Dissolved inorganic carbon dynamics and air-sea carbon dioxide fluxes during coccolithophore blooms in the northwest European continental margin (northern Bay of Biscay)

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[1] We report a data set of dissolved inorganic carbon (DIC) obtained during three cruises in the northern Bay of Biscay carried out in June 2006, May 2007, and May 2008. During these cruises, blooms of the coccolithophore Emiliania huxleyi occurred, as indicated by patches of high reflectance on remote sensing images, phytoplankton pigment signatures, and microscopic examinations. Total alkalinity showed a nonconservative behavior as a function of salinity due to the cumulative effect of net community calcification (NCC) on seawater carbonate chemistry during bloom development. The cumulative effect of NCC and net community production (NCP) on DIC and the partial pressure of CO2 (pCO2) were evaluated. The decrease of DIC (and increase of pCO2) due to NCC was overwhelmingly lower than the decrease of DIC (and decrease of pCO2) due to NCP (NCC:NCP ≪ 1). During the cruises, the northern Bay of Biscay acted as a sink of atmospheric CO2 (on average ∼ 9.7 mmol C m−2 d−1 for the three cruises). The overall effect of NCC in decreasing the CO2 sink during the cruises was low (on average ∼12% of total air-sea CO2 flux). If this is a general feature in naturally occurring phytoplankton blooms in the North Atlantic Ocean (where blooms of coccolithophores are the most intense and recurrent), and in the global ocean, then the potential feedback on increasing atmospheric CO2 of the projected decrease of pelagic calcification due to thermodynamic CO2 “production” from calcification is probably minor compared to potential feedbacks related to changes of NCP.


1. Introduction

[2] Balch et al. [2007] evaluated from remote sensing data the contemporary global calcification related to coccolithophores to 1.6 ± 0.3 Pg PIC yr−1 (1 Pg = 1015 g; PIC, particulate inorganic carbon). Other estimates of contemporary global pelagic calcification range between 0.7 Pg PIC yr−1, based on accumulation rates and sediment trap data [Milliman et al., 1999], and 1.4 Pg PIC yr−1, based on the seasonal cycle of total alkalinity (TA) in the euphotic zone [Lee, 2001]. Each of these estimates of global pelagic calcification suffers from specific shortcomings. For instance, the estimate of Milliman et al. [1999] might be underestimated due to supralysoclinal dissolution of calcium carbonate (CaCO3) [e.g., Wollast and Chou, 1998; Beaufort et al., 2007; Berelson et al., 2007], and the TA analysis of Lee [2001] could be affected by other processes than calcification such as nutrient uptake and release or mixing of water masses. The estimate of Balch et al. [2007] is probably less biased by the sparseness of data coverage compared to the two other approaches, although strongly dependent on the predictive capability of the algorithm used to process the remote sensing data. Three-dimensional circulation models mostly tuned to reproduce the observed TA distributions also provide a wide range of global pelagic calcification values from 0.6 to 1.8 Pg PIC yr−1 [Bacastow and Maier-Reimer, 1990; Yamanaka and Tajika, 1996; Archer et al., 1998; Murnane et al., 1999; Heinze et al., 2003; Moore et al., 2004; Jin et al., 2006; Gehlen et al., 2007; Hofmann and Schellnhuber, 2009]. The fact that the estimate of Balch et al. [2007] of contemporary global pelagic calcification related to coccolithophores is comparable to the other estimates would imply that coccolithophores are the most important pelagic calcifiers in the oceans.

[3] The development of coccolithophore blooms affects the seawater carbonate chemistry, and air-sea CO2 fluxes, through the organic carbon pump and the carbonate counterpump. The organic carbon pump relies on organic carbon...
production by photosynthesis and leads to an uptake of CO₂ from surface waters, according to:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$$

The carbonate counterpump relies on the production of CaCO₃, leading to a thermodynamic shift of HCO₃⁻ to CO₂, hence, a release of CO₂ to surrounding surface waters, according to:

$$\text{Ca}^{2+} + 2 \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$

The ratio between calcification (carbonate counterpump), and organic carbon production (organic carbon pump), the C:P ratio, depends on the life cycle (bloom development) and growth conditions of coccolithophores [Fernández et al., 1993; Paasche and Brubak, 1994; Paasche, 2002; Delille et al., 2005]. At the onset of the coccolithophore bloom, when nutrients are available for growth, organic carbon production dominates over calcification (C:P ∼ 1, the so-called organic phase). At the end of the bloom, in nutrient-depleted conditions and high irradiances (due to stronger stratification), organic carbon production decreases and calcification increases (C:P ≤ 1, the so-called inorganic phase).

The accumulation of anthropogenic CO₂ in the oceans [e.g., Sabine et al., 2004] has altered carbonate chemistry in surface waters (ocean acidification) since preindustrial times, and is expected to continue to do so in the coming centuries [e.g., Caldeira and Wickett, 2003; Orr et al., 2005; Cao et al., 2007; McNeil and Matear, 2007]. Changes of the carbonate chemistry of surface waters related to ocean acidification can alter the rates and fates of primary production and calcification of numerous marine organisms and communities [as reviewed by Raven et al., 2005; Kleypas et al., 2006; Fabry et al., 2008; Doney et al., 2009]. Such changes can provide either positive or negative feedbacks on increasing atmospheric CO₂ by modifying the flux of CO₂ between the ocean and the atmosphere.

Several manipulative experiments to test the effect of ocean acidification on coccolithophores have shown that while calcification would decrease, the export of organic carbon would increase mainly through increasing production of transparent exopolymer particles (TEP) [Riebesell et al., 2000; Engel et al., 2004a, 2004b; Delille et al., 2005; Riebesell et al., 2007]. On the other hand, the reduction of pelagic calcification due to ocean acidification could also lead to a reduction of carbon export due to the decrease of the ballast effect of CaCO₃ on marine particles [e.g., Armstrong et al., 2002; Klaas and Archer, 2002; Barker et al., 2003; Hofmann and Schellnhuber, 2009]. The modelling study of Hofmann and Schellnhuber [2009] suggested that the positive feedback on increasing atmospheric CO₂ related to the decrease of carbon export from the reduction of ballast effect of CaCO₃ on marine particles would represent ~40% of the negative feedback related to the decrease of the CO₂ emission to the atmosphere due to the reduction of pelagic calcification. For a credible implementation in mathematical models of such feedback mechanisms to allow the projection of a future evolution of marine carbon biogeochemistry under global change, it is required to understand present day biogeochemistry and ecology of naturally occurring pelagic calcifying communities. In particular, the overall effect of phytoplankton communities on the C:P ratio, carbonate chemistry, and air-sea CO₂ fluxes.

In the northwest European continental margin, blooms of the coccolithophore Emiliania huxleyi have been frequently reported [Holligan et al., 1983; Garcia-Soto et al., 1995; Wollast and Chou, 1998, 2001; Godoi et al., 2009; Harlay et al., 2009, 2010]. Here, we report a data set of carbonate chemistry in surface waters obtained during three cruises in the northern Bay of Biscay (Figure 1). We evaluate the relative effect of calcification and organic carbon production on seawater carbonate chemistry and air-sea CO₂ fluxes.

2. Material and Methods

2.1. Cruises and Sampling

Three cruises were carried out in the northern Bay of Biscay from 31 May to 9 June 2006 (BG06/11 cruise), 10 May to 24 May 2007 (BG07/12 cruise), and 7 May to 23 May 2008 (BG08/12 cruise). Sampling of pH, TA, oxygen (O₂), and phosphate (PO₄³⁻) was carried out with a rosette of 12 Niskin bottles (12 L) coupled to a conductivity-temperature-depth probe (Seabird SBE21). Depths of sampling covered surface waters, thermocline, and bottom waters down to the seafloor over the continental shelf and down to maximum 1400 m over the continental slope. Because of shorter ship-time, sampling during the June 2006 cruise was limited to the area around the La Chapelle Bank.
Bank, while during the other two cruises sampling was also carried out further north along the continental shelf break (Figure 1).

2.2. Analytical Methods

[10] Underway measurements of the partial pressure of CO₂ (pCO₂) were carried out in surface waters (2 m depth) using an equilibrator [Frankignoulle et al., 2001], and a nondispersive infrared CO₂ analyzer (Li-Cor 6262) calibrated with pure nitrogen (Air Liquide Belgium) and two gas mixtures with a CO₂ molar fraction of 366 and 810 ppm (Air Liquide Belgium), that were calibrated against standards with a CO₂ molar fraction of 361 and 774 ppm acquired from National Oceanic and Atmospheric Administration (NOAA, Global Monitoring Division, Carbon Cycle Greenhouse Gases Group). Temperature at the outlet of the equilibrator was measured with a Metrohm Pt-100 temperature sensor. The correction of pCO₂ for the difference between equilibrator and in situ temperature was carried out with the algorithm given by Takahashi et al. [1993]. Sea surface temperature (SST) and salinity were measured underway (2 m depth) with a Seabird thermosalinograph (SBE 21).

[11] Measurements of pH were carried out with a combined electrode (Metrohm 6.0232.100), calibrated on the total hydrogen ion concentration scale, using TRIS (2-amino-2-hydroxymethyl-1,3-propanediol) and AMP (2-amino-pyridine) buffers prepared at a salinity of 35 according to Dickson [1993]. Measurements of TA were carried out by open-cell titration with HCl 0.1 M according to Gran [1952] on 100 mL filtered (GF/F Whatman) seawater samples, and data were quality checked with certified reference material acquired from Andrew Dickson ( Scripps Institution of Oceanography, University of California, San Diego). Dissolved inorganic carbon (DIC) and the saturation state of calcite (ΩCAL) were computed from pH and TA using the carbonic acid dissociation constants of Mehrbach et al. [1973] refitted by Dickson and Millero [1987], and the calcite solubility of Mucci [1983].

[12] Concentrations of dissolved O₂ were measured by Winkler titration with a potentiometric end point determination. Reagents and standardizations were similar to those described by Knap et al. [1996]. The O₂ saturation level (%) of O₂ was calculated from the measured O₂ concentration and the O₂ concentration at saturation computed with the algorithm given by Benson and Krause [1984]. PO₄⁻ was measured colorimetrically with the molybdate and ascorbic acid method described by Grasshoff et al. [1983].

2.3. Evaluation of the Effect of Biological Activity on Carbonate Chemistry of Surface Waters and Air–Sea CO₂ Fluxes

[13] The effect on DIC, pCO₂, and ΩCAL in surface waters of net community production (NCP) and net community calcification (NCC) was estimated on the basis of the changes between the surface layer and the deep layer of nutrients and of TA, respectively. Changes in nutrients and TA were computed as the difference of the average concentration in the surface layer (top 20 m, ⟨X⟩₀−20m) and the average concentration of the deep layer (80 m to seafloor, ⟨X⟩₈₀m−bottom). The lower limit of the surface layer (20 m) was chosen to include data within the euphotic layer (euphotic depth typically of ~30 m during the cruises, not shown), while the upper limit of the deep layer (80 m) was chosen to avoid the base of the thermocline (at some stations down to 70 m, not shown). For the deeper stations on the continental slope, the averaging of the deep layer data was made down to 150 m.

[14] TA and DIC were normalized to a constant salinity of 35.5 (TA₃₅.₅ and DIC₃₅.₅, respectively) according to:

\[
TA_{35.5} = 35.5 \frac{TA}{S}
\]

\[
DIC_{35.5} = 35.5 \frac{DIC}{S}
\]

where TA and DIC are the observed values at the observed salinity (S).

[15] Hereafter, pCO₂@SST refers to pCO₂ at SST and pCO₂@13°C refers to the pCO₂ normalized to a temperature of 13°C applying the algorithm of Takahashi et al. [1993]. The change of pCO₂ due to temperature (T) changes (ΔpCO₂SST) was computed with the algorithm of Takahashi et al. [1993] and the change of T (ΔT):

\[
ΔT = ⟨T⟩₀−20m − ⟨T⟩₈₀m−bottom
\]

[16] For the anomaly of TA (TAanomaly) to only represent CaCO₃ production and dissolution and to exclude the effect of organic matter production and degradation, TA values have to be corrected for PO₄³⁻ and nitrate (NO₃⁻) assimilation and release [Brewer and Goldman, 1976]. PO₄³⁻ assimilation is given by the term (PO₄³⁻)₈₀m−bottom − (PO₄³⁻)₀−20m. In absence of NO₃ data during the June 2006 cruise, NO₃ assimilation was computed for the three cruises from PO₄³⁻ assimilation, using the Redfield ratio (16:1). During the May 2007 and May 2008 cruises, the measured NO₃:PO₄³⁻ ratios were 16.7 and 15.7, respectively (not shown), hence close to the Redfield ratio. The TAanomaly was computed according to:

\[
TA_{anomaly} = ⟨TA⟩₃₅.₅ₐₜ₏₉₀m−bottom − 16 × ((PO₄³⁻)₈₀m−bottom − (PO₄³⁻)₀−20m) − ((PO₄³⁻)₈₀m−bottom − (PO₄³⁻)₀−20m) − (TA₃₅.₅)₈₀m−bottom
\]

[17] The change of DIC in surface waters due to net organic carbon production (ΔDICorg) was computed from the change of PO₄³⁻ converted to carbon using the Redfield ratio (106:1), according to:

\[
ΔDIC_{org} = 106 × ((PO₄³⁻)₀−20m − (PO₄³⁻)₈₀m−bottom)
\]

[18] The change of DIC in surface waters due to net CaCO₃ production (ΔDICinorg) was computed using the TA anomaly technique [e.g., Smith and Key, 1975] according to:

\[
ΔDIC_{inorg} = 0.5 \times TA_{anomaly}
\]

[19] To estimate the change of pCO₂ due to ΔDICorg and ΔDICinorg (ΔpCO₂org and ΔpCO₂inorg, respectively), we first computed DIC at atmospheric CO₂ equilibrium (DICeq)
from an average $TA$ of 2340 $\mu$mol kg$^{-1}$, a $pCO_2$ of 380 ppm, an average temperature of 13°C, and an average salinity of 35.5.

[20] The value $\Delta pCO_2$ was computed as the difference between atmospheric equilibrium (380 ppm) and $pCO_2$ computed from $DIC$, a $TA$ of 2340 $\mu$mol kg$^{-1}$, a temperature of 13°C and a salinity of 35.5, where $DIC$ is given by:

$$DIC_{org} = DIC_{eq} + \Delta DIC_{org}$$

$\Delta pCO_2$ was computed as the difference between atmospheric equilibrium (380 ppm) and $pCO_2$ computed from $DIC$, a $TA$ of 2340 $\mu$mol kg$^{-1}$, a temperature of 13°C and a salinity of 35.5, where $DIC$ and $TA$ are given by:

$$DIC_{inorg} = DIC_{eq} + \Delta DIC_{inorg}$$

$$TA_{inorg} = 2340 + TA_{anomaly}$$

[21] The change of $\Omega_{CAL}$ due to net organic carbon production ($\Delta \Omega_{CALorg}$) was calculated as the difference between $\Omega_{CALorg}$ and $\Omega_{CALorg}$, where $\Omega_{CALorg}$ was computed from $DIC$, a $TA$ of 2340 $\mu$mol kg$^{-1}$, a temperature of 13°C, and a salinity of 35.5, and $\Omega_{CALorg}$ was computed from $DIC$, a $TA$ of 2340 $\mu$mol kg$^{-1}$, a temperature of 13°C and a salinity of 35.5. The change of $\Omega_{CAL}$ due to net CaCO$_3$ production ($\Delta \Omega_{CALinorg}$) was calculated as the difference between $\Omega_{CALinorg}$ and $\Omega_{CALinorg}$, where $\Omega_{CALinorg}$ was computed from $DIC$, $TA$, a temperature of 13°C, and a salinity of 35.5. The change of $\Omega_{CAL}$ due to $T$ change ($\Delta \Omega_{CALST}$) was calculated as the difference between $\Omega_{CALST}$ and $\Omega_{CALST}$, where $\Omega_{CALST}$ was computed from $DIC$, $TA$, a $TA$ of 2340 $\mu$mol kg$^{-1}$, a temperature $= 13 + \Delta T$, and a salinity of 35.5.

The net effects of NCP and NCC on DIC, $pCO_2$, and $\Omega_{CAL}$ were calculated according to:

$$\Delta DIC_{computed} = \Delta DIC_{org} + \Delta DIC_{inorg}$$

$$\Delta pCO_2_{computed} = \Delta pCO_2_{org} + \Delta pCO_2_{inorg}$$

$$\Delta \Omega_{CAL_{computed}} = \Delta \Omega_{CAL_{org}} + \Delta \Omega_{CAL_{inorg}} + \Delta \Omega_{CAL_{ST}}$$

The observed changes of DIC, $pCO_2$, and $\Omega_{CAL}$ were calculated according to:

$$\Delta DIC_{observed} = \langle DIC_{35.5} \rangle_{0-20 m} - \langle DIC_{35.5} \rangle_{80m-bottom}$$

$$\Delta pCO_2_{observed} = pCO_2@13^\circ C - 380$$

$$\Delta \Omega_{CAL_{observed}} = \langle \Omega_{CAL} \rangle_{0-20 m} - \langle \Omega_{CAL} \rangle_{80m-bottom}$$

[22] Air-sea $CO_2$ fluxes ($F$) were computed according to:

$$F = \alpha \times k \times \Delta pCO_2_{air-sea}$$

where $\Delta pCO_2_{air-sea}$ is the air-sea gradient of $pCO_2$, $\alpha$ is the solubility coefficient of $CO_2$ computed using the algorithm given by Weiss [1974], and $k$ is the gas transfer velocity computed from wind speed using the $k$-wind parameterization given by Ho et al. [2006].

[23] Wind speed data were obtained from the National Centers for Environmental Prediction reanalysis daily averages surface flux (http://www.cdc.noaa.gov/) at five grid points covering the sampled region (50.475°N, 7.080°W; 50.475°N, 7.120°W; 48.571°N, 7.150°W; 48.571°N, 7.650°W; 48.571°N, 8.030°W). $F$ was computed using daily wind speed values (average of the five grid points) for a time interval of 30 days centered on the date of the middle of the cruises. $\Delta pCO_2_{air-sea}$ was computed from measured $pCO_2$ in seawater and the monthly atmospheric $pCO_2$ at Mace Head (53.33°N, 9.00°W, Southern Ireland) obtained from the NOAA Climate Monitoring and Diagnostics Laboratory air sampling network (http://www.cmdl.noaa.gov/). Atmospheric $pCO_2$ was converted to wet air using the water vapor algorithm given by Weiss and Price [1980].

3. Results and Discussion

3.1. General Setting of the Cruises

[24] Time series of remotely sensed surface chlorophyll-a (Chl-a) in the study area indicate that seasonal cycles of phytoplankton biomass were remarkably similar during the 3 years at the La Chapelle Bank and Goban Spur regions (Figure 2). The main spring bloom associated to diatoms peaked in mid-April, followed by a strong increase in normalized water leaving radiance at 550 nm ($L_{wn}(555)$) indicative of the occurrence of coccolithophore blooms from early May to late June. Overall, higher Chl-a as well as $L_{wn}(555)$ values were observed at Goban Spur than at La Chapelle Bank during the 3 years. Some interannual variability in remotely sensed Chl-a was observed with highest concentrations in 2008 (up to 5 $\mu$g L$^{-1}$ at Goban Spur). The three cruises were carried out after the main spring bloom, during the period of peak to declining $L_{wn}(555)$.

[25] During the three cruises, remote sensing images revealed several patches of cold water (SST < 14°C) along the shelf break in the whole study area (Figure 3) corresponding to the signature of enhanced vertical mixing due to turbulent dissipation related to the generation of internal tides [Pingree and New, 1995; Wollast and Chou, 2001]. The highest Chl-a concentrations (>0.8 $\mu$g L$^{-1}$) at the continental margin were observed inshore of the 200 m isobath. The upwelled nutrient rich cold water at the shelf break, characterized by lower Chl-a values (<0.4 $\mu$g L$^{-1}$), warmed and stratified as it propagated from the shelf break both offshore and onshore, leading to enhanced biological activity [Wollast and Chou, 2001; Harlay et al., 2010]. As these water masses propagated further on the shelf, phytoplankton development caused nutrient depletion, hence, the highest Chl-a waters were confined close to the shelf break. The high Chl-a waters were also associated to high reflectance patches indicating the presence of coccolithophores at the end of the inorganic phase, since coccoliths that are shed from coccolithophores increase reflectance. High performance liquid chromatography (HPLC) pigment measurements (N. Van Oostende and K. Sabbe, personal communication,
not shown) indicate that prymnesiophytes (i.e., coccolithophores) accounted, depending on the station, for 10%–71%, 0%–59%, and 2%–49% of the total Chl-a during the June 2006, May 2007, and May 2008 cruises, respectively. The other most abundant phytoplankton community in terms of total Chl-a was usually composed of diatoms, and at some rare occasions of dinoflagellates or chlorophytes. Scanning electron microscopy (SEM) of coccolithophores in samples obtained during the June 2007 and June 2008 cruises identified *Emiliania huxleyi* as the dominant species (N. Van Oostende and K. Sabbe, personal communication; A. Engel, personal communication).

### 3.2. Distribution of pCO₂ and TA in Surface Waters

The distribution of pCO₂ during the three cruises was patchy and strong horizontal gradients of pCO₂ were observed (Figure 4). At the continental margin, the range of pCO₂ variations in surface waters was 248–270 ppm, 288–342 ppm, and 250–269 ppm, during the June 2006, May 2007, and May 2008 cruises, respectively. The pCO₂ values were systematically below atmospheric equilibrium (378 ppm, 382 ppm, and 385 ppm in June 2006, May 2007, and May 2008, respectively), hence, the area acted as a sink for atmospheric CO₂. Average air-sea CO₂ fluxes were −9.8, −11.9, and −7.4 mmol C m⁻² d⁻¹ in June 2006, May 2007, and May 2008, respectively (Table 1), in agreement with air-sea CO₂ fluxes reported previously in the area at this time of the year [Frankignoulle and Borges, 2001; Borges et al., 2006; Padin et al., 2009; de la Paz et al., 2010; Harlay et al., 2010].

During the three cruises, TA in surface waters showed a strong nonconservative behavior with respect to salinity compared to the climatological TA-S relationship for the North Atlantic Ocean surface waters reported by Millero et al. [1998] (Figure 5). Some of the TA data points (in particular during the June 2008 cruise) were above the climatological TA-S relationship of Millero et al. [1998]. While these TA data points remained within the standard deviation of the linear fit of the climatological TA-S relationship of Millero et al. [1998] (±9 μmol kg⁻¹), this could be due to local influence in the northern Bay of Biscay of river inputs [Kelly–Gerrey et al., 2006] characterized by high TA values, such as the Loire river [TA ∼2800 μmol kg⁻¹ in the freshwater end member, Abril et al., 2003] and the Gironde river [TA ∼2400 μmol kg⁻¹ in the freshwater end member, Abril et al., 1999]. Yet, the nonconservative behavior of TA as a function of salinity indicated the drawdown of TA by calcification. This is consistent with the presence of coccolithophores in the area during the three cruises as indicated by the high reflectance patches in remote sensing images (Figure 3), HPLC and SEM measurements.
Figure 3. Remote sensing images of SST (Advanced Very High Resolution Radiometer), Chl-a (SeaWiFS), and reflectance (unitless, false-color [443, 490, and 555 nm bands], SeaWiFS) contemporary to the May 2006, June 2007, and 2008 cruises in the Bay of Biscay (6 May 2006; composite 20–22 May 2007; composite 18 May 2008) (courtesy of S. Groom, Remote Sensing Group of the Plymouth Marine Laboratory), and bathymetry (200 m and 2000 m isobaths).
3.3. Distribution of Variables as Function of the Degree of Stratification

[28] Stratification is one of the most important variables controlling the intensity of primary production, and the succession of phytoplankton communities [e.g., Margalef, 1997]. Increasing stratification enhances light availability but leads to the decrease of vertical input of inorganic nutrients, imposing a succession of phytoplankton communities with variable light and inorganic nutrient requirements. Coccolithophores (and especially Emiliania huxleyi)

### Table 1.

<table>
<thead>
<tr>
<th>Date</th>
<th>Longitude (°W)</th>
<th>Latitude (°N)</th>
<th>ΔpCO₂air-sea (ppm)</th>
<th>F (mmol C m⁻² d⁻¹)</th>
<th>Change of F Due to NCC (%)</th>
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<td>47.749</td>
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<tr>
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have a high tolerance to elevated irradiances [Nanninga and
Tyrrell, 1996] as well as a high affinity for inorganic
[Holligan et al., 1993] and organic nutrients [Riegman et al.,
2000]. Emiliania huxleyi has the ability to use organic
sources for nitrogen and phosphorus when inorganic
nutrients are limiting for the development of other phyto-
 planktonic species [Palenik and Henson, 1997; Riegman et al.,
2000]. Hence, Emiliania huxleyi usually blooms in
stratified and inorganic nutrient-depleted conditions typically
after the blooms of diatoms [e.g., Margalef, 1997].

[30] The degree of stratification was computed as the
difference between seawater density at 100 m depth and the
seawater density at 10 m depth. These depths were chosen to
make sure that the upper value was within the mixed layer
(where density was homogeneous), and that the bottom
value was below the base of the thermocline (down to 70 m
at some stations, not shown). Variables from different stations
were plotted as a function of the degree of stratification
as a way of reconstructing the effect of the bloom develop-
ment on seawater carbonate chemistry and other biogeo-
chemical variables. Such an approach is useful and
appropriate in the study area, where there is a more or less
continuous generation of low stratified and nutrient rich
waters at the continental shelf break that propagate on shelf,
stratify, and host high phytoplankton biomass at the period
of the year when the cruises were carried out (section 3.1).
It should be noted that the changes of the biogeochemical
variables as a function of the stratification degree corre-
spond to a cumulative signal of biological activity, and these
patterns do not necessarily indicate an increase of biological
rates with stratification. Prior to the May 2007 cruise, a
major storm occurred in the area that induced enhanced
vertical mixing compared to the June 2006 and May 2008
 cruises, and this might have added additional variability in
the 2007 data set as a function of the degree of stratification.
Hence, linear regressions of variables as a function of the
degree of stratification were computed either on the basis of
the 2006 and 2008 data sets or on the 2006, 2007, and 2008
data sets.

[31] The patterns of the variables in surface waters as a
function of the stratification degree were remarkably consis-
tent considering that data from three cruises carried out in
different years were merged together (Figure 6). The increase
of %O₂ and decrease of PO₄³⁻ were consistent with organic
carbon production during the bloom development (increas-
ing stratification). The pattern in TA_anomaly was consistent
with CaCO₃ production during the bloom development
(increasing stratification) of mixed phytoplanktonic com-
munities. The strongest TA_anomaly (−32 µmol kg⁻¹) was
comparable to the strongest values of −28 µmol kg⁻¹
reported by Holligan et al. [1993] in the North Atlantic in
June 1991, and of −35 µmol kg⁻¹ reported by Bates et al.
[1996] in the Sargasso Sea in February 1992, but weaker
than the value of −82 µmol kg⁻¹ reported by Murata and
Takizawa [2002] in the Bering Sea in October 2000. These
TA_anomaly values observed in naturally occurring blooms
remain well below the TA drawdown observed in confined
environments with coccolithophores of ∼300 µmol kg⁻¹ in
mesocosms [e.g., Delille et al., 2005] and of ∼1000 µmol kg⁻¹
in batch cultures [e.g., De Bodt et al., 2010]. pCO₂@13°C
showed a decreasing pattern with stratification, indicative
that the net effect on pCO₂ of organic carbon production
dominated over the net effect of calcification. The pattern
with stratification of pCO₂@SST has lower statistical sig-
nificance than that of pCO₂@13°C due to the increase of
SST with stratification and subsequent effect on the CO₂
solubility and pCO₂@SST. DIC decreased during the bloom
development (increasing stratification) due to the combined
effect of NCC and NCP, as discussed hereafter. Although
the linear regression has a low statistical significance, the
general increasing pattern of Ω_CAL during the bloom de-
velopment (increasing stratification) suggests that the combined
(increasing) effect of NCP and SST change dominated over the
decreasing effect of NCC, as discussed hereafter. Also, the
values of Ω_CAL were higher than the wintertime value of ∼3.7
(computed from a TA of 2340 µmol kg⁻¹, a salinity of 35.5,
a SST of 12°C and pCO₂ at atmospheric equilibrium, based
on wintertime data in the area reported by Frankignoulle
and Borges [2001]). This shows that NCP increased Ω_CAL
values with regards to wintertime values. A temperature
increase from the wintertime value of 12°C to 13°C (average
SST during the cruises) can only account for an increase of
Ω_CAL of 3%, while the increase between observed Ω_CAL
values and the wintertime Ω_CAL value ranged between 9% and
34%.

[32] The low values of pCO₂ and DIC in surface waters
observed in the area during the cruises could be in part due
to NCP during the diatom blooms that occurred prior to
the cruises and peaked in mid-April (Figure 2). However,
mixing at the shelf break (section 3.1) also induced the
increase of pCO₂ and DIC in surface waters as indicated by
the high values of these quantities for the lowest degree of
stratification (Figure 6). The mixing at the shelf break
and injection of nutrients to surface waters are assumed to be
the factors that trigger the coccolithophore blooms in the area
at the period of the year the cruises were carried out [Harlay
et al., 2010]. Since the stations sampled over the continental
shelf and slope were close to the shelf break, we assume that the sampled water masses were derived from the cold and nutrient rich source waters at the shelf break. Hence, we also assume that the patterns of biogeochemical variables as a function of stratification in Figure 6, and the effects of NCP and NCC on seawater carbonate chemistry evaluated hereafter are mainly related to the activity of the recently bloomed mixed phytoplanktonic assemblages dominated by coccolithophores.

Figure 6. Average values in surface waters (top 20 m) of %O$_2$, TA$_{anomaly}$, DIC, $\Omega_{\text{CAL}}$, and PO$_4^{3-}$, and underway pCO$_2$@13°C and pCO$_2$@SST, and SST (2 m) as a function of the degree of stratification, during the June 2006 (grey circles), May 2007 (open circles), and May 2008 (black circles) cruises in the northern Bay of Biscay. The solid line corresponds to the linear regression based on the 2006 and 2008 data sets (corresponding $r^2$ is not italicized), the dotted line corresponds to the linear regression based on the 2006, 2007, and 2008 data sets (corresponding $r^2$ is italicized).
3.4. Evaluation of the Effect of NCP, NCC, and SST on DIC, pCO$_2$, and $\Omega_{\text{CAL}}$

The cumulative effects of NCP, NCC, and SST change on DIC, pCO$_2$, and $\Omega_{\text{CAL}}$ were evaluated as described in section 2.3. $\Delta$DIC$_\text{org}$ and $\Delta$pCO$_2$$_\text{org}$ decreased, and $\Delta$DIC$_\text{inorg}$ increased with increasing stratification, consistent with a cumulative effect of NCP as the water mass stratified and the bloom developed (Figure 7). $\Delta$DIC$_\text{inorg}$ and $\Delta$DIC$_\text{org}$ increased, and $\Delta$pCO$_2$$_\text{inorg}$ increased with increasing stratification, consistent with a cumulative effect of NCC as the water mass stratified and the bloom developed. $\Delta$pCO$_2$$_\text{SST}$ and $\Delta$DIC$_\text{SST}$ increased with increasing stratification, consistent with the warming of surface waters as the water mass stratified. The cumulative effect of NCP on DIC as well as on pCO$_2$ was stronger ($\Delta$DIC$_\text{org}$ down to $-60$ mmol kg$^{-1}$ and $\Delta$pCO$_2$$_\text{org}$ down to $-100$ ppm) than the effect of NCC ($\Delta$DIC$_\text{inorg}$ down to $-20$ mmol kg$^{-1}$ and $\Delta$pCO$_2$$_\text{inorg}$ up to $+20$ ppm). The cumulative effect of NCC on pCO$_2$ was also weaker than the effect of SST change ($\Delta$pCO$_2$$_\text{SST}$ up to $+60$ ppm). The highest $\Delta$pCO$_2$$_\text{inorg}$ values we report were close to maximal values reported by Robertson et al. [1994] in northeast North Atlantic Ocean in June 1991 (~15 ppm), and those given by the model of Buitenhuis et al. [2001] (~25 ppm) calibrated with data from the northern North Sea in June 1993 [Buitenhuis et al., 1996]. However, the $\Delta$pCO$_2$$_\text{inorg}$ values we report were lower than the highest value reported by Murata and Takizawa [1992] in the Bering Sea in October 2000 (~100 ppm). This is mainly due to very high TA drawdown (~82 mmol kg$^{-1}$) [Murata and Takizawa, 2002], and to a lesser extent due to the lower seawater buffering capacity in the Bering Sea (salinity ~32). The cumulative effect of NCP as well as SST change on $\Omega_{\text{CAL}}$ was stronger ($\Delta$DIC$_\text{org}$ up to $+0.9$, $\Delta$DIC$_\text{inorg}$ up to $+0.4$) than the effect of NCC ($\Delta$DIC$_\text{org}$ down to $-0.3$).

[33] The $\Delta$DIC$_\text{inorg}$:DIC$_\text{org}$ ratio increased with stratification (Figure 8), in agreement with the life cycle of coccolithophores. As the water mass stratifies and nutrients become depleted in surface waters, coccolithophores shift from the organic carbon production and growth phase to the stationary and calcification phase [Fernández et al., 1993; Paasche and Brubak, 1994; Paasche, 2002; Delille et al., 2005]. The $\Delta$DIC$_\text{inorg}$:DIC$_\text{org}$ values (0.00 to 0.42, on average 0.13 for the three cruises) were in relatively good agreement with C:P values based on calcification and primary production rates derived from $^{14}$C incubations reported.
during several studies in the North Atlantic Ocean: 0.14–0.19 in the northeast North Atlantic Ocean in June 1991 [Fernández et al., 1993], 0.03–0.18 in the northern North Sea in July 1993 [van der Wal et al., 1995], 0.14–0.16 in the northern North Sea in July 1994 [Marañón and González, 1997], 0.03–0.18 in the northern North Sea in June 1999 [Rees et al., 2002], 0.02–0.31 in the northern Bay of Biscay in June 2004 [Harlay et al., 2010].

[34] The much larger effect of NCP than NCC on seawater carbonate chemistry is confirmed by the value of the Revelle factor of 8.4 in the top 30 m of the water column (for the whole data set). This value is closer to the theoretical value of 10.0 if only DIC uptake and release by net organic carbon production and degradation occurred in the water column, than the theoretical value of −7.5 if only DIC uptake and release by CaCO3 precipitation and dissolution occurred in the water column (computed for a temperature of 13°C, salinity of 35.5, pCO2 of 300 ppm, and TA of 2340 μmol kg−1) [Frankignoulle, 1994]. Based on the Revelle factor computed from measured profiles in the top 30 m of the water column from the whole data set (8.4), we evaluated theoretically the C:P ratio yielding a value of 0.12, in close agreement with the average DICinorg:DICorg ratio (0.13) derived independently.

[35] The computed changes of DIC, pCO2, and ΩCAL (ΔDICcomputed, ΔpCO2computed, and ΔΩCALcomputed, respectively) were remarkably consistent with the observed changes of DIC, pCO2, and ΩCAL (ΔDICobserved, ΔpCO2observed, and ΔΩCALobserved, respectively), considering that these quantities were evaluated independently (Figure 9). Yet, the values of ΔDICobserved and ΔpCO2observed were almost always systematically lower than the values of ΔDICcomputed, ΔpCO2computed, and the values of ΔΩCALcomputed were almost always systematically higher than the values of ΩCALcomputed. This could indicate that additional processes affecting seawater carbonate chemistry dynamics in surface waters were not taken into account in the computations. First, phosphorous was assumed to be assimilated by phytoplankton exclusively as PO43−, however, coccolithophores can rely on dissolved organic phosphorous (DOP) to meet part of their phosphorous requirements [Egge and Heimdal, 1994; Paasche, 2002; Lessard et al., 2005]. Secondly, in low or depleted nutrient conditions, a significant amount of carbon fixed by photosynthesis is released as dissolved organic carbon (documented for coccolithophores by Fernández et al. [1996] and Engel et al. [2004a, 2004b]), which cannot be accounted for in our computations since it is independent of nutrient assimilation (carbon overconsump-

**Figure 9.** The ΔDICobserved versus ΔDICcomputed, ΔpCO2observed versus ΔpCO2computed, and ΔΩCALobserved versus ΔΩCALcomputed during the June 2006 (grey circles), May 2007 (open circles), and May 2008 (black circles) cruises in the northern Bay of Biscay. The solid line corresponds to the linear regression (forced through 0) based on the 2006 and 2008 data sets (corresponding r2 is not italicized), the dotted line corresponds to the linear regression (forced through 0) based on the 2006, 2007, and 2008 data sets (corresponding r2 is italicized). The 1:1 line is in bold.
3.5. Effect of Calcification on Air-Sea CO₂ Fluxes

[36] Air-sea CO₂ fluxes were computed at each sampled station (Table 1), and the cumulative effect of NCC on air-sea CO₂ fluxes was evaluated by recomputing the air-sea CO₂ fluxes with ΔpCO₂air-sea from which ΔpCO₂inorg was removed. The cumulative effect of NCC in decreasing the CO₂ sink in the study area ranged between 0% and 72% depending on the station, but on average it was small, ~12%. If this finding is confirmed in other oceanic regions, it would imply that the potential feedback on increasing atmospheric CO₂ of the projected decrease of pelagic calcification [e.g., Gehlen et al., 2007; Ridgwell et al., 2007; Hofmann and Schellnhuber, 2009] due to thermodynamic CO₂ “production” from calcification is probably minor. Furthermore, in naturally occurring blooms, the cumulative effect of NCP leads to an increase of Ω_{CAL} above wintertime values (at or close to CO₂ atmospheric equilibrium). Hence, a future increase of NCP [e.g., Riebesell et al., 2007] could to some extent counteract the effect of ocean acidification on Ω_{CAL}, in addition to the predicted effect of SST increase on Ω_{CAL} [Cao et al., 2007; McNeil and Matear, 2007].

4. Conclusions

[37] We report a data set of seawater carbonate chemistry obtained during blooms of the coccolithophore Emiliania huxleyi at the continental margin of the northern Bay of Biscay. Physical settings were the major factors controlling phytoplankton dynamics under the springtime high irradiance conditions. The cold, nutrient rich upwelled water at the shelf break moved over the shelf, warmed and stratified and then became depleted in nutrients, constraining the bloom close to the shelf break. Coccolithophores were present during these cruises as testified by high reflectance patches in remote sensed images, HPCL and SEM measurements. On the basis of HLPC measurements, coccolithophores accounted up to 70% of total Chl-a. Calcification by coccolithophores led to a marked drawdown of TA. Yet, the decrease of DIC (and increase of pCO₂) due to NCC was overwhelmingly lower than the decrease of DIC and pCO₂ due to NCP (NCC:NCP [ΔDIC_{inorg}:ΔDIC_{org}] ratios, on average 0.13 for the three cruises). The NCC:NCP (ΔDIC_{inorg}:ΔDIC_{org}) ratios could in fact be lower, since the computed effect of NCP on DIC was probably underestimated due DOP assimilation and/or dissolved primary production (carbon overconsumption).

[38] The overall effect of NCC in decreasing the CO₂ sink in the area during the cruises was low (on average ~12%). The primary production and calcification rates based on 14C incubations measured in the study area [Harlay et al., 2010; J. Harlay, unpublished data, 2009] are consistent with those typically reported in literature in the North Atlantic Ocean during blooms of coccolithophores [Fernández et al., 1993; van der Wal et al., 1995; Marañon and González, 1997; Rees et al., 2002]. The NCC:NCP (ΔDIC_{inorg}:ΔDIC_{org}) ratios are also consistent with those reported in literature for the North Atlantic Ocean. The North Atlantic Ocean is one of the main regions of the global ocean where coccolithophore blooms are the most intense and recurrent [Brown and Yoder, 1994; Balch et al., 2005, 2007]. Also, Emiliania huxleyi is the most abundant and ubiquitous coccolithophore in the modern ocean [Paasche, 2002]. Hence, if one assumes that the overall low effect of NCC in decreasing the CO₂ sink is a general feature in naturally occurring blooms in the global ocean, then the potential feedback on increasing atmospheric CO₂ of the projected decrease of pelagic calcification [e.g., Gehlen et al., 2007; Ridgwell et al., 2007; Hofmann and Schellnhuber, 2009] due to thermodynamic CO₂ “production” from calcification is probably minor. Furthermore, in naturally occurring blooms, the cumulative effect of NCP leads to an increase of Ω_{CAL} above wintertime values (at or close to CO₂ atmospheric equilibrium). Hence, a future increase of NCP [e.g., Riebesell et al., 2007] could to some extent counteract the effect of ocean acidification on Ω_{CAL}, in addition to the predicted effect of SST increase on Ω_{CAL} [Cao et al., 2007; McNeil and Matear, 2007].


Nanninga, H. J., and T. Tyrrell (1996), "Importance of light for the forma-


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