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The seasonal cycle of δ^3C_{DIC} in the North Atlantic subpolar gyre

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Abstract. This study introduces for the first time the $\delta^{13}C_{DIC}$ seasonality in the North Atlantic subpolar gyre (NASPG) using $\delta^{13}C_{DIC}$ data obtained in 2005–2006 and 2010–2012 with dissolved inorganic carbon (DIC) and nutrient observations. On the seasonal scale, the NASPG is characterized by higher $\delta^{13}C_{DIC}$ values during summer than during winter, with a seasonal amplitude between 0.70 ± 0.10 ‰ (August 2010–March 2011) and 0.77 ± 0.07 ‰ (2005–2006). This is mainly attributed to photosynthetic activity in summer and to a deep remineralization process during winter convection, sometimes influenced by ocean dynamics and carbonate pumps. There is also a strong and negative linear relationship between $\delta^{13}C_{DIC}$ and DIC during all seasons. Winter data also showed a large decrease in $\delta^{13}C_{DIC}$ associated with an increase in DIC between 2006 and 2011–2012, but the observed time rates (-0.04 ‰ yr^{-1}and $+1.7$ µmol kg^{-1} yr^{-1}) are much larger than the expected anthropogenic signal.

1 Introduction

The stable isotopic composition of dissolved inorganic carbon (DIC) in the ocean is a useful semi-conservative tracer for various oceanic analysis (e.g., water masses, paleocirculation) and global carbon studies (constraint for the global carbon budget, interpreting anthropogenic carbon). This is reported relative to the reference V-PDB (Vienna–Pee Dee Belemnite) in terms of $\delta^{13}C$ in ‰ (Craig, 1957):

$$\delta^{13}C = \left[\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{reference}} - 1 \right] \times 1000. \quad (1)$$

The mean annual large-scale distribution of this tracer is now relatively well documented at the sea surface and at depth. Values range typically between 0.5 ‰ and 2.5 ‰ in the modern surface ocean (Gruber et al., 1999). Regular observations conducted since the 1970s–1980s at a few time series stations or repetitive tracks were used to describe and interpret its temporal variability. In subtropical oceanic regions, the seasonal $\delta^{13}C$ amplitude of 0.2–0.3 ‰ at the BATS (Bermuda Atlantic Time series) station and of 0.1 ‰ at the ALOHA station (Pacific time series north of Hawaii) reflect the local balance between air–sea CO_2 exchange, biological activity and vertical mixing (Gruber et al., 1998, 1999; Gruber and Keeling, 1999; Quay and Stutsman, 2003). This is also observed in the Southern Indian Ocean, with a seasonal $\delta^{13}C$ amplitude of 0.3 ‰ in the western part of the basin (Racapé et al., 2010), whereas it reaches 0.45 ‰ south of Tasmania (McNeil and Tilbrook, 2009). Studies have also highlighted a significant decrease in $\delta^{13}C_{DIC}$, attributed to the anthropogenic CO_2 uptake in the ocean. This results from human-induced perturbations that reduce the $\delta^{13}CO_2$ in the atmosphere with a time rate of change of -0.024 ‰ yr^{-1} (estimate for the 1985–2008 period with the Alert station data set; Keeling et al., 2010), as the combustion of the organic carbon pool produces CO_2 gas that is strongly depleted in the heavy carbon isotope (^{13}C). This signal, known as the oceanic ^{13}C Suess effect, provides an additional constraint to estimate the anthropogenic carbon uptake in the ocean.

This has been estimated as less than -0.007 ‰ yr^{-1} in polar regions (McNeil et al., 2001; Olsen et al., 2006; Sonnerup and Quay, 2012) and as large as -0.025 ‰ yr^{-1} in subtropical regions (Bacastow et al., 1996; Gruber et al., 1999; Sonnerup and Quay, 2012). The high latitudes of the North Atlantic Ocean are considered to be one of the strongest anthropogenic CO_2 sinks, a consequence of the large heat loss and deep convection during winter as well as strong biological activity during spring and summer. In this region, the temporal variability (seasonal to decadal) of the $\delta^{13}C_{DIC}$ still needs to be investigated. The winter–summer difference is expected to be as large as 1 ‰ (Gruber et al., 1999), which could potentially mask the oceanic ^{13}C Suess effect in surface water (McNeil et al., 2001). In this context, this study introduces for the first time the $\delta^{13}C_{DIC}$ seasonality in the North Atlantic subpolar gyre using $\delta^{13}C_{DIC}$ surface data obtained in 2005–2006 and 2010–2012 from merchant vessels *Skogafoss* and *Reykjafoss* (14 cruises) along with DIC and nutrient measurements. Driving processes will be identified from isotopic data and from the semi-quantitative tracer ($\Delta\delta^{13}C_{bio}$) of Gruber et al. (1999), which enables us to isolate the biological contribution to the seasonal amplitude from the physical contributions (e.g., air–sea gas exchange fractionation, ocean dynamics). The time rate of change in $\delta^{13}C_{DIC}$ will be investigated over the short period of 5 to 7 years and compared to other regions.

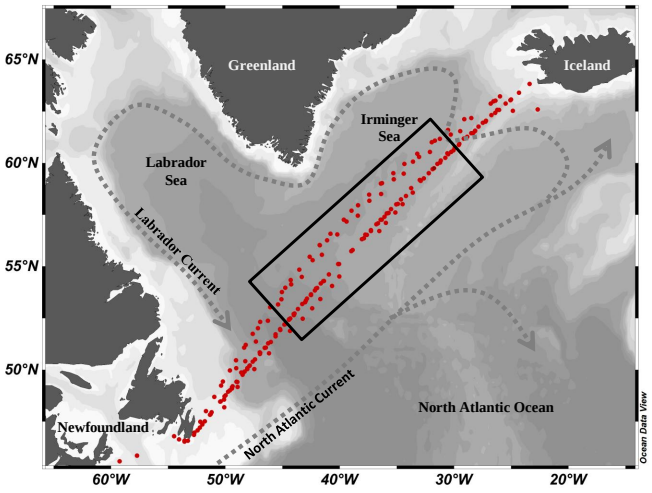

Fig. 1. Cruises track where $\delta^{13}C_{DIC}$ was sampled in 2005–2006 and 2010–2012 (red dots). Dashed lines indicate schematically surface main currents in the North Atlantic Ocean. The interior of the North Atlantic subpolar gyre (NASPG, 53° N–62° N), our study area, is delimited by the black box.

2 Materials and methods

2.1 Data collection

Data used in this study were collected in the North Atlantic subpolar gyre, mostly from merchant vessels *Skogafoss* and *Reykjafoss* between Iceland and Newfoundland (Fig. 1) over two periods in 2005–2006 and 2010–2012. This is part of sampling efforts carried from vessels of opportunity within the SURATLANT project initiated in 1993. The sampling periods for each cruise and vessel are summarized in Table 1.

During all cruises, seawater was pumped from a depth of $\sim$ 3–5 m, depending on the ship. Sea surface salinity (SSS) was from discrete salinity samples. Sea surface temperature (SST) was either from the continuously recording ThermoSalinoGraph (TSG seabird Electronics, Inc. USA, model 21) corrected for an average bias to sea surface temperature, or from nearly simultaneous XBT temperature profiles (at 3 m). SST and SSS accuracies were estimated at 0.2 °C and 0.01, respectively. $\delta^{13}C_{DIC}$, DIC and nitrate concentrations (NO_3^-) were also obtained from discrete samples collected every 4 h and analyzed later in land laboratories. Over the 2005–2006 period, DIC concentrations were estimated manometrically during the acid CO_2 extraction procedure for $\delta^{13}C_{DIC}$ measurements from the helium stripping technique. This analytical method has been described previously by Quay et al. (1992, 2003). These measurements have an accuracy of ± 0.02 ‰ for $\delta^{13}C_{DIC}$ based on a helium stripping technique adapted from the one used by Kroopnick (1974) and ± 5 µmol kg^{-1} for DIC, based on a comparison to coulometric DIC values and to the Certified Reference Material (CRM) provided by Prof. A. Dickson (Scripps Institution of Oceanography, San Diego, USA). Over the 2010–2012 period during the SURATLANT cruises, $\delta^{13}C_{DIC}$ were measured via an acid CO_2 extraction method in a vacuum system developed by Kroopnick (1974), whereas DIC were determined at the same time as total alkalinity (Alk) by a potentiometric titration derived from the method developed by Edmond (1970) using a closed cell and a CRM calibration. Further details on the sampling methods and analytical techniques are provided in Racapé et al. (2010, 2013) for $\delta^{13}C_{DIC}$ and in Corbière et al. (2007) for DIC. Both parameters were analyzed at the LOCEAN-IPSL Laboratory (Paris, France). $\delta^{13}C_{DIC}$ values have a precision of ± 0.01 ‰ (Vangriesheim et al., 2009) and a reproducibility of ± 0.02 ‰, whereas DIC concentrations have an accuracy of ± 3 µmol kg^{-1}. Finally, nutrient concentrations were measured for all cruises with standard colorometric methods at the Marine Research Institute (Reykjavik, Iceland). The analytical procedure and the quality control for the nutrient analyses have been described in detail in Olafsson et al. (2010), where the long-term accuracy has been estimated as ± 0.2 µmol L^{-1} for nitrate and silicate, and ± 0.03 µmol L^{-1} for phosphate.

2.2 $\Delta\delta^{13}C_{bio}$ and $\delta^{13}C_{phys}$ estimation

To determine the major process driving the seasonal $\delta^{13}C_{DIC}$ distribution ($t_1 \rightarrow t_2$), we used two isotopic and semi-quantitative tracers, noted $\Delta\delta^{13}C_{bio}$ and $\Delta\delta^{13}C_{phys}$, which

Table 1. Summary of sampling periods conducted on board the merchant vessels *Skogafoss* and *Reykjafoss* between Reykjavik (64° N, Iceland) and Newfoundland (47° N, Canada) over the 2005–2006 and 2010–2012 periods, respectively. The average values of $\delta^{13}C_{DIC}$, DIC and salinity normalized DIC (nDIC) as well as their standard deviation (SD) were estimated for the interior of the North Atlantic subpolar gyre (NASPG 53° N–62° N). The number of data (n) used to calculate these mean values are indicated in the last column.

	NASPG (53° N–62° N)				
	Date	Mean $\delta^{13}C_{DIC} \pm$ SD (‰)	Mean DIC $\pm$ SD ($\mu mol\,kg^{-1}$)	Mean nDIC $\pm$ SD ($\mu mol\,kg^{-1}$)	n
M/V *Skogafoss*	23 to 27 Jul 2005	1.65 ± 0.10	2077.4 ± 10.0	2093.6 ± 5.3	15
	17 to 24 Sep 2005	1.46 ± 0.11	2089.9 ± 9.3	2107.9 ± 4.3	8
	12 to 16 Nov 2005	1.06 ± 0.07	2120.7 ± 10.6	2137.7 ± 9.7	16
	7 to 11 Feb 2006	0.87 ± 0.05	2142.4 ± 4.5	2144.1 ± 7.3	20
	18 to 28 Apr 2006	0.90 ± 0.09	2137.7 ± 8.5		12
	25 to 27 Jun 2006	1.64 ± 0.08	2058.7 ± 8.4	2094.9 ± 9.1	4
	11 to 15 Nov 2006	0.99 ± 0.12	2114.3 ± 11.6	2118.6 ± 10.3	13
M/V *Reykjafoss*	21 to 25 Aug 2010	1.36 ± 0.11	2054.4 ± 9.9	2074.0 ± 9.2	21
	15 to 19 Dec 2010	0.97 ± 0.10	2114.6 ± 7.6	2131.2 ± 5.3	11
	13 to 18 Mar 2011	0.66 ± 0.08	2149.4 ± 5.9	2150.8 ± 6.3	15
	16 to 20 Dec 2011	0.69 ± 0.05	2150.6 ± 4.1	2151.0 ± 6.9	23
	11 to 13 Mar 2012	0.61 ± 0.04	2152.5 ± 2.4	2152.1 ± 9.5	16
	30 Jun to 4 Jul 2012	1.28 ± 0.09	2089.7 ± 9.1	2100.4 ± 17.2	11
	21 to 25 Sep 2012	1.33 ± 0.12	2095.7 ± 13.5	2115.6 ± 5.0	13

reveal the biological and physical signatures, respectively, as shown by Eqs. (2) and (3).

$$DIC^{t_2}(\delta^{13}C^{t_2}_{DIC}) = DIC^{t_1}(\delta^{13}C^{t_1}_{DIC}) + \left[\Delta DIC(\delta^{13}C)\right]^{t_1\to t_2}_{bio} + \left[\Delta DIC(\delta^{13}C)\right]^{t_1\to t_2}_{phys} \quad (2)$$

$$\delta^{13}C^{t_2}_{DIC} = \frac{DIC^{t_1}}{DIC^{t_2}}(\delta^{13}C^{t_1}_{DIC}) + \Delta\delta^{13}C^{t_1\to t_2}_{bio} + \Delta\delta^{13}C^{t_1\to t_2}_{phys}. \quad (3)$$

Described by Gruber et al. (1999), the biological processes contribution ($\Delta\delta^{13}C_{bio}$) results from the combined photosynthesis, respiration and remineralization processes (the soft-tissue pump) as well as the formation–dissolution of the calcium carbonate shells (the carbonate pump). In this study, the $\Delta\delta^{13}C_{bio}$ will be expressed according to observed biogeochemical conditions from one month or season (t_1) to another one (t_2) by Eq. (4), with the stoichiometric carbon–nitrate ratio ($r_{c:n}$) of 117 : 16 from Anderson and Sarmiento (1994), the $\delta^{13}C$ value of the carbonate ($\delta^{13}C_{carb}$) of 2 ‰ like Gruber et al. (1999), and the $\delta^{13}C$ value of organic matter ($\delta^{13}C_{org}$) of −24 ‰ from Goericke and Fry (1994). This last value depicts the average for the northern North Atlantic where sea surface temperature is around 10 °C in summer.

$$\Delta\delta^{13}C^{t_1\to t_2}_{bio} = r_{c:n} \times \delta^{13}C_{org} \times \frac{\left(NO_3^{t_2} - NO_3^{t_1}\right)}{DIC^{t_2}} + \delta^{13}C_{carb} \times \frac{\left(Alk^{t_2} - Alk^{t_1} + NO_3^{t_2} - NO_3^{t_1}\right)}{2DIC^{t_2}} \quad (4)$$

As the $\delta^{13}C$ variation associated with the carbonate pump (< 0.02 ‰ of the measurement error) does not contribute much to the biological signature, this mechanism will be afterwards neglected.

According to Eq. (3), the physical processes contribution (air–sea CO_2 exchange fractionations and ocean dynamics; $\Delta\delta^{13}C_{phys}$) corresponds to the difference between the $\delta^{13}C_{DIC}$ at t_2 and the expected $\delta^{13}C_{DIC}$ if biological activity was the only process controlling the t_1 to t_2 distribution. This is expressed in Eq. (5).

$$\Delta\delta^{13}C^{t_1\to t_2}_{phys} = \delta^{13}C^{t_2}_{DIC} - \left(\frac{DIC^{t_1}}{DIC^{t_2}}(\delta^{13}C^{t_1}_{DIC}) + \Delta\delta^{13}C^{t_1\to t_2}_{bio}\right). \quad (5)$$

As t_1 to t_2 DIC change due to physical and biological processes (up to 100 $\mu mol\,kg^{-1}$) is lower than the mean DIC concentration observed in the surface water of this region (between 2050 and 2150 $\mu mol\,kg^{-1}$), we assume that DIC^{t1}/DIC^{t2} equals 1.

3 Results and discussion

3.1 Surface $\delta^{13}C_{DIC}$ distribution

During each transect, surface $\delta^{13}C_{DIC}$ is distributed according to a north–south gradient, with an amplitude between 0.2 ‰ and 0.4 ‰ depending on the season and with higher values close to the Newfoundland coast (up to 1.8 ‰; Fig. 2, bottom panel). This is opposite to the DIC distribution

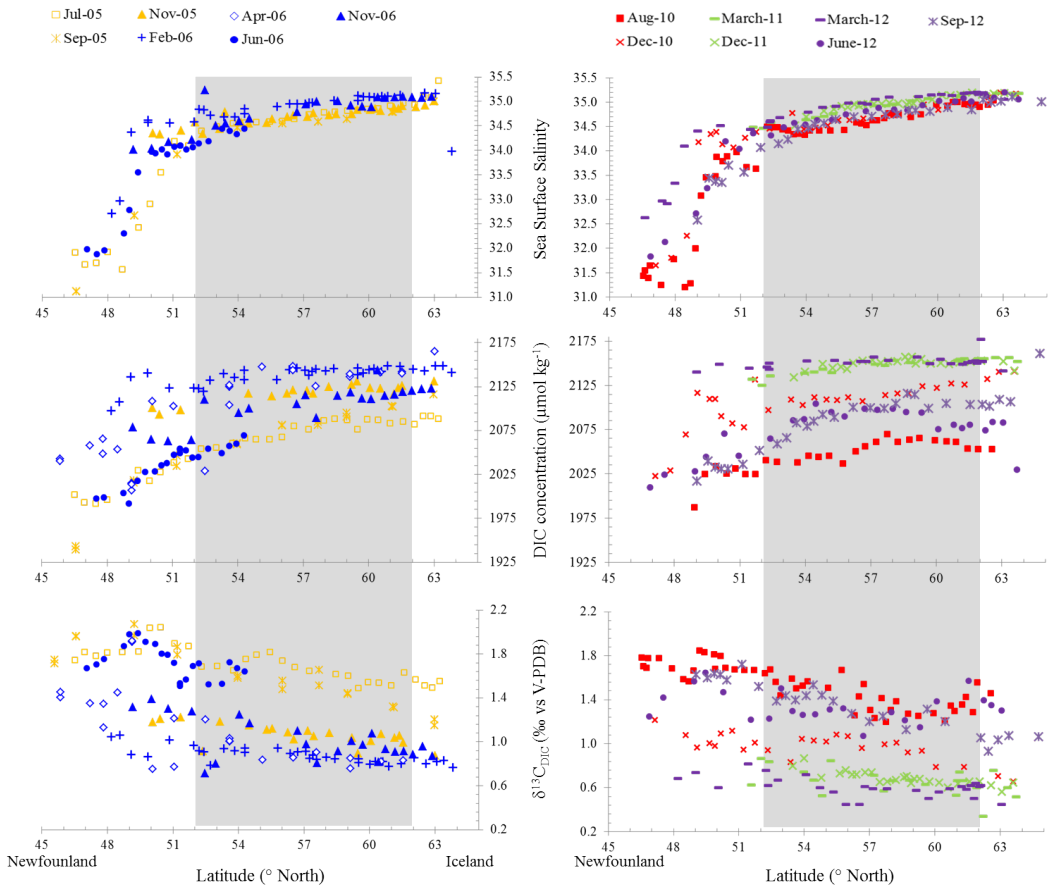

Fig. 2. Surface distribution of salinity (top panel), dissolved inorganic carbon concentration (DIC, middle panel) and $\delta^{13}C_{DIC}$ (bottom panel) between Reykjavik (Iceland, 64° N) and Newfoundland (Canada, 47° N) over the periods 2005–2006 (left panel) and 2010–2012 (right panel). The interior of the North Atlantic subpolar gyre (NASPG, 53° N–62° N), our study area, is delimited by the light grey box. Any salinity measurements are realized in April 2006. August 2010 (full red square) distinguishes itself by a lower DIC concentration observed over both periods but without higher $\delta^{13}C_{DIC}$ values.

(variation up to 100 µmol kg^{-1}; Fig. 2, middle panel), which increases northward as observed previously by Corbière et al. (2007). These authors have also shown that the area south of 53° N was characterized by large spatial variability in SSS (Fig. 2, top panel), SST, DIC (Fig. 2, bottom panel) and nutrient concentrations when crossing the Labrador Current and approaching the Newfoundland coast (Fig. 1). Influence of coastal waters was also identified north of 62° N near Iceland and on $\delta^{13}C_{DIC}$ distribution (Fig. 2, bottom panel). Thus, we selected a region where both hydrological and carbon properties (including $\delta^{13}C_{DIC}$) are much more homogeneous between 53° N and 62° N, which corresponds to the interior of the North Atlantic subpolar gyre, denoted NASPG, west of the Reykjanes Ridge.

In the NASPG, the $\delta^{13}C_{DIC}$ meridional gradient is weaker (close to 0.1 ‰). Highest values were observed during summer (up to 1.65 ± 0.10 ‰ in 2005–2006 and 1.36 ± 0.11 ‰ in 2010–2012), while minima were measured during winter (down to 0.87 ± 0.05 ‰ in 2005–2006 and 0.61 ± 0.04 ‰ in 2010–2012, Fig. 2, bottom panel and Table 1). Compared to 2005–2006, $\delta^{13}C_{DIC}$ values collected in 2010–2012 are lower, suggesting a potential impact of anthropogenic carbon uptake. This would then require the correction of $\delta^{13}C_{DIC}$ observations by this anthropogenic signal to compose the "climatological" seasonal cycle. If this change in $\delta^{13}C_{DIC}$ (decrease) represents the oceanic ^{13}C Suess effect only, this should also be observed on DIC, with an expected theoretical increase of 5–7 µmol kg^{-1} in winter (Corbière et al., 2007; Metzl et al., 2010).

3.2 $\delta^{13}C_{DIC}$ versus DIC in NASPG

Figure 3a highlights a strong and negative link between $\delta^{13}C_{DIC}$ and DIC concentration in the NASPG over both sampling periods. Lower $\delta^{13}C_{DIC}$ in winter are associated with higher DIC concentrations, conversely for summer. According to this figure, August 2010 is clearly outside the general trend observed here. This is a linear relationship from winter to winter, nevertheless with a difference in the values

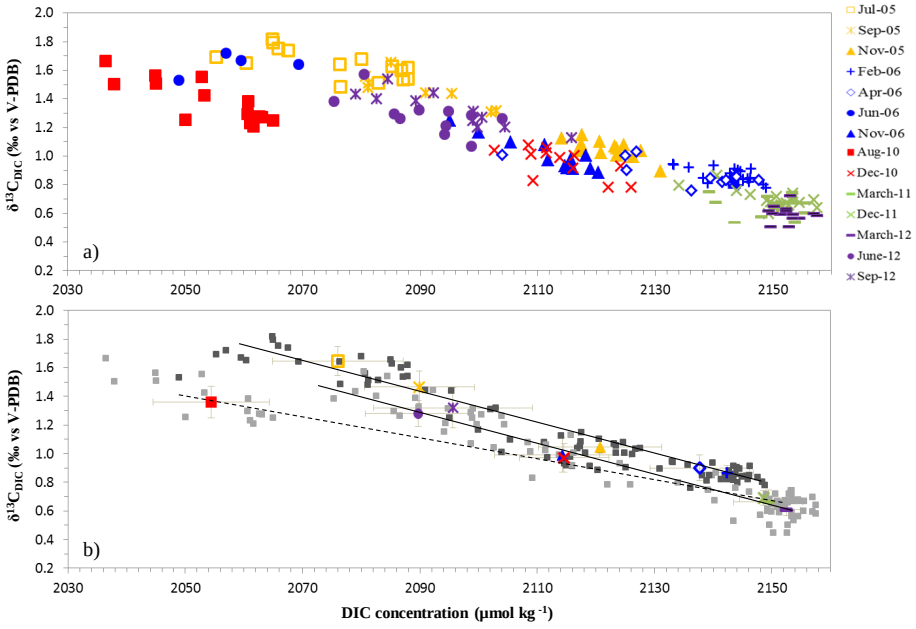

Fig. 3. (a, b) $\delta^{13}C_{DIC}$ versus dissolved inorganic carbon (DIC) concentration collected in the surface waters of the North Atlantic subpolar gyre (NASPG, 53° N–62° N) in 2005–2006 and 2010–2012. **(b)** Dark grey squares represent the 2005–2006 data set, light grey squares symbolize the 2010–2012 data set and colored symbols (like the Fig. 3a legend) show mean values (and standard deviation) of $\delta^{13}C_{DIC}$ and DIC concentration for each sampling period, but without June 2006 because only four data were sampled in the south of the transect. The linear regressions indicated with dark lines were estimated for the periods from July 2005 to June 2006 and from March 2011 to September 2012 (from the bottom up: $y - 0.0108x + 23.81$, $r^2 = 0.95$ and $y = -0.0108x + 24.10$, $r^2 = 0.94$), and with dashed lines were estimated for the period from August 2010 to March 2011 ($y - 0.007x + 16.58$, $r^2 = 0.94$).

detected between all data collected in 2005–2006, except for November 2006 and those sampled in 2010–2012. If we focus on the winter data set (February–March) like Corbière et al. (2007) and Metzl et al. (2010), we notice an increase in DIC by 7 to 10 µmol kg^{-1} over the 5- to 6-year period. This is much larger than those expected from the anthropogenic effect (∼ 5–7 µmol kg^{-1}). To remove natural variation due to a potential salinity anomaly (Fig. 2, top panel), we evaluated the trend for salinity normalized DIC (nDIC reported in Table 1) of 1.3 µmol kg^{-1} yr^{-1} during this period (the 5- to 6-year period). This suggests a significant additional contribution of the natural variability, thus masking the impact of the anthropogenic carbon uptake in the NASPG region. This comment is supported by the observed time rates of change in $\delta^{13}C_{DIC}$ (−0.04 ‰ yr^{-1}) that are much larger than those observed by Quay et al. (2007) in the NASPG (−0.017 ‰ yr^{-1} over the 1993–2007 period), Sonnerup and Quay (2012) in the Labrador Sea (−0.014 ‰ yr^{-1} over the 1970–1995 period), Olsen et al. (2006) in the Nordic seas (up to −0.024 ‰ yr^{-1} over the 1981–2003 period) and by Keeling et al. (2010) in the atmosphere (−0.024 ‰ yr^{-1} over the 1985–2008 period). As the residence time of the surface water (∼ 1 yr) is shorter than the time needed for CO_2 to reach isotopic equilibrium with the atmosphere (∼ 10 yr; Broecker and Peng, 1974; Lynch-Stieglitz et al., 1995), this large decrease in $\delta^{13}C_{DIC}$ cannot be attributed to the anthropogenic signal only. In addition, the mixed layer depth time series depicted in Fig. 4b reveals two winter episodes, with the deepest layers between 2005 and 2012, which should be associated with a higher $DI^{12}C$ input of subsurface water, thus contributing to the $\delta^{13}C_{DIC}$ decrease during this period (and DIC increase). As we suspect a large impact of the natural variability that we cannot estimate, observations are not corrected for an anthropogenic signal and the mean $\delta^{13}C_{DIC}$ seasonal cycle will be composed for each detected period.

Study of the relationships between $\delta^{13}C_{DIC}$ and DIC over both sampling periods reveals, in fact, another important signal to compose and interpret the $\delta^{13}C_{DIC}$ seasonal cycle. According to Fig. 3b, observations are actually distributed within three periods: from July 2005 to June 2006, August 2010 to March 2011 and from March 2011 to September 2012. These are characterized by the following linear regressions (Eqs. 6 to 8):

From July 2005 to June 2006,

$$\delta^{13}C_{DIC}^{2005-2006} = -0.0108 \times [DIC] + 24.10;$$
$$r^2 = 0.94;\ \text{slope error} = 3.3 \times 10^{-4}. \quad (6)$$

From August 2010 to March 2011,

$$\delta^{13}C_{DIC}^{\text{August 2010–March 2011}} = -0.0074 \times [DIC] + 16.58;$$
$$r^2 = 0.94;\ \text{slope error} = 3.1 \times 10^{-4}. \quad (7)$$

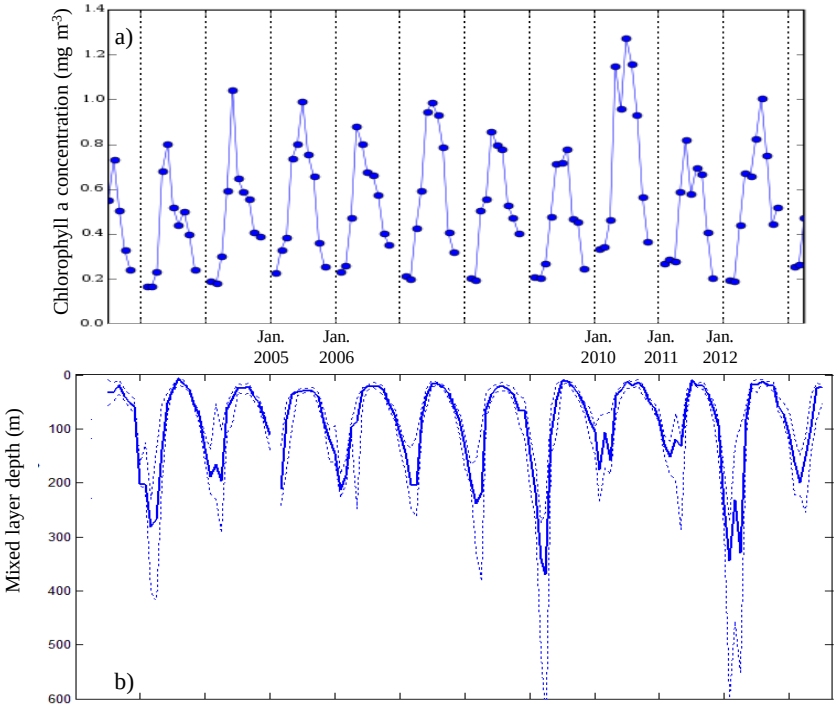

Fig. 4. Distribution of **(a)** chlorophyll *a* concentration from MODIS-Aqua 4 km (disc.sci.gsfc.nasa.gov/giovanni, time series generated between 44° W–27° W and 53° N–62° N) and of **(b)** mixed layer depth (MLD, m) from Argo-float observations in NASPG. The MLD is estimated on each profile as the depth at which temperature deviates by 0.1 °C from the temperature at 5 m. The full line represents the median depth, whereas the dashed lines correspond to the first and third quartiles.

From March 2011 to September 2012

$$\delta^{13}C_{DIC}^{2011-2012} = -0.0108 \times [DIC] + 23.81;$$
$$r^2 = 0.95; \quad \text{slope error} = 2.9 \times 10^{-4}. \qquad (8)$$

Based on a Student's *t* test and its associated error, there is no significant difference between the slopes of regression 1 (Eq. 6) and 3 (Eq. 8). These are also equivalent to those expected if the soft-tissue pump (photosynthesis/respiration/remineralization) were the only mechanism affecting DIC and $\delta^{13}C_{DIC}$ seasonal distributions (-0.011 ‰ (µmol kg^{-1})$^{-1}$ with $\delta^{13}C_{org}$ of -24 ‰ and $r_{c:n}$ of 117 : 16). As a result, the slope of regression 2 (Eq. 7), estimated from August 2010 to March 2011, is significantly different from the other two (-0.007 ‰ (µmol kg^{-1})$^{-1}$). This is influenced by the August 2010 DIC values that are the lowest concentrations reported in this study (Table 1, as well as for nDIC) but are not associated with the highest $\delta^{13}C_{DIC}$ as expected. Indeed, high productivity recorded in the whole region during the summer of 2010 (Fig. 4a) would explain the low DIC values (2054.40 ± 9.92 µmol kg^{-1}, Table 1) but, according to previous results, an enhanced photosynthetic activity would increase $\delta^{13}C_{DIC}$ linearly with a ratio of -0.011 ‰ (µmol kg^{-1})$^{-1}$ to reach a maximum value. This suggests that additional processes also contribute to DIC and $\delta^{13}C_{DIC}$ seasonal distributions during this period, thus changing their relationship. The estimate of the isotopic tracers ($\Delta\delta^{13}C_{bio}$ and $\Delta\delta^{13}C_{phys}$) might be clarified to interpret this peculiar situation.

3.3 $\delta^{13}C_{DIC}$ seasonal cycle and driving processes in NASPG

3.3.1 The period July 2005–June 2006

Based on satellite information (the monthly SST composite of MODIS Aqua 9 km, disc.sci.gsfc.nasa.gov/giovanni), the SURATLANT data set (NO_3^- and DIC) and Eq. (6), we built the climatological seasonal cycle of SST, NO_3^-, DIC and $\delta^{13}C_{DIC}$ for 2005–2006 (Fig. 5). Because DIC concentrations have slightly changed during this period (by less than the climatological cycle standard deviation; Corbière et al., 2007; Ullman et al., 2009), we chose to consider the available DIC (and NO_3^-) data set sampled between 2001 and 2006, which is much more complete for composing the seasonality. The observations collected on board M/V *Skogafoss* during this period fit well within this climatology (Fig. 5b and c).

Figure 5 thus reveals the mean seasonal cycle for $\delta^{13}C_{DIC}$ in 2005–2006, with an amplitude of 0.77 ± 0.07 ‰, in phase with SST (6 °C) and in opposite phase with NO_3^- (9 µmol kg^{-1}) and DIC (70 µmol kg^{-1}). Minima are observed in February–March, whereas maxima are estimated

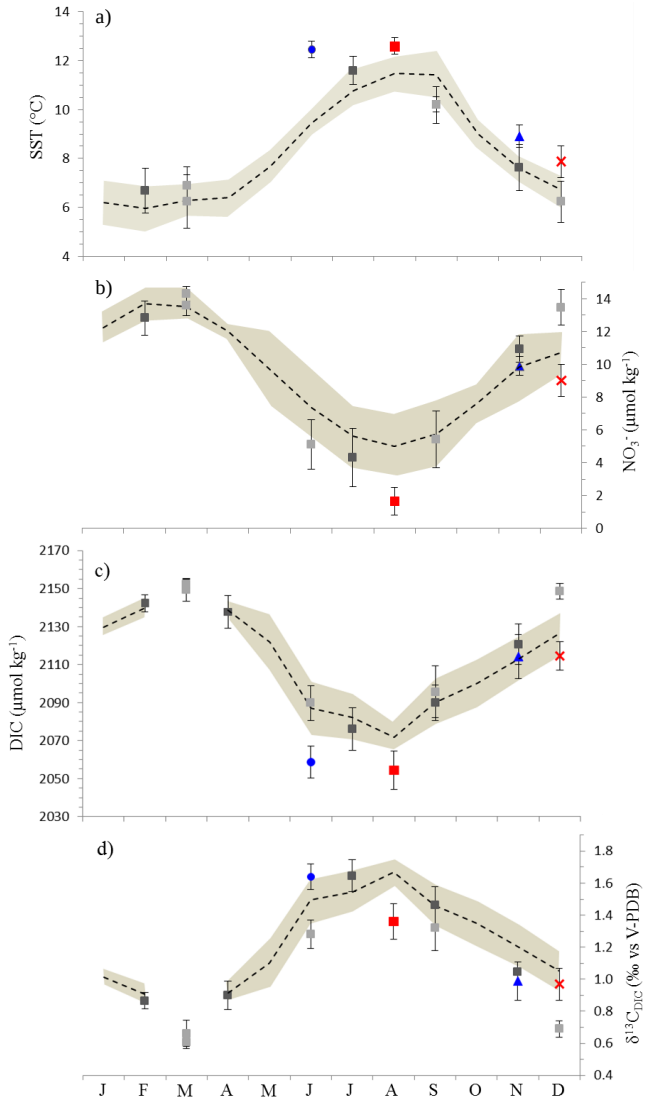

Fig. 5. Mean seasonal cycle of **(a)** sea surface temperature (SST), **(b)** nitrate (NO_3^-), **(c)** dissolved inorganic carbon (DIC), and **(d)** $\delta^{13}C_{DIC}$ in the surface waters of the NASPG (53° N–62° N). Light grey squares (and standard deviation) symbolize the 2010–2012 data set, whereas dark grey squares (and standard deviation) represent the 2005–2006 data set. Black dashed curves and their standard deviation were established from **(a)** the MODIS-aqua data set recorded in 2005–2006 (monthly composite with a spatial resolution of 9 km, generated by NASA's Giovanni, disc.sci.gsfc.nasa.gov/giovanni), **b** and **c**) both NO_3^- and DIC measurements collected during SURATLANT cruises between 2002 and 2006 and **(c)** from the 2005–2006 $\delta^{13}C_{DIC}$–DIC relationship presented in Fig. 3b. Anomalies are identified by colored symbols following the legend of Fig. 3a.

in August during the summer bloom (Antoine et al., 2005; Corbière et al., 2007). Based on Eqs. (4) and (5), processes controlling this seasonality could be identified. Table 2 summarizes the results. The standard deviation displays the meridional gradient reported previously. Positive $\Delta\delta^{13}C_{bio}$ is associated with phytoplankton activity, which preferentially uses the light carbon isotope during the photosynthetic mechanism ($\Delta NO_3^{W\rightarrow S} < 0\,\mu mol\,kg^{-1}$, nutrient consumption), whereas negative $\Delta\delta^{13}C_{bio}$ highlights the remineralization process, which releases much more $DI^{12}C$ ($\Delta NO_3^{W\rightarrow S} > 0$, nutrient input). Based on 2005–2006 values (Fig. 5), we estimate a $\Delta\delta^{13}C_{bio}$ of 0.74 ± 0.12 ‰ for the winter to summer amplitude of 0.77 ± 0.07 ‰. During this period, the $\delta^{13}C_{DIC}$ seasonality observed in the NASPG surface waters is largely controlled by biological activity, which increased $\delta^{13}C_{DIC}$ values during summer (photosynthesis) and decreased them during winter (remineralization). These high concentrations of NO_3^- and DIC related to remineralization are attributed to the winter entrainment of subsurface water (Takahashi et al., 1993).

According to the previous section, data from November 2006 do not get into line with other data collected in 2005–2006. Results obtained from isotopic tracers indicate that physical processes also contribute to controlling the $\delta^{13}C_{DIC}$ and DIC distributions from summer to November 2006 ($\Delta\delta^{13}C_{phys} = -0.23 \pm 0.15$ ‰; Table 2). As no anomaly was detected in November 2006 (e.g., SST, MLD), this is difficult to assess further.

3.3.2 The period August 2010–March 2011

There were only three cruises conducted between August 2010 and March 2011 (Table 1), but $\delta^{13}C_{DIC}$ were measured during winter and summer, when maximal and minimal values are expected. According to this comment, we cannot compose the mean $\delta^{13}C_{DIC}$ seasonal cycle for this period but, we can evaluate a seasonal amplitude of 0.70 ± 0.10 ‰ for $\delta^{13}C_{DIC}$ and of $92.9 \pm 5.9\,\mu mol\,kg^{-1}$ for DIC concentration. The biological and physical $\delta^{13}C_{DIC}$ signature estimated from summer 2010 to winter 2011 is much higher (-0.97 ± 0.06 ‰ and 0.27 ± 0.13 ‰, respectively; Table 2) than those obtained from the 2005–2006 data set. This is in agreement with the hypothesis of high productivity that is masked by additional processes.

The extensive winter mixed layer observed in 2009 (Fig. 4b) could have lowered $\delta^{13}C_{DIC}$ at the sea surface and persisted through to August 2010. The lack of $\delta^{13}C_{DIC}$ measurements in the winter of 2010 precludes estimating $\Delta\delta^{13}C_{phys}$ directly. If photosynthesis were the only process controlling the seasonal amplitude, as was observed during the 2005–2006 cycle, the $\delta^{13}C_{DIC}$ values of the winter of 2010 would be around 0.36 ‰ ($\delta^{13}C_{DIC}^{August\ 2010} + \Delta\delta^{13}C_{bio}^{W\rightarrow August\ 2010} = 1.36$–$1.00$). However, such low values have not yet been observed in the NASPG (Quay et al., 2007; Racapé et al., 2013) and are unlikely.

The NASPG also experienced a significant anomalous warming (+2 °C) during 2010. According to Zhang et al. (1995), a warming of 2 °C would decrease $\delta^{13}C_{DIC}$ by

Table 2. Seasonal (t_1 to t_2) amplitude of $\delta^{13}C_{DIC}$ ($\Delta\delta^{13}C_{DIC}$) and their standard deviation (SD). The biological and physical contributions ($\Delta\delta^{13}C_{bio}$ and $\Delta\delta^{13}C_{phys}$, respectively) for the 2005–2006 and 2010–2012 periods estimated from Eqs. (4) and (5).

t_1	to	t_2	$\Delta\delta^{13}C_{DIC} \pm$ SD (‰)	$\Delta\delta^{13}C_{bio} \pm$ SD (‰)	$\Delta\delta^{13}C_{phys} \pm$ SD (‰)
2005–2006 period					
Mean Feb	to	mean Aug	0.77 ± 0.07	0.74 ± 0.12	0.03 ± 0.14
of black dashed curves in Fig. 5					
Mean Aug	to	Nov 2006	-0.65 ± 0.14	-0.42 ± 0.10	-0.23 ± 0.15
2010–2012 period					
Mar 2010	to	Aug 2010	NA	1.00 ± 0.10	NA
Aug 2010	to	Dec 2010	-0.44 ± 0.09	-0.61 ± 0.11	0.18 ± 0.11
Aug 2010	to	Mar 2011	-0.70 ± 0.10	-0.97 ± 0.06	0.27 ± 0.13
Mar 2012	to	Jun 2012	0.68 ± 0.14	0.76 ± 0.11	-0.08 ± 0.12

0.2 ‰ at the isotopic equilibrium conditions, thus masking the biological signal on $\delta^{13}C_{DIC}$. In the subpolar region, the surface $\delta^{13}C_{DIC}$ is never in isotopic equilibrium with the atmospheric $\delta^{13}CO_2$ (Quay et al., 2003). Nevertheless, if we assume that change in SST affects $\delta^{13}C_{DIC}$ substantially at the seasonal scale in this region, this is in opposite effect to the uptake of ^{13}C poor CO_2 in surface water. Data collected in December 2010 are relatively higher in $\delta^{13}C_{DIC}$ and lower in DIC than those sampled in December 2011. This suggests either that the impact due to the change in SST in 2010 is dominated by the CO_2 uptake effect, or that additional physical driving processes, like horizontal transport, influenced the $\delta^{13}C_{DIC}$ and DIC seasonal distributions in 2010.

In the subpolar region, phytoplanktonic bloom is regularly dominated by the coccolithophore species, which are promoted by specific environmental conditions like high SST and shallow MLD (Fig. 4b; Raitsos et al., 2006) observed during this period. Coccolithophores are photosynthetic calcifying algal species. As we mentioned in Sect. 3.2, a small ^{13}C fractionation occurs during the formation of the calcium carbonate coccoliths so that it is insignificant for the $\delta^{13}C_{DIC}$ variation. Coccolithophores bloom starts generally in June and would induce by their soft-tissue pump a winter to summer increase in $\delta^{13}C_{DIC}$ and decrease in DIC according to a ratio of -0.011 ‰ µmol kg^{-1} and by their carbonate pump, an additional decrease in DIC without change in $\delta^{13}C_{DIC}$ (conversely from summer to winter), thus impacting the seasonal relationships observed between these both parameters over the period August 2010–March 2011. There is no information on $\delta^{13}C_{DIC}$ in the spring of 2010, and the cloudy conditions during summer precluded observations with satellite imagery, so that it is difficult to confirm this hypothesis.

According to regression slope 2 (Eq. 7), the lowest DIC values associated with low $\delta^{13}C_{DIC}$ and the isotopic tracers ($\Delta\delta^{13}C_{bio}$ and $\Delta\delta^{13}C_{phys}$), DIC and $\delta^{13}C_{DIC}$ seasonal distributions may be controlled by these combined processes.

3.3.3 The period March 2011–September 2012

In 2011–2012, the seasonal minimum was sampled two times but the seasonal maximum was never reached (Table 1). As all DIC data collected in the NASPG region between March 2011 and September 2012 are presented in this study, it is impossible to complete the seasonal DIC cycle like in 2005–2006 and to deduce that of $\delta^{13}C_{DIC}$ (Fig. 5). Based on 2012 values (from March 2012 to June 2012; Fig. 5), we can nevertheless observe a seasonal $\delta^{13}C_{DIC}$ amplitude of at least 0.68 ± 0.14 ‰, with a biological contribution of 0.76 ± 0.11 ‰ (Table 2). These results are comparable to those observed in 2005–2006, suggesting that the soft-tissue pump was the major driving process of $\delta^{13}C_{DIC}$ seasonality in the NASPG region.

4 Conclusions

In this study, we present new sea surface observations of $\delta^{13}C_{DIC}$ and associated hydrological and biogeochemical properties (DIC, NO_3^-) in the NASPG (53° N–62° N) based on 14 transects conducted in 2005–2006 and 2010–2012. During all transects, we observe a positive north–south gradient coherent with model studies of Gruber et al. (1999) and Tagliabue and Bopp (2008), and opposite to DIC gradients (high DIC in the north, low in the south). We also detect a very large range of $\delta^{13}C_{DIC}$ depending on the periods. Coupling $\delta^{13}C_{DIC}$–DIC observations enables to reveal strong parallel relationships in 2005–2006 and in 2011–2012. For both tracers and for winter (February–March) the change from 2005–2006 to 2011–2012 is coherent with anthropogenic carbon uptake (increase in DIC, decrease in $\delta^{13}C_{DIC}$), but with a time rate of change much larger than the theoretical value due to anthropogenic effect. Deeper winter mixing recorded in the winter of 2008–2009 and in the winter of 2011–2012 most likely contributed to reduce $\delta^{13}C_{DIC}$ and increase DIC, thus masking the anthropogenic signal.

During these both periods, the seasonality of $\delta^{13}C_{DIC}$ was investigated taking into account the observed changes and was totally computed for the years 2005–2006. Our "climatological" seasonal cycle shows a large $\delta^{13}C_{DIC}$ variation of 0.77 ± 0.07 ‰ (larger in summer, lower in winter), which represents the largest seasonal amplitude recorded at the sea surface in this region by Gruber et al. (1999) and built by Jonkers et al. (2013). This is coherent with large DIC (70 µmol kg^{-1}), nutrients and pCO_2 seasonal signals previously observed in the region (Corbière et al., 2007). A diagnostic process model suggests that the biological processes control the $\delta^{13}C_{DIC}$ seasonality, thus masking air–sea CO_2 exchange and the ocean dynamics effect. The comparison between the slope obtained from the $\delta^{13}C_{DIC}$–DIC relationship and those expected if the soft-tissue pump is the only driving process emphasized the importance of the biological pump in DIC seasonality in the subpolar North Atlantic region.

The $\delta^{13}C_{DIC}$–DIC relationship has also helped to identify a third period (from August 2010 to March 2011) characterized by a lower regression slope, significantly different from the other two. This may be due to a combination of processes such as the formation of a carbonate shell associated with a coccolitophore bloom, the temperature effect on the carbon isotopic fractionation, and the ocean dynamics processes. Coccolithophore bloom being common in the NASPG surface water, it will be interesting to estimate the relationship between $\delta^{13}C_{DIC}$ and DIC in such a bloom in order to validate one of these hypotheses and to better understand the carbon cycle evolution in this region.

The observed $\delta^{13}C_{DIC}$ seasonal cycle now being well established, a challenge for future analysis will be to investigate this seasonality in ocean models. We strongly recommend maintaining such observations in the future to better separate natural and anthropogenic signals. The $\delta^{13}C_{DIC}$ is also able to estimate the oceanic $\delta^{13}C$ in disequilibrium with the atmosphere ($\delta^{13}C_{des}$) used in the atmospheric inversion models to evaluate CO_2 flux. This study has revealed a large seasonal variability of $\delta^{13}C_{DIC}$ that strongly influenced the $\delta^{13}C_{des}$ seasonality, although we have observed a winter to summer change in SST of 6 °C. Taking into account this variability would improve the CO_2 flux uncertainty due to the evaluation of the $\delta^{13}C_{des}$. This highlights the need to continue measuring both parameters to investigate the anthropogenic carbon signals, as well as to better constrain atmospheric inversions and validate ocean carbon models.

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