Trends in inorganic and organic carbon in a bloom of *Emiliania huxleyi* in the North Sea

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**ABSTRACT:** During a survey of the end phase of an *Emiliania huxleyi* bloom in the northern part of the North Sea we measured total inorganic carbon (TIC) and the fugacity of CO₂ (fCO₂), as well as standing stocks of CaCO₃ and particulate organic carbon (POC). Production of CaCO₃ by *E. huxleyi* resulted in an immediate increase of fCO₂, but led to a long-term decrease in fCO₂. Observations during a surface survey and at 24 h stations showed a large increase of fCO₂ with the standing stock of CaCO₃. The immediate increase of fCO₂ is caused by a shift in the chemical equilibria in the inorganic carbon system when alkalinity decreases relative to dissolved inorganic carbon (DIC). Average fCO₂ in the high reflectance area (with high numbers of detached coccoliths) was lower than average fCO₂ in the reference areas, located outside the *E. huxleyi* bloom. The long-term decrease in fCO₂ is due to an enhanced sedimentation of both organic and inorganic carbon in faecal pellets containing heavy calcite. This enhanced sedimentation is reflected in the vertical gradient of TIC between the surface mixed layer and the aphotic zone, which increased from the POC-rich zone to the CaCO₃ maximum. The overall effect of production, air-sea exchange, mineralisation and sedimentation was a decrease of fCO₂ due to a net transport of carbon to below the pycnocline. We tentatively calculate an atmospheric carbon sink of 1.3 mol m⁻² for this bloom of *E. huxleyi*.

**KEY WORDS:** TIC, fCO₂, CaCO₃, POC, Algal bloom, Coccolithophorid

**INTRODUCTION**

*Emiliania huxleyi* (Lohmann) Hay & Mohler is a coccolithophorid of the class of Prymnesiophyta. It is a unicellular alga that produces organic carbon through photosynthesis and inorganic carbon through coccolithogenesis. The coccoliths of *E. huxleyi* are oval platelets which are formed intracellularly by precipitation of CaCO₃ in a coccolith vesicle (Westbroek et al. 1989). After completion they are transported out of the cell and retained on the cell surface.

Massive blooms of this species are a regular (yearly) phenomenon, especially in the temperate regions. Surface waters with spectral signatures similar to that of *Emiliania huxleyi* blooms annually covered an average of 1.4 × 10⁶ km² (Brown & Yoder 1994). *E. huxleyi* may influence global climate with 3 mechanisms: (1) by affecting the inorganic carbon system of the sea water; (2) by altering the heat exchange between the sea water and the atmosphere, due to increased light scattering by detached coccoliths; and (3) by contributing to emissions of dimethylsulphide (DMS), which increases cloud albedo. In this paper we focus mainly on the first mechanism and to some extent on the second.

All algae contain the enzyme ribulose bisphosphate carboxylase oxygenase (Rubisco). Rubisco fixes CO₂ into organic carbon (Eq. 1), which decreases the CO₂ concentration in the sea water. Besides organic carbon, *Emiliania huxleyi* also produces CaCO₃ (Eq. 2). Production of CaCO₃ generates CO₂ intracellularly (Eq. 3). The ratio between the production of organic carbon and CaCO₃ determines the net effect on the CO₂ concentration in the sea water. Production of organic carbon and CaCO₃ in a ratio of 1:1 (Eq. 4) results in a small decrease of the CO₂ concentration. This decrease is caused by the buffering effect of sea water: removal of bicarbonate is partially compensated for by hydration of CO₂. The concentration of CO₂ remains constant if the ratio is 1:1.2. Higher ratios result in elevated CO₂ concentrations.

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**Materials and Methods**

During a cruise in the northern part of the North Sea (Fig. 1A) from 28 June until 12 July 1993 total inorganic carbon (TIC), fCO2, standing stocks of CaCO3 and particulate organic carbon (POC) [see Table 1] were measured on board the research vessel 'Pelagia'. For TIC, fCO2, and CaCO3, both discrete samples at CTD stations and on-line measurements, when the ship was sailing, were taken. For POC only discrete samples were taken.

Laboratory experiments have shown that the ratio between organic carbon and CaCO3 production is affected by the growth conditions of *Emiliania huxleyi*. CaCO3 production has been observed to exceed photosynthesis when cells are limited by phosphate (Paasche & Brubak 1994, van Bleijswijk et al. 1994b). Such a situation may occur at the end of a bloom.

In the field the situation is complicated by the variability of environmental factors. Furthermore, sedimentation may play an important role in the field, whereas it cannot be measured in the laboratory. Therefore no a priori conclusions can be drawn with respect to the effect of *Emiliania huxleyi* blooms on the CO2 concentration of surface waters. In order to resolve this question we measured the concentrations and standing stocks of carbon (fCO2, TIC, CaCO3, POC) in various stages of a bloom of *E. huxleyi* in the summer of 1993 in the North Sea. We derive a carbon budget for the development of the bloom (in time) based on the various stages of the bloom encountered on a transect from the edge to the centre of the bloom (in space).

The fugacity of CO2 (fCO2) is proportional to the chemical activity (µ) of CO2 in air (equivalent to the activity of a dissolved ion). fCO2 is about 0.5% lower than the partial pressure of CO2 (pCO2, equivalent to the concentration of a dissolved ion). Total inorganic carbon (TIC) is the sum of dissolved inorganic carbon (DIC) and CaCO3. Calcium carbonate (CaCO3) is precipitated by *Emiliania huxleyi* into coccoliths in the mineral form calcite (Young et al. 1991). Particulate organic carbon (POC) here designates the organic carbon in algae, calculated from flow cytometer data. Alkalinity is the excess of strong cations over strong anions or the amount of acid needed to titrate weak bases to their protonated forms. Alkalinity was calculated from DIC and fCO2.

**Sampling.** Discrete samples were taken from a CTD rosette sampler (Neil Brown) equipped with 10.5 l NOEX bottles. Samples were not poisoned; they were stored in the dark and analysed shortly after sampling. Discrete samples for TIC were taken in gas tight bags made of Mailar (aluminium foil coated with plastic) fitted with gas tight tubing (Masterflex 6542-24). TIC was measured within 2 h after sampling. Discrete samples for fCO2 were taken in 1100 ml bottles of dark glass, which were flushed with 3 volumes of sea water. The fCO2 was measured within 1 h after sampling.

On-line samples for TIC were taken at approximately 10 min intervals from a 10 l debubbling tank. This tank was flushed with water from the aqua flow system (flow approximately 8 l min⁻¹) which took in water at a depth of approximately 3 m at the bow of the ship. On-line samples for fCO2 were taken directly from the aqua flow system. Water temperature, salinity, fluorescence and atmospheric pressure were logged automatically at 1 min intervals.

**Total Inorganic Carbon.** Total inorganic carbon (TIC) was measured with an automated coulometer (DOE). Measurements were calibrated with standard water obtained from A. G. Dickson (Scripps Institution of Oceanography, CA, USA). The extraction efficiency as determined with this standard water was 99.3%. The standard deviation was 8 μmol kg⁻¹ (n = 19). This relatively large standard deviation was probably caused by variation between titration cells (A. A. J. Majoer, Netherlands Institute for Sea Research, NIOZ, The Netherlands, pers. comm.), which were not calibrated separately. All measurements at a station were performed with the same cell, probably leading to less variation.

**Fugacity of CO2.** The mole fraction of CO2 (xCO2) in air equilibrated with sea water was measured with an IRGA (infra-red gas analyser, Licor 6252). The instrument resembles the underway system described by Wanninkhof & Thoning (1993), with 3 improvements (design by M. H. C. Stoll and J. M. J. Hoppema, NIOZ). The xCO2 is measured in non-flowing gas to guarantee that measurements are taken at atmospheric pressure and to obtain a stable signal. Typical standard deviation of 10 measurements was 0.05 ppm. (2) During equilibration the gas is circulated through both the sample cell and the equilibrator. This prevents the flow of unequilibrated air into the system which Wanninkhof & Thoning (1993) mentioned as a possible source of error. (3) Measurements were performed in dry gas to circumvent the need for water vapour correction, and to facilitate comparison between samples and calibration gases.

The IRGA was calibrated every hour with 3 mixtures of CO2 in synthetic air. The raw data were fitted by a second order function. The polynomial function sup-
Fig. 1. The research area. (A) Cruise track (from 28 June until 12 July) with station numbers. Stns 19N and 19S are represented by a single dot. Stns 20 to 34 are referred to as the transect. Shaded area indicates the average position of the high reflectance area between 27 June and 13 July. (B) On-line data in the high reflectance area. Bold lines: on-line data in the reference areas. (B) AVHRR photograph of the investigated area on 27 June 1993. The high reflectance area can be recognised as a light spot between The Shetlands and Norway. Dark spots are cloud cover. (C) Contour plot of the fluorescence (arbitrary units) at 3 m depth in the investigated area.
plied by the manufacturer gives less reproducible results for xCO$_2$, because the zero and span settings vary with changes in pressure and temperature (F. A. Koning, NIOZ, pers. comm.).

The 3 calibration gases were calibrated on a gas chromatograph (GC) against 3 standards of the NMI (Dutch Bureau of Standards). Similarly, a calibration gas of NOAA (National Oceanographic and Atmospheric Administration, USA) was measured on the GC. The difference between the measured value based on the NMI calibration and the value given by NOAA was +1.3 ppm. The reproducibility of the IRGA, calculated as the standard deviation of air samples \( n = 133 \), was 1.2 ppm.

Discrete samples for xCO$_2$ were measured in bottles of dark glass after equilibration of 1 l sea water with 100 ml laboratory air plus the volume of air in the instrument. On-line samples were taken by equilibrating a circulated flow of air with a continuous flow of sea water from the aqua flow system \( \approx 2 \) l min$^{-1}$) in an equilibrator equipped with a calibrated temperature sensor. The design of the equilibrator was adopted from A. Watson (Robertson et al. 1993). Every hour we measured 10 samples from the sea water equilibrator and 1 sample of air, taken at about 15 m above the sea surface.

For the discrete samples, fCO$_2$ was calculated using xCO$_2$, the temperature measured by the CTD and the ambient pressure (Weiss 1974). This calculated fCO$_2$ was higher than the in situ fCO$_2$ due to warming of the samples. We estimate an increase of less than 10 \( \mu \)atm for surface samples and less than 60 \( \mu \)atm for samples taken at 125 m.

For the on-line samples, fCO$_2$ in the equilibrator was calculated using the temperature in the equilibrator and the ambient pressure. fCO$_2$ at the in situ temperature was calculated from TIC and alkalinity according to Goyet et al. (1993). The use of TIC instead of DIC introduced an error smaller than 0.1 \( \mu \)atm. TIC at the time of measurement of fCO$_2$ was obtained by linear interpolation. Alkalinity was calculated using TIC and fCO$_2$ in the equilibrator.

Dissolved inorganic carbon and alkalinity. Dissolved inorganic carbon (DIC) was calculated by subtracting CaCO$_3$ from TIC. Alkalinity was calculated from DIC and fCO$_2$, using the dissociation constants of Goyet & Poisson (1989). The uncertainty in alkalinity due to the standard deviation of 8 pmol kg$^{-1}$ in TIC is about 10 \( \mu \)equivalents kg$^{-1}$. The uncertainty due to the standard deviation of 1.2 ppm in fCO$_2$ is about 1 \( \mu \)equivalent kg$^{-1}$.

Standing stock of CaCO$_3$. Particulate calcium \( >0.8 \mu \)m standing stock was determined according to van Bleijswijk et al. (1994a) using atomic absorption spectroscopy. The reproducibility of the measurements (average standard deviation of duplicates) was 6%.

Dissolution of CaCO$_3$. The dissolution rate of CaCO$_3$ was determined by incubating 5 l of sea water in the dark. Duplicate samples were taken in the dark from single 10.5 l NOEX bottles. Samples were incubated unfiltered or after filtration over 10 and 200 \( \mu \)m filters to remove micro- and mesozooplankton respectively. Samples were incubated in a sea water tank on deck of the ship. Subsamples were taken after 0, 24 and 48 or 72 h, until the bottles were empty. Three series of subsamples in which a decrease in CaCO$_3$ alternated with an increase were discarded. Apparently the bottles had not been shaken sufficiently to resuspend the coccoliths and algae before taking one of the subsamples.

Saturation of sea water with CaCO$_3$. The concentration of calcium ([Ca$^{2+}$]) was measured by atomic absorption spectroscopy. The concentration of carbonate ([CO$_3^{2-}$]) was calculated from DIC and fCO$_2$, using the dissociation constants of Goyet & Poisson (1989). The extent of undersaturation of CaCO$_3$ in sea water was calculated according to Mucci (1983).

Particulate organic carbon. Particulate organic carbon (POC) standing stock of the phytoplankton was calculated from cell numbers and estimated spherical diameters (ESDs), as determined by flow cytometry (Veldhuis et al. in press). ESD was calibrated with standard beads (high density 2.0 and 10.0 \( \mu \)m, Coulter Counter), and checked by fractionated filtration and microscopical observations. ESDs were used to estimate cell volumes (assuming spherical cells), that were converted to carbon. For cyanobacteria a constant factor of 400 \( \mu \)g C \( \mu \)m$^{-3}$ was used (Takahashi et al. 1985). For pico-eukaryotes a factor of 1800 to 3000 \( \mu \)g cell$^{-1}$ was used, depending on size (Campbell & Vaulot 1993). For larger cells the formula $\log C =-0.422+0.758 \log V$ was used (Strathmann 1967). Detritus was not included.

RESULTS

Research area

Before the start of the cruise the research area was located by AVHRR (advanced very high resolution radiometry). An area with high reflectance was observed in the North Sea. During the cruise this area was located east of the Shetland Islands (Fig. 1B). The high reflectance area could be recognised from the ship as a milky white colouring of the sea. It was characterised by low nutrient concentrations (NO$_3^-$ and
PO_{4}^{3-} < 0.1 \mu mol \ell^{-1}), low particulate organic carbon (-4 \mu mol \ell^{-1} POC), low numbers of living *Emiliania huxleyi* (-2000 ml^{-1}) and high numbers of detached coccoliths (-100000 ml^{-1}). These conditions are typical for the end phase of a bloom of *E. huxleyi*. Small cyanobacteria (-100 000 ml^{-1}) contributed about 50% to POC.

To the northwest of the high reflectance area we observed a POC-rich zone (cf. Fig. 1C). This zone was characterised by high nutrient concentrations (4 \mu mol 1^{-1} NO_{3}^{-}, 0.3 \mu mol 1^{-1} PO_{4}^{3-}) and a high standing stock of POC (-30 \mu mol 1^{-1}). A mixed phytoplankton community was present, with *Emiliania huxleyi* (-3500 ml^{-1}) constituting about 40% of POC. In the Atlantic Ocean and to the east and south of the high reflectance area nutrient concentrations (0.1 to 6 \mu mol 1^{-1} NO_{3}^{-} and 0.1 to 0.4 \mu mol 1^{-1} PO_{4}^{3-}) and POC (2 to 15 \mu mol 1^{-1}) were variable. In these areas, which we will call the reference areas (Fig. 1A), the numbers of *Emiliania huxleyi* cells (-2000 ml^{-1}) and detached coccoliths (-16 000 ml^{-1}) were low.

**On-line measurements**

Total inorganic carbon (TIC; Table 1) averaged 2048 ± 31 \mu mol kg^{-1} (n = 172) in the high reflectance area, and 2058 ± 31 \mu mol kg^{-1} (n = 182) in the reference areas. TIC varied between 1970 and 2110 \mu mol kg^{-1} in both areas. fC_{O2} in the high reflectance area was 303 ± 24 \mu atm on average (n = 464, ranging from 257 to 440 \mu atm). In the reference areas fC_{O2} was 324 ± 29 \mu atm on average (n = 416, ranging from 227 to 421 \mu atm).

Apparently, the 2 regions, while showing large differences in detached coccoliths, do not show significant differences in average TIC and fC_{O2}. However, we found a positive correlation between fC_{O2} and on-line CaCO_{3} standing stock measured at the same time fC_{O2} (\mu atm) = 259.7 + 3.5 CaCO_{3} (\mu mol 1^{-1}), n = 94, p < 0.05. When fC_{O2} was corrected to a constant temperature of 10.6°C it increased slightly less with CaCO_{3} [Fig 2; fC_{O2}-corrected (\mu atm) = 260.0 + 3.0 CaCO_{3} (\mu mol 1^{-1}), n = 94, p < 0.05]. We also observed a positive correlation between temperature and CaCO_{3} standing stock [T (°C) = 10.6 + 0.03 CaCO_{3} (\mu mol 1^{-1}), n = 94, p < 0.02]. Ackleson et al. (1988) and Holligan et al. (1993) found a much larger temperature difference between CaCO_{3}-rich and CaCO_{3}-poor waters.

The mole fraction of CO_{2} (xCO_{2}) in dry air was 358.8 ± 1.2 ppm (n = 133) during the first week of the cruise. The same average xCO_{2} was presented in Boden et al. (1994) for June 1993 north of 35° N (357.6 ± 3.7, n = 8, excluding the data of the industry-influenced Waldhof station). fC_{O2} in the air, at a pressure of 1.013 X 10^{5} Pa and an average water temperature of 11.6°C, was 357.5 \mu atm.

**24 h stations**

At four 24 h stations (Stns 12, 19N, 19S and 15; Fig. 1A) we measured several vertical profiles of TIC, fC_{O2}, CaCO_{3} and POC over a 24 h period. The position of the ship was maintained in relation to the sam-

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**Table 1. Parameters mentioned in this paper**

<table>
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<th>Parameter</th>
<th>Abbreviation</th>
<th>Unit</th>
<th>Description</th>
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<tr>
<td>Alkalinity</td>
<td>Alk</td>
<td>uequivalents kg^{-1}</td>
<td>2[HCO_{3}^{-}] + [HCO_{2}^{-}] + [B(OH)_{4}]^{-} + [OH^{-}] − [H^{+}] etc.</td>
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<tr>
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<td>Measured fluometrically or with HPLC</td>
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<tr>
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<td>Activity of CO_{2} gas in water</td>
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<td>Gas mixing ratio (\mu mol mol^{-1})</td>
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<td>\mu atm</td>
<td>Phytoplankton carbon (flow cytometer)</td>
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<td>\mu mol 1^{-1}</td>
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</tr>
<tr>
<td>Total inorganic carbon</td>
<td>TIC</td>
<td>\mu mol 1^{-1}</td>
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pleased water mass by using a drifting buoy with sediment traps at 10 and 50 m depth. Stn 12 was located just outside the high reflectance area. To the west of the high reflectance area there were two 24 h stations on the same day (sampled alternatingly). One (Stn 19N) was located in the POC-rich zone, and the other (Stn 19S) was located 9 nautical miles to the south, towards the high reflectance area. The fourth 24 h station (Stn 15) was in the high reflectance area.

At none of the stations did fCO2 or TIC show a distinct diel rhythm. In order to better distinguish the differences between stations, data of all CTD casts were averaged to produce a single profile per station. We order these stations as progressive stages of the bloom: first the reference areas, then the POC-rich zone and then the high reflectance area (successively Stns 12, 19N, 19S and 15). During these stages concentrations of TIC decreased in the upper mixed layer (from 2070 to 2060 μmol kg⁻¹). In contrast, below the pycnocline TIC increased (from 2120 to 2150 μmol kg⁻¹) (Fig. 3A). These observations indicate that sedimentation was higher in the high reflectance area than in the reference areas. Sedimentation decreases TIC in the upper mixed layer, and subsequent mineralisation below the pycnocline increases TIC. The fCO2 increased from Stn 12 to Stn 15 over the entire water column (from 286 to 354 μatm at the surface, Fig. 3B). Stns 19S and 19N showed intermediate values.

![Fig. 3. Depth profiles of 24 h stations, averaged values over all CTD casts at a single station, with standard deviations (a) Stn 12, outside the bloom (n = 3, except CaCO3); (x) Stn 19N, at the fluorescence maximum (n = 3, except CaCO3); (+) Stn 19S, at the lower fluorescence (n = 4, except CaCO3); (D) Stn 15, at the high reflectance area (n = 5, except CaCO3). (A) Total inorganic carbon, TIC; (B) fCO2; (C) CaCO3; (D) POC (n = 1 or 2 for Stns 19N, 19S).](image-url)
The standing stock of CaCO$_3$ increased from Stn 19N via 19S to Stn 15, whereas the standing stock of POC decreased (Fig. 3C, D). At Stn 12 the standing stocks of CaCO$_3$ and POC were intermediate between those at Stns 19N and 19S.

At Stn 15 a high standing stock of CaCO$_3$ (8 µmol l$^{-1}$) and a low standing stock of POC (11 µmol l$^{-1}$) coincided with a high fCO$_2$ (354 µatm at the surface). Most likely, this high fCO$_2$ is the result of the acidification of the sea water due to CaCO$_3$ production (Eqs. 2 & 3). At another station in the high reflectance area (Stn 7, Fig. 1A) a high CaCO$_3$ standing stock (15 µmol l$^{-1}$) and low POC (4 µmol l$^{-1}$ at the surface) coincided with a low fCO$_2$ (330 µatm at the surface, data not shown). The vertical gradient in TIC (2040 µmol kg$^{-1}$ at the surface; 2150 µmol kg$^{-1}$ at 125 m depth) was even sharper here than at Stn 15. We conclude that so much carbon was removed from the upper mixed layer through sedimentation that this had a greater effect on fCO$_2$ than did the production of coccoliths.

**Dissolution experiments**

At Stns 7, 12 and 15 (Fig. 1A) samples were incubated in the dark for determination of the dissolution rate of CaCO$_3$. In order to determine the effect of grazing on the dissolution rate we compared samples that had been filtered before incubation (either 10 or 200 µm) with unfiltered samples. Removal of grazers had no significant effect on the dissolution rate of CaCO$_3$ (data not shown). Therefore the results were averaged per station (Fig. 4). At all stations 25% (±11%, n = 27) of the CaCO$_3$ standing stock dissolved per 24 h.

The sea water at Stns 7, 12 and 15 was 3.8 to 4.5 times oversaturated with respect to CaCO$_3$. Even if all the POC in the samples had been mineralised to CO$_2$ during the incubations the sea water would still be oversaturated 3.6 to 4.1 times with respect to CaCO$_3$.

**Transact**

Within a period of 24 h vertical profiles were taken along a transect (Stns 20 to 33; Fig. 1A). This transect ran from the edge of the Atlantic Ocean, through the POC-rich zone, along the edge of the high reflectance area where coccoliths were abundant.

TIC and the density of the water (SigmaT) showed comparable patterns (Fig. 5A, B). Towards the high reflectance area the gradients of TIC and SigmaT with depth became more pronounced. An increased gradient of TIC with depth was noted above (in the section '24 h stations'), and indicates increased sedimentation. The fCO$_2$ was clearly influenced by uptake of CO$_2$ by algae, expressed as POC (Fig. 5C, D). A minimum of fCO$_2$ was located in the POC-rich zone. Low values of fCO$_2$ persisted in the high reflectance area. There was no apparent relationship between CaCO$_3$ and fCO$_2$ (Fig. 5D, E). Calculated alkalinity in the upper mixed layer decreased from the POC-rich zone to the high reflectance area. This agrees with the observed increase of the standing stock of CaCO$_3$ (Fig. 5E, F).

The CaCO$_3$ standing stock, as measured by atomic absorption, showed a close correlation with the CaCO$_3$ standing stock calculated from flow cytometer data (CaCO$_3^{\text{AAS}}$ = 0.99CaCO$_3^{\text{flow cytometer}}$ - 0.052, p < 0.001, n = 39). For Stns 20, 22, 30 and 32 we assumed that each Emiliania huxleyi cell was covered with 20 coccoliths. The total number of coccoliths (attached and detached) was multiplied by 0.26 pg C coccolith$^{-1}$ (Balch et al. 1992). At Stns 24, 26 and 28 (the POC-rich zone) CaCO$_3$ was calculated from detached coccoliths only, because the numbers of *E. huxleyi* cells were probably overestimated due to the presence of small diatoms (P. van der Wal, NIOZ, pers. comm.). At Stn 33 (95 nautical miles from the start of the transect) CaCO$_3$ was not measured by atomic absorption spectrophotometry (AAS), but estimated using this equation.

The organic carbon to chlorophyll ratio [POC (µmol l$^{-1}$)/chlorophyll a (µg l$^{-1}$)] was 6.7 ± 3.8 (n = 43) on average. In the POC-rich zone the ratio was 9 ± 5 (n = 17). In the high reflectance area it was 4 ± 2 (n = 15). Because organic carbon was calculated from flow cytometer data for living algae, the ratio is a direct measure of the average algal composition.

Total carbon content (TIC + POC; Fig. 6) was calculated over the photic zone (0 to 40 m, penetration depth of 0.5% of surface irradiance) and the aphotic zone (40 to 80 m), and over the entire sampled depth (0 to 80 m). Proceeding from the POC-rich zone towards the high reflectance area the total carbon content decreased in
Fig. 5. Contour plots (using least squares method) of the transect, with distance from the first station in nautical miles and depth in meters. Diamonds represent sampling depths. $f\text{CO}_2$ and CaCO$_3$ were not measured at the last station. (A) SigmaT is the density excess calculated as [density (kg l$^{-1}$) - 1] x 1000. (B) TIC in µmol kg$^{-1}$. (C) POC in µmol l$^{-1}$. (D) $f\text{CO}_2$ in µatm. (E) CaCO$_3$ in µmol l$^{-1}$ at 95 nautical miles was calculated from flow cytometer data using the correlation of flow cytometer data with atomic adsorption measurements at the other stations (see text). (F) Calculated alkalinity in µequivalents kg$^{-1}$. 
In a bloom of *Emiliania huxleyi* in the North Atlantic in 1991 Robertson et al. (1994) found that the fugacity of CO$_2$ ($f$CO$_2$) was 15 μatm higher in waters with high CaCO$_3$ standing stocks (>18 μmol l$^{-1}$) than in waters with low CaCO$_3$ standing stocks (<5.5 μmol l$^{-1}$). We will argue here that while the short-term effect of CaCO$_3$ precipitation was a rise in $f$CO$_2$ due to a decrease in alkalinity, the long-term effect of this bloom of *E. huxleyi* was a decrease in $f$CO$_2$ by enhanced sedimentation. First we discuss the influences that the physical properties of the water column and biological activities have on the concentrations of inorganic and particulate organic carbon and the speciation of the dissolved inorganic carbon system. Then we derive a carbon budget that shows that this bloom acted as a carbon sink for the atmosphere.

**DISCUSSION**

In a bloom of *Emiliania huxleyi* in the North Atlantic in 1991 Robertson et al. (1994) found that the fugacity of CO$_2$ ($f$CO$_2$) was 15 μatm higher in waters with high CaCO$_3$ standing stocks (>18 μmol l$^{-1}$) than in waters with low CaCO$_3$ standing stocks (<5.5 μmol l$^{-1}$). We will argue here that while the short-term effect of CaCO$_3$ precipitation was a rise in $f$CO$_2$ due to a decrease in alkalinity, the long-term effect of this bloom of *E. huxleyi* was a decrease in $f$CO$_2$ by enhanced sedimentation. First we discuss the influences that the physical properties of the water column and biological activities have on the concentrations of inorganic and particulate organic carbon and the speciation of the dissolved inorganic carbon system. Then we derive a carbon budget that shows that this bloom acted as a carbon sink for the atmosphere.

The influence of the physical structure was apparent from the similarity between the contour plots for total inorganic carbon (TIC) and the density of the water column (Fig. 6A, B). In the high reflectance area the stratification was more pronounced than in the northern part of the research area (Atlantic Ocean side). As a result the phytoplankton was mixed over shallower depths, and the concentration gradient of inorganic carbon was steeper (Fig. 5B, see also Fig. 6A). The enhancement of stratification is not necessarily the result of physical processes only. *Emiliania huxleyi* may generate a positive feedback for an increase of the temperature in the upper mixed layer: the reflectance of coccoliths may increase the temperature by light scattering (Holligan & Balch 1991, Westbroek et al. 1993), this will make the upper mixed layer shallower which will increase the average light intensity, and this will stimulate growth. The observed positive correlation between temperature and the CaCO$_3$ standing stock illustrates these processes of calcification, stratification and positive feedback.

The influence of biological activities on the carbon speciation was manifested by the occurrence of the $f$CO$_2$ minimum in the POC-rich zone, and by the increase of $f$CO$_2$ with biologically produced CaCO$_3$. Furthermore TIC was strongly depleted in the upper mixed layer of the high reflectance area, because in this area sedimentation was high due to the elevated sinking speed of faecal pellets containing CaCO$_3$ (van der Wal et al. 1995).

In a plot based on a surface survey over the entire cruise track, $f$CO$_2$ (corrected to a constant temperature) increased with an increase of the standing stock of CaCO$_3$ (Fig. 2). This demonstrates that precipitation of CaCO$_3$ shifts the DIC equilibria in favour of CO$_2$ according to Eqs. (2) and (3). The $f$CO$_2$ increased 3.0 μatm per μmol l$^{-1}$ CaCO$_3$. This is much
higher than the increase of $fCO_2$ that is predicted from CaCO$_3$ precipitation (1 $\mu$atm per $\mu$mol 1$^{-1}$ CaCO$_3$) at typical concentrations of alkalinity and DIC. The enhanced increase results from the apparent inverse correlation between the standing stocks of POC and CaCO$_3$ (Figs. 3C, D & 5C, E). There are 3 compatible explanations for this inverse correlation. Firstly, the production of CaCO$_3$ continues after the culmination of the bloom, so that the peak in CaCO$_3$ standing stock occurs after the peak in POC standing stock (P. van der Wal pers. comm.). Secondly, other phytoplankton species may contribute relatively less to POC at the end of the bloom, when nutrient concentrations are low. At low nutrient concentrations Emiliania huxleyi will outcompete other phytoplankton species as it has a high affinity for nutrients, especially phosphate (Egge 1993). Thirdly, POC is degraded faster than CaCO$_3$, so the relative contribution of CaCO$_3$ increases.

The relatively high $fCO_2$ in the surface water at Stn 15 (which has a high standing stock of CaCO$_3$) is in accordance with the trend shown in Fig. 2. The profiles of the other 24 h stations do not show a clear increase of $fCO_2$ with CaCO$_3$. Other data also seem to contradict a positive correlation between CaCO$_3$ and $fCO_2$. At Stn 7, where the highest standing stock of CaCO$_3$ was found, $fCO_2$ was relatively low. Along the transect $fCO_2$ at the surface was fairly constant between Stns 24 and 33. On-line surface measurements of $fCO_2$ integrated over wider areas were lower inside the high reflectance area than in the reference areas. The explanation is found in the trend in TIC along the transect towards lower concentrations in the upper mixed layer and higher concentrations below the pycnocline. This is consistent with sedimentation, which results in a decrease of $fCO_2$ at time scales that are slower than the increase of $fCO_2$ caused by production of CaCO$_3$. We conclude that whether calcification is seen as a sink or source of CO$_2$ depends on the time scale on which these processes are observed: while on the basis of chemical equilibria production of CaCO$_3$ will lead to an instantaneous increase of $fCO_2$, the overall processes of production, remineralisation, dissolution, air-sea gas exchange and sedimentation lead to a net export of carbon from the upper mixed layer, and hence a decrease of $fCO_2$.

About 25% of the standing stock of CaCO$_3$ was found to dissolve per 24 h in the dark, despite the fact that the sea water at Stns 7, 12 and 15 was about 4 times oversaturated with respect to CaCO$_3$. Degradation of the standing stock of POC would not change this. Since there was no significant difference between filtered (either 10 or 200 $\mu$m) and unfiltered samples, we conclude that dissolution was not caused by micro- or mesozooplankton. Therefore dissolution was probably caused by respiration of bacteria and algae, and by lysis of cells, which creates an acidified micro-environment around the coccoliths.

Photosynthesis accompanied by production of CaCO$_3$ in a molar ratio of 1:1 amounts to bicarbonate utilisation, and leads to a smaller decrease in $fCO_2$ than in the case of CO$_2$ utilisation by photosynthesis alone. In either case there is an additional decrease in $fCO_2$ due to an increase in pH since uptake NO$_3^-$ by the cell is coupled to OH$^-$ excretion (Brewer & Goldman 1976). This increase of pH is equivalent to an increase of alkalinity (Table 1). The ratio between calcification and photosynthesis (C/P ratio) indicates how uptake of dissolved inorganic carbon will affect $fCO_2$. When the effect of simultaneous production of CaCO$_3$ and POC is calculated, $fCO_2$ remains constant at a C/P ratio of 1.2:1. When the effect of PON production is also taken into account the C/P ratio required for maintaining a constant $fCO_2$ increases to 1.3:1. The highest C/P production ratio that was observed in this bloom was 0.18 (Stn 7, van der Wal et al. 1995). The highest C/P sedimentation ratio was 1.3 (Stn 15, the unpoisoned trap at 50 m depth; van der Wal et al. 1995). Thus no indication for an increase of $fCO_2$ was observed at any stage of this bloom.

The particulate organic carbon to chlorophyll a ratio in the POC-rich zone was about twice the ratio in the high reflectance area. Although the difference is not significant, there is an explanation for this difference. The beam attenuation coefficient c$530$ was twice as large in the high reflectance area as in the POC-rich zone. This would lead to a higher chlorophyll content per cell as an adaptation to low light conditions.

Consecutive stages of the bloom development were encountered travelling southward along the transect. Therefore we tentatively interpret Fig. 6 as the development of the bloom in time. This interpretation is suggested by the seasonal northwesterly migration of the high reflectance area on satellite images taken before the cruise. This is corroborated by the observed decrease of nutrient concentrations from north to south. We have calculated the transport of carbon during the bloom from changes in the total carbon content (TIC + POC) of the sampled water column along the transect. For this purpose the water column was divided into en upper (0 to 40 m), an intermediate (40 to 80 m) and a deep (80 to 130 m) box (Fig. 7). The thermocline resides at approximately 40 m depth (Fig. 5A), whereas no samples were taken below 80 m depth. The mass balance for the upper box involves an influx of CO$_2$ from the atmosphere, changes in carbon pools and downflux of biogenic particles:

\[ \text{Influx} = \Delta \text{DIC} + \Delta \text{POC} + \Delta \text{CaCO}_3 + \text{Downflux} \]  

(5)
This latter downflux is the source term for a similar balance for the intermediate box, where any residual carbon is assumed to represent an excess sedimentation term into the deep box:

\[ \text{Downflux} = ADIC + APOC + ACaCO_3 + \text{Excess sedimentation} \]  

In the first 20 nautical miles of the transect from the Atlantic Ocean to the POC-rich zone the \( fCO_2 \) decreased to 286 \( \mu \text{atm} \) at the surface, while the total carbon content from 0 to 80 m increased by 0.7 mol m\(^{-2} \) (Figs. 5D & 6B). This indicates uptake of \( CO_2 \) from the atmosphere. The air to sea flux (influx; Fig. 7) was calculated with the exchange coefficient for average wind speeds given by Wanninkhof (1992) using the average wind speed during the cruise and the \( fCO_2 \) gradient at the chlorophyll maximum (20 nautical miles from the beginning of the transect). At a fugacity gradient of 72 \( \mu \text{atm} \) and an average wind speed during the cruise of 7.7 m s\(^{-1} \) it would have taken 64 d for an amount of 0.7 mol m\(^{-2} \) to be taken up from the atmosphere. This 64 d period is only an approximation since \( fCO_2 \) was only measured once at Stn 24 and the wind speed represents an average in time (13 d) and space. Blooms tend to be visible by AVHRR for shorter periods of typically 15 to 30 d (Westbroek et al. 1993). This would mean that either the air to sea flux has been underestimated or diffusion from below the thermocline plays an important role. We have not included the latter diffusion in our calculations.

In the subsequent stretch (20 to 100 nautical miles) from the POC-rich zone (Stn 24) to the high reflectance area (Stn 33) the stratification increased (Fig. 5A). As discussed above, this led to a decrease of DIC in the photic zone (0 to 40 m; Fig. 6A). This decrease cannot be ascribed to increased photosynthesis since neither POC (Figs. 5C & 6A), nor chlorophyll \( a \) (data not shown) increased, due to nitrogen limitation. Since the total carbon content in the aphotic zone increased while the total carbon content in the photic zone decreased (Fig. 6A) we assume that these changes are caused by sedimentation.

From the POC-rich zone to the high reflectance area the decrease in total carbon content of 1.6 mol m\(^{-2} \) in the upper mixed layer was larger than the increase of 0.9 mol m\(^{-2} \) in the intermediate layer (Fig. 6B). Since the upper mixed layer remained undersaturated (Fig. 5D), the difference of 0.7 mol m\(^{-2} \) cannot have escaped by sea to air outflux. The most straightforward explanation is that from 80 m to the bottom the total carbon content increased as well, as was found elsewhere at the 24 h stations at 125 m depth (Fig. 3). When the measured total carbon content at 80 m depth was extrapolated to the 80 to 130 m interval an increase of 2.4 mol m\(^{-2} \) for the aphotic zone (40 to 130 m) was calculated over the whole transect (downflux + excess sedimentation in Fig. 7).

In the photic zone the total carbon content decreased 1.1 mol m\(^{-2} \). This would yield an overall atmospheric carbon sink of 1.3 mol m\(^{-2} \) for this bloom of *Emiliania huxleyi*. This is consistent with the relatively high sedimentation rate of 45 mmol m\(^{-2} \) d\(^{-1} \) that was measured at Stn 7 (van der Wal et al. 1995), if it is multiplied by 30 d.

If we calculate the global significance of this carbon sink of 1.3 mol m\(^{-2} \) by multiplying it by the average area of *Emiliania huxleyi* blooms of 1.4 \( \times 10^9 \) km\(^2 \) (Brown & Yoder 1994) we arrive at 2.2 Mt C yr\(^{-1} \) or 0.4% of the export production at 100 m depth (Berger et al. 1989).
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