UNIVERSITY OF SOUTHAMPTON



Primary production and nitrate budgets in the temperate Northeast Atlantic estimated from ocean gliders

by

Victoria Hemsley A thesis submitted in partial fulfillment for the degree of Doctor of Philosophy

in the

Faculty of Natural And Environmental Sciences Department of Ocean and Earth Sciences

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"And above all, watch with glittering eyes the whole world around you because the greatest secrets are always hidden in the most unlikely places."

-Roald Dahl

UNIVERSITY OF SOUTHAMPTON

Abstract

FACULTY OF NATURAL AND ENVIRONMENTAL SCIENCES Department of Ocean and Earth Sciences

Doctor of Philosophy

PRIMARY PRODUCTION AND NITRATE BUDGETS IN THE TEMPERATE NORTHEAST ATLANTIC ESTIMATED FROM OCEAN GLIDERS by Victoria Hemsley

Phytoplankton in the ocean are a key component of the global carbon cycle and the base of most marine food webs. They contribute approximately one half of total global primary production, but are restricted to the euphotic zone, where sunlight is sufficient for photosynthesis. Due to ocean stratification nutrients become limiting in the near-surface ocean and the distribution of phytoplankton is influenced by the upward flux of nutrients from below. In situ measurements of primary production and nutrient fluxes are generally sparse and questions still remain about quantifying how the physical mechanisms supplying nutrients balance the amount of growth. Using a year long observational dataset from ocean gliders and mooring data this thesis investigates primary production in the North East Atlantic and the associated vertical nitrate fluxes into the euphotic zone. A method was developed to estimate primary production from glider chlorophyll fluorescence and photosynthetic active radiation data using a primary production algorithm designed for satellite data. Primary production in the subsurface was quantified from the model, showing the formation of a subsurface primary production maximum, which contributed 23% of the total annual primary production. Concurrent nitrate fluxes are calculated from mooring vertical velocities and diffusivity measurements using a density-nitrate relationship derived from cruise CTD bottle samples. An estimate of the convective flux was also estimated using glider mixed layer depths. An annual timeseries of sub-daily estimates of primary production and nitrate fluxes was therefore obtained. Annual budgets show that nitrate fluxes could support between 75 and 102% of the observed primary production. The vertical advective flux contributes the largest vertical flux to the nitrate supply, and is therefore of greater significance than previously considered. Notable small scale temporal variability was observed in both the timeseries of primary production and nitrate fluxes, demonstrating an important influence from submesoscale and mesoscale processes on phytoplankton growth.

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Abbreviations

PAP-SO	$\mathbf{P} or cupine \ \mathbf{A} by ssal \ \mathbf{P} lain \ \mathbf{O} bservatory$
PAR	$\mathbf{P} hotosynthetic \ \mathbf{A} ctivel \ \mathbf{R} adiation$
\mathbf{SCM}	${\bf S}$ ubsurface ${\bf C}$ hlorophyll ${\bf M}$ aximum
\mathbf{SPM}	$\mathbf{S} ubsurface \ \mathbf{P} roduction \ \mathbf{M} aximum$
RMSE	Root Mean Square Error
CDOM	Chromophoric Dissolved Organic Matter

Symbols

a	distance	m
g	gravity	${\rm m~s^{-1}}$
z	depth	m
E	irradiance	${\rm W}~{\rm m}^{-2}$
r	reflectance	%
K_w	attenuation coefficient of water	m^{-1}
K_c	attenuation coefficient of chlorophyll	m^{-1}
a^*	absorption cross section per unit chlorophyll	m^{-1}
T	temperature	°С
t	time	seconds
p	pressure	dbar
U, V	horizontal speeds	${\rm m}~{\rm d}^{-1}$
w	vertical velocity of water	${\rm m}~{\rm d}^{-1}$
N	buoyancy frequency	
C	concentration	$\rm mmol \ m^{-3}$
λ	wavelength	m
ϕ_{μ}	net growth rate	mol C (mol quanta) ⁻¹
β	photoinhibition parameter	unitless
ρ	density	$\rm kg \ m^{-3}$
κ_z	diffusivity	${\rm m~s^{-1}}$
Γ	mixing efficiency	0.2
α^B	initial slope of photosynthesis-irradiance curve	mg C m ⁻³ h ⁻¹ (W m ⁻²) ⁻¹

Chapter 1

Introduction

This thesis will investigate an annual cycle of primary production and vertical nitrate fluxes at a site in the North East Atlantic.

In this chapter I will introduce primary production and give a brief summary of the mechanisms of nitrate supply to the surface ocean and work that has been previously done in this field. I will then introduce gliders and how they may be applied to ocean research, in particular biogeochemical studies. Finally I will introduce the region of study near the Porcupine Abyssal Plain Sustained Observatory (PAP-SO) in the North Atlantic and the data that was collected during this project. The aim of this poject is to use glider and mooring data to quantify primary production and nitrate fluxes over a whole annual cycle.

1.1 Primary Production in the Ocean

Primary production is a measure of the carbon fixed by plants over time through the process of photosynthesis. In the ocean it is fuelled by nutrients but is powered by sunlight and is therefore restricted to the ocean euphotic layer (depth of 1% of the surface irradiance). Marine phytoplankton fix between 45 and 50 Gt C yr⁻¹, which accounts for approximately one half of total global primary production (Field, 1998; Carr *et al.*, 2006). Primary production and the mechanisms that influence it are therefore important to quantify because of their influence on climate regulation via the associated drawdown of carbon dioxide and because they supply energy to the majority of the oceans' food webs.

Direct measurements of primary production in the ocean are sparse as they are time consuming, and research cruises that collect the necessary samples tend to be conducted in regions of subjective interest, avoiding winter months. Fixed point observations with regular sampling may not allow spatial extrapolation due to high spatial variability of phytoplankton. Algorithms have therefore been developed that use satellite ocean colour data to estimate regional and global primary production, allowing a variety of spatial and temporal scales to be resolved. Earth Observation (EO) derived surface chlorophyll fields capture the variability in primary production better than any other remotely sensed parameter (Jacox et al., 2015). However EO is limited as it relies on cloud free skies to estimate chlorophyll and can only observe approximately the first optical depth of the euphotic zone (1/k), where k is the attenuation coefficient, approximately 10 m in temperate latitudes), thereby omitting features such as subsurface chlorophyll maxima (SCM) and deeper biomass distributions (Gordon & Clark, 1980). As a result, primary production estimates derived exclusively from satellite data typically underestimate spatial and temporal variability (Carr *et al.*, 2006). Methods have been developed to accommodate SCM (Morel & Berthon, 1989), but are based on broad statistical relationships (Cullen, 2015), with the result that they may not be able to capture the SCM in all areas with equal accuracy.

The North Atlantic Ocean is of particular interest because it has a strong seasonal cycle of phytoplankton growth leading to high levels of primary production in the spring bloom, that resulting in a sink of atmospheric CO_2 (Taylor *et al.*, 1991). The seasonal cycle (phenology) of primary production in the North Atlantic is well studied and controlled by a number of physical factors (Longhurst et al., 1995; Körtzinger et al., 2008). During winter, deep mixing ensures plenty of nutrients are available, however when phytoplankton are mixed out of the euphotic zone they become light limited and growth rates remain low. In spring, solar irradiance increases, which warms the surface waters and shoals the mixed layer, ultimately resulting in shallow mixed layers (typically 20 m) that are stratified throughout summer. Reduced mixing and stratification of the water column in summer traps phytoplankton near the surface where there is plenty of available light but isolates them away from the deeper nutrient reservoirs. Due to a lack of vertical mixing, nutrients are quickly depleted from the surface layer and often a subsurface chlorophyll maximum forms at the base of the mixed layer (Cullen, 1982). In the transition between winter and summer while nutrients are still abundant and light is not yet limiting a spring bloom often occurs. This description of annual phytoplankton phenology is somewhat simplified and other factors, such as grazing and storm events can also have a significant impact on phytoplankton growth. For example storm events in early autumn may result in an autumn phytoplankton bloom through a deepening of the mixed layer which entrains nutrients from below (Martinez et al., 2011; Painter et al., 2016), and grazing may delay the spring bloom (Sambrotto et al., 1986; Gifford et al., 1995; Henson et al., 2009).

Although the general phenology of spring blooms is well known, phytoplankton growth is highly non-uniform throughout the North Atlantic. That phytoplankton exhibit spatial variability has been known since explorers in the eighteenth century observed changes in the colour of the ocean coincident with abundant phytoplankton (Bainbridge, 1957). This is known as phytoplankton patchiness (Martin, 2003). Regions with high mean chlorophyll also tend to have a high spatial variance (Mahadevan, 2016). Temperature, nutrient availability and predation all influence the biogeography of phytoplankton, however the dynamic movement of the ocean also plays an important role as phytoplankton are continually being dispersed or concentrated by surface currents. The distribution of phytoplankton therefore becomes a balance between growth, competition and dispersal (Lévy *et al.*, 2015). This thesis will focus on phytoplankton primary production and the influence of nutrient availability and nutrient fluxes into the euphotic zone.

The Earth's rotation dominates oceanic flow at scales more than a few kilometres resulting in largely horizontal currents, in geostrophic and thermal wind balance (Mahadevan, 2016). This flow restricts the flux of nutrients from the nutrient rich deeper waters to the illuminated euphotic zone. However at smaller scales processes can overcome these constraints allowing for vertical motion and increasing mixing in localised regions (Pidcock *et al.*, 2010). Although they are localised in space and time, submesoscale processes have been shown to be important for primary production because the timescale at which they occur are similar to phytoplankton growth rates (Mahadevan, 2016, and references therein).

The vertical flux of nitrate is dependent not only on physical processes resulting in vertical velocities or mixing, but also on the distribution of nitrate at depth, the depth of the nitricline and the vertical gradient of nitrate. Furthermore the community composition of the phytoplankton can also come into play. Faster growing phytoplankton will uptake nutrients more quickly maintaining nutrient depletion in the euphotic zone, resulting in a stronger nitrate gradient. Therefore, for the same velocity field, the flux of nitrate is greater for a phytoplankton community that consumes nutrient inputs quickly, as compared with one that consumes nutrients more slowly, although this is more important in stratified waters (Painter *et al.*, 2014*b*; Mahadevan, 2016).

The balance of control over primary production is also not well known, and quantitative estimates of regional nutrient supply contributing to primary production vary significantly (Lévy *et al.*, 2001). One of the main reasons that we still have a limited understanding of primary production and the influence of nutrient supply over a full annual cycle is that few studies simultaneously measure primary production and nutrient fluxes at high resolution time or space scales and for sufficiently long periods of time to resolve and annual cycle. Most studies are conducted over short periods or with very

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few stations and therefore the temporal and spatial scales are not fully captured. In addition, on tradiational ship based programmes, water samples for primary production are collected from CTD casts that typically come from only a few discrete depths, which may underestimate vertical variability, such as in chlorophyll thin layers.

Ocean gliders can expand our understanding of these processes as they can be deployed for long durations (up to 6 months), with vertical sampling resolution of up to half a meter and with the ability to simultaneously measure or infer a number of different variables, such as primary production, Photosynthetically Active Radiation (PAR), and mixed layer depth.

1.2 New and Regenerated Production

It is generally thought that phytoplankton growth in the North Atlantic Ocean is nitrogen limited (e.g. Capone *et al.*, 2008; Howarth, 1988). Under this assumption primary production can be separated into new and regenerated production (Dugdale & Goering, 1967). New production uses allochthonous nitrate brought into the euphotic zone from a number of processes (described below, Section 1.3). Regenerated production uses nitrogen formed locally, generally in the form of ammonium (NH_4^+) or dissolved organic nitrogen. Assuming steady state over appropriate time scales, what comes up in the ocean must come down, new production can therefore be used to estimate the amount of carbon export by phytoplankton (Eppley & Peterson, 1979). Estimates show that global new production is 11 Pg C yr⁻¹ with regenerated production contributing to 78% of global primary production (Laws *et al.*, 2000). The *f*-ratio is the fraction of primary production fuelled by nitrate as opposed to other sources of nitrogen (Eppley & Peterson, 1979). This can be explained by the following equation:

$$f = \frac{[\rho N O_3^-]}{[\rho N O_3^-] + [\rho N H_4^+] + [\rho U rea]}$$
(1.1)

where ρ is the uptake rate. If the value of the *f*-ratio is 1 all production is new production, if the value is 0 all production is reliant on regenerated forms of nitrogen. If nitrogen fixation is assumed to be negligible the nitrogen supplied to the euphotic zone can be used as a proxy for new production (Eppley & Peterson, 1979; Henson *et al.*, 2003). However the process of nitrification, the conversion of ammonia or ammonium to nitrite then nitrate by bacteria, complicates the *f*-ratio as it relies on the fundamental assumption that nitrification in the euphotic zone is negligible (Yool *et al.*, 2007; Zehr & Kudela, 2011). It is now known that nitrification can occur throughout the euphotic zone and therefore new production may have been overestimated in the past. Although measurements of nitrification are relatively rare, they do suggest that using new production as a proxy for the biological pump may be misleading (Yool *et al.*, 2007). There are also questions over how long the nitrogen has to be subducted out of the euphotic zone before it can be called new nitrogen. Conventionally an annual time period is used and therefore any nitrate returned to the euphotic zone in under a year is not considered to be new.

1.3 Mechanisms of Nutrient Supply to the Surface Ocean

When phytoplankton die they sink, and bacterial remineralisation deeper in the water column helps maintain a vertical gradient in nutrient concentrations across the thermocline. In the North Atlantic nutrient concentrations typically become limiting for growth in the euphotic zone during late spring and throughout summer as they are rapidly consumed by phytoplankton to support growth. Further growth is inhibited by weak upward transport of nutrient rich deep water, due to seasonal stratification. There are a number of mechanisms which contribute to nutrient fluxes in the open ocean, which include: i) atmospheric deposition, ii) nitrogen fixation, iii) winter convective mixing, iv) sub- and mesoscale advective upwelling and v) small-scale turbulent mixing (Figure 1.1). I will now discuss the last three mechanisms listed, which are those controlled by oceanic circulation and will be covered in Chapter 5 of this thesis. Atmospheric deposition and nitrogen fixation are beyond the scope of this thesis, but both have been shown to contribute low inputs of nitrate in this region. Nitrogen fixation is mostly constrained to low latitudes and is therefore assumed to be negligible in the North Atlantic (e.g. Lipschultz & Owens, 1996; Coles & Hood, 2006), while atmospheric deposition contributes low concentrations in the North East Atlantic, between 15 and 40 mmol N m⁻² yr⁻¹ (Duce *et al.*, 2008).

Winter convective mixing

Winter convective mixing occurs when colder temperatures and higher wind speeds during winter deepen the surface mixed layer, sometimes to several hundreds of meters. This deepening of the mixed layer mixes up deep nutrient rich waters from below the euphotic zone increasing surface concentrations. Phytoplankton cells become dispersed within the mixed layer, which is below the euphotic depth and as such prevents growth due to low light levels (Sverdrup, 1953). Re-stratification of the water column is fundamental for phytoplankton growth and the onset of the spring bloom and, convective mixing may also influence phytoplankton growth by regulating the amount of light available during spring (Dutkiewicz *et al.*, 2001). Zooplankton survival may also be impacted by winter



FIGURE 1.1: Schematic showing the supply of nitrate in the surface ocean.

convective mixing and their subsequent grazing on the phytoplankton as deeper winter mixed layer depths mean that phytoplankton are too dispersed to allow herbivore populations to reach high enough levels for grazing to have an impact on the spring bloom (Fasham, 1995; Behrenfeld, 2010; Behrenfeld & Boss, 2014).

In the North Atlantic the convective nitrate supply generally increases northward and ranges from 0.05 to 1.4 mol N m⁻² yr⁻¹ (Williams *et al.*, 2000; Williams & Follows, 2003). Inter-annual variability in nutrient supply is thought to occur from inter-annual changes in convection, mostly controlled by local heat loss to the atmosphere (Williams *et al.*, 2000).

Winter convective mixing has been shown to increase springtime nutrient and chlorophyll concentrations and is generally thought to be the largest source of nutrients into the euphotic zone in the sub-tropical and sub-polar gyres (Michaels & Knap, 1996; McGillicuddy *et al.*, 1998; Williams *et al.*, 2000). This supply may regulate spring production by setting the magnitude of nutrients available for new production (Dutkiewicz *et al.*, 2001). Williams & Follows (2003) show data from the Bermuda Atlantic Timeseires Station (BATS) demonstrating that years with a deep winter mixed layer resulted in an increase in surface nutrients and a corresponding increase in chlorophyll. However, convection only redistributes nutrients when the mixed layer is deepening. If there is loss of organic matter from the base of the mixed layer nutrient concentrations in the surface will decrease and other sources of nutrients are needed to off-set this loss (Williams & Follows, 2003). Hartman *et al.* (2015) found that increases in nutrient concentration did not correlate with a deepening of the winter mixed layer at the Porcupine Abyssal Plain Sustained Observatory (PAP-SO), indicating the importance of other fluxes into the euphtoic zone in this region, such as horizontal and vertical advective transport (Hartman *et al.*, 2010).

Vertical turbulent diffusive mixing

At scales less than a few tens of meters the turbulent motion of the surface ocean is three dimensional such that the horizontal and vertical components are more or less equal. Turbulence results in the transfer of properties such as heat, salinity and other tracers, such as nutrients. To maintain turbulent motion a steady supply of energy is required. Turbulent diffusive mixing at the surface is driven by atmospheric cooling and wind-mixing and is generally several orders of magnitude larger than that at depth which tends to be dominated by breaking internal waves and interactions with topography. In the North Atlantic turbulent mixing has been shown to contribute a lower proportion of the total nutrient flux than in other regions, such as the tropics. Law et al. (2001) found that turbulent mixing supplied only 16% of the nitrate needed for the observed nitrate uptake in the sub-polar North Atlantic. Further observations, between subpolar and subtropical gyres, by Martin et al. (2010a) demonstrated that convective mixing supplied nearly 40-fold more nitrate to the euphotic zone at the site studied here (PAP-SO) in the North Atlantic than turbulent mixing. An eddy-resolving modelling study ($\sim 0.1^{\circ}$) showed that at the North Atlantic Bloom Experiment site $(47^{\circ}N \ 20^{\circ}W)$ the diffusive flux of nitrate supported approximately 20% of the modelled annual new production. On the other hand at the equator, where the ocean is strongly stratified, Carr et al. (1995) found that the turbulent diffusive supply accounted for approximately one third of production, becoming negligible further from the equator as other processes began to dominate, such as winter convective mixing (Williams & Follows, 2003). The turbulent flux is therefore of more significance in strongly stratified oligotrophic regions, where phytoplankton growth is nutrient limited and other processes for supplying nutrients are small. However rates of turbulent diffusivity are still poorly known in the ocean as it is difficult to measure and because it fluctuates in both space and time and may be dominated by episodic events (Rippeth et al., 2009). Munk (1966) estimated that diffusivity needed to be 10^{-4} m² s⁻¹ in the interior ocean in order to explain the vertical profile of tracers. However this tends to be larger than direct observations in the ocean of $10^{-5} \text{ m}^2 \text{ s}^{-1}$ (Ledwell *et al.*, 1993), suggesting that diffusive mixing does not dominate or explain the nutrient supply to the euphotic zone. However, turbulent mixing is heterogeneous in the ocean, with enhanced diffusivity in certain areas, such as over ocean ridges (Ledwell *et al.*, 2000), and occurs at intermittent times making peaks in dissipation difficult to observe (Burchard & Rippeth, 2009).

Submesoscale and Mesoscale upwelling

The mesoscale (10 - 100 km, weeks) and the submesoscale (0.1 - 10 km, days) can have a strong influence over the distribution of chlorophyll and nutrient supply (Lévy *et al.*, 1998, 2001; Klein & Lapeyre, 2009). Wind driven vertical velocities within the mixed layer tend not to result in exchange between the surface layer and the ocean interior, apart from during winter convection or during storm events when the mixed layer deepens (Giordani *et al.*, 2005). Exchanges during the rest of the year are driven by vertical velocities below the mixed layer caused by mesoscale and submesoscale processes (Klein & Lapeyre, 2009).

The influence of the mesoscale can be observed from space in the swirls and filaments seen in ocean colour data and strongly influences the patchy distribution of phytoplankton (e.g. Martin *et al.*, 2005). Mesoscale upwelling occurs throughout the year and also contributes large fluxes, with vertical velocities between 5 and 100 m d⁻¹ (Allen & Smeed, 1996; Allen et al., 2005; Pidcock et al., 2013). However they are irregular in space and time, associated with mesoscale eddies and fronts. Mescoscale eddies are a common feature in the ocean (McDowell L & Rossby, 1978). They can be generated by a number of processes including deep winter mixing (Marshall & Schott, 1999), barotropic and baroclinic instability of large scale flows (Richardson, 1993), and high intensity shortlived wind events (Willett et al., 2006). Mesoscale eddies can persist for several weeks or even months, therefore on timescales much longer than phytoplankton growth. There are a number of mechanisms by which mesoscale eddies can influence the chlorophyll signature. In the eddy pumping mechanism eddies (cyclones) can uplift isopyncnals into the euphotic zone, increasing nutrient concentrations and resulting in an increase in primary production (McGillicuddy et al., 1998; Siegel et al., 1999). Eddy pumping occurs during the formation and intensification phases of an eddy, and generally takes place in the interior of the eddy, isolating it from surrounding waters (McGillicuddy et al., 2003). When analysing nutrient budgets it is often assumed that all the nutrients uplifted are consumed by phytoplankton (McGillicuddy, 2016). Modelling studies have shown that as eddies weaken and start to decay net downwelling of nutrients can occur in the centre of the eddy as the isopycnals subside (McGillicuddy et al., 2003).

Eddy-eddy interactions can also intensify features and lead to an uplift of the nutricline (McGillicuddy & Robinson, 1997). Eddies can also lead to increased stratification caused

by baroclinic slumping of fronts, increasing light availability for phytoplankton and leading to an onset of growth (Lévy *et al.*, 1998; Mahadevan *et al.*, 2012). At fronts nutrients may be transported into the euphotic zone along sloping isopycnals due to ageostrophic secondary circulation (Mahadevan & Archer, 2000; Klein & Lapeyre, 2009).

Mesoscale eddies have been suggested as a mechanism of nitrate supply to the surface, which enables the discrepancy between estimates of traditional nutrient transportation mechanisms (vertical diffusive and convective fluxes) and biological requirements to be resolved (McGillicuddy et al., 1998). These estimates have often been in disagreement by an order of magnitude or more (Williams & Follows, 1998). However further studies have shown that assumptions that phytoplankton are able to utilise all the upwelled nitrate before isopycnals are subducted again to initial positions are unlikely to be realistic (Oschlies, 2002; Martin, 2003). It is suggested instead that mesoscale eddies may supply 20 - 30% of the nitrate needed for biological uptake (McGillicuddy et al., 2003, 2007). However an eddy-resolving modelling study by McGillicuddy et al. (2003) has shown that over an annual cycle, the supply of nitrate by vertical advection may be negative at the North Atlantic Bloom Experiment site $(47^{\circ}N \ 20^{\circ}W)$ and convective mixing is the main contributor of nitrate to supply primary production. This is due to the role that mesoscale and submesoscale features play in restratification (McGillicuddy et al., 2003; Mahadevan et al., 2012). A proportion of nutrients supplied by winter convection are subducted back down as the near surface of the water column stratifies.

Submesoscale transport of nutrients is considered more episodic and impacts a smaller area than transport by the mesoscale. Submesoscale processes are particularly relevant to phytoplankton as the timescales (hours to days) over which they occur are similar to those of phytoplankton growth rates (Mahadevan, 2016). These processes can result in vertical velocities of more than 100 m d⁻¹. Although vertical velocities work in both directions, the vertical nutrient gradient generally ensures that nutrient rich water is advected upwards into the euphotic zone whilst water with lower nutrient concentrations is transported out of the euphotic zone, resulting in a net transport of nutrients to the surface ocean. Klein & Lapeyre (2009) suggest that the discrepancy in the nutrient budget, between observed fluxes and primary production, may be due to a lack of high spatial resolution studies capturing the submesoscale, as vertical fluxes are much stronger at the submesoscale than the mesoscale (Capet *et al.*, 2008).

1.4 Gliders for Ocean Sampling

In 1989 Henry Stommel (Stommel, 1989) envisioned a fleet of inexpensive underwater platforms for observing the ocean. A large number of small platforms would help overcome the problem of observing a turbulent fluid at scales ranging from ocean basins to meters. The number of platforms and their density could be scaled to what was being observed. Argo floats partially fulfill this vision. Argo floats are profiling floats that are an important component of the ocean observing system with around 3000 floats in the Argo network. However the floats cannot be directed and instead drift with the currents, which restricts observing some features in the ocean, especially in areas of divergence, or tracking of a feature such as an eddy. Gliders are the next step as they can be directed instead of drifting.





Gliders are buoyancy driven autonomous vehicles which profile the ocean in a saw-tooth pattern to a depth of 1000 m (Figure 1.2). Gliders are highly energy efficient due to a pressure hull with nearly equivalent compressibility to that of seawater, a low drag hydrodynamic shape and a limited number of low powered instruments. Gliders also profile relatively slowly at a speed of approximately 20 cm s⁻¹. As the loss of energy to drag is proportional to the cube of the speed through water, this also allows the glider to be efficient and have long duration deployments (Rudnick, 2016). The glider typically

travels 6 km between surfacings for a profile to 1000 m. After each dive-climb profile the glider reports data via Iridium satellite in near-real time. Fuller details on glider engineering can be found in Eriksen *et al.* (2001).

Gliders can be equipped with a variety of sensors depending on the purpose of the mission. The standard suite of sensors includes un-pumped Conductivity Temperature Depth (CTD), triplet puck (including fluorescence, optical backscatter and Chromophoric Dissolved Organic Matter (CDOM), and an oxygen optode. Other sensors can also be included depending on the available payload and energy usage such as a broad-band Photosynthetically Available Radiation (PAR) sensor, microstructure, Submersible Ultraviolet Nitrate Analyser (SUNA) nitrate sensor (Rudnick, 2016), with many more sensors currently being developed. This means that gliders can be used for a variety of purposes. A balance between the sensor sampling rate, number of sensors and duration of mission needs to be considered when planning a deployment due to limited battery power.

Gliders allow high resolution measurements with samples taken up to every half a metre vertically for months at a time. They can be piloted from land and the sampling strategy can be changed remotely at every glider surfacing during the deployment. Gliders are also easy to transport and can be deployed off small vessels to monitor events which are localised or irregular. The cost of a glider is small compared to other sampling methods, such as ships and mooring arrays and they can continue collecting data in harsh weather conditions when ship sampling is not possible, making them ideal platforms to survey the ocean. However a large amount of post processing of the data is needed to have an accurate representation of the ocean. Sensor validation and calibration is also challenging when sampling with gliders as it is difficult to take water samples near to the glider while it is deployed to validate the measurements.

Gliders have been shown to have a wide range of applications despite the use of such data being relatively new and a lack of comprehensive protocols or guidelines on processing the data (Heslop *et al.*, 2015).

1.4.1 Glider Applications

Since 2007 the number of studies using autonomous gliders has increased rapidly (Johnson *et al.*, 2009; Rudnick, 2016). However the full potential of gliders for ocean research has yet to be demonstrated. Gliders can be used to acquire data on a number of oceanic variables, from temperature and salinity to the biogeochemisty and even the vertical motion of the water. The ability to make several concurrent measurements, including

physical and biogeochemical, allows the oceanic environment to be interpreted more fully.

Applications for gliders can scale the entire food web. They have frequently been used to measure chlorophyll fluorescence as a proxy for phytoplankton biomass (Perry *et al.*, 2008; Swart *et al.*, 2015). Recently, active acoustic sensors have been used to observe krill off Antarctica (Guihen *et al.*, 2014). Further up the food chain, Wall *et al.* (2012) detected red grouper and toadfish with a glider mounted hydrophone on the West Florida Shelf, while Klinck *et al.* (2012) were able to monitor beaked whales off the coast of Hawaii. Monitoring whole food chains in an ecosystem, from primary production to feeding sites with one relatively cheap platform could provide vital information for fisheries and conservation as well as changing patterns caused by the changing climate.

As well as taking standard physical parameters such as temperature, conductivity and pressure, gliders are now being used for a number of other physical measurements. They have been shown to be able to measure vertical water velocities using the glider flight model (Merckelbach *et al.*, 2010; Frajka-Williams *et al.*, 2011). Vertical velocities are typically difficult to measure because they are generally very small (less than 1 cm s⁻¹). Also when using computational methods such as the omega equation high resolution sampling in three dimensions is required (Sévellec *et al.*, 2015). However vertical flow is an important part of ocean circulation, transporting water and tracers, such as nutrients, between the deep ocean and the surface mixed layer and therefore being able to estimate this from a glider is extremely important. As gliders are slow and stable platforms, turbulent dissipation can also be measured using a microstructure sensor mounted on the front of the glider (Palmer *et al.*, 2015). However Beaird *et al.* (2012), have shown that gliders also have the potential to estimate dissipation using the glider flight model. Although the latter method is not as sensitive, this can be extremely useful for longer deployments as the microstructure sensor has a limited battery life.

Measurements from gliders therefore have the possibility to open up many multidisciplinary studies to determine how the ocean environment and circulation impact the growth of phytoplankton and how this may propagate up the food chain.

Glider data have a potential when used in conjunction with other data collections techniques, such as ship, satellite and moorings, which together put the observations into the context of the larger environment. The study in the thesis utilises a number of different data sources for validation of glider measurements and to complement the data to understand the wider context. Measurements from gliders therefore have the possibility to open up many multidisciplinary studies to determine how the ocean environment and circulation impact the growth of phytoplankton and how this may propagate up the food chain.

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1.5 OSMOSIS Project

The data used in this thesis were collected as a supplement to the Ocean Surface Mixing, Ocean Submesoscale Interaction Study (OSMOSIS), a NERC research project to improve our understanding of the physics of the ocean surface boundary layer. A large portion of the project was an observational campaign conducted from September 2012 to September 2013 in the North Atlantic Ocean, ($48^{\circ}41 \text{ N}$, $16^{\circ}11 \text{ W}$). This site is approximately 40 km south east of the Porcupine Abyssal Plain sustained observatory (PAP-SO, Figure 1.3) (Lampitt *et al.*, 2001; Hartman *et al.*, 2010). Currents in this area are generally weak with mean currents of 11 cm s⁻¹. Patchy phytoplankton distributions with fine spatial scales (< 10 km) have been observed in this region (Painter *et al.*, 2010*a*). Diatoms dominate the spring bloom, succeeded by prymnesiophytes and dinoflagellates (Barlow *et al.*, 1993; Henson *et al.*, 2012). In summer, diatoms form a subsurface chlorophyll maximum at the base of the mixed layer (Lochte & Pfannkuche, 1987; Painter *et al.*, 2010*b*). Due to the patchy nature of phytoplankton distribution, advection of spatial variability can result in apparent variations in the phytoplankton community structure on daily time scales (Smythe-Wright *et al.*, 2010).

Year long coverage of glider data was obtained between September 2012 to September 2013 in a 15 km x 15 km area. One glider completed a north-south butterfly pattern, while the other completed an east-west butterfly (Figure 1.3b). Vertical sampling was approximately every half to one meter depending on battery usage. In total, 8458 vertical profiles of simultaneous observations of temperature, salinity, chlorophyll-a fluorescence, particulate optical backscatter, photosynthetically available radiation and oxygen were obtained. Biological sensors sampled to 300 m depth only to save on power. Figure 1.4 shows a picture of one of the deployed iRobot gliders and the sensors used in this thesis.

The OSMOSIS project also made measurements near surface (from 50 to 500 m deep) from moorings, of parameters that include temperature, salinity, horizontal velocity



FIGURE 1.3: Study location and glider flight paths from September 2012 to September 2013, overlaid on monthly mean chlorophyll maps from August 2013.

and turbulent dissipation. Nine instrumented moorings were arranged with one central mooring. A number of cruises to the region also took place to deploy/recover equipment which were used to collect data for calibration of sensors. Details of cruises and available data are given in Chapter 2.

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FIGURE 1.4: iRobot Seaglider with sensors labelled.

turbulent dissipation. Nine instrumented moorings were arranged with one central mooring. A number of cruises to the region also took place to deploy/recover equipment which were used to collect data for calibration of sensors. Details of cruises and available data are given in Chapter 2.

This study uses the glider deployments to study the biogeochemistry of the area, using other datasets, such as cruises, moorings and satellite data to enhance the observations made and put them into a larger context. The glider data available from the OSMOSIS project allows an extensive analysis of primary production over a whole year. In this thesis, I will show how we can use glider data as a powerful observational tool to estimate rates of primary production and how this is influenced by fluxes of nutrients into the euphotic layer to sustain growth.

1.6 Thesis Objectives

The overall aim of this thesis is to measure and investigate rates of primary production over a whole annual cycle using glider data and to determine how the flux of nutrients from different processes contribute to the observed biological requirements. The OSMOSIS dataset will allow the whole annual cycle to be explored in detail.

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Aims

- 1. To quantify the rate of primary production in the study area, both annually and at daily resolution.
- 2. To quantify the nitrate fluxes including mixing, convection and vertical advection over the study area.
- 3. To determine how nitrate fluxes contribute to rates of primary production in the North East Atlantic and if they balance the requirements of the observed primary production.
- 4. To illustrate the suitability of gliders for studying biogeochemical cycles.

The data and methods used will be explained in Chapter 2, going into a further explanation of the OSMOSIS project and the data available for this study. Chapter 3 will derive a new method for measuring primary production using glider data and has been published as Hemsley *et al.* (2015). The method involves using the glider chlorophyll and PAR data as input into a primary production model developed by Smyth *et al.* (2005). This method will be used for all the gliders in the OSMOSIS project allowing the annual cycle of primary production to be examined in Chapter 4, to address the first aim of the project. Nitrate fluxes associated with convection, vertical velocities and dissipation estimates will be examined in Chapter 5 as a way of calculating the nutrient fluxes for the second aim. In the same chapter the nutrient fluxes will be compared to the annual cycle of primary production to address the third aim. Chapter 6 has the conclusions of the project and a broarder view will be taken to use the results of the thesis to address how suitable gliders are for examining biogeochemical cycles in the ocean (Aim 4).

Chapter 2

Data Collection, Calibration and Processing

This chapter explains the OSMOSIS project in more detail and some of the previously published methods used for data collection and processing. Ancillary data used throughout the thesis, such as satellite, cruise, and mooring data, are described.

2.1 The OSMOSIS Project

The Ocean Surface Mixing, Ocean Submesoscale Interaction Study (OSMOSIS) is a NERC research project to improve our understanding of the ocean surface boundary layer. A large component of the project was an observational campaign conducted from September 2012 to September 2013 in the North Atlantic Ocean, ($\sim 48^{\circ}$ 41 N, 16° 11 W). This site is approximately 40 km south east of the Porcupine Abyssal Plain sustained observatory (Lampitt *et al.*, 2001; Hartman *et al.*, 2010). Pairs of gliders were deployed for the whole year (Table 2.1 shows the time of all the deployments). Measurements from 50-500 m were also made from moorings, including temperature, salinity, horizontal velocity and ADCP. Nine moorings were arranged with one central mooring, four were approximately 2 km apart around the central mooring and another four were spaced approximately 15 km apart (Figure 2.1). This allows measurements to be made of the mesoscale (outer moorings) and submescale (inner moorings). This study focuses on the glider deployments to study the biogeochemistry of the area.



FIGURE 2.1: Locations of the nine moorings in the array and distances from moorings

2.2 Glider Data and Processing

An ocean glider is an autonomous, buoyancy driven vehicle that profiles to a depth of typically 1000 m. This project used pairs of gliders that were deployed from September 2012 to September 2013. There were short periods of overlap when gliders were turned around, during several research cruises, due to limitations with battery power (see Table 2.1 for the timeline of glider deployments). In total, 6 separate glider deployments were used for this study. SG502 did not have a PAR sensor and was therefore not included. This resulted in a whole year of data with two different gliders deployed coincidentally, apart from between January and April when only one glider could be used. The gliders profiled along orthogonal butterfly patterns (Figure 1.3), profiling to a depth of 1000 m. Each butterfly took approximately one week to complete. The instrument sampling rate was every 5 or 10 seconds, equating to approximately one measurement every half to one meter at typical vertical speeds of 0.1 m s^{-1} , along a saw-tooth trajectory (Eriksen et al., 2001; Davis et al., 2002; Rudnick et al., 2004).
Glider	Deployment Number	Start Date	End Date	Details
SG566	1	09/12	01/13	
SG533	1	09/12	01/13	Problems with conductiv-
				ity cell
SG579	2	01/13	04/13	Chlorophyll fluorescence;
				nutrients
SG502	2	01/13	04/13	No PAR sensor
SG566	3	04/13	09/13	
SG510	3	04/13	06/13	Problems with conductiv-
				ity cell
SG533	4	06/13	09/13	

TABLE 2.1: Glider deployments for the OSMOSIS project

The gliders were equipped with an unpumped Seabird SBE13 CT sail (conductivitytemperature; Seabird Electronics, Bellevue, USA), a Paine pressure sensor (Paine Electronics, East Wenatchee, USA), a Triplet Ecopuck (Wetlabs, Philomath, USA) measuring chlorophyll fluorescence and optical back scatter, and a broadband 4π cosine Photosynthetically Active Radiation (PAR) sensor (400-700 nm; Biospherical Instruments, San Diego, USA). Raw measurements from the CT sail were initially calibrated using manufacturer-supplied coefficients, with further corrections to account for thermal lag (Garau *et al.*, 2011). Glider salinities were calibrated against cruise data (Damerell *et al.*, 2016). Pressure measurements were corrected to remove long term drift and to account for pressure hysteresis within each dive (Damerell *et al.*, 2016).

Manufacturer calibrations were initially applied to data from the Wetlabs Triplet and 4π PAR by subtracting the instrument blank and applying a scaling factor. The manufacturer's calibration for chlorophyll fluorescence is based on the sensor's response to a culture of the phytoplankton species *Thalassiosira weissflogiiat* at a known chlorophyll-*a* concentration (UserManual10, 2014). Our secondary calibration methodology is outlined below. Other empirical methods have been developed to calibrate fluorescence profiles (Stramski *et al.*, 2004), but by using in situ PAR data, a scale factor can be derived which may indicate changes in phytoplankton physiology (Hemsley *et al.*, 2015). The manufacturer's PAR sensor calibration uses a traceable 1000 watt type FEL Spectral Irradiance Standard and is reported in units of μ Einsteins cm⁻² (Biospherical, 2013). All data were depth binned to 2 m depth intervals.

2.2.1 Fluorescence Data Processing

Chlorophyll is contained within phytoplankton cells and is relatively easy to measure as it has specific fluorescent properties, with maximum absorption near 440 nm and fluorescence at 685 nm (Huot & Babin, 2010). Fluorescence can therefore be used as a proxy for chlorophyll-a concentrations (Lorenzen, 1966), using the unique wavelength of fluorescence (685 nm). However the fluorescence-to-chlorophyll-a ratio can vary depending on species and pigment composition, phytoplankton size and nutrient stress (Cullen, 1982).

Quenching Correction

Fluorescence quenching is a depression in the fluorescence signal during daylight especially when irradiance is high, such as at noon (Figure 2.3). It represents a number of different photoprotective mechanisms, which allow the phytoplankton to avoid damage under high irradiance energy (Maxwell & Johnson, 2000).

Night time profiles were determined by extracting profiles where the surface PAR was less than 25 W m⁻². Day time profiles were extracted if PAR was higher that 25 W m⁻². A linear regression was obtained between 2132 night-time profiles of chlorophyll and backscatter counts to a depth of 60 m. This regression represented by the equation:

$$chlorophyllconcentration = 0.0455 * backscatter - 3.2$$
 (2.1)

and was used to correct daytime chlorophyll profiles affected by quenching (Spearman (1904) $R^2 = 0.87$, p <0.001, n = 31980 Figure 2.2). Due to the dominance of diatoms in the pre-bloom phytoplankton community structure (Lochte & Pfannkuche, 1987; Barlow *et al.*, 1993; Painter *et al.*, 2010*b*; Henson *et al.*, 2012), to our knowledge diel vertical migration should not impact heavily on the quenching corrections.

Subsurface chlorophyll maxima were defined when the maximum in chlorophyll concentration was below the mixed layer depth. When a subsurface chlorophyll maxima (SCM) were present the night-time relationship between optical backscatter and chlorophyll weakened, with \mathbb{R}^2 values reducing from ~0.87 to ~0.54. The poor relationship may be due to physiological changes in the phytoplankton due to low light levels, such as the packaging effect (Swart *et al.*, 2015). The decision was made not to correct for quenching when an SCM was present for several reasons: first surface chlorophyll concentrations were substantially lower when a SCM was present, second there was little difference in surface and SCM chlorophyll concentrations between night and day profiles



FIGURE 2.2: Regression between glider backscatter and chlorophyll concentration. Blue diamonds show well mixed chlorophyll profile, black stars show when there was a SCM present.



FIGURE 2.3: Example chlorophyll profiles (a) for day (solid) and night (dashed) and the corrected profile (blue). Panel b) shows the backscatter profiles for day (solid) and night (dashed)

(<5%), third the method assumes a constant carbon to chlorophyll ratio and no cellular changes with depth, which is unlikely to hold in the SCM as changed due to light adaptation occur, such as chlorophyll packaging (Swart *et al.*, 2015), finally if the correction was made to the SCM it resulted in an artificial increase of chlorophyll at the surface that was not present in the night profiles. For glider SG566 out 589 profiles 257 were found to be in the SCM and therefore 43 % of profiles were not corrected for quenching. In late spring the mean difference in surface chlorophyll concentrations between night and day profiles was 2.1 mg chl m⁻³. However when a persistent SCM was present the mean difference in surface chlorophyll concentrations was <0.2 mg chl m⁻³. Figure 2.4 shows a histogram of the differences between night and day profiles during the period of the SCM, the shape is Gaussian and centred on zero and therefore there is no evidence of quenching within the day time profiles within the SCM. There are slightly higher values of chlorophyll during the day shown in the histogram (Figure 2.4), which may indicate growth, whereas at night there may be losses due to grazing.



FIGURE 2.4: A histogram of the night minus day profiles when there is a SCM present

2.2.2 PAR Processing

Although absolute PAR values are not needed to calibrate chlorophyll fluorescence they are needed for input into the primary production algorithm. Validating the glider PAR instrument on the Seaglider was done with a linear least squares regression between the ship and glider surface PAR. All observations were coincident to within 100 km, a distance over which any minor differences in irradiance were expected to be due to significant differences in cloud cover and/or type, assuming identical sun angle and intensity. Ship-based PAR data were extracted within one minute of each glider surfacing and the resultant time series correlated to irradiance just above the surface $(E(0^+))$ estimates from the glider, which were calculated using the following equations:

$$r_{tot} = r_d + r_{diff} \tag{2.2}$$

Where r_{tot} is the reflectance of the water, which is the sum of direct reflectance (r_d) and diffusive reflectance (r_{diff}) . The direct reflectance was calculated from the solar declination at the time of the glider surfacing and the wind speed. The diffuse reflectance is calculated from the wind speed, which impacts the amount of foam present at the water surface. The full equations can be seen in Appendix A.

Glider PAR was then extrapolated to just below the surface by assuming exponential attenuation. The following equation was then applied to calculate PAR just above the surface, $E(0^+)$

$$E(0^+) = \frac{E(0^-)(1 - R\bar{r})}{(1 - r_{tot})}$$
(2.3)

where $E(0^-)$ is the irradiance just below the surface and R the irradiance reflectance (0.1 in ocean waters). The water-air Fresnel reflection for the whole diffuse upwelling radiation (\bar{r}) has a value of 0.48 Kirk (2011). R and \bar{r} are needed to obtain the upwelling irradiance flux, which is subsequently reflected back down upon reaching the water surface (Kirk, 2011). The resulting correlation was significant (Spearman R²= 0.48, p < 0.005, n = 83) but revealed substantial variation between ship-based and glider-based measurements particularly at midday. The standard deviation of differences over 10 minutes of the measurement was calculated for the ship-based PAR; reaching up to 100 W m⁻², with a mean standard error of ± 14 W m⁻². This is likely due to patchy cloud cover shading the ship and or glider. The coefficient of variation was generally less than 0.6 suggesting a high variance. Errors calculated for the ship-based PAR increased late in the evening and early morning when PAR values are low and sensor geometry can play a significant role due to the low angle of the sun.

To evaluate the strength of the linear regression between glider and ship PAR a bootstrapping method was applied, 90% of the data points were randomly selected, 10,000 times, and calculated the regression for each subset. The distribution of the slopes was normal with a mean of 0.96 and a standard deviation of 0.076. I concluded that the true slope and intercept were indistinguishable from one and zero. Based on this analysis, glider and shipped-based PAR estimates agree so the glider PAR data were used with the manufacturer's calibration applied.

2.2.3 Temperature and Salinity Calibration

The CT sensor is unpumped and therefore thermal lag can become a problem especially when there is a steep thermocline or halocline. This was corrected for following the method of Garau *et al.* (2011). "Bad" data caused by biofouling, and/or poor flushing of the CT cell, is flagged and discarded (Damerell *et al.*, 2016). Salinity was calibrated against salinity taken from CTD sensor data from a number of cruises to the region (see below, Section 2.3). The CTD data were calibrated against discrete water samples taken on the same cruises, analysed with an Autosal salinometer. After calibration temperature and salinity concentrations are accurate to $0.01^{\circ}C$ and 0.01 g kg⁻¹ respectively (Damerell *et al.*, 2016).

2.2.4 Mixed Layer Depth Calculation

A threshold density or temperature at 10 m depth was used to calculate the Mixed Layer Depth (MLD) by finding the depth where there is a change of more than $0.2^{\circ}C$ or 0.03 kg m⁻³ from the threshold value (Damerell *et al.*, 2016) (this data was kindly processed and given to me by Dr Gillian Damerell at University of East Anglia). The value which showed the shallowest MLD is used (de Boyer Montégut *et al.*, 2004).

2.3 Cruise Data

Five cruises were conducted to the region during the project; D381 in September 2012, CE13001 in January 2013, JC085 in April 2013, JC087 June 2013 and JC089 September 2013 (see Table 2.2 for exact dates and measurements taken).

Cruise	Start Date	End Date	Relevant Measurements Taken	
D381	Sep 2012	Sep 2012	Chlorophyll; nutrients	
CE13001	05 Jan 2013	11 Jan 203		
JC085	Apr 2013	Apr 2013	Chlorophyll; nutrients	
JC087	Jul 2013	Jul 2013	Chlorophyll; nutrients; ¹³ C uptake	
JC090	Sep 2013	Sep 2013	Chlorophyll; nutrients	

TABLE 2.2: Cruises conducted to the study site during the OSMOSIS project

2.3.1 Chlorophyll Samples

Water samples for chlorophyll-*a* were collected on all cruises from up to six depths across the euphotic zone using a Seabird 911 plus CTD-Niskin rosette system. Chlorophyll-*a* concentrations were measured using 250 ml water samples filtered onto 25 mm Whatman glass fibre filters (GF/F; nominal pore size 0.7 μ m). This involved chlorophyll-*a* pigment extraction in 6 ml of 90% acetone at 4°C in the dark for ~20 hours before measurement on a Turner Designs Trilogy fluorometer calibrated against a pure chlorophyll standard (spinach extract, Sigma Aldritch) (Welschmeyer, 1994).

2.3.2 Primary Production In situ

Measurements of PP using the ¹³C method of Slawyk et al. (1977) were made between 30th May and 18th June on JC087 only. Water samples were collected from pre-dawn CTD casts at five depths corresponding to 55%, 20%, 7%, 5% and 1% of surface irradiance based on profiles obtained from previous midday CTD casts and an estimate of the diffuse attenuation coefficient obtained by linear regression of the natural log of PAR against depth. Each 1 litre water sample was added to an acid-rinsed Nalgene polycarbonate bottle, which was wrapped with optical filters (Lee Filters, Hampshire, UK) to replicate the appropriate irradiance levels. Each bottle was spiked with 200 μ L of ¹³C labelled sodium bicarbonate (0.65g in 50 ml of pH adjusted milli-Q water), corresponding to an addition of 255 μ mol L⁻¹ (or ~1% of ambient (~2084 μ mol L⁻¹) dissolved inorganic carbon concentrations). Sealed sample bottles were placed in on-deck incubators, which were flushed with surface seawater for 24 hours. After incubation, each sample was filtered onto an ashed (450°C, 6 hours) 25mm GF/F (Whatman) filter and rinsed with a weak HCl solution (1-2%) to remove inorganic carbon before being stored frozen at -20°C. Filters were oven dried and encapsulated in tin capsules. Samples were analysed for ¹³C isotopic enrichment at the Scottish Association for Marine Science (OBAN, Scotland) using an ANCA NT preparation system coupled to a PDZ 20-20 Stable Isotope Analyser (PDZ Europa Scientific Instruments, Northwich, UK). Daily primary production rates were calculated from the stable isotope results using standard equations (Legendre & Gosselin, 1997).

2.3.3 MSS Data Collection

Turbulence measurements were collected with a MSS90 microstructure profiler to a depth of approximately 200 m (Tech, 2013). The MSS measurements were taken on a number of days (shown in Table 2.3). Estimates of the turbulent kinetic energy dissipation rate (ϵ) were obtained from raw shear data using the MSSPRO software standard processing sequence (this data was kindly processed and given to me by Dr Natasha Lucas at Bangor University).

Cruise	Start Date	End Date	Number of profiles
D381	16/09/12	18/09/12	238
D381	21/09/12	22/09/12	202
D381	26/09/12	28/09/12	175

TABLE 2.3: MSS profiles

2.4 Mooring Data

The OSMOSIS mooring data has a number of different sensors and uses. Figure 2.1 shows the locations of the moorings and the distances between them. The current meters are used in this thesis to estimate budgets of nitrate into and out of the study site, the position of the instruments are show in Figure 2.5 (figure was made by Xiaolong Yu at National Oceanography Centre Southampton). The density from the moorings is also used to estimate the amount of nitrate used in the budgets by calculating a nitrate density relationship from CTD data (Chapter 5). The mooring data has been binned to 10 m bins and interpolated onto an hourly grid (this was kindly processed and given to me by Xiaolong Yu at the National Oceanography Centre Southampton).

2.5 Satellite Ocean Colour Data

Chlorophyll composites of MODIS Aqua 1 km daily resolution data were obtained from the NERC Earth Observation Data Acquisition and Analysis Service (NEODAAS). These data are used for comparison with the method described in Chapter 3, which estimates primary production from ocean gliders. The 1 km data was used to validate the method as a stringent match up. For each glider surfacing the satellite data pixel that matched the position and date was extracted. I opted to use a stringent 1 km match-up between glider and satellite observation to minimise the introduction of potential artefacts. Due to persistent cloud cover the number of retrieved match-ups is reduced. Although relaxing the spatial criteria would likely increase the number of data points this would also be at the cost of increased variability in the comparison between glider and satellite. It is also for this reason that I do not use a cruder satellite product (i.e. 4 km or 9 km spatial resolution) or longer satellite averaging period (i.e. 3 or 8 day averages) which would both provide additional data. Cloud cover resulted in data gaps



FIGURE 2.5: A 3D diagram of the mooring array. Shows the locations of the sensors on the moorings. The centre mooring also has the the ADCP used for the dissipation measurements. Figure made by Xiaolong Yu at the National Oceanography Centre Southampton

in satellite coverage and surface match ups; these time periods were omitted from the analysis. Approximately 21% of glider surfacings could be matched to satellite data.

For an annual estimate of primary production I used 4 km 8-day MODIS Aqua chlorophyll product. Pixels were extracted for the 15 x 15 km area of the OSMOSIS site. A less stringent match-up is required for estimating the seasonal cycle of primary production (Chapter 4) and so in this case it is more advantageous to have more data points for a comparison. The same method to model the chlorophyll depth profile described below was used for both sets of data 2.5.1.

Average daily integrated PAR fields from MODIS Aqua were also used in the primary production algorithm. To estimate primary production from the satellite I used the algorithm described by Smyth *et al.* (2005), with inputs of the chlorophyll profiles, surface spectral light, date, time and location. This couples the model of Morel (1991) with the HYDROLIGHT radiative transfer code (Mobley, 1998), allowing light through the water column to be more accurately modelled. When calculating the integrated yearly value of primary production the satellite pixels in the area were averaged for each 8-day period to produce a time-series.

Satellite 8-day 4 km estimates of particulate inorganic carbon (PIC) was also used as an indication for change in community composition, specifically indicating the presence of coccolithophores (Gordon *et al.*, 2001; Balch *et al.*, 2005). This was extracted for the same 15 km square grid over the glider deployment site (Figure 1.3).

2.5.1 Modelling a Satellite Chlorophyll Profile

The satellite estimate for chlorophyll (c) was used to calculate full depth profiles using relationships derived by Morel and Berthon relating satellite chlorophyll to the shape of the profile at depth(Morel & Berthon, 1989). A Gaussian curve, with a maximum value (C_{max}) situated at (ζ_{max}) and a thickness controlled by $(\Delta\zeta)$, is fitted over a background (C_b) , Equations are shown below:

$$\frac{C(\zeta)}{\bar{C}_{ze}} = C_b + C_{max} exp\left[-\left\{\frac{\zeta - \zeta_{max}}{\Delta\zeta}\right\}\right]$$
(2.4)

with

$$C_b = 0.768 + 0.087 \log c - 0.179 (\log c)^2 - 0.025 (\log c)^3$$
(2.5)

$$C_{max} = 0.299 - 0.289 \log c + 0.579 (\log c)^2$$
(2.6)

$$\zeta_{max} = 0.600 - 0.640 \log c + 0.0021 (\log c)^2 + 0.115 (\log c)^3 \tag{2.7}$$

and

$$\Delta \zeta = 0.710 + 0.159 \log c + 0.021 (\log c)^2 \tag{2.8}$$

Where $C(\zeta)/\bar{C}_{ze}$ is normalised chlorophyll; chlorophyll divided by the mean pigment concentration in the euphotic layer, where $C_{ze}=1.12 \ c^{0.803}$. The full methods are described in Morel and Berthon Morel & Berthon (1989).

For an alternative estimate of primary production for comparison to the glider-based estimates, the profiles of MODIS Aqua satellite chlorophyll and PAR data were also used as inputs to the primary production algorithm developed by (Smyth *et al.*, 2005). This model couples the photosynthesis model (section 3.2.6) to the HYDROLIGHT radiative transfer code (Mobley, 1998), allowing for the inclusion of CDOM, suspended particulate matter, sea surface temperature, PAR and day length to more accurately estimate irradiance with depth.

2.6 Continuous Plankton Recorder Data

Continuous Plankton Recorder (CPR) is towed at a depth of 7-10 m behind ships of opportunity. It contains a silk mesh that winds into a tank of formalin, preserving the plankton. The method of collecting and counting the plankton has not changed since 1958 resulting in a consistent time series over several decades. The data used in this study are from the E5 standard area, showing abundances of diatoms and dinoflagellates analysed for the period of the survey. These data were used to describe changes in the community composition for the region (see Chapter 4).

Chapter 3

Calculating Primary Production for vertical chlorophyll and irradiance profiles



3.1 Primary Production

This chapter describes the methods used to estimate primary production using the glider measured chlorophyll fluorescence and photosynthetic active radiation (PAR). This allows me to quantify the rates of primary production at high frequency and vertically resolved over a whole year, at the study site. This chapter also explains how the chlorophyll is corrected using irradiance profiles to derive a scale factor for each dive and climb profile. As the purpose is to describe the method, this chapter focuses on a single glider deployed from April to September 2013, the next chapter examines primary production over the year. This chapter has been published in Environmental Science and Technology (Hemsley *et al.*, 2015).

3.2 Method

3.2.1 Irradiance corrections, calibrations and calculation

Primary production is best parametrised using spectral irradiance, as irradiance attenuates preferentially from red to blue wavelengths (Kirk, 2011). Non-spectral methods can overestimate primary production by as much as 50% if only broadband PAR is used (Sathyendranath *et al.*, 1989). A number of calculations are necessary to spectrally resolve the glider broadband PAR observations.

The glider only records subsurface PAR, so first an estimate of surface irradiance is made from glider data, for comparison with a surface irradiance model. The surface irradiance is then decomposed into spectral components. Irradiance at depth was calculated using spectrally-weighted algorithms (Xing *et al.*, 2011). Details are described below.

Seaglider SG566 returned 1325 simultaneous profiles of chlorophyll and PAR (downcast and upcast counted separately). Profiles where PAR intensity increased with depth (due to passing cloud cover and/or glider rolls) (Xing *et al.*, 2011) were excluded from the analysis (319 profiles). Night-time profiles were also excluded due to the lack of irradiance (417 profiles) leaving a total of 589 simultaneous PAR and fluorescence profiles for analysis.

3.2.2 Estimating surface irradiance from subsurface glider measurements

The fraction of solar irradiance entering the water column depends on the amount of sunlight reflected by the sea surface. This is calculated by separating the diffuse and direct components of irradiance using determinations of the Fresnel reflectance and the amount of foam (same method as used in Section 2.2.2, Equation 2.3).

3.2.3 Calculating spectral irradiance

Surface PAR from the Seaglider (Equation (2.3)) was spectrally decomposed into 5 nm wavelengths, E_0 (λ), using a look-up table (Smyth *et al.*, 2005) created by generating a clear sky run of a radiative transfer model (Gregg & Carder, 1990), which is specific for oceanographic applications and adapted to include the effects of cloud cover (Reed, 1977). For a given day, this model is run for noon using the glider surfacing position and relevant meteorological parameters to attenuate irradiance through the atmosphere (British Atmospheric Data Centre, BADC). The model outputs a spectrally resolved, full day irradiance time series just above the surface of the ocean for the location of interest. The integrated irradiance over all wavelengths for the time of the glider measurements was calculated in $\mu mol \ quanta \ m^{-2} \ s^{-1}$. The ratio between $E(0^+)$ from Equation(2.3) and the integrated clear sky run is used to scale the spectral values for the day in question using each profile in that day to get spectral irradiance over the whole day at half hour intervals.

3.2.4 Spectral irradiance through the water column

To calculate spectral irradiance $(E(z,\lambda))$ at a given depth in the water column I used the equation (Carr, 1986),

$$E(z,\lambda) = E_0(\lambda) \int_z^0 exp - \left([K_w(\lambda) + K_c(\lambda)], z \right)$$
(3.1)

where $K_w(\lambda)$ is the attenuation coefficient associated with water and $K_c(\lambda)$ is the attenuation coefficient associated with chlorophyll and other dissolved material at specific wavelengths, λ . Morel & Maritorena (2001) calculate $K_c(\lambda)$ as

$$K_c(\lambda) = \chi_c(\lambda) Chl^{e(\lambda)}$$
(3.2)

The coefficient $\chi_c(\lambda)$ and the exponent $e(\lambda)$ are both functions of wavelength and Chl is chlorophyll concentration (mg m⁻³). Wavelengths within the PAR broadband range are used at 5 nm intervals.

3.2.5 PAR-based chlorophyll correction

The fluorescence was converted to chlorophyll using a laboratory standard of single species diatom. However that is not necessarily representative of the mixed community being measured in the field and therefore it is necessary to further correct the chlorophyll profiles to better represent reality.

The chlorophyll fluorescence sensor was corrected using the PAR measurements and Eq.(3.1) to model the irradiance attenuation due to chlorophyll (Carr, 1986). The uncorrected-chlorophyll profile (with dives and climb treated separately) was divided by a scaling factor ranging from 0.2-25 in intervals of 0.2. The spectral irradiance profile was recalculated from the glider measured surface irradiance and the attenuation due to the scaled chlorophyll profile (Eq. (3.1) and (3.2)). The calculated values of spectral irradiance were then integrated over all wavelengths (400-700 nm) to compare to glider PAR measurements. A root mean squared error (RMSE) was calculated between the modelled and measured PAR values, over all depths (typically 50 points), for each scale factor.

For each profile the scale factor with the lowest RMSE was then used to scale the uncorrected-chlorophyll concentration. This approach produces an independent scaling factor for each dive/climb, allowing for drift in the fluorometer to be corrected. The method assumes Case I water characteristics where CDOM and particulates co-vary with phytoplankton (Morel, 1988; Boss *et al.*, 2008). This method can be used if the glider PAR sensor is uncalibrated provided the fluorescence-chlorophyll relationship is linear as the method relies on matching the attenuation due to chlorophyll using the surface PAR value. For example, if the PAR sensor is reading twice as high the surface value will also be twice as high and therefore the modelled profile, which uses this surface value, can still be used to determine the attenuation due to chlorophyll. Although the PAR profile is used to correct chlorophyll and used as input into the primary production model, the PAR-corrected chlorophyll and PAR profiles are still largely independent as one used the attenuation and the other the absolute values.

Variation in the scaling factor over a deployment period may result from poorly resolved PAR profiles (e.g. significant glider rolls or cloud cover). Profile-to-profile variability was reduced by using the median scaling factor calculated for a 10-day moving window. A 10-day window was picked arbitrarily, but no significant difference was seen using 6, 8 or 10 days. Longer time intervals resulted in over-smoothing of the scaling factor.

Final PAR-corrected chlorophyll concentrations for each profile were obtained using the appropriate 10-day median scale factor (Figure 3.1). These corrected chlorophyll profiles (Figure 3.2) were used as input into the primary production model, along with the spectral downwelling PAR (Section 3.2.3).



FIGURE 3.1: The scale factors derived from scaling fluorescence to match the modelled PAR to the observed PAR. The solid black line is the scale factor for a 10 day moving window and is the value used to scale the chlorophyll. The dashed grey lines are \pm one standard deviation within each window.



FIGURE 3.2: Timeseries of calibrated chlorophyll from the glider data. The dashed white line is the euphotic depth (1% of surface irradiance) and the solid white line shows the mixed layer depth (calculated in 2.2.4. Gaps in the data were from the sensor being turned off due to battery consumption.

3.2.6 Calculating Primary Production

Primary production was calculated with the spectrally split glider profiles of irradiance and PAR-corrected chlorophyll using depth, time and wavelength-resolved irradiance (Morel, 1991). Primary production is represented by a triple integral, integrating over day length (L), depth (D) and wavelength λ from $\lambda_1 = 400$ nm to $\lambda_2 = 700$ nm,

$$PP = 12 \int_0^L \int_0^D \int_{\lambda_1}^{\lambda_2} Chl(Z) PAR(\lambda, Z, t) a^*(\lambda) \phi_\mu(\lambda, Z, t) d\lambda dZ dt$$
(3.3)

where a^* is the absorption cross section per unit of chlorophyll (m⁻¹), ϕ_{μ} is the net growth rate (mol C (mol quanta)⁻¹). Each separate dive and climb were assigned an average time (t) and position (latitude and longitude) for the profile. The model requires surface downwelling spectral irradiance (W m⁻² nm⁻¹), which is provided by the glider PAR sensor (Section 3.2.3). Parameters are calculated as in Morel *et al.* (1996), where a^* is 0.033 m⁻¹. Temperature from the glider CTD (°C) is used to parameterise ϕ_{μ} using the following equations:

$$\phi_{\mu} = \phi_{\mu \max} f(x) \tag{3.4}$$

$$f(x) = x^{-1}(1 - e^{-x})e^{-\beta(x)}$$
(3.5)

$$x = PUR/KPUR \tag{3.6}$$

and

$$\phi_{\mu} KPUR(T) = KPUR(20^{\circ}) 1.065^{(T-20^{\circ}C)}$$
(3.7)

where $\phi_{\mu\text{max}}$ is set to 0.06 mol C (mol quanta)⁻¹ and f(x) is formulated according to the photosynthesis-irradiance curve (Platt *et al.*, 1981). β is a unitless photoinhibition parameter set to 0.01. PUR is the Photosynthetic Useful Radiation (PAR weighted by chlorophyll-*a* specific absorption spectrum and KPUR is derived from temperature (T), which is provided by the glider PAR sensor.

The model used here represents net primary production. Net primary production is the gross primary production minus respiration by plants. This differs from net community production, which is a measure of the net amount of carbon removed from the atmosphere and therefore also includes respiration by zooplankton.

Choice of model and sensitivity study

There are several primary production models available, the choice of primary production model was based on the good performance of this model in the North Atlantic region. A number of papers show that the Morel (1991) model performs well in the area (Smyth *et al.*, 2005; Carr *et al.*, 2006; Tilstone *et al.*, 2009; Saba *et al.*, 2011). Furthermore, as described above primary production is best calculated using a wavelength resolved model as changes in the proportion of each wavelength changes with depth, blue light penetrates deeper in the water column (Kirk, 2011).

A sensitivity study was conducted to test the parameters, a^* and ϕ_{μ} , used in the model and how much they influence primary production. Parameter values were chosen from the literature using the maximum and minimum observed values for the North Atlantic (Table 3.1; Bricaud *et al.*, 2004; Morel *et al.*, 1996; Babin *et al.*, 1996; Cleveland, 1995; Bricaud *et al.*, 1983). A range was chosen of 0.01 to 0.1 m⁻¹ for a^{*} and 0.01 to 0.06 mol C (mol quanta)⁻¹ for ϕ_{μ} . The model was run for all the PAR-corrected chlorophyll profiles for a combination of the parameters, including the standard values used in the model of 0.033 and 0.06, for a^{*} and ϕ_{μ} respectively (Smyth *et al.*, 2005).

An error was also placed on the PAR-corrected chlorophyll by using the root mean squared error (RMSE) between all the bottle samples taken within 10 km of the glider and the glider PAR-corrected chlorophyll concentration (RMSE = $0.3 \text{ mg Chl-}a \text{ m}^{-3}$). The RMSE was added and subtracted from the PAR-correction chlorophyll profiles and input into the model.

Reference	$a^{*} (m^{-1})$	$\phi_{\mu} \pmod{\mathrm{C} \pmod{\mathrm{Quanta}}^{-1}}$		
Bricaud et al. (2004)	0.01 - 0.1	_		
Morel <i>et al.</i> (1996)	—	0.01 - 0.06		
Babin <i>et al.</i> (1996)	—	0.03 - 0.06		
Cleveland (1995)	0.01 - 0.05	_		
Bricaud et al. (1983)	0.01 - 0.1	_		

TABLE 3.1: Sensitivity study on the primary production model

3.3 Results

3.3.1 Glider chlorophyll

3.3.1.1 PAR-Corrected Chlorophyll data

The scale factor used to calibrate the chlorophyll data (Figure 3.1) has a mean of 3 (range 0.6 - 11). In May there is a peak of 5 but only 4 profiles were used to calculate this scale factor (range 1.2-8.8), as the sensors were turned off for a time to save battery, so it is not as well constrained as in other months when more profiles were available. In July the scale factor became less variable (range 1.2 - 1.8) for the remainder of the deployment.

The chlorophyll profiles are shown in Figure 3.2 for the whole deployment period. Maximum chlorophyll concentrations were typically < 1.5 mg Chl-a m⁻³ from May until July, when they increased to > 2 mg Chl-a m⁻³. Before July the chlorophyll concentration varied little within the top 30 m. A subsurface chlorophyll maximum (SCM) started to form towards the end of July, with maximum chlorophyll concentrations > 4 mg Chl-a m⁻³ at a depth of 30 m. Surface concentrations during August were very low, < 0.6 mg Chl-a m⁻³. By the end of August the SCM deepened to 40 m and maximum concentrations in the SCM decreased to < 2.5 mg Chl-a m⁻³, with surface concentrations < 0.4mg Chl-a m⁻³.

3.3.1.2 Comparison of glider and bottle-sample estimates of chlorophyll

Figure 3.3 compares discrete bottle-sample chlorophyll and PAR-corrected glider chlorophyll for the 3 cruises. In late April, prior to the spring bloom, the discrete chlorophyll concentrations were comparable to the PAR-corrected chlorophyll concentrations (JC085). Surface concentrations ranged from 0.25 - 0.7 mg Chl-a m⁻³ and 0.15 - 0.8 mg Chl-a m⁻³ for the discrete samples and PAR-corrected glider estimates, respectively. The range in the PAR-corrected glider-based chlorophyll concentrations was slightly larger than the discrete samples; likely due to the greater number of glider profiles detecting a wider range of concentrations. At depths between 75 - 150 m, bottle samples were approximately 0.1 - 0.2 mg Chl-a m⁻³ higher than the glider, which effectively measured close to zero at these depths, which is below the euphotic depth (60 m).

In July the majority of discrete chlorophyll measurements were elevated compared to the PAR-corrected glider estimates, particularly throughout the upper 50 m. Surface concentrations ranged from 0.05 - 1.2 mg Chl-a m⁻³ for the PAR-corrected glider compared with 0.08 - 1.8 mg Chl-a m⁻³ from bottle samples (Figure 3.3). There was no

offset between the PAR-corrected glider and discrete measurements below 75 - 150 m, suggesting no systematic error. Chlorophyll values below 100 m were < 0.4 mg Chl-a m⁻³, with the majority of the glider and discrete measurements < 0.2 mg Chl-a m⁻³. The panel on the left (Figure 3.3b) shows that the bottle chlorophyll are below the one-to-one line and therefore higher than the PAR-corrected chlorophyll. On the other hand the bottle measurements are notably further in distance from the glider at the time of measurement (generally > 10 km), whereas the other two cruises show that the measurements were taken within < 6 km of the glider, so the relatively poorer fit could be due to increased spatial heterogeneity.

For the final cruise, in September (JC90), discrete and PAR-corrected glider chlorophyll estimates were comparable (Figure 3.3). Surface values ranged between 0.4 and 1 mg Chl-a m⁻³ in the discrete water samples, whereas the PAR-corrected glider chlorophyll ranged from < 0.1 to 0.75 mg Chl-a m⁻³. A SCM around 40 m was measured by both data sets, with similar maximum values (3.3 mg Chl-a m⁻³).

The lateral distances between CTD and glider profiles were compared with the differences in surface chlorophyll concentrations (Figure 3.4, Spearman $R^2 = 0.47$, p < 0.001, n = 21). Surface chlorophyll differences increase with distance, suggesting that spatial differences remain an important consideration in the comparison of glider and in situ data. Many of the CTD profiles were located >10 km away from the glider making it possible that spatial variability affects the comparison. This is also consistent with the glider data, which can show significant variations in water mass properties and chlorophyll concentrations along a single 15-km transect. Cloud cover hinders examining this from satellite images in more detail.

3.3.2 Depth Integrated Primary Production

3.3.2.1 Depth integrated glider estimates of primary production

Glider based estimates of primary production ranged from 0.38 to 30 g C m⁻² d⁻¹ over the 5 months, displaying strong temporal variability. These estimates have been compared to ship-based ¹³C measurements and 1 km satellite estimates (Figure 3.5).

The ¹³C primary production estimates, integrated to the base of the euphotic depth, from June are compared to glider estimates in Figure 3.5a. Glider profiles on the same day were averaged together for comparison. ¹³C primary production increased from day 157 to 165 (06 June to 14 June), with values ranging from 0.5 to 1.9 g C m⁻² d⁻¹, whereas the glider estimates of primary production were relatively consistent, varying from 1.1 to 1.6 g C m⁻² d⁻¹ over the same time period. Glider primary production



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FIGURE 3.3: Chlorophyll measurements from CTD and glider with depth for the three cruise periods a) JC085 - April 2013 b) JC087 - July 2013 c) JC090 - September 2013. The solid lines show the mean profiles. The panels on the right are for the same cruise, showing the regression between the CTD bottle chlorophyll and the glider corrected chlorophyll. The solid black lines are the one to one line.

measurements were higher on average by 0.17 g C m⁻² d⁻¹ (or 39%) but offsets were also highly variable (Figure 3.5a).

In Figure 3.5b a time series of water column integrated primary production over the five month glider deployment is presented, in conjunction with ¹³C measurements already shown in Figure 3.5a. The glider estimates were higher than the ¹³C measurements but not unreasonably so. Integrated primary production rates from late April to May were 1 g C m⁻² d⁻¹ increasing to a maximum of 3 g C m⁻² d⁻¹ in July. Towards the end of July and through August rates decreased to 1.5 g C m⁻² d⁻¹ but remained highly variable, fluctuating by ± 0.6 g C m⁻² d⁻¹.

Integrated primary production estimates from the glider and satellite were also compared (Section 2.5 Figure 3.5c). Due to the high level of cloud cover there were no satellite pixel matches during the time period when the in situ measurements were taken and

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FIGURE 3.4: Difference between surface bottle and PAR-corrected glider chlorophyll concentrations (mg chl m⁻³) compared with the distance from the CTD from the ship (km)

therefore a comparison with satellite and ship-based measurements was not possible. The correlation between the satellite and glider estimates of surface primary production was modest but nevertheless statistically significant (Figure 3.6, Spearman, $R^2 = 0.374$, P < 0.0001, n=122). In general the glider shows higher integrated estimates of primary production than the satellite. Dissimilarity between estimates is likely due to differences in the PAR values and between the modelled and observed SCM. The root mean squared error between the modelled and observed chlorophyll profiles was 0.9 mg Chl-a m⁻³ (range 0.58 – 1.36 mg Chl-a m⁻³).

Figure 3.6 shows that the satellite and glider have reasonably good agreement during the deployment with similar variability, trends and magnitude in primary production. Both datasets show an increase in production from May to June (spring bloom Figure 3.5c) and a production maximum in July, with maximum rates of 3 and 2 g C m⁻² d⁻¹ for the glider and satellite respectively. Both data sets then show a decrease in primary production during late July. Although glider estimates of primary production are on average 16% higher than satellite estimates, it is possible that the modelled satellite data may be underestimating primary production in this region due to the failure to capture the depth and/or magnitude of the SCM accurately (see Chapter 4).



FIGURE 3.5: Panel a) shows the glider PAR-corrected and uncorrected integrated primary production estimates against the integrated ¹⁴C in situ measurements. Panel b) shows the timeseries of primary production depth integrated from the surface to the base of the euphotic zone for the PAR-corrected and uncorrected glider primary production estimates along with the in situ measurements. Panel c) shows the PAR-corrected against the Modia-AQUA primary production estimates.

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FIGURE 3.6: Comparison between integrated primary production estimates from satellite and gliders. Both have been integrated to the euphotic depth. The black dots show the well mixed profiles and the grey show where there is a significant subsurface production maximum. The solid black line is a linear regression through all the points and the dashed black line is the one to one line.

3.3.2.2 Primary production sensitivity analysis

The sensitivity of the primary production model was evaluated using a range of literature values for the maximum quantum yield for growth (ϕ_{μ}) , the absorption cross section of chlorophyll (a^*) and the PAR-corrected chlorophyll concentrations (Table 3.2).

When using the maximum $(0.1 \text{ m}^{-1} \text{ and } 0.06 \text{ mol C} (\text{mol quanta})^{-1}$ for a^{*} and ϕ_{μ} respectively) values of each parameter primary production was increased by 195% (Table 3.2). By just changing the a^* parameter from 0.1 to 0.01 primary production was increased by 195% and decreased by 70%, respectively. Both minimum values (0.01 m⁻¹ and 0.01 mol C (mol quanta)⁻¹ for a^{*} and ϕ_{μ} respectively) produced a percentage decrease of 95%.

The error on the primary production produced from the changing the chlorophyll values (± 0.3 mg Chl-a m⁻³, the RMSE between the bottle samples and PAR-corrected chlorophyll) shows a range of plus or minus 20% of the primary production values (Table 3.2).

TABLE 3.2: Sensitivity study on the primary production model

Chapter 3. Calculating Primary Production from vertical chlorophyll and irradiance profiles

Change in model	Mean Primary Production	Percentage increase or decrease		
	$(g C m^{-2} d^{-1})$	from standard run		
Standard run				
$a^* = 0.033$	1.59	0		
$\phi_{\mu} = 0.06$				
$a^* = 0.1$				
$\phi_{\mu} = 0.06$	4.7	195		
$a^* = 0.1$				
$\phi_{\mu} = 0.01$	0.79	-50		
$a^* = 0.01$				
$\phi_{\mu} = 0.06$	0.47	-70		
$a^* = 0.01$				
$\phi_{\mu} = 0.01$	0.08	-95		

3.3.2.3 Glider estimates of seasonal primary production vs literature estimates

Due to the limited number of ¹³C in situ measurements a comparison with productivity estimates from the literature for the same region has also been made (Table 3.3) (Chipman *et al.*, 1993; Marra *et al.*, 1995; Savidge *et al.*, 1995; Bury *et al.*, 2001; Painter *et al.*, 2010*b*). The literature values span 0.3 - 2 g C m⁻² d⁻¹, comparable with our ¹³C measurements. The glider primary production compares fairly well with the literature values throughout May and June. However, towards the end of June and July the literature observations are lower than those estimated from the glider and our ¹³C measurements. This may be due to inter-annual variability.

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Beference	Sampling period	Position	n	$mean(\pm standard deviation)$
Itelefence				$(g C m^{-2} d^{-1})$
This study	June 2013	$48^{o}N \ 16^{o}W$	6	1.16(0.5)
	May 2013	$48^{o}N \ 16^{o}W$	253	0.72 (0.4)
Glider Monthly Mean	June 2013		439	1.65(0.6)
	July 2013		339	2(0.6)
Chipman et al. (1993)	May 1989	$47^{o}N 20^{o}W$	11	0.84 (0.19)
Marra <i>et al.</i> (1995)	June 1991	$59.5^{o}N 21^{o}W$	4	1 (0.46)
Savidge et al. (1995)	May/June 1990	$47-60^{\circ}N \ 20^{\circ}W$	25	0.70 (0.32)
Bury et al. (2001)	May 1990	47^{o} N 20^{o} W	8	0.84 (0.50)
Painter $et al. (2010b)$	July 2006	49^{o} N 16^{o} W	3	0.55 (0.22)

TABLE 3.3: Primary production estimates in the same regions from the literature. All values integrated to the euphotic depth

3.3.3 Depth resolved primary production

Depth resolved primary production over the deployment (Figure 3.7) shows that throughout May and June primary production was highest at the surface and decreased with depth due to irradiance attenuation. In July, as chlorophyll and irradiance concentrations increased primary production also increased with maximum surface rates of 0.45 g C m⁻³ d⁻¹. In late July a subsurface production maximum formed with primary production rates of 0.2 - 0.3 g C m⁻³ d⁻¹. The production maximum deepened throughout August from 15 to 30 m, coincident with the SCM. The productivity maximum was located just beneath the mixed layer but also below the optical sampling depth for remote sensing (~ 10 m).

The euphotic depth was 60-80 m throughout May and June, with variable mixed layer depths (MLD) of between 40 and 130 m. The euphotic depth shoaled to 35 m in July coincident with increasing chlorophyll concentrations and associated greater irradiance attenuation and a shoaling of the MLD due to either surface forcing (heating) or a re-stratification through physical processes such as Ekman transport, mixed layer instabilities and lateral advection. The subsurface production maximum in late July and August was around the same depth as the mixed layer. However the SCM was deeper by 10 m than the production maximum, and below the mixed layer, suggesting that the SCM was preferentially located where nutrient concentrations were higher. In August the SCM was located between the MLD and the euphotic depth (Figure 3.2).

Depth profiles of the ¹³C productivity measurements are shown in Figure 3.8 alongside the range and mean of the coincident glider profiles. Although the ¹³C productivity rates were lower than the mean glider profile, they lie mostly within the range of glider



FIGURE 3.7: Depth resolved primary production from glider. The dashed white line is the euphotic depth and the solid white line is the mixed layer depth

data. Some of the ¹³C profiles show a production maximum around 30 m whereas the glider estimated profiles do not. Two profiles also show higher production at depth than estimated from the glider.



FIGURE 3.8: Profiles of the CTD ¹³C measurements (blue) against the range (dashed) and mean (solid) of glider profiles for the same time period.

3.4 Discussion

3.4.1 Advantages of calculating Primary Production using gliders

Fine scale measurements are important since submesoscale features are often present, such as highly productive filaments (Painter *et al.*, 2010*b*). Furthermore, primary production may change over daily time scales due to changes in irradiance and mixed layer depth. Such short timescales (hours) are not resolved by remote sensing, but with several profiles a day a glider can observe these changes. Early June showed differences in integrated production rates between sequential dives of between 0.3 and 1 g C m⁻² d⁻¹. The average daily production was < 2 g C m⁻² d⁻¹, so this difference was significant. Small scale temporal variations in primary production may be important in determining the carbon budget (Painter *et al.*, 2010*b*), especially in areas of high variability of phytoplankton. Submesoscale features (1 - 10 km) have been shown to account for up to 50% of the variability observed in primary production (Lévy *et al.*, 2001). Gliders are an important platform for monitoring and observing these features (Thomalla *et al.*, 2015; Swart *et al.*, 2015).

In addition to being able to resolve scales of variability in both time and space, a key advantage of using gliders is their ability to resolve subsurface features, previously only possible using ship-based measurements. Satellite production estimates are only resolved to the first optical depth and it has been shown that including fluorescence profiles significantly improves estimates (Jacox et al., 2015). Knowing the distribution of chlorophyll at depth is considered vital for ecological studies (Uitz et al., 2006). Glider integrated primary production rates were 16% higher than satellite estimates during the deployment suggesting that satellite-based estimates of production may be significantly underestimating primary production during summer months in this region. Subsurface chlorophyll maxima contribute significantly to integrated primary production in temperate latitudes (Anderson, 1969). Subsurface production maxima are common globally and this contribution is often modelled incorrectly for specific regions when using satellite colour to estimate primary production (Weston et al., 2005; Martin et al., 2010b; Cullen, 2015). Therefore gliders have considerable potential to improve satellite estimates of primary production (Jacox et al., 2015), as demonstrated here. The subsurface production maximum is explored more fully in Chapter 4.

Gliders also have the benefit of being able to continuously sample in all weather conditions. Ship-based measurements are weather and time dependent. For this study only six in situ ¹³C profiles were available as a comparison to the glider primary production estimates. Satellite coverage is restricted by cloud cover, which can introduce sampling bias (Longhurst *et al.*, 1995) (Gregg & Casey, 2007). During this deployment 467 profiles out of 589 (79%) had no direct satellite matchup due to high levels of cloud cover, equating to a loss of 105 days of satellite coverage over the whole deployment of 141 days.

3.4.1.1 Limitations of glider estimated primary production

The spectral constants for chlorophyll used in the irradiance attenuation calculations (Eq. 3.2) differ within the literature probably due to regional differences in community composition and/or temperature (Carder *et al.*, 1999; Morel & Maritorena, 2001; Werdell *et al.*, 2013). Additional uncertainty is introduced when broadband PAR is split spectrally. The method assumes that clouds, changes in atmospheric absorption and season, influence spectral values of PAR linearly (Smyth *et al.*, 2005). The photosynthetic rate per unit of biomass (Eq. 3.3) remains the largest unknown in the primary production algorithm because of its high variability in the ocean (Huot *et al.*, 2007).

Fluorescence measurements, which are only a proxy for chlorophyll-*a*, can be difficult to interpret. The fluorescence yield per unit of chlorophyll is known to change in response to changes in community structure (Falkowski & Kolber, 1995). The changing scale factor used to calibrate glider chlorophyll and the rapid decrease in the scale factor seen in July (Figure 3.1) may therefore be indicative of post bloom changes to the community composition. However this cannot be verified with the data available. However, using a time-dependent scale factor to probe community structure would be an interesting topic to explore.

Measurements from autonomous platforms present their own challenges. Sensor calibrations may drift with time or with biofouling (Perry *et al.*, 2008). Additional calibration measurements collected at deployment and recovery could indicate this. For this deployment no biofouling was noted at recovery and there was no drift in dark counts at depth, so fouling is unlikely to have negatively influenced the quality of the data set. As discussed in Section 3.3.1.2, discrepancies were however seen between bottle data and the PAR-corrected glider chlorophyll. As few CTD casts were made near the glider and this area is known to display patchy chlorophyll distributions (Painter *et al.*, 2010*b*), comparisons can be complicated. All the methods shown here, ¹³C, satellite and glider show broadly consistent results, however each method shows primary production at different timescales and resolution, which could be a major factor contributing to any differences seen between them. However the data are broadly consistent suggesting that glider productivity rates calculated here are generally appropriate for the region.

3.4.1.2 Primary Production Model

It is difficult to put an error on the primary production estimates from the model (Morel, 1991; Smyth et al., 2005). However, there is likely to be an error associated with the primary production algorithm and some algorithms tend to better represent certain areas. The algorithm used here performs well in the North East Atlantic (Carr et al., 2006; Saba et al., 2011). The validation of the model is shown in Smyth et al. (2005) and demonstrates that all the modelled points are within a factor of two of measured values (RMSE in log space is 0.16). A comparison between ship based ¹³C production measurements in June and coincident glider production estimates have been presented. The glider primary production measurements were higher on average by 0.17 g C m⁻² d^{-1} (or 39%) but offsets were also highly variable (Figure 3.5a). There are very few studies which have looked into putting error estimates on net primary production model estimates. Generally values of production are published without an associated error. Producing error estimates from complex models is a very complicated procedure due to the complexities of primary production algorithms. Pemberton et al. (2006) used a simple primary production algorithm to estimate errors on primary production estimates using variations in two parameters used in the algorithm, P^B_{max} the maximum rate of net photosynthesis (amount of carbon fixed per unit of chlorophyll biomass and per unit time) and α^B the initial slope of the photosynthesis-irradiance curve (the relationship between irradiance, I, and photosynthesis, P^B). They found that uncertainty varied depending on the experiment, making it difficult to assign a constant error term for each parameter. The maximum standard deviation varied by no more than a factor of two but was usually less (Pemberton et al., 2006). Morel et al. (1996) found that altering P_{max}^B had a greater effect on primary production estimates than α^B , although it is mainly dependent on the ratio between the two parameters and the surface irradiance. The study by Pemberton et al. (2006) shows that large error can be associated with just two parameters in a simple algorithm, but does not take into account error in chlorophyll concentrations or PAR, assuming the values are accurate. More complex algorithms such as the one used here could incur larger errors as there are more parameters. However the process of photosynthesis is represented in more detail and therefore the forcing can be more subtle and in particular wavelength resolved algorithms tend to perform better in algorithm comparison studies (Carr et al., 2006).

It is currently assumed that biomass retrieval is the largest error in satellite models (Platt *et al.*, 1995; Joint & Groom, 2000). In this study chlorophyll profiles from the glider have been corrected and compared against CTD measurements (Figure 3.3), with good results and little offset between different gliders (Section 4.2.1). The PAR data was also compared to ship based measurements (Section 2.2.2). A comparison with

modelled satellite profiles and glider profiles showed that the satellite failed to properly capture the subsurface distribution (Section 4.4.1, Figure 4.6). Therefore the primary production profiles used here have less associated error with the chlorophyll and PAR than satellite estimates.

I have mentioned previously that the algorithm may not represent the change in carbon to fluorescence with depth (Section 4.4.1). However rates of primary production seen in the subsurface chlorophyll maximum were similar to previous observations in the same location and for similar chlorophyll concentrations (Painter *et al.*, 2010*a*). The relationship between integrated chlorophyll and integrated carbon fixation was fairly similar (Figure 4.7). The adaptation of chlorophyll with light levels are taken into account in the algorithm in the equations 3.4 and 3.5 in Chapter 3, where f(x) describes the photosynthesis-irradiance curve. However if the carbon to fluorescence ratio changes with depth it may still incur an error in the estimated photosynthesis when using chlorophyll fluorescence as a proxy.

Milutinovi & Bertino (2011) did a further study of error using the Vertical Generalised Production Model (VGPM) (Behrenfeld & Falkowski, 1997), they found that the physiological state of phytoplankton contributed most to the random error, whereas the largest contributor to the systematic uncertainty came from the description of the change in photosynthesis with depth. The study showed that the VGPM has a percentage bias in primary production of between -3 to +15%, with an average bias of +6%.

Sensitivity testing of the primary production model used here (Morel, 1991) showed that the choice of parameter can significantly impact the rates of primary production derived by the model from increasing primary production by 200% and decreasing it by 95%. Typically these two parameters (absorption cross section of chlorophyll a^{*} and the maximum quantum yield ϕ_{μ}) would be considered physiologically independent. The values used in the sensitivity study are the maximum parameters found in the literature (Table 3.1 0.1 and 0.06 for a^{*} and ϕ_{μ} respectively) and are also likely to change seasonally as the maximum quantum yield for growth depend on both community structure and the light and nutrient environments (Babin et al., 1996) and the absorption cross section per unit of chlorophyll can vary due to the package effect and pigment composition. The package effect occurs under light limitation and has a greater impact on larger cells as their low surface-to-volume ration limits an increase in the absorption cross section. (Bricaud et al., 2004) found that a* varied most due to the package effect and not pigment composition. The parameter therefore had a strong relationship with chlorophyll concentration (Bricaud et al., 2004, 1998). It may be possible that the scale factor takes into account some of the variation in the a^{*} parameter, however further investigation would be needed to investigate this.

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The error shown from the difference between co-located CTD bottle samples and the PAR-corrected chlorophyll was much lower at 20%. This error may be more representative as it is taken from actual measurements. The sensitivity study from the parameters shows a maximum range (Table 3.1 0.01 to 0.1 and 0.01 to 0.06 for a^{*} and ϕ_{μ} respectively), however no measurements of the parameters were taken and therefore it is unlikely that the error would be so large, especially as the parameters may vary. Although the sensitivity test gives an idea of how much primary production could vary depending on the parameters used the error presented in the subsequent chapters, of $\pm 20\%$, is therefore taken from the RMSE between the bottle samples and glider PAR-corrected chlorophyll, this is also more similar method to the error calculated on the nitrate fluxes and allows for a better comparison.

3.4.2 Scale factor for chlorophyll correction

The scale factor derived from the attenuation of light observed by the glider has a number of benefits. Firstly, it allows the glider fluorescence to be corrected even if there are no CTD measurements, as might happen if the glider is deployed from a small boat from shore. Second, there were different fits between the observed CTD chlorophyll and the glider chlorophyll fluorescence for each of the three cruises, which leads to problems when correcting the chlorophyll, when does the change occur and which fit would you use for which proportion of glider data? The PAR-correction method shows when the change in scale factor occurs allowing a scale factor to be produced separately for each dive and climb.

In general for the deployment and recovery cruises (JC085 and JC090) the CTD bottle chlorophyll measurements match well with the glider PAR-corrected chlorophyll (\mathbb{R}^2 0.89 and 0.78, RMSE 0.08 and 0.23, respectively). All the bottle measurements for these two cruises were taken within 6 km of the glider (Figure 3.3). The cruise in July (JC087) showed a discrepancy between the glider PAR-corrected chlorophyll and the bottle measurements (\mathbb{R}^2 0.64, RMSE 0.18). This cruise was not a deployment or recovery cruise for this glider and therefore no CTD's were specifically taken for glider calibration, resulting in a larger distance of separation between the bottle measurements and the glider (> 10 km, Figure 3.3). This demonstrates the need for careful placement of CTD casts for glider calibration. These results suggest that casts need to be < 10 km (preferable < 6 km) from the glider to achieve a good representation of the chlorophyll field in this area.

Glider fluorescence measurements have generally been calibrated using a regression between co-located bottle samples and the glider fluorescence measurements (e.g. Swart

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et al., 2015). Figure 3.9 shows the regression between the uncorrected glider chlorophyll and the bottle samples. The scatter appears much larger with lower \mathbb{R}^2 values for each cruise than when the PAR-corrected glider chlorophyll is used. A simple regression does not capture the relationship well and which in any case changed from cruise to cruise. It is therefore not clear how a single regression would be applied across all the glider data. Furthermore, glider to glider (or sensor to sensor) variation would make use of a single regression unwise despite the manufacturers calibration supposedly correcting for any difference between sensors. The next chapter will introduce a comparison between the uncorrected and PAR-corrected chlorophyll, where there is an obvious offset between sensors over the year when using uncorrected data (Section 4.2.1).



FIGURE 3.9: Regression between the bottle chlorophyll measurements and co-located glider measurements of uncorrected chlorophyll.

It is difficult to determine the cause of the large scatter which occurs within the scale factor at short timescales (Figure 3.1). It could be due to changes in the light level during a dive. For example, dives where the light profile increased with depth were removed as it was most likely due to a lessening (increase) of cloud cover during the dive (climb), however if the cloud cover increases (decreases) during a dive (climb) the profile will not be removed and may be the cause of some of the scatter in the scale factor. To remove some of this uncertainty and to prevent large spikes in the chlorophyll timeseries a ten day moving window was used to smooth the scale factor. This highlights the problem that gliders measure in both space and time. As it takes several hours to complete a dive climb cycle, the light field and chlorophyll distribution may change significantly between the beginning and end of the profile.

3.4.3 Future applications

While I have used gliders to quantify primary production in a region of the North Atlantic, this approach will allow improved estimates of primary production more widely in the future, particularly in regions with SCMs and/or considerable cloud cover. I have demonstrated the suitability of gliders for capturing fine-scale temporal changes in production at daily timescales over a single season. Gliders allow coincident and simultaneous measurements of physical parameters, including density, temperature, oxygen and vertical water velocity (Merckelbach *et al.*, 2010; Frajka-Williams *et al.*, 2011). The coincident analysis of the physical environment allows an improved understanding of influences on phytoplankton growth. Small-scale physical processes may account for a significant amount of new production (Lévy *et al.*, 2001; Frajka-Williams *et al.*, 2009). Several recent studies have used high resolution data from gliders to analyse biological and physical connections (Pietri *et al.*, 2013; Webber *et al.*, 2014; Omand *et al.*, 2015). Simultaneous estimates of primary production will help further resolve biological and physical connections.

An unexpected result of this study was the post bloom change in the scaling factor (Figure 3.1). This clearly shows that the use of a single scaling factor for long deployments is insufficient when interpreting chlorophyll from fluorescence profiles, and may additionally indicate a change in phytoplankton community composition.
Chapter 4

A Yearly Cycle of Primary Production



4.1 Introduction

The seasonal cycle (phenology) of primary production in the North Atlantic has been described in Chapter 1. Modelling studies have shown that high spatial resolution surveys are necessary in order to test predictions for how physical drivers at the submesoscale control rates of primary production in the ocean (Lévy *et al.*, 2001). Submesoscale processes can introduce variability at small spatial and temporal scales. Autonomous vehicles may help resolve these scales and better link other methods of observation such as satellites, moorings and cruises.

In this chapter I will describe the annual cycle of primary production as observed by the gliders (see Chapter 3 for the method). This dataset is unique in the North Atlantic as it has depth estimates of primary production from the surface to the base of the euphotic zone throughout the year, at sub-daily frequency. This allows me to discuss three questions within this chapter regarding the annual cycle of primary production. First, how much annual primary production occurs below the mixed layer, particularly in the subsurface chlorophyll-a maximum? Second, how significant are patchiness and variability over the year? Third, how do changes in the scale factor for the glider fluorescence correction (derived in the method described in Chapter 3 (Hemsley *et al.*, 2015)) relate to changing phytoplankton communities?

4.2 Data and Methods

The data collected for this chapter are described in Chapter 2 and the methods used to estimate primary production are described in Chapter 3 and Hemsley *et al.* (2015). In this chapter I examine the seasonal cycle of primary production and so below I describe briefly how the primary production data were compiled and then the statistical methods used to investigate the data.

4.2.1 Calculating Primary Production

The method for calculating primary production is described in Chapter 3. I have applied this method to 5 other gliders that were deployed in the same region over the entire year (see Table 2.1 for dates and duration of deployments). There are a total of 2094 primary production profiles between all the gliders, with some neglected due to problematic PAR profiles (Section 3.2.3). Worth noting is that the Morel (1991) algorithm uses equations for net growth rate and so the production calculated is closer to net primary production rather than gross as it includes repiration by plants, this is significant when looking at the nitrate fluxes in Chapter 5.

Chlorophyll concentration was estimated from fluorescence and PAR, as described in Chapter 3 and Hemsley *et al.* (2015). When only the manufacturers' calibration was used on the fluorescence sensor the time series of integrated chlorophyll-*a* showed offsets between gliders that were deployed at the same time (Figure 4.1 a). For example from September 2012 to January 2013 SG566 continuously read higher chlorophyll concentrations than SG533, often by more than 5 mg Chl-a m⁻², approximately 15% higher on average. This occurred again between the same two gliders when they were both deployed in the summer of 2013. SG510 was also deployed at the same time as SG566 in April to June and read significantly higher values of chlorophyll than SG566 by more than 20 mg Chl-a m⁻² on average, which equated to a 68% difference. There is thus significant sensor to sensor variability that negates the usefulness of multiple sensors for understanding relative spatial differences (patchiness) and therefore further calibration is essential.

Once the scale factor derived from the PAR sensor was applied to the fluorescence data, the persistent offsets between the gliders chlorophyll was much reduced (Figure 4.1 b). For example, after the fluorescence was adjusted based on radiative transfer calculations, SG566 and SG533 had daily differences of just 0.05 mg Chl-a m⁻², representing a difference of only 3%, from September 2012 to January 2013. The R² value between the chlorophyll from the two gliders, 0.31 was relatively low. However, the correlation



FIGURE 4.1: The chlorophyll time series from the 6 glider deployments a) with manufacturer's calibration and b) adjusted by PAR.

between the two gliders was significant (p-value < 0.001). This may be due to small spatial scale variability. An analysis of the difference of chlorophyll concentrations between profiles compared with distance of separation showed that the differences in chlorophyll profiles could be just as large at 1km than at 15 km separations and that this difference was not dependent on the time of year (Figure 4.2). Furthermore in the summer when the same two gliders were deployed, the percentage difference was 10% but the \mathbb{R}^2 increased to 0.8 with a p-value of < 0.001. Post correction a linear regression between chlorophyll from SG510 and SG566 in the summer also had a high \mathbb{R}^2 of 0.61 and a p-value of < 0.001, demonstrating that the two gliders were showing very similar results



FIGURE 4.2: The difference in glider profiles of chlorophyll compared with their distance of separation

(not shown).

4.2.2 Defining Subsurface Production

Primary production was quantified for a number of different scenarios; 1) over the full depth of the euphotic zone, 2) within the mixed layer, 3) below the mixed layer in the subsurface chlorophyll maximum and 4) below the mixed layer in the absence of a subsurface chlorophyll maximum.

To estimate the contribution of primary production in the subsurface, production below the mixed layer depth was extracted from the glider profiles and integrated over the depth from the mixed layer to the base of the euphotic depth. However it was then necessary to determine further if the production below the mixed layer was within a subsurface production maximum. For each profile the depth of the production maximum was found and profiles were selected if the production maximum was found to be below the mixed layer depth, allowing me to quantify primary production in the subsurface production maximum. This is the same criteria used in recent studies of subsurface chlorophyll maximum (Martin *et al.*, 2010*b*; Joo *et al.*, 2012; Brown *et al.*, 2015).

4.2.3 Coefficient of Variation

The coefficient of variation (CV) was calculated for primary production for 7 day periods over the year. The CV provides a relative estimate of variability in the data (Everitt, 1998). Because primary production values cannot be less than zero, but are often very close to zero, the data are skewed and not normally distributed. For this reason the natural log of primary production was determined before the coefficient of variation was calculated. However as the data is logged the mean may now be negative. Therefore, to calculate the CV using the log-transformed data the following equation was applied (Limpert *et al.*, 2001), to calculate the variability in the non-transformed data:

$$CV = (exp(\sigma^2) - 1)^{\frac{1}{2}}$$
(4.1)

The CV was also calculated for the glider density data for the same 7 day windows, in the standard way by dividing the standard deviation by the mean. The two methods were used for both data sets to determine any discrepancies.

4.2.4 Satellite Data

It is useful to have another source of primary production estimates to compare to those from the glider. For this comparison the MODIS Aqua 8-day 4 km resolution chlorophyll product was used for the whole year of the deployment (September 2012 to September 2013). All the pixels within the gliders' $15 \ge 15 \ge 15 \ge 15 \ge 10$ more fully in Chapter 2, however I will briefly give an overview here. To estimate primary production from satellite data the chlorophyll profile was estimated using statistical relationships derived from Morel & Berthon (1989) (See Section 2.5.1). Average daily-integrated PAR fields from MODIS Aqua were also utilised and split spectrally using the same method described for the glider data (Section 3.2.3). To estimate primary production we used the algorithm described by Smyth *et al.* (2005), which inputs the chlorophyll profiles, surface spectral light, date, time and location. When calculating the integrated yearly value of primary production the satellite pixels in the sampled area were averaged for each 8-day period to produce a time-series. A grid of 100 x 100 km around the survey area was also extracted to investigate the variability in satellite data from a larger area.

Satellite-estimated particulate inorganic carbon (PIC) was also examined for changes in community composition, as PIC can indicate the presence of coccolithophores (Gordon *et al.*, 2001; Balch *et al.*, 2005). Satellite PIC was extracted for the same 15 x 15 km area over the glider deployment site.

4.3 Results

A year long timeseries of primary production was returned by the gliders, from September 2012 to September 2013, providing detailed observations of daily and seasonal variability.

4.3.1 Biogeophysical Setting

The mixed layer was relatively shallow (less than 50 m) at the beginning of the deployment, September 2012 (Figure 4.3). From December 2012 to April 2013 the surface layer was well mixed, with mixed layer depths between 100 and 350 m, indicative of winter mixing due to high winds and sea state (Figure 4.3). Over this period the mixed layer was highly variable, with fluctuations of more than 100 m in less than a day. The mixed layer shoaled at the beginning of May to 20 m but deepened again to 120 m by the end of the month. Throughout June, July and August the water column was strongly stratified with mixed layer depths less than 20 m, apart from a short period in June when it deepened to 50 m. Surface temperatures reached a minimum of 11°C in February when the water column was well mixed and peaked in summer at 20°C. Euphotic depths (depth where irradiance is 1% of surface value) were consistently around 50 m at the beginning of the deployments until November. During winter, euphotic depths were deeper as there was little growth and low particulate levels in the surface allowing light to penetrate further into the water column and reached a maximum of 100 m from January to March. In April, the euphotic depth shallowed and became more variable and with several periods throughout May when it shallowed to 50 m. From mid-June it remained < 50 m deep and reached its shallowest in July at a depth of 30 m. During this period (July to September 2013) the euphotic depth was deeper than the mixed layer.



FIGURE 4.3: The mixed layer depth estimated from glider data (black) and the euphotic depth (orange) calculated as the depth where PAR reaches 1% of the surface value. Gaps in the euphotic depth occur due to "bad" PAR profiles, which increase with depth (Section 2.2.2)

Figure 4.4 shows the mean profile of nitrate collected from CTD bottle samples for the three cruises, D381 (September 2012, n = 20), JC87 (June 2013, n = 23) and JC90 (September 2013, n = 8), where n is the number of CTD casts. Surface concentrations were low for both of the September cruises, 0.1 and 0.04 mmol m⁻³ for D381 and JC90 respectively. Concentrations were much higher in June, 4 mmol m⁻³. Nitrate concentrations are considered limiting when below 0.5 mmol m⁻³ (Eppley *et al.*, 1969). Concentrations increased steadily with depth during JC87 reaching a maximum of 5.7 mmol m⁻³ at 52 m. JC90 showed an increase in concentrations at 55 m to 3 mmol m⁻³. Concentrations during D381 were below 2 mmol m⁻³ for the full depth shown.

4.3.2 Chlorophyll-a timeseries

Chlorophyll concentrations integrated to 100 m demonstrated a clear seasonal cycle (Figure 4.1 b). At the beginning of the survey in September 2012, water column integrated chlorophyll concentrations varied between 20 and 30 mg Chl-a m⁻². Concentrations



FIGURE 4.4: The mean nitrate profiles collected from CTD bottle data for the three cruises, D381 (September 2012, n = 20), JC87 (June 2013, n = 23) and JC90 (September 2013, n = 8)

steadily decreased between September 2013 and February 2013, apart from a small increase at the end of October. In February integrated chlorophyll concentrations were low (< 10 mg Chl-a m⁻²), coincident with a deep mixed layers and euphotic depths. Throughout March and April, integrated chlorophyll concentrations increased but also became more variable. At the beginning of May, chlorophyll concentrations peaked at 45 mg Chl-a m⁻², coincident with a shallowing of the mixed layer depth above 50 m. During this peak in chlorophyll the mixed layer depth was shallower than the euphotic depth. After this, the mixed layer deepened again to 60 m and chlorophyll concentrations decreased to less than 20 mg Chl-a m⁻². Concentrations then increased steadily as the mixed layer depth shoaled throughout June and July. There was a small spike in June but then concentrations increased to a maximum of 50 mg Chl-a m⁻² in July. After this integrated chlorophyll concentrations gently decreased to a monthly mean of 28 mg Chl-a m⁻² by mid September, with fluctuations from 20 to 35 mg Chl-a m⁻². This was slightly higher than observed during the previous September 2013 (between

18 and 30 mg Chl-a m^{-3} , with a monthly mean of 20 mg Chl-a m^{-3}), demonstrating important year to year variability.

4.3.3**Depth-Integrated Primary Production over Time**

The primary production estimates derived from the glider and integrated to the euphotic depth show a similar pattern to those of the integrated chlorophyll (Figure 4.1, 4.5), with a strong seasonal cycle. Rates of production were relatively low in autumn and winter, decreasing from ~ 1 g C m⁻² d⁻¹ in September 2012 to less than 0.5 g C m⁻² d⁻¹ throughout February and March 2013. Rates then increased in April. A strong peak in primary production developed in May, with production rates reaching 2.5 gC m⁻² d⁻¹. Towards the end of May production decreased to less than 1 g C m⁻² d⁻¹. A later, more dominant peak (the spring bloom) then developed in June reaching up to 3 g C m⁻² d⁻¹ at the beginning of July. The rates of production decreased slightly to between 1 and 2 g C m $^{-2}$ d $^{-1}$ throughout August and into September when the gliders were recovered.

A linear regression between mixed layer depth and depth integrated primary production to the euphotic depth gave a low correlation (\mathbb{R}^2 between 0.05 and 0.2 depending on the glider, Table 4.1). However for all gliders the p-value was < 0.001 and therefore there was a significant relationship between shallower MLD and increased primary production, although it is important to note that this may not imply causality. However, for a long timeseries and where there is a lot of variability, where each data point is independent, the p-value can still be significant. The glider with the highest \mathbb{R}^2 was SG579 (0.2), deployed from January to April, as chlorophyll concentrations increased and the mixed layer began to shoal.

Glider	\mathbb{R}^2	P-value	Regression Equation
SG566	0.15	< 0.0001	PP = -0.002MLD + 0.4
SG533	0.17	< 0.0001	PP = -0.002MLD + 0.5
SG579	0.2	< 0.0001	PP = -0.001MLD + 0.4
SG566	0.05	< 0.0001	PP = -0.004MLD + 1.7
SG510	0.15	< 0.0001	PP = -0.003MLD + 0.9
SG533	0.03	< 0.0001	PP = -0.009MLD + 2.1

TABLE 4.1: Regressions between glider primary production with mixed layer depth

The satellite timeseries of primary production is also shown in Figure 4.5 for comparison with the glider data. Cruise data were fairly limited and satellite data provide a full year for comparison. I will use it to assess when and how the two methods (glider and satellite) may differ. The grey area in the figure shows the range of satellite estimates



FIGURE 4.5: Time series of glider derived primary production integrated over the euphotic depth at the study site (the 15 x 15 km area where the gliders flew Figure 1.3). The range of production values around the study site in the 100 x 100 km area are shown in grey calculated from the satellite data, also integrated to the euphotic depth. The solid black line is the satellite estimate from pixels within the survey region. The glider production values are shown as dark grey dots. The mean daily primary production from the glider is a solid red line.

in a 100 x 100 km box around the deployment site and the solid black line indicates the average of the pixels extracted over the 15 x 15 km survey region. There is very little difference in the satellite estimates of primary production over the larger area compared with the smaller survey site. The general trends in the glider and satellite data sets are similar, with low rates of productivity in winter, increasing throughout spring and peaking in July. However, the satellite timeseries does show several differences to the glider timeseries. The satellite estimates of primary production are generally higher than those from the glider, apart from in the summer, when the subsurface maximum is present. The satellite estimates also missed the spike in primary production in May. A closer inspection suggests that this may be due to the statistical relationship used to estimate chlorophyll at depth from the satellite data (Morel & Berthon, 1989). At the beginning of the deployment the satellite method showed an increase in chlorophyll at depth that the glider did not observe, whereas toward the end of the timeseries when the glider observed a subsurface production maximum the satellite underestimated the amount of chlorophyll present at that depth. The root mean square error, which provides a useful measure of the differences between measured and predicted values, was calculated between each glider and satellite chlorophyll profile to determine which

times of year the profile was best modelled (Figure 4.6). The RMS of the glider profiles over each day is also plotted on the same figure, this allows a visual to determine if the RMSE is large. For example if the RMSE is much lower than the RMS the error is of less significance whereas if the values are similar the error is very large. The error was low in January, March and towards the end of May, however there were significant differences between the measured and observed profiles for most of the year, in particular when chlorophyll concentrations are high. A comparison between satellite chlorophyll and glider chlorophyll can be seen in Appendix B.



FIGURE 4.6: The root mean squared error between the glider chlorophyll profiles and the profiles modelled from the satellite chlorophyll using Morel and Berthon (orange), against the root mean square of the glider profiles for each day (black), the RMS gives a reference for determining if the RMSE is large compared with the concentrations observed in the timeseries

Chlorophyll normalised production is shown in Figure 4.7. The correlation between primary production and chlorophyll is significant (p-value < 0.001). However there is a large amount of scatter in the data and the relationship changes over the year.

From the glider estimates of primary production an annual rate of production can be estimated for this region. By integrating all the values of primary production from the glider over time and the euphotic depth, primary production in this area was 255 g C m⁻² year⁻¹. A yearly estimate from the satellite data over the deployment site was similar to the glider 225 ± 7.5 g C m⁻² year⁻¹, the error estimate comes from the standard deviation of the yearly integrated estimates for each of the 16 pixels within the PAP site.



FIGURE 4.7: The top panel (a) shows the ratio of integrated chlorophyll to integrated primary production. The bottom panel (b) shows one against the other coloured by date, demonstrating how the relationship changes throughout the year. The black line is the relationship between integrated chlorophyll and carbon fixation for bottle data found by Painter *et al.* (2010*a*) at the PAP site in 2006. $R^2 = 0.25$ p-value < 0.001 RMSE 0.6. The blue line is the line of best fit (y = 0.03x -0.37)

4.3.4 Variability in Integrated Primary Production

The timeseries of integrated primary production shows high frequency variability, with changes in primary production from one dive to the next within a spatial distance of 6 km and within approximately 2.5 hours; the time it takes to complete one dive or climb. The percentage difference in primary production from profile to profile ranges from 0 to > 100%, the median percentage change over the whole deployment is 9%. Using daily averaged primary production the percentage change on a day to day basis increases to a maximum of 320% in October, with an average of 37% over the year (Figure 4.8). There was also a general trend over the annual cycle. The percentage change in September 2012 was moderate, mostly below 50%, but this increased over winter, though usually varying under 150% until March. After March the percentage change became moderate again, until the end of June and beginning of July where it decreased to < 25%. The daily percentage change increased again in August, but generally remained below 100%.

The variance of primary production for each glider was calculated for each month over



FIGURE 4.8: Percentage change of primary production from day to day

the deployments (Figure 4.9). There were differences seen in the variance between gliders. However in the winter months when there was less growth the gliders all showed a similar variance. This suggests that the differences between gliders was due to real spatial variability. In general the gliders showed a variance of ~0.1 g C² m⁻⁴ d⁻² in September and October, which then decreased to negligible values in December and January. In February the variance increased until May, where it reached its highest value of 0.325 gC² m⁻⁴ d⁻². After this, throughout the summer, it gradually decreased again to 0.125 gC² m⁻⁴ d⁻² at the end of the deployments in September 2013.

The variance in primary production was also calculated for the 8-day satellite data, by calculating the variance including every pixel in the 15 x 15 km box for each month that the glider was deployed. The seasonal shape is similar to that of the glider, with the highest variance found in the summer months (May) and the lowest during the winter (December). However the total variability is much lower, suggesting that the gliders observe features not detected by satellite. The highest variance seen in the satellite data was $0.052 \text{ gC}^2 \text{ m}^{-4} \text{ d}^{-2}$ in June. To further examine variability a 100 x 100 km grid was extracted from the MODIS Aqua satellite data with the glider study region in the centre. The grid was split into 15 x 15 km boxes and the variance in each box found for each month (Figure 4.9). This was done to determine if the larger region (100 by 100 km) showed similar patterns in the primary production variability. There was little difference between each grid box during the winter months, however during the summer the variances ranged from negligible to $0.064 \text{ gC}^2 \text{ m}^{-4} \text{ d}^{-2}$. The variance observed from the satellite is consistently lower than that observed from the glider, particularly between April and September. It is important to note the differences in scale between the satellite pixels (4 km) and the glider point measurements.



FIGURE 4.9: Variance of primary production each month from each glider. Each black dot represents one of the 15 x 15 km grids in the the larger area around the study site. The red dot represents the 15 x 15 km grid centred over the study site.

The coefficient of variation (CV) is also a useful measure as it is unit-less, demonstrating the extent of variability relative to the mean. Figure 4.10 shows the CV of density and primary production for two slightly different methods of calculation. The density is calculated from the standard method and the primary production method, which is specifically for logged primary production values (Equation 4.1). The shape of the CV for density is unchanged using the different calculation, although the magnitude is slightly lower for the alternative method, for log normal data. The primary production CV on the other hand showed a large difference depending on the method used, where it is much lower and flatter for the standard method (not shown). For the alternative method it showed peaks in January to March and another at the end of May. The density showed highest CV in June and July. It also showed peaks in the CV in September and October. The CV for primary production showed highest values in winter but also a peak at the end of June.

4.3.5 Primary production below the mixed layer depth

The primary production maximum began to deepen in July, around the same time as the formation of the SCM (Figures 4.11 and 4.12). The production maximum deepened at approximately 1 m per day until reaching a depth of 25 m. The production maximum (SPM) remained at this depth throughout August and into September when the glider deployments finished. The productivity of the subsurface production maximum peaked in July at 0.3 g C m⁻³ d⁻¹ at the surface and then decreased to 0.15 g C m⁻³ d⁻¹ as the productivity maximum deepened to a depth of 25 m.



FIGURE 4.10: Coefficient of variation for primary production (a) and density (b). The black lines show the standard method for calculating the CV and the blue line is the method used for the logged primary production

Figure 4.13 shows the fraction of integrated primary production that occurred below the mixed layer depth. There is a proportion of primary production below the mixed layer in September and October 2012, as the production was decreasing and the mixed layer shallowing. After winter mixing the proportion of production below the mixed layer started to increase again in April, accounting for 30% of the years' primary production, at 74 g C m⁻² yr⁻¹. Using the criteria for subsurface production maximum, where the production maximum is below the mixed layer, this gives a slightly different result, also shown in Figure 4.13. The subsurface production associated with the SPM started later at the beginning of July and in total accounts for 23% of the yearly production, 55 g C m⁻² yr⁻¹. On average the SPM accounted for 52% of daily water column production, during the stratified period.

A correlation between subsurface production in the SPM and mixed layer depth was significant although the R^2 value was low ($R^2 = 0.3$ p-value < 0.001). However, the correlation between production integrated below the mixed layer and mixed layer depth ($R^2 = 0.1$ p-value 0.06), was insignificant.



FIGURE 4.11: Depth resolved primary production from the glider data. The white dashed line depicts the mixed layed depth and the white solid line depicts the euphotic depth (1% of the surface light level).



FIGURE 4.12: Depth resolved corrected chlorophyll concentrations from the glider data.



FIGURE 4.13: The fraction of primary production below the mixed layer depth (black) and the primary production within the subsurface maximum (red)

4.3.6 Chlorophyll Scale Factor

A scale factor for each glider dive and climb profile of chlorophyll is produced from the method described in Chapter 3 and in Hemsley *et al.* (2015). This scale factor gives a relationship between the irradiance observed and the amount of chlorophyll present in the water column. The scale factor varied over time and in a consistent way for gliders deployed at the same time (Figure 4.14). At the beginning of the mission in September the scale factor varied very little between 1.8 and 2.5. It then increased to between 3 and 4 during March and April when SG579 was in the water. The scale factor then gradually increased again in May up to its maximum of 6 and remained at a value of 5 throughout June. In July the scale factor significantly decreased to a value of 1.5 by August and September.

Figure 4.15 shows the scale factor along with the ratio of dinoflagellates against diatoms, from the CPR data. During the end of June and beginning of July there was a large shift from diatom to dinoflagellate dominance, with slight increases in dinoflagellates in December and March. The figure also displays the satellite PIC product as an indication of coccolithophore abundance. This also shows an increase in March and June.



FIGURE 4.14: The scale factor derived from irradiance and fluorescence for each glider, smoothed over 10 days



FIGURE 4.15: The scale factor for each glider in black shown next to the change in community composition derived from CPR data as the ratio of dinoflagellates to diatoms. PIC from satellite data is shown in red multiplied by 1000. The horizontal green line indicates where the population switches from being diatom to dinoflagellate dominant.

4.4 Discussion

4.4.1 Primary Production Seasonal Cycle

I show for the first time, a complete annual cycle of primary production in the North Atlantic from gliders, with multiple daily estimates and at high vertical resolution from the surface of the ocean to the bottom of the euphotic zone (Figure 4.11). Underwater gliders enable us to estimate primary production at high vertical and temporal resolution (Hemsley *et al.*, 2015). Most profiles show a reduction of primary production with depth as light is absorbed quickly by the water column. However in summer the glider showed the formation of a subsurface primary production maximum in July that persisted throughout August and into September. These are common globally and have been shown to contribute significantly to rates of primary production (Cullen, 1982).

The glider data shows two distinct peaks in production for 2013, although the later peak is the larger. The first significant peak in primary production in May was coincident with the mixed layer depth being shallower than 50 m for a period of three days for the first time. This allowed the phytoplankton to have access to the increasing irradiance at the surface causing an increase in growth. However after this the mixed layer deepened again, diluting the phytoplankton causing an observed decrease in growth. Although the mixed layer shoaled again after this period it did not coincide with another increase in primary production until towards the end of June and into July when the main peak in primary production occurred. This may be due to high levels of grazing keeping phytoplankton populations low (Gifford *et al.*, 1995; Henson *et al.*, 2009).

Normalised Primary Production Ratio

Previous studies in this region have found similar rates of primary production (see Table 3.3). The chlorophyll to carbon fixation ratio varies over the year, although the correlation is positive and significant, although the two are not independent ($\mathbb{R}^2 = 0.25$ p-value < 0.001, Figure 4.7). The ratio is much lower from September to April, however after April the ratio becomes larger, following the general trend of the primary production timeseries. It does not change significantly during the formation of the subsurface chlorophyll maximum suggesting that the formation of the subsurface maximum does not impact the ratio of chlorophyll to production. From the scatter plot of Figure 4.7b it is apparent that the production increased for the same chlorophyll concentration during May to August compared with previous months. It appears that there are two relationships separated in time, one from September 2012 until April 2013 and a different relationship after April which leads to higher carbon fixation to chlorophyll values. As chlorophyll is a large determinant of the primary production and the two are not independent of each other the changes in the ratio may be surprising. Light levels were highest in June and July a maximum of 300 W m⁻², but decreased in August to similar levels as observed in May, 150 W m⁻², leading to more primary production. However this would not be expected during August as the light levels at the subsurface production maximum are lower ~ 35 W m⁻². Previous studies have found a good relationship between integrated chlorophyll and carbon fixation rates in July 2006 at the PAP-SO site (Painter *et al.*, 2010*a*). The relationship from Painter *et al.* (2010*a*), which is independent, is plotted on Figure 4.7 in black and is more similar to the relationship pre-May than the relationship throughout June, July and August. The only other input into the production algorithm other than chlorophyll and irradiance was temperature. Increasing temperatures increase the net growth rate. During May surface temperatures at around 12° and increase steadily untill the beginning of August when they reach the annual maximum and remain fairly constant at 19°C (Damerell *et al.*, 2016).

Interannual variability

Figure 4.16 shows satellite primary production for this study and previous years. Large year to year variability is apparent, with the maximum peak in primary production varying from May to July. The earliest peak in May is observed in 2011. Both 2012 and 2013 are distinct with larger than average peaks in production in the summer. The peak in primary production for this study (2013) was later than usual in this region (July) and the rates of primary production were higher into late summer, suggesting that there were sufficient nutrients available in the surface to support growth later in the year. Nitrate samples taken in June 2013 show relatively high concentrations in the surface of $\sim 4 \text{ mmol m}^{-3}$, and therefore nutrient concentrations were not considered limiting. Nitrate is considered limiting when concentrations move below 0.5 mmol m^{-3} (Eppley et al., 1969). Previous studies to the region have found that surface nitrate values are generally lower for this time of year, probably because the peak in the spring bloom is generally earlier. For example at the PAP-SO site surface values in June and July in 2006 ranged from negligible to 2 mmol m⁻³ (Martin *et al.*, 2010*a*; Painter *et al.*, 2010*a*) and in June, July and August in 2003 and 2004 levels were well below 2 mmol m^{-3} (Körtzinger et al., 2008; Hartman et al., 2010). Painter et al. (2010a) found that values of normalised active fluorescence, a measure of the efficiency of photosynthesis, were low in the surface waters at the PAP-SO in 2006, indicating nutrient stress (Cleveland & Perry, 1987; Moore *et al.*, 2006). Although 2 mmol m^{-3} of nitrate would not normally be assumed to be limiting, growth may be limited by other micronutrients, such as iron or silicate (Moore *et al.*, 2006).



FIGURE 4.16: MODIS Aqua chlorophyll for all years from 2007 to 2013, average in 15 x 15 km area. Note the later peak in chlorophyll at the study site in July for 2013

Many factors influence the timing and magnitude of the spring bloom and there are a number of theories as to what processes influence the start date, which is a major cause of inter-annual variability. The original theory proposed by Sverdrup (1953) suggested that the spring bloom was initiated when light levels are high enough and the convective mixing rate is less than a critical threshold (Colebrook, 1982; Siegel *et al.*, 2002). Other theories include the 'Convection-Shutdown-Hypothesis' (Ferrari *et al.*, 2015), as well as a number of top-down biologically orientated hypotheses such as the decoupling of phytoplankton biomass from zooplankton grazing pressure (Behrenfeld, 2010; Behrenfeld & Boss, 2014). Determining the start date of the spring bloom is also debated. It has been described as starting at the onset of exponential or explosive growth (Platt *et al.*, 1991), however sometimes blooms develop more slowly and therefore the start can also be determined by the onset of net positive growth (Behrenfeld, 2010).

Comparison with Satellite

Although the time series for satellite primary production and glider primary production look slightly different (Figure 4.5), the integrated yearly estimates are very similar, with the glider estimating only 6% higher annual primary production. However when looking at the seasonal change in primary production the two methods look notably different and therefore the similarities between yearly estimates may be coincidence. Levels of primary production estimated by satellite tend to be higher than glider estimates from the beginning of the glider deployment from September 2012 to the end of April 2013 (Figure 4.5). Following which, glider estimates of production tend to be higher than satellite estimates from July to September. This could be due to one or more of several methodological limitations. For example, when evaluating the profiles of chlorophyll constructed from the satellite data using the Morel and Berthon equations the glider and modelled profiles often did not agree. Figure 4.6 shows the root mean squared error of each satellite profile against the glider chlorophyll. The mean RMSE was 0.27 mg Chl-a m $^{-3}$. This was high relative to the mean RMS of the glider profiles of 0.6 mg Chl-a m^{-3} , which suggests a large significant error compared to the measurements. The RMSE decreased as chlorophyll decreased over autumn (September to December). During this period the equations used to estimate the chlorophyll profile from satellite data (Morel & Berthon, 1989), resulted in a chlorophyll maximum at depth when there was none present in the glider data. This resulted in the satellite data overestimating the chlorophyll concentration compared to the glider. The error was lower during March and towards the end of May as chlorophyll was mostly found at the surface. There was a peak in the error at the beginning of May when the glider observed a peak in chlorophyll concentrations. Throughout May, July and August integrated satellite chlorophyll was underestimated compared to the glider concentrations. During August the error increases when the subsurface maximum was present, as the relationships used for the satellite data did not fully capture the subsurface chlorophyll maximum. These observations highlight the problems faced when inferring the subsurface chlorophyll distribution using satellite near surface observations.

As mentioned previously, during May the glider observed a spike in primary production which the satellite did not. This spike was found in all 12 of the glider profiles, over 2 days. During this time there was high cloud cover and the satellite most likely missed a short lived spike in chlorophyll concentrations. Because the spike was only 2 days long the 8-day satellite product may have smoother out some of the short-term temporal variability. Similarly, from a spatial averaging perspective, in the 100 km grid only 50% of pixels had a chlorophyll value. Figure 4.17 shows the percentage of pixels obscured by cloud cover throughout the year, note the high percentage throughout the winter and summer months. High levels of cloud cover were prevalent throughout the year, which reduced both the spatial and temporal variability of chlorophyll that can be observed by the satellite, demonstrating a benefit of using gliders for determining the timing of primary production over satellites, especially in areas with high cloud cover.

The subsurface production maximum

A subsurface primary production maximum formed in July, which deepened to a maximum depth of 28 m by the end of August. There was sufficient light at this depth to support production. The production maximum was approximately 10 m above the euphotic depth (Figure 4.11). The deepening of the production maximum generally



FIGURE 4.17: The percentage of satellite pixels obscured by cloud cover in a 15 x 15 km grid centred over the study region.

followed the deepening of the 35 W m⁻² isolume (appoximately 25% of surface light levels). With midday PAR values just below the surface measuring a maximum of 150 W m⁻².

Two months prior to the formation of subsurface production maximum, in April, there was already significant production below the mixed layer depth, approximately 15% of the total water column production, but no subsurface maximum (Figure 4.13). There may be a lag in the formation of subsurface production maximum after the stabilisation of the mixed layer depth (to less than 10 m), with some phytoplankton starting to grow lower in the water column while others remain at the surface. The phytoplankton below the mixed layer may be present because some phytoplankton have sunk out of the mixed layer or due to competition in the surface (Jerlov, 1958).

As defined here production in the SPM accounted for 23% of annual production in this area and 52% of the daily water column productivity, when the water column was stratified. Studies have shown that production in the subsurface can significantly contribute to total primary production (Goldman, 1993; Weston *et al.*, 2005). Estrada (1985) has estimated that in the Mediterranean subsurface production accounts for between 15 and 30% of annual production and is closely associated with the nitricline. Painter *et al.* (2010*a*) found similar levels of carbon fixation at 20 m compared to those observed by the glider, approximately 0.1 - 0.3 g C m⁻³ d⁻¹ (from ¹⁴C uptake experiments, for a 12 hour day), compared to values of 0.1 to 0.4 g C m⁻³ d⁻¹ from the glider. The observed chlorophyll concentrations are also about the same at this depth as in Painter *et al.* (2010*a*). The SPM in this study was located slightly shallower (25 m) than the chlorophyll maximum (35 m). This was because glider primary production is a function of both chlorophyll and irradiance, and as irradiance attenuates rapidly through the water column there is less available for phytoplankton growth deeper in the water column. The production maximum was located above the euphotic depth, where there was sufficient

irradiance and below the mixed layer, where nutrient concentrations were higher. The lack of change in depth and magnitude of the production maximum throughout August and into September suggests that the phytoplankton are actively growing. As declining growth rates and further deepening of the SPM would suggest that the observed increase in depth may be due to a passively sinking post-bloom community (Brown *et al.*, 2015). The rates of growth therefore must equal losses (grazing and sedimentation) as the concentration remains constant throughout August.

The primary production in the SPM starts later, in July, compared with the production below the mixed layer when the SPM is absent (Figure 4.13). The fraction of primary production in the SPM increased rapidly from 0 to $0.85 \text{ gC m}^{-2} \text{ d}^{-1}$ within one day. The rate of deepening of the subsurface chlorophyll maximum (SCM) is 1 m d^{-1} calculated from the chlorophyll data. Campbell & Aarup (1992) found that the nitrcline deepened by 10 m per month, slower than the deepening of the SCM observed here. The chlorophyll maximum has generally been shown to be located at the top of the nutricline, where nutrients and light are optimal (Cullen, 2015). Growth was low in the surface during the period of the subsurface production maximum (July to September), although nutrients are non-limiting in June when there is still surface growth by mid-July surface nitrate concentrations may have been depleted. In September nitrate concentrations at 5 m were limiting and had fallen from $\sim 4 \text{ mmol m}^{-3}$ in June to 0.03 mmol m⁻³ (Figure 4.4). The difference between 4mmol in June and 0.03 mmol in September equates to 0.5 $g C m^{-3}$, using the Redfield ratio of 6.6 for C:N, which at a mean surface growth rate of $0.2 \text{ g C m}^{-2} \text{ d}^{-1}$ (for this time period) would take approximately 3 days (Figure 4.11). Once a subsurface chlorophyll maximum is established it acts as a nutrient trap preventing any vertical fluxes from reaching the surface (Taylor et al., 1986; Banse, 1987). The rate of new production is strongly related to the nutrient fluxes that become trapped and therefore also related to the light levels at the nutricline (Cullen, 2015). Here the production maximum is not too deep and light levels are sufficient for significant growth, therefore if the nitrate fluxes are high during the subsurface production maximum, new production may also be high.

4.4.2 Variability and Patchiness

Phytoplankton are free floating and are advected by ocean currents. Satellite ocean colour images show the high variability in the distribution of phytoplankton, with filaments of phytoplankton from thousands of kilometres to less than 1 km. The mechanisms that control this variability are still largely debated. Problems arise when measuring a spatial distribution that changes faster than current sampling capabilities (Martin,

2003). Understanding phytoplankton variability is important as it can influence ecosystem stability (Steele, 1974) and diversity (Bracco et al., 2000). Previous studies have shown that this region of the North Atlantic can experience variability in production due to sub-mesoscale features such as highly productive filaments (Painter et al., 2010b; Lévy et al., 2001). The primary production from the glider shows strong variability with day to day changes from negligible to 320%, the mean percentage change per day over the whole year was 37% (Figure 4.8). The observed high day to day variability can be the result of both temporal variability: through the complex interplay between growth and loss processes as well as dilution (through MLD excursions), and spatial variability: through submesoscale patchiness (i.e. in a 24 hour period the glider moves into a different filament of different production. The percentage changes per day were high for the whole timeseries, but tended to be highest throughout autumn and winter (150%). They were also high throughout May and June at the onset of the bloom (100%), suggesting that the start of the bloom develops in a patchy manner (Mahadevan et al., 2012). In July the percentage change was low (<20%) suggesting that growth and losses were now relatively balanced per day, which could be due to high light levels, persistent stratification and non-limiting nutrients or a reduction in submesoscale patchiness. Reduced mixing as the mixed layer became shallow and strongly stratified may reduce a source of phytoplankton patchiness (Figure 4.3). In August the fluctuations from day to day increase again and could be an indication that growth is fuelled by episodic inputs of nutrients into the euphotic zone as nutrients have become limiting late into summer. Input of nitrate by submesoscale and mesoscale events would have a larger impact on the growth of phytoplankton than when there are still abundant nutrients in the surface. Bibby et al. (2008) show that in summer the uplift of deep isopycnals into the euphotic zone by mesoscale eddies can have a large impact on phytoplankton growth specifically at the SCM as density surfaces become vertically displaced increasing light availability.

To estimate the amount of production that may be caused by short term mesoscale and submesoscale effects the minimum of the primary production data was found in a seven day moving window, this was then subtracted from the production timeseries. This method, which I call "data mowing", assumes that all small spikes in the primary production data were caused by submesoscale events. This is an upper estimate of the impact on primary production as it assumes that all effects cause a positive impact on growth. Integrated over the whole year these spikes in production contributed to 175 g C m⁻², or 68% of the total yearly production estimate. The spikes were largest in summer particularly towards the beginning of August. A continuous wavelet analysis on the mowed timeseries showed which temporal scales were dominant in the timeseries. An analysis of the "mowed" primary production timeseries showed that there was significant variability on scales of two to eight days (submesoscale) from April to June, however it is not uniform over the whole period (Figure 4.18, Grinsted *et al.*, 2004). There was less variability shown in the beginning of July, consistent with the percentage changes in day to day production. August showed high variability on scales from one to four days, again consistent with high percentage changes per day, and suggesting an influence on production from mesoscale events. Modelling studies have shown that mesoscale and submesoscale effects can increase observed primary production up to 30 to 100%, respectively (Lévy *et al.*, 2001).



FIGURE 4.18: A continuous wavelet analysis of mowed primary production over the whole year (integrated to the euphotic depth). The black contours marks the 5% significance level. The light shaded area shows the edges that may be effected by the cone of influence (Grinsted *et al.*, 2004). The bottom panel shows the 'mowed' primary production timeseries.

The glider observed much higher variance than satellite data (Figure 4.9), suggesting that the distribution of phytoplankton was controlled at very small scales and was observed by the glider because the observations are at much higher resolution in time and space compared to the satellites. The satellite data represents 8-day composites which greatly reduces the spatial and temporal variability observed. Martin *et al.* (2015) found that 8-day composites only explained 66% of the coefficient of variation of chlorophyll compared to daily chlorophyll fields. Daily satellite products were examined, however due to high cloud cover in this region it was difficult to properly estimate the variance

using the daily fields, as there were few pixels available. It is difficult to use other tracers to observe patchiness, such as sea surface temperature, as biological uptake response occurs on much shorter time scales than changes to the heat flux, leading to additional patchiness (Mahadevan & Campbell, 2002).

Global estimates of nitrate use have been argued to exceed estimates of nutrient fluxes from large-scale circulations, winter convection and mesoscale eddies (McGillicuddy *et al.*, 1998; Klein & Lapeyre, 2009). Submesoscale physics has been proposed as one of the missing mechanisms for supplying the remaining nutrients to bridge the gap between supply and demand. Submesoscale processes such as filaments and fronts produce strong gradients in density, resulting in vertical velocities which can upwell nutrients and result in the subduction of chlorophyll below the euphotic zone (Thomas *et al.*, 2013). Variability in density can therefore be used as a simple proxy for the amount of submesoscale features present (Liu & Levine, 2016). The coefficient of variation in surface density was calculated over a 7 day moving window (Figure 4.10). This showed stronger variability in the surface during the summer when primary production was highest.



FIGURE 4.19: Coefficient of variation for density correlated to estimated glider primary production integrated to the euphotic depth. R^2 0.48 p-value < 0.001

The coefficient of variation for primary production showed a different pattern to the variability in density with a large peak in January and February, declining throughout March and April with another peak in the beginning of June (Figure 4.10). The peak in winter occurred because the standard deviation at this time was higher together with a low mean. The lack of coherence in the coefficient of variation seen between density and primary production suggests that the relationship between density and primary production is more complex interplay between physical drivers and the impact on the biological response. The density CV has a significant correlation with total primary

production, suggest that it may influence production, however this requires further study as it may be coincidence (4.19). The density CV was high during times of stratification as the isopycnals move closer together in the surface so internal waves would show up as high variability. Internal waves can increase light available to phytoplankton by uplifting isopycnals, which can lead to enhanced but intermittent growth (Holloway, 1984; Lande & Yentsch, 1988), which may partly explain the high variability in primary production seen in August, when the water column is stratified.

Each of these methods for looking at variability produces slightly different results. For example the variance shows the distribution around the mean, whereas the percentage change shows day to day variability. The wavelet analysis depicts which temporal scales the data varies over. The CV is a standard measure of dispersion. Because the CV was calculated on logged data, the spikes during periods of high primary production rates will be dampened. During January and February there are some very low primary production rates leading to a large dispersion in the logged data and consequently the spikes in the CV during this time are high. There is an indication that during the summer months there is higher variability, shown from the variance, wavelet analysis and daily percentage changes, as well as a peak in the CV. Without more supplementary data, it is difficult to say which method gives the most accurate assessment. In the future it would be useful to have more data on grazing rates and zooplankton distributions to determine if the variability seen in primary production is controlled by bottom up or top down processes. Grazing rates may induce phytoplankton variability in a number of ways, such as swarming, feeding and predator avoidance and may also depend on the species and or life stage of the organism (Omori & Hamner, 1982). Vertical migration of zooplankton in the presence of shear can result in different distributions of migrating and non-migrating species, which may have different grazing rates (Martin, 2003, and references therein).

Mahadevan & Campbell (2002) show that high resolution sampling and modelling is needed for more patchy distributions of tracers. Biological uptake and growth respond quickly to changes in the ocean surface, such as nutrient supply and therefore it is important to model and sample primary production at high resolution. Gliders can be an important tool for looking into patchiness and the response of phytoplankton to physical forcing. The results here show the highly patchy nature of primary production.

4.4.3 Community Composition

The scale factor for correcting the chlorophyll concentrations varies throughout the year (Figure 4.14) and could potentially give an indication of important changes occurring

within the phytoplankton community throughout the year. It has been shown that phytoplankton species can have different carbon (biomass) to chlorophyll fluorescence ratios (Cullen, 1982; Kruskopf & Flynn, 2006), which may explain the change in scale factor. For example, if a species has a high carbon to fluorescence ratio, the irradiance would be attenuated at a similar rate for the same number of cells with a low carbon to fluorescence ratio but would have a higher fluorescence reading. Therefore the scale factor would be larger than a low carbon to fluorescence community if the attenuation was the same (Carr, 1986).

Studies have shown that the community composition in the North Atlantic changes over the development of the bloom (Barlow et al., 1993). Typically diatoms dominate the peak of the bloom although prymnesiophytes are also present. The post bloom stage is dominated by prymnesiophytes, with an increase in dinoflagellates (Barlow *et al.*, 1993; Henson et al., 2012). After the bloom the subsurface maximum is generally dominated by diatoms (Lochte & Pfannkuche, 1987; Painter et al., 2010a). CPR (Continuous Phytoplankton Recorder) data collected at the same time as this study, from the E5 standard region, which encompassed the study site, provided an indication of a shift in the species composition (Figure 4.15). The abundance of diatoms increased throughout March and April as the scale factor increased, which could indicate a shift from smaller species to larger species as the bloom develops. There was then a shift from a community dominated by diatoms to one dominated by dinoflagellates during June and July. A regression between the ratio of diatoms to dinoflagellates with monthly averaged values of the scale factor was however insignificant. This was possibly because the area used for the CPR dataset was much larger than our study site and changes in this extended area may influence the timing of the shift in community. For example, the spring bloom tends to develop first in the South and propagates to the North at about 20 km per day (Siegel et al., 2002) and therefore there may also be differences from North to South in the timing of phytoplankton community succession. The CPR would only show an average of this change over the whole area, rather than the specific change at the study site. From the North to the South the length of the E5 standard area is approximately 550 km and therefore it could take a month for the spring bloom to propagate from the South to the North, which would encompass the lag observed here between the change in scale factor and community. Although this may explain the lag it does not prove there would be a correlation between community composition and the scale factor. This may particularly be true for the beginning of the survey (September to March) when community changes little. There may be other factors that contribute to the change in scale factor such as nutrient stress or light limitation.

During the period when the subsurface chlorophyll maximum was present the CPR data showed a decrease in diatoms. Diatoms are generally present in the subsurface maximum (Smythe-Wright *et al.*, 2010), but the CPR cannot capture the subsurface community. The SCM was at a depth of 30 - 40 m, deeper than the general depth at which CPR data is collected at approximately 5-10 m (Batten *et al.*, 2003). The production maximum was also deeper than this at 20 m.

Satellite estimates of calcite concentrations can be used as a proxy for the abundance of coccolithophores using PIC estimates from satellite data (Gordon *et al.*, 2001). Satellite PIC showed an increase in PIC concentration slightly before the shift to a dinoflagellate dominated community and coincident with the increase in scale factor (Figure 4.15), suggesting that high PIC concentrations may correspond to a low scale factor. Although the difference between peaks could be caused by the difference in the frequency of the data, the satellite is an 8-day composite whereas the glider data has daily values. However there was also a sharp decrease seen in PIC at the beginning of March but no increase in the scale factor with low PIC in July to September when the scale factor was low. A correlation between the scale factor and PIC concentration was insignificant.

Although both indications of community change were not significantly correlated to the scale factor it nevertheless appears that there may be considerable changes in the community composition of phytoplankton in June and July. Within the space of one week there was a dramatic change in the ratio of diatoms to dinoflagellates and an increase in PIC, along with a deepening of chlorophyll in the water column. This corresponded with the decrease in the scale factor in July. Cetinić et al. (2015) found that community composition varied together with the ratio of chlorophyll fluorescence to backscatter measurement in the North Atlantic just South of Iceland, with an increase in the ratio signalling a shift from a winter phytoplankton community dominated by pico- and nanophytoplankton to a community dominated by diatoms in spring. An analysis of the glider PAR-corrected chlorophyll to back scatter ratio demonstrates a similar pattern to the scale factor (Figure 4.20). The ratios are high when diatoms are present in the CPR data, as found by Cetinić et al. (2015). The surface pattern, however, is different from that seen at 20 m depth where the production maximum is located. The ratio at 20 m remains high later into the year, at a time when the subsurface production maximum is present and therefore could indicate that the community of diatoms had migrated to the subsurface maximum.

The carbon to chlorophyll ratio can also vary due to nutrient stress and/or photoacclimation (Riemann *et al.*, 1989; Kruskopf & Flynn, 2006; Llewellyn *et al.*, 2005). Nutrient stress can cause a decline in chlorophyll to carbon, however this may be somewhat compensated for by an increase in chlorophyll to carbon caused by photoacclimation during subsurface blooms (Kruskopf & Flynn, 2006). This could also be a contributing factor to the changing scale factor, as the rapid decrease in scale factor occurs around the same time as the formation of the subsurface chlorophyll maxima and could therefore be related to both nutrient stress and photoacclimation as the phytoplankton grow deeper in the water column.

At the present time changes in the scale factor (which represents changes to bulk community chlorophyll fluorescence) cannot be linked unequivocally to changes in dominant phytoplankton taxa but the coincident timings of changes in the ratio of dinoflagellates to diatoms and formation of the subsurface chlorophyll maximum, is strongly suggestive of a link between changing species or physiology and changing scale factors in summer. This is clearly an avenue for future research.



FIGURE 4.20: The ratio of the corrected chlorophyll from the glider to glider measured backscatter. The blue line shows the scale factor, which decreases at the same time as the surface ratio of chl:bb

4.5 Conclusions

I have presented a high resolution full annual timeseries for primary production in the North Atlantic from September 2012 to September 2013, derived from glider data. The yearly integrated primary production estimate from the glider of 255 g C m⁻² d⁻¹ was 6% higher than estimated by the satellite chlorophyll product.

The three questions posed in Section 4.1 have been discussed:

- 1. It has been demonstrated that the formation of a subsurface production maximum in July, which persists throughout August and into the beginning of September, contributed to 23% of annual production.
- 2. High variability is evident at small spatial scales throughout the primary production timeseries, with several different methods pointing to increased variability throughout the summer months.

3. The scale factor derived from the chlorophyll-*a* fluorescence and irradiance data showed changes over the period of the formation of the subsurface chlorophyll maximum, indicating a change in the community composition, the phytoplankton carbon to chlorophyll ratio, or an indication of nutrient stress or photoaclimation.

High variability in the primary production estimates was observed from the gliders, with large day to day percentage changes in production particularly in the summer. Much of this variability is missed from the satellite data establishing the usefulness of gliders for monitoring small spatial and temporal scales. There was evidence that increased variability in density, indicating submesoscale processes, increased primary production, this will be explored more by calculating nitrate fluxes in the next chapter.

The glider dataset also demonstrates evidence of a change in the carbon to chlorophyll ratio of phytoplankton during the formation of the subsurface maximum, this could demonstrate a change in community composition, photoacclimation of cells or nutrient limitation. There are indications from other datasets of changes to the community composition, however the other two factors cannot be tested with the current dataset.

Chapter 5

Advective and Diffusive Fluxes of Nitrate



5.1 Introduction

In this chapter, I will investigate nitrate fluxes into the euphotic zone. I will quantify a number of different processes which result in the vertical supply of nitrate: advective, convective and diffusive fluxes. I will then relate the nitrate fluxes to the rates of primary production presented in Chapter 4.

Inorganic nitrogen is an important macronutrient for phytoplankton growth, forming 16% of the stoichiometric biomass of phytoplankton cells (Redfield, 1958). Nitrate is often depleted in surface waters in the North Atlantic throughout summer due to uptake by phytoplankton and subsequent sinking and remineralisation at depth. Higher concentrations are therefore found at depth, and phytoplankton are dependent on fluxes of nitrate into the euphotic zone from the subsurface. Nitrate fluxes in the ocean are difficult to measure directly, especially over long time periods. Processes in the ocean which result in the flux of nitrate into the euphotic zone, largely dictate patterns of primary production in the ocean, in the absence of light limitation (Figure 1.1 shows a schematic of mechanisms of nutrient supply). This chapter quantifies the flux of nitrate into the euphotic zone at a range of timescales from days to a full year and relates this to the observed primary production described in Chapter 4.

5.2 Methods

The dataset available (Section 2.4) allowed an estimate of the nitrate budget to be calculated by using the mooring and glider data together. Briefly, the moored velocity data are used to estimate the horizontal advective flux into and out of the survey box. Vertical velocities were calculated from the mooring data by Xiaolong Yu (National Oceanography Centre Southampton) and kindly contributed towards this study, which allows calculation of the vertical advective flux into the euphotic zone. The convective flux is estimated from the glider data using mixed layer depth estimates. The diffusive flux of nitrate is estimated using the ADCP mooring data, kindly contributed by Natasha Lucas (Bangor University). The calculations of all the fluxes and data interpretation have been carried out by myself.

Before explaining the methods used to estimate nitrate fluxes, an appropriate depth over which to do the calculations has to be chosen. For this project a depth of 50 m was used. The measurements used are situated at different depths: dissipation approximately 48 m, vertical velocities 50 - 500 m and horizontal current measurements 50 - 500 m. 50 m is the minimum depth possible for most of the measurements, but it is also conveniently situated just below the euphtotic depth for most of the year (Figure 4.3).
5.2.1 Density Nitrate Relationship

To estimate nitrate from the data collected by the gliders, a relationship between a measured parameter and nitrate was needed, because nitrate was not measured directly by the glider. There is extensive evidence that there is a strong relationship between nitrate concentrations and density. A number of global databases for nitrate have been assembled from ship-board measurements (Kamykowski & Zentara, 1985; Levitus et al., 1993). Several studies have shown that density (or temperature) and nitrate are highly correlated in the ocean (Johnson et al., 2010; Lucas et al., 2011; Johnson et al., 2013). This correlation is present at small spatial and temporal scales at a given depth because of the vertical movement of isopycnals (Johnson et al., 2010; Ascani et al., 2013). The vertical movement of water across isopycnals is inhibited. As rates of diapycnal mixing are generally weak the flux of nitrate into the surface is restricted. This leads to a vertical gradient of nitrate, with higher concentrations below the euphotic zone. The sources and sinks of nitrate are depth dependent; phytoplankton production is dependent on irradiance, which decays exponentially with depth, and remineralisation of organic matter occurs at depth falling off with a power law below the euphotic layer (Martin *et al.*, 1987). It might therefore be assumed that nitrate would have a stronger association with isobars rather than isopycnals. However the relationship of nitrate with density occurs at global scales. Using measured nitrate profiles from the World Ocean Atlas While & Haines (2010) found that variability of nitrate concentrations are higher at a constant depth than on isopyncal surfaces. At large scales eddies mix properties along isopyncals and diapycnal mixing is weak causing the correlation to persist (Omand & Mahadevan, 2013). Density was therefore decided to be the most appropriate parameter.

This study uses CTD data from the 3 cruises to the study site that have available nutrient data: D381 in September 2012, JC087 in July 2013 and JC090 in September 2013 (Table 2.2). Following Sharples *et al.* (2007) bottle data from the CTDs were used to form a density-nitrate relationship (Figure 5.1). A fit to the data was obtained using Matlab's polyfit function, with a fourth order polynomial giving the best fit ($y = -2.9x + 1.2x10^4x - 1.86x7^{10}x + 1.3x10^{10}x - 3.3x10^{12}$), the observations against the calculated values are shown in Figure 5.2 (R² 0.83, n = 1024). This relationship was then applied to the glider and mooring density profiles to produce a time-series of nitrate within the study area (Figure 5.3). The RMSE was calculated from the data and was found to be 1.6 mmol N m⁻³, this was used to estimate error on the fluxes by calculating the fluxes using nitrate plus or minus the RMSE.

Temperature nitrate relationships were also investigated. However there was a larger difference, especially at depth but also within the top 50 m, between the different cruises

leading to a low \mathbb{R}^2 of 0.23 between the fitted and observed values (Figure 5.4). Therefore density was used as an estimate of nitrate concentrations.



FIGURE 5.1: Density nitrate relationship from 3 cruises. The dotted line is the fourth order fit $(y = -2.9x + 1.2x10^4x - 1.86x7^{10}x + 1.3x10^10x - 3.3x10^{12})$



FIGURE 5.2: The observed nitrate calculated from CTD density data compared with the calculated nitrate derived with the density nitrate relationship.



FIGURE 5.3: Surface glider nitrate calculated from the density nitrate relationship.



FIGURE 5.4: Temperature nitrate relationship from 3 cruises.

5.2.2 Diffusive Nitrate Fluxes

The diffusive flux of nitrate can be calculated from turbulent diffusion estimated using a structure function from the ADCP mooring data (Lucas *et al.*, 2014) and profiles of nitrate derived from the density-nitrate relationship. The flux, NO_{3flux} (mmol m⁻² s⁻¹), can be estimated as the product of turbulent diffusivity and the gradient of nitrate at depth z using the equation (Tennekes & Lumley, 1972):

$$NO_{3flux} = -\kappa_z \left(\frac{\partial N}{\partial z}\right),$$
(5.1)

where N is the concentration of nitrate (mmol m⁻³) and κ_z (m² s⁻¹) is the turbulent diffusivity. Nitrate gradients (mmol m⁻⁴) are traditionally calculated from CTD bottle samples, which are vertically sparse. This can lead to underestimates in gradients. An advantage of the nitrate-density relationship is that it allows nitrate estimates at the same high resolution as density data. Here the gradient between 10 m depth bins either side of the ADCP instrument was used. The depth changes slightly over the year as the moorings were prone to knock down, but in general the ADCP was situated around 48 m and therefore the gradient was calculated from between 45 and 55 m bins.

The turbulent diffusivity (κ_z) represents the magnitude of turbulent mixing and is related to dissipation of turbulent kinetic energy (ε) by (Osborn, 1980):

$$\varepsilon = \frac{\kappa_z N^2}{\Gamma} \tag{5.2}$$

where Γ is a constant mixing efficiency, for which a value of 0.2 was used (Rippeth *et al.*, 2003; Moum *et al.*, 1995; Osborn, 1980), and N (s⁻²) is the buoyancy frequency (Gill, 1982),

$$N^2 = -\frac{g}{\rho} \frac{\partial \rho}{\partial z} \tag{5.3}$$

where g is acceleration due to gravity and ρ is the potential density.

5.2.3 Vertical Advective Nitrate Fluxes Using Mooring Data

Mesoscale Vertical Advective Flux

The outer moorings are approximately 13 km apart (Figure 2.1) and the calculations for the vertical advective flux (Equation 5.5) therefore estimates the temporal vertical flow over this spatial scale. The vertical velocities calculated at the outer moorings therefore represent vertical flow at the mesoscale. The vertical advective flux is calculated by multiplying the vertical velocity (w) by the nitrate concentration (N) at a single depth and time:

$$NO_{3\,flux} = wN \tag{5.4}$$

The vertical velocities were calculated from the mooring density measurements by Xiaolong Yu using the method of Sévellec *et al.* (2015) based on the equation:

$$w = \underbrace{-\frac{\partial_t \rho}{\partial_z \rho}}_{\text{Time Variation}} - \underbrace{\frac{\text{Divergence}}{(u\partial_x \rho + v\partial_y \rho)}}_{\partial_z \rho}$$
(5.5)

Where the first term on the right hand side is a time varying component and broadly represents the vertical velocity in terms of internal waves and the second term represents the vertical velocity due to horizontal divergence/convergence. The vertical velocities were interpolated onto an hourly grid with 10 m depth bins.

The vertical velocities within the mixed layer are not well constrained, due to the homogeneous density profile. Therefore when the mixed layer depth was deeper than 50 m no vertical flux was calculated. Moreover it was assumed that when the mixed layer was deeper than my chosen depth of 50 m then the advective flux was zero because the nitrate gradient in the mixed layer was zero. At other times if the velocities were going downward the nitrate concentration used in the calculation was taken from the 10 m bin above 50 m. If the velocities were going upward the 10 m bin below 50 m was used. This assumes that the water was coming from the 10 m bin upstream of the vertical velocity measurement. On average, between the two depths the concentration in the deeper depth bin was 20% higher than the shallower depth bin.

An upper and lower estimate of the advective flux is calculated here as there are assumptions attached to each estimate. This therefore allows a range to be calculated. It also allows an assessment of how these assumptions might impact on the estimated nitrate fluxes. As there are no direct measurements of nitrate taken, fluxes out of the euphotic zone are difficult to constrain, particularly in summer when phytoplankton uptake may cause the density-nitrate relationship to deviate. To achieve an upper estimate of the nitrate fluxes into the mixed layer the downward fluxes were set to zero, assuming that all the nitrate in the mixed layer has been assimilated by the phytoplankton. In reality this is unlikely as some processes causing the vertical velocities may be on shorter timescales than phytoplankton growth, causing nitrate to move up and down into and out of the mixed layer without consumption. This may be particularly true in winter when phytoplankton are light limited. To estimate a lower limit on the vertical flux the same method was used but the downward velocities were not removed, which represents the extreme of no consumption by phytoplankton.

As a third estimate of the average flux over the year the root mean square of the vertical velocities was multiplied by the root mean square of the nitrate field. For this the nitrate concentration was taken at 50 m.

Submesoscale Vertical Advective Flux

From the inner moorings, which are approximately 1.3 km apart (Figure 2.1), the submesoscale component of vertical velocities can also be calculated in the same way as the mesoscale fluxes. Unfortunately, due to the loss of the top instrument off one of the inner moorings the shallowest vertical velocity estimate is at a depth of 120 m (Figure 2.5). This is 70 m deeper than the euphotic depth, and therefore may not influence the growth of phytoplankton in the top 50 m. However, the vertical advective fluxes for the mesoscale and submesoscale have been calculated at this depth to estimate how different the contribution from the submesoscale may be.

Vertical Velocity Components

The two components of the vertical velocities, time varying and divergent, were separated and the associated nitrate fluxes calculated. This allowed an estimate of how much of the flux was contributed from features that induce isopycnal displacement, such as internal waves (time varying component Unnikrishnan & Antony (1990)) and how much from the eddy field and frontogenesis (divergent component) propagating through the site (Thomas *et al.*, 2013; Sévellec *et al.*, 2015).

5.2.4 Horizontal Advection

The shallowest available mooring data is at 50 m (discussed previously), therefore a horizontal flux within the top 50 m cannot be calculated, instead the horizontal flux between 50 and 100 m is calculated. Although these will not be used directly to measure a nitrate flux into the euphotic zone, the fluxes are still useful to put the other fluxes in context.

To estimate the advective flux of nitrate into the survey area, geostrophic calculations were used as the water budget did not sum to zero for the current meter measurements. Although the current meters themselves are very accurate the compasses could be out by several degrees. This could lead to large discrepancies between the current meters leading to a loss or gain of water in the study site, over time this could become a significant error in the flux estimates. When using the current meters to estimate water budgets there was a large loss of water from the site over the whole year, approximately 5×10^{10} m³ over the survey volume of 105,000 m³.

Geostrophic flow in the ocean is where the pressure gradient force is balanced by the Coriolis effect (see Appendix ?? for theory). The direction of flow is parallel to the

isobars, with the high pressure to the right of the flow in the Northern Hemisphere. Geostrophy assumes that the ocean is in geostrophic and hydrostatic balance. A consequence of this is that fluxes due to winds and even submesoscale currents will be neglected.

For each depth the lateral buoyancy gradient between pairs of moorings was found by taking the difference between the two moorings and dividing by the distance between them. The ADCP velocity at this depth was multiplied to the geostrophic shear integrated from the reference depth. The reference depth was the average between 450 and 500 m, as this is the deepest mooring measurement, far from the surface effects such as wind.

As a check to determine the accuracy of the nitrate fluxes the water budget was first calculated. Due to conservation of volume it can be assumed that the water budget over time should average to zero, with water coming into the study site equalling the water leaving it, as the area used is a closed volume. An average current was determined for each section over all depths and multiplied by the distance between the moorings (Figure 2.1) and the depth of each depth bin (50 m). This allows a volume flux through the area from between 50 - 100 m depth. For all sections, the water entering the box was assigned a positive flux and if the water was leaving the box the flux was negative. The water budget, when calculated using geostrophic velocities, sums to zero at each time interval.

An average profile of nitrate for each face of the box was constructed using the average of the density profiles for the two corner moorings for each side. This was then multiplied in each depth bin by the volume flux resulting in an estimate for the amount of nitrate per time period going through the box. As a nitrate-density profile is derived using data from across the year, short term fluctuations in transport may be missed.

5.2.5 Convective Flux

The convective flux of nitrate from winter convective mixing, can be estimated simply by taking the nitrate concentration at the maximum winter mixed layer depth and integrating over the euphotic depth (Forryan *et al.*, 2012; Painter *et al.*, 2014*a*). For example the maximum mixed layer depth derived from the glider data of 360 m shows a concentration of 12.4 mmol N m⁻³ at this depth. The cruise data from JC090 shows that the concentration of nitrate at 5m depth is 0.03 mmol m⁻³ in September. Taking this as the annual minimum which persists until winter convective mixing, with an initial nitrate concentration of 12.4 mmol N m⁻³, therefore, a depth integrated total to 50 m equates to 620 mmol N m⁻² supplied by deep winter mixing.

5.2.6 Wind Stress

The wind stress is the shear stress exerted by the wind on the ocean surface and depends on the wind speed, waves and atmospheric stratification (Bentamy & Fillon, 2012). Wind stress was used to compare the fluxes and observe if wind events lead to an increase in the nitrate flux. The data on a regular grid was obtained as Daily Advanced Scatterometer (ASCAT) Surface Wind Fields Level 3 from the Centre de Recherche et d'Exploitation Satellitaire (CERSAT), at IFREMER, Plouzan (France), which gives daily-averaged wind stress fields (Figure 5.5). The spatial resolution was 0.25 degrees and the wind data was extracted for the grid point centred on 48.75° N, 16.25° W. The method for wind stress estimation from the scatterometer surface wind retrievals is described by (Milliff & Morzel, 2001).



FIGURE 5.5: Timeseries of wind stress at the OSMOSIS site.

5.3 Results

5.3.1 Summary of Nitrate Fluxes

In this section I will present the year-long results of the vertical nitrate fluxes, from advection, diffusion and convection. The horizontal advective fluxes between 50 and 100 m will also be presented. First I will summarise the main results.

The annual nitrate fluxes of the individual processes are summarised in Table 5.1. The largest vertical flux, at 50 m, was the maximum estimate of the mesoscale advective flux at 1.5 mol N m⁻² yr⁻¹. The diffusive and convective fluxes and the minimum estimate for vertical advection were all very similar ranging from 0.62 to 0.74 mol N m⁻² yr⁻¹.

At a depth of 120 m the mesoscale vertical advective fluxes were lower than the submesoscale fluxes. Annually the maximum estimates were 2.6 and 3 mol N m⁻² yr⁻¹, for the mesoscale and submesoscale fluxes respectively. The minimum estimates at this depth were negative and were -1.9 and -3.8 mol N m⁻² yr⁻¹ for the mesoscale and submesoscale fluxes respectively.

The vertical advective fluxes were split into the time-varying and divergent components. For both the mesoscale fluxes at 50 and 120 m and the submesoscale fluxes at 120 m the time-varying flux was the largest component for the maximum flux estimates. When the minimum flux was taken into account the time-varying component became very small, whereas the divergent flux showed little change.

The diffusive and advective fluxes (both the vertical and horizontal) showed strong temporal variability throughout the year. In general, most months showed high variability apart from July, where the fluxes tend to be much lower, especially for the mesoscale vertical advective flux at 50 m.

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Flux	Amount	Contribution to
		Primary Produc-
		tion
Mesoscale Vertical advective flux 50	$1.5 \pm 0.8 \text{ mol m}^{-2} \text{ N yr}^{-1}$	$55\pm 30\%$
m (maximum estimate)		
Mesoscale Vertical advective flux 50	$0.48 \text{ mol N} \text{m}^{-2} \text{yr}^{-1}$	17%
m (RMS estimate)		
Mesoscale Vertical advective flux 50	$0.74 \pm 0.28 \text{ mol N m}^{-2} \text{ yr}^{-1}$	$27 \pm 10\%$
m (minimum estimate)		
Winter Convective mixing (50 m	$0.62 \pm 0.08 \text{ mol N} \text{ m}^{-2}$	$22 \pm 3\%$
MLD)		
Diffusive Flux (50 m)	$0.7 \pm 0.03 \text{ mol N} \text{ m}^{-2} \text{ yr}^{-1}$	$25 \pm 1\%$
Mesoscale Vertical advective flux	$2.6 \pm 0.75 \text{ mol N m}^{-2} \text{ yr}^{-1}$	$96\pm28\%$
120 m (maximum estimate)		
Mesoscale Vertical advective flux	$0.4 \text{ mol N} \text{ m}^{-2} \text{ yr}^{-1}$	2.2~%
120 m (RMS estimate)		
Mesoscale Vertical advective flux	$-1.9 \pm 0.55 \text{ mol N m}^{-2} \text{ yr}^{-1}$	- $68 \pm 20\%$
120 m (minimum estimate)		
Submesoscale Vertical advective	$3.0 \pm 0.8 \text{ mol N m}^{-2} \text{ yr}^{-1}$	$112\pm32\%$
flux 120 m (maximum estimate)		
Submesoscale Vertical advective	$0.07 \text{ mol N} \text{ m}^{-2} \text{ yr}^{-1}$	-2.5 %
flux 120 m (RMS estimate)		
Submesoscale Vertical advective	$-3.8 \pm 0.3 \text{ mol N m}^{-2} \text{ yr}^{-1}$	$-140 \pm 13\%$
flux 120 m (minimum estimate)		

TABLE 5.1: Summary of nitrate fluxes and the contribution to the calculated primary production

An annual flux was calculated by summing the different fluxes together (Table 5.2). The minimum flux has both upward and downward fluxes, whereas the maximum flux was the upward fluxes only, assuming all the nitrate is consumed by phytoplankton. The maximum flux at 50 m used the maximum vertical advective flux, the convective flux and the diffusive flux. Over the year the maximum estimate was 2.82 mol N m⁻² yr⁻¹ and accounted for 102% of the total annual primary production (Chapter 4). The minimum flux at 50 m used the minimum vertical advective flux, the convective flux and the diffusive flux. The annual total of the minimum flux was therefore 2.06 mol N m⁻² yr⁻¹ and accounts for 75% of the total annual primary production. The mesoscale

and submesoscale vertical advective fluxes at 120 m are all treated separately, i.e. not summed together as the submesoscale velocities incorporate the mesoscale velocities.

Flux	Amount	Contribution to Pri-
		mary Production
Maximum estimate at 50 m	$2.82 \pm 1.26 \text{ mol m}^{-2} \text{ N yr}^{-1}$	$102 \pm 48\%$
Minimum estimate at 50 m	$2.06 \pm 0.75 \text{ mol m}^{-2} \text{ N yr}^{-1}$	$75\pm25\%$

 TABLE 5.2: Annual Vertical Fluxes

5.3.2 Diffusive Flux

The nitrate gradient at 50 m was highest in autumn at around 0.15 mmol N m⁻⁴ decreasing to near zero in winter when the water column was well mixed and there was little gradient in density and consequently nitrate (Figure 5.6). As the water column becomes stratified in the summer the nitrate gradient increased to 0.1 mmol N m⁻⁴. These values were similar to those found by Martin *et al.* (2010*a*), from a study conducted in the same region. The opposite pattern was found in κ_z , with the highest values in winter (10⁻¹ m² s⁻¹) and lowest values in summer (10⁻⁴ m² s⁻¹). There was also a decrease in k_z in May after which it increased again temporarily in mid-May (Figure 5.6). k_z was highest when the mixed layer was deeper than 50 m where turbulent diffusivity was typically 10^{-2} m² s⁻¹. Below the mixed layer depth, the values were orders of magnitude smaller, 10^{-4} m² s⁻¹, although this tends to be slightly higher than the background diffusivity of the ocean of 10^{-5} m² s⁻¹ (Polzin, 1997; Ledwell *et al.*, 1998).

The seasonal variations in turbulent diffusivity and the nitrate gradient cancelled each other out to a certain extent resulting in a relatively uniform pattern in the diffusive nitrate flux. However there was still a seasonal pattern. Throughout Autumn and Spring (September to November and April to June) the nitrate flux was slightly higher and more variable, ranging from 0.026 to 36 mmol m⁻² d⁻¹. In the later summer (July and August) the diffusive flux of nitrate was the lowest and least variable with values around 0.1 mmol m⁻² d⁻¹ (Figure 5.6). These fluxes were similar to those observed in 2006 by Martin *et al.* (2010*a*) for the same time of year. For the two studies the diffusivity measurements $(10^{-4} - 10^{-5} \text{ m s}^{-1})$ and the gradient (0.1 mmol N m⁻⁴) showed similar values at 50 m. There were several periods of mooring knock down, down to more than 150 m (Figure 5.7). This may lead to diffusivities used in the calculation that are at the wrong depth. If the depth is deeper it may result in a lower flux as diffusivities tend to decrease with depth. For the daily results, the values were logged and then the mean was taken, which may reduce the effects of spikes due to mooring movement.



FIGURE 5.6: Timeseries of (a) the gradient in nitrate over 55 to 45 m depth (b) diffusivity at 50 m (c) diffusive nitrate flux over 50 m.



FIGURE 5.7: The depth of the ADCP, used to estimate K_z , note the large knock down in May and June

5.3.3 Vertical Advective Flux

Mesoscale fluxes at 50 m

There were measurements from the moorings for vertical velocities at hourly intervals. However the results have been presented as daily means to match the primary production measurements. Looking at the daily means compared with the hourly fluxes, shows that the latter can be variable but that the daily means are a good representation of the advective hourly fluxes.

The advective nitrate flux into the euphotic zone was positive for both the maximum and minimum estimates (Table 5.1), contributing between 27 and 55% of the total annual flux, respectively. The vertical velocities average over the year to 1.6 m d⁻¹ at the depth of 50 m, for the periods when the mixed layer was shallower than 50 m. If a survey adequately samples features that have associated vertical velocities the mean vertical velocity should average to zero due to mass conservation, i.e. what comes up must come down (Frajka-Williams *et al.*, 2011). The calculated mean for the vertical velocities at 50 m was very close to zero, as found previously for mesoscale upwelling (Sévellec *et al.*, 2015). The largest daily averaged flux occurred at the beginning of August, 90 mmol N m⁻² d⁻¹. The largest daily averaged downward flux was -63 mmol N m⁻² d⁻¹, in mid June.

The vertical advective flux was zero throughout winter and spring (December to April) because the chosen depth level of 50 m was within the mixed layer, as described earlier. During May when the mixed layer was shallower than 50 m there was no flux due to mooring knock down (Figure 5.7). Fluxes in autumn (September to December) ranged from -9 to 40 mmol N m⁻² d⁻¹ (Figure 5.8).

There were several spikes in the advective flux throughout the summer, particularly throughout June and August. Fluxes throughout June range from -60 to 46 mmol N m⁻² d⁻¹. In August fluxes were also quite variable and range from -7 to 90 mmol N m⁻² d⁻¹, the downward fluxes are lower because the nitrate concentration at 40 m was used which has lower nitrate, as concentrations increase with depth (Figure 5.3). Activity throughout July is lower, with maximum fluxes reaching 23 mmol N m⁻² d⁻¹.



FIGURE 5.8: Mesoscale Advective Nitrate Flux at 50 m, maximum (black) and minimum (red) estimates. Time period shown where mixed layer depth is less than 50 m. The top panel shows the nitrate concentration at 50 m and the middle panel shows the mesoscale vertical velocity at the same depth.

Submesoscale and Mesoscale Fluxes at 120 m

Figures 5.9 and 5.10 show the mesoscale and submesoscale vertical fluxes at 120 m. The first thing to note is that the submesoscale fluxes were larger than those at the mesoscale, by approximately 15%, with 3.0 ± 0.84 and 2.6 ± 0.96 mol N m⁻² yr⁻¹ annual fluxes for the sub mesoscale and mesoscale respectively. As the nitrate concentrations were the same for both calculations this is entirely due to the larger submesoscale vertical velocities. The mesoscale fluxes were more often negative than the submesoscale fluxes, with 62% more fluxes being negative than positive. The submesoscale fluxes showed a higher flux in November (maximum of 580 mol N m⁻² d⁻¹), whereas the mesoscale fluxes were stronger in December peaking at 520 mol N m⁻² d⁻¹ (note the scale of the axes are different, Figures 5.9 and 5.10). Both fluxes were lower during summer. Furthermore, at this depth the mesoscale fluxes were larger than those observed shallower at 50 m by 42% (Figure 5.8).

There were more available estimates of vertical velocities at 120 m than at 50 m because the shallower instruments were more affected by mooring knock down resulting in a loss of some data at 50 m depth, particularly during May.



FIGURE 5.9: Mesoscale Advective Nitrate Flux at 120 m, maximum (black) and minimum (red) estimates. Time period shown where mixed layer depth is less than 120 m. The top panel shows the nitrate concentration at 120 m and the middle panel shows the mesoscale vertical velocity at the same depth.



FIGURE 5.10: Submesoscale Advective Nitrate Flux, maximum (black) and minimum (red) estimates. Time period shown where mixed layer depth is less than 120 m. The top panel shows the nitrate concentration at 120 m and the middle panel shows the submesoscale vertical velocity at the same depth.

Fluxes Associated with Vertical Velocity Components

The annual fluxes were calculated for the mesoscale moorings at a depth of 50 m. The upper estimates (with no downward fluxes) equated to 0.64 ± 0.3 and 1.16 ± 0.6 mol N m⁻² yr⁻¹, for the divergent and time varying components respectively. For the maximum estimate of the components the time varying component was the largest contributor to the vertical advective flux. The minimum estimates for the vertical advective fluxes were also calculated for each of the velocity components and resulted in a flux of 0.5 ± 0.2 and 0.24 ± 0.01 mol N m⁻² yr⁻¹, for the divergent and time varying components and resulted in a flux of 0.5 ± 0.2 and 0.24 ± 0.01 mol N m⁻² yr⁻¹, for the divergent and time varying components respectively.

Scale and depth	Divergent Flux	Time-varying flux
	$(mol N m^{-2} yr^{-1})$	$(mol N m^{-2} yr^{-1})$
Mesoscale 50 m	Maximum 0.64	Maximum 1.16
	Minimum 0.5	Minimum 0.24
Mesoscale 120 m	Maximum 0.87	Maximum 1.74
	Minimum -0.19	Minimum -0.024
Submesoscale 120 m	Maximum 1.26	Maximum 1.74
	Minimum -0.54	Minimum 0.014

TABLE 5.3: The divergent and time-varying components of the vertical advective flux

The mesoscale fluxes at 120 m have a maximum estimate of flux components of 0.87 \pm 0.43 mol N m⁻² yr⁻¹ and 1.74 \pm 1 mol N m⁻² yr⁻¹ for the divergent and time varying components respectively. The minimum estimates were both negative, at -0.19 \pm 0.02 mol N m⁻² yr⁻¹ and -0.024 \pm 0.07 mol N m⁻² yr⁻¹. The submesoscale fluxes were higher at the same depth (120 m) and showed a maximum estimated flux of 1.26 \pm 0.14 mol N m⁻² yr⁻¹ and 1.74 \pm 0.24 mol N m⁻² yr⁻¹ for the divergent and time varying components respectively (Figure 5.11). The minimum estimates for the submesoscale fluxes were fluxes were -0.54 \pm 0.06 mol N m⁻² yr⁻¹ and 0.014 \pm 0.006 mol N m⁻² yr⁻¹.



FIGURE 5.11: The time varying (black) and divergent (orange) components of the nitrate flux calculated as vertical velocities components. The top panel shows the mesoscale at 50 m. The middle panel shows the the mesoscale flux at 120 m and the bottom panel shows the submesoscale flux at 120 m.

5.3.4 Horizontal Geostrophic Flux

The horizontal fluxes through the study area were much larger, by several orders of magnitude, than any of the other mechanisms of nitrate supply calculated here (Table 5.4). Over the whole year the total geostrophic flux of nitrate into the site, between 50 and 100 m, was $1.9 \ge 10^9$ mol N yr⁻¹. However most of the nitrate goes straight through the site, resulting in a small net positive flux into the site of 0.8 mol N yr⁻¹ into the site over the whole year. The fluxes balance well because of the method used, which conserves volume transport and the use of a constant density-nitrate relationship. The difference between the fluxes entering the site and leaving the site was in between the maximum and minimum estimates of the vertical advective flux suggesting the discrepancy was due to vertical advection.

The horizontal advective flux was below the euphotic zone and therefore you would expect little uptake at this depth, which could also explain why the difference between the nitrate entering and leaving the site is so small.

The highest lateral fluxes into the box occurred in the winter and spring months, with the largest fluxes in February, March and April displaying a maximum of 1.78×10^6 mol N d⁻¹ (Figure 5.12). The fluxes reduced over summer to a minimum in July but increased again slightly in the summer.

Flux	Amount
Transit time through box (v)	4 days
Transit time through box (u)	$3.7 \mathrm{~days}$
Net Horizontal Flux through box	$0.8 \text{ mol N m}^{-2} \text{ yr}^{-1}$
Horizontal Flux into box	$1.9 \ge 10^9 \text{ mol N m}^{-2} \text{ yr}^{-1}$

TABLE 5.4: Summary of the horizontal fluxes



FIGURE 5.12: The flux of nitrate into the study site between 50 and 100 m depth.

5.4 Discussion

5.4.1 Primary Production Annual Cycle

Primary production over the year is described in Chapter 4, but I will briefly refresh the reader here on the annual cycle (Figure 4.5). The total annual (near) net primary production was 255 ± 51 g C m⁻² yr⁻¹ (2.75 ± 0.5 mol N m⁻² yr⁻¹). The error estimates are taken from the chlorophyll sensitivity study, as the RMSE between the PAR-corrected glider chlorophyll and the CTD bottle chlorophyll, which resulted in approximately a 20% error in primary production (Section 3.2.6). Mean daily productivity levels declined from September 2012 to February 2013 when productivity rates were lowest (negligible). The rate of primary production increased in March as light became stronger. There was a spike in primary production at the beginning of May at ~ 2.5 g C m⁻² d⁻¹, after which it declined again to about 0.5 - 0.7 g C m⁻² d⁻¹. Throughout June rates increased, reaching the annual maximum at the beginning of July (3.5 g C m⁻² d⁻¹). After this a subsurface production maximum formed and remained throughout August. Production migrated to the subsurface as the water stratified, mixing decreased and nitrate concentrations in the surface waters were depleted due to phytoplankton consumption. Over the whole year primary production was highly variable over daily timescales (Section 4.4.1).

5.4.2 Previous Estimates of Nitrate Fluxes

Using the assumption of eddy pumping the nitrate flux can be estimated directly from the vertical displacement of density surfaces from the mean position outside the eddy (McGillicuddy & Robinson, 1997). This method assumes that there is a strong relationship between nitrate and potential density. Another main assumption of this method is that phytoplankton are able to assimilate the upwelled nitrate with 100% efficiency. McGillicuddy *et al.* (1998) and Siegel *et al.* (1999) found that mesoscale nitrate fluxes from eddies, using satellite sea level anomaly data, was 0.19 and 0.35 ± 0.1 mol N m⁻² yr⁻¹ in the Sargasso Sea, respectively. These values are lower than the mesoscale estimates in this study of 0.74 - 1.5 mol N m⁻² yr⁻¹. However the modelled annual primary production for these studies was also much smaller, and therefore as a proportion the fluxes contribute to 48 and 70%, of the annual production in Siegel *et al.* (1999) and McGillicuddy *et al.* (1998) respectively. As a proportion this is more similar to the estimates here of 27 to 55% of annual primary production. Note that the earlier studies by McGillicuddy *et al.* (1998) and Siegel *et al.* (1999) may be considered to overestimate nitrate fluxes because it would not be possible for phytoplankton to consume all Spatial resolution in models can significantly change simulated nutrient budgets. For example a course resolution model (~2°) by Oschlies *et al.* (2000) found that at the North Atlantic Bloom Experiment site horizontal advection resulted in a net sink of nitrate whereas an eddy-resolving model (~0.1°) found that it was a net source of nitrate for biological uptake (McGillicuddy *et al.*, 2003). McGillicuddy *et al.* (2003) found that in this area convective mixing supplied the largest flux of nitrate, 1.04 \pm 0.09 mol N m⁻² yr⁻¹. Whereas the supply by vertical advection was slightly negative at -0.09 \pm 0.07 mol N m⁻² yr⁻¹. The negative transport occurred primarily in winter during periods of deep convection. There are no measurements of vertical advective fluxes during winter in this study, which may explain the differences in the sign of the flux term.

Modelling studies show that resolving mesoscale fluxes may not be adequate for estimating the contribution to primary production (McGillicuddy, 2016). Lévy *et al.* (2001) found that productivity was nearly three times higher at 2 km resolution than at 10 km resolution. Further modelling studies by Lévy *et al.* (2012) show that a higher resolution models $(1/9^{\circ} \text{ compared with } 1/54^{\circ})$ depict more energetic submesoscale fronts and therefore have greater fluxes of nutrients into the surface. This supports the results here as the submesoscale fluxes of nitrate are higher and could therefore support more growth. Global models are currently not eddy resolving due to computational limitations, which could result in differences between different model resolution over long term simulations (Lévy *et al.*, 2012).

5.4.3 Seasonality in Nitrate Fluxes

5.4.3.1 Mesoscale fluxes at 50 m

I will first examine the fluxes at 50 m and therefore there is no submesoscale component. Aggregating all the nitrate fluxes together per month allows a seasonal cycle of nitrate supply into the euphotic zone to be produced (Figure 5.13). The convective flux is evenly split between the months from when the mixed layer starts to deepen in winter to when it reaches the deepest point, on February 4th 2013, when the convective flux was calculated. The convective flux was therefore split between 5 months from September to January. First I will discuss the maximum estimate of nitrate fluxes at 50 m (Figure 5.13 (a)). In September 2012 the fluxes were quite high, at 384 mmol m⁻² and were dominated by the advective flux and by winter convective mixing. Autumn storms most likely cause the supply of nutrients during this time (Painter *et al.*, 2016), the advective fluxes were high during September, with peaks up to 40 mmol m⁻² d⁻¹ (Figure 5.8).

began to shallow, indicating the end of convection. Although the convective flux is shown as a constant supply, it is more likely to be variable over the winter depending on wind speeds and storm events. Winter convection is often thought to set the concentration of nutrients available over summer, but here it was smaller than the vertical advective flux and the diffusive flux (Table 5.1). Williams & Follows (2003) show that it can range from 0.05 to 1.4 mol N m⁻² yr⁻¹, increasing with latitude. The estimate here of 0.62 \pm 0.08 mol N m⁻² yr⁻¹ is within the range predicted by Williams & Follows (2003). Martin *et al.* (2010*a*) measured the diffusive flux from cruise data during June 2006 and found that their estimate for winter convective mixing (same method as used here) was forty-fold higher than the measurements of dissipation. However, this study shows that the diffusive flux can change dramatically from day to day and month to month. It may be possible that observational campaigns miss discrete nutrient pulses, which can increase dissipation by an order of magnitude (Rippeth *et al.*, 2005). This demonstrates that short studies cannot be extrapolated over an annual cycle.

In the summer, when the mixed layer depth was shallower than 50 m, the supply was again dominated by the advective nitrate fluxes. Although the diffusive flux in summer was low, as diffusivity decreases below the mixed layer, the constant but relatively small supply of nitrate through diffusive mixing still contributes a significant amount to phytoplankton productivity over the whole year (Forryan *et al.*, 2012). Although much smaller than the advective fluxes per month (Figure 5.13), this study shows that it still contributed up to 25 % of the annual primary production (Table table:flux).

Looking at daily fluxes, there were periods of high advective fluxes throughout July, although overall the fluxes tended to be smaller than the adjacent months. The maximum flux in July reached 23 mmol m⁻² d⁻¹ (Figure 5.8), whereas August had much higher advective fluxes reaching 90 mmol m⁻² d⁻¹. This may be an indication of high mesoscale activity, such as eddies and fronts, resulting in increased vertical velocities, which could explain the very patchy production at this time (Chapter 4). A number of studies have shown that submesoscale and mesoscale events can have a greater effect on nitrate fluxes into the euphotic zone when the water column is stratified (Bibby *et al.*, 2008; Alonso-González *et al.*, 2013). During the summer, when nutrients are limiting, episodic nitrate fluxes could have a proportionally greater impact on phytoplankton growth than when nitrate is already present in the water column.

The diffusive flux ranged from 0.01 to 14.7 mmol N m⁻² d⁻¹ and the mean was 0.9 mmol N m⁻² d⁻¹. These values are higher than those observed in the literature. Martin *et al.* (2010*a*) found that the diffusive flux was uniformly low over the PAP-SO site in 2006, with a mean of 0.09 mmol N m⁻² d⁻¹, which is similar to the diffusive fluxes

observed here over the same period (June to July). When the diffusive flux was higher (e.g. May) this was mostly due to higher diffusivities as the nitrate gradients were smaller (Figure 5.6). The diffusive flux was highest in May with values ranging from mean values of $0.5 - 3.9 \text{ mmol N m}^{-2} \text{ d}^{-1}$ and a mean of 1.5 mmol N m⁻² d⁻¹. It seems counter intuitive that this month had the largest fluxes as the wind speeds and horizontal fluxes decrease during this period (Figures 5.5 and 5.12). However there was significant mooring knock down (Figure 5.7), which may lead to an error associated with the diffusivity measurements. From the daily estimates in Figure 5.6, the high monthly value appears to come from one large spike in the diffusivity measurements during mid may, which actually occurs when the mooring is stable, after a period of knock down. The limit of detection for the diffusivity measurements is currently unknown and needs to be addressed. The lowest diffusivity measured here was 1.7×10^{-5} over the whole year, whereas values have often been observed to be lower than 10^{-5} m s^{-1} (Martin *et al.*, 2010*a*; Forryan *et al.*, 2012).

Figure 5.13 (b) shows the minimum estimate of nitrate fluxes. Although the advective fluxes dominate most of the year when the maximum estimate is used, the upward and downward advective fluxes cancel out in most months for the minimum estimate with only significant contributions in September 2012 and August and September 2013. This suggests that the summer advective fluxes, when the water column is stratified, contribute significantly to primary production. Overall there is still a positive supply of nitrate to the euphotic zone by the minimum vertical advective flux, 0.74 mol N m⁻² yr⁻¹ (Table 5.1).

The horizontal advective flux into the study site also shows seasonality, with larger more variable fluxes in winter and spring (December to April, 0.25 to $3.4 \ge 10^4$ mol N m⁻² d⁻¹) and lower fluxes in the summer (May to September, 0.18 to $1.4 \ge 10^4$ mol N m⁻² d⁻¹, Figure 5.12). Although the magnitude of the horizontal flux below 50 m may not be the same as in the upper 50 m, due to a different nitrate field, it shows there is significant movement of water through the site, which could bring in nitrate from elsewhere, as demonstrated by Hartman *et al.* (2010). However if there is phytoplankton growth in the regions outside the study site it would be likely that the surface nitrate concentrations in the water advecting from outside would also be depleted in the top 50 m.

I will now explore a period of interest in the autumn as it is possible for me to validate the nitrate fluxes with measurements taken during cruise D381 and published by Rumyantseva *et al.* (2015). During Autumn there was a storm event captured by cruise data (Rumyantseva *et al.*, 2015; Painter *et al.*, 2016). The storm occurred from 22 -27 September, with maximum wind speeds on the 25th of ~18 m s⁻¹, gusting to over



FIGURE 5.13: Nitrate supply to the euphotic zone at 50 m from vertical mesoscale advective, convective and diffusive fluxes for the maximum (a) and minimum (b) estimates.

 20 m s^{-1} . Looking at the fluxes calculated over this time the diffusive flux shows an order of magnitude increase from background levels of 0.75 mmol $m^{-2} d^{-1}$ to 5 mmol $m^{-2} d^{-1}$. Figure 5.14 shows the diffusive flux changing rapidly over the space of a few hours, due primarily to κ_z as the nitrate gradient changes little over this period. These diffusive fluxes are higher than those observed in the nutrient pulses by Rumyantseva et al. (1 mmol $m^{-2} d^{-1}$), although the main peak in the diffusive flux does occur on the same day. The reason for the discrepancy in the daily fluxes is that the spikes seen in dissipation by Rumyantseva *et al.* (2015) were of much shorter duration (1 hour) than the spikes calculated from the ADCP (approximately 12 hours). This may be due to differences between the two methods, although currently there are no error estimates associated with the dissipation measurements. Nutrient pluses may occur after storm events if inertial currents are still present (Rumyantseva et al., 2015). These nutrient pulses are discrete features and may often be missed in observational campaigns (Burchard & Rippeth, 2009). Surface nitrate concentrations increased after the storm period, which Rumyantseva et al. (2015) and Painter et al. (2016) have attributed to nutrient entrainment from depth. There was no increase in the calculated advective fluxes or the nitrate concentation during the storm period (Figure 5.14). For the minimum estimate the advective fluxes go from being positive with values ranging from 4 to 50 mmol m^{-2}

 d^{-1} to becoming negative and ranging from -8 to +7 mmol m⁻² d⁻¹. The vertical velocities may not show a signal of the storm if mixing is predominantly diapycnal. The use of a climatology for nitrate concentrations may smooth out the fluxes if no change in the nitrate concentration is observed and therefore not pick out events which alters the nitrate density relationship. This will be discussed further below.



FIGURE 5.14: Figure of fluxes during the storm. The top panel shows the hourly diffusive flux. The middle panel shows the vertical advective flux and the bottom panel shows the concentration of nitrate at the surface from the glider (black dots) and the the corresponding CTD values (organe dots).

5.4.4 Relation to Primary Production

Annual Rates

The nitrate fluxes into the euphotic zone, calculated from the mooring data, can be related to the primary production estimates from Chapter 4. The maximum estimate assumes no downward vertical advective flux as all nitrate is consumed by phytoplankton, whereas the minimum estimate incorporates both upward and downward fluxes. I first compare the estimates as yearly fluxes and rates. Table 5.5 shows the contributions from each flux to a maximum and minimum estimate of the total nitrate flux (if all the fluxes are summed together). It shows that if the maximum estimate of the vertical advective flux is taken then it is by far the largest contributor to the annual nitrate supply into the euphotic zone contributing 53%. The minimum estimates makes the three fluxes about equal contributors of nitrate. The true flux would more likely be between the two estimates, i.e. 36 - 53%. High resolution modelling studies that capture the mesoscale do not agree with this observation, and have shown that the supply of nitrate is dominated by convective mixing and contributions from diffusion and vertical advection are low (McGillicuddy *et al.*, 2003). This may partly be due to a large negative vertical advective flux in winter modelled by McGillicuddy *et al.*, where this study has no measurements.

	<u>.</u>	
Flux	Contribution to	Contribution to
	maximum total	minimum total
	estimate	estimate
Mesoscale Vertical advective flux	53%	36%
Winter Convective mixing (50 m MLD)	22%	30%
Diffusive Flux (50 m)	25%	34%

TABLE 5.5: Contribution of different processes to the nitrate flux at 50 m

With all the vertical fluxes summed together, the maximum estimated flux into the euphotic zone (1% surface light level) is 2.82 ± 0.91 mol N m⁻² yr⁻¹ and the minimum estimate is 2.05 ± 0.39 mol N m⁻² yr⁻¹ (Table 5.2). Using the nitrogen molar mass of 14 and the Redfield ratio of 6.6:1 for C:N, this results in maximum and minimum estimates of 260.6 g C m⁻² yr⁻¹ and 190 g C m⁻² yr⁻¹, respectively. The yearly estimate from the glider of primary production is 255 ± 51 g C m⁻² yr⁻¹ (2.75 ± 0.5 mol N m⁻² yr⁻¹). Therefore the equivalent flux of nitrogen is enough to support the estimated primary production if the maximum estimate is taken (102 ± 34 %). If the minimum estimate is used the total is 75 ± 14 % of primary production. It is likely that some nitrate is subducted below the euphotic zone throughout the year before it can be utilised by phytoplankton and the maximum flux is probably therefore an overestimate. Although

there are large uncertainties on the nitrate fluxes it could be assumed that the fluxes calculated here may be insufficient to support the observed net primary production, if the primary production estimate is accurate and precise. This would be expected as a proportion of primary production over the year is likely to be supported by horizontal advection of nitrogen from outside the study region, by the submesoscale component of the vertical advective flux, or by regenerated production.

Monthly Rates

Figure 5.15 shows monthly rates of primary production compared to monthly maximum and minimum estimates of the summed nitrate fluxes, converted to grams of carbon using the redfield ratio for ease of comparison. The upper estimates of nitrate fluxes are similar in magnitude to the primary production, although the seasonal cycle is different. There are six months of the year where the primary production exceeds the nitrate fluxes for both the maximum and minimum estimates, from February to July, which explains the reduction of surface nitrate at this time. During this time surface nutrients are not limiting (Figure 4.4), as production is high and can use up the nitrate already present in the system, from winter convective mixing and high vertical advective fluxes in autumn. There is a large input of nitrate into the euphotic zone during August, but this does not result in a corresponding increase in primary production. This may be somewhat compensated for if the negative flux seen during June had an adverse effect on phytoplankton growth, for the minimum estimate only. The only indication of this is that the rate of growth slows down and then starts to decrease in July and August. The downward flux of nitrate during this time may also subduct phytoplankton below the euphotic depth causing some of the variability seen in the production, as some areas may have a net loss of phytoplankton whereas in times of upwelling there would be net growth (Chapter 4).

Daily Rates

I will now explore in more detail a few periods of interest over the spring and summer when phytoplankton growth rates are high to try and relate the fluxes to daily rates of primary production (Figure 4.5).

The peak observed in daily primary production estimates (Figure 4.5) on 1st May cannot be explained by the calculated nitrate fluxes. It cannot be determined if there was a vertical advective flux as there were no vertical velocity measurements at this time, due to mooring knock down (Figure 5.7). Furthermore, diffusive fluxes were low, with only one short-lived spike on 26th April (Figure 5.6). The mixed layer depth shoaled above



FIGURE 5.15: The monthly rate of primary production shown next to monthly total nitrate fluxes for the maximum and minimum estimates.

50 m for a period of 9 days over this period (Figure 4.3), which may have trapped the phytoplankton closer to the surface irradiance, causing a temporary bloom. However this cannot be the only explanation as the mixed layer depth remained shallow for a few days after the peak in primary production occured and rates decreased again. Bottle samples on cruise JC087 in June showed that the surface nitrate concentrations were still high enough for nitrate not to be limiting growth ($\sim 4 \text{ mmol m}^{-3}$, Figure 4.4) and therefore fluxes into the euphotic zone would not have a significant impact on primary production at the same time. There may therefore have been top down factors influencing the growth during this time, such as grazing, as the primary production peak decreased rapidly in spite of non-limiting nitrate concentrations and a shallow mixed layer.

In all the measured fluxes in summer, July had the lowest activity. The minimum and maximum estimates of advective fluxes showed estimated fluxes of between 44 and 110 mmol N m⁻² month⁻¹ (Figure 5.13). The diffusive flux was also low at 11 mmol N m⁻² month⁻¹ for July (Figure 5.6). The flux of nitrate into the box below 50 m also decreased during July (Figure 5.12), and again was much less variable. This also corresponds to a decrease in the dive averaged horizontal currents. During this time daily estimates of primary production started to decline and there was much less day to day variability compared to other months, such as August (Section 4.4.1, Figure 4.5). In July the largest daily difference was 0.5 g C m⁻² day⁻¹, whereas in August this increased to changes of more than 1.5 g C m⁻² day⁻¹. The mixed layer depth during this period was very stable remaining shallower than 16 m from the 5 - 30 July (Figure 4.3). During August, on the other hand, it deepened with larger fluctuations. July was also the month during which the subsurface production maximum started to form (Figure 4.13). With reduced nitrate fluxes into the euphotic zone and a strongly stratified water

column, it is no surprise that primary production decreased and a subsurface maximum started to form. Nitrate concentrations had become depleted in the surface to effectively zero (Figure 5.3, derived from the glider density), phytoplankton were therefore unable to continue growing in the surface. August was relatively contrasting with larger and more variable fluxes and higher wind stress, up to 0.2 N m^{-2} . It is interesting to see that primary production estimates showed a similar pattern with higher fluctuations during August, which indicates the importance of nitrate fluxes on primary production when nutrients are limiting. As discussed above these intermittent fluxes in August may have been caused by mesoscale or submesoscale activity, enhancing primary production. However there were also sharp decreases in production, over the period of a day, which could be caused by the subduction of phytoplankton below the euphotic depth by the same features advecting the nutrients upwards (Gruber *et al.*, 2011). The subduction of phytoplankton may occur before the nutrients are fully consumed (Mahadevan, 2016).

Colebrook (1986) showed that phytoplankton and zooplankton stocks remain relatively stable throughout June to October. The zooplankton graze daily primary production and therefore growth should also depend on nutrients recycled from the zooplankton (Colebrook, 1984). However this study shows that there are still significant nitrate fluxes during August, likely contributing to the growth of phytoplankton in the subsurface.

New Production

Nitrate fluxes are often assumed to contribute to new production. If this was the case for this study it would imply an f-ratio of 0.7 - 1, which is much higher than previous estimates (Table 5.6). However there are issues with using the nitrate fluxes calculated here to estimate new production. Regeneration of nitrate occurs throughout the water column and a proportion of nitrate used to calculate the fluxes here may have already been consumed and converted back to nitrate. It is often assumed that anything returned to the euphotic zone in under a year is not new. Therefore it is likely that the fluxes in this study are counting nitrate that has already been regenerated and therefore it is not appropriate to suggest that the fluxes represent new production.

Fluxes of new nitrogen should be smaller than the total primary production. Current estimates of new production in the North Atlantic are varied, ranging from 5 to 77% of total production (e.g., Bury *et al.*, 2001; Bender *et al.*, 1992; Alkire *et al.*, 2012; Fernndez *et al.*, 2005), using a variety of different methods (Table 5.6). Export rates can be used to estimate the nitrate flux into the euphotic zone. Assuming that the system is in balance export is equivalent to new production, i.e. the flux of nitrogen into the euphotic zone should balance the flux out. Current estimates for export production

in the North Atlantic are all relatively consistent, at approximately 0.5 mol N m⁻² yr⁻¹ (Eppley & Peterson, 1979; Campbell & Aarup, 1992; Antia *et al.*, 2001; Sanders *et al.*, 2014). These estimates are again much lower than the fluxes calculated in this study, of the amount of production supported by new inputs of nitrate. It is, however, difficult to make a broad comparison of export production over the North Atlantic compared to the small site studied here as fluxes may vary significantly depending on location and physical forcing, as well as the method used (Torres Valdés *et al.*, 2014).

Reference	New Produc-	Method	Location
	tion $(\%)$		
Buesseler <i>et al.</i> (1992)	5 - 42	234 Thorium	47^{o} N 20^{o} W
Martin $et al.$ (1993)	45 - 50	POC flux from sedi-	47^{o} N 20^{o} W
		ment traps	
Bury et al. (2001)	45 - 77	Bottle incubations	47^{o} N 20^{o} W
Sambrotto et al. (1993)	20 - 46	Bottle incubations	$59.5^{o}N 21^{o}W$
Alkire et al. (2012)	30 - 70	Lagrangian profiling	59^{o} N 20^{o} W
		float	
Fernndez et al. (2005)	33	Dual isotopic labelling	38 - 45°N 16 -
		$^{13}C/^{15}N$	$22^{o}W$
Boyd & Newton (1995)	22 - 47	Modelling study	

TABLE 5.6: New Production Estimates from the Literature

5.4.5 Other fluxes that may contribute to the budget

There are other sources of nitrate that may enter the euphotic zone over the year to contribute to the budget calculated here. For example, horizontal advection, atmospheric deposition and nitrification.

Because there were no measurements of the horizontal advective flux above 50 m, the fluxes between 50 and 100 m were used to put the other fluxes into context. The horizontal fluxes are orders of magnitude larger than any of the other fluxes calculated and suggest that there was a lot of nitrate being advected through the site relative to vertical advection (Figure 5.12). This complicates the interpretation of the results as strong horizontal advection will also advect chlorophyll from elsewhere. It would therefore be a plausible assumption that water advected from outside the site during summer already has its own chlorophyll stock and that the surface waters would already be depleted in nitrate. Phytoplankton respond on short time scales (~ 1 day) to physical perturbations (Letelier et al., 2004). Therefore if the horizontal flux does bring nitrate and the water transit time through the study site is approximately 4 days, this would allow sufficient time for nitrate uptake. There is evidence from previous studies that horizontal advection of nutrient rich water does occur in this area (Painter et al., 2008; Hartman et al., 2010), which could affect the budget by influencing both the nitrate calculations and the primary production estimates. Figure ?? shows the monthly MODIS AQUA chlorophyll composites, during May and June 2013. Growth over the region begins in a very patchy distribution, suggesting that the nitrate concentrations around the study site might vary, either due to different rates of phytoplankton uptake or supply. Damerell et al. (2016) show that the glider dive average currents in May and June are mostly from the East. The chlorophyll concentration in this area is similar to the study site. Assuming that an area with similar chlorophyll distributions would also have a similar nitrate concentration can lead to the assumption that horizontal advection may be bringing in a similar nitrate concentrations to the study site, which would not impact the nitrate budget. However this is a broad assumption and more measurements would be needed to fully assess the horizontal advective flux within the top 50 m.

Regenerated production has been shown to be significant in this area over summer, approximately equal to one third of primary production (Fernndez et al., 2005). Regenerated production will also be a component of the observed primary production, which is mainly ammonium (NH4⁺) and is produced in situ. Nitrification may also be present (Clark *et al.*, 2008). Nitrification is the process of oxidising NH_4^+ to nitrite (NO_2^-) and subsequently nitrate (NO_3^-) . These three forms of nitrogen are all bioavailable, but nitrate supplied by nitrification should be classed as regenerated nitrogen. Current estimates of nitrification in the euphotic zone in the North Atlantic are relatively low, at 0.01 mmol N m⁻³ d⁻¹ (Martin *et al.*, 2010*a*), compared to other regions, such as subtropical gyres where nutrients are limiting all year round. There is however significant variability in measurements of nitrification so these estimates are broad approximations (Yool *et al.*, 2007). Integrating these estimates over the euphotic depth (50 m) and assuming that the daily rate is constant over the whole year, gives an approximate value for nitrification of 0.19 mol N m⁻² yr⁻¹ only. This supply of nitrate is lower than all the calculated fluxes but could support approximately 6% of the estimated annual primary production, and is therefore assumed to be a minor component of the nitrate budget. Furthermore, as discussed above the fluxes here may encompass a proportion of the regenerated production if it sinks below 50 m.

Another input worth considering, which was not measured here is atmospheric input of nitrogen. Globally, this has been shown to contribute approximately 3% of annual new production and is likely to increase in the future due to anthropogenic inputs from fertilisers (Duce *et al.*, 2008). Atmospheric deposition varies from region to region, but is generally higher closer to the coasts. Modelling studies estimate that the North Atlantic receives between 15 and 40 mmol N m⁻² yr⁻¹ (Duce *et al.*, 2008), equivalent to just between 0.5 and 1.3% of the estimated primary production in this study.

5.4.6 Mesoscale and Submesoscale Fluxes

The vertical velocities presented here are derived from the outer moorings, which are spaced approximately 13 km apart (Figure 2.1), and therefore represent the mesoscale

velocity field. There are also vertical velocities associated with the submesoscale (~ 1 - 10 km, Section 5.2.3). These have been shown, by models, to contribute significantly to the flux of nitrate into the euphotic zone (Mahadevan & Archer, 2000; Lévy *et al.*, 2001; Martin *et al.*, 2002; Lévy, 2008; Klein & Lapeyre, 2009). It is still largely unknown how the mesoscale and submesoscale processes interact with each other, mostly due to a lack of high spatial resolution field studies (< 10 km) and the theory is uncertain. The inner mooring estimates of submesoscale likely also include the mesoscale velocities and therefore summing the two fluxes together for an annual budget will result in an overestimate of the nitrate flux.

Estimates of vertical velocities from the inner moorings are available, which were spaced approximately 1.5 km apart (Figure 5.10). Unfortunately there were no measurements above 120 m, due to the loss of the upper instruments on one of the moorings, and therefore it is difficult to assess how a flux at this depth might influence primary production 70 m or more above. It is possible however to look at the fluxes at 120 m to assess the difference between the meso and submeso-scales. The submesoscale fluxes are significantly larger than the mesoscale fluxes at the same depth (Figures 5.10 and 5.9). Lévy et al. (2001) found that in a modelling study vertical velocities increased with increasing resolution. They found that submesoscale processes could contribute to 100% of primary production in the surface. For my study the submesoscale fluxes at this depth could contribute to between +112 to -140% of the observed primary production (Table 5.1), for the maximum and minimum estimates respectively. For the maximum and minimum fluxes at 120 m for the mesoscale can contribute approximately +96 to -68% of the observed integrated primary production, respectively. The RMS mid-estimate fluxes are both very small for the mesoscale and submesoscale at 120 m (Table 5.1), because the RMS velocities are very small over the whole year. The mesoscale fluxes at 120 m were larger by 73% than those at 50 m, and therefore it can be assumed that the submesoscale velocities would be smaller at 50 m than 120 m. Therefore the submesoscale fluxes at 50 m could influence primary production in the euphotic zone less than suggested by the fluxes at 120 m. The flux at 120 m was larger because the nitrate concentrations at this depth were higher than those at 50 m by 133 %. Louanchi & Najjar (2001) found that there is little seasonality in nutrient concentrations at a depth of 125 m. The vertical mesoscale velocities at 120 m are on average lower than those at 50 m, which would result in a smaller flux at depth and therefore it can be assumed it mostly results from the nitrate concentration. There are also fewer estimates of vertical velocity at 50 m than 120 m because the mixed layer depth is below 50 m for a longer period of time, resulting in larger fluxes during winter when the mixed layer depth is between 50 and 120 m (Figures 5.10 and 5.9). If it is assumed that the submesoscale vertical velocities at 50 m were 73% of those at 120 m, the same difference observed in the mesoscale, they could contribute to 81% of the observed primary production. Although this is an upper limit it would mean that summing together the submesoscale, diffusive and convective fluxes would supply 130% of the total annual primary production.

The vertical advective nitrate fluxes observed at 120 m in this study (-1.9 to 2.6 mol N m⁻² yr⁻¹, Table 5.1) are much larger than those currently in the literature. Garabato et al. (2002) found maximum and minimum mesoscale vertical advective nitrate fluxes of -0.35 to 0.79 mol N m⁻² yr⁻¹ at 100 m depth in the Southern Ocean using a SeaSoar survey and the Omega equation. Using a similar method Pidcock (2011) found fluxes of -0.4 to 0.3 mol N m⁻² yr⁻¹ at 98 m depth in an eddy dipole in the Icelandic Basin. These studies use perturbations from the areal mean to diagnose the vertical flux i.e. w'N' rather than wN as used here (Equation 5.4). Using wN Pidcock (2011) shows that the vertical nitrate flux is much larger and comparable to the flux seen here, with maximum values of 1.61 and 3.86 mol N m⁻² d⁻¹ and an annual flux of -0.76 to +0.59 mol N m⁻² yr⁻¹ and -1.54 to +1.41, at 50 and 100 m respectively.

The vertical velocities are within the range of those in models and field studies, from -40 to 40 and -100 to 100 m d⁻¹ for the mesoscale and submesoscale respectively at 120 m depth and -20 to 20 m d⁻¹ for the mesoscale velocities at 50 m. Previously observed upwelling rates have been shown to range from 10 to 100 m d⁻¹ (Martin & Richards, 2001; Garabato *et al.*, 2002; Mahadevan *et al.*, 2008). These studies tend to be shorter and therefore may be missing the variability in the fluxes seen here.

At the depth of 120 m both the mesoscale and submesoscale nitrate fluxes were negative for the minimum estimates (-1.9 and - 3.8 mol N m⁻² yr⁻¹), suggesting that the downward velocities are dominant (Table 5.1). Submesoscale processes are associated with both upward and downward vertical velocities (Mahadevan, 2016). It is possible that the submesoscale fluxes also subduct a significant amount of phytoplankton out of the euphotic zone, as well as upwelling nutrients (Lévy *et al.*, 2001).

5.4.7 Time Varying and Divergent Components of the Nitrate Flux

The two components of the vertical velocities show the fluxes for different processes (Figure 5.11). The time varying component represents processes that displace isopycnals, such as internal waves (Thomas *et al.*, 2013) and the divergent component represents the eddy field and frontogenesis (Unnikrishnan & Antony, 1990). When examining the minimum estimates of the time-varying component the annual flux is very low (Table 5.3), almost summing to zero, which would be expected for internal waves as they move the water up and down at regular intervals. However it is by far the largest component when looking at the upward fluxes only (maximum estimate), 65, 66 and 62% for the

mesoscale at 50 m, the mesoscale at 120 m and the submesoscale at 120 m. Damerell *et al.* (2016) use temperature, salinity and oxygen concentrations from the same glider data as this thesis to demonstrate that there is a strong internal tide signal in the spectra, which could influence primary production. Internal waves can influence primary production by uplifting isopycnals and thereby increasing the light intensity (Holloway, 1984; Lande & Yentsch, 1988). However the isopycnals are also subducted downwards and therefore the flux is not permanent, which explains why the mean for upward and downward fluxes is low (0.24, -0.024 and 0.014 mol N m⁻² yr⁻¹, for mesoscale 50 and 120 m and submesoscale fluxes respectively).

Taking the annual flux of the divergent components there is less change between the minimum and maximum estimates at 50 m. Whereas at 120 m this component becomes negative at both the mesoscale and submesoscale, -0.19 and -0.54 mol N m⁻² yr⁻¹. If the minimum estimate is taken the divergent component is larger than the time-varying component for all depths and scales (Table 5.3), which suggests that the resulting fluxes are dominated by mesoscale and submesoscale eddies propagating through the study site. However, if all nitrate is assumed to be consumed with no downward fluxes, for the maximum estimate, the the dominant feature contributing to the upward flux of nitrate is internal waves (Sévellec *et al.*, 2015).

5.4.8 Limitations

The main limitation to the methods used here to calculate nitrate fluxes is that nitrate is not measured directly but is derived from a density nitrate relationship created from data from several cruises conducted throughout the year. Lapeyre & Klein (2006) found that vertical motions do not necessarily have the same impact on tracer distribution as density if the sources and sinks are different. As nitrate is taken up by biological activity in the upper ocean and increases at depth due to the sinking of particles and remineralisation, it would be expected that the distribution would be different to density. Upward vertical velocities could have a significant impact on nitrate distribution, whereas downward velocities transporting nitrate depleted water would have little or no impact. Conversely, upward or downward transport of density will both have a contribution to the density distribution. Although the relationship seen here is reasonably tight ($\mathbb{R}^2 = 0.83$) there is still significant scatter and therefore the true nitrate value for a given density could lie within a range of values (Figure 5.2). The root mean square error is 1.61 between the observed and calculated values. When normalised by the mean of the measurements there is a 24% error.



FIGURE 5.16: Density against bottle nitrate coloured by date for D381. Note the higher scatter in nitrate concentrations between 1026.2 and 1026.7 kg m⁻³ on 28th September.

The largest scatter occurs at lowest densities, which is to be expected as phytoplankton uptake of nitrate at the surface may cause the relationship to deviate. Uptake of nitrate by phytoplankton would result in a lower nitrate concentration at the same density. However at densities between approximately 1026.7 to 1026.2 km m⁻³ the observed nitrate values are often higher than those calculated from the relationship (Figure 5.16). The density at 50 m is below 1026.7 km m⁻³ from September to mid December 2012 and therefore this bias would affect the budget. This is predominantly observed from one cruise in September 2012 (D381, Figure 5.1). Further examination of the CTDs taken from this cruise show that the water samples with higher nitrate concentrations at lower densities were taken after the passage of a storm measured on D381 from 22 to 27 September 2012 (Painter et al., 2016), mentioned previously (Figure 5.14). Figure 5.16 shows the same as Figure 5.1 but for D381 only with the points coloured by date. During the storm event the nitrate density relationship does not pick up this increase in surface nitrate concentrations, that was observed from the cruise data, which may explain why there was no corresponding increase in the vertical advective flux observed during the storm event described in the previous section (Rumyantseva et al., 2015; Painter et al., 2016). The glider data shows that the surface temperature decreases during the storm, probably due to wind cooling, however there is no corresponding change in salinity, explaining why the relationship changes during this period.

In the summer (June to September 2013) two cruises (JC087 and JC090) both show a slightly different nitrate density relationship to D381 (Figure 5.1), with lower nitrate concentrations on isopycnals. It is therefore likely that nitrate concentrations at 50 m

have been overestimated slightly during the summer months, particularly from June onwards when density at 50 m goes below 1026.8 kg m⁻³. The calculated nitrate fluxes would therefore be lower during this period, this may only impact the advective fluxes as the diffusive flux uses the gradient in nitrate rather than absolute values and therefore may not have a significant change. If a fit of the density nitrate relationship is used for the two summer cruises only, the total flux over the whole year would have been reduced by 16%. This would be a lower overall impact to the total flux as the relationship would not be valid over autumn (September, October 2012).

These two periods demonstrate the limitations of using the same density nitrate relationship for a full year as it can vary when diapycnal mixing occurs. This could be somewhat mitigated by using different relationships for different times of year or seasons. Unfortunately there were no nitrate measurements taken over winter and only three periods within summer months were available, so the same relationship was extrapolated to the full year. The fluxes calculated here would have benefited from a nitrate sensor deployed on the glider or mooring. However looking at annual fluxes, periods of over and under estimation may cancel out and the fluxes are still a good representation of the nitrate supply to the euphotic zone.

A further limitation to this study is that there were no nitrate uptake measurements taken from any of the cruises to the study region. It is therefore difficult to put a firm estimate on the amount of nitrate used for phytoplankton growth. The Redfield ratio describes the elemental composition of phytoplankton, and assumes that the composition of the deep sea is a result of the synthesis or decomposition of organic matter (Redfield, 1958). It is largely used in ocean models and in oceanography for the calculation of export production and nutrient-based productivity estimates. The Redfield ratio assumes C:N:P equates to 106:16:1. The Redfield ratio is an average based on deep water nutrient ratios so is constant for the whole year. The ratio of C:N has been shown to deviate due to phytoplankton community structure and rate of nitrogen fixation (Singh et al., 2015, 2013; Martiny et al., 2013). A number of studies have shown that large deviations from the Redfield ratio can occur, especially after the spring bloom when nutrient stress is prevalent (Körtzinger et al., 2001; Koeve, 2004; Painter et al., 2010a). This occurs because of carbon overconsumption in the summer leading to a higher C:N ratio. Körtzinger et al. (2001) shows that the C:N ratio is lower in the early bloom, from 5-6, and higher in the post-bloom 10-16. For my study the difference between using a ratio of 5 and of 16 was estimated for the post-bloom month of August using the primary production data, resulting in a difference of 15 mmol N m⁻² d⁻¹, which equates to a difference of 400 mmol N m^{-2} over the month of August. If the C:N ratio does increase over the year the nitrate fluxes would contribute to an even larger proportion of primary production. Over the whole year this could result in a difference of 2.46 mol N m⁻² yr⁻¹
with primary production ranging from 1.14 to 3.6 mol N m⁻² yr⁻¹, for a ratio of 16 to 5, respectively. Using a value of 6.6 gives a production value nearly equal between these two extremes (2.75 mol N m⁻² yr⁻¹) and therefore when looking at annual contributions of fluxes the results should be fairly representative. Furthermore, the ratio tends to be lower for diatoms (Martiny *et al.*, 2013) and as the subsurface chlorophyll maximum is generally made up of diatoms in this region (Painter *et al.*, 2010*a*) it is unlikely that the ratio will reach as high as 16.

There are also limitations due to the depth of measurements. Because the moorings shallowest measurements are at 50 m, I am unable to quantify the horizontal advective flux into the study site for the same water (0 - 50 m) used for the other fluxes and primary production calculations, which would allow me to complete the budget of nitrate entering the area. There are also periods with no vertical velocity observations due to mooring knock down, such as during May leading to a loss of flux estimates. However there is still significant data available to determine flux measurements and observe which processes are dominating during times of high phytoplankton growth.

Finally, currently it is not possible to put an error estimate on the dissipation measurements from the ADCP. As the lowest measurement observed is $1.7 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, it may be possible that the limit of detection cannot encompass low measurements of diffusivity $(< 1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1})$ that can occur in the ocean (Ledwell *et al.*, 1993). There are a number of considerations when converting the dissipation values into diffusivity. The value used in Equation 5.2 of 0.2 for the mixing efficiency is an assumption, although it generally is in line with past studies (e.g., Prandke, 2007; Rippeth *et al.*, 2003). A recent study by Salehipour *et al.* (2016) found that the mixing efficiency can range from 0.1 to 0.3 with a mean value of 0.25.

5.4.9 The Nitrate Budget

There are four possible reasons why the nitrate fluxes may exceed or equal the observed primary production that have been discussed in this chapter; 1) the vertical fluxes are overestimated, 2) primary production is underestimated, 3) primary production is equal to the observed fluxes, 4) vertical fluxes are overestimated and primary production is underestimated.

It is possible that the maximum estimate of the vertical fluxes are an overestimate as some nitrate may be subducted back out of the euphotic zone, but also due to changes in the density nitrate relationship discussed above. Nitrate may be overestimated in summer leading to a larger calculated flux. However this could equally lead to an underestimation, particularly in winter. However it is important to note that the submesoscale component is not included at 50 m and therefore the vertical advective flux would be larger.

Primary production could be underestimated, although it matches well with previous measurements in the literature in both integrated values and in the subsurface (Section 4.4.1). However the C:N ratio likely increases over the year making the contribution of nitrate fluxes to primary production even larger (Section 5.4.8). If the primary production was overestimated by 6% as Milutinovi & Bertino (2011) calculated for a different primary production model, it would equate to an annual primary production of 240 g C m⁻² (2.6 mol N m⁻²). This would alter the budget and the nitrate fluxes would supply between 79 to 108%. This is not a huge change to the budget and would not alter the main conclusions of the project. Furthermore, there is error associated with both measurements and this could result in the budget either diverging further or converging if the errors are taken into account.

To my knowledge no one has previously measured submesoscale and mesoscale fluxes. Although there is error associated with all the measurements here it is still significant that the fluxes are such a good match to the primary production estimates and that the vertical advection contributes to a large proportion of the annual nitrate supply.

5.5 Conclusion

This chapter has presented an annual timeseries of nitrate fluxes into the euphotic zone at 50 m. To the best of my knowledge this is the first time observations have been able to quantify nitrate fluxes and primary production over a full annual cycle at (sub) daily resolution and at small spatial scales. The nitrate fluxes show that all the vertical physical processes analysed, convective, diffusive and advective, contribute significantly to (near) net primary production, and when combined contribute between 75 to 102% of the observed production.

The dominant mechanism for nitrate supply into the euphotic zone is the vertical advective flux, which accounted for between 27 and 55% of total primary production. Using the submesoscale velocities would increase the contribution of the vertical advective flux into the euphotic zone, as the nitrate fluxes calculated at 120 m were larger than the mesoscale flux at the same depth. The diffusive flux was smaller but persistent and therefore contributed 25% of the annual primary production. Annually winter convective mixing supplied 22% of the nitrate supply to primary production. The vertical advective and diffusive fluxes also showed strong variability, highlighting the importance of mesoscale and submesoscale features in this region. Breaking down the divergent and time varying components of the vertical advective flux suggests that the fluxes in the area are influenced by internal waves as well as eddies propagating through the area. There is evidence that when stratification is strong and nutrients in the surface are limiting, fluxes into the euphotic zone may contribute to patchy phytoplankton growth during August.

Chapter 6

Discussion

6.1 Overview of Results

In this thesis I use glider and mooring data, from the OSMOSIS project, to investigate the balance between phytoplankton net primary production and nutrient fluxes in the upper ocean.

To accomplish the thesis aims (reiterated below) I first developed a method to calculate (near) net primary production as described in Chapter 3. The first aim was then addressed in Chapter 4 where primary production derived from the gliders was quantified and the annual production was estimated to be 255 g C m⁻² (2.7 mol N m⁻² yr⁻¹). The production followed a general seasonal cycle with low levels in winter when the mixed layer was deep and light levels were low. It increased throughout spring, peaking with the bloom at the beginning of July. However, an interesting result of the primary production data was the large amount of small scale variability observed throughout the year, which demonstrates the importance of measuring small spatial and temporal scales. During the summer a subsurface production maximum evolved contributing to 23% of the total annual primary production.

Chapter 5 covers the second aim, where vertical nitrate fluxes were calculated using a density-nitrate relationship, derived from cruise data and applied to the glider and mooring data. Mixing was calculated from dissipation data from the mooring ADCP (contributed by Natasha Lucas, Bangor University) and supplied 700 mmol N m⁻² yr⁻¹. The vertical advective flux supplied between 737 and 1508 mmol N m⁻² yr⁻¹ and was calculated from vertical velocities estimated from the mooring data (contributed by Xiaolong Yu, National Oceanography Centre Southampton). The convective flux was estimated from the winter depth of the mixed layer from the glider data and the concentration of nitrate at that depth and resulted in a flux of 620 mmol N m⁻² yr⁻¹. Chapter 5 also addressed the third aim. By assuming the stoichiometry of the Redfield ratio the fluxes supplied between 75 and 102% of the nitrate needed to support the observed production. Although submesoscale vertical advection would increase the nitrate flux further. Furthermore, non Redfield stoichiometry may also change the proportion of nitrate flux to primary production.

There was evidence that mesoscale and submesoscale processes, acted to increase vertical velocities, and subsequently the nutrient fluxes, which has a significant impact on primary production.

This study gives a comprehensive view of one small area over one year in the North-East Atlantic, thereby allowing quantification of annual vertical nitrate fluxes and primary production. Using the comprehensive dataset available I have been able to look at annual budgets, seasonal changes and day to day variation. Using gliders in this study has helped demonstrate the usefulness of gliders in studying biogeochemical cycles (Aim four).

Project Aims

- 1. To quantify the rate of primary production in the study area, both annually and at daily resolution.
- 2. To quantify the nitrate fluxes including mixing, convection and vertical advection over the study area.
- 3. To determine how nitrate fluxes contribute to rates of primary production in the North East Atlantic and if they balance the requirements of the observed primary production.
- 4. To illustrate the suitability of gliders for studying biogeochemical cycles.

6.2 Discussion of Results

6.2.1 Primary Production and Chlorophyll

Glider data have allowed daily estimates of primary production over a whole year to be estimated from irradiance and chlorophyll fluorescence profiles. Some of the key findings are:

- there is strong seasonal cycle in primary production on top of which is overlaid with submesoscale variability (2 to 8 days), with increased variability in the summer months
- primary production in the subsurface maximum contributes 23% of the total annual primary production
- the scale factor proved to be an effective method for correcting glider chlorophyll which requires further investigation into the dominant drivers of variability (e.g. adjustments in chlorophyll to carbon ratios through community structure and /or physiological adjustments to a changing environment)

This thesis has demonstrated the suitability of ocean gliders to measure primary production, with estimates comparing well with in situ samples, satellite estimates and previous measurements from the literature. There are a number of advantages of using gliders to measure primary production. They allow primary production to be measured at depth and at high temporal and spatial resolution. This has benefits over traditional methods as satellites only measure the top optical depth and ships tend to only sample for short time periods. Here I show that satellite products may underestimate primary production when there is a subsurface chlorophyll maximum present. The glider data shows that the subsurface production maximum contributes significantly to the annual primary production budget (23%) and therefore it is important that this is represented properly when looking at annual rates of primary production.

The high resolution glider measurements show strong variability in primary production at submesoscale and mesoscale timescales (Section 4.4.2). This compares well with previous observations (Painter *et al.*, 2010*b*) and modelling studies in the North Atlantic (Lévy *et al.*, 2012, 2001). The seasonal cycle displayed by the glider is useful for interpreting how phytoplankton respond to the physical environment. Satellite data has been shown to be largely impacted by cloud cover, resulting in the loss of data, in particular the first peak in primary production observed by the glider in May. This may be vital for understand the onset of the spring bloom (Rumyantseva *et al.*, In Review).

The method of deriving a scale factor to calibrate chlorophyll profiles using the glider PAR data has been shown to represent chlorophyll well from bottle cruise data, which are co-located less than 6 km apart. It is useful as it can determine when a change in the scale factor need to be applied as cruises at different times of the year may show a different regression between glider fluorescence and bottle chlorophyll. This also makes it a useful method to apply to glider that have been deployed from small vessels or from shore where it is difficult to take calibrating water samples. Further work needs to be undertaken to properly understand what the scale factor represents and how it may relate to phytoplankton community or physiology and would be an interesting topic for future investigation, as it may show indications to the change in community over time.

6.2.2 Vertical Velocities

Generally the vertical velocities were significantly smaller than horizontal velocities due to vertical stratification, which creates a barrier to vertical motion. Their location and magnitude in the ocean are thought to play an important role in the distribution of tracers, such as heat and nutrients (Strass, 1992). Using simple scaling arguments mesoscale velocities can range from 10 - 100 m d⁻¹ (Allen *et al.*, 2001), with the submesoscale being larger.

Currently vertical velocities are difficult to measure in the ocean, partly because they are small, but also because most studies require high resolution spatial data taken over a relatively short time period. There are several methods used to estimate vertical velocities. The omega equation uses density measurements to obtain vertical velocities from geostrophic flow and requires high resolution ship surveys (Allen et al., 2002). These mesoscale surveys should have about 3-4 km along track spatial resolution and be synoptic, i.e. completed in a time shorter than the time taken for the feature to propagate or for properties to significantly alter. Using this method it has been shown that vertical velocities in the mesoscale range from 5 - 100 m d^{-1} (Allen & Smeed, 1996; Allen et al., 2005; Pidcock et al., 2013). This encompasses the range of vertical velocities seen in this study, with the mean absolute velocity as 5 m d^{-1} and the range from negligible to 35 m d^{-1} . Most of these studies target areas with known high vertical velocities, such as strong ocean fronts, geostrophic jets and strong eddy features and therefore in general vertical velocities in the ocean are likely to be smaller. On the other hand, significant smoothing in the Omega method may occur due to sparse sampling leading to an underestimate of vertical velocities by up to 55% (Allen et al., 2001).

Vertical velocities have also been calculated from gliders using the glider flight model and minimising for flight parameters, lift, drag, compressibility, thermal expansion and glider volume (Merckelbach *et al.*, 2010; Frajka-Williams *et al.*, 2011). I used the glider flight model to estimate vertical velocities, using the method of Frajka-Williams *et al.* (2011). However confidence in the results was low and therefore it was decided not to use these in the flux calculations. The vertical velocities calculated were very large (on the order of 1000 m d⁻¹) and did not compare well with the velocities calculated from the moorings. There were indications that the parameters (volume, lift, drag, thermal expansion, compressibility) are poorly constrained, and problems with the glider flight in general, as there are considerable differences between the climb and dive velocities.

6.2.3 The Nitrate Budget

The main findings of the nitrate fluxes that:

- there is strong variability in the diffusive and vertical advective nitrate fluxes
- the vertical advective flux is the largest contributor of nitrate supply to the euphotic zone
- the summed fluxes support between 75 and 102% of annual primary production.

There has been much debate in the literature about closing the nutrient budget. Global geochemical estimates of new production are significantly higher than estimates of nutrient supply from winter convection by a factor of two and nutrient fluxes from mesoscale eddies account for only 20 - 30% of the annual budget (McGillicuddy et al., 2003, 2007). Much of this discrepancy is thought to be a lack of observations at high spatial resolution, to capture the submesoscale (Klein & Lapeyre, 2009). I have shown here that vertical nitrate fluxes into the euphotic zone are in balance with primary production (Chapter 5). The fluxes at 50 m from convection, mesoscale vertical advection and diffusion, can support all the observed primary production (75 - 102%). The submession fluxes could contribute an upper estimate of an extra 24% of the total primary production at 50 m, if the proportion of mesoscale to submesoscale is the same at 50 m as at 120 m(Section 5.4.6). Some of the fluxes may include recycled nitrate that has already been used in production and has sunk out of the euphotic zone, been regenerated and brought back up by ocean movement. It is also likely that the upper estimate used here is an overestimate as nitrate could be subducted back below the euphotic zone before it has been fully consumed by phytoplankton. The assumption of the Redfield ratio would also have an impact on the influence of the fluxes on the phytoplankton primary production (see section 5.4.8). Furthermore there is a potentially significant error associated with the nitrate-density relationship, which is particularly apparent on the vertical advective fluxes (Table 5.1).

The vertical advective flux was the most important flux of nitrate into the euphotic zone, followed by the diffusive flux and winter convective mixing, which both supplied similar amounts (Table 5.1). A modelling study by McGillicuddy *et al.* (2003) shows that the most important flux at the North Atlantic Bloom Experiment site was the convective flux, which differs from the observation here. They found that the vertical advective flux was negative, but was mostly controlled by strong negative fluxes during the restratification of the water column in winter. As there are no flux measurements during winter I cannot explicitly say that this would not lead to an annual downward

flux with the method used here. With more measurements at 120 m the minimum overall nitrate flux is negative. Large negative fluxes are seen at the beginning of May in the minimum estimate of the mesoscale fluxes at 120 m (Figure 5.9) at the same time as the water column begins to stratify (Figure 4.3). This could be an indication that nitrate is subducted out of the euphotic zone during restratification. However if assuming that all the nitrate is consumed, as for the maximum estimate, the flux would still be positive. This may be evidence that assuming total consumption is an overestimate, especially during certain times of year. However this is not seen in the submesoscale fluxes at 120 m, as the mixed layer shoals above 120 m in May the submesoscale fluxes are positive (Figure 5.10). This study effectively demonstrates the difference between the mesoscale and submesoscale fluxes (Figures 5.9 and 5.10).

The most important component of the maximum vertical advective flux, at depths of 50 and 120 m, for both the mesoscale and submesoscale, was the time varying component for the maximum flux estimates, suggesting that the fluxes were dominated by internal waves. Whereas for the minimum estimates the timevarying component largely cancelled out, which is unsurprising for internal waves. Therefore for the minimum estimate at 50 m the divergent component was more important indicating that eddies propagating through the site were also important (Sévellec *et al.*, 2015). The minimum estimates at 120 m had negative fluxes for the divergent component, which leads to the conclusion that eddies contribute to the subduction of nitrate at this depth found by (McGillicuddy *et al.*, 2003).

The modelling study by McGillicuddy *et al.* (2003) found that the diffusive flux at the North Atlantic Bloom Experiment contributed to 20% of the modelled production, very similar to the result here (25%). On the other hand, observations by Martin *et al.* (2010*a*) showed that convective mixing supplied 40-fold more nitrate to the euphotic zone than turbulent diffusion at the Porcupine Abyssal Plain-Sustained Observatory (PAP-SO) site. However, as the fluxes by Martin *et al.* were taken over just 2 weeks (between June and July), it is possible that over the whole year spikes in turbulent diffusivity were missed as they are sparse. The diffusive flux calculated here showed low values during the same time of year, with the highest fluxes in Autumn and May, demonstrating that it may be difficult to extrapolate short surveys to a yearly budget. There is less error associated with the nitrate-density relationship on the diffusive fluxes as it uses the nitrate gradient rather than absolute values. There will be additional error associated with the diffusivity measurements, but that is beyond this study to quantify.

6.2.4 Variability

The high resolution data collected as part of the OSMOSIS project is ideal for looking at small scale temporal or spatial events in the ocean. Both Thompson *et al.* (2016) and Damerell *et al.* (2016) use the same glider data set to demonstrate the presence of submesoscale activity and variability in physical parameters in the water column, such as temperature, salinity and buoyancy gradients.

There was a large amount of small scale temporal variability in both the primary production estimates and the nitrate fluxes throughout the whole timeseries. A number of methods to assess the variability of primary production were presented in Section 4.4.1 and demonstrated that in general variability was high throughout the whole year. Large day to day percentage changes in primary production are particularly prevalent throughout October, November and December. These become lower in summer, from May to July. The coefficient of variation also peaks in the winter when primary production is low but variable. Mahadevan & Campbell (2002) has shown that chlorophyll tends to have a more patchy distribution than sea surface temperature because biological response times to changes in the environment are faster the changes to the heat flux.

In August when the water column is stratified there was evidence of submesoscale processes shown in the wavelet analysis, with a significant signal less than 7 days. The distribution of phytoplankton will be effected by the intermittency of the nitrate fluxes, especially when nitrate is limiting. The nitrate fluxes reduced and became less variable during July as a subsurface chlorophyll maximum started to form. The variability seen in primary production also decreased over this time. In August however the nitrate fluxes increased, with many pulses into the euphotic zone, coincident with the high variability seen in the primary production (Section 5.4.4). Although primary production variability may also have been influenced by grazing pressure this is an important indication of the influence of mesoscale activity enhancing the growth and/or subduction of phytoplankton. Modelling studies have previously demonstrated the importance of small scale processes on phytoplankton growth (Lévy *et al.*, 2001; McGillicuddy *et al.*, 2003).

Submesoscale time and space scales are an important feature in the ocean. Studies have shown that primary production can be in error of up to 50% by not including these processes in models (?Lévy *et al.*, 2001) and vertical velocity variance increases ten fold when using resolutions of 6 to 1 km (?). Swart *et al.* (2015) used glider to show that mesoscale and submesoscale processes have an important role in driving stratification and the onset of the spring bloom in the Southern Ocean, by regulating light and iron in the euphotic zone. It is therefore important that we study these features and gliders are an important tool to observe small scale features and processes over long time periods.

6.3 Glider Suitability for Assessing Biogeochemical Cycles

As described above, this project has fulfilled the first three aims, using a combination of glider and mooring data. It has not been possible to fulfil all the aims of this project with glider data alone. Mooring data has been used to estimate the nitrate fluxes. The last aim, to determine how suitable gliders are for studying biogeochemical cycles, will be addressed here.

Gliders are still a relatively new technology and the possibilities for applying them to study processes in the ocean are still being explored. To understand global biogeochemical cycles and their responses to global environmental change more observations are needed at high resolution spatial temporal scales to resolve the submesoscale and mesoscale (Johnson et al., 2009). Satellite ocean colour has been extremely valuable in interpreting temporal variability in biogeochemical processes, along with several longterm time-series stations (e.g. PAP-SO, Hawaii Ocean Time-Series, HOTS, Bermuda Atlantic Time-Series, BATS, European Station for Time-Series in the Ocean Canary Islands, ESTOC). However there are still gaps between these two observation methods. Gliders may help bridge the gap in observing biogeochemical cycles, such as those studied here (nitrate fluxes and depth resolved primary production) at the relevant temporal and spatial scales. Satellite data are often obscured by cloud cover (Figure 4.17) and only observe the surface layer of the ocean. This study has shown errors are incurred where assumptions are made for extracting the depth resolved chlorophyll from surface values. This study found that methods used to predict chlorophyll at depth, which are commonly used (Morel & Berthon, 1989) often poorly represent subsurface chlorophyll distributions (Section 4.4.1). Submesoscale processes are typically difficult to measure in the ocean as they are small and lasts too quickly to be observed by satellites. Time series stations measure the temporal but not spatial scales and therefore assumptions are needed to be extrapolated to larger areas. Cruises can take all the relevant data needed for more comprehensive studies, however they tend to be over short time periods and therefore quantifying annual or even seasonal scales is not possible.

This study has shown the high variability in primary production in the North Atlantic (Section 4.4.1). Other studies have used high resolution glider data to determine the dominant scale of temporal variability (Thomalla *et al.*, 2015). Swart *et al.* (2015) used two gliders to determine the causes of the variability of the mixed layer depth.

There are several other benefits from using underwater gliders for ocean research. One of these is that they are relatively cheap (approx $\pounds 100,000$) compared to other methods of data collection, such as ships (~ $\pounds 30,000$ per day). Gliders can be deployed from small ships or even from the coast. However there are implications with calibration because of the difficulty of taking accurate matching water samples. Deployment from research ships allows more appropriate water samples to be taken for calibration. In this study I have developed a method to calibrate the fluorometer without the need for alternative samples (Hemsley et al., 2015), although there are still issues with calibrating the other sensors (Damerell et al., 2016). The cost and easy deployment of gliders means they can be used as a network, such as the ARGO network, with many gliders deployed at the same time all taking high resolution measurements. A network allows the upper ocean to be measured systematically in real time. The benefit of gliders over ARGO floats is that they can be steered allowing them to be directed to specific areas of interest, repeat transect lines or be used as virtual moorings. Here two gliders were used to repeatedly fly around a mooring array, resulting in a comprehensive dataset over a full annual cycle, with both physical and biogeochemical measurements. However piloting gliders currently requires a significant amount of man power as they need monitoring regularly and re-directing if necessary. Work is underway to fly fleets of gliders in coordination, without the need for constant monitoring (Leonard et al., 2010).

When studying seasonal cycles a benefit of gliders is their continual presence, as they can be deployed for up to six months (Rudnick, 2016). In this study, 7 gliders were deployed in pairs resulting in 4096 dive-climb profiles over a whole annual cycle, encompassing observations of many different processes, physical (Damerell *et al.*, 2016; Thompson et al., 2016) and biogeochemical (Hemsley et al., 2015; Rumyantseva et al., In Review; Binetti, Unpublished Data). The direct measurements throughout winter of the mixed layer and density (via the density nitrate relationship) allowed an estimate to be made of the amount of winter convective mixing (Section 5.2.5). Winter measurements are not easy to obtain from ships due to poor weather conditions and therefore gliders can make observing these periods easier. The gliders also showed that there was still chlorophyll present over winter and enough irradiance to allow a small amount of phytoplankton growth. This type of study can therefore allow important observations to be taken e.g. on the causes of the onset of spring bloom, allowing different hypotheses to be tested against the data (Rumyantseva et al., In Review; Thomalla et al., 2015). Generally it is difficult to catch the beginning of the North Atlantic spring bloom on research cruises, as the timing is unpredictable.

A number of studies have used glider data to investigate biogeochemical cycles in the ocean and glider data can be extended into many areas. Perry *et al.* (2008) used several years of glider deployments to show that interannual changes in stratification influence

the onset of the spring bloom. They also show the benefit of gliders for observing the ocean's subsurface, to distinguish between true blooms and the vertical redistribution of phytoplankton during the autumn. Without the constant monitoring of gliders it would have been difficult to obtain subsurface data on the onset of the spring bloom each year as changes in timing would make it difficult to predict when monitoring should start. Furthermore for this study the full annual cycle of depth resolved production allowed me to demonstrate the importance of the subsurface chlorophyll maximum contributing up to 23% of the annual net primary production. The high temporal resolution of a few hours and horizontal spatial resolution of a few kilometres made glider profiles ideal for collecting data on small eddies off the Southern California Bight (Todd *et al.*, 2009) finding that isopycnals were elevated in the centre of the eddies coincident with higher chlorophyll concentrations, due to uplift of nutrients into the euphotic zone. The presence of the gliders over long time scales allowed the transition in conditions from summer to winter to be captured. Constant monitoring by gliders is also useful for monitoring episodic events in the ocean, when timing and location may be difficult to predict for ship based surveys. Four mesoscale eddy events were observed by gliders in the subtropical North Pacific between February and November 2005 (Nicholson et al., 2008). The glider data allowed net community production (NCP) to be quantified by assessing the seasonal build-up of oxygen in the euphotic zone. Local production was enhanced by the shoaling of isopycnals causing an increase in oxygen concentrations and fluorescence. This helped strengthen the hypothesis that in the subtropics NCP occurs in episodic events while heterotrophic conditions exist the rest of the time.

Gliders can be present through poor weather conditions. They have been flown in strong currents and hurricanes, making it much easier to monitor the development of storms (Miles *et al.*, 2013; Aragon *et al.*, 2015). Measurements from ships are difficult during poor weather conditions, due to dangers when deploying equipment and satellite data is obscured by cloud. Gliders can be used to investigate how storms may impact on the growth of phytoplankton either by decreasing light available to the phytoplankton by deepening the mixed layer or increasing nutrient fluxes (Rumyantseva *et al.*, 2015).

On the other hand there are still several obstacles faced by the glider community. Currently about 10% of gliders are lost on missions of a few months (Testor *et al.*, 2010). The OSMOSIS project was lucky as no gliders were lost and there were only a few periods with data gaps, due to instrument failure. The post processing of glider data is time consuming and often requires that each dive be checked by hand. There are problems with thermal lag, because the CTD cell is unpumped, often leading to spikes in salinity at the base of the thermocline. The compromise between payload and battery power to sensors means that many measurements made by gliders are proxies, for example fluorescence is a proxy for chlorophyll, which is a proxy for phytoplankton biomass. This thesis has tried to remove some of the errors associated with converting fluorescence to chlorophyll by using irradiance profiles, however more work needs to be done on how this changes with community composition and phytoplankton stress.

Interpreting glider data can also be difficult. Gliders move slowly through the water (2 cm s^{-1}) and this raises the question of whether the data accurately represent the spatial structure. Doppler smearing can occur, which is where temporal variability can appear as spatial structure. Aliasing due to discrete time between samples may also be a problem. Rudnick & Cole (2011) found that there was considerably more variability on isopycnal depths from glider data than in the same section completed by a towed vehicle. This is because the glider moves more slowly and therefore variability at high frequencies, such as internal waves, gets projected onto lower observed wavenumbers. Spatial variability was not specifically looked at in this project and the data were treated as a time series, and data was depth binned to 2 m intervals. Originally slanted glider profiles were assumed to be vertical (typical glide angles of 30°). However in this study problems were found when intermittent cloud cover caused irradiance to increase with depth because of glider speed as the light field may change as it completes the dive or climb profile. To mitigate this problem profiles where PAR increased with depth were removed.

Data from gliders should, over a relatively short time frame, be improved as the number and range of sensors that can be carried is extended. There are a number of sensors in trial or under development that will increase the scope of gliders for measuring biogeochemical processes. The list is long and I will not go into all the sensors in development but several are discussed below (Section 6.4.1), which may have added to this thesis. For this study a key sensor would have been a nitrate sensor as a significant error was potentially associated with the density-nitrate relationship. However other sensors for looking at different nutrients would also be useful, e.g. iron or silicate. It is often suggested that iron may be limiting growth when nitrate is present (Moore et al., 2006; Painter *et al.*, 2014a) and therefore to study how or when iron may become limiting in summer it would be useful to have an iron sensor deployed on a glider. Looking further up the food chain if numbers of zooplankton could be measured from a glider it would be useful to study how grazing might impact phytoplankton populations. Krill density has been estimated from gliders in the Southern Ocean using a glider mounted echo-sounder (Guihen et al., 2014). To properly analyse biogeochemical cycles a number of different sensors are needed. However gliders are currently limited by their payload capacity and battery power. One possibility is to deploy a fleet of gliders measuring a number of different properties until this limitation is overcome either by increased payload capacity or miniaturisation of sensors.

There are several hurdles that need to be overcome before gliders can be used as a global observing system (Johnson *et al.*, 2009). First, it needs to be demonstrated that the sensors can generate the very high quality data needed for climate research. Oxygen measurements need to be as accurate as $\pm 0.5\%$ in measurements of biological rate estimates to avoid bias (Johnson *et al.*, 2009). However factory calibrations are often not accurate enough (Körtzinger *et al.*, 2005; Riser & Johnson, 2008), making it difficult to compare data from different platforms.

Observed biogeochemical data needs to be integrated into models to improve their ability to forecast the ocean climate, although it also requires knowledge of the physical environment from which the data was collected. Temperature and salinity are already integrated in some regional (Mediterranean, MSF; Pacific, NCOM) and global (MER-CATOR) models, with glider profiles treated like those from profiling floats or ships (Testor et al., 2010). ARGO data are collected into a single data management system. A similar set up would be a benefit for glider data as it would be useful for quality control and for data access. This would require all gliders to be calibrated and processed with standard control procedures. Currently different methods are used in different institutes around the world. GROOM (Gliders for Research, Ocean Observation and Management) has the objective to design a European Research Infrastructure for glider use, with the infrastructure able to deploy, maintain and operate both individual and fleets of gliders continuously. This will be developed in line with GOOS (Global Ocean Observing Systems) to benefit users globally. The aim is to integrate gliders into existing observing systems, when this has been fully realised gliders will make a more important contribution to marine science.

In the future primary production measured from gliders may be incorporated into global observing systems, allowing the subsurface to be fully resolved.

6.4 Future Work

During this study ideas for a number of improvements and possible future work has come to light.

6.4.1 Glider Sensors

There are many sensors available or in development that would have improved upon the work in this project. I will go into a few of those sensors in more detail here. wavelengths change with depth. The method used in this study uses broadband PAR and assumes the ratios of these wavelengths remain relatively constant throughout the year when it is split spectrally, although weather conditions are taken into account (Section 3.2.3). Ideally to reduce error it would be beneficial to measure the irradiance spectrally throughout the water column to better resolve the amount of irradiance available for primary production. Hyperspectral sensors exist but they tend to be too large to fit into the gliders payload capacity. A seven-channel Satlantic OCR507 irradiance sensor is available however and has been deployed on a Slocum glider (English *et al.*, 2009).

One of the main limitations of the gliders in this project was calculating nutrient fluxes using a density nitrate relationship based on data collected over the entire year. Error estimates using standard error from the CTD cruise observations and the density relationship often resulted in errors of more than 50%, especially for the advective flux calculations (Table 5.1). The cruise data presented in Chapter 5 shows that deviations from this relationship can occur. It has been shown from high resolution measurements that small scale variations on isopyncals can result in a 10% error of nitrate concentrations and that vertical velocities and nitrate concentrations are poorly correlated (Pidcock, 2011). There are a number of nitrate sensors available that could have been used as part of this project, but were unfortunately unavailable. The SUNA Satlantic nitrate sensor, uses optical detection, and has detection limits of approximately 0.0005 to 0.001 mmol. Although this may not be sufficient to measure nitrate in the upper ocean where phytoplankton have depleted concentrations, it would have been sufficient to measure the flux at 50 m, where the lowest nitrate concentration that occurred was 0.48 mmol during September 2012. The sensors have been used to assess a low-oxygen mode water eddy off the West coast of North Africa (Karstensen et al., 2016). Alkire et al. (2012) shows the use of these nitrate sensors deployed on floats. As well as the commercially available optical sensors a miniaturised lab-on-chip nitrate sensor is being developed at the National Oceanography Centre (Beaton et al., 2012), with the aim of being deployed on gliders. Trials of this sensor have been done as part of the NERC Shelf Seas Biogeochemistry programme and the concentrations from the sensor look similar to those from cruise CTD casts (Vincent et al., In Press). It would be beneficial to have the nitrate sensor on the same platform as the productivity measurements to obtain coincident concentrations of the surrounding nitrate fields to reduce the error estimates of the flux calculations caused by the use of the nitrate-density relationship.

It is also possible to have a glider equipped with an ADCP or microstructure probe (Davis, 2010; Todd *et al.*, 2011; Fer *et al.*, 2014; Peterson & Fer, 2014; Palmer *et al.*, 2015). Although these sensors are power hungry and can only be deployed for shorter periods of time (several weeks rather than months), there would be several benefits to

having these sensors on a glider. First, it would allow measurements in real time and there would be little need for a mooring array. Moorings are costly and there is a risk of instrument loss or failure, which would not become apparent until the array has been recovered. Instrument loss was why the submesoscale fluxes can only be calculated from 120 m in this study. Furthermore, this study was specifically focused on one small area, however many glider studies use long transects or try to follow features of interest in the ocean, such as an eddy, which would not be possible if using a mooring array. It would be useful to be have velocity and dissipation estimates on a movable platform, for example to measure fluxes associated with mesoscale features. The ADCP would allow diagnosis of currents at high resolution and from the surface to the depth of a glider dive (1000 m), which would allow the calculation of fluxes of other observable parameters, such as heat or nutrients. However unless bottom-tracking is available there is no method currently available that can reference the currents relative to the glider, making it difficult to obtain their direction. In this project the mooring data had no measurements in the top 50 m, the most important part of the water column when looking at phytoplankton production in this region. This was mostly a problem for measuring the horizontal fluxes into the top 50 m (Section 5.3.4). If currents can in the future be reliably measured from a glider, it would be an important step for measuring horizontal advective fluxes, especially if there is no mooring data available. Methods have been developed to calculate shear velocities and utilise the dive averaged currents as reference horizontal velocities to obtain accurate currents from glider mounted ADCPs (Ordonez et al., 2012). For this study it would have been useful for the nitrate budget by assessing how chlorophyll and nitrate are advected to the study site within the euphotic zone (<50 m). The variance in velocity shear could be used to explain the formation of phytoplankton thin layers (Siegel & Rusello, 2013). An ADCP specific for use on gliders, AD2CP, has been developed by Nortek AS (Oslo, Norway Rusello et al. (2012)). Deployments have been made for testing purposes, however to my knowledge no data has yet been published. It is small, with low power consumption and incorporates a tilt sensor and compass to measure the pitch of the glider.

All these measurements cannot be taken by a single glider due to payload capacity and battery power, using currently available glider technology. However it would be possible to have a number of gliders equipped with different sensors, as was envisioned by Henry Stommel in 1989 (Stommel, 1989). Problems may arise from using several gliders, namely the issue of the submesoscale. This study has shown that there is significant patchiness in a small area (15 x 15 km), with a large variability in primary productivity measurements within one day from multiple dive climb profiles (standard deviations ranging from 0 to 0.68 g C m⁻² d⁻¹) to large changes from day to day estimates (0 -320%). It may therefore be difficult to compare different measurements from different gliders, as variability is high and two gliders may be observing different features, even if they are less than 1 km away from each other. Looking at differences in chlorophyll concentrations compared with the distance of separation of the profiles from the glider data here, showed that there was no relationship and even at distances less than 1 km the difference in the two chlorophyll concentrations could be as large as if the gliders were separated by 15 km (Figure 4.2).

6.4.2 Community Composition

Fluorescence is now used ubiquitously as a proxy for measuring chlorophyll, which is itself a proxy for biomass, despite it being known that the ratio of fluorescence to phytoplankton biomass varies with phytoplankton community (Cullen, 1982). In this thesis I have tentatively related the change in scale factor, which was used to calibrate the fluorescence measurements (Chapter 3), to a change in the community composition. It would be interesting to explore this relationship further and fully investigate how the scale factor for fluorescence measurements may change with phytoplankton community structure and chlorophyll to carbon ratio. This may have a significant impact on the estimates of chlorophyll concentration and primary production in this study and hence how the nitrate fluxes contribute to production. Cruise data would be needed on the phytoplankton community composition and the ratio between chlorophyll and phytoplankton specific carbon along with measurements of irradiance, fluorescence and nutrients so that the scale factor can be derived and then compared to the phytoplankton community and physiology (e.g. nutrient light stress responses). It was not possible at this time due to a lack of data on the phytoplankton community and phytoplankton specific carbon data. It would also be useful to have in situ primary production measurements from different cruises to assess if there are significant changes to the production to chlorophyll ratio with the changes to the community. The C:N relationship may also change depending on the phytoplankton species or also due to nutrient stress and light limitation. Therefore it would also be useful to this project to determine how this may change throughout the year, as it would make the determination of the nitrate budget more accurate as currently the Redfield ratio of 6.6 is used to convert between carbon and nitrogen uptake.

6.4.3 Nitrate Uptake

In situ net primary production in this study was obtained from ¹⁴C measurements (Chapter 3). Dual labelling with ¹³C and ¹⁵N allows better constraint on C:N uptake ratios. These measurements would therefore have been an improvement for this study

by reducing errors when assuming Redfield stoichiometry (Chapter 5). Changes in the C:N ratios may also change over time for a number of reasons, such as community composition or nutrient stress (Geider & La Roche, 2002; Ptacnik *et al.*, 2010; Painter *et al.*, 2010*a*). This could lead to an over or underestimate of how much the nitrate fluxes contribute to the observed primary production. The C:N ratio has been shown to be as high as 16 in the post bloom phytoplankton community (Körtzinger *et al.*, 2001), which would lead to a difference of 400 mmol N m⁻² over the month of August, relative to an initial estimate of 500 mmol N m⁻², when converting the primary production data to nitrate.

6.4.4 Primary Production Parameters

In situ primary production measurements were only taken from one cruise in this study. It would have been beneficial to have measurements taken on different cruises in particular when the subsurface production maximum was present. This would be beneficial for several reasons. Primarily it would give different primary production measurements to ground truth over a variety of different scale factors. Furthermore primary production may be overestimated in the subsurface due to changes in chlorophyll to carbon ratios and therefore an alternative estimate of primary production during this time would be a beneficial comparison.

To better estimate primary production from the bio-optical model, measurements of the parameters used in the algorithm would have been beneficial (Equation 3.3), such as, $a^*(\lambda)$ the absorption cross sections per unit of chlorophyll to the spectral light field (m^{-1}) and ϕ_{μ} the maximum growth rate. Babin *et al.* (1996) showed that the chlorophyll-specific absorption coefficient and the quantum yield for fluorescence varied significantly. Variability in $a^*(\lambda)$ has been observed among different species, which has been attributed to pigment packaging effects depending on cell size, pigment content per cell and concentration of accessory pigments relative to chlorophyll-a (Morel & Bricaud, 1981; Bricaud et al., 1983, 1995; Sathyendranath et al., 1987). This can be measured from water samples. Particulate matter is concentrated on filter paper and then scanned by a spectrophotometer to produce an absorption spectrum (Yentsch, 1962; Mueller & Austin, 1995). The filter is washed in methanol to remove pigments and re-scanned, what is left is assumed to be the detrital material. The difference between the two spectra gives an estimate of phytoplankton pigment absorption. High performance liquid chromatography (HPLC) can also be used to construct the spectrum from the quantity of pigments and pigment-specific absorption coefficients (Bidigare *et al.*, 1990). ϕ_{μ} also varies among species (Falkowski et al., 1985) and can be calculated from two measurements of biomass separated by a period of time, assuming that the phytoplankton are

not becoming diluted (Behrenfeld, 2010). If these parameters are known, error in the estimates of primary production can be reduced by inputting the values into an algorithm rather than using values used for global estimates of production as I used here (Section 3.2.6).

6.5 Closing Comments

Primary production in the ocean is an important process for food chains and global carbon cycles. The impact of nutrient fluxes in supporting primary production is difficult to quantify as measurements are generally sparse. I have presented here a full annual cycle of depth resolved, primary production alongside estimates of nitrate fluxes into the euphotic zone.

The calculated primary production annual estimate is 255 g C m⁻² yr⁻¹. The observations show that there is significant production in the subsurface accounting for 23% of total annual net primary production. The calculated nitrate fluxes balance that of the rates of primary production and can contribute to between 75 to 102% of the annual primary production. The largest contribution to the nitrate supply was from the vertical advective flux, which demonstrates the dominant role of mesoscale and submesoscale processes in this region. Both the primary production and the nitrate fluxes show a strong seasonal cycle, but with high temporal variability imposed on top. This strong variability indicates the importance of mesoscale and submesoscale processes influencing phytoplankton growth in the surface ocean.

Changes in primary production are expected in the future due to increasing sea temperatures. Stratification in the ocean may increase which could reduce nutrients available for phytoplankton growth, but in some areas could increase growth by increasing light availability (Behrenfeld *et al.*, 2006). It is important that we understand the processes that influence growth and nutrient inputs in the ocean and continue to monitor the changes that are occurring. I have shown that gliders will be a vital tool to help survey these processes over small temporal and spatial scales and annual cycles.

Appendix A

Water Reflectance

Equations to calculate water reflectance. First the solar declination (δ) at a given time needs to be calculated:

$$\delta = 0.39637 - 22.9133 \times \cos(t) + 4.02543 \times \sin(t) - 0.38772 \times \cos(2t) + 0.052 \times \sin(2t) \quad (A.1)$$

where t is time. Next the solar elevation (α) needs calculated:

$$\alpha = \sin(lat) \times \sin(\delta) - \cos(lat) \times \cos(\delta) \times \cos(h) \tag{A.2}$$

where *lat* is the latitude and *h* is the hour angle, which is a coordinate system ($ha = 360^{\circ} \ge (hour/24)$). The solar elevation (α) is equal to the cosine of the solar zenith angle θ_s :

$$\theta_s = a\cos(\alpha) \tag{A.3}$$

The index of refraction of pure seawater (n_s) is 1.341 and the density of air (ρ_a) is 1.2 $\times 10^3$ g m⁻³.

$$cn = 0.49 \times 10^{-3} + 0.065 \times 10^{-3} \times s_w \tag{A.4}$$

where s_w is the wind speed. The reflectance due to foam (r_f) can be calculated from the wind speed following Mobley (1999):

$$r_f = (\rho_a \times cn \times 4.5 \times 10^{-5} - 4.0 \times 10^{-5}) \times s_w^2$$
(A.5)

To convert degrees to radians:

$$r\theta = 0.0174533\theta \tag{A.6}$$

If the solar zenith angle is less that 40° then the following equations are used to calculate the direct reflectance (r_d) (Mobley, 1999):

$$r_{min} = r\theta - asin(\frac{sin(r\theta)}{rn})$$
(A.7)

$$r_{max} = r\theta + asin(\frac{sin(r\theta)}{rn})$$
(A.8)

$$sinp = \frac{sin(r_{min}) \times sin(r_{min})}{sin(r_{max}) \times sin(r_{max})}$$
(A.9)

$$tanp = \frac{tan(r_{min}) * tan(rmin)}{tan(r_{max}) \times tan(r_{max})}$$
(A.10)

$$r_d = 0.5(sinp + tanp) \tag{A.11}$$

If θ is large than 40° an empirical fit can be used (Mobley, 1999):

$$r_d = 0.0253 e^{b(\theta - 40.0)} \tag{A.12}$$

where b = -7.14 x $10^{-4} \times s_w + 0.0618$. The total surface reflectance is then equal to:

$$r_{tot} = r_d + r_{diff}.\tag{A.13}$$

Appendix B

Chlorophyll

A comparison between the glider primary production and modelled satellite profiles, shows a large discrepancy (Figure 4.6). Just comparing satellite chlorophyll with the glider chlorophyll before the profiles are modelled shows better results. The satellite data was extracted, for the nearest glider data point in date and location, from 1 day MODIS-Aqua 4 km data (NEODAAS). The satellite chlorophyll was compared with 1) glider surface concentrations (Figure B.1) 2) mean glider chlorophyll in the first optical depth (Figure B.2) and 3) mean glider chlorophyll within the euphotic zone (Figure B.3). The R² for all three comparisons are low. Interesting the best comparison is between the satellite data and glider surface chlorophyll, which has the highest R² and lowest root mean square error. It is generally assumed that the satellite views the first optical depth of the water column, however here that is the worst comparison with a low R² of 0.06 and the highest root mean squared error.



FIGURE B.1: Comparison between glider surface chlorophyll and satellite data. RMSE 0.398



FIGURE B.2: Comparison between mean glider chlorophyll concentrations over the first optical depthl and satellite data. RMSE 0.419



FIGURE B.3: Comparison between mean glider chlorophyll concentration over the euphotic depth and satellite data. RMSE 0.405

Appendix C

Geostrophic Theory

Geostrophy in the ocean can be represented as:

$$\frac{\partial}{\partial z} \left[-fv \right] = \frac{\partial}{\partial z} \left[-\frac{1}{\rho_0} \frac{\partial p}{\partial x} \right]
\frac{\partial}{\partial z} \left[fu \right] = \frac{\partial}{\partial z} \left[-\frac{1}{\rho_0} \frac{\partial p}{\partial y} \right]$$
(C.1)

where (u, v, w) are the velocity components in the (x, y, z) = (east, north, vertical directions; p is pressure, ρ_0 is density of seawater; f is the Coriolis parameter; and v is the coefficient of kinematic viscosity. These equations use the assumptions that seawater is an incompressible Newtonian fluid. In hydrostatic balance $\frac{\delta p}{\delta z}$ is equal to $-\rho g$. It is assumed there is no acceleration (steady-state), no viscosity and the pressure is hydrostatic (Gill, 1982).

$$-f\frac{\partial v}{\partial z} = +\frac{g}{\rho_0}\frac{\partial \rho}{\partial x}$$

$$f\frac{\partial u}{\partial z} = +\frac{g}{\rho_0}\frac{\partial \rho}{\partial y}$$
 (C.2)

The geostrophic equations satisfy the continuity equation in steady-state:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0. \tag{C.3}$$

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