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Biogeochemical variations at the Porcupine Abyssal Plain Sustained Observatory (PAP-SO) in the northeast Atlantic Ocean, from weekly to inter-annual time scales

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Abstract

We present high-resolution autonomous measurements of carbon dioxide partial pressure $p(CO_2)$ taken in situ at the Porcupine Abyssal Plain sustained observatory (PAP-SO) in the Northeast Atlantic (49°N, 16.5°W; water depth of 4850 m) for the period

- ⁵ 2010 to 2012. Measurements of $p(CO_2)$ made at 30 m depth on a sensor frame are compared with other autonomous biogeochemical measurements at that depth (including chlorophyll *a*-fluorescence and nitrate concentration data) to analyse weekly to seasonal controls on $p(CO_2)$ flux in the inter-gyre region of the North Atlantic. Comparisons are also made with in situ regional time-series data from a ship of opportunity
- ¹⁰ and mixed layer depth (MLD) measurements from profiling Argo floats. There is a persistent under saturation of CO_2 in surface waters throughout the year which gives rise to a perennial CO_2 sink. Comparison with an earlier dataset collected at the site (2003 to 2005) confirms seasonal and inter-annual changes in surface seawater chemistry. There is year-to-year variability in the timing of stratification and deep winter mixing.
- ¹⁵ The 2010 to 2012 period shows an overall increase in $p(CO_2)$ values when compared to the 2003–2005 period. This is despite similar surface temperature, wind speed and MLD measurements between the two periods of time. Future work should incorporate daily CO₂ flux measurements made using CO₂ sensors at 1 m depth and the in situ wind speed data now available from the UK Met Office Buoy.

20 **1** Introduction

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A persistent feature of the subpolar North Atlantic is under-saturation of carbon dioxide (CO_2) in surface waters throughout the year, which gives rise to a perennial CO_2 sink (Körtzinger et al., 2008). This makes the north east Atlantic a region of great importance in the global carbon cycle. However, there is evidence for inter-annual variation in the CO_2 sink (1–3 mol m⁻² a⁻¹) due to changes in wintertime mixing and stratification (Schuster and Watson, 2007). Changes in the amount of CO_2 absorbed by the



ocean may have implications for the global carbon cycle now and as a carbon sink in the future. Studies of the physical and biological processes regulating surface water partial pressure of $CO_2 \ p(CO_2)$ are required to estimate future trends in the ability of the ocean to act as a sink for increasing CO_2 in the atmosphere. Frequent observations from fixed positions are critical to make these calculations (McGillicuddy et al., 1998).

Accurate, high-resolution, long-term datasets are offered by time series studies such as the Porcupine Abyssal Plain sustained Observatory (PAP-SO) in the Northeast Atlantic at 49° N, 16.5° W (4850 m water depth) where a fixed-point mooring has been in place since 2002 (Hartman et al., 2012).

- The PAP-SO is in the North Atlantic Drift Region (NADR), a biogeographical province defined by deep winter convective mixing (Longhurst, 2006; Monterey and Levitus, 1997). The surface mixed layer depth changes from 25 m in the summer to over 400 m in winter. A twofold decrease in winter nitrate concentration over a three year period from 2003 has been attributed to a combination of shallower winter convective mixing
- ¹⁵ and changes in surface circulation (Hartman et al., 2010). The PAP-SO is in an area with relatively high wind speeds, frequently greater than 10 m s^{-1} . High wind speeds have a significant effect on CO₂ flux (Takahashi et al., 2002). The CO₂ flux at the PAP-SO was calculated from $p(CO_2)$, the water partial pressure of CO₂, between 2003 and 2005 as a net flux into the ocean of over $3 \text{ mol m}^{-2} \text{ a}^{-1}$ (Körtzinger et al., 2008). This
- ²⁰ is a significant sink compared with subtropical time series sites such as ESTOC (near the Canary Islands, 29.17° N, 15.5° W), which is an overall annual CO_2 source region (0.05 mol m⁻² a⁻¹, Gonzalez-Davila et al., 2003).

Recently, the decline in North Atlantic CO_2 uptake from 1994/1995 to 2002–2005 has been linked to a variation in the North Atlantic Oscillation (Schuster and Watson,

²⁵ 2008; Padin et al., 2011). The decreased uptake may be a consequence of declining rates of wintertime mixing and ventilation between surface and subsurface waters due to increasing stratification. Enhanced stratification forms a barrier to nutrient exchange, which may result in a progressive decline in primary production (Field et al., 1998), as was seen in the North Atlantic between 1999 and 2004 (Behrenfeld et al., 2006). The



observed decrease in nitrate concentration and productivity in this region (Behrenfeld et al., 2006), may in turn affect the oceanic uptake of $p(CO_2)$.

In this paper, we present recent year round time-series data of temperature, salinity, nitrate concentration, chlorophyll *a*-fluorescence and $p(CO_2)$ collected from 30 m depth

- ⁵ from 2010 to 2012. The data are compared with an earlier published dataset (from 2003 to 2005) and additional $p(CO_2)$ measurements made from a ship of opportunity. The in situ dataset is considered in relation to convective mixing processes using mixed layer depth (MLD) estimates calculated from profiling Argo floats. The weekly air-sea CO_2 flux at the PAP-SO site was calculated from in situ $p(CO_2)$ measurements and ancillary satellite wind speed datasets. The objective of this study is to examine the
- ancillary satellite wind speed datasets. The objective of this study is to examine the biogeochemical variations at the PAP-SO in the northeast Atlantic over different periods from weekly, seasonal to annual.

2 Materials and methods

2.1 Study site

¹⁵ The position of the Porcupine Abyssal Plain sustained observatory (PAP-SO) at 49° N, 16.5° W is shown in Fig. 1. Lampitt et al. (2001) has summarised the hydrography, meteorology and upper mixed layer dynamics in the region.

2.2 In Situ data

The instrumentation of the PAP-SO observatory has been described in detail by Hart-²⁰ man et al., 2012 (see Table 1 and Fig. 1 therein) and is briefly summarized here. Since 2002 instruments on a mooring at the PAP-SO (49° N, 16.5° W) have recorded a suite of biogeochemical parameters in the mixed layer. Measurements of nitrate concentration, chlorophyll *a*-fluorescence and $p(CO_2)$, carbon dioxide partial pressure, have been made since 2002, using biogeochemical sensors on a frame at a nominal depth of 30 m often within the deep chlorophyll maxima. Between 2002 and 2007 the sensor

 $_{\rm 25}$ $\,$ of 30 m, often within the deep chlorophyll maxima. Between 2002 and 2007 the sensor



frame depth varied from 20 m to 225 m, deflecting in response to local currents. A surface buoy was added in 2007 so biogeochemical measurements were consistently made at 30 m depth. In 2010 collaboration with the UK Met Office led to a redesigned infrastructure, providing simultaneous surface physical and biogeochemical measure-5 ments with surface meteorological data.

The two periods of time examined here were collected using different instrumentation. Twice daily $p(CO_2)$ measurements, from 2010 to 2012, were made using a PRO-CO₂ sensor (Pro-Oceanus, Canada), which uses an infrared detector and is internally calibrated through an auto-zero calibration function (see Jiang et al., 2014 for further dataile). A nume was used (Sashird Inc.) to improve water flow serves the senser mem

- ¹⁰ details). A pump was used (Seabird Inc.) to improve water flow across the sensor membrane to accelerate the equilibrium, and a gas tension device (Pro-Oceanus, Canada) measured the total gas pressure to improve gas estimates. The data are compared here with the published $p(CO_2)$ data from 2003–2005 (Körtzinger et al., 2008) measured using a SAMI (Sunburst Sensors LLC, USA) sensor, which is based on equilibra-
- ¹⁵ tion of a pH indicator solution, contained in a gas-permeable membrane, with ambient $p(CO_2)$ and subsequent spectrophotometric determination in the equilibrated solution (DeGrandpre et al., 1995). The surface in situ $p(CO_2)$ time-series ceased between 2006 and 2009 and for the early part of 2011.

A Hobi Labs Inc., HS-2 fluorometer (Arizona, USA) was used on the PAP-SO mooring to estimate chlorophyll *a* until 2005 when an alternative ECO FLNTU (WETIab, USA) fluorometer came into use. As described by Hartman et al., 2010 fluorescence output provides an approximation of chlorophyll *a*; the fluorescence/chlorophyll *a* calibration ratio changes throughout the year, due to variations in the phytoplankton species composition. On the mooring, chlorophyll *a*-fluorescence measurements were

taken every 2 h over the 1 yr deployments and biofouling was controlled using motorised copper shutters on each of the fluorometers.

Nitrate concentration measurements were initially made using wet chemical "NAS Nitrate Analysers" (EnviroTech LLC, USA) as described in Hydes et al. (2000) with twice daily sampling frequency and internal calibration as described by Hartman et al. (2010).



From 2010 additional higher frequency inorganic nitrate measurements were made using UV detection methods (ISUS, Satlantic).

For each instrument the manufacturer's calibration was checked at the start of each deployment and instrument drift was corrected using a second calibration check on

- ⁵ recovery of the instruments. Biogeochemical data from the PAP-SO are available from www.eurosites.info/pap and the British Oceanographic Data Centre BODC. Data presented here cover the period when $p(CO_2)$ measurements are available, July 2003 to the end of June 2005 (with deployments in July 2003, November 2003, June 2004) and the period from May 2010 to June 2012 (with sensor deployment in May 2010, September 2010, July 2011, May 2012). All of the measurements are within the mixed
- ¹⁰ September 2010, July 2011, May 2012). All of the measurements are within the mixed layer although the depth of measurements is closer to the 30 m nominal depth after mooring redesign to incorporate a surface float in 2007.

2.3 Other observational data sources

and are internally consistent.

Temperature and salinity data were taken from Argo floats (http://www.coriolis.eu.org),
extracting 30 (± 5) m depth data. The Argo data have a potentially lower accuracy than the in situ microcat data, with a quoted accuracy of 0.005 °C for temperature and 0.1 for salinity. A comparison of Argo temperature with in situ 30 m microcat data (n=112, comparison not shown) suggests errors of up to 2 % for salinity and 1 % for temperature in the Argo data compared with the in situ data (when available). The errors will be compounded further when eddies pass the site or with an increase in search radius around the PAP-SO. To obtain a continuous seasonal description, a large region was selected (45° N to 52° N and 26.08° W to 8.92° W, excluding the shelf area). However the Argo data were chosen over the in situ data as they have a larger temporal coverage

The $p(CO_2)$ time-series was compared with surface data from a ship of opportunity (SOO) running from Portsmouth, UK to the Caribbean (Schuster et al., 2007). Onboard the SOO continuous $p(CO_2)$ measurements are made using a calibrated system with a showerhead equilibrator (Schuster et al., 2007). Discrete nutrient samples were col-



lected at 4 h intervals along the route and were analysed ashore (Hartman et al., 2008). This provides an approximately monthly nutrient sample and $p(CO_2)$ data point close to the PAP-SO on the return route of the ship. The nominal depth of these samples is 5 m, which is shallower than the 30 m samples from the PAP-SO. We selected SOO data

₅ between 52° N and 45° N and 8.92° W and 26.08° W, and then took the average $p(CO_2)$ values that were within that area on the same day as the sample from the PAP-SO site.

Through collaboration with the UK Met Office in situ wind speed data are available since 2010. However for consistency in calculations of CO₂ flux between the two time periods (2003-2005 and 2010-2012) considered here we took wind speed data from weekly satellite data: Fleet Numerical Meteorology and Oceanography Center (FN-MOC) 1° by 1°. We calculated a weekly mean from the 6 hourly, 10 m height data; available from http://las.pfeg.noaa.gov/.

The air-sea CO₂ flux (in mmol $m^{-2} d^{-1}$) was calculated from the air-sea $p(CO_2)$ difference, temperature and salinity (30 m) and wind speed at 10 m height, using the following equation:

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$$F_{\rm CO_2} = k \cdot K_0 (\rho \rm CO_{2sea} - \rho \rm CO_{2air})$$

Where k is the transfer coefficient based on the wind speed-dependent formulation of Nightingale (2000), scaled to the temperature-dependent Schmidt number according to Wanninkhof (1992), K_0 is the CO₂ solubility at the in situ temperature and salinity after

- Weiss and Cohen (1974). While pCO_{2sea} and pCO_{2air} are the CO₂ partial pressures 20 of seawater and air, respectively. As $p(CO_2)$ was reported throughout this manuscript, we used $p(CO_2)$ for the air-sea flux calculation. Using $f(CO_2)$ for calculation would generate the same results of flux estimates. The atmospheric $p(CO_2)$ is calculated from monthly averaged $x(CO_2)$ measured at Mace Head (53.33° N, 9.90° W) assuming 100% water vapour saturation under 1 atm air pressure. Please note that 1 atm = 25
- 1.01325 bar.

The alkalinity was calculated from Argo temperature and salinity (30 m), following the relationship for the North Atlantic developed by Lee et al. (2006). The dissolved



(1)

inorganic carbon (DIC) concentration was then calculated from alkalinity and $p(CO_2)$ measurements using the "seacarb" package (Lavigne and Gattuso, 2011), with Argo temperature and salinity (30 m) and nutrient concentrations set to zero. The chosen constants were Lueker et al. (2000) for K_1 and K_2 , Perez and Fraga (1987) for K_f and the Dickson (1990) constant for K_c , as recommended by Dickson et al. (2007).

The monthly MLD was calculated from density profiles using global gridded fields of temperature and salinity collected by Argo floats, XBTs, CTD/XCTDs and moorings. These data are collected and made freely available by the Coriolis project and programmes that contribute to it (http://www.coriolis.eu.org). We used the near realtime mode data as these datasets have been quality control checked. The depth of the mixed layer was defined by a density difference of 0.03 kg m⁻³ from the density at a reference depth (in this case 10 m to avoid diurnal changes in temperature and salinity

at the surface). We followed the method of Holte and Talley (2009) by using their algorithm to calculate the MLD based on density difference. This algorithm incorporates linear interpolation to estimate the depth at which the density difference is crossed.

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

3 Results

Figures 2a–c show the in situ observations from the PAP-SO at 30 m depth (including $p(CO_2)$, chlorophyll *a*-fluorescence and nitrate concentration). Figure 2a shows that $p(CO_2)$, the partial pressure of carbon dioxide, between 2010 and 2012 had a 57 µatm range (327 to 384 µatm) with a mean of 353 µatm. This compares with the 2003 to 2005 data (also shown in Körtzinger et al., 2008), where the range was 74 µatm (300 to 374 µatm) and the mean was 339 µatm. The $p(CO_2)$ data for the 2010–2012 period are confirmed by SOO data from the Portsmouth to Caribbean route in Fig. 2a, (see Fig. 1 for positions of the SOO samples). The 2003–2005 SOO comparison is shown in Körtzinger et al. (2008). The higher $p(CO_2)$ values in the 2010 to 2012 period are

Discussion Paper BGD 11, 12415–12439, 2014 **Biogeochemical** variations at the **Porcupine Abyssal Discussion** Paper Plain S. E. Hartman et al. **Title Page** Introduction Abstract Discussion Paper Conclusions References Tables Figures Close Back **Discussion** Paper Full Screen / Esc **Printer-friendly Version** Interactive Discussion

confirmed and the SOO data fill in the gap in the time series when PAP-SO $p(CO_2)$ data were not available due to failure of the instrument logger.

In situ chlorophyll data in Fig. 2b shows the characteristic chlorophyll *a*-fluorescence increase for this area during the spring bloom. There is large inter-annual variability in both the timing and magnitude of the spring bloom. For example there was a larger

spring bloom in 2011 compared with the other years shown. It also started earlier in the year (in April) compared with the spring bloom in 2004 that started in late May.

Nitrate concentration data in Fig. 2c shows the characteristic seasonality, with increased winter nitrate concentrations and depletion following the spring bloom (seen

- ¹⁰ in Fig. 2b). The seasonality in the nitrate concentration is similar for the two periods shown (2003–2005 and 2010–2012). However, winter nitrate concentrations are significantly lower in the 2004/2005 winter compared with other years as has been discussed in Hartman et al., 2010. Overall, the in situ data show a characteristic increase in inorganic nitrate concentrations, and $p(CO_2)$, through the winter months whilst chlorophyll
- ¹⁵ *a*-fluorescence decreases. SOO nitrate concentration data show a good agreement throughout 2010–2012 and fill in the gaps in early 2011 when nutrient measurements at the PAP-SO are not available.

To put the in situ data in context Fig. 3a shows the Argo temperature data, extracted at 30 m depth for the time period that biogeochemical measurements were available at the PAP-SO. The temperature variations in these years are very similar showing a summer-winter difference of 6 °C. Temperature data shows an opposite trend to the $p(CO_2)$ and nitrate concentration from in situ data.

The seasonality of the in situ data can be put in context when looking at the MLD in Fig. 3b. The increase in winter nitrate concentration and $p(CO_2)$ due to convective mixing at the site is shown. The MLD range varies little over the winters considered here and the maximum MLD does not exceed 260 m. However the timing of the maximum winter mixed layer depth varies from year to year. For example the maximum MLD for the 2010/2011 winter was 215 m in February 2011 compared with earlier and deeper mixing (to 257 m) in December 2011 (for the 2011/2012 winter).



The calculated DIC concentrations are shown in Fig. 3c as the data show a closer relationship to the MLD seasonality than nitrate concentration data. Seasonal variation in the concentration of both DIC and nitrate is similar apart from the 2004/2005 winter; low DIC concentrations were not seen at the same time as the low nitrate concentra-

tions. Both DIC and nitrate concentrations increase earlier in the winter at the end of 2011, compared with 2004, and this can be related to the earlier increase in the winter MLD at that time.

The interrelation between DIC and nitrate concentrations can be considered by looking at the Redfield ratio (Redfield, 1958), which is illustrated in Fig. 4. The changes in calculated DIC concentrations at the PAP sustained observatory, in relation to changes in the in situ nitrate concentrations, are represented for the different seasons. The C : N ratio differed from the Redfield ratio of 6.6 with especially high values in spring (12.7) and post bloom in the autumn (8.7).

Figure 5a shows the sea-to-air CO_2 flux (where a positive flux is defined as from sea ¹⁵ to the atmosphere). This was calculated from in situ $p(CO_2)$ data and satellite wind speed data (Fig. 5b). The week by week variation in CO_2 flux is shown and an overall average for the two periods of time has been calculated as $-1.52 \text{ mmol m}^{-2} \text{ d}^{-1}$ for the 2003–2005 period and $-1.36 \text{ mmol m}^{-2} \text{ d}^{-1}$ for the 2010–2012 period. The peak sink is $-2.55 \text{ mmol m}^{-2} \text{ d}^{-1}$ in the summer of 2011. This is compared with a maximum sink of $-3.52 \text{ mmol m}^{-2} \text{ d}^{-1}$ in the summer of 2004 (which was also reported by Körtzinger, 2008).

Figure 5b shows weekly satellite wind speed data used to calculate the CO_2 flux. The wind speeds were similar in the two periods. Wind speeds peak before the peak in nitrate concentration and $p(CO_2)$ and this corresponds to an increase in convective

²⁵ mixing at the PAP-SO. There is an earlier period of days with high wind speeds towards the end of 2011 that can be compared with the CO_2 data presented. The average wind speed was 8.2 m s⁻¹ for both time periods. The maximum was 14 m s⁻¹, although in situ winds of up to 20 m s⁻¹ were seen from the Met Office data (eurosites.info/pap), this is not seen in the weekly averaged satellite wind speed data presented.



There is little variation in CO_2 flux and MLD between the years shown but for completeness the NAO index is shown in Fig. 5c. There is a large range in the winter NAO in the 2010/2011 winter when the NAO changed from -4 to +3. Also in the winter of 2011/2012 there was a relatively high NAO of +3. In contrast the 2003/2004 winter NAO was near zero and the 2004/2005 winter NAO was also low, between -2 to +1. Overall the range in the NAO values was smaller for the 2003 to 2005 time period shown.

4 Discussion

4.1 PAP-SO seasonal variation

- The 2003–2005 and 2010–2013 datasets show very similar seasonal patterns between the years. Concentrations of nitrate and DIC exhibit a seasonality, which varied inversely with temperature and MLD. The seasonal variation in nitrate and DIC concentrations is controlled by the convective mixing (resulting in the winter maximum) and biological uptake during the spring bloom period (resulting in the summer minimum).
- ¹⁵ The $p(CO_2)$ distribution pattern at the PAP-SO site is characterized by a single annual peak (high in winter and low in summer), which is similar to that of nutrient and DIC concentrations, but in antiphase to the temperature signal. Körtzinger et al. (2008) report a good comparison with a SOO route from Kiel, to the north of the Portsmouth to Caribbean route, for the 2003–2005 data. In this paper we show that the $p(CO_2)$ values
- ²⁰ for 2010–2012 are confirmed by SOO measurements, this time from the Portsmouth to the Caribbean route.

Jiang et al. (2013) compared seasonal carbon variability between different sites in the North Atlantic and suggested a latitudinal change in the $p(CO_2)$ seasonality from the temperature-dominated oligotrophic subtropical gyre to the subpolar region where

 $_{25}$ $p(CO_2)$ is dominated by changing concentrations of DIC. Our $p(CO_2)$ observations at the PAP-SO site show the subpolar-like seasonal pattern, which is similar to that of



the Ocean Weather Station M (Skjelvan et al., 2008). The surface $p(CO_2)$ at this site is mainly governed by the varying DIC concentration while the seasonal cooling and warming have a contrasting effect.

The time integrated uptake of DIC and nitrate during the spring bloom is reflected by
the slope of the linear regression between them (Fig. 4). The ratio of DIC and nitrate concentrations shows higher values than the Redfield C : N ratio of 6.6. For example the spring-time ratio of 12.7 (±4) was considerably higher than the Redfield ratio, in agreement with similar "carbon overconsumption" ratios seen for the North Atlantic (e.g. 14.2, Sambrotto et al., 1993). It is also in agreement with the single C : N ratio reported
previously at the PAP-SO of 11.0 (Körtzinger et al., 2008). We have demonstrated seasonal variation in the C : N ratio at the PAP-SO, with an autumn C : N value that is closer to the Redfield ratio (8.7±4) and large deviations from the Redfield ratio in

4.2 Air-sea CO₂ flux

winter.

- ¹⁵ Wind speeds have an indirect impact on the biogeochemistry, in particular the $p(CO_2)$. In the North Atlantic long-term wind speed values have been increasing and high wind events are generally starting earlier in the winter. Wind speeds are similar for the two time periods considered here. However there is some suggestion of an earlier increase in winds at the start of the 2011/2012 winter coinciding with an earlier increase in mixing (Fig. 5). Although the CO₂ flux is not linked linearly to the wind speed there is
- a corresponding decrease in CO_2 flux into the ocean at this time. There is also an early increase in $p(CO_2)$ and DIC concentrations as deeper water is mixed to the surface (Fig. 3).

It is well known that Northeast Atlantic is a strong CO_2 sink with large variability. The observations at the PAP-SO provide high frequency data to follow the variability in CO_2 exchange. The largest CO_2 flux shown here was in September 2004, as a combined result of low seawater $p(CO_2)$ and high wind speed (Fig. 2). Larger CO_2 flux into the ocean may have occurred in 2011 considering the large, early spring bloom seen in



that year but we do not have $p(CO_2)$ data to calculate the flux at that time. The average CO_2 flux is lower in the 2010–2012 period, although again this may be biased by the missing data in early 2011. However, increases in productivity do not necessarily result in enhanced oceanic CO_2 uptake as the gas exchange is also affected by other factors such as temperature and wind speed (Dumousseaud et al., 2010; Jiang et al., 2013). The average is similar for the years presented with values of $-1.52 \text{ mmol m}^{-2} \text{ d}^{-1}$ in 2003–2005 and $-1.36 \text{ mmol m}^{-2} \text{ d}^{-1}$ from 2010–2012.

4.3 PAP-SO inter-annual variations

The Gibraltar minus Iceland version of the NAO (North Atlantic Oscillation) index is really most applicable to the winter half of the year. During positive NAO periods, the PAP-SO region experiences subpolar-like conditions, with strong wind stress and deep mixed layers (Henson et al., 2012). However the MLD did not vary significantly at the PAP-SO between the 2003–2005 and 2010–2012 time periods shown here (with a range of only 215 to 257 m for deepest winter MLD between the years, when in previ-

- ous years such as 2009/2010 deep winter mixing of 390 m has been seen with an NAO reaching –3, not shown). So NAO is unlikely to have a large role as the PAP-SO winter sea surface temperature and MLD were similar in the time periods from 2003–2005 and 2010–2013. Data from a winter with deeper mixing would need to be put into the comparison to resolve this.
- However, there was a twofold decrease in nitrate concentrations in the 2004/05 winter despite sea surface temperature and MLD values being close to other years. The low values were confirmed by SOO data in Hartman et al. (2010). As discussed in Hartman et al. (2010) the lower winter nitrate concentration seen in 2004/2005 did not correlate with a decrease in the MLD and this showed the influence of horizon-
- tal mixing at the PAP-SO. It was suggested that lateral advection to the site at that time introduced a subtropical water mass with a lower nitrate concentration. Earlier time-series studies largely ignored circulation at the PAP-SO site, assuming convective mixing is a dominant process influencing mixed layer temperature and nitrate concen-



tration in the region (Williams et al., 2000; Körtzinger et al. 2008). However, fixed-point time-series observations are influenced by spatial variability passing the point of observation (McGillicuddy et al., 1998; Painter et al., 2010). It is clear from Hartman et al. (2010) that lateral advection cannot be ignored and may significantly influence the surface temperature and nitrate concentrations in the region of the PAP-SO site.

Both DIC and nitrate concentrations increase earlier in the winter at end of 2011 compared with 2004. This can be related to the earlier increase in the winter MLD at that time. Despite similar maximum winter MLD in 2003–2005 and 2010–2013, the timing and intensity of the spring bloom is also quite different. Additionally, the observed seawater $p(CO_2)$ increased from an average of 339 µatm in 2003 to 353 µatm in 2011. The cause of these differences requires further investigation.

5 Conclusions and further work

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We have presented recent year round surface time-series biogeochemical data at the PAP time-series observatory and compared it with previous observations. The surface $p(CO_2)$, and concentrations of DIC and nitrate, all show a clear seasonal cycle, which 15 is mainly controlled by winter convective mixing and biological activity in the spring bloom. However the suggestion that inter-annual variability is dominated by convection (Bennington et al., 2009) is not clear as the MLD did not vary significantly between the winter periods shown. An especially low winter nitrate concentration in 2005 was observed thought to be due to surface advection and this highlights the need to con-20 sider advection when dealing with time series data. Despite the similar winter physical conditions (temperature and MLD), the differences in timing and intensity of the spring blooms requires further investigation. At the PAP-SO, increasing mean seawater $p(CO_2)$ from 2003 to 2011 (339 ± 17 µatm to 353 ± 15 µatm) was observed. The mean air-sea CO₂ flux did not show a significant change $(-1.52 \pm 0.7 \text{ mmol m}^{-2} \text{ d}^{-1} \text{ to})$ 25 $-1.36 \pm 0.6 \,\mathrm{mmol}\,\mathrm{m}^{-2}\,\mathrm{d}^{-1}$).



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

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Figure 1. Map of the inter-gyre region of the Northeast Atlantic showing the position of the PAP observatory (black diamond) and the ship of opportunity programme (SOO) sampling positions (red circles) from 2010 to 2012.

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





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





Figure 4. The relationship between concentrations of DIC and nitrate at the PAP-SO in 4 different seasons (Winter: January–March, red squares; Spring: April-June, green triangles and green line; Summer: July-September, blue diamonds; Autumn: October to December, dark blue crosses and blue line), showing the Redfield ratio 6.6 (dashed line) for reference.





Figure 5. PAP-SO data from 2003–2005 (blue circles) and 2010–2012 (red diamonds) follow (red diamonds) with the following text – with vertical lines to represent the start of each year showing: **(a)** calculations of weekly sea-to-air CO_2 flux (negative: into the ocean); **(b)** weekly satellite wind speed data; **(c)** the monthly NAO index.

