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

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Abstract

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

Keywords: nitrates, time-series, ship of opportunity

Regional Index terms: North East Atlantic, Bay of Biscay

1 Introduction

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

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

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

In 2002 we initiated year round in situ measurements on a SOO to study the physical and biogeochemical drivers of productivity on and off shelf from the English Channel to the deep water Bay of Biscay. In this study we present an 8 year time-series (2003 to 2010) of

continuous SOO data from *in situ* FerryBox measurements, with additional nutrient samples from 2003 onwards taken each month over most of the period except for August 2007 to August 2008. MLD estimates, calculated from Argo profiling float temperature profiles (available in increasing resolution from 2004 onwards) were used to look at year to year variations in surface nitrate measurements in relation to convective mixing processes. Measurements of Sea Surface Temperature, PAR irradiance, wind speed and turbulence and phytoplankton concentration for the years 1997-2007 along the same FerryBox line using remote sensing can found in Garcia-Soto & Pingree (2009).

We use here the *in situ* SOO dataset to look at seasonal timescales to investigate periods of mixed layer deepening and if they are associated with increases in nitrate or productivity. The nitrate, oxygen and MLD data are used to estimate net community production (NCP) and this study provides a direct opportunity to study seasonal and interannual variations in surface nutrient concentrations and how this may affect phytoplankton production.

2 Materials and methods

2.1 Study Site

Surface water data were collected from P & O European Ferries Ltd ship *MV Pride of Bilbao* operating between Portsmouth (UK, $50.8^{\circ}N$, $1.1^{\circ}W$) and Bilbao (Spain, $43.4^{\circ}N$, $3.0^{\circ}W$) (Fig. 1). The ship made approximately two crossings weekly between these ports. The FerryBox system ran from April 2002 to September 2010, operating year round except for January when the ship was in dry dock for its annual refit. The distance is approximately 1000 km and the journey time is about 35 hours each way. This gives a repeat sampling rate of between 4 hours and 4 days, depending on location. Over the 8 years the FerryBox measurements cover 0.8×10^{6} km of ship's track. The map in figure 1 is reproduced from Bargeron *et al* (2006) and identifies persistent regional features as identified by Pingree & Griffith (1978).



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

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

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

2.2 Ship measurements

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

The sampled water was taken from the ship's cooling water supply at a depth of 5 metres. The Ferrybox system consisted of sensors to measure conductivity (precision 0.005 mmho cm⁻¹) to calculate salinity; dissolved oxygen, temperature (precision 0.003 °C) and chlorophyll-fluorescence (precision 0.01 ± 0.01 mg m⁻³). The flow rate in the Ferrybox system was 15-20 litres per minute. A comparison between the flow through temperature readings and a hull mounted temperature sensor showed that the flow through temperature readings were 0.5 ± 0.3 °C higher than the in situ water (offset ±1s) from 2005 through August 2008. Subsequent to August 2008 this reduces slightly to 0.3 ± 0.3 °C. These small offsets suggests a low residence time of water in the Ferrybox system. Underway data were logged at a rate of 1 Hz on a NOC (National Oceanography Centre, Southampton) designed logging and control system. Public domain Matlab routines

(http://marine.csiro.au/~morgan/seawater) provided the calculations for salinity based on UNESCO (1983) algorithms. All sensors were cleaned on an approximately weekly basis to reduce bio-fouling, when the ship was berthed in Portsmouth.

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

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

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

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

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

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

Argo floats (http://www.coriolis.eu.org) provide temperature profiles in the Bay of Biscay for the estimation of the mixed layer depth (MLD). As the thermal gradient of the permanent thermocline in the Bay of Biscay is very weak, mixed layer depth estimates based on threshold algorithms may provide biased results. Instead a topology-based algorithm (Gonzalez-Pola *et al.*, 2007) was used that performs the best-fit of the temperature profiles to a prescribed functional form. The fitting allows a series of parameters to be extracted, that can be identified with properties of the vertical structure of the water column, including the MLD. MLD data are presented for the off-shelf Bay of Biscay region as the Argo float data are only available for water deeper than 1000m. In the selected region, from 0 to 10°W and 43 to 48°N, over 900 profiles were used in the calculation of MLD. Prior to the 2005/2006 winter there were not sufficient Argo profiles within the Bay of Biscay to calculate MLD. MLD was compared with the North Atlantic Oscillation (NAO) winter index (December to March) assuming this to be the dominant mode of atmospheric pressure variation over the North Atlantic (Visbeck *et al.*, 2003)

3 Results and discussion

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

3.1 Regional and inter-annual variations in temperature and nutrients

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



Figure 2: In situ temperature measurements from the FerryBox on route between Portsmouth and Bilbao from 2003-2010. The colour bar shows the temperature range encounted (in deg C).

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



Figure 3: Inter-annual variation in winter sea surface temperature shown as the minimum in-situ temperature identified each year from 2003-2010, along the route between Portsmouth and Bilbao and the region, as identified in Figure 1

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



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

In the off-shelf Bay of Biscay region (45-47.5 °N) the nitrate: temperature relationship is correlated in the winter months (when the temperature is <16 °C) as shown in figure 5. Linearity in the nitrate: temperature signal is widely reported (e.g.: Henson *et al*, 2003). Although a single line is shown this relationship varies through the autumn and winter months and there will be a range of nitrate concentrations for a given temperature (Garcia-Soto & Pingree, 1998). At temperatures above 16 °C, in the summer the relationship no longer holds although small increases in nitrate concentration at may arise due to processes such as for example internal tides, internal waves, eddies and slope current mixing processes (Garcia-Soto & Pingree, 1998)



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

3.2 Variation in nutrients related to mixing

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



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

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

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



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

The position and temperature profiles from all available Argo floats during March (from 2006 to 2009) are shown in figure 8. Estimates of mixed layer depth based on the temperature profiles confirm that the vertical structure is very different in cold winters (2006 and 2009) compared with warm winters (2007 and 2008). The MLD is roughly double in cold winters (approx 170 m vs. 340 m). Despite spatial and temporal variability in the profiles this is a coherent signal across the Bay of Biscay.



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

3.3 Variation in nutrients on and off-shelf

The variation in surface nitrate concentration and salinity along the track at different times of year is illustrated in figure 9, where selected individual months illustrate the beginning of winter mixing (October), the winter maximum (March) and depleted levels (April). There are clear boundaries to the changes in nitrate and salinity as the ship travels north. These changes were used to define the on-shelf, off-shelf and slope regions shown in figure 1.

In the winter the highest nitrate concentrations are seen off shelf (between 46 °N and 46.5 °N) where concentrations tend to be greater than 6 micro mol kg⁻¹ (in the March 2005 example shown in figure 9) peakingnear the shelf break (at 46.5 °N). Concentrations are lowest around (47.5 °N), which can be defined as a half slope, half stratified shelf environment. Slope processes such as internal tides, waves and eddies maintain high nutrient concentrations to the north, on the shelf (Garcia-Soto & Pingree, 1998), as is seen in each of the months shown in figure 9. The springtime decline in nitrate is observed to occur over a

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





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

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

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

3.4 Variation in net community production in relation to nutrients and mixing In figure 10 seasonal and inter-annual variability in MLD is shown in relation to the monthly oxygen anomaly (DO_{anom}) data from 2005-2010, which was used as a measure of productivity (Bargeron *et al.* 2006).



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

The peak in DO_{anom} indicates the main phytoplankton bloom in spring. In the Bay of Biscay the main spring bloom is dominated by diatoms (Smythe-Wright, *et al.*, 2013) and follows a period of sustained positive net heat flux into the ocean (on the scale of 8-10 days, Garcia-Soto & Pingree, 1998; Waniek, 2003).

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

In having a year round *in situ* dataset some of the assumptions used to calculate NCP can be minimised. For example, there is no need to estimate wintertime nitrate with the associated errors (Glover & Brewer, 1998; Koeve, 2001) and there is no need to make assumptions on the length of the productive cycle (Waniek *et al.*, 2003). However the calculation of NCP is heavily dependent on the choice of MLD and require assumptions on the C:N ratio (Körtzinger *et al.*, 2001). The relative merit in using chlorophyll-fluorescence or DO_{anom} as an indicator of surface and subsurface phytoplankton growth is beyond the scope of this paper. The high frequency data available from each of these variables could be used to further investigate the timing of the spring bloom in this area although there are numerous studies that have investigated bloom timing in this region using both in situ and remote sensing data (eg: Pingree, 1975; Garcia-Soto & Pingree, 1998; Garcia-Soto et al., 2002; Garcia-Soto & Pingree, 2009).

Table 1 summarises inter-annual variations from 2005 to 2010, highlighting each winter period (December to March) and integrated NCP_{MLD} for the following spring. The winter NAO index, temperature minima, maximum winter MLD; the annual change in dissolved inorganic nitrate and the integrated net community production are shown.

	NAO	Temperature	MLD	NO ₃ change	NCP _{MLD}
Year	index	minima (deg C)	(m)	(micro mol kg ⁻¹)	$(mol C m^{-2})$
2005/2006	-0.24	11.76	469	7.73	20.91
2006/2007	0.63	13.06	212	3.91	10.07
2007/2008	0.51	12.61	265		10.53
2008/2009	0.09	11.89	439	7.41	19.91
2009/2010	-1.48	11.81	476	7.13	16.91

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

In the Bay of Biscay the MLD (Table 1) was found to vary from 212 m in relatively mild winters (such as 2006/2007) to 476 m in cold winters (2009/2010). Deeper mixing was associated with an increase in nitrate concentrations in the surface waters. Hydes *et al*, (2001) showed that nutrient concentrations below 300 m remained relatively consistent between cruises and from Hydes *et al*., 2001 nitrate profiles an increase in mixing from 200m to 400m would be expected to increase the surface nutrients by up to 2 micro mol kg⁻¹.

The inter-annual changes seen in the maximum winter nitrate in this study were in the order of 3 micro mol kg⁻¹ (Table 1) which suggests a further source of winter nitrate or a decreased surface advection of low nutrient waters in some years. The currents were not

measured in this study although the water properties reported will reflect changes in the water masses, surface circulation and vertical mixing of depth accumulated nitrate. The slope current and internal tide mixing is particularly important for phytoplankton growth and the slope region will experience a continuous injection of nitrate which can enhance productivity (Pingree, 1975; Garcia-Soto & Pingree, 1998).

This is a simple illustration of year-to-year variations in winter nitrate in the Bay of Biscay and how productivity is affected the following spring. Our data suggests that low production corresponds to low winter nitrate concentrations and warmer surface water in the 2006/2007 winter, compared with the previous and following years. Overall, the data indicate year to year variation in nutrients and productivity that can be related to changes in sea surface temperature and mixing depth and these changes could be linked to climate indices. A very negative North Atlantic Oscillation index will cool sea surface temperatures from the Azores region to the Bay of Biscay (Pingree, 2005; Garcia-Soto & Pingree, 2012). Negative winter NAO indices are associated with high seasonal ranges of nitrate concentrations with deep winter mixing (Garcia-Soto & Pingree, 2012). In contrast warm winters, such as 2007 and 2008, correspond to positive winter NAO indices and warmer sea surface temperatures. These positive winter NAO years are associated with shallow winter MLDs, lower seasonal amplitudes of nitrate and winter nutrient concentrations with correspondingly reduced spring time productivity as shown in the dataset (see also Jiang *et al.*, 2013).

4 Conclusions

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

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

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