	528	0.35
PAP	2.49	2251	0.02	7.11	2063	0.91	-6.5	444	0.69

The Celtic Sea receives freshwater from rivers with both high TA (e.g. the Rivers Barrow, Nore and Suir into Waterford Harbour) and low TA (e.g. the River Lee in Cork Harbour), depending of the presence or lack of calcareous riverbeds, although the effect of this will be seen nearer the coast (McGrath et al., 2016). Region 6 (Minches) shows especially low TA values which may be due to dilution from the low TA and low nutrient rivers around Scotland. Despite the high alkalinity of the river Liffey this river has a low discharge (McGrath et al. 2016) and we do not see a negative relationship between TA:S in the Irish Sea (region 5) where the TA:S relationship is positive.

A large component of the apparent noise in Figure 7 is from the large variation in alkalinity values in the southern North Sea (region 2). Table 2 suggests a negative TA:S correlation which may be due to high TA from riverine input influencing this shallow region. Alkalinity is also influenced by the oxidation of organic material in marine sediments, leading to an increase in alkalinity, CO_2 and phosphate (Froelich et al., 1979); this may be important in the shallower regions around the shelf (eg: the southern North Sea region 2).

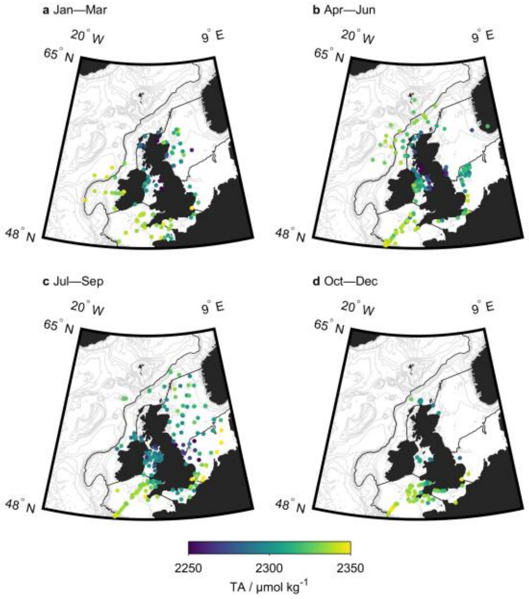


Figure 6: Seasonal SSB maps with winter data (Jan-Mar), spring (Apr-Jun), summer (Jul-Sep) and autumn (Oct-Dec) for Total alkalinity (TA) measurements

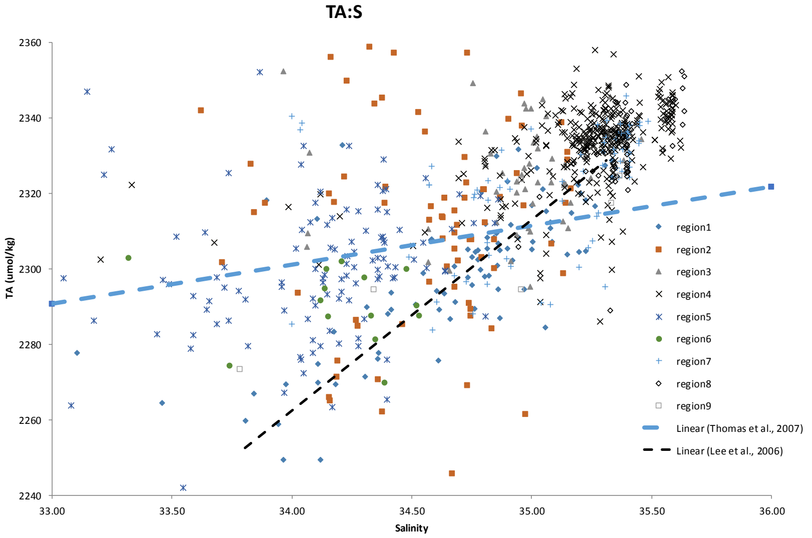


Figure 7: Regional variation in Total alkalinity (TA) against salinity relationship. The linear relationships derived for the North Sea (Thomas et al., 2007) and the North Atlantic (Lee et al., 2006) are shown (blue and black dashed lines respectively).

Dissolved Inorganic Carbon

Surface maps of SSB sampled DIC (Figure 8) show there is a characteristic seasonal pattern of DIC distribution, which shows a close relationship to nutrients as both increase in winter due to remineralisation and convective mixing of colder, DIC and nutrient rich waters towards the surface (Kortzinger et al., 2008). Classically phytoplankton assimilate DIC and nutrients during photosynthesis in spring, producing organic matter; this ‘spring bloom’ results in a decrease in DIC (and nutrients).

Additionally, however DIC distribution is influenced by air sea CO_2 exchange and dissolution of calcium carbonate (Lee et al., 2000). From the seasonal maps a decrease in DIC and nitrate is seen in the spring and summer in most regions. DIC remains relatively high in the Celtic Sea (region 4) in spring, even when nitrate is depleted. The high DIC in the Celtic Sea (region 4) could be due to the high DIC source in Irish rivers from the dissolution of limestone bedrock (McGrath et al., 2016) along with a high source of DIC from offshore waters of the eastern North Atlantic, carried with the predominantly northward flow into the Irish Sea.

From the average (and standard deviation), for each variable and each region (Table 1) it is clear that the highest DIC (and nitrate concentrations) are seen in the winter with a significant decrease in summer and this is true for all regions aside from Region 7 (the continental shelf). Figure 8 also shows that DIC concentrations remain relatively high on the continental shelf (region 7) in spring (as was seen with nitrate in this region).

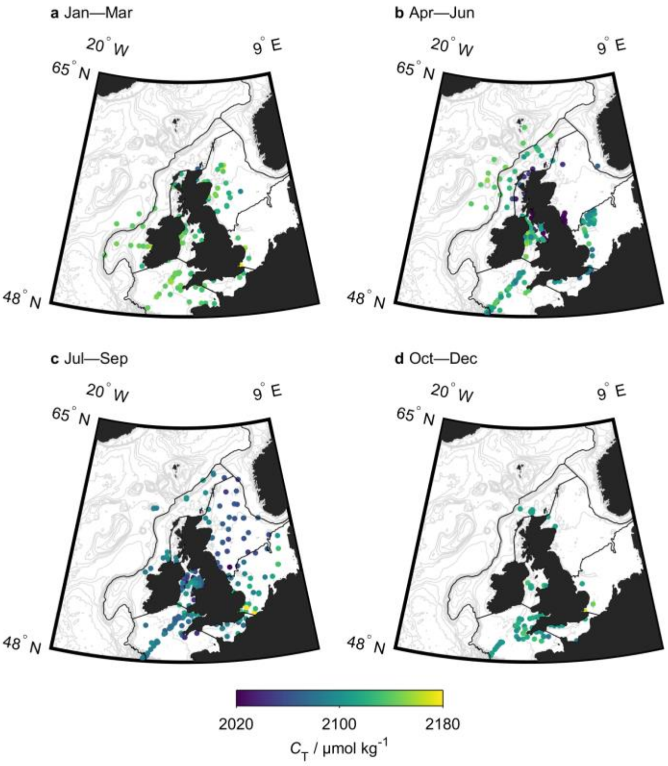


Figure 8: Seasonal SSB maps with winter data (Jan-Mar), spring (Apr-Jun), summer (Jul-Sep) and autumn (Oct-Dec) for Dissolved Inorganic Carbon (DIC).

Productivity can be calculated from the depletion in DIC or nitrate (Frigstad et al., 2015 and references therein) and productivity calculated this way relies on a constant Redfield C:N ratio (Redfield et al., 1963) of 6.6. Data from the present study suggest that the C:N relationship varies from 3-9 around the NW European Shelf (see figure 9) which will have implications for calculations of productivity.

The slope of DIC:NO_3 (see Table 3) suggests possible carbon overconsumption in the Northern North Sea (region 1 where the slope of the line is 9.4) and in the Minches (region 6 where the slope of the line is 11.5). However, for region 6 (the Minches) DIC values are lower that than the Redfield line at very low nitrate concentrations (as seen in Figure 9). This contrasts with the Southern North Sea (region 2) where DIC remains high when nitrate is depleted resulting in a high C:N at very low nitrate concentrations (although not reflected in the whole year C:N reported in Table 2). Denitrification is significant in the North Sea (Hydes et al, 1999) and this could contribute to the relatively low nitrate values seen in Region 2 (southern North Sea).

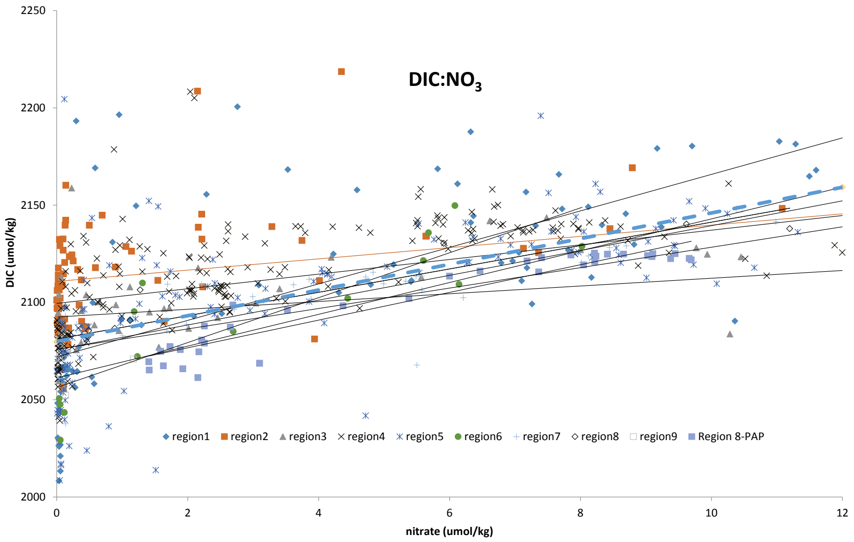


Figure 9: Data from the SSB surveys showing the relationship between DIC and nitrate and the (dashed) 6.6 Redfield et al. (1963) C:N line.

The summary diagram in Figure 10 shows regions 1 to 8 (9 is not included as there is insufficient seasonal data). Large seasonal changes in both TA and DIC are seen in the North Sea, for example in the northern North Sea (region 1), there is a steeper slope in the relationship during winter compared with summer possibly due to sediment or riverine influences in this region. This contrasts with regions 4 (Celtic Sea) and 8 (Atlantic western approaches off shelf), where there is little variability in TA. In these regions, the highest DIC values are clearly in autumn and winter (due to mixing) with lower values in spring and summer (due to productivity).

In region 7 (continental shelf) there are two clusters in the alkalinity data; the lower values are predominantly, although not exclusively, to the north of Scotland with higher values seen around the Outer Hebrides (using supplementary data here from DY017). This grouping of values is also reflected in the salinity data (not shown), with the cluster of low TA data corresponding to low salinity data to the North of Scotland. Region 2 (southern North Sea) and region 3 (Eastern Channel) show larger variability in TA as these are shallow areas and influenced by riverine input.

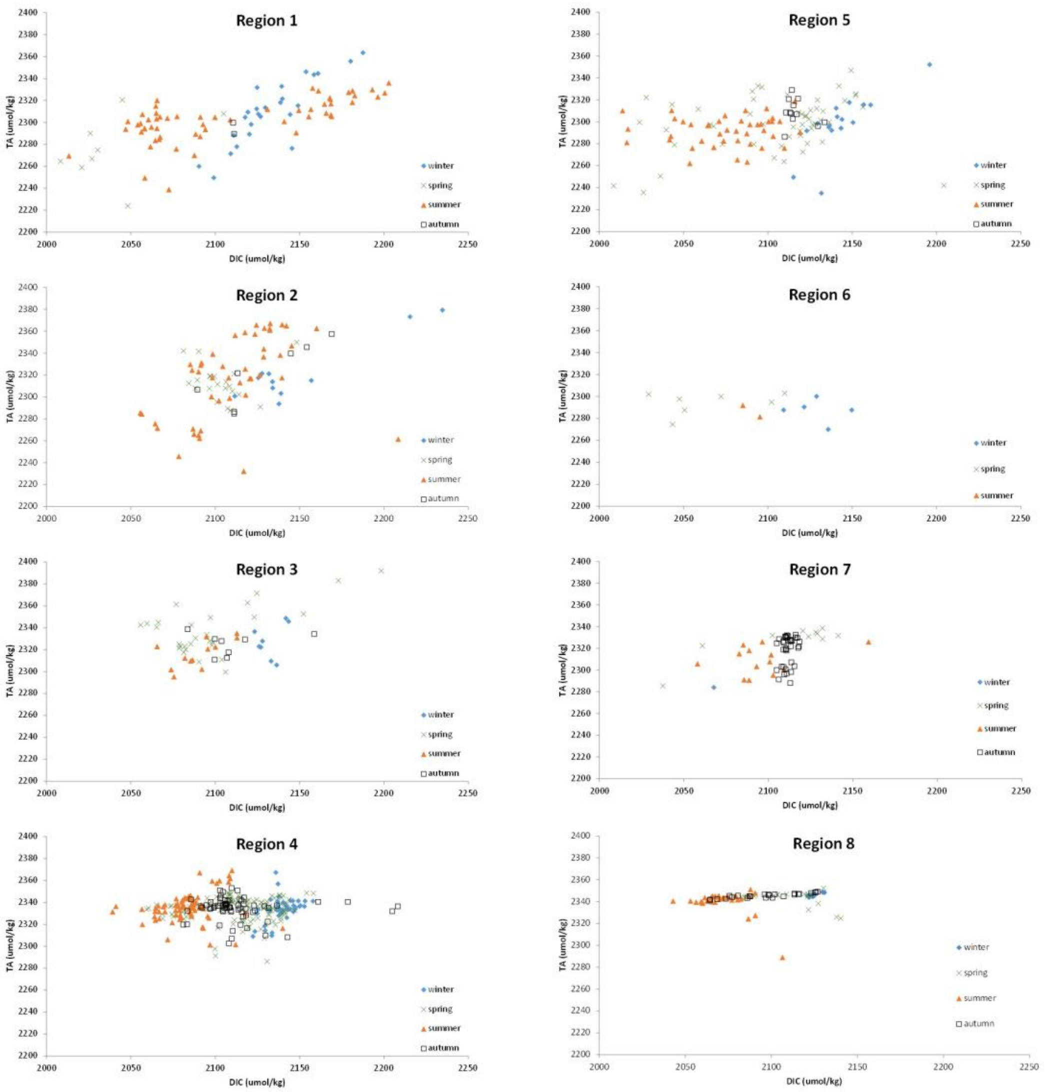


Figure 10: Seasonal relationship between DIC and TA for regions 1 (Northern North Sea), 2 (Southern North Sea), 3 (Eastern Channel), 4 (Celtic Sea), 5 (Irish Sea), 6 (Minches), 7 (on shelf Atlantic approaches) and 8 (off-shelf Atlantic approaches)

Carbon Dioxide

The CO_2 results in Figure 11 include pCO_2 calculated from SSB bottle DIC and TA measurements and underway pCO_2 measurements and show a strong seasonal variation in pCO_2. The map in Figure 11 shows that in the North Sea (region 2) and in the English Channel (region 3) there is an increase in pCO_2 values from the winter to summer (also seen in Table 1). The largest seasonal variation in pCO_2 is seen in the North Sea with over ~ 90 µatm increase between the winter and summer (Table 1) in the average pCO_2.

The difference between the surface seawater and air CO_2 (along with the strength of the wind) drives the flux of CO_2 between the atmosphere and ocean. Concentrations above 400ppm, shown clearly in Figure 11, are above the atmospheric CO_2. Where the pCO_2 is higher than the atmospheric levels there is the potential for outgassing and these regions tend to be CO_2 source regions. The flux of CO_2 into the ocean increases due to productivity and decreases with temperature increases but the dominance of these processes varies with region (Jiang et al., 2013). Jiang et al., (2013) showed that the

English Channel was characterized as a CO_2 sink during the winter and spring months because of the low temperature and biological production but it was a CO_2 source during the summer and autumn due to the increasing temperature and the heterotrophic processes involving degradation of the organic matter. Our study suggests that the Eastern Channel (Region 3) is a potential source of CO_2 in the autumn when the pCO_2 is above the atmospheric levels. Frankignoulle et al., (1996) and Kitidis et al., (2012) also showed the autumn oversaturation of CO_2 in the English Channel.

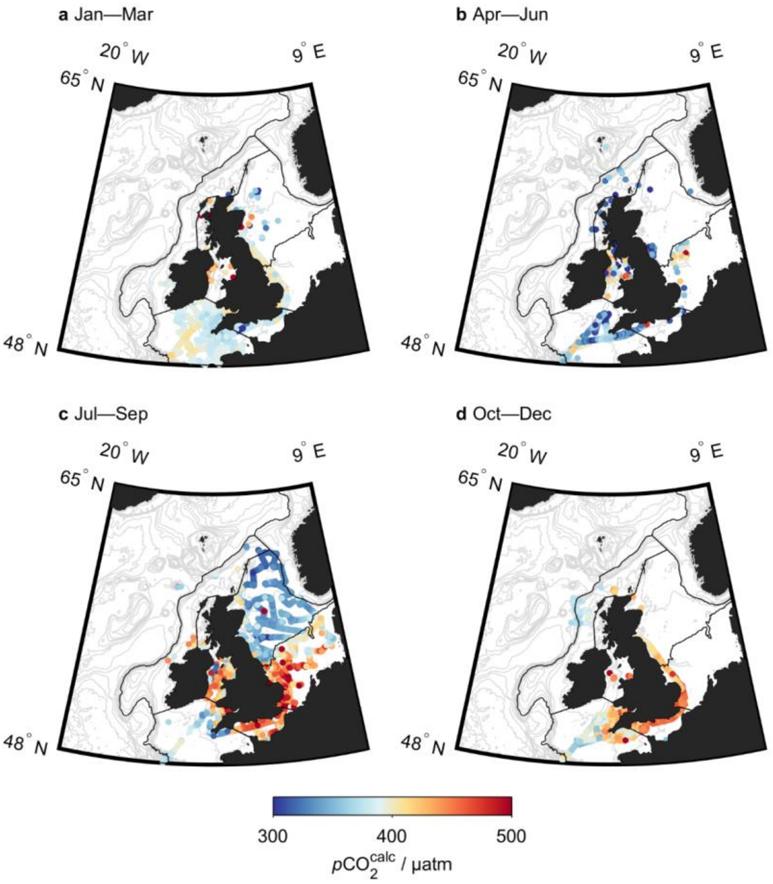


Figure 11: Seasonal SSB maps with winter data (Jan-Mar), spring (Apr-Jun), summer (Jul-Sep) and autumn (Oct-Dec) for pCO_2 calculated from bottle samples analysed for DIC/TA (using CO_2SYS) and measured pCO_2 from underway systems on the NERC and CEFAS vessels (2014-2015)

In contrast, regions 4 (Celtic Sea), 5 (Irish Sea) and 6 (Minches) show a decrease in pCO_2 between winter and summer of 3-50 µatm (Table 1) when these regions become CO_2 sinks. For example, in region 4 (Celtic Sea), pCO_2 decreases as temperature starts to increase in spring and summer due to the dominance of biological processes over physics at this time. Kitidis et al., (2012) also showed that the seasonal variations are dominated by biology rather than advection in the western English Channel.

In the wider sub-polar Atlantic, the seasonal cycle of CO_2 is dominated by the mixing of high carbon water from depth in the winter, so CO_2 is higher in the winter (Kortzinger et al., 2008). It decreases in the spring and summer due to photosynthesis and uptake of CO_2 by phytoplankton. This is the case for the off-shelf region in this study, region 8 (the Atlantic north-west approaches). Here there is a decrease in CO_2 as the temperature increases, from the mixing of deeper high CO_2 waters brought to the surface in winter to the decrease due to the CO_2 uptake during the spring bloom. This is also seen at the PAP-SO site throughout the year and, although the slope is not as steep as in region 8 (Atlantic), the R^2 is more significant (R^2=0.69, see Table 2).

In our study the southern North Sea (Region 2) and region 3 (Eastern Channel) are relatively shallow so there is little mixing of high CO_2 water to the surface in winter, although both show a large seasonal range (Table 1). The well-mixed, shallower regions (eg: the southern North Sea) show the dominance of temperature control on CO_2. The varying relationship between pCO_2 and temperature over the annual cycle was first recognised for sub-tropical regions such as the Sargasso Sea (Bates et al., 1998) and the European Station for Time series in the ocean (ESTOC) Gonzalez-Davillia et al, 2003). At both of these sub-tropical sites there is a positive relationship between pCO_2 and temperature throughout the year. In autumn, there is a decrease in pCO_2 as temperature decreases due to cooling. However, the slope of this relationship is shallower for the spring-summer period. At this time, the CO_2 increase per degree of temperature rise is lower than in the autumn, as CO_2 is being decreased by phytoplankton productivity. There is an opposite curve relationship in winter as CO_2 increases (with a decrease in temperature) due to mixing. There is also a negative slope between CO_2 and temperature (Table 2) in region 6 (Minches & west Scotland) although the relationship is not significant as there are still very few data points in this region. Of the regions considered, pCO_2 is lowest at the PAP-SO (in region 8); where, throughout the year, there is a net uptake of CO_2. (Kortzinger et al., 2008).

CO_2 in the Western shelf (region 4) is close to the atmospheric CO_2, as shown by McGrath et al., (2016). Figure 12 shows underway pCO_2 data from region 4 (the Celtic Sea) and the relevant process on a seasonal cycle. This illustrates that a straightforward linear relationship cannot be assumed between CO_2 and temperature on the shelf as there are many processes involved. For example, the underway CO_2 data collected in the Celtic Sea shows the large decrease in pCO_2 due to the spring bloom and phytoplankton growth on the April and May cruises (Figure 12).

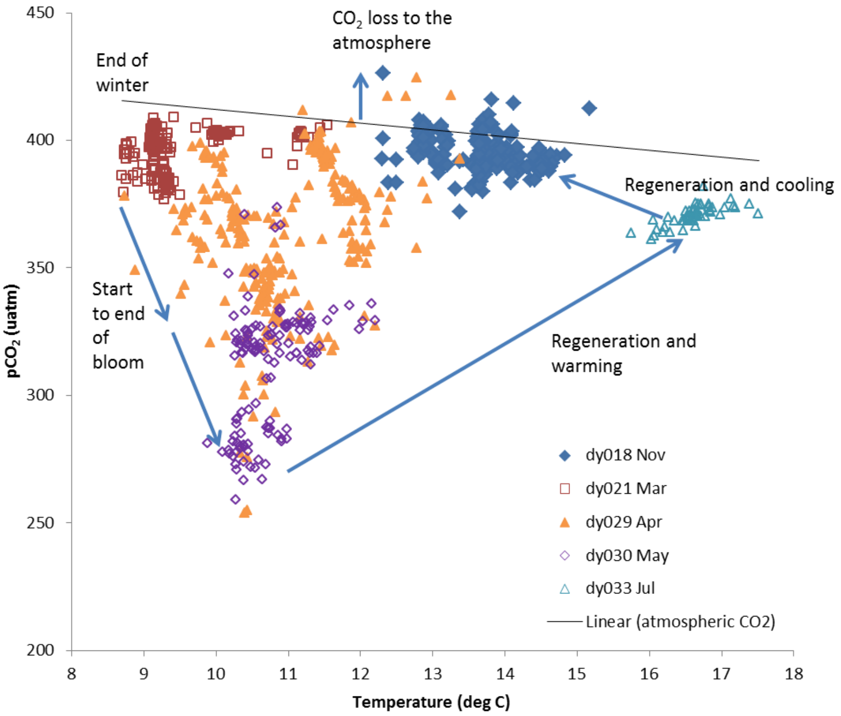


Figure 12: Seasonal variation in the underway CO_2 measurements in relation to temperature for the Celtic sea, showing 5 cruises from 2014/2015 and dominant processes (as shown by the labelled arrows)

Calculated pH

The calculated pH maps in Figure 13 show a similar but inverse distribution to pCO_2 due to an increase in H^+ ions (decreased pH) when CO_2 dissolves in seawater. In the northern North Sea (region 1) pH is high in the winter (8.23 ±0.2) when CO_2 is low (Table 1 and Figure 11) whereas CO_2 is high in the Irish Sea (region 5) in winter and this is reflected by a lower pH. Table 1 shows a winter to summer decrease in pH in the North Sea (region 1 and 2) and region 3 (the Eastern Channel). This is particularly significant in the Eastern Channel (region 3) where there is a seasonal decrease in pH from 8.14 (±0.03) in winter to 8.09 (±0.02) in summer. This reflects the increase in CO_2 in summer, due to the influence of temperature and the remineralisation of organic matter in these shallower regions.

The opposite seasonal changes are seen in the Western Channel (region 4), Irish Sea (region 5) and the Minches (region 6) where there is low winter pH and an increase in pH in summer (Table 1) due to the winter to summer decrease in CO_2 in these productive regions. The Atlantic Northwest approaches (region 8) is a region of deep winter mixing when DIC is replenished in the winter and there is a seasonal increase in pH from winter values of 8.06 (±0.01) to summer values of 8.13 (±0.1) as pCO_2 decreases. A recent synthesis report (Ostle et al., 2016) combined all UK carbonate data collected to date and also found large seasonal variations in pH around the NW European Shelf, of up to 0.2 units in some years and regions such as the Stonehaven site off north east Scotland.

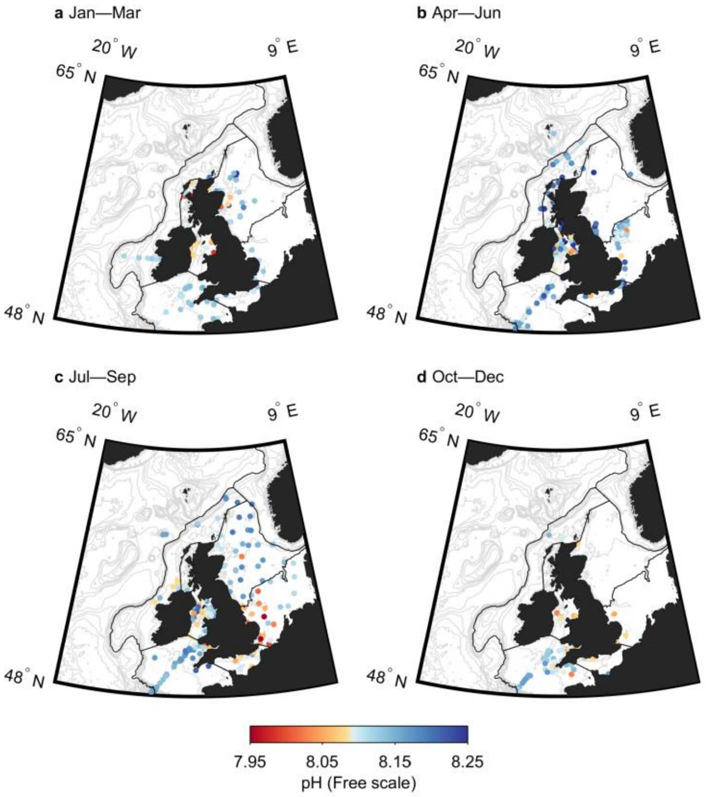


Figure 13: Seasonal SSB maps with winter data (Jan-Mar), spring (Apr-Jun), summer (Jul-Sep) and autumn (Oct-Dec) for pH calculated from bottle samples analysed for DIC/TA (using CO_2SYS)

Conclusions and further work

From data collected in 2014-2015 we divided the shelf into 9 ecohydrodynamic regions, described the seasonal and regional variations in nutrients and carbonate parameters around the whole shelf and made comparisons to the wider Atlantic. A comparison of winter and summer averages for all measured variables give an indication of seasonal variations in all regions and the largest seasonal changes in temperature were seen in the shallower southern North Sea (region 2) and western English Channel (region 3) areas. There was little seasonal variability in salinity although the lowest values were seen in the Irish Sea (region 5), which is classed as a region of freshwater influence.

Nutrient concentrations were highest offshore, especially in the Atlantic approaches. The expected pattern of seasonal variability was of high DIC and nutrients in winter, with a decrease in spring due to productivity, as was generally seen around the shelf in this study. Seasonal changes in nutrients can be used as an indication of potential productivity and the largest seasonal changes in nutrients were seen in the Irish Sea (region 5) due to freshwater inputs. Generally, nutrients were depleted in the spring around the shelf although they were not fully depleted in spring to the north of Scotland.

Around the NW European Shelf the dissolved inorganic carbon data broadly followed the nitrate data with an increase in both during winter. We have shown variations in the C:N ratio around the NW European shelf, this will have implications for the calculation of productivity. Variability in C:N is pronounced at very low nitrate concentrations when carbon stays well above the expected ratio in the southern North Sea (region 2) possibly due to denitrification in this region.

There is a large natural variation in both pH and CO_2 between seasons and regions, for example high pCO2 in winter compared with summer (with associated low pH) was seen in regions 4 (Celtic Sea), 5 (Irish Sea) and 6 (Minches). The opposite was seen in regions 1 and 2 (North Sea) and region 3 (Western Channel) where there was a dominant temperature control on CO_2 with a winter to summer increase in pCO_2 (and associated pH decrease), possibly influenced too by remineralisation of organic matter in these shallower regions. The largest seasonal changes in CO_2 were seen in the North Sea, with an increase from winter to summer of over 90µatm.

The highest alkalinity measurements generally corresponded to the higher salinity waters in the Atlantic (region 8) although there is less seasonal variability in alkalinity offshore where there is a positive correlation between TA and salinity. The largest seasonal variability in alkalinity was seen in the North Sea (regions 1 and 2), potentially from increased riverine input as the lower salinity waters have high alkalinity for example in the Southern North Sea (region 2).

Where underway pCO_2 measurements are available there is improved seasonal coverage over what is possible with bottle sampling alone and we have closely followed the relationship between pCO_2 and temperature plus the effects of processes such as remineralisation and photosynthesis on this relationship.

Once we have a longer time series, we could use this data set to quantify trends in pH and CO_2 (see Ostle et al., 2016), so we recommend that the sampling be continued if we are to comment on year-to-year variability and elucidate trends in the data. Generally the winter time period and regions 9 (Norwegian Trench) and 6 (the Minches) are still under sampled and this could be the focus for further sampling campaigns. The increased use of autonomous measurements on robust platforms (buoys, buoyancy gliders, autonomous surface vehicles, etc.) would help in this regard.

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Synthesis of results and general discussion

This thesis presents time-series measurements in the northeast Atlantic, including over 10 years of measurements from biogeochemical sensors at the PAP-SO, 8 years of SOO data and two years of shelf wide sampling. Ultimately the study attempts to collate the results obtained at the PAP-SO site and make comparisons with the wider Atlantic.

Discussion of the methodology

This synthesis includes a critical review of instrument choice and the methods used to collect the biogeochemical data (described in **Chapter 1**; Hartman et al., 2012). The review considers both the accuracy and precision plus the reliability of instruments over time. The robustness of the whole mooring system is also considered.

Access to remote sites such as the PAP-SO is limited by the availability of time on the research vessels needed for service visits. To understand how the biogeochemistry varies over the year between service visits reliable sensors must be selected to make continuous measurements. There is always a compromise between power requirements and the need for high temporal resolution data when choosing the sensors to use at the PAP-SO. Power requirements determine the frequency of measurements that can be made. Solid state sensors, with minimal moving parts, reduce both the power requirements and complexity.

Temperature and salinity are measured at the PAP-SO using Seabird Microcats. These sensors are reliable and the data compare favourably with Argo float data (as shown in **Chapter 2**, Hartman et al., 2010). Until 2009 these sensors were used on a string down to 1000m. However since 2010 the UK-Met Office mooring has been in place so the sensors are now at 1m, 30m and on the sediment traps at 3000m. It should be pointed out that the early PAP-SO mooring design (2003-2006) meant that the sensors were frequently knocked down to deeper depths. The average depth of the sensor frame was 30m but the sensor could experience from 20m to 225m depths. The sensors in use, depths and dates of use are detailed in Table 1 (which has been updated from **Chapter 1**).

The following sub-section shows the sensors that are currently available for use at the PAP-SO. The UK to Spain Ferry-Box included some of these sensors (such as temperature, salinity, oxygen and chlorophyll-fluorescence). In addition, there was an opportunity to take biogeochemical samples along the ferry route on a monthly basis. As this is not yet possible, at the relatively remote PAP-SO, biogeochemical sensors have been introduced to measure nutrients and carbonate variables and samples are taken each year for validation. The data quality obtainable has been considered relative to the processes that we aim to measure.

Dissolved oxygen

Some of the Seabird microcat instruments also have the capability to measure dissolved oxygen (DO). These Seabird instruments have a dissolved oxygen resolution of 0.2µM and offer high accuracy (3uM, 2%). Since 2010 dissolved oxygen has also been measured using Aanderra optodes (on a SeaGuard) which make measurements based on a principle called dynamic luminescence quenching (see Hydes et al., 2009 for details of the optode, also used on the UK to Spain Ferry-Box route reported in **Chapter 5**, Hartman et al., 2014). The optode resolution is lower than the Seabird microcat, at 1 µM and accuracy is <8µM (5%) but the data quality for both instruments is sufficient for detecting bloom timing. Calculation of oxygen saturation, as offered by the optodes for example, can be used as an indication of the spring bloom. Oversaturation of oxygen (~110%) can be encountered in surface waters during harmful algal blooms (as was shown from the UK to Spain Ferry-Box data, Hartman et al., 2014a).

Chlorophyll-fluorescence

As can be seen in Table 1 a number of systems for measurement of chlorophyll-fluorescence have been used at the PAP-SO site (Wetlabs and Turner fluorometers are currently in use and these replaced the HobiLabs HS2). These instruments are all capable of measuring the optical properties of seawater and *in situ* fluorescence measurements provide a semi-quantitative assessment of chlorophyll-*a*. Using fluorescence data to predict chlorophyll concentration and primary production remains a challenge because of physiological and community structure variability in phytoplankton (Suggett et al., 2004). However a similar problem is experienced when interpreting remote sensing data and the link between fluorescence and chlorophyll concentration, biomass, or productivity is therefore semi-quantitative. In addition, atmospheric effects, surface films, turbidity, and variable depth all add significantly to the error in satellite chlorophyll estimates (Mowlem et al., 2008).

Nitrate

The subsurface inorganic nitrate concentrations at the PAP-SO have been measured using both wet chemistry and ultra-violet (UV) detection. Nitrate concentrations were initially measured using wet chemical instruments known as the NAS (NAS-3X, EnviroTech LLC) analysers. As the NAS is reagent based it produces higher accuracy data (e.g. 0.1µM nitrate resolution) than UV detection, and the data are validated with on-board standards. However the NAS has a maximum deployment duration of only about six months due to reagent stability. Since 2010 nitrate concentrations at the PAP-SO have been measured by using ultraviolet (UV) detection. Two different UV spectrophotometric sensors are currently in use, both available from Satlantic (the SUNA and ISUS instruments). UV detectors are relatively insensitive (~0.5µM, or 20% of open ocean maximum concentrations) but offer high temporal resolution and detection without the need for reagents.

Carbon dioxide

Currently the only carbon variables that can be easily measured with sensors are pCO_2 and pH. pCO_2 in the ocean depends on the dissociation constants (see introduction Figure 3) which in turn depend on the temperature, salinity and pressure so it is very important to have accurate measurements of these. Until 2005 a wet chemistry sensor was used to measure seawater CO_2; a SAMI pCO_2 (Sunburst Sensors). This chemical based instrument used the colorimetric detection of a pH induced colour change of an indicator solution (meta cresol blue) and was equilibrated with ambient seawater pCO_2 through a gas-permeable membrane. Chemical sensors may drift up to 1µatm over 6 months although this is corrected for by using on-board standards.

The pCO_2 in the seawater at the PAP-SO site is currently measured directly using nondispersive infrared absorption (NDIR) spectrometry using a sensor from Pro-Oceanus. Pro-C sensors are based on the equilibration of the CO_2 gas dissolved in water through a gas permeable membrane. In the inner air-filled compartment of the analyser the mole fraction of the CO_2 concentration in air is measured optically. The NDIR sensors have the potential for an increased measurement frequency and the manufacturers claim that <1 µatm resolution of CO_2 is achievable (*in situ* studies suggest that 5 µatm resolution is more realistic, Jiang et al., 2014). However NDIR sensor drift is potentially large and frequent auto-zero measurements are taken throughout the deployment to correct for any drift (Jiang et al., 2014). The response time of the instrument is generally in the order of 2.5 minutes although this time may increase following zero readings and at different temperatures.

Table 1: shows sensors deployed at the PAP-SO (updated 2016 from Chapter 1, Hartman et al., 2012).

Depth	Parameters/variables	Sensor	Frequency
Atmospheric (UK Meteorological Office buoy) from 2010			
3.5 m above surface	Wind speed and direction	Gill acoustic sensor and revolution magnetic compass	Hourly (10 min mean)
2 m above surface	Relative humidity	Rotronic Hygroclip R/S sensor	Hourly (instantaneous)
1.5 m above surface	Air temperature	Electrical resistance thermometer (ERT)	Hourly (10 s mean)
1.5 m above surface	Irradiance	Radiometer (Satlantic OCR, 7-channel with standard wavelengths) (from 2010)	1 h
1 m (subsurface)	sea temperature	Electrical resistance thermometer (ERT)	Hourly (10 s mean)
1 m (subsurface)	CO_2 (IR absorbance after equilibration)	PRO-OCEANUS (from 2013)	6 h
1 m (subsurface)	pH	Satlantic SeaFET pH (from 2014); Sensor lab from 2014	2 h
1.75 m above surface	Atmospheric pressure	Druck RPT350 pressure sensor	Hourly (20 s mean)
Surface	Significant wave height and period	Datawell heave sensor; 17.5 min average	Hourly (over 17.5 min)
Surface ocean (fixed frame depth of 25-30m from 2007, Met office buoy from 2007)			
25-30m	CTD	Seabird MicroCAT	10 min
25-30m	CTD + dissolved oxygen	Seabird MicroCAT IDO	30 min
25-30m	Nitrate and nitrite (chemical)	NAS (2002-2010)	4 h
25-30m	Nitrate and nitrite (UV absorption)	Satlantic ISUS and SUNA (from 2010)	1 h
25-30m	Chlorophyll	HobiLab HS2 (2002-2005), WETlabs (FLNTUSB) from 2007, Cyclops (from 2010)	6 h, 1 h
25-30m	Dissolved oxygen	Aanderaa optode on Seaguard (from 2010)	1 h
25-30m	Currents	DCS (from 2010)	1 h
25-30m	CO_2 (colorimetric)	SAMI-CO2 (2002-2005)	12 h
25-30m	CO_2 (IR absorbance after equilibration)	PRO-OCEANUS (from 2010)	12 h
25-30m	Dissolved gases	PRO-OCEANUS gas tension device (from 2010)	12 h
25-30m	Radiance Lu upwelling radiance	Radiometer (Satlantic OCR, 7-channel with standard wavelengths)	1 h
25-30m	Irradiance Ed, Eu downwelling	Radiometer (Satlantic OCR as above)	1 h
25-30m	Irradiance Es total irradiance	Radiometer (Satlantic OCR as above)	1 h
25-30m	pH	Satlantic SeaFET pH (from 2014)	30 min
25-30m	Phosphate	WETLabs CYCL-P Phosphate Analyser (from 2016)	8 h
25-30m	Zooplankton sampler	McLane zooplankton sampler	Every 2 d
Deep ocean (subsurface mooring)			
25–1000 m	CTD	Seabird MicroCAT (2002-2009)	10 min
3000 m	Particle flux (sediment traps)	McLane sediment trap	Variable (d)
3000 m	Currents	Aanderaa RCM9	4 h
3000 m	Particle flux (sediment traps)	McLane sediment trap	Variable (d)
100 m above seabed	Particle flux (sediment traps)	McLane sediment trap	Variable (d)
100 m above seabed	Currents	Aanderaa RCM9	4 h
Seafloor (lander)			
Seafloor (4800 m)	Time-lapse photos	Imenco AS (SDS 12100) stills camera	8 h

Measurements of pH

SeaFET sensors (from Satlantic) have been used at the PAP-SO to directly measure pH since 2014. The SeaFET instrument is a potentiometric system based on ion-sensitive field-effect transistors (ISFET; Martz et al., 2010). SeaFETs have both internal and external chloride-sensitive electrodes. The internal one uses an internal gel as reference while the external one uses the ambient seawater. In order to obtain high quality data from the sensors accurate temperature and salinity data are required for processing raw sensor data. In addition a spectrophotometric Sensorlab pH system has recently been introduced, which uses pH-sensitive indicator dye. M-cresol purple dye is usually the choice for spectrophotometric measurements of pH (Byrne and Breland, 1989). This method of pH measurement should not be influenced by drift, and it is highly accurate and precise (0.003 pH). Recent comparisons between the SeaFET and spectrophotometric measurements in the Arctic Ocean yielded similar pH measurements between the two methods, within 0.01 pH units (Rérolle et al., 2016).

Bio-fouling

The subsurface ocean is biologically active and surface measurements are vulnerable to bio fouling, especially the shallower measurements at 1m. Bio-fouling is less of an issue for the sensors at 30m depth. However various methods are employed to deter fouling at the PAP-SO as it is in such a productive region. Bio-fouling protection at the PAP-SO includes copper guards (on the SeaFET pH and ISUS nitrate sensors), brushes (on the SUNA nitrate sensor and Turner fluorometer), shutters (on the HS2 and Satlantic irradiance sensors) or wipers (on the Wetlab FLNTUSB sensor). The sensors are replaced at each service visit (from 1 to 2 times a year). On SOOs it is possible to replace or clean the sensors more frequently. The sensors on the UK to Spain Ferry-Box were cleaned weekly for example and compared with samples taken on a monthly basis (Jiang et al., 2013).

Sensor data validation

All of the sensors are initially calibrated by the manufacturers. However sensor output can drift, even when sensors are in storage so it is important to validate the sensor output pre and post deployment. There are numerous methods for performing pre and post deployment calibrations both ashore and at sea. The procedures used currently at the PAP-SO have made a substantial contribution to the FixO3 best practices report (Coppola et al., 2016). Some sensors cannot go onto the frame that supports sampling bottles (known as the CTD frame as it also holds the on-board conductivity, temperature and depth sensors). For example the sensors may only work in shallow water or they may use wet chemistry and have a low sampling frequency. Where a sensor can be placed onto the CTD frame at sea it is profiled and data are extracted at the same depth as the bottle samples are taken. Then a simple linear correction is done based on the calibration points. The salinity data for example are validated pre and post cruise at the PAP-SO, profiling the microcats on a CTD frame. The salinity data obtained is then compared with the salinity measured on the CTD (which in turn has been calibrated using bottle samples, analysed using a salinometer on-board the ship). On the UK to Spain SOO *in situ* sampling on a monthly basis was used to validate the sensor measurements.

Dissolved oxygen

Validation of oxygen sensors is done on a CTD cast at the PAP-SO pre and post deployment. The sensor data are compared against bottle samples, which are fixed and titrated on-board using a modified Winkler technique (Dickson, 1994; Holley and Hydes, 2004). The Ferry-Box oxygen sensors were validated in a similar way using Winkler titration on-board the ferry between the UK and Spain. Additional conversions must also be done to take into account temperature, salinity and pressure effects.

Chlorophyll-fluorescence

At the PAP-SO the accuracy of the fluorometer is improved by validating the calibration *in situ*. Petihakis et al., (2007) also minimise the error by performing site-specific calibrations using cultures of seawater collected from the deployment site. Without this the manufacturer's factory calibrations can produce an order of magnitude error in the results. These calibrations may only hold as long as the phytoplankton community structure remains constant which is unlikely to be true over extended time periods, such as the year-long deployment at the PAP-SO. At the PAP-SO the fluorometers are attached onto the CTD frame pre and post deployment and a comparison is made with extracted chlorophyll at the depths of sampling within the top 200m (due to depth requirements of the sensor). Good agreement (within 0.08µg/L) has been shown in repeated *in situ* calibrations at the PAP-SO for the same instrument (Mowlem et al., 2008) using pre and post deployments of a fluorometer on a CTD frame. The fluorescence sensors were also validated using *in situ* sampling along the route of the UK to Spain ferry, on a monthly basis.

Nitrate

Both the UV and wet chemistry based methods of detecting nitrate at the PAP-SO require validation of the calibration to improve accuracy. This is done at the pre and post deployment. In each case a standard curve can be produced by introducing a range of known concentrations of nitrate in seawater to the sensor inlets. Additionally the UV based sensors can also be attached to the CTD rosette to get a profile. At each depth a bottle sample is obtained and inorganic nutrients are analysed ashore using an auto-analyser. A linear comparison of the discrete samples and sensor data extracted from the profiling instruments is then used for sensor validation. The wet chemistry instruments for the measurement of nitrate cannot be attached to a CTD frame for the calibration as it is difficult to determine when the sample will be taken. In this case the 30m output is compared pre and post deployment with the 30m discrete nutrient sample concentration. Accuracy of the chemical based nitrate sensor can also be assured through the use of on-board standards throughout the deployment.

Carbon dioxide

The NDIR CO_2 detection instruments are calibrated by the manufacturers against known CO_2 concentration gas (from the National Oceanic and Atmospheric Administration, NOAA). However the manufacturers calibration often by-passes the membrane so the instrument has to be validated *in situ*, both pre and post deployment. At the PAP-SO validation of the pCO_2 measurements is done through a comparison with samples taken at the depth of the sensor deployment and analysed for DIC and TA. CO_2 is then calculated from the DIC and TA results using the CO_2SYS toolbox (Lewis et al., 1998).

Measurements of pH

Wet chemical analysers such as the Sensorlab pH instrument are not recommended for profiling as it is difficult to determine at what depth the samples are taken. These instruments cannot be attached to the CTD frame for pre and post deployment calibration. Likewise the PAP-SO SeaFETs cannot be put onto the CTD frame, as their depth rating is only 50m. Therefore the pH sensors are validated in the laboratory using Certified Reference Material (CRMs, available from Andrew Dickson at Scripps). For the SeaFETS the CRM is introduced directly to the electrodes and (along with an accurate measurement of temperature) the pH of the CRM solution is determined using the CO_2SYS toolbox (Lewis et al., 1998). The PAP-SO methods have contributed to the FixO3 Best Practice document (Coppola et al., 2016). For the SeaFET a comparison of the external and internal reference electrode is used to track instrument drift, possible fouling, and malfunction of the electrodes throughout deployment. A small difference between the internal and external junction will indicate fouling whereas larger offsets may indicate that the calibration needs to be redone.

Discrete samples

Ideally frequent discrete samples should be taken alongside the sensor measurements throughout a deployment as was the case in validating the UK to Spain Ferry-Box measurements. However for the PAP-SO this would require an auto-sampler. As these are not yet fully developed bottle samples are taken on ship-based service visits both pre and post deployment. Discrete samples are taken for the analysis of dissolved oxygen and inorganic nutrients as described. Samples for TA and DIC are also collected (into 250ml Duran glass bottles) and these samples are preserved with 100ul of a saturated mercuric chloride solution for analysis ashore. DIC and TA are determined using a Vindta (Versatile INstrument for the Determination of Titration Alkalinity; Mintrop, 2010; Hartman et al., 2011). The VINDTA instrument uses a coulometric titration method (based on Johnson et al., 1987) for DIC and an open-cell potentiometric titration (Haraldsson et al., 1997) for TA. The precision from replicate analyses for both TA and DIC is ±1.5 µmol kg^{-1}.

pH and CO_2 are calculated using the CO_2SYS toolbox. There are potential errors associated with the CO_2SYS calculations, propagating both from measurement errors and the errors in the selected dissociation constants (Millero, 2007; Hydes et al., 2010; Ribas- Ribas et al., 2014). These errors can be difficult to fully assess but the DIC/TA pair is currently the most commonly measured of the carbon parameters largely due to the CRM program for ocean CO_2 measurements (Dickson et al., 2003; Dickson et al., 2007) which allows assessment of the accuracy for DIC and TA measurements.

There is a seasonal bias in bottle sampling at the PAP-SO, as sampling is restricted to periods of mooring turnaround (usually spring and summer). Seasonal bias should not be a problem for sensor validation as the relationship between bottle sample data and the sensor readings will hold throughout the year for many of the biogeochemical measurements. However sensors could drift within the year in which case it would be useful to have more frequent bottle samples for reference.

Validation of measurements between different platforms and depths

A further validation of the sensor data from the mooring can be done using ships of opportunity as a platform for sampling. The nitrate data in **Chapter 2** (Hartman et al., 2010) was validated using nitrate samples taken from the UK to Caribbean SOO route that passes the PAP-SO site each month. In **Chapter 3** (Hartman et al., 2015) the sensor CO_2 output is also compared directly with data from the UK to Caribbean SOO route. In 2012 this SOO was used as a sampling platform for DIC and TA samples and provides monthly crossovers between bottle sampling and sensor measurements. Figure 1 shows all of these sampling frequencies relative to weekly averages of calculated DIC from the PAP-SO mooring data (calculated using the CO_2SYS toolbox, inputting monthly estimates of CO_2 from the sensor output and total alkalinity derived from salinity measurements using Lee et al., 2006).

The frequency of DIC ‘sampling’ at the PAP site is better than implied in Figure 1, as DIC is determined from the twice daily CO_2 measurements. This comparison shows that the calculated DIC from the PAP-SO are comparable to the bottle samples that were analysed ashore.

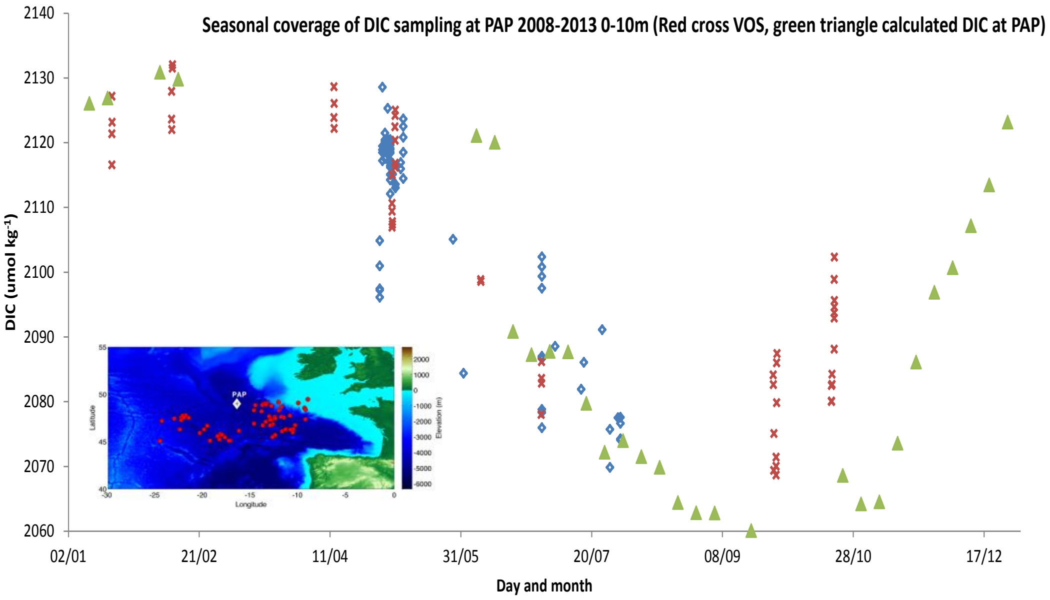

Figure 1: Annual cycle of DIC results at the PAP-SO from a) sampling at the PAP site (0-10m, shown in blue) from 2008-2013; b) from year round sampling from the UK-Caribbean voluntary observing ship (VOS) in 2012 (5m samples, shown in red) and c) DIC results calculated from 30m pCO_2 and TA (calculated from salinity sensor data) at the PAP-SO (shown in green triangles). The inset image shows the distribution of sampling sites on the SOO (in red) relative to the position of the PAP-SO site (white diamond).

A comparison of the 1m and 30m data could also be used to validate the data in the case of duplicate sensors. This is especially valid if the top 30m is well mixed, as was assumed for the PAP-SO by Körtzinger et al., (2008). However Microcat temperature data from the PAP-SO suggests that although the top 30m is well mixed in winter the 1m and 30m temperature readings start to deviate in the summer (as shown in Figure 2).

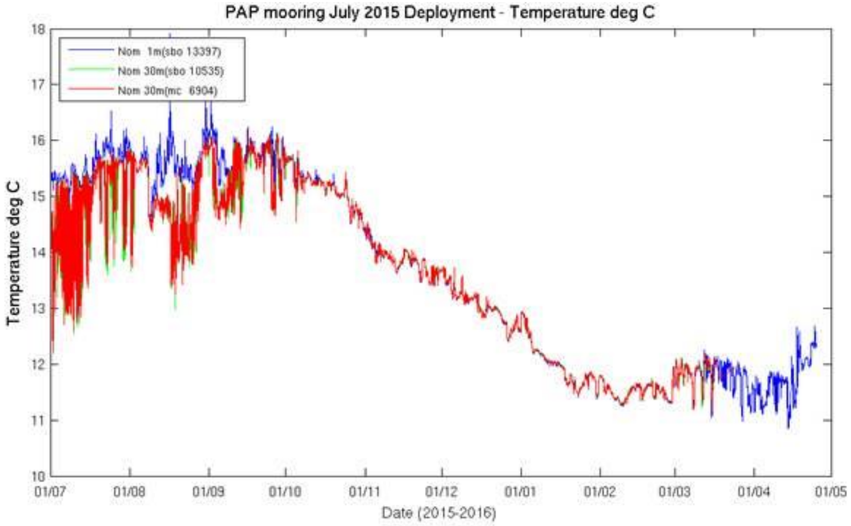

Figure 2: Microcat temperature data from the PAP-SO suggests that the top 30m is well mixed in winter but the 1m and 30m temperature readings start to deviate in August.

The output from all of the 30m sensors at the PAP-SO suggests large variability in measurements over the top 30m in the summer. The 30m data look ‘noisy’ as the sensors are frequently below the shallow summer mixed layer depth and therefore comparing the 1m and 30m readings as a method of validation should be used with care in the summer.

Variability in the top 30m of the water column can be also illustrated by looking at data from a bio-Argo float, for example float 0276 that is currently located near to the PAP-SO site (Figure 3). The annual cycle of nitrate data from the 0-30m depth range selected from the Bio-Argo float suggests some high nitrate measurements in summer. The Bio-Argo float measurements, taken over the top 30m, show that there are some measurements below the mixed layer in the summer. Glider data can also be used to validate the sensor data at the PAP-SO. A recent glider survey gave a particularly detailed picture of the top 150m of the water column (Hemsley et al., 2015). The chlorophyll-fluorescence measurements from gliders at the PAP-SO site (Figure 4) were useful to identify the position of the Deep Chlorophyll Maxima (DCM). The average depth of the DCM at the PAP-SO site was calculated as 17.82 ± 12.6m from the glider data. This suggests that the DCM can be captured for most of the year using the 30m sensor package on the PAP-SO site mooring.

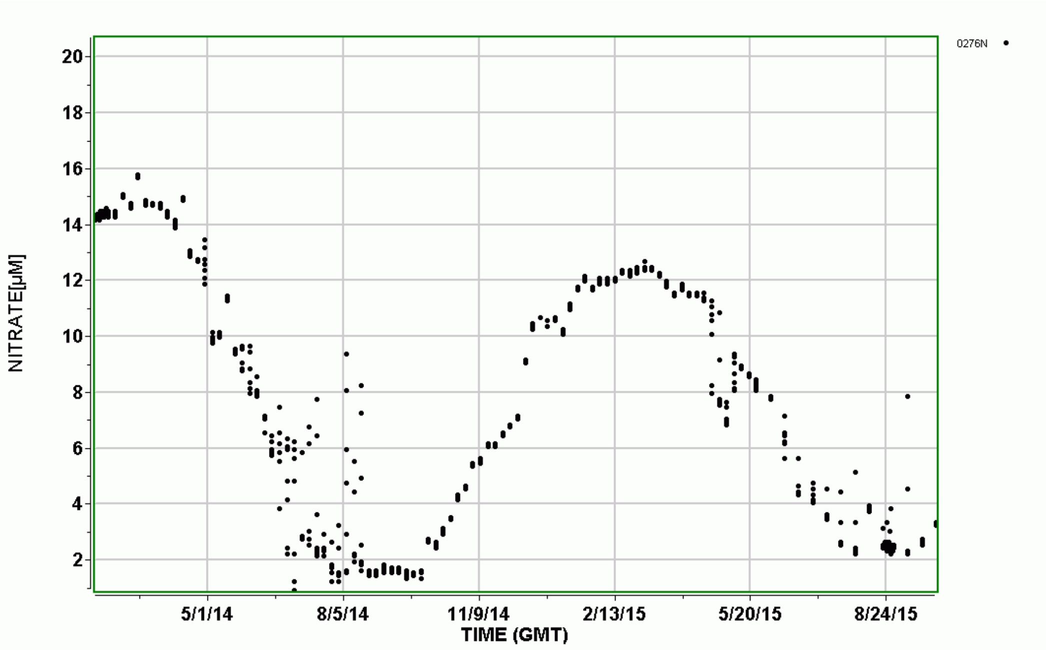

Figure 3: Nitrate data from a BioArgo Float (0276) in the Northeast Atlantic showing 0-30m data. The high values in August suggest that 30m is below the MLD at this time.

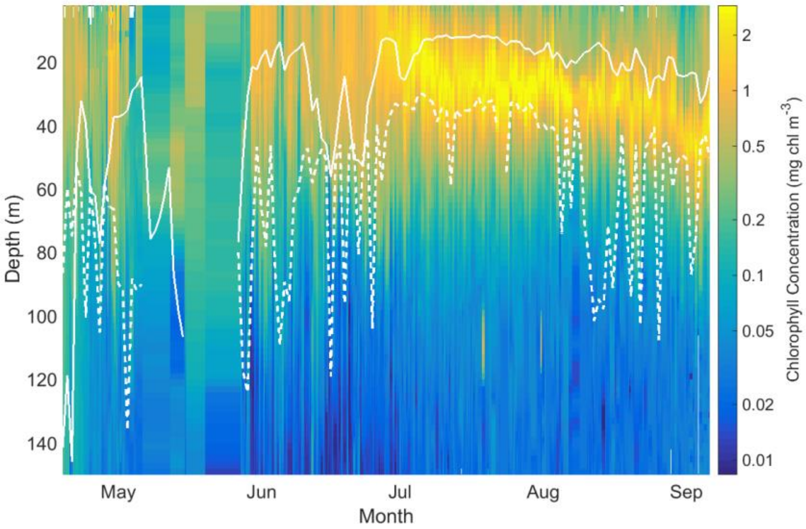

Figure 4: Chlorophyll-fluorescence from glider data at the PAP-SO site (from Hemsley et al., 2015) shows the DCM relative to the MLD (solid white line) and euphotic depth (dashed line).

Biogeochemical variability

The PAP-SO observatory site and the Bay of Biscay (on the SOO route) are in the inter gyre region of the North Atlantic where convective mixing ranges from 25m in the summer to over 400m in winter (when nutrients are supplied to the surface). In the temperate well-lit ocean nutrient supply and the subsequent CO_2 draw down and productivity would be largely sustained by convective mixing. Year to year variations in convective mixing will then have a large impact on nutrient supply and productivity. **Chapters 2-6** all deal with biogeochemical variability, highlighting the consequences for CO_2 draw down and productivity in the Northeast Atlantic and Northwest European shelf.

Variability in nutrients and productivity

Chapter 2 (Hartman et al., 2010) considered three-years of the PAP-SO time-series (2003–2005) of physical and biogeochemical data, which was analysed for both seasonal and inter-annual variation. There was a decrease in the maximum winter nitrate concentrations over the three-year period, from 10 mmol m^{-3} in 2003 to 7 mmol m^{-3} in 2005. However the surface nutrient trend could not be explained by convective mixing as it was no shallower in 2005. The MLD varied by about 40m between years when a MLD variation of about 150m would be required to explain the nitrate concentration variations. Körtzinger et al., (2008) had suggested that vertical convective mixing was the main driver behind inter-annual variation in the surface signals at the PAP-SO and that lateral advection could be ignored at the site. However it was clear from the results in **Chapter 2** that the influence of lateral advection should be considered.

In **Chapter 2** trajectories leading to the PAP-SO site were computed from altimetry-derived geostrophic velocities. The trajectories reaching the PAP-SO in March are considered in terms of water mass influence. In 2005 there was clearly a reduced influence of water from the north-east of the site. From water mass analysis two variants of Eastern North Atlantic Central Water (ENACW) were seen at the PAP-SO: sub-tropical and sub-polar ENACW as identified by Ríos et al., (1992). The relative influence of each would be expected to change from year to year due to the location of the PAP-SO in the transition zone (Henson et al., 2009) at the boundary of the SPG and STG. The sub-tropical variant is associated with lower nitrate concentrations than the sub-polar variant. As there was a reduced influence of the sub-polar variant in 2005 this would have contributed to the apparent trend towards the decreasing surface nutrient concentrations. **Chapter 2** therefore showed that lateral advection is an important process, along with convective mixing, and it cannot be ignored at the PAP-SO.

Progressive warming at the PAP–SO site from winter 2003 to winter 2005 was also observed in both the National Centre for Environmental Prediction (NCEP) sea surface temperature (SST) and subsurface (25 m) temperature records from the PAP–SO mooring. The increasing temperature and salinity trend over the three-year period was confirmed by other observations including coastal *in situ* observations at the L4 buoy in the western English Channel (Smyth et al., 2010). Bower and Van Appen (2008) showed a shift in the position of the NAC from the southern mode between 2003 and late 2004. The hypothesis is that a shift in the position of the NAC will have influenced the surface nitrate measurements; when the NAC was to the north of the PAP-SO site more tropical water masses would prevail. Associated decreases in the maximum winter nitrate concentrations may therefore be attributable to a combination of shallower convective mixing, changes in surface circulation, and mode waters supplying the region.

The winter nitrate concentration influences productivity the following year. Over the three years considered in **Chapter 2**, there was also a decrease in productivity at the PAP-SO as seen in the new production calculated from nitrate assimilation, which decreased from 85.4 g C m^{-2} a^{-1} in 2003 to 40.3 ±4.3 g C m^{-2} a^{-1} in 2005. The decrease in productivity was confirmed by year-to-year variability in primary production calculated from remote (satellite) observations of chlorophyll-*a* fluorescence around the PAP-SO site. Both the satellite and *in situ* sensor measurement estimates of productivity showed a spring and summer bloom. However there was an offset between the 30m sensor data and the surface satellite measurements which was attributed to the presence of a seasonal Deep Chlorophyll Maxima (DCM) at the PAP-SO that could not be detected by satellite measurements. In summary both data sets showed a decline in productivity which can be seen in the wider context of a progressive primary production decline in the open ocean from 1999 to 2004 (Behrenfeld et al., 2006).

The high resolution data from 2003-2005 was used to resolve short term variation in the timing of the spring bloom. Net heat flux (NHF) was used as an indicator of the local convective mixing. Timing of the spring bloom can then be correlated to the local shoaling of the mixed layer. NHF showed a direct influence on the timing of the spring bloom and that sustained periods of positive NHF were necessary for the bloom to start. Periods of positive sustained NHF earlier in the year in 2005 explained the earlier spring bloom seen in that year compared with 2004. These relationships have since been expanded in Smyth et al., (2014) to show that the NHF need only be positive to trigger the spring bloom.

In summary, results from the analysis in **Chapter 2** showed evidence of increased temperature in surface waters from 2003 to 2005, with increased stratification, decreased nitrate concentration and a consequent decline in productivity, with a delay in the start of the spring bloom. These are all predicted scenarios for a warming ocean.

Variability in surface carbonate chemistry

Chapter 3 (Hartman et al., 2015) moved on to look directly at the carbonate system. The seasonal air-sea exchange of CO_2 and new production were studied at the PAP-SO site to learn more about the CO_2 flux into the surface ocean. Changes in temperature and the related changes in the measured CO_2 were investigated. Productivity is a major driver of CO_2 flux in the Northeast Atlantic. In **Chapter 3** the influence of production on CO_2 uptake between 2003 and 2005 was compared with the 2010 to 2012 period. Both nitrate supply and chlorophyll-florescence were used to determine productivity. MLD, C:N and CO_2 flux were derived and compared between the two periods of time. Total alkalinity was calculated from Argo temperature and salinity using the Lee et al., (2006) equation, with error estimates of up to 6.4 µmol kg^{-1}. DIC was then calculated from TA and pCO_2 using the CO_2SYS toolbox (Lewis et al., 1998).

There is a persistent under-saturation of CO_2 in surface waters around the PAP-SO throughout the year, which gives rise to a perennial CO_2 sink. Comparison with an earlier data set at the PAP-SO collected from 2003 to 2005 (Körtzinger et al., 2008) confirms seasonal and inter-annual changes in surface seawater chemistry. The 2010–2012 period shows an overall increase in pCO_2 values when compared to the 2003–2005 period as would be expected from increases in atmospheric concentrations due to anthropogenic CO_2 emissions. High frequency subsurface measurements of pCO_2 from sensors at the PAP-SO showed an increase in seawater pCO_2 of 14 µatm over the last 8 years: from 339 ±17 µatm in the 2003-2005 period to 353 ±15 µatm in the 2010 to 2012 period. The increase in pCO_2 at the PAP-SO is consistent with the 1.84 µatm per year increase expected from Takahashi et al., (2009).

CO_2 flux was calculated as -5.7 (±2.8) mmol m^{-2} d^{-1} in 2003-05 compared with -5.0 (±2.2) mmol m^{-2} d^{-1} in 2010-12. Therefore there was little variability in the mean air to sea CO_2 flux between the years considered here. Note that in Körtzinger et al., (2008) the annual estimate for CO_2 flux was calculated as 3 mol m^{-2} a^{-1} (a daily flux of 8.2 mmol m^{-2} d^{-1}). The annual estimates from the present study would be lower that the estimates made by Körtzinger et al., (2008) as it was calculated from weekly rather than daily averages. For comparison multiplying the mean daily values by 365 days results in annual estimates of 2.08 mol m^{-2} a^{-1} and 1.83 mol m^{-2} a^{-1} respectively for the two time periods. These calculations of CO_2 flux at the PAP-SO all show that this region is still a significant sink.

There is some indication of earlier spring bloom timing in 2008-2010 compared with 2003-2005. As in **Chapter 2** there were year to year variations in the timing and intensity of the spring bloom between all years considered despite similar winter physical conditions (temperature and MLD) between the years. Variations in the timing and intensity of the spring bloom may be due to changes in the net heat flux as suggested in **Chapter 2**.

In **Chapter 3** the seasonal variation in C:N was investigated and the ratio was close to the Redfield ratio of 6.6 for most of the year. However in the spring the C:N ratio changed to higher values (14.3) suggesting carbon overconsumption (Sambrotto et al., 1993). As a C:N of 6.6 is used routinely in productivity calculations changing this to 14.3 would impact the productivity calculation.

Further work following **Chapter 3** shows the contribution of thermal and non-thermal forcing on the surface pCO_2 at the PAP-SO. These processes were separated by using the equations of Takahashi et al., (2002) shown below, where 'obs' is the observed values and 'ave' is the annual average.

$$1)\quad pCO_{2,therm} = (pCO_2)_{ave}.\ e^{\,0.0423.(Tobs-Tave)}$$

$$2)\quad pCO_{2,nontherm} = pCO_{2,obs}.\ e^{0.0423.(Tave-Tobs)}$$

Equation 1 gives an indication of the seasonal thermal forcing on the surface pCO_2 at the PAP-SO. Whereas equation 2 removes the thermal effect by correcting to the annual mean sea surface temperature. These non-thermal changes include biological carbon fixation, vertical mixing, advection and air-sea CO_2 transfer. The results are shown in Figure 5.

The seasonal range of SST is approximately 6°C at the PAP-SO. Figure 5 shows that if SST alone controlled pCO_2 at PAP-SO there would be a winter to summer increase of about 80 µatm pCO_2. In turn there is a decrease of 110 µatm pCO_2 by the non-thermal effects, which compensates for the thermal changes. The results show that the non-thermal effects are dominant at the PAP-SO largely due to biological effects in summer which result in the pCO_2 minima. The pCO_2 maximum in winter is associated with the deepening of the mixed layer which brings DIC and CO_2 back to the surface.

Linking the surface and deep ocean

Figure 6 shows the full depth profiles for physical and biogeochemical variables at the PAP-SO. Figure 6 shows that the 1000m water for example is associated with a high salinity, high alkalinity and low oxygen due to Mediterranean Overflow Water (MOW) influences. At 3000m the influence of North Atlantic Deep Water (NADW) is seen (with high oxygen values). The profiles of DIC and nitrate show similar trends as they co-vary, with an increase towards the Lower Deep Water (LDW). There is an opposing trend between pH and CO_2 as expected. This is an update on the water mass analysis at PAP (from Laes et al., 2003) summarised below in Table 2.

In **Chapter 4** (Frigstad et al., 2015) the biological pump at the PAP-SO was considered, from the surface uptake of CO_2 and nutrients to the sinking and recycling of fixed carbon at depth. Two productivity calculations were made at the surface: seasonal net community production (NCP) and new production (NP). NCP was calculated from the carbon measurements and NP from changes in nitrate, at 30m at the PAP-SO. NCP was calculated as 4.57 ± 0.27 mol C m^{-2} and NP as 0.37 ± 0.14 mol N m^{-2}. The production results from **Chapter 4** are indicative of carbon overconsumption (Sambrotto et al., 1993).

In **Chapter 4** the link between surface productivity at the PAP-SO and the amount of material in the sediment traps at 3000m was investigated. The mean surface productivity was calculated by taking a 100km box around the PAP-SO and comparing the results with a particle tracking approach, to examine the source region of material arriving at the traps. By using the particle tracking approach it was found that there were large variations, both between and within years, in where the material originated from.

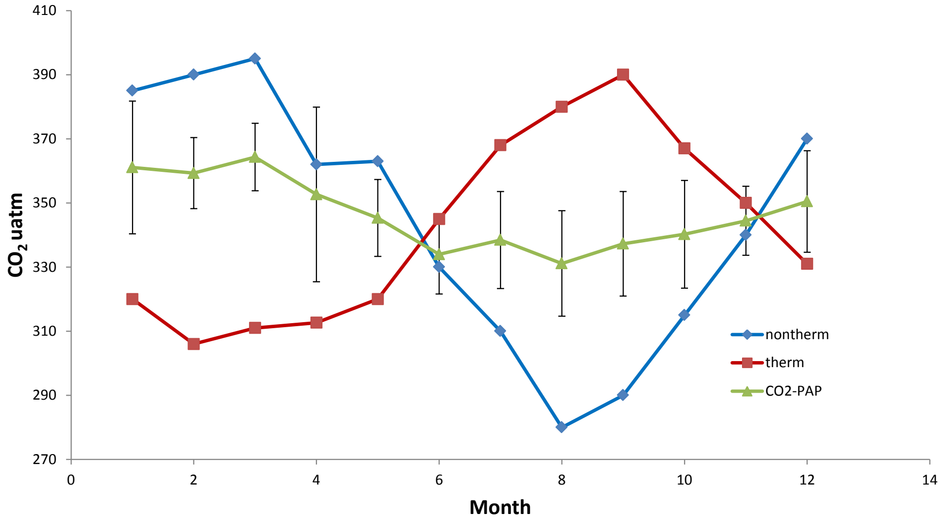

Figure 5: Calculated thermal (red) and non-thermal (blue) effects on surface pCO_2 at the PAP-SO (green). The annual cycle of pCO_2 at the PAP-SO is shown as average values ± 1 standard deviation indicating inter-annual variability (from 2003-2012).

There were higher correlations between surface productivity and export flux when using the particle-tracking approach, than by comparing with the mean productivity in a 100 km box around the PAP-SO site. However, the differences in correlation coefficients were not significant, and a longer time-series is needed to draw conclusions on the validity of this approach of applying particle tracking in sediment trap analyses.

The fraction of production that is exported (export efficiency), and how efficiently this material is transferred to depth (transfer efficiency), varies on regional scales. It is uncertain what factors control this regional variability (Buesseler & Boyd, 2009; Cavan et al., 2015). In **Chapter 4** the export ratio and transfer efficiency were calculated as 16% and 4 %, respectively. The PAP-SO site thereby showed low transfer to depth and a high attenuation of this flux as is expected in productive, high latitude ecosystems (Cavan et al., 2015).

The seasonal cycles summarised in **Chapter 4** are shown in Figure 7. From these figures it is clear that the seasonal cycle in nitrate and carbon is linked to the seasonal cycle in MLD and PP. DIC and nitrate co-vary, with an increase prior to spring and decrease at the time of the spring bloom. The seasonal data shown in **Chapter 4** is based on all data collected at the PAP-SO site so the variability (error bars) relates to the inter-annual variability. Some months are still poorly sampled especially in the winter as it is a challenge to obtain a whole year of data.

Table 3 shows the time line of sensors deployed at the PAP-SO (updated from **Chapter 1**). A critical assessment of the PAP-SO site biogeochemical data reveals large gaps in the data. To maintain a long time-series at the PAP-SO it is important to improve on the length of each record and to avoid gaps in the data. Longer data streams have been possible since 2010 when the more robust UK Met office buoy was first used at the site. However the real-time data is still susceptible to some communications failures. Most data can still be retrieved from the instruments post deployment so data retrieval is not fully reliant on real time data transmission.

Table 2: Water mass summary (after Laes et al., 2003) showing the typical water mass qualities (in temperature, salinity and oxygen) on depth and density surfaces at the PAP-SO

	Depth (m)	Salinity		Temperature (° C)		Oxygen (µM)	
Density		27	28	27	28	27	28
LDW	>3000	34.92	34.91	2.29	2.21	238.12	239.2
NADW	2300–3000	34.97	34.99	2.94	3.42	239.98	244.96
LSW	2000	34.99	35.02	3.6	4.01	251.75	254.39
MOW	1000	35.74	35.74	9.5	9.61	185.88	186.92
ENACW	700–50	35.55	35.56	11.04	11.06	214.1	199.53
Surface	waters	35.6	35.64	12.31	12.57	262.81	258.57

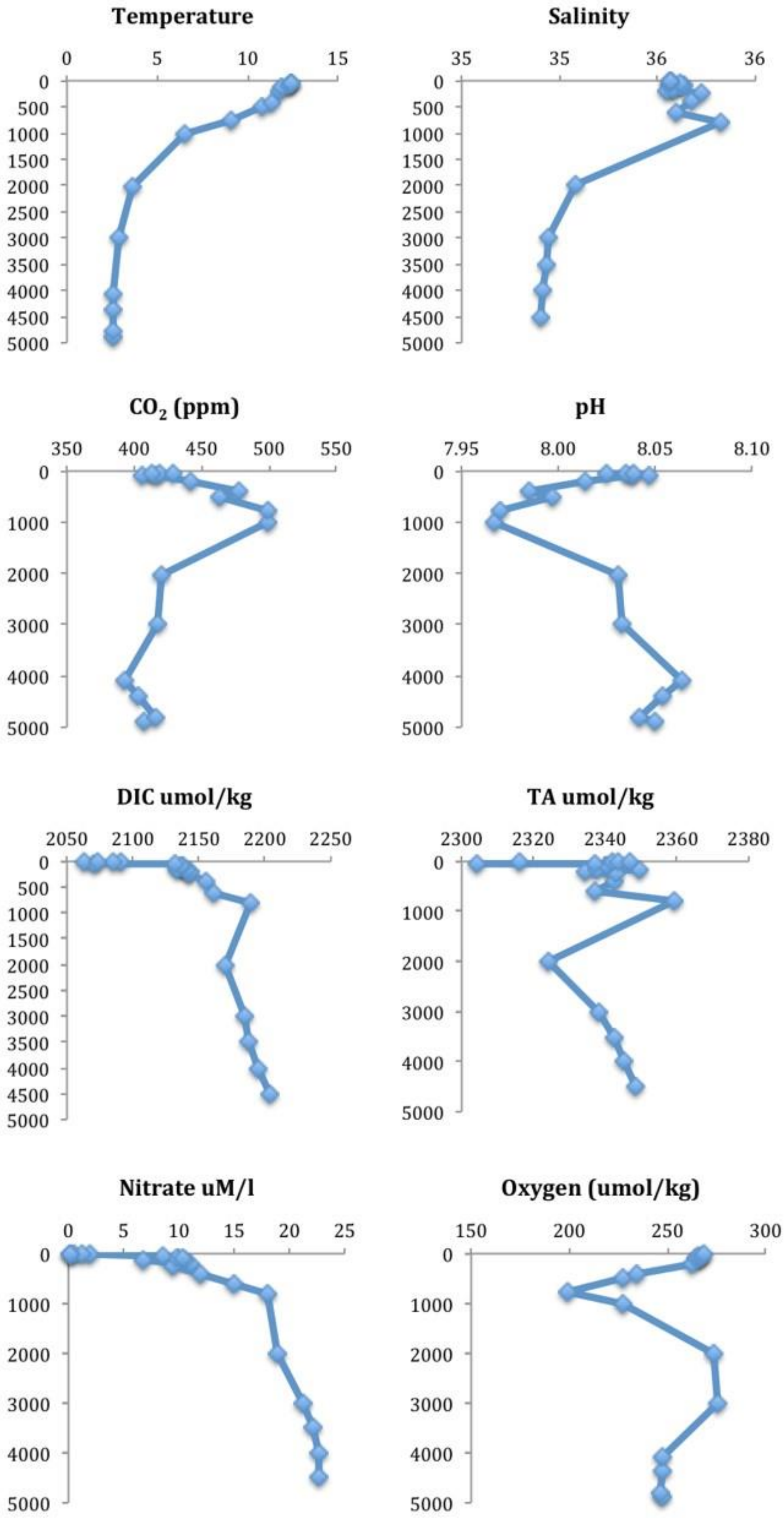

Figure 6: Full depth profiles from the PAP-SO taken on an annual service visit in spring (2016)

For a trend to be detected and attributed to climate change a long time-series is needed. Any changes in the instrumentation or gaps in the data set will increase the number of years needed to detect a trend (Beaulieu et al., 2013). Signorini & McClain (2012) show a decrease in productivity in the sub-tropical gyres from a 13 year time-series of satellite measurements. In the high latitude North Atlantic a longer time-series may be required to detect such trends. **Chapter 2** (Hartman et al., 2010) suggested that there was a decrease in productivity (a decrease in NCP from about 85 to 40 gC m^{-2} a^{-1} over 3 years of *in situ* measurements) confirmed by a decrease in Primary productivity calculated from satellite data. However it is clear that a longer time-series is needed to attribute this to a real decreasing trend in oceanic production (Henson et al., 2016).

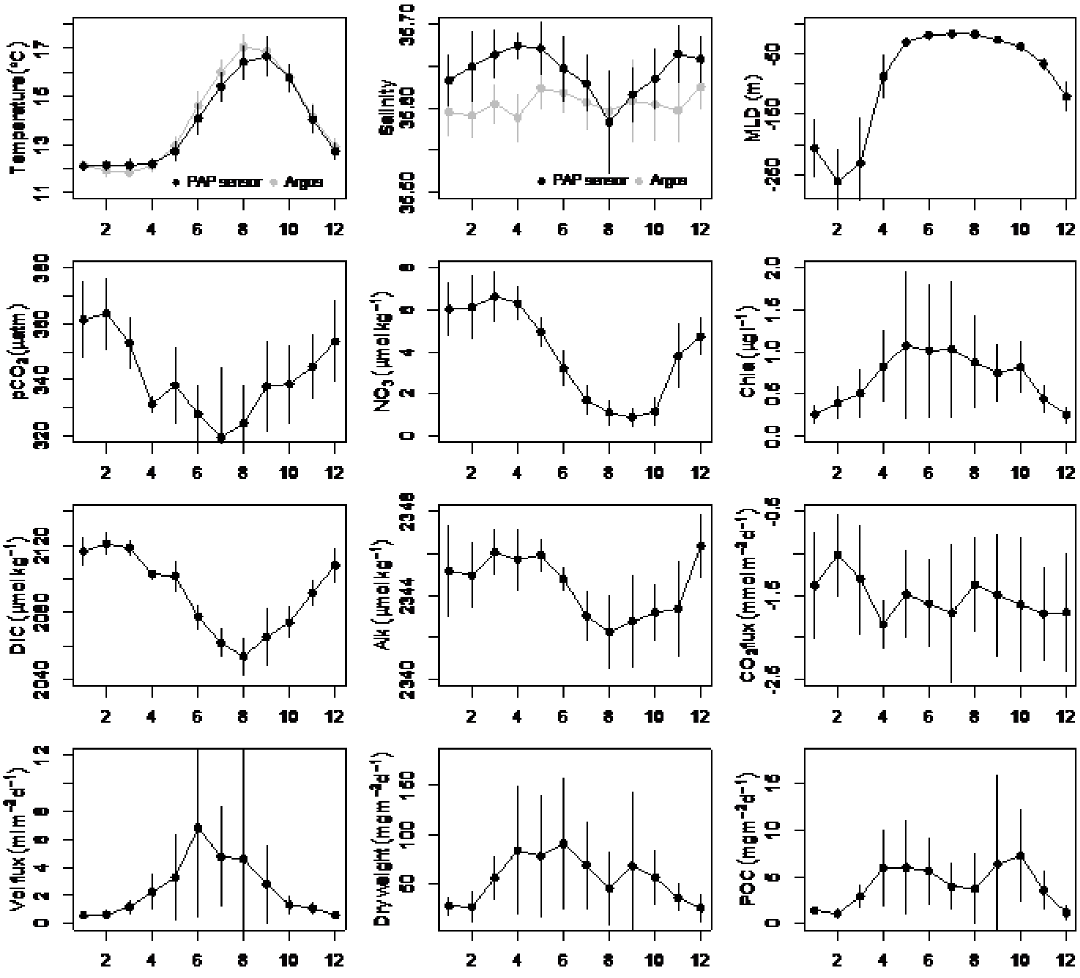

Figure 7: Shows broad seasonal variation in biogeochemistry and physics at PAP. The 'error bars' show the year to year variation (from Frigstad et al., 2015)

Table 3: The types of sensors deployed and the number of months of high quality data available for each year of the PAP-SO mooring deployment (updated from chapter 1 in 2016).

Year	**deployed**	**nitrate, chl, CO_2, O_2, pH instruments**	**Comments**
2002	07/10/2002	NAS nitrate, HS2 chl, SAMI CO_2	9 month full record until 8/7/2003
2003	12/07/2003	NAS nitrate, HS2 chl, SAMI CO_2	4 month full record until 16/11/2003
2003 (2)	18/11/2003	NAS nitrate, HS2 chl, SAMI CO_2	7 month full record until 20/6/2004
2004	23/06/2004	NAS nitrate, HS2 chl, SAMI CO_2	1 month record until 18/7/2004
2005	Jun-2005	no data	1 month then mooring drift from 27/7/2005
2006	Jul-2006	not deployed	not deployed due to long line fishing damage
2007	22/06/2007	11 day ISUS, Wetlab chl , no CO_2	2 month full record until 9/8/2007
2008	2008	not deployed	not deployed 2008
2009	23/05/2009	Wetlab chl only	2 month record until 20/7/2009
2010	03/06/2010	NAS, Wetlabs chl, no CO_2, O_2 optode	3 month record to 15/9/2010, NAS to August 2010
2010 (2)	20/09/2010	ISUS, Wetlabs chl, PRO-c	4 month record to 11/1/11 (wetlab to 28/7/2010)
2011	30/07/2011	ISUS, Wetlabs chl, PRO-c, O_2 optode	10 month chl to 2/5/2012, ISUS and pro-c to 28/2/12
2012	07/05/2012	ISUS, wetlabs chl, PRO-c, O_2 optode & SeaFET pH	2 month record to 3/7/2012 comms fail (pH to 21/5/2012)
2013	25/04/2013	ISUS, wetlabs chl, PRO-c, O_2 optode, SeaFET pH	8 month pro-c 1m to 11/12/13, others to 15/5/2013
2014	15/07/2014	SUNA, wetlabs chl, PRO-c, O_2 optode, SeaFET pH	7 month record to 28/2/15 (comms fail in storms)
2015	01/07/2015	ISUS, wetlabs chl, PRO-c , O_2 optode, SeaFET pH	7 month pro-c at 30m odd from 1/1/16 but still recording

The extent to which any time-series station is representative of the larger region was assessed by Henson et al., (2016). They correlated the sampled output from models with the surrounding area to find the ‘footprint’ of each ocean observatory (Figure 8). The footprint of the PAP-SO site was largest for pH and chlorophyll, extending towards but not into the northern Bay of Biscay (in **Chapter 5**).

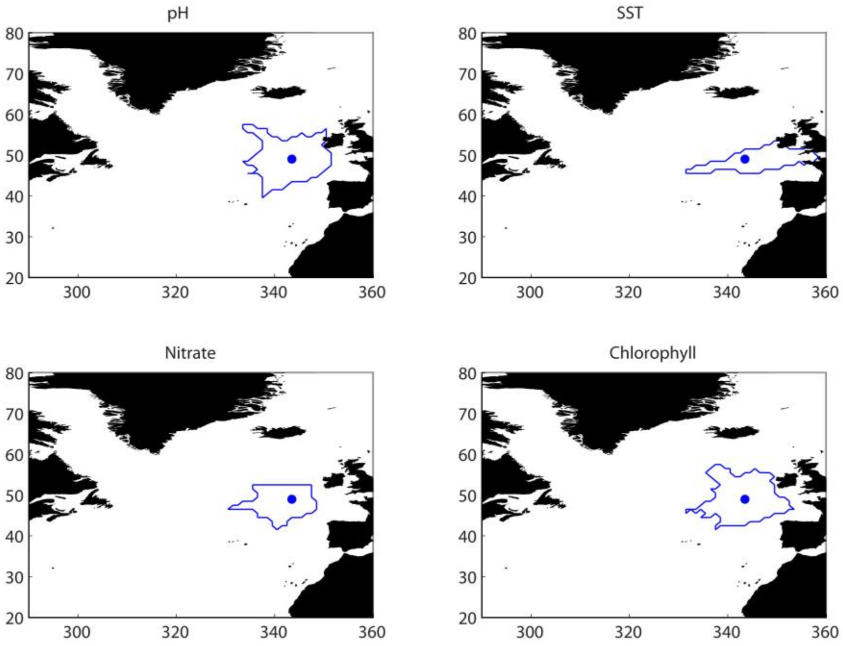

Figure 8: The footprint of the PAP-SO site shows the extent to which biogeochemical measurements for a) chlorophyll; b) SST; c) nitrate concentrations and d) pH are representative of neighbouring regions (adapted from Henson et al., 2016).

Other regions of the Northeast Atlantic

The annual SST, CO_2 and DIC cycles at four different sites across the Atlantic is shown in Figure 9 (adapted from Bates et al., 2014). The sites that were chosen are in contrasting regions to look at the variations in biogeochemistry. The Bermuda Atlantic Time-series (BATS) is in the tropical western STG; Ocean Weather Station Mike (OWSM) in the SPG; the Bay of Biscay (Bbay) SOO time and the PAP-SO site both represent the inter-gyre region between the STG and SPG.

At the OWSM (Olsen et al., 2008) in the sub-polar region there is a single peak in CO_2 in the winter, due to the influence of deep winter mixing. The seasonal cycle of CO_2 in the SPG is opposite to that in the oligotrophic STG, represented here by BATS. At BATS the influence of temperature dominates and there is a single peak in CO_2 in summer (Bates et al., 1996; Takahashi et al., 2002).

In the Bay of Biscay Jiang et al., (2013) distinguished the contributions of biological and physical processes to the monthly carbonate variables. The separate effects of gas exchange, biological production and mixing processes were quantified. The temperature effect on the seawater pCO_2 was dominant in summer and non-thermal effects such as mixing were dominant in winter. Biological processes dominated during the spring bloom, which resulted in a double CO_2 peak (Jiang et al., 2013) in this inter gyre region of the Northeast Atlantic.

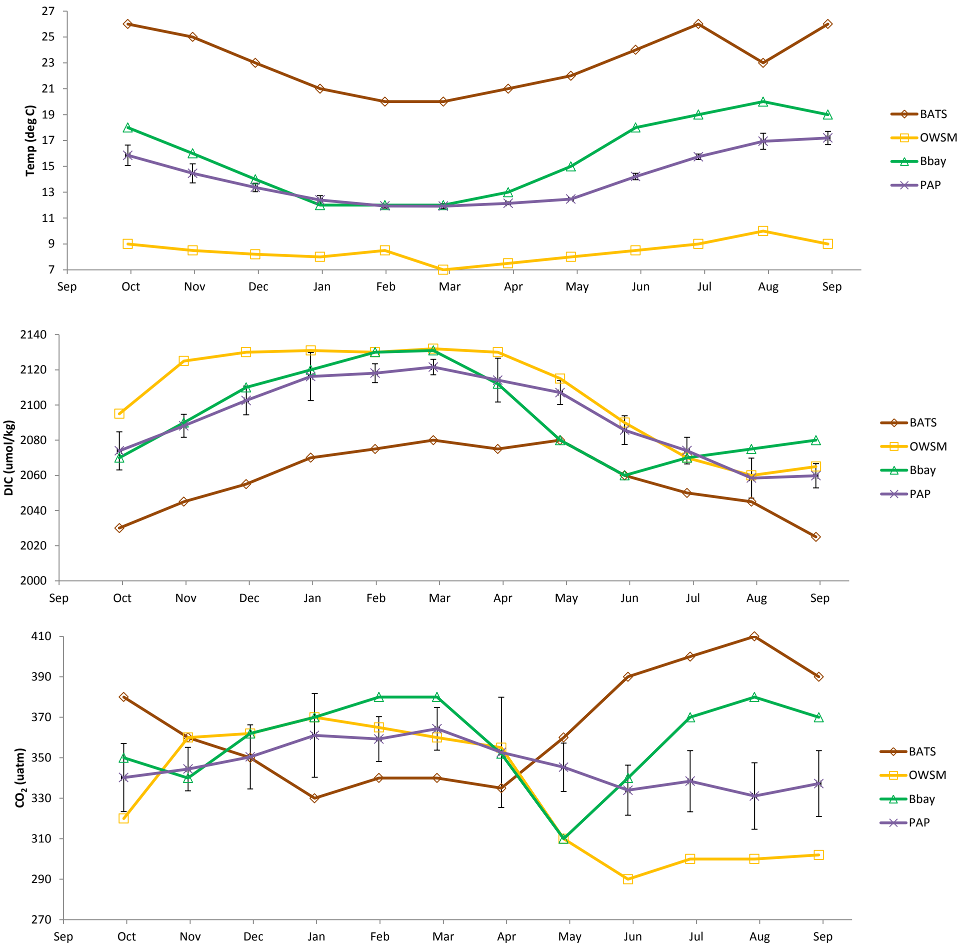

Figure 9: The seasonal variations of (a) SST, (b) DIC and (c) pCO_2 in regions at different latitudes in the North Atlantic. The available data during 2003–2010 are presented as monthly averaged values at BATS (in brown), Ocean Weather Station Mike (in yellow) and the Bay of Biscay (Bbay) data in green (from Jiang et al., 2013). The PAP-SO site data from this study is also shown (in purple) with ± 1sd around the mean to show year to year variability.

Figure 9 suggests that the temperature and DIC data at the PAP-SO site data closely resembles the Bay of Biscay data set (from Jiang et al., 2013). Generally at the PAP-SO site the changes in pCO_2 occurred in parallel to those of DIC with a single-peak in the annual cycle. The winter peak in pCO_2 and DIC corresponded to the colder winter temperatures. There is a decrease in pCO_2 and DIC during the spring bloom when temperature increases. Both the Bbay and PAP-SO data are from the inter gyre region of the North Atlantic, with the influence of both the sub-tropical and sub-polar gyre waters so it is postulated that the double CO_2 peaks would be seen at the PAP-SO site. A recent study by Benson et al., (2016) suggests a double CO_2 peak at the PAP-SO site from model output. However this was not seen in the *in situ* CO_2 data or in the calculated DIC at the PAP-SO.

Chapter 5 considers biogeochemical variability across the Bay of Biscay from the UK to Spain Ferry-Box time-series. Winter nitrate concentrations were found to be decrease by about 3µmol kg^{-1} in years with shallow mixing (such as 2007 and 2008). Mixing was assessed using Argo floats and the mild winters were associated with an approximate halving of the MLD. In the relatively mild winter of 2007/08 the MLD was 212m compared with cold winters such as 2009/10 when the MLD reached 476m. There was a more direct link between decreased winter mixing, decreased winter nitrate and the NAO index in the Bay of

Biscay (compared with the PAP-SO). The warm winter of 2007/08 corresponded to a positive NAO index and warmer surface temperatures, associated with a shallower MLD. Decreased concentrations of nutrients in these milder winters resulted in a decrease in productivity the following spring. Table 3 (and **Chapter** 3) shows that these years (with a positive NAO) are underrepresented in the PAP-SO time-series.

Körtzinger et al. (2008) used a 0.6°C temperature difference from the surface to distinguish the surface water at the PAP-SO although it has since been determined that this criterion is not ideal (eg: Steinhoff et al., 2010). Two estimates of MLD based on temperature differences (0.3°C and 0.5°C) were used to distinguish the mixed layer depth in **Chapter 2**. In **Chapters 3 , 4 and 5** the MLD criterion was modified further and a density difference criterion was used. MLD calculations are important for the calculation of productivity and the calculated productivity would potentially vary depending on the criteria selected.

As at the PAP-SO (**Chapter 2**, Hartman at al., 2010) productivity was calculated from the depletion in nutrients. The increase in oxygen anomaly was used along the Ferry-Box route (**Chapter 5**, Hartman et al., 2014). Chapter 5 showed that the timing of the bloom was earlier offshore in the Bay of Biscay compared with on the shallower Northwest European shelf (towards the UK).

Chapter 6 (Hartman et al., 2017) extends the measurements further onto the Northwest European shelf. It considers biogeochemical variability at the PAP-SO in contrast to the Northwest European shelf. Seasonal maps show clear divisions between the low salinity, high nutrient and low dissolved inorganic carbon in coastal waters compared with off-shelf regions, throughout the year. Nutrients remain higher year-round in the colder waters to the north of Scotland, compared with other regions where they are depleted by the annual spring bloom. Nutrient concentrations recover sooner (in the summer) following the spring bloom in the shallow Irish Sea and Eastern English Channel compared with the other regions.

The Northwest European shelf is a weak CO_2 sink although **Chapter 6** shows that there is some variation in the capacity to take up CO_2 around the coast. The underway pCO_2 data (Figure 10, adapted from a figure shown in **Chapter 6**) highlights the contrast between the low pCO_2 waters of the northern North Sea and higher pCO_2 (above atmospheric concentrations) in the shallower southern North Sea. This confirms the suggestion by Thomas et al., (2006) and Van Leeuwen et al., (2015) that the northern North Sea is a net sink of CO_2 and biological control dominates pCO_2 over the annual cycle. Whereas water temperature is the dominant control on pCO_2 in the southern North Sea, which is a net source region of CO_2 to the atmosphere.

pCO_2 is relatively low at the PAP-SO compared with the Bay of Biscay (Figure 11) and data from the Northwest European shelf (**Chapter 6**, Hartman et al., 2017). There is a net uptake of CO_2 at the PAP-SO throughout the year. CO_2 decreases as the temperature increases due to CO_2 uptake during the spring and summer blooms and in turn mixing brings deeper high CO_2 waters to the surface in winter. This results in a strong inverse relationship between the seawater pCO_2 and temperature (Figure 11). This inverse relationship between CO_2 and temperature is seen at the PAP-SO site throughout the year and shows the dominance of biological control on pCO_2 in this region, in contrast to the Northwest European shelf (shown in **Chapter 6**).

Over 10 years of measurements at the PAP-SO there is a trend of ~1.8 μatm yr^{-1} increase in CO_2 (from **Chapter 3**, Hartman et al., 2015). The annual increase in pCO_2 reflects the broader oceanic trend from Takahashi et al., (2009). This is likely to accompany a decreasing pH as shown by Bates et al., (2014) using other time-series data. However pH measurements were only introduced in 2014 and it has been calculated that a 14 year time-series is needed at the PAP-SO site to detect real trends in pH; other biogeochemical variables require over 25 years of data (Henson et al., 2016).

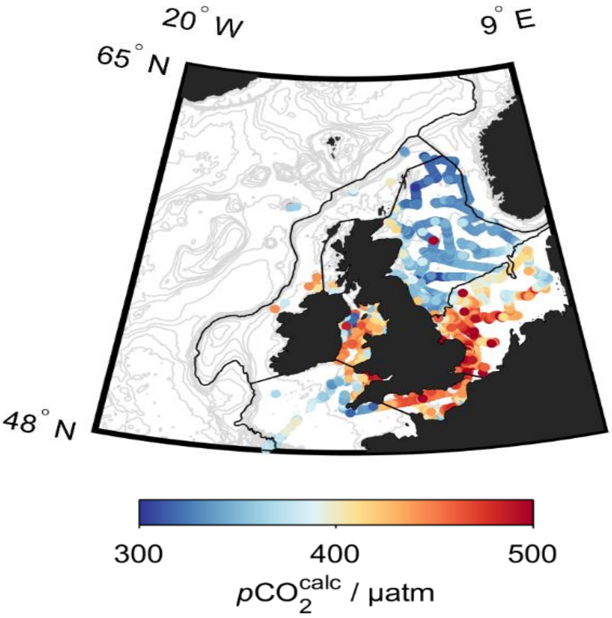

Figure 10: One of the seasonal maps (summer; July to September) from chapter 6 (Hartman et al., 2017) showing calculated and underway pCO_2 measurements around the Northwest European shelf. The data were collected during the UK Shelf Sea Biogeochemistry programme (2014-2015).

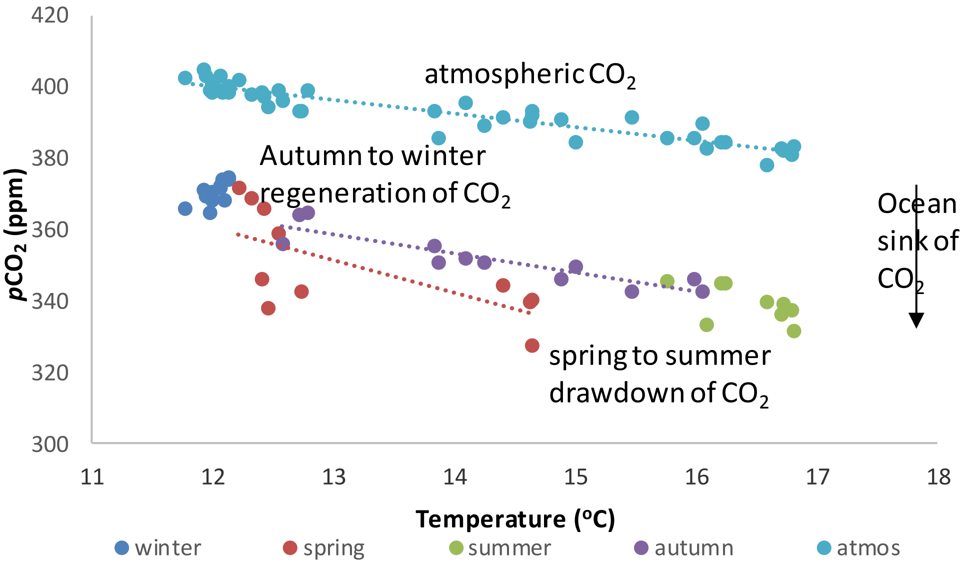

Figure 11: Seasonal variation in the pCO_2 measurements in relation to temperature for the PAP-SO, showing weekly averaged data from 2010-2012 and dominant processes.

Conclusions

- Experience gained at the PAP-SO in the use of biogeochemical sensors and in validating the measurements have made a valued contribution to international Best Practice for sensor deployment and validation (for example in Coppola et al., 2016).
- The seasonal variation of biogeochemistry at the PAP-SO has been described here. There is an annual winter peak in nitrate (up to 10 µmol kg^{-1}) and DIC (2130 µmol kg^{-1} in 2012), which corresponds to colder surface temperatures (around 12°C) and deep mixing (up to 400m). Generally there is a summer decrease in nitrate (to zero) and DIC (2060 µmol kg^{-1} in 2012), due to stratification (MLD decreases to 25m) and phytoplankton growth. There is a summer increase in chlorophyll-fluorescence (up to 5 µg/l) and temperature (to 18°C). The seasonal cycle is typical of the productive sub-polar regions.
- This study confirmed the winter to summer decrease in surface pCO_2 at the PAP-SO and showed that this is largely controlled by non-thermal processes, including biological drawdown in the spring and vertical mixing in the winter. The seasonal variation (for example from 327 µatm in August 2012 to a winter maxima of 384 µatm in 2012) was opposite to the seasonal variations at sub-tropical sites such as BATS and ESTOC.
- Surface ocean observations at the PAP-SO represent both the natural variability of biogeochemical variables and the anthropogenic forcing acting on these. Year to year there are large variations in the biogeochemical measurements at the PAP-SO. For example the results suggest increases in temperature (eg: a winter temperature increase from 12.25 ±0.2 °C in 2003 to 12.61 ± 0.16 °C in 2005) which was accompanied by a decrease in winter nitrate concentrations (from 10 mmol m^{-3} to 7 mmol m^{-3} from 2003 to 2005).
- One of the aims of this thesis was to look at causes of year to year variations in the biogeochemistry at the PAP-SO site and see if there is a link to climate forcing. The NAO is the dominant mode of atmospheric variability in the Northeast Atlantic and it has been associated with biogeochemical variability. However there was little variability in the NAO for the two time periods chosen for the PAP-SO so the effect of changes in the NAO has yet to be shown for that site. However the mild winters in the Bay of Biscay (for example 2007/08) were associated with a positive NAO and warmer surface ocean. The MLD halved at this time (212m in 2007/08 compared with 476m in the colder, low NAO winter of 2009/10). This was associated with a decrease in winter nitrate of 3µmol kg^{-1} and decreased productivity the following spring.
- Work in this thesis shows that the PAP-SO region is influenced by variations in the source regions of the Eastern North Atlantic Surface Water. Years with low winter nitrate concentrations (eg: 2005 which had a low winter nitrate of 7 µmol kg^{-1}) may in part be linked to the lateral advection of low nitrate sub-tropical waters or a decrease in the higher nutrient, low temperature and salinity sub-polar variant of this water mass (as shown for 2005). The results of this study support the hypotheses that lateral advection is important at the PAP-SO.
- The real strength of the sustained observatory data from the PAP-SO is to detect short term changes at the surface. Work presented here shows that the net heat flux calculations can be a good indicator for the timing of the spring bloom at the PAP-SO and a positive net heat flux triggers the start of the spring bloom (within 7-9 days). Productivity is one of the main controls on the CO_2 uptake by the sub-polar North Atlantic Ocean. In the future productivity may decrease due to increased stratification of the water column and decreased supply of nitrate to fuel the spring bloom (Behrenfeld et al., 2006). Productivity calculations were derived from the time-series measurements at the PAP-SO and showed year to year variability. There was a decrease in productivity (from 85.4 gC m^{-2} a^{-1} to 40.3 gC m^{-2} a^{-1}) from 2003

to 2005, which demonstrates the need to sustain monitoring at the PAP-SO.

- Productivity calculations from both carbon and nutrients suggested that the consumption of inorganic carbon relative to inorganic nitrate was in excess of the Redfield ratio at the surface. The seasonal net community production was calculated as 4.57 ± 0.85 mol C m^{-2}. The new production calculated from nitrate was 0.37 ± 0.14 mol N m^{-2} suggesting a C:N of 12.0. So there was evidence of carbon overconsumption at the PAP-SO, with more carbon removal than expected. This may be due to preferential remineralisation or it could indicate that regenerated nitrate is refuelling production.
- The persistent under-saturation of CO_2 throughout the year makes the PAP-SO area a significant CO_2 sink, especially in comparison with sub-tropical sites and also in comparison with the Northwest European shelf. The average pCO_2 concentration at the PAP-SO increased from 339 ±17 (2003-2005) to 353 ±15 (2010-2012), which is consistent with the annual increase of 1.84 ±0.4 μatm reported by Takahashi et al., (2009).
- CO_2 flux was calculated from the time-series at the PAP-SO to assess the changing capacity for the North Atlantic as a carbon sink. Initial aims were to look for year to year variation in CO_2 flux (as shown by Schuster & Watson, 2007). However no large year to year changes in flux were seen at the PAP-SO. The CO_2 flux varied from -5.7 ± 2.8 mmol m^{-2} day^{-1} in the 2003-2005 period to -5.0 ± 2.2 mmol m^{-2} day^{-1} in the 2010-2012 period which is not a significant variation. A satellite wind product was used rather than *in situ* wind measurements in the calculations which may have averaged out some of the relatively high wind speeds at the PAP-SO, which could have a significant effect on CO_2 flux.
- CO_2 from the atmosphere is sequestered to depth through the production of organic material. An export ratio of 16% was calculated which represents organic material exported below the euphotic zone. The efficiency of the biological pump is represented by the transfer efficiency (calculated as 4% at the PAP-SO). There was large variation both within and between years in where material reaching the PAP-SO sediment traps originated from. There were higher correlations between surface productivity and export flux when using the particle-tracking approach, than by comparing with the mean productivity in a 100 km box around the PAP-SO site. However, the differences in correlation coefficients were not significant, and a longer time-series is needed to draw conclusions on the validity of using the particle tracking approach.
- The surface waters from the region of the PAP-SO influence the Northwest European shelf and this study showed how the seasonal biogeochemical cycles at the PAP-SO site compared with the shelf region. For example winter alkalinity is generally higher offshore at the PAP-SO as is salinity. There is also an inverse relationship between surface pCO_2 and temperature at the PAP-SO and on the Irish and Scottish shelf due to productivity.

Further work

High resolution, long time-series data are needed to assess both short term events and trends in open ocean biogeochemistry and productivity. Recent studies in the Atlantic have shown how nutrients are resupplied from deeper waters during storms (Rumyantseva et al., 2015). Such short term variation in nitrate supply could easily be investigated in future studies at the PAP-SO site.

In this study satellite wind speed data was used to calculate air-sea CO_2 flux in order to be consistent over the 10 years of sensor data that exists. Future CO_2 flux calculations should consider using the *in situ* wind data from the Met office buoy. Satellite data shows average wind speed and the maximum was recorded as 14 ms^{-1}. However *in situ* data from the Met office buoy suggests wind speeds of up to 20 ms^{-1}. There is an apparent increase in CO_2 uptake around October 2010 for example (corresponding to high wind speeds) which could be examined more closely as it may correspond to a storm event.

Future studies should also include the 1m CO_2 data to be compatible with datasets such as SOCAT (which use the top 15m data). When using the *in situ* temperature and 1m CO_2 data to calculate CO_2 flux at the PAP-SO site the values were similar to the 30m data reported in **Chapter 3**. For example net CO_2 uptake in 2013 was -5.0 ± 2 mmol m^{-2} d^{-1} which is similar to the values found in **Chapter 3** (-5.7 and -5.0 mmol m^{-2} d^{-1}). The new calculations used *in situ* wind speed from the Met Office buoy (and the atmospheric CO_2 from Mace Head). A recommendation would be to report all future flux calculations using the *in situ* meteorological data and to introduce local measurements of atmospheric CO_2 on the buoy.

Recently 7-channel radiometers have collected light data both on the buoy and the mooring frame. Output from the radiometers could be used to improve the chlorophyll-fluorescence data following the methods in Hemsley et al., (2015), which was an intensive study of largely non biogeochemical measurements around the PAP-SO site using gliders. As smaller, less power hungry biogeochemical sensors become available in the future more intensive glider studies at the PAP-SO site will be possible and will provide increased depth resolution.

The Northeast Atlantic has the highest proportion of anthropogenic CO_2 compared with other oceans. Anthropogenic carbon cannot be calculated from surface measurements so a further recommendation would be to have similar sensors throughout the water column. As biogeochemical sensors are increasingly available that can cope with high pressures of the deep ocean it is a recommendation of this study that CO_2 sensors be added to the PAP-SO site time-series at deeper depths. Currently full depth profile measurements of biogeochemical variables are only made at the annual service visits (both pre and post deployment). Ideally profiles would be done throughout the year. This could also be achieved using auto samplers at various depths, which would additionally help in sensor data validation.

Ship of opportunity data could be used to extend the time-series measurements made at the PAP-SO. The PAP-SO site sits between regions 4 and 5 as defined by Ostle et al., (2015). Ostle et al., (2015) selected biogeochemical provinces from the UK to Caribbean ship of opportunity track (that passes through the PAP-SO site) based on correlations of temperature, density and chlorophyll. The method used to select the biogeochemical provinces was preferred over static biogeochemical provinces such as Longhurst, (2006) so that the boundaries could shift from year to year. The PAP-SO site is also defined as being in the inter gyre or ‘transition’ region between the SPG and STG (Henson et al., 2009), so it will have both sub-tropical and sub-polar influences. In future studies years with increased sub-tropical influence should be distinguished at the PAP-SO site beyond the descriptive approach in **Chapter 2**, especially if the sub-tropical gyre is expanding as predicted by Henson et al., 2009.

A comparison of biogeochemical cycles at the PAP-SO with the Northwest European shelf showed large seasonal and regional variations in pH. To determine a trend in pH would require a longer time-series. Further work at the PAP-SO will include a full description of year to year changes in pH. These time-series measurements should be continued to elucidate trends in the data.

Models and interpolation methods are used to fill the gaps between time-series sites and where data are sparse. Although not explored in this thesis the importance of models and interpolation methods are recognised. Further work would be to couple the time-series measurements with models to increase understanding of the underlying processes and interactions

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Introducción general

Conocimientos previos

El Dióxido de Carbono (CO_2) es el Segundo gas más común de efecto invernadero después del vapor de agua. El CO_2 absorbe la radiación de onda larga, aumentando el forzamiento radiactivo y el calentamiento de la superficie de la Tierra. La concentración de CO_2 atmosférico ha aumentado un 40% desde tiempos pre-industriales, principalmente debido a la combustión de carburantes fósiles y en segundo lugar por el cambio en el uso de la tierra (Quéré et al., 2015). En 2014, la concentración atmosférica en la estación de Mauna Loa alcanzó por primera vez 400 ppm (co2now.org) y se ha predicho que los niveles podrán alcanzar las 490 ppm al final del siglo XXI.

El océano actúa como un importante almacén de carbono, absorbiendo más de una cuarta parte de las emisiones antropogénicas anuales (Quéré et al., 2015 and Figure 1). Los océanos absorben cerca de 2 Pg C yr^{-1} (Wanninkhof et al., 2013), el cual modera el cambio en el total de CO_2 en la atmósfera.

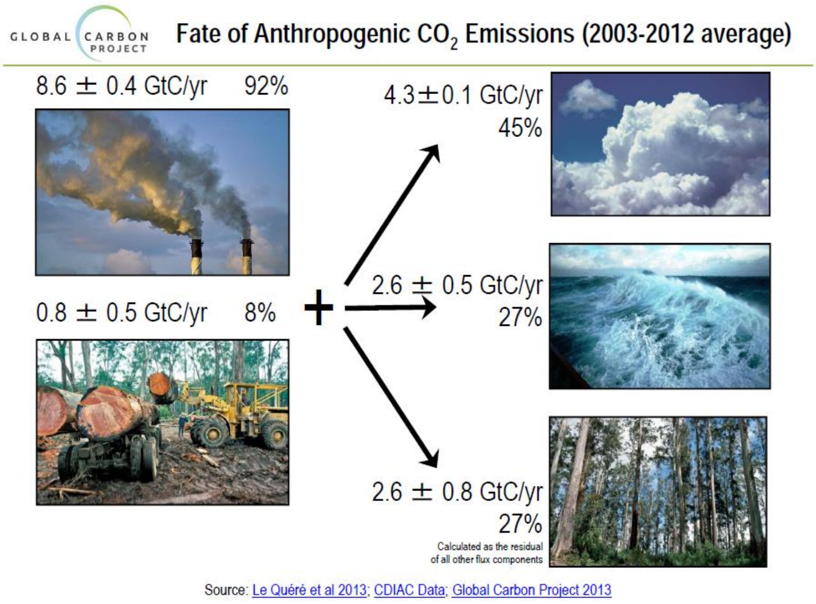

Figura 1: Emisiones antropogénicas de CO_2 (a partir de Le Quéré et al., 2013)

La cantidad de CO_2 disuelta en agua de mar se describe generalmente a través del equilibrio del CO_2 entre el aire y el agua. El CO_2 en agua de mar se mide y se presenta a través de su presión parcial en la superficie (de forma más precisa se debe utilizar expresado como fugacidad o fCO_2). El intercambio o flujo de CO_2 entre el aire y el agua superficial se puede calcular a partir de la diferencia entre ambas fases junto con medidas de la temperatura del agua de mar, la salinidad y la velocidad del viento. El flujo se ve afectado por procesos físicos y biogeoquímicos que varían ambos de manera temporal y espacial. Al igual que las variaciones en temperatura y viento, el flujo de CO_2 se puede ver afectado por advección y por la circulación termohalina de larga escala en los océanos. El flujo de CO_2 también se ve afectado por la incorporación biológica debido a los cambios en la disponibilidad de nutrientes y luz.

Existen tres mecanismos principales que afectan la incorporación de CO_2 in los océanos: la bomba física o de solubilidad; la bomba biológica o del carbono orgánico y la contrabomba de carbonatos (Heinze et al., 1991). La influencia de las tres cambia temporalmente y espacialmente a lo largo de los océanos, como así se muestra en la estimación a escala global del mapa de flujo de CO_2 (Figura 2), que presenta regiones con grandes y pequeñas incorporaciones anuales de CO_2. Por ejemplo, el Atlántico Norte, productivo, tiene una incorporación anual particularmente importante de CO_2.

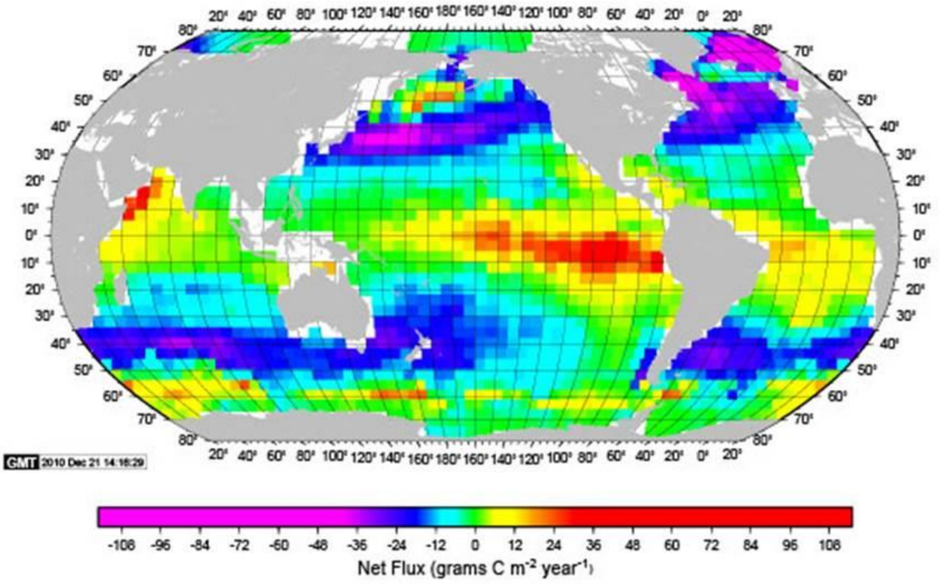

Figura 2: Valores medios climatológicos de flujo de CO_2 en una malla de 4° Latitud por 5° Longitud. Publicado por Takahashi, et al. (2009)

La bomba física o de solubilidad describe los procesos físicos que afectan a la cantidad de CO_2 disuelto en la columna de agua, que es mucho más soluble a bajas temperaturas. El flujo termodinámico de CO_2 hacia o desde el agua superficial (Figura 2) es debido a la diferencia entre los valores de pCO_2 entre el agua y la atmósfera. Se ve afectado por el coeficiente de transferencia ‘k’, que se base en formulaciones dependientes de la velocidad del viento (ej.: Nightingale et al., 2000) incluyendo el número de Schmidt que depende de la temperatura (ej.: Wanninkhof, 1992 y la revisión Wanninkhof, 2014).

La bomba de carbono orgánica se refiere a la rápida eliminación de CO_2 del agua a través de la producción primaria (PP), es decir, a través de la síntesis de compuestos orgánicos a partir de dióxido de carbono y nutrientes gracias a la fotosíntesis. Este proceso es seguido, a su vez, por una lenta compensación de un flujo de CO_2 hacia los océanos. La bomba orgánica tiene un importante impacto en el ciclo del carbono global oceánico ya que favorece la incorporación de CO_2 desde la atmósfera que se convierte en material orgánica (McGillicuddy et al., 1998). La eliminación de carbono y nutrientes en el océano se muestra en la siguiente ecuación (Anderson et al., 1995) que describe la fotosíntesis y el proceso inverso de la remineralización. El ratio atómico (o estequiometría) del carbono, nitrógeno, fósforo y oxígeno se deriva de la misma. Se conoce como la relación de Redfield (Redfield et al., 1963), que se cumple ampliamente en el fitoplancton y en los océanos profundos.

$$106\ CO_2 + 16\ HNO_3^- + H_3PO_4 + 78\ H_20 = C_{106}H_{175}O_{42}N_{16}P + 150\ O_2$$

dióxido de carbono + nitrato + fosfato + agua = carbohidratos + oxígeno

La PP produce una reducción del CO_2 superficial y de nutrientes y se produce ampliamente en el océano superficial eufótico, (donde la atenuación de la luz solar va desde ~1 hasta el ~10% del total superficial; Mackey et al., 1995). El CO_2 y los nutrientes forman material orgánico y una porción de la misma se exporta fuera de la capa fótica. La materia orgánica es remineralizada en aguas más profundas y produce un aumento con la profundidad de nutrientes y carbono inorgánico disuelto (DIC). Una parte de esos compuestos vuelven a la superficie a través de procesos de mezcla y en los afloramientos, los cuales favorecen de nuevo la producción. El DIC es la suma de las formas de las especies de carbono inorgánico y se corresponde aproximadamente con un 90% de bicarbonato y un 8% de carbonato.

El CO_2 es un gas muy soluble (comparado con el oxígeno), reacciona con el agua de mar para formar ácido carbónico (Figura 3), que se disocia rápidamente para formar bicarbonato (HCO_3^-), carbonato (CO_3^{2-}) e iones hidronio (H^+). La reacción se muestra en la Figura 3.

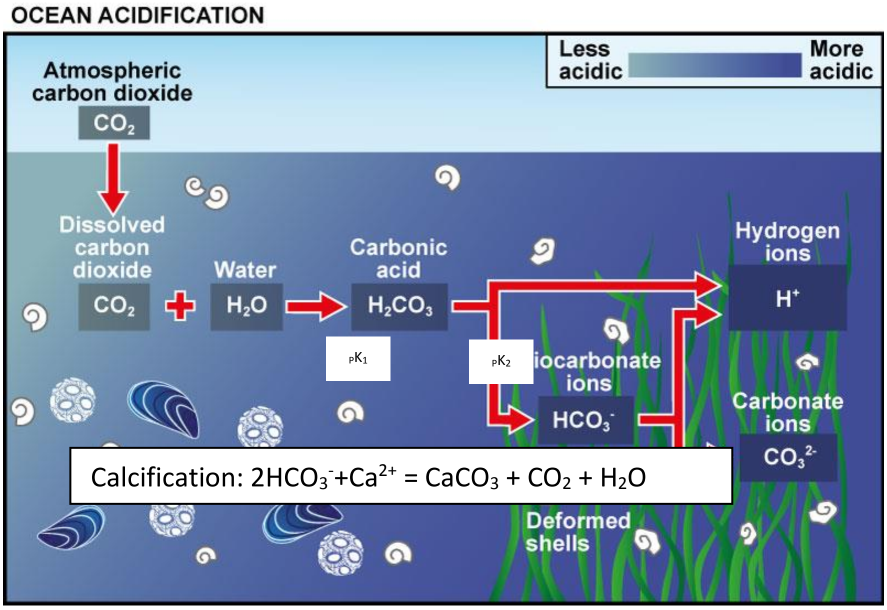

Figura 3: Ilustración esquemática del sistema del carbonato en los océanos incluyendo las reacciones reversibles y las constantes de disociación, que producen la acidificación oceánica (adaptado de una gráfica de la University of Maryland, www.oceanacidification.org.uk) y la ecuación de calcificación.

El aumento del CO_2 en el agua sigue el incremento de la concentración de CO_2 atmosférico que está modificando el balance de equilibrio del sistema del carbonato (Figura 3). La calcificación libera CO_2, por lo que esta bomba tiene un efecto opuesto al de la bomba orgánica y es conocida como la contra-bomba de los carbonatos. La calcificación se relaciona con la incorporación de bicarbonato por parte de los cocolitofóridos y otros grupos de organismos que crean conchas de carbonato cálcico. La ecuación de calcificación se muestra superpuesta en la Figura 3.

Los océanos son actualmente ligeramente alcalinos (~pH 8.1, donde el pH se define como el logaritmo negativo de la concentración de iones hidrógeno), pero el incremento de la incorporación de CO_2 y de concentración de iones hidrógeno en el agua de mar está produciendo una disminución en el pH oceánico, conocido como proceso de acidificación oceánica (OA). Existen muchos estudios que muestran el impacto potencial de la OA en detrimento de la calcificación (ej.:

Riebesell et al., 2011; Smith et al., 2012; Schermer et al., 2016).

Las tendencias en el pH oceánico (y en CO_2) se han detectado en las posiciones de las estaciones de series temporales oceánicas tal como la estación ALOHA cerca de Hawaii (http://aco-ssds.soest.hawaii.edu/ALOHA). Los datos de ALOHA (Figura 4) muestran un gran aumento del CO_2 marino y su asociada disminución en el pH a lo largo de un periodo de 20 años. Existe además una gran variación estacional, que hace necesario medidas a lo largo de todo el año. La tendencia observada es de una disminución de 0.002 unidades de pH por año y una disminución de hasta 0.5 unidades de pH hacia finales del siglo XXI (Bates et al., 2014). El trabajo de Bates et al., (2014) incluye tendencias en las series temporales oceánicas del Atlántico Norte en Bermuda (BATS) y en las Islas Canarias (ESTOC).

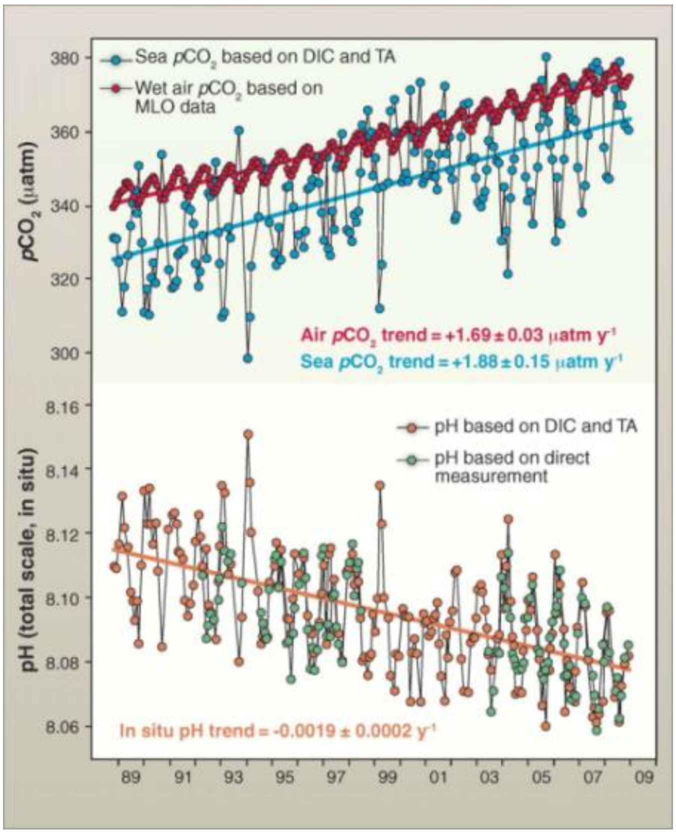

Figura 4: Datos de la estación de series temporales ALOHA, mostrando el aumento de CO_2 tanto en la atmósfera como en el agua de mar, con la correspondiente disminución en el pH oceánico.

Los cambios en el pH pueden no ser directamente proporcionales al aumento en el CO_2 ya que otras características de las masas de agua se ven afectadas, tales como la alcalinidad. La alcalinidad es la habilidad del agua de mar para neutralizar a los protones (H^+), por lo que suministra una medida de la capacidad tamponante hacia el cambio en el pH. La alcalinidad total (TA) se define como el número de moles de ion hidrógeno equivalente al exceso de aceptores de protones (bases formadas a partir de los ácidos débiles) sobre los donadores de protones que hay en 1 Kg de agua de mar. TA se relaciona con la concentración de iones bicarbonato y carbonato en el agua de mar, con una menor contribución de otros aceptores tales como el ácido bórico, fosfato y silicato. El valor de la alcalinidad determinará el cambio potencial del pH por la adición de CO_2. Por este motivo si el DIC aumenta más rápido que la TA entonces el pH disminuirá**.** El proceso de calcificación elimina el DIC superficial, que a su vez aumenta con la profundidad (Heinze et al., 1991) con la disolución de carbonato cálcico en las aguas profundas, aumentando así a la alcalinidad del sistema. Los mapas globales de alcalinidad superficial (Carter et al., 2014; Fry et al., 2015) revelan un aumento de la alcalinidad hacia los polos. Su distribución se ve afectado por los procesos físicos y biogeoquímicos, pero es independiente de la disolución de CO_2.

Los procesos competitivos de calcificación y disolución de carbonato, incorporación y eliminación de CO_2, fotosíntesis y respiración y sus efectos en DIC, TA y pH se resumen en la Figura 5.

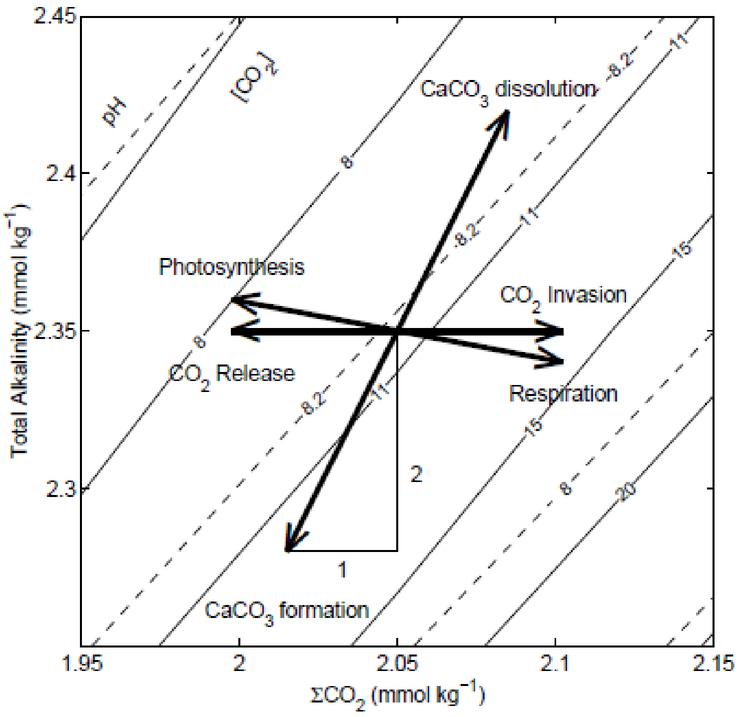

Figura 5: Esquema de la alcalinidad total y de la suma de las especies de carbonato (DIC, ΣCO_2), con contornos de CO_2 (líneas continuas) y pH (líneas discontinuas), mostrando los procesos competitivos actuando en las cuatro variables (Después de Zeebe & Wolf-Gladrow, 2001).

Parte del CO_2 tomado por los océanos y por la formación de material orgánica se recicla en la columna de agua. Además, parte de la materia orgánica se hunde y de esta manera el carbono se secuestra en profundidad. El Atlántico Norte es una región importante del estudio de la incorporación de CO_2 por los océanos al ser un importante reservorio de carbono antropogénico (Khatiwala et al., 2013). Alrededor de un 38% del carbono antropogénico se encuentra almacenado en el Atlántico Norte (Sabine et al., 2004). Estos grandes inventarios se encuentran recogidos en el mapa de la Figura 6 y son consecuencia directa de la formación de masas de agua profunda en el Atlántico Norte.

A pesar del aumento en las observaciones, las variaciones temporales y regional en los parámetros del sistema del carbonato superficial (también en el conocimiento de sus controles físicos y biogeoquímicos) se conocen muy poco (Steinberg et al., 2001; Wanninkhof et al., 2013). Hay una gran necesidad de medir la variabilidad biogeoquímica en los océanos y comprender las relaciones entre las diferentes partes de los ciclos del carbono y de los nutrientes para poder realizar cualquier predicción futura de potencial incorporador del CO_2 por los océanos.

Esta tesis se centra en los ciclos del carbono y nutrientes y por qué son importantes. Cuatro de sus capítulos se centran en una serie temporal oceánica en el Atlántico Norte, el Observatorio situado en la platafroma abisal Porcupine (PAP-SO). El primero presenta las medidas realizadas en PAP-SO, centrándonos en su hecho inicial y contexto, así como en los métodos de medida. Los siguientes dos capítulos presentan ya resultados de las medidas estacionales y de variabilidad interanual en la biogeoquímica superficial. El cuarto capítulo caracteriza la influencia de los procesos más profundos y críticos de la columna de agua para el almacenamiento a larga escala. Los datos de PAP-SO se suplementan con otras fuentes que también se describen en este capítulo. Los resultados se resumen mostrando los principales hechos y poniéndolos en un contexto mucho más global. Con una comparación regional en mente, el capítulo Quinto considera datos biogeoquímicos de dentro y fuera de la plataforma oceánica utilizando una serie temporal obtenida a través de un buque de oportunidades entre UK y España. El capítulo final considera los datos de PAP-SO en relación con datos biogeoquímicos en la zona Noroeste de la plataforma oceánica europea.

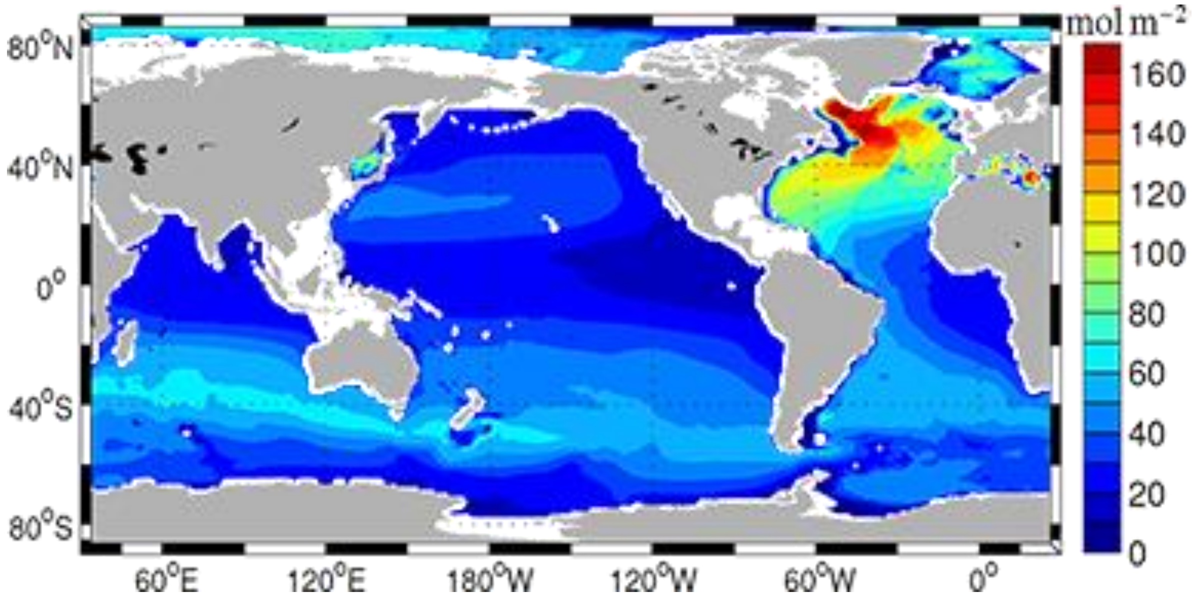

Figura 6: Contenidos de carbono antropogénico en la columna oceánica mostrando la importante incorporación de CO_2 en el Océano Atlántico Norte. (Fuente: Khatiwala et al., 2013).

Carbono oceánico y ciclo de los nutrientes en el Atlántico Norte

La producción primaria (PP) depende de la luz, nutrientes y pastaje en las latitudes templadas consideradas en este estudio. La luz se ve limitada en invierno (y con la profundidad) por lo que la luz y la temperatura controlan el ciclo diario y estacional del CO_2 y su incorporación a través de la fotosíntesis. La hipótesis clásica del desarrollo del florecimiento en el Atlántico

Norte (Sverdrup, 1953) es que la entrada de calor en primavera produce la estratificación de la columna de agua. El desarrollo del florecimiento tiene entonces lugar en esa agua estratificada cuando hay suficiente luz y nutrientes. El florecimiento primaveral ocurre al disminuir la profundidad de la capa de mezcla hasta un punto en el que la producción es mayor que la respiración. Como la productividad tiene lugar con una disminución de nutrientes, hace que el crecimiento se limite hasta que esos nutrientes vuelvan a entrar de nuevo en la superficie en otoño. La profundidad crítica es el límite de la zona productiva producida entre el balance de la penetración de la luz y la mezcla vertical, cuantificado inicialmente por Sverdrup (1953), y reformulada por Nelson & Smith (1991). Existen otras muchas hipótesis sobre la formación del florecimiento, ya que estos pueden producirse bajo la ausencia de estratificación (Townsend et al., 1992). Por ejemplo, la hipótesis de la turbulencia crítica (Huisman et al., 1999) sugiere que ésta se puede producir cuando la mezcla convectiva se reduce lo suficiente. Otro ejemplo es dado por Behrenfeld (2010), que sugiere que el desacople entre el fitoplancton y el micro-zooplancton después del invierno puede resultar en un crecimiento neto fitoplanctónico a través de una reducción en el pastaje.

Conforme el florecimiento primaveral continua, los nutrientes son usados y llegan a limitar el crecimiento, aunque algunos procesos tormentosos pueden favorecer su incorporación y posterior utilización (Rumyantseva et al., 2015). De los nutrientes mayoritarios, el nitrato (NO_3) es uno de los medidos ya que limita el crecimiento fitoplanctónico en muchas regiones de los océanos superficiales. Globalmente hasta un 75% de la superficie de los océanos está limitada por nitrato (Duce at al., 2008). El crecimiento de algunas especies se puede favorecer por el incremento de CO2 (Riebesell et al., 2011), pero el carbono no limita el crecimiento de los organismos fotosintetizadores.

La producción primaria se puede estimar a través de imágenes de sensores satelitales (Falkowski et al., 1998). Sin embargo, después del periodo inicial de florecimiento se desarrolla un máximo en la concentración de clorofila debajo de la superficie, generalmente entre la termoclina y la nutriclina alrededor del 1% en el nivel de penetración de la luz. Este máximo subsuperficial de clorofila se produce en las regiones templadas y se conoce como máximo de clorofila profundo (DCM). Las causas, el tiempo y localización del DCM varía ampliamente (Cullen, 1982). La aparición del DCM significa que las técnicas de sensores remotos no podrán detectar toda la clorofila, por lo que, para conseguir una estimación correcta de la productividad, se necesitan medidas in situ subsuperficiales del contenido de clorofila.

Desde un punto de vista del ciclo del carbono oceánico, la medida de la productividad se puede relacionar mejor con el sistema del carbonato a través de la producción comunitaria neta (NCP). NCP es la suma de la producción nueva y regenerada, donde la producción nueva es la estimada considerando los cambios en la concentración de nitrato (Dugdale & Goering, 1967). La producción nueva se sustenta en la entrada de nitrato en la capa fótica a través del afloramiento y mezcla horizontal, así como por procesos de deposición atmosférica y de fijación de nitrógeno (Gruber, 2009; Sarmiento & Gruber, 2006). El crecimiento de autótrofos o productividad se puede determinar a través de la incorporación neta de nutrientes o de DIC (Bargeron et al., 2005) o por el aumento de oxígeno disuelto (Ostle et al., 2015) en la zona fótica. NCP representa al carbono orgánico (tanto particulado como disuelto) disponible de ser exportado fuera de la zona fótica o ser utilizado por niveles tróficos superiores. Sobre una base anual, asumiendo que el sistema está en estado estacionario, la producción exportada se considera equivalente a la producción nueva (Eppley & Peterson, 1979).

Para calcular la producción nueva a partir del flujo anual de nitrato (Eppley & Peterson, 1979; Henson et al., 2003) se debe convertir en unidades de carbono. Esa conversión se realiza en base a la ratio de Redfield (Redfield et al., 1963), que es considerado una variable clave en la biogeoquímica marina (Falkowski et al., 2000). En particular la ratio de Redfield C:N es una constante importante utilizada en muchos modelos que relacionan la capacidad de incorporar carbono a unidades de nitrógeno en los océanos. Muchos estudios recientes sugieren, no obstante, que esta ratio no es constante, aunque exista un gran consenso de que es relativamente constante a nivel global (Sterner et al., 2008). En los océanos abiertos, se suele asumir un valor medio de 6.6 para la ratio C:N (Redfield et al., 1963) para los cálculos de la producción nueva.

La ratio Redfield suele variar con la región y profundidad (Sterner et al., 2008). Los cambios en la relación C:N se pueden deber a muchos factores tales como la forma de los nutrientes, la intensidad de la luz y la composición de las especies. Estos factores se pueden controlar a escala de laboratorio, pero en el medio natural existe una mezcla heterogénea y de esta manera existen muchos estudios que muestras valores C:N mayores que el dado por Redfield. Por ejemplo, la relación C:N varía con los niveles de luz y ello puede producir un aumento en su valor observado desde primavera a verano en las latitudes norte (Bates at al., 2005). Valores altos de C:N pueden ser debido a una mayor eliminación de DIC y una mineralización preferente de material orgánico rico en carbono, conocido como sobreconsumo de carbono (Sambrotto et al., 1993). Los sistemas costeros tienden a eliminar CO_2 hacia la atmósfera debido a la composición estequiométrica elemental C:N de la descomposición de la materia orgánica terrestre con respecto a la producida en medios marinos. El material orgánico traído a las costas desde los ríos tiene un alto C:N (30:1) mientras que la materia orgánica producida por el fitoplancton en los sistemas costeros tiene un C:N cercano a 7:1 (Bauer et al., 2013).

El Atlántico Noreste

La circulación general en el Atlántico Noreste está dominada por la extensión en dirección noreste de la corriente del golfo, conocida como Corriente Noratlántica (NAC). La NAC es una importante corriente en la advección y transporte de agua superficial relativamente cálida, rica en nutrientes y en oxígeno hacia las costas europeas (Williams et al., 2011). La NAC también marca el límite entre el gripo Subpolar (SPG) y el Subtropical (STG) en torno a 40°N. La posición del NAC varía de año a año en el Noratlántico templado. La posición aproximada se muestra en el mapa de la Figura 7.

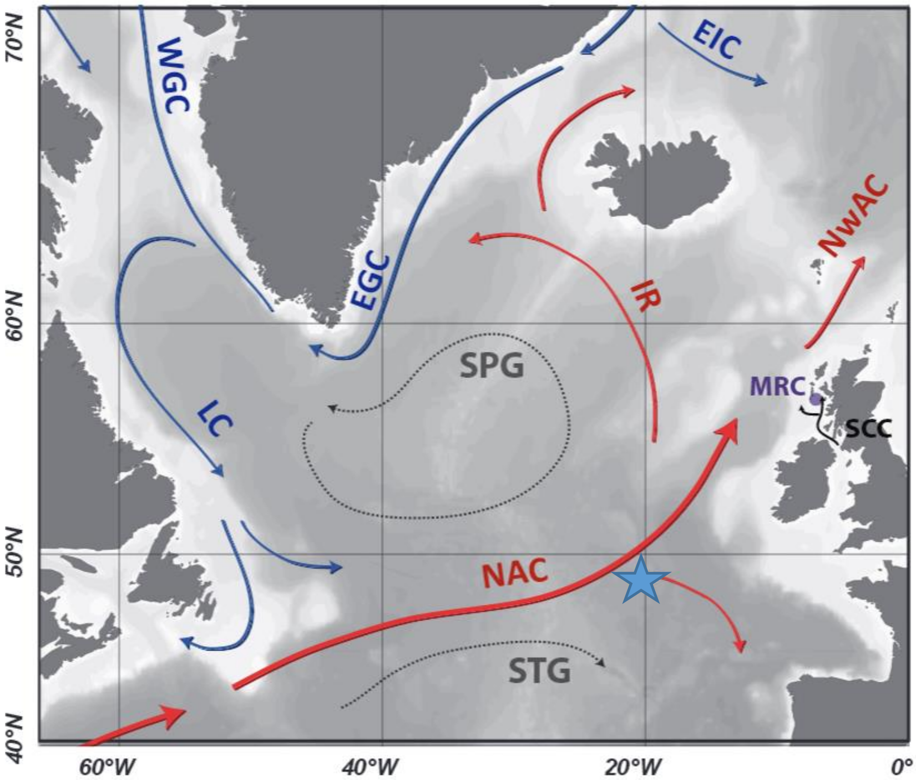

Figura 7: Circulación superficial en el Noratlántico mostrando cómo se encuentran y mezclan las aguas subpolares y subtropicales (SPG y STG) y retroalimentan la corriente noratlántica (NAC). Las flechas rojas muestran la posición media de las aguas cálidas y salinas de la corriente noratlántica. Las líneas azules muestran las aguas más frías y menos salinas de la corriente este de Groenlandia (EGC) y la corriente del Labrador (LC). La estrella azul muestra la posición de la estación PAP-SO. Adaptado de Dourarin et al., 2016 quien utilizó el mapa para ilustrar el MRC (Complejo Mingulay Reef) y el SCC (corriente costera de Escocia) en las costas noroestes europeas, que no se consideran en este estudio.

La variación estacional en los valores de pCO_2 en agua de mar difieren entre localizaciones en el Atlántico (Bates et al., 2014), ya que el calentamiento y enfriamiento de las aguas afecta a la solubilidad del CO_2. Las aguas cálidas superficiales tienen una capacidad menor para disolver el CO_2 mientras que el enfriamiento eleva esa solubilidad y favorece su absorción. La posterior incorporación biológica, el intercambio de gases atmósfera-océano y la cantidad de CO_2 suministrado por los procesos de afloramiento y mezcla con aguas más profundas alterarán posteriormente esos procesos (Takahashi et al., 2014).

En el giro oligotrófico Subtropical (STG) la columna de agua superficial está permanentemente estratificada por lo que la productividad anual es menor y menos variable estacionalmente. Los nutrientes y DIC se suministran a las aguas productivas superficiales a través de bombeo por giros y procesos convectivos. La convección de invierno es importante en el este del STG; mientras que el bombeo por giros es más importante como fuente de nitrato a las aguas superficiales en oeste del STG (Cianca et al., 2007). El ciclo estacional del pCO_2 en agua de mar en el STG viene dominado por la temperatura, con un máximo único en verano y un mínimo en invierno (Bates et al., 1996; González-Dávila et al., 2003). En general, el STG es un pequeño sumidero de carbono e incluso una ligera Fuente de CO_2 (McKinley et al., 2016).

En el SPG, el ciclo estacional de nutrientes y carbono están controlados por el fuerte ciclo estacional de la mezcla de aguas profundas y de la producción primaria. La convección produce un aumento en el suministro de nutrientes y DIC hacia la superficie en el invierno; a continuación, se produce una disminución en primavera debido al desarrollo del florecimiento primaveral. El SPG es productivo unos 7 meses al año (Ostle et al., 2015) donde el CO_2 es incorporado a través de la fotosíntesis en la producción de material orgánica.

Existe una alta solubilidad de CO_2 en el SPG debido a la menor temperatura superficial (SST) y la importante intensidad de la mezcla de invierno. El control dominante en la distribución espacial de DIC es la temperatura superficial, pero el nitrato juega también un papel esencial debido a su relación con la incorporación biológica y procesos de afloramiento. El DIC y los nutrientes tiendan a covariar y muestran un comportamiento estacional predecible, por lo que la relación entre SST y nitrato se puede utilizar para describir la distribución global del DIC superficial (Lee et al., 2000).

La región del Atlántico noreste es importante en el ciclo del carbono y es un importante sumidero de CO_2 con acumulación de carbono antropogénico en las profundidades. El Atlántico noreste subpolar es un sumidero de CO_2 aunque la cantidad de CO_2 tomada por los océanos varía, debido a la variación de la mezcla y la productividad del océano (Schuster & Watson, 2007). Por ello, es esencial que los procesos que pueden afectar a esa variación sean estudiados para conocer el futuro de capacidad de los océanos para incorporar CO_2.

Importancia del cambio climático

Los cambios en la cantidad de CO_2 absorbido por los océanos tiene implicaciones en el ciclo global del carbono y en el papel de los océanos como sumideros en el futuro. Existen diferentes procesos en el sistema del carbono que hacen complejo el predecir esos efectos. Por ejemplo, el aumento en la estratificación de la columna de agua esperada en un océano más cálido potencialmente disminuiría el suministro de nitrato a la superficie, así como una disminución en la PP y en la consecuente incorporación de CO_2 (Duce et al., 2008; Behrenfeld et al., 2010). Cambios en la entrada de CO_2 afectará a la tendencia futura en acidificación. Igualmente, la transferencia de CO_2 hacia la formación de materia orgánica y hacia aguas más profundas disminuiría con una mayor estratificación. Como el STG se expande (Henson et al., 2009), el escenario futuro del Atlántico Noreste puede ser una disminución en la productividad de la misma. Esas variaciones en la productividad afectarán la distribución de zooplancton y consecuentemente la dinámica de los organismos superiores (Henson et al., 2009).

La oscilación del Atlántico norte (NAO) es el modo dominante en la variación de la presión en el Atlántico Norte (Marshall et al., 2001). El NAO se utiliza como un indicador de la variabilidad atmosférica en el hemisferio norte (Osborn et al., 1999) y se suele expresar en función de sus valores en invierno. El NAO es un indicador de la variabilidad en el Atlántico Norte ya que afecta la hidrografía superficial (Schuster & Watson, 2007) y se ha relacionado con cambios en el suministro de nutrientes hacia las aguas superficiales (Cianca et al., 2007). Un NAO elevado produce condiciones más cálidas y húmedas en el norte de Europa y más secas en el sur y una mayor profundidad en la capa de mezcla en el giro subpolar (Cullen et al., 2001; Jiang et al., 2013). Se ha sugerido que hay una tendencia a disminuir en el NAO a lo largo de este siglo (Osborn et al., 1999). La disminución en la mezcla de invierno (bajo NAO) implicaría una mayor estratificación y una barrera al intercambio de nutrientes y una correspondiente disminución en productividad.

El NAO también es un indicador importante de la variabilidad interanual en el flujo de CO_2. El cambio de valores negativos a positivos en el NAO se ha asociado con una disminución en los valores de pCO_2 superficial en el giro subtropical (Watson et al., 2009). El detectar la influencia del NAO debe considerar que a menudo existe un retardo en la observación de los efectos debido al tiempo que toma la advección de las masas de agua y que depende también de dónde son realizadas las medidas. Por ejemplo, en la estación ESTOC la respuesta oceánica es retardada 3 años relativa al cambio en el NAO, si bien esa respuesta está más directamente relacionada con otro indicador climático, el comportamiento del Atlántico Este (González-Dávila et al., 2007; Santana-Casiano et al., 2007).

Henson et al., (2009) mostraron una variabilidad decadal en la aparición del florecimiento del Atlántico Noreste entre 1959 y 2004. Sin embargo, no se observaba una tendencia en la productividad que se pudiera relacionar con el cambio climático. Henson et al., (2009) identificaron una zona de transición entre el SPG y el STG donde había una gran variabilidad en el tiempo de aparición del florecimiento primaveral (ver Figura 8). Una fase positiva NAO se asociaba con una expansión del SPG, cuando la zona de transición se desplazaba al sur resultando en un retardo en el florecimiento. En una fase negativa NAO la zona de transición se desplazaba al norte y el florecimiento primaveral comenzaba antes. Un cambio en esa zona de transición tendría consecuencias para el periodo de incorporación de CO_2 en dicha región del Atlántico Noreste.

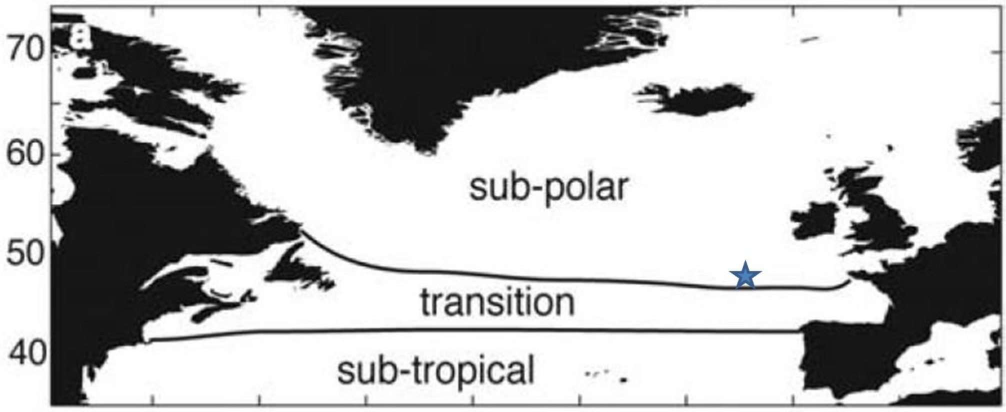

Figura 8: Posición de la estación PAP-SO (mostrada como una estrella) con respecto a las condiciones medias de las posiciones del SPG, STG y la zona de transición (según Henson et al., 2009).

Técnicas de medida

Para predecir los efectos de los estresores antropogénicos y de cambio climático se requiere el conocimiento del papel de los océanos en el ciclo global del carbono (Steinberg et al., 2001). Son de especial importancia los estudios del control físico y biológico del CO_2 *in situ*. Esto requiere medidas a larga escala, alta resolución en las observaciones de nutrientes y carbono para poder caracterizar la variabilidad natural y cuantificar las perturbaciones y tendencia que puedan ser debidas a cambios globales.

Algunos de los parámetros oceanográficos comunes mas medidos además de la salinidad y temperatura son el oxígeno disuelto y los nutrientes inorgánicos. El oxígeno disuelto (DO) es la cantidad de oxígeno contenida en un volumen de agua y depende de la temperatura y del balance entre la producción primaria y la respiración. El oxígeno entra en las aguas superficiales oceánicas a través de difusión desde la atmósfera o es producido *in situ* por los organismos fotosintetizadores (fotosíntesis) y es eliminado por respiración. El oxígeno en agua de mar se puede medir en laboratorio utilizando Winkler (Dickson, 1994) o con sensores *in situ* (ej.: Hydes et al., 2009).

Los nutrientes mayoritarios son los nitritos y nitratos (NO_2^- y NO_3^-, juntos por lo general indicados como nitrato), fosfatos y silicatos. Se miden utilizando un autoanalizador en el laboratorio con técnicas colorimétricas (ej.: Grasshoff, 1976). Autoanalizadores miniaturizados y sensores para la medida *in situ* de nutrientes han comenzado a desarrollarse en los últimos años (ej.: Johnson et al., 2009).

Las cuatro variables del sistema del carbonato se pueden medir: DIC, alcalinidad total (TA), pH y CO_2. El sistema de carbonato se puede caracterizar mediante la medida de dos de ellas utilizando la herramienta CO_2SYS (Lewis et al., 1998). El CO_2SYS se puede utilizar con las constantes de disociación apropiadas (Dickson & Millero, 1987; Dickson, 1990). Cualquier error en las medias e incertidumbre en las constantes de disociación se propagarán en esos cálculos con lo que se aumenta la incertidumbre en los datos obtenidos. Aunque existe un conocimiento de esos errores en los cálculos (Lee et al., 1997) algunas parejas de variables poseen menores errores asociados que otros (Ribas-Ribas et al., 2014). Para esos cálculos, el disponer de datos de salinidad, temperatura y nutrientes mayoritarios es vital.

Carbono Inorgánico Disuelto (DIC, C_T) es la suma de la concentración del CO_2 disuelto, bicarbonato (HCO_3) y carbonato (CO_3). El DIC muestra los cambios en el contenido de carbono y es independiente de la presión y temperatura.

Alcalinidad Total (TA, TALK, AT) se define como el número de moles de protones H^+ equivalente al exceso de aceptores de protones en un kilo de muestra e indica la habilidad del agua de mar para neutralizar protones (H^+), su 'capacidad buffer'. En el océano abierto, la alcalinidad se considera que es un parámetro casi-conservativo ya que se ve influenciado por los mismos procesos que la salinidad a través de la evaporación, precipitación y mezcla (Lee et al., 2006), aunque la alcalinidad también se ve afectada por la fotosíntesis y la remineralización. La salinidad del océano abierto se puede utilizar para predecir la TA utilizando relaciones lineales entre la TA y la salinidad, que se definen a nivel regional (Lee et al., 2006).

pH es la medida de la acidez o basicidad de una disolución y es definida como el logaritmo en base 10 cambiado de signo de la concentración de ion hidrógeno de una disolución. El pH se expresa en diferentes escalas válidas en agua de mar como la escala de protones totales, la escala de agua de mar y la escala libre (Schuster et al., 2009). El pH no es independiente de los cambios en la temperatura y en la presión.

Dióxido de Carbono (CO_2), se disuelve en los océanos para formar ácido carbónico (H_2CO_3), bicarbonato (HCO_3^-) y carbonato (CO_3^{2-}) como se muestra en la Figura 3. La concentración de CO_2 en agua de mar se expresa como la presión parcial (pCO_2) que cambia con la temperatura y la presión. Las medidas de pCO_2 no consideran su comportamiento no ideal del gas en agua de mar a la presión atmosférica por lo que es necesario calcular su valor real expresado como fugacidad (fCO_2). De esta manera, fCO_2 es la presión parcial del CO_2 (pCO_2) corregida por el comportamiento no ideal del gas (Bakker et al., 2013; Pfeil et al., 2012).

Actualmente las medidas de DIC y TA se realizan en laboratorio (Mintrop, 2010), mientras que sólo las de pH y CO_2 se pueden realizar con el uso de sensores (Johnson et al., 2009; Fiedler et al., 2013).

Plataformas de medidas

Los programas de monitorización de larga duración son necesarios para detectar tendencias en estas variables, pero el desarrollo de sensores biogeoquímicos *in situ* son aún un reto. Se trata de un ambiente hostil (ej. remoto, oscuro, corrosivo) y caracterizado por un gran rango de temperatura y presión. A todo esto, hay que unir el requerimiento de un alto nivel de precisión y exactitud en periodos largos de tiempo (Mowlem et al., 2008).

Las técnicas remotas satelitales pueden suministrar estimaciones en grandes áreas para muchas variables, tales como la temperatura superficial del agua, salinidad y producción primaria. Se basan en algoritmos derivados de medidas *in situ,* aunque muchas variables aún no se pueden estimar de las medidas satelitales.

Hay pocas restricciones a los tipos de variables que se pueden analizar a bordo de buques oceanográficos o en laboratorios en tierra siguiendo el muestreo *in situ* y preservación. Los estudios de procesos a partir de investigación en buques se pueden centrar en escalas regional o grandes cuencas, existiendo gran número de ejemplos de estudios que muestran la variación temporal y espacial de CO_2 (ej.: Sabine et al., 2002; Bates et al., 2006; Clargo et al., 2015). Actualmente hay grandes esfuerzos por reunir bases de datos de décadas de cruceros que consideran perfiles profundos dentro de proyectos como Carina (CARbon dioxide IN the Atlantic Ocean, dióxido de carbono en el Océano Atlántico) y GLODAP (Global Ocean Data Analysis Project, proyecto para el análisis de datos oceánicos globales) (ej.: Key et al. 2004 y 2010). La repetición de secciones oceánicas también ofrece la posibilidad de crear series temporales de grandes cuencas oceánicas. La ocupación anual de la línea Ellet en el Atlántico Noreste ha suministrado ocho años de medidas de carbono en toda la columna de agua y el cálculo de la incorporación de carbono antropogénico. (Humphreys et al., 2016).

Los barcos de oportunidades (SOOs) (VOS) son efectivos para suministrar medidas superficiales si mantienen rutas repetitivas, todo el año (Hydes et al., 2003). Cuando el SOO es un ferry el paquete de sensores a bordo se suele definir como ‘Ferry-Box’. Un ejemplo era la ruta UK-España en el buque *Pride of Bilbao* (P&O ferry) que tuvo un Ferry-Box durante 8 años (Jiang et al., 2013). Las medidas *in situ* en un SOO se pueden comparar con medidas estándares y muestreo para asegurar su calidad. Existe un gran esfuerzo para reunir esos datos de dióxido de carbono de las líneas VOS con control de calidad en bases tales como SOCAT (Atlas de CO_2 superficial oceánico; Bakker et al. 2014; Pfeil et al. 2012). Por ejemplo, la ruta entre UK y el Caribe recorre el Atlántico mensualmente al que se une medidas de muestras puntuales para asegurar la validez de las mismas (Hartman et al., 2010a). Los resultados de esta línea han identificado la variabilidad interanual en la incorporación de dióxido de carbono en el Atlántico norte (Schuster & Watson et al., 2007).

Los perfiladores Argo cubren grandes regiones de los océanos y tienen la ventaja de proporcionar perfiles de profundidad. Argos con medidas biogeoquímicas (ej.: Johnson et al., 2009; Fiedler et al., 2013; Hemsley et al., 2015) son aún escasos comparados con los de medidas hidrográficas, especialmente cuando los sensores son grandes y con altos requerimientos de potencia eléctrica (Henson et al., 2016).

Los fondeos de océano abierto suministran datos de alta resolución en un punto oceánico. Se pueden reunir en grandes redes como es el caso de la red Neptuno de Canadá, donde estos fondeos son cableados para suministrar potencia y que no exista restricciones en el tamaño o potencia de los mismos (Barnes et al., 2008). En Europa, la iniciativa FixO3 (Lampitt et al. 2014; www.fix03.eu) incorpora los sitios de series temporales en una red de fondeos de océano abierto e incluye medidas biogeoquímicas, estandarizando medidas y procedimientos. A escala global, ‘Oceansites’ (Send et al., 2010; www.oceansites.org) es la red mundial de fondeos oceánicos. Teniendo en cuenta las características propias de cada sitio (y para cada variable biogeoquímica) esta red representa entre el 9% y el 15% de la superficie global oceánica (Henson et al., 2016). El mapa de la Figura 9 muestra los observatorios que tiene (o planean) tener medidas biogeoquímicas.

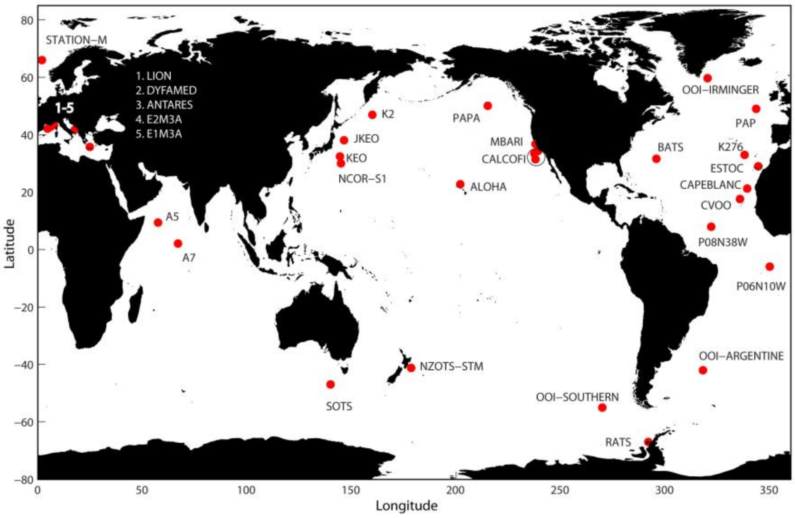

Figura 9: Localización de observatorios con componentes biogeoquímicos, incluyendo plataformas actuales y planificadas (a partir de Henson et al., 2016).

La serie temporal en la plataforma abisal Porcupine

El trabajo de esta tesis se centra en el observatorio de la plataforma abisal Porcupine (PAP-SO). PAP-SO es una serie temporal en las aguas templadas del Atlántico Noreste y es parte tanto de 'Oceansites' como de la red europea FixO3. PAP–SO es una serie temporal multidisciplinar de océano abierto en el Noreste Atlántico Subpolar (49°N, 16.5°W) con una profundidad de 4800 m, donde se han realizado medidas *in situ* desde finales de los 80. PAP-SO es un punto especial para estudiar las conexiones entre la superficie y el océano profundo. PAP-SO posee datos de series temporales de relevancia climática y medioambiental desde la columna de agua hasta el mismo fondo oceánico. Antes de 2003, las medidas biogeoquímicas se realizaban a partir de muestreo discretos tanto en el sitio PAP como en la estación JGOFS cercana localizada a 47°N, 20°W (Lochte et al., 1993; Lampitt et al., 2010). El fondeo se estableció desde 2002, con una boya superficial añadida en el 2007. En 2010 y en colaboración con el Centro Británico de Investigación del Medioambiente Natural (NERC) y de la oficina Meteorológica, la estructura se rediseño y se fondeó el 1 de junio de 2010.

La localización (Figura 10) se considera remota fuera de la plataforma continental y de la cordillera Atlántica central. Como muestra la Figura 8, PAP-SO está localizada en el giro entre el SPG estratificado estacional y el permanentemente estratificado (McKinley et al., 2016), donde existe influencia tanto de masas de agua polares como tropicales (Waniek, 2003; Henson et al., 2009).

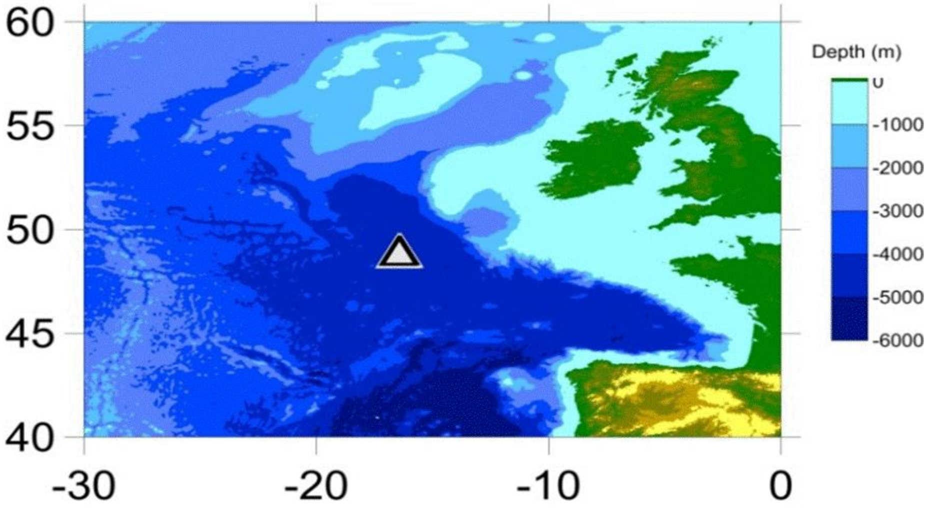

Figura 10: El Atlántico Noreste con la posición del observatorio abisal Porcupine (PAP-SO) a 49°N, 16.5°W, y la profundidad en metros (m).

Los sensores multidisciplinares en el fondeo han suministrado datos *in situ* desde 2002, incluyendo medidas subsuperficiales (~25-30 m) de temperatura, salinidad, clorofila-a a través de fluorescencia, pH, nitrato, luz, oxígeno y pCO_2. Desde 2012, se han adicionado medidas en aguas más someras biogeoquímicas aprovechando la boya superficial (sensores a 1 m). Además, en la boya se dispone de sensores meteorológicos registrando altura de ola, velocidad del viento y dirección y temperatura del aire. Los datos se envían en tiempo real vía telemetría Iridium al Centro Oceanográfico Nacional (NOC), UK. Todos los datos de PAP-SO son de acceso abierto a través de sitios web y la cualidad de los mismos controlados continuamente para su uso por diferentes entradas ftp, así como descargados diariamente para su uso en MyOcean y en los sistemas de telecomunicaciones globales para su uso en actividades de modelado.

En el agua templada del Atlántico norte, el crecimiento de fitoplancton está limitado por la luz en el invierno y el florecimiento se produce en primavera siguiendo la estratificación de la columna de agua (Sverdrup, 1953). Con el incremento de la producción, los nutrientes se consumen y el florecimiento se para hasta que la mezcla vuelve a comenzar en otoño suministrando más nutrientes hacia la superficie gracias a la mezcla de invierno. El ciclo estacional esperado en PAP-SO es así un pico en invierno de nutrientes y DIC, coincidiendo con la mezcla más profunda y menor temperatura superficial (Körtzinger et al., 2008). Lampitt et al. (2010) mostraron que la extensión de la mezcla profunda en PAP-SO varía con los años, alcanzando 400m en algunos de ellos. Por ello, la concentración de nutrientes y DIC cambiará de igual manera. De la misma forma, el tiempo del florecimiento primaveral, tanto en duración como en magnitud cambia con los años.

Un hecho persistente en el Atlántico Norte es la no saturación de las aguas superficiales con respecto al CO_2 a lo largo del año. Esto es un hecho característico del Atlántico Norte subpolar, consecuencia del enfriamiento general de las aguas superficiales durante el paso desde las bajas a las altas latitudes. Esta instauración sugiere que existirá un sumidero continuo de CO_2 con una incorporación neta calculada en el orden de 3 mol m^{-2} a^{-1} en PAP-SO (Körtzinger et al., 2008). La región es un gran sumidero de CO_2, especialmente cuando se compara con estaciones subtropicales tales como ESTOC donde la incorporación es de sólo 0.05 mol m^{-2} a^{-1} (González-Dávila et al., 2003), por lo que es de gran importancia su medida a nivel del ciclo del carbono global.

Objetivos

El principal objetivo de esta Tesis es la identificación de los controladores de la variación estacional e interanual de la biogeoquímica del Atlántico noreste. Este estudio se construye sobre la base de datos biogeoquímicos de más de 10 años recogida en el observatorio de la plataforma abisal Porcupine (PAP-SO); de los 8 años de serie temporal a través de un buque de oportunidades (SOO) entre UK y España y de dos años de muestreo biogeoquímico en la plataforma noreste europea. Este objetivo general se puede subdividir en otros más específicos como son:

- Considerar como los datos biogeoquímicos se pueden obtener y validar utilizando instrumentos autónomos. Las medidas de invierno utilizando buques son bastante escasas por lo que utilizar sensores permite obtener datos todo el año. La meta es combinar esas medidas con datos complementarios procedente de flotadores Argo, datos de satélite, y barcos de oportunidades.
- Capturar procesos que ocurren a diferentes escalas de tiempo, ya que las tendencias a corta escala y su variabilidad pueden contribuir a tendencias de procesos controlados climatológicamente a escalas más amplias. Por ejemplo, el estudiar a escala estacional la química del carbono, el suministro de nutrientes y la productividad permitirá comprender los valores en agua de mar de pCO_2 y los procesos que controlan su variabilidad.
- Comprender los cambios interanuales en la química del carbono, suministro de nutrientes y productividad en el Atlántico Noreste considerando la influencia entre la concentración de invierno de nutrientes y la mezcla profunda de invierno al tiempo que se define cómo se calcula la mezcla de invierno. Se debe considerar que la advección lateral de nutrientes hacia PAP-SO puede también contribuir a la variabilidad interanual, siendo este un proceso que ha sido despreciado con anterioridad en esta localización
- Investigar la variación anual en nitrato con respecto a la de carbono en PAP-SO. La relación carbono a nitrato se utiliza para calcular productividad y se ha considerado anteriormente constante en muchos estudios.
- Investigar la variación anual en el flujo de CO_2 en PAP-SO. El área PAP-SO es un sumidero neto de CO_2, sin embargo, en un clima cambiante la capacidad de los océanos para incorporar CO_2 puede verse modificada.
- Buscar episodios (ej. florecimientos primaverales) utilizando datos de sensores de alta frecuencia en PAP-SO. La meta es ver cómo la variación en el nitrato de invierno se relaciona con la productividad de la siguiente primavera y ver cómo la variación anual en el momento de comienzo del florecimiento se puede relacionar con el flujo de calor neto.
- Considerar las relaciones entre la productividad superficial y los flujos de carbono hacia el océano profundo considerando medidas de trampas de sedimentos. Además, considerar la región de influencia del flujo de material desde la superficie a fondo considerando procesos de advección lateral.
- Expandir los resultados de PAP-SO hacia el Atlántico buscando las variaciones estacionales e interanuales en nutrientes en relación con la mezcla y productividad de la Bahía de Vizcaya, utilizando datos SOO.
- Buscar los tiempos de aumentos en la concentración de nutrientes (debido a mezcla de invierno) y su disminución (a partir del florecimiento primaveral) dentro y fuera del talud utilizando datos SOO.
- Considerar PAP-SO como parte del Atlántico y su extrapolación hacia la costa europea noreste, comparando las variaciones biogeoquímicas en el observatorio con esas en la plataforma costera.

El estudio se base en el trabajo presentado en los capítulos que se corresponden con otras tantas publicaciones científicas (o sometidas) de la doctoranda.

Capítulo 1: El observatorio de la plataforma abisal Porcupine (PAP-SO): Variaciones y tendencias a partir de una serie temporal en el Atlántico Noreste

En este capítulo (Hartman et al., 2012) se describe PAP-SO y los sensores que se han situado desde 2002. PAP-SO en el Atlántico Noreste (49°N, 16.5°W; 4800 m) produce una serie de datos de alta resolución, incluyendo variables medioambientales y ecológicas relevantes desde la superficie hasta el fondo marino. Desde 2002, se estableció un fondeo con sensores autónomos de temperatura, salinidad, clorofila, nitrato y pCO_2. Estos se complementan con observaciones mesopelágicas y de fondo con flujo de partículas y de determinación de la función y estructura del ecosistema bentónico. El capítulo considera cómo estos sensores se seleccionan y como su uso ha evolucionado con el tiempo. En la parte de la síntesis, se discute las diferentes opciones de sensores y la validación de sus datos.

Capítulo 2: Variación estacional e interanual de los datos biogeoquímicos en el observatorio abisal Porcupine entre 2003-2005 asociado con la mezcla de invierno y la circulación superficial

En este capítulo (Hartman et al., 2010) se utilizan medidas autónomas de alta resolución incluyendo temperatura, salinidad, clorofila-a (derivada de valores de fluorescencia) y nitrato inorgánico. Considera los tres primeros años de medidas autónomas (2003-2005) en PAP-SO, utilizando la estructura situada a 30 m por debajo de la superficie. Los datos *in situ* se comparan con datos de: 1) datos de clorofila satelitales, 2) datos regionales a partir de un buque de oportunidades, 3) medidas de la profundidad de capa de mezcla a partir de datos de perfiladores Argo y 4) estimaciones de advección lateral a partir de medidas de satélite de altimetría. Este conjunto de datos combinados su utilizó para interpretar la variabilidad estacional e interanual en la hidrografía y concentración de nitratos en PAP-SO. La hipótesis de partida es que la advección lateral en PAP-SOP es importante. La influencia de la mezcla convectiva y la advección lateral en el suministro de nitratos hacia la superficie se explica ya que afecta a la productividad de la primavera posterior. Se utilizan datos de alta resolución de fluorescencia y cálculos de flujo neto de calor para caracterizar el tiempo en el que se produce el florecimiento en la estación PAP-SO.

Capítulo 3: Variaciones biogeoquímicas en el observatorio Abisal Porcupine en el Atlántico Noreste, en escalas de tiempo de semanas o años

En este capítulo (Hartman et al., 2015) se discuten las medidas autónomas de alta resolución de presión parcial de dióxido de carbono (pCO_2) tomadas *in situ* en PAP-SO. Se comparan los datos de los años 2010-2012 con los de los años 2003-2005. Las medias de pCO_2 se realizaron a 30m en la estructura donde se disponen los sensores y se compara con otras medidas autónomas biogeoquímicas a esa profundidad (incluyendo clorofila-a y nitrato). También se comparan con medidas *in situ* regionales a partir de un buque de oportunidades y de la profundidad de la capa de mezcla (MLD) a partir de perfiladores Argo. La variabilidad interanual en pCO_2 y en los flujos de CO_2 confirmaron que la región es un sumidero permanente de CO_2. Se investigó las variables que controlan el flujo de CO_2 en esta región noratlántica. La hipótesis de partida es que el flujo de CO_2 cambia cada año, relacionado con los cambios en productividad contralada por la concentración de nutrientes en el invierno.

Capítulo 4: Relación entre la productividad superficial y el flujo de partículas hacia el océano profundo en el observatorio abisal Porcupine

En este capítulo (Frigstad et al., 2015) se utilizaron datos hidrográficos y biogeoquímicos entre 2003 y 2012 junto con observaciones de trampas de sedimentos. La serie temporal es única en el Atlántico Noreste para la relación entre productividad y flujo de carbono hacia el océano profundo. En el Capítulo 4 los valores medidos se comparan con los calculados de NCP y producción nueva a partir de datos de eliminación de DIC y nitrato, respectivamente. Se calcularon las relaciones de exporte comparando estimaciones de productividad derivadas por medidas de satélite y los publicados a partir del flujo de carbono orgánico particulado superficial en PAP-SO. En segundo lugar, se investigó la relación entre la producción en la superficie y el flujo de partículas a 3000 m de profundidad. A continuación, se calcula la eficiencia de la transferencia de carbono entre la superficie y el océano profundo. También se describe la localización de la fuente de material exportado, utilizando técnicas de seguimiento de partículas.

Capítulo 5: Variabilidad estacional e interanual en el suministro de nutrientes en relación con los procesos de mezcla en la Bahía de Vizcaya

En este capítulo (Hartman et al., 2014) se presentan datos de alta resolución y autónomas de un Ferry-Box entre UK y España. Una serie de 8 años de datos hidrográficos del Ferry-Box (2002-2010) se complementan con muestras tomadas mensualmente para el análisis de nutrientes inorgánicos disueltos. En este capítulo se cuantificó la variabilidad año a año en la concentración de nutrientes y su relación con los procesos de mezcla de invierno y el índice NAO. La productividad se calculó a partir de los datos de oxígeno del Ferry-Box y se utilizó para caracterizar el momento del florecimiento primaveral tanto dentro como fuera del talud.

Capítulo 6: Heterogeneidad estacional y espacial del sistema de carbonato superficial en la plataforma europea noroeste

En este capítulo (Hartman et al., 2017, enviado) se presenta un complejo estudio coordinado de los parámetros de carbonato alrededor de la plataforma europea noroeste. Las muestras diarias superficiales se obtuvieron entre 2014 y 2015. Esas muestras discretas se analizaron para nutrientes, DIC y TA y se utilizaron para calcular pH y pCO_2. PAP-SO se consideró como parte del Atlántico oeste en su aproximación a la costa. La variación estacional hidrográfica y biogeoquímica hacia la costa es de esa manera presentada. La plataforma se dividió en 9 regiones ecohidrodinámicas determinando los valores promedios estacionales tanto medidos como derivados para cada una de ellas.

Conclusiones

- La experiencia obtenida en PAP-SO en el uso de sensores biogeoquímicos y en la validación de las medidas ha contribuido al conocimiento de las mejores prácticas internacionales para el fondeo de sensores y su validación (por ejemplo, en Coppola et al., 2016).
- Se ha descrito la variación estacional de la biogeoquímica en PAP-SO. Hay un pico anual en invierno (hasta 10 µmol kg^{-1}) y DIC (2130 µmol kg^{-1} en 2012), que corresponde con aguas más frías superficiales (alrededor de 12°C) y mezcla profunda (hasta 400m). Generalmente existe una disminución en verano de nitrato (a cero) y DIC (2060 µmol kg^{-1} en 2012), debido a la estratificación (MLD disminuye a 25m) y en el crecimiento del fitoplancton. Existe un aumento en verano de la clorofila (hasta 5 µg/l) y temperatura (a 18°C). El ciclo estacional es típico de las regiones productivas subpolares.
- Este estudio confirma la disminución entre invierno y verano en el pCO$_2$ superficial en PAP-SO y mostró que no es controlado de forma preferencial por procesos térmicos, incluyendo la eliminación biológica en primavera y la mezcla vertical en el invierno. La variación estacional (por ejemplo, entre 327 µatm en agosto 2012 a un máximo en invierno de 384 µatm en 2012) era opuesta a la variación estacional en lugares subtropicales tales como BATS y ESTOC.
- Las medidas superficiales oceánicas en PAP-SO representan tanto la variabilidad natural de las medidas biogeoquímicas y el forzamiento antropogénico que actúan sobre ellos. Año a año existe una gran variación en las medidas biogeoquímicas en PAP-SO. Por ejemplo, los resultados sugieren un aumento de temperatura (ej.: un aumento de temperatura de invierno desde 12.25 ±0.2 °C en 2003 a 12.61 ± 0.16 °C en 2005) que fue acompañado con una disminución en la concentración en invierno de nitrato (de 10 mmol m^{-3} a 7 mmol m^{-3} de 2003 a 2005).
- Uno de los objetivos de esta tesis era buscar las causas de la variación interanual en la biogeoquímica de PAP-SO y ver si existe una relación con el forzamiento climático. El NAO es el modo dominante de la variabilidad atmosférico en el Atlántico Noreste y se ha asociado con la variabilidad biogeoquímica. Sin embargo, existió una ligera variabilidad en el NAO en el periodo de dos años seleccionado por lo que el efecto de los cambios en el NAO no se ha mostrado para este sitio. Sin embargo, los inviernos suaves en la Bahía de Vizcaya (por ejemplo, entre 2007/08) se asociaron con un NAO positivo y aguas oceánicas más cálidas. La MLD se redujo a la mitad en ese periodo (212m en 2007/08 comparado con 476m en los más fríos con bajo NAO de invierno del 2009/10). Esto se asoció también con una disminución en el nitrato de invierno de 3 µmol kg^{-1} y con la disminución de la productividad en la siguiente primavera.
- Se mostró que la región PAP-SO está influenciada por las variaciones en las regiones fuentes de las aguas superficiales del Atlántico Noreste. Años con bajos valores de nitrato en invierno (ej.: 2005 que tuvo un valor de 7 µmol kg $^{-1}$) puede relacionarse en parte con la advección lateral de aguas de bajo contenido en nutrientes subtropicales o una disminución en la variante subpolar de mayor contenido en nutrientes y baja temperatura (como se observó en 2005). Los resultados de este estudio confirman la hipótesis de que la advección lateral es importante en PAP-SO.
- La fortaleza de los datos procedentes de observatorios permanentes como PAP-SO es la de detector cambios a corta escala en la superficie. El trabajo presentado muestra que los cálculos de flujo neto de calor pueden ser un buen indicador del tiempo del florecimiento primaveral en PAP-SO y que un flujo neto de calor positivo desencadena el comienzo del florecimiento primaveral (dentro de 7-9 días). La productividad es uno de controladores de la incorporación de CO$_2$ por el océano Atlántico norte subpolar. En el futuro, la productividad puede disminuir debido a una estratificación más reforzada de la columna de agua y que disminuye el suministro de nitrato para acelerar el

florecimiento primaveral (Behrenfeld et al., 2006). Los cálculos de productividad se realizan a partir de datos de la serie temporal en PAP-SO y mostraron una variabilidad interanual. Disminuía la productividad (de 85.4 gC m^{-2} a^{-1} a 40.3 gC m^{-2} a^{-1}) desde 2003 a 2005, lo que demuestra la necesidad de continuar con las medidas en PAP-SO.

- Los cálculos de productividad a partir tanto de datos de carbono como de nutrientes sugirieron que el consumo de carbono inorgánico con respecto a nitrato estaba en exceso con respecto al ratio Redfield en la superficie. La producción comunitaria neta estacional calculada fue de 4.57 ± 0.85 mol C m^{-2}. La producción nueva calculada a partir de nitrato fue 0.37 ± 0.14 mol N m^{-2} sugiriendo a C:N de 12.0. Esto evidenció un sobreconsumo de carbono en PAP-SO, con mayor eliminación de carbono que el esperado. Esto puede ser debido a una remineralización preferencial o podría indicar que el nitrato regenerado está recargando la producción.
- La insaturación persistente en CO_2 a lo largo del año hace de PAP-SO un sumidero significante de CO_2, especialmente cuando se compara con los sitios subtropicales y con las costas europeas del noroeste. La concentración media de pCO_2 en PAP-SO aumento desde 339 ±17 (2003-2005) a 353 ±15 (2010-2012), lo cual es consistente con un incremento anual de 1.84 ±0.4 µatm reportado por Takahashi et al. (2009).
- El flujo de CO_2 calculado a partir de los datos de series temporales en PAP-SO han servido para confirmar la capacidad de cambio del Atlántico Norte como sumidero de carbono. El objetivo inicial era estudiar la variación año a año del flujo de CO_2 (como mostró Schuster & Watson, 2007). Sin embargo, no se observaron cambios interanuales importantes en los flujos medidos en PAP-SO. El flujo de CO_2 varió desde -5.7 ± 2.8 mmol m^{-2} dia^{-1} en el periodo 2003-2005 a -5.0 ± 2.2 mmol m^{-2} dia^{-1} en el periodo 2010-2012 periodo, lo cual no es una variación significante. En los cálculos un producto satelital de viento se utilizó más que vientos medidos *in situ* lo cual puede haber suavizado alguno de los grandes vientos en PAP-SO, lo cual podría tener un efecto importante en el flujo de CO_2.
- El CO_2 atmosférico se secuestra hacia aguas más profundas a través de la producción de material orgánico. Se calculó una ratio de exporte del 16%, que representa el material orgánico exportado debajo de la zona eufótica. La eficiencia de la bomba biológica se representa por la eficiencia de la transferencia (calculada como un 4% en PAP-SO). Hubo una gran variación tanto dentro como entre los años del tipo de material que alcanzaba las trampas de sedimentos en PAP-SO. Hubo una mayor correlación entre la productividad superficial y el flujo exportado cuando se utilizaba la aproximación del rastreo de partículas que por la comparación entre la producción media en una caja de 100 km alrededor de PAP-SO. Sin embargo, las diferencias en los coeficientes de correlación no eran significantes y una serie temporal más larga es necesaria para extraer conclusiones en la validez de usar la aproximación del rastreo de partículas.
- Las aguas superficiales de la región de PAP-SO influye en las costas europeas noroeste y este estudio mostró cómo la estacionalidad de los ciclos biogeoquímicos en PAP-SO se comparaban con la región costera. Por ejemplo, la alcalinidad de invierno es generalmente más alta fuera de la costa en la posición de PAP-SO como es el caso de la salinidad. Hubo también una relación inversa entre el pCO_2 superficial y la temperatura en PAP-SO y en la costa irlandesa y escocesa debido a la productividad.

Trabajo futuro

Los datos de series temporales de alta resolución y larga escala son necesarios para caracterizar tanto eventos de corta escala y tendencias biogeoquímicas y de productividad en océano abierto. Los estudios recientes en el Atlántico han mostrado cómo los nutrientes se resuministran desde las aguas profundas durante las tormentas (Rumyantseva et al., 2015). Tal variación a corta escala en el suministro de nitrato podría ser fácilmente investigado en estudios futuros en PAP-SO.

En este estudio se han utilizado datos de velocidad de viento satelitales para calcular los flujos de CO_2 atmósfera-océano para ser consistente con los 10 años de datos del sensor que existen. Los cálculos de flujo futuros deberían considerar datos de viento *in situ* de la boya de la oficina del Met. Los datos de satélite muestran velocidades de viento medios con valores máximos de 14 ms^{-1}. Sin embargo, los datos de la boya Met sugieren velocidades de viento de hasta 20 ms^{-1}. Existe un aumento aparente en la incorporación de CO_2 en octubre 2010 por ejemplo (correspondiente con velocidades de viento más altos) lo cual podría ser examinado con más detalle ya que podría corresponder con un evento tormentoso.

Los estudios futuros deberían también incluir los datos a 1m de CO_2 compatibles con las bases de datos tal como SOCAT (que utiliza datos de los primeros 15m). Cuando se utilizan datos *in situ* de temperatura y los datos medidos a 1m de CO_2 para calcular el flujo en PAP-SO, los valores eran similares a los medidos a 30m que son los que utilizan en el **Capítulo 3**. Por ejemplo, la incorporación neta de CO_2 en 2013 fue -5.0 ± 2 mmol m^{-2} d^{-1} que era similar a los valores encontrado en el **Capítulo 3** (-5.7 and -5.0 mmol m^{-2} d^{-1}). Los nuevos cálculos utilizan velocidades de viento *in situ* de la boya de la oficina Met (y con los valores atmosféricos de CO_2 en Mace Head). Una recomendación sería calcular los datos futuros de flujos utilizando datos meteorológicos *in situ* e introducir medidas locales de CO_2 atmosférico en la boya.

En la actualidad, un radiómetro de 7 canales está registrando datos de luz tanto en la boya como en superficie y en la estructura del fondeo. Esas salidas podrían ser utilizadas para mejorar las medidas de datos de clorofila por fluorescencia siguiendo el método de Hemsley et al., (2015), que ha realizado un importante estudio de medidas no biogeoquímicas en las cercanías de PAP-SO utilizando gliders. Conforme se desarrollen en un futuro sensores biogeoquímicos más pequeños y menos consumidores de potencia, una mayor cantidad de estudios utilizando gliders en PAP-SO será altamente positivo y aumentará la resolución en profundidad.

El Atlántico Noreste tiene la mayor proporción de CO_2 antropogénico con respecto a otros océanos. El carbono antropogénico no se puede calcular a partir de medidas superficiales por lo que una recomendación sería tener sensores similares a lo largo de la columna de agua. Conforme lo sensores biogeoquímicos se desarrollen y sean capaces de trabajar a las altas presiones de la columna de agua, se recomienda la inclusión en este estudio de sensores de CO_2 a profundidades mayores. En la actualidad solo es posible medidas en toda la columna de agua de variables biogeoquímicas en las visitas anuales de servicio de la estación (tanto en el pre como en el post fondeo. Sería ideal disponer de perfiles a lo largo del año. Esto podría ser también conseguido utilizando automuestreadores a varias profundidades, que además ayudaría en la validación de los datos de sensores.

Los datos de barcos de oportunidades podrían ser utilizados para extender las medidas de series temporales realizadas en PAP-SO. La estación PAP-SO se sitúa entre las regiones 4 y 5 (Ostle et al.,2015). Ostle et al. (2015) seleccionó las provincias biogeoquímicas desde UK hasta el Caribe siguiendo la ruta del buque de oportunidades (que pasa por PAP-SO) basado en la correlación entre temperatura, densidad y clorofila. El método utilizado para seleccionar la provincia biogeoquímica se prefirió sobre el de las provincias biogeoquímicas estáticas de Longhurst, (2006) ya que las fronteras podrían cambiar de año a año. PAP-SO también se define por estar en la zona de entre giro o zona de transición entre el SPG y el STG (Henson et al., 2009), por lo que tendrá tanto influencia subtropical como subpolar. En estudios de años futuros con un incremento de la influencia subtropical debería poder ser distinguido en PAP-SO más allá de la aproximación descriptiva del **Capítulo 2**, especialmente si el giro subtropical se expande como predice Henson et al., 2009.

Una comparación de los ciclos biogeoquímicos en PAP-SO con los costeros del noroeste europeo mostró grandes variaciones estacionales a escala regional en el pH. Para determinar las tendencias en el pH se requieren series temporales más largas. El trabajo futuro en PAP-SO debe incluir una descripción completa de los cambios interanuales en pH. Por ello, las medidas de series temporales deben continuar para elucidar esas tendencias en los datos.

Los modelos y los métodos de interpolación se utilizan para rellenar los huecos de datos entre los sitios de series temporales y donde los datos son escasos. Aunque no se ha considerado en esta tesis, la importancia de modelos y los métodos de interpolación deben ser considerados. Los trabajos futuros deben acoplar los datos de medidas de las series temporales con las salidas de modelos para aumentar el conocimiento de los procesos que los controlan y de sus interacciones.

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