



## Pelagic community production and carbon-nutrient stoichiometry under variable ocean acidification in an Arctic fjord

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**Abstract.** Net community production (NCP) and carbon to nutrient uptake ratios were studied during a large-scale mesocosm experiment on ocean acidification in Kongsfjorden, western Svalbard, during June–July 2010. Nutrient depleted fjord water with natural plankton assemblages, enclosed in nine mesocosms of  $\sim 50\text{ m}^3$  in volume, was exposed to  $p\text{CO}_2$  levels ranging initially from 185 to 1420  $\mu\text{atm}$ . NCP estimations are the cumulative change in dissolved inorganic carbon concentrations after accounting for gas exchange and total alkalinity variations. Stoichiometric coupling between inorganic carbon and nutrient net uptake is shown as a ratio of NCP to a cumulative change in inorganic nutrients. Phytoplankton growth was stimulated by nutrient addition half way through the experiment and three distinct peaks in chlorophyll *a* concentration were observed during the experiment. Accordingly, the experiment was divided in three phases. Cumulative NCP was similar in all mesocosms over the duration of the experiment. However, in phases I and II, NCP was higher and in phase III lower at elevated  $p\text{CO}_2$ . Due to relatively low inorganic nutrient concentration in phase I, C : N and C : P uptake ratios were calculated only for the period after nutrient addition (phase II and phase III). For the total post-nutrient period (phase II + phase III) ratios were

close to Redfield, however they were lower in phase II and higher in phase III. Variability of NCP, C : N and C : P uptake ratios in different phases reflects the effect of increasing  $\text{CO}_2$  on phytoplankton community composition and succession. The phytoplankton community was composed predominantly of haptophytes in phase I, prasinophytes, dinoflagellates, and cryptophytes in phase II, and haptophytes, prasinophytes, dinoflagellates and chlorophytes in phase III (Schulz et al., 2013). Increasing ambient inorganic carbon concentrations have also been shown to promote primary production and carbon assimilation. For this study, it is clear that the pelagic ecosystem response to increasing  $\text{CO}_2$  is more complex than that represented in previous work, e.g. Bellerby et al. (2008). Carbon and nutrient uptake representation in models should, where possible, be more focused on individual plankton functional types as applying a single stoichiometry to a biogeochemical model with regard to the effect of increasing  $p\text{CO}_2$  may not always be optimal. The phase variability in NCP and stoichiometry may be better understood if  $\text{CO}_2$  sensitivities of the plankton's functional type biogeochemical uptake kinetics and trophic interactions are better constrained.

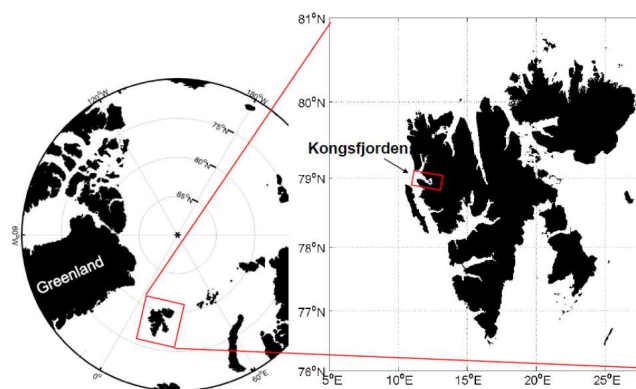
## 1 Introduction

The Arctic Ocean is a key player in global carbon cycling (e.g. Bates et al., 2009) and the Arctic shelves are currently amongst the most productive areas of the world's oceans (Wassmann et al., 2011). Over the past decades, the Arctic Ocean has experienced significant change (e.g. Christensen et al., 2007 and references therein) including warming (Loeng, 2005, Trenberth et al., 2007), sea-ice decline (Polyakov et al., 2010; Stroeve et al., 2012), freshening (McPhee et al., 2009 and reference therein) and increasing surface carbon dioxide (CO<sub>2</sub>) concentrations (Cai et al., 2010) with concomitant ocean acidification (Bellerby et al., 2005; Yamamoto-Kawai et al., 2009, 2011).

Due to naturally low carbonate ion concentrations and thus a lower buffer capacity than most of the global ocean, rapid ocean warming, diminishing ice cover facilitating greater ocean CO<sub>2</sub> uptake and a rapidly increasing freshwater fraction, waters of the Arctic Ocean are and will continue to exhibit the fastest rate of ocean acidification of all the world's oceans (Bellerby et al., 2005; Steinacher et al., 2009). Undersaturation with respect to aragonite is already found in surface waters of the Canada Basin (Yamamoto-Kawai et al., 2009; Chierici et al., 2009; Bates et al., 2012). Model studies show that the Arctic Ocean may become entirely undersaturated with respect to aragonite already by 2050 (Anderson et al., 2010).

These chemical changes may induce modifications in organism physiology and ecosystem functioning, as have been observed in many laboratory and mesocosm experiments (Nisumaa et al., 2010). Common responses are deleterious effects of ocean acidification on calcium carbonate production by marine calcifying phytoplankton (Riebesell et al., 2000; Delille et al., 2005; Ridgwell et al., 2009; Lohbeck et al., 2012) and organisms at higher trophic levels (e.g. Comeau et al. 2009; Lischka et al., 2011). Increasing ambient inorganic carbon concentrations have also been shown to enhance primary production and carbon assimilation in various photoautotrophs, including seagrasses (Palacios and Zimmerman, 2007; Hall-Spencer et al., 2008) and freshwater and marine phytoplankton (Hein and Sand-Jensen, 1997; Schippers et al., 2004; Levitan et al., 2007; Riebesell et al., 2007; Engel et al., 2008; Tortell et al., 2008).

Increasing carbon assimilation by marine phytoplankton could cause a shift in pelagic ecosystems towards higher carbon-to-nutrient utilization ratios (Riebesell et al., 2007; Bellerby et al., 2008). Model studies show that by consuming more carbon in the surface layer, marine phytoplankton may potentially increase the oceanic sink of CO<sub>2</sub> (Schneider et al., 2004). However, the Arctic Ocean is characterized by high heterotrophic bacterioplankton concentrations (Li et al., 2009) leading to net heterotrophy, which is responsible for the rapid turnover of carbon through a highly efficient microbial loop (Rokkan Iversen and Seuthe, 2011; Tremblay et al., 2012).



**Fig. 1.** Map of the Arctic Ocean with the Svalbard archipelago highlighted in red and enlarged map of the latter with a red square indicating the location of Kongsfjorden.

Despite Arctic marine ecosystems experiencing the strongest ocean acidification, no specific ocean acidification mesocosm study has been conducted in the northern high latitudes. This study presents results from the first large-scale pelagic ocean acidification mesocosm experiment conducted in the Arctic. The aim of this work is to investigate the effect of increased  $p\text{CO}_2$  on net community production – the balance between CO<sub>2</sub> assimilation due to photosynthesis by autotrophs and CO<sub>2</sub> release due to organic matter respiration by autotrophs and heterotrophs – and net community stoichiometry.

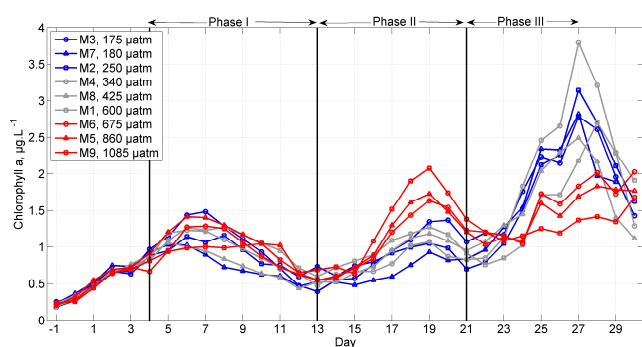
## 2 Material and methods

### 2.1 Study area

The mesocosm experiment was performed in Kongsfjorden (78°56.2' N, 11°53.6' E, Fig. 1), on the west coast of Spitsbergen, Svalbard archipelago. The water in Kongsfjorden is a mixture of Arctic water masses (which are transported by the coastal current flowing from the Barents Sea over the West Spitsbergen Shelf), Atlantic water masses (West Spitsbergen Current), and freshwater input from melting glaciers and precipitation (Cottier et al., 2005). In winter the hydrography is dominated by Arctic water masses and in summer it is under Atlantic influence (Svendsen et al., 2002).

### 2.2 Experimental set-up

Nine mesocosm bags two metres in diameter and 17 m long were deployed in Kongsfjorden in late May of 2010. The bags, attached to hard floating frames, were made of thermoplastic polyurethane (TPU). Each mesocosms enclosed 43.9–47.6 m<sup>3</sup> of fjord water (Schulz et al., 2013; Czerny et al., 2013a). Closing the mesocosms at the bottom isolated the interior waters assuring there was no further exchange with the fjord water. Above the bottom plate inside each mesocosm



**Fig. 2.** Temporal evolution of chlorophyll *a* concentrations in different mesocosms. Vertical lines on  $t_4$ ,  $t_{13}$  and  $t_{22}$  show the start and the end of each experimental phase. Blue colour of the lines indicates low  $p\text{CO}_2$  level, grey – intermediate  $p\text{CO}_2$  level and red – high  $p\text{CO}_2$  level. Numbers in a legend next to every line with symbol are the rounded  $p\text{CO}_2$  levels for  $t_8$ – $t_{27}$  period.

was a cone of a sediment trap (see Czerny et al., 2013c, Fig. 1a), which separated the main water column and water below the cone. The water below the cone was not directly manipulated, and had a slow exchange with the main water column. This space below the cone was approximately 8% of the total enclosures' volume (Riebesell et al., 2013), and is called hereafter “dead volume” (Czerny et al., 2013b). On top of each floating frame there was a hood made of transparent polyvinyl chloride (PVC) to minimize precipitation and external sources of particulate carbon and nitrogen (e.g. aeolian supply and bird excrement) to the mesocosms.

The experiment lasted for 31 days from 7 June (day  $t_0$ ) to 7 July (day  $t_{30}$ ).  $\text{CO}_2$  addition was implemented in four steps (Schulz et al., 2013). Filtered seawater, enriched with  $\text{CO}_2$  was injected into the mesocosms and evenly distributed throughout the water column. Exchange of  $\text{CO}_2$ -enriched water with unperturbed water in the dead volume caused an initial abrupt decline in  $p\text{CO}_2$  levels from day  $t_4$  until day  $t_8$ . Therefore  $p\text{CO}_2$  levels on  $t_8$  were used as initial values ranging in the different mesocosms from 185 to 1420  $\mu\text{atm}$ . Table 1 shows mean  $p\text{CO}_2$  and  $\text{pH}_T$  values in seven perturbed (M1, M2, M4, M5, M6, M8, M9) and two control mesocosms (M3, M7) for different periods of the experiment, defined according to temporal changes in chlorophyll *a* concentrations (Riebesell et al., 2013): phase I, end of  $\text{CO}_2$  manipulation until nutrient addition ( $t_5$ – $t_{12}$ ), phase II, nutrient addition until 2nd chlorophyll minimum ( $t_{13}$ – $t_{21}$ ), and phase III, 2nd chlorophyll minimum until end of the experiment ( $t_{22}$ – $t_{30}$ ). However, the variables for calculating NCP (net community production), C : N and C : P uptake ratios are only available from  $t_8$  onwards, when the perturbed water column had exchanged with the dead volume, and only until  $t_{27}$  due to logistical constraints. Therefore, in this study, phase I was defined as  $t_8$ – $t_{12}$  and phase III as  $t_{22}$ – $t_{27}$ . In addition we evaluated C : N and C : P uptake ratios in the post-nutrient period  $t_{14}$ – $t_{27}$  (phase II + phase III).

Nutrients, (5  $\mu\text{M}$  of nitrate ( $\text{NO}_3^-$ ), 0.31  $\mu\text{M}$  of phosphate ( $\text{PO}_4^{3-}$ ), and 2.5  $\mu\text{M}$  of silicate ( $\text{Si}(\text{OH})_4$ ), were added to the mesocosms on day  $t_{13}$  to simulate the upwelling of nutrient rich deep waters to the surface (Schulz et al., 2013).

Water samples were collected daily using a 5 L depth-integrated sampler lowered down to 12 m. A more detailed description of the experimental set-up can be found in Riebesell et al. (2013), Czerny et al. (2013a, b, c), and Schulz et al. (2013).

### 2.3 Data

Concurrent with sampling for other biogeochemical and biological variables, seawater samples for determining the carbon dioxide system were taken daily from the integrated water sampler. Samples for total alkalinity ( $A_T$ ) and total dissolved inorganic carbon ( $C_T$ ) were drawn into 500ml borosilicate bottles. No filtering of samples prior to analysis was done due to the lack of significant calcifying plankton (Schulz et al., 2013; Brussaard et al., 2013; Niehoff et al., 2013).  $A_T$  was measured using Gran potentiometric titration (Gran, 1952) on a VINDTA system (Mintrop et al., 2000) with a precision of 2  $\mu\text{mol kg}^{-1}$ .  $C_T$  was determined using coulometric titration (Johnson et al., 1987) with a precision of  $\leq 2 \mu\text{mol kg}^{-1}$ . Measurements for both  $C_T$  and  $A_T$  were calibrated against certified reference material and values adjusted according to the offsets for each measurement series (CRM; Batch No. 101, [http://cdiac.esd.ornl.gov/oceans/Dickson\\_CRM/rmdata/Batch101.pdf](http://cdiac.esd.ornl.gov/oceans/Dickson_CRM/rmdata/Batch101.pdf)).

### CO<sub>2</sub> system calculations

The measured  $C_T$  and  $A_T$ , with associated temperatures, salinity and dissolved nutrient data, were applied to the CO2SYS program for Matlab (van Heuven et al., 2011) to calculate additional carbon dioxide system variables. To be consistent with Bellerby et al. (2008), we used the dissociation constants for carbonic acid of Dickson and Millero (1987), boric acid from Dickson (1990a), sulphuric acid following Dickson (1990b) and the  $\text{CO}_2$  solubility coefficients from Weiss (1974). Values are reported as in situ concentrations. Seawater pH is reported on the total hydrogen scale ( $\text{pH}_T$ ) and  $p\text{CO}_2$  in  $\mu\text{atm}$ .

To estimate NCP and the stoichiometric rates of carbon to nutrient uptake, we used measurements of total inorganic carbon concentration ( $C_T$ ), total alkalinity ( $A_T$ ), inorganic nutrient concentrations (phosphate –  $\text{PO}_4^{3-}$ , nitrate –  $\text{NO}_3^-$ , nitrite –  $\text{NO}_2^-$ , and ammonium –  $\text{NH}_4^+$ ) (Schulz et al., 2013) and air/sea  $\text{CO}_2$  gas exchange ( $\text{CO}_{2(\text{ex.})}$ ), estimated by measured loss of  $\text{N}_2\text{O}$  added to the mesocosms as a deliberate tracer (Czerny et al., 2013b). We also show the temporal evolution of chlorophyll *a* concentrations (Fig. 2), measured using HPLC according to Welschmeyer (1994) (Schulz et al., 2013).

**Table 1.** Mean values of  $p\text{CO}_2$  and  $\text{pH}_T$  (total scale) levels in mesocosms for every phase, post-nutrients period  $t_{14-t_{27}}$  and the overall period  $t_{8-t_{27}}$ .  $p\text{CO}_2$  and  $\text{pH}_T$  are calculated from total carbon and total alkalinity using CO2SYS for Matlab (van Heuven et al., 2011). The dissociation constant for carbonic acid was adopted from Dickson and Millero (1987), for boric acid from Dickson (1990a), for sulfuric acid from Dickson (1990b);  $\text{CO}_2$  solubility coefficient was adopted from Weiss (1974).

|    | phase I       |                                       | phase II      |                                       | phase III     |                                       | phase II + phase III |                                       | $t_{8-t_{27}}$ |                                       |
|----|---------------|---------------------------------------|---------------|---------------------------------------|---------------|---------------------------------------|----------------------|---------------------------------------|----------------|---------------------------------------|
|    | $\text{pH}_T$ | $p\text{CO}_2$<br>( $\mu\text{atm}$ ) | $\text{pH}_T$ | $p\text{CO}_2$<br>( $\mu\text{atm}$ ) | $\text{pH}_T$ | $p\text{CO}_2$<br>( $\mu\text{atm}$ ) | $\text{pH}_T$        | $p\text{CO}_2$<br>( $\mu\text{atm}$ ) | $\text{pH}_T$  | $p\text{CO}_2$<br>( $\mu\text{atm}$ ) |
| M3 | 8.33          | 185                                   | 8.34          | 176                                   | 8.35          | 170                                   | 8.34                 | 174                                   | 8.34           | 177                                   |
| M7 | 8.32          | 187                                   | 8.33          | 179                                   | 8.35          | 170                                   | 8.34                 | 175                                   | 8.33           | 179                                   |
| M2 | 8.18          | 270                                   | 8.20          | 253                                   | 8.24          | 233                                   | 8.22                 | 245                                   | 8.21           | 252                                   |
| M4 | 8.06          | 375                                   | 8.09          | 344                                   | 8.13          | 309                                   | 8.10                 | 329                                   | 8.09           | 342                                   |
| M8 | 7.96          | 480                                   | 8.01          | 422                                   | 8.04          | 389                                   | 8.02                 | 409                                   | 8.01           | 426                                   |
| M1 | 7.82          | 690                                   | 7.87          | 594                                   | 7.92          | 533                                   | 7.89                 | 568                                   | 7.87           | 598                                   |
| M6 | 7.74          | 820                                   | 7.82          | 665                                   | 7.89          | 578                                   | 7.85                 | 629                                   | 7.82           | 676                                   |
| M5 | 7.64          | 1050                                  | 7.73          | 838                                   | 7.78          | 746                                   | 7.75                 | 800                                   | 7.72           | 861                                   |
| M9 | 7.52          | 1420                                  | 7.64          | 1033                                  | 7.71          | 891                                   | 7.67                 | 974                                   | 7.63           | 1084                                  |

**Table 2.** The results of the  $F$  test on linear regressions between NCP, C:N, C:P uptake ratios in different phases and the mean  $p\text{CO}_2$  for the corresponding phase.

|           | Period               | Slope  | $R^2$ | $p$     |
|-----------|----------------------|--------|-------|---------|
| NCP       | phase I              | 0.007  | 0.849 | < 0.001 |
|           | phase II             | 0.007  | 0.367 | 0.084   |
|           | phase III            | -0.029 | 0.902 | < 0.001 |
|           | $t_{8-t_{27}}$       | -0.010 | 0.348 | 0.094   |
| C:N ratio | phase II + phase III | -0.004 | 0.757 | 0.002   |
|           | phase II             | 0.000  | 0.001 | 0.952   |
|           | phase III            | -0.008 | 0.409 | 0.064   |
| C:P ratio | phase II + Phase III | -0.073 | 0.739 | 0.003   |
|           | phase II             | -0.005 | 0.044 | 0.588   |
|           | phase III            | 0.219  | 0.379 | 0.078   |

## 2.4 Net community production derived from changes in $C_T$ concentration

To estimate the net effect of  $C_T$  uptake by phytoplankton during photosynthesis and  $C_T$  release due to auto- and heterotrophic respiration, we calculated NCP with a method previously employed in the PeECE mesocosm studies (Delille et al., 2005; Bellerby et al., 2008).

$A_T$  was corrected to cumulative changes in inorganic nutrient concentrations (Eq. 1), as for each mole of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{PO}_4^{3-}$  consumed through biosynthesis, total alkalinity increases by 1 mole (Brewer and Goldman, 1976). Additionally, each mole of consumed  $\text{NH}_4^+$  decreases total alkalinity by 1 mole (Wolf-Gladrow et al., 2007).

$$A_{T\text{corrected}} = A_{T\text{measured}} - \Delta\text{NO}_3^- - \Delta\text{PO}_4^{3-} - \Delta\text{NO}_2^- + \Delta\text{NH}_4^+ \quad (1)$$

The incremental change in  $C_T$  concentration was corrected for the  $\text{CO}_2$  air/sea gas exchange (Eq. 2).

$$C_{T\text{corrected}} = C_{T\text{measured}} - \text{CO}_2(\text{ex.}) \quad (2)$$

Corrected  $A_T$  and  $C_T$  concentrations were normalized to salinity to account for evaporation from the first day of every phase (Eqs. 3, 4) (Schulz et al., 2013).

$$A_{T\text{norm.}}(x_n) = A_{T\text{corrected}}(x_n) \frac{S(x_n)}{S(x_1)} \quad (3)$$

$$C_{T\text{norm.}}(x_n) = C_{T\text{corrected}}(x_n) \frac{S(x_n)}{S(x_1)}, \quad (4)$$

where,  $S$  is salinity,  $x_n$  and  $x_1$  correspond to day  $n$  and day 1, respectively, of the time period for which  $A_T$  and  $C_T$  are normalized.

Net community calcification (NCC) was estimated as cumulative change in  $A_{T\text{norm.}}$  (Eq. 5):

$$\text{NCC} = -0.5 \frac{\Delta A_{T\text{norm.}}}{\Delta t} \quad (5)$$

Calcification was insignificant during the experiment, therefore calculated NCC expresses the precision of  $A_T$  measurements ( $2 \mu\text{mol kg}^{-1}$ ).

Finally, net community production was computed as the cumulative change in  $C_{T\text{norm.}}$ , accounting for the cumulative change in  $A_{T\text{norm.}}$  (Eq. 6):

$$\text{NCP} = -\frac{\Delta C_{T\text{norm.}}}{\Delta t} + 0.5 \frac{\Delta A_{T\text{norm.}}}{\Delta t} \quad (6)$$

## 2.5 Statistical analysis

A gradient of eight  $\text{CO}_2$  levels with no replicates allowed for linear regression analysis (Riebesell et al., 2013) in order

**Table 3.** C : N uptake ratios (Slope), standard deviations (SD) and the results of the  $F$  test on linear regression analysis in phases II and III and the post-nutrient period (phase II + phase III) (see explanations in text).

| CO <sub>2</sub> level     | phase II ( $n = 8$ ) |       |       |        | phase III ( $n = 6$ ) |       |       |       | phase II + phase III ( $n = 14$ ) |       |       |        |
|---------------------------|----------------------|-------|-------|--------|-----------------------|-------|-------|-------|-----------------------------------|-------|-------|--------|
|                           | Slope                | SD    | $R^2$ | $p$    | Slope                 | SD    | $R^2$ | $p$   | Slope                             | SD    | $R^2$ | $p$    |
| Low (M3, M2, M7)          | 4.428                | 0.437 | 0.888 | <0.001 | 15.167                | 0.394 | 0.947 | 0.001 | 8.889                             | 0.611 | 0.927 | <0.001 |
| Intermediate (M1, M4, M8) | 4.507                | 0.605 | 0.960 | <0.001 | 15.731                | 2.167 | 0.935 | 0.002 | 8.743                             | 1.104 | 0.918 | <0.001 |
| High (M5, M6, M9)         | 4.551                | 0.745 | 0.933 | <0.001 | 13.833                | 5.311 | 0.814 | 0.014 | 6.581                             | 0.825 | 0.913 | <0.001 |

**Table 4.** C : P uptake ratios, standard deviations and the results of the  $F$  test on linear regressions analysis in phases II and III and the post-nutrient period (phase II + phase III) (see explanations in text).

| CO <sub>2</sub> level     | phase II ( $n = 8$ ) |       |       |        | phase III ( $n = 6$ ) |         |       |       | phase II + phase III ( $n = 14$ ) |        |       |        |
|---------------------------|----------------------|-------|-------|--------|-----------------------|---------|-------|-------|-----------------------------------|--------|-------|--------|
|                           | Slope                | SD    | $R^2$ | $p$    | Slope                 | SD      | $R^2$ | $p$   | Slope                             | SD     | $R^2$ | $p$    |
| Low (M3, M2, M7)          | 62.001               | 7.730 | 0.875 | 0.001  | 276.242               | 41.622  | 0.902 | 0.004 | 136.325                           | 18.264 | 0.892 | <0.001 |
| Intermediate (M1, M4, M8) | 54.616               | 1.618 | 0.902 | <0.001 | 290.583               | 20.009  | 0.879 | 0.006 | 127.303                           | 16.402 | 0.859 | <0.001 |
| High (M5, M6, M9)         | 55.317               | 9.639 | 0.857 | 0.001  | 408.084               | 123.390 | 0.596 | 0.072 | 92.866                            | 14.426 | 0.824 | <0.001 |

to test for the relationship between NCP, and C : N and C : P uptake ratios in each phase and the mean  $p\text{CO}_2$  level in the corresponding phase. For the regression analysis we used cumulative NCP on the final day of each phase and C : N and C : P uptake ratios, which were derived from a linear regression described below. The slope of linear regression analysis,  $R^2$  and  $p$  values of the  $F$  test are shown in Table 2.

A linear regression analysis was performed to define the relationship between NCP in each time period (phase) and the corresponding cumulative change in inorganic nitrogen ( $\Delta\text{N}$ ) and phosphorus ( $\Delta\text{P}$ ). The cumulative change in inorganic nitrogen resulted from a sum of a cumulative change in nitrate, nitrite and ammonia. The relationships for each time period were defined with an equation type  $Y = \alpha X + \beta$ , where coefficient  $\alpha$  corresponded to the C : N or C : P uptake ratio. Tables 3 and 4 show averaged coefficients  $\alpha$  for low, intermediate and high  $p\text{CO}_2$  levels (slope), as well as corresponding standard deviations. All statistical analyses were performed with the Statistics toolbox in Matlab.

### 3 Results

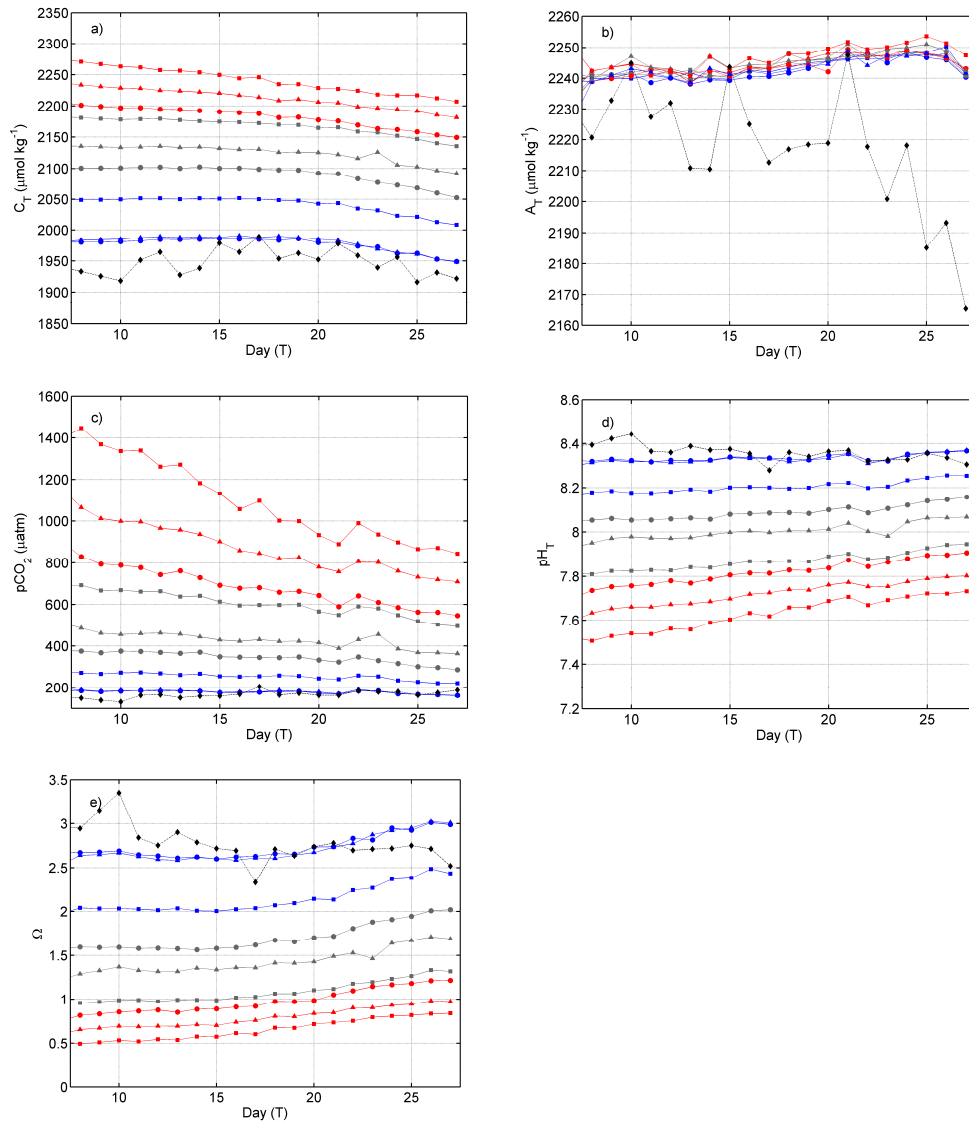
The initial characterization of the CO<sub>2</sub> system in the mesocosm and the fjord was performed on  $t_{-3}$  prior to the CO<sub>2</sub> addition (Riebesell et al., 2013). The initial  $p\text{CO}_2$  of the ambient water in the fjord was  $\sim 170 \mu\text{atm}$ , corresponding to a  $\text{pH}_T$  of  $\sim 8.3$ . The mesocosm values agreed to  $\pm 1.2 \mu\text{mol kg}^{-1}$ , i.e. within the measurement precision, for both  $C_T$  and  $A_T$ . This confirmed that the closing of the bags isolated water of very similar biogeochemical properties in each mesocosm; a significant feat due to the typical small scale heterogeneity of the fjord (Svendsen et al., 2002). Following the final carbon dioxide perturbations on  $t_4$  (Schulz et al., 2013; Riebesell et al., 2013) it took a further four days

for the CO<sub>2</sub> system to settle down in the mesocosms due to slow exchange with dead volume in the base of the bags and thus, all changes to the CO<sub>2</sub> fields were referenced to  $t_8$ . A phytoplankton bloom developed in the mesocosm (Schulz et al., 2013) and CO<sub>2</sub> was drawn down due to high primary productivity (Engel et al., 2013). Primary production (Engel et al., 2013) showed significant sensitivity to the initial and bloom phase CO<sub>2</sub> conditions. A breakdown of the CO<sub>2</sub> sensitivity on the development of the particulate and dissolved elemental pools is described in Czerny et al. (2013c).

The daily measurements of the measured carbonate system variables ( $C_T$  and  $A_T$ ) and the calculated variables ( $p\text{CO}_2$ ,  $\text{pH}_T$  and  $\Omega_{\text{ar}}$ ) for all mesocosms and the background fjord values are shown in Fig. 3. The net changes in these variables, relative to  $t_8$ , are illustrated in Fig. 4.

Total alkalinity increased steadily in all the bags from 2242 on  $t_8$  to 2247  $\mu\text{mol kg}^{-1}$  on  $t_{25}$  falling back to the original 2242  $\mu\text{mol kg}^{-1}$  by  $t_{27}$  (Figs. 3, 4). The increase was due to freshwater losses, following evaporation, and nutrient uptake as, in the absence of significant numbers of calcifiers (Schulz et al., 2013; Brussaard et al., 2013; Niehoff et al., 2013), there were no significant  $A_T$  changes due to calcification. The effect of nutrient addition on  $t_{13}$  could not be seen in  $A_T$  as the addition was alkalinity neutral due to the concomitant addition of acid (Riebesell et al., 2013). As there were no other changes in other associated biogeochemical variables and salinity, it is likely that the drop in  $A_T$  on  $t_{27}$  was a calibration offset.

$C_T$  concentrations showed high variability between the mesocosms in response to the deliberate additions of CO<sub>2</sub> (Figs. 3, 4). From an original fjord value of about 1982  $\mu\text{mol kg}^{-1}$ , the perturbations spanned a range from 1982 to 2270  $\mu\text{mol kg}^{-1}$ . In the high CO<sub>2</sub> scenarios,  $C_T$  drops rapidly and consistently throughout the experiment with net  $C_T$  changes between 52 and 63  $\mu\text{mol kg}^{-1}$ . In the



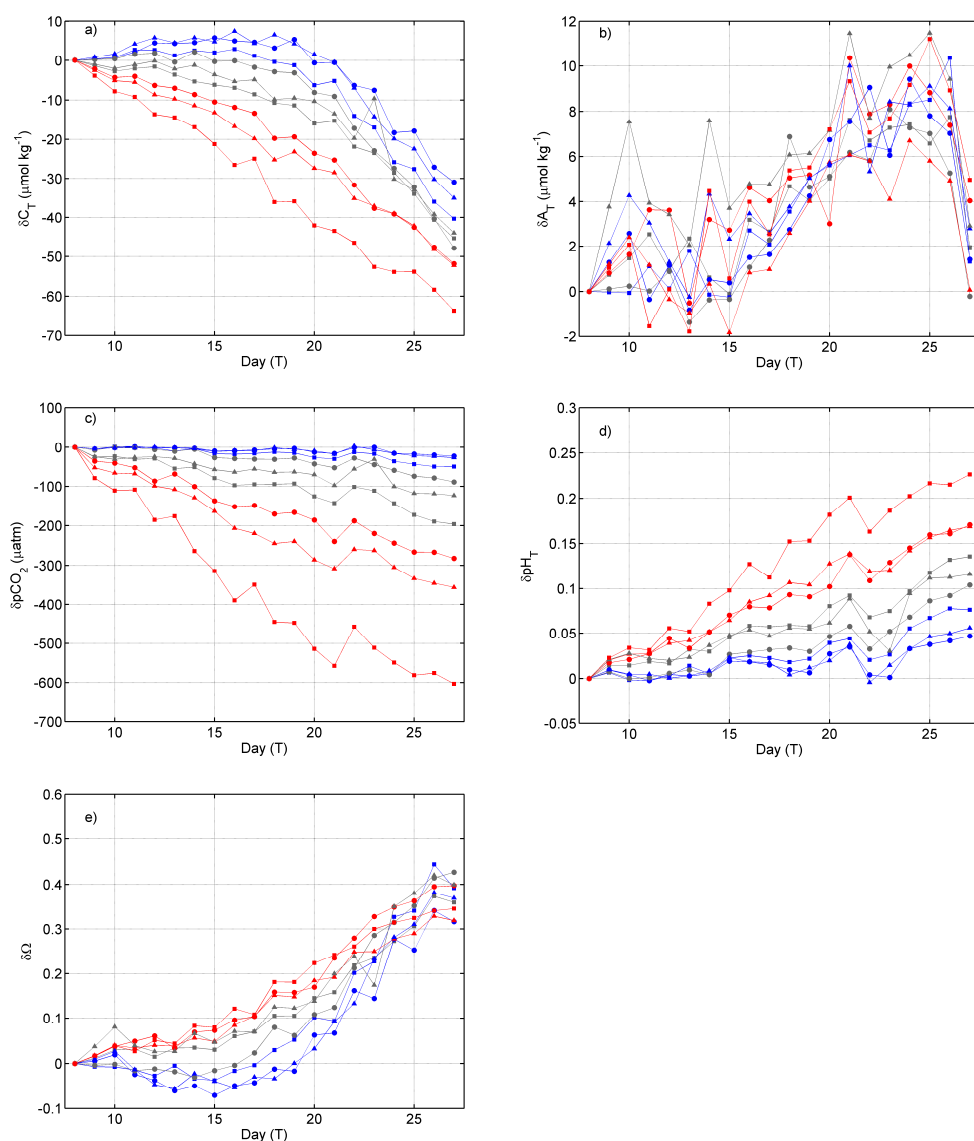
**Fig. 3.** Absolute values for the marine carbonate system variables. Measured values are **(a)** total inorganic carbon ( $C_T$ ) and **(b)** total alkalinity ( $A_T$ ). Calculated values are **(c)** partial pressure of carbon dioxide ( $pCO_2$ ), **(d)**  $pH_T$  on the total hydrogen scale and **(e)** aragonite saturation state ( $\Omega_{ar}$ ). Red symbols: high  $pCO_2$  mesocosms (M5, M6, M9), grey symbols: medium  $pCO_2$  mesocosms (M1, M4, M8), blue symbols: low  $pCO_2$  mesocosms (M2, M3, M7). The black line represents the natural fjord background variability.

intermediate  $CO_2$  scenarios,  $C_T$  concentrations change much more slowly until about  $t_{23}$  after which there is a much faster reduction. Total reductions in the intermediate scenario were between 54 and  $58 \mu\text{mol kg}^{-1}$ . In the low  $CO_2$  scenario mesocosms,  $C_T$  increases until  $t_{19}$  before exhibiting the fastest decline of all the scenarios towards the end of the experiment resulting in a net change of between 31 and  $40 \mu\text{mol kg}^{-1}$ .

The initial mesocosm  $pCO_2$  concentrations were chosen to represent a range of atmospheric values corresponding to anticipated carbon fossil fuel release scenarios.  $pCO_2$  showed very large inter- and intra-mesocosm variability, particularly in the high  $CO_2$  scenarios (Figs. 3, 4). This is

due to the poor buffer capacity of the seawater that results in increasing sensitivity in  $pCO_2$  to even small changes in  $C_T$  and  $A_T$  that result from both net ecosystem perturbations and from measurement sensitivity. The higher  $CO_2$  scenario mesocosms also exhibited the largest reductions in  $pCO_2$  enhanced by rapid exchange with the atmosphere (Czerny et al., 2013b).

Initial  $pH_T$  levels ranged from 7.5 to 8.3 and, in all bags, increased through the experiments according to the relative amounts of  $CO_2$  exchange with the overlying atmosphere and biological net carbon production (Figs. 3, 4). The high  $CO_2$  mesocosm exhibited the greatest  $pH_T$  changes.



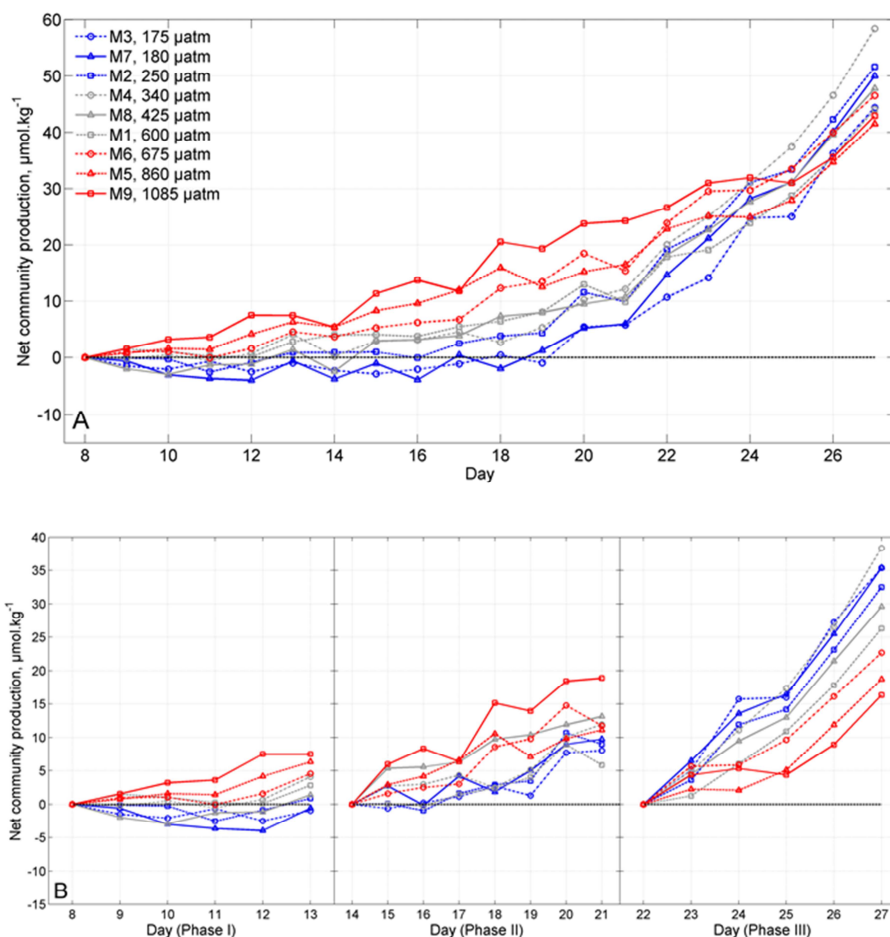
**Fig. 4.** Cumulative changes relative to the start of the post  $\text{CO}_2$  perturbation ( $t_8$ ). **(a)** total inorganic carbon ( $C_T$ ), **(b)** total alkalinity ( $A_T$ ), **(c)** partial pressure of carbon dioxide ( $p\text{CO}_2$ ), **(d)**  $\text{pH}_T$  on the total hydrogen scale and **(e)** aragonite saturation state ( $\Omega_{\text{ar}}$ ). Red symbols: high  $p\text{CO}_2$  mesocosms (M5, M6, M9), grey symbols: medium  $p\text{CO}_2$  mesocosms (M1, M4, M8), blue symbols: low  $p\text{CO}_2$  mesocosms (M2, M3, M7). The black line represents the natural fjord background variability.

The aragonite saturation state ( $\Omega_{\text{ar}}$ ) displayed the highest values (2.6) in the control mesocosms (Fig. 3). The seawater was undersaturated with respect to aragonite in the four highest  $\text{CO}_2$  mesocosms with the lowest  $\Omega_{\text{ar}}$  of the experiment being 0.5. Seawater was undersaturated with respect to aragonite for the entire experimental period under the highest  $\text{CO}_2$  scenario (Fig. 3).

Concentrations of nitrate and phosphate in the water were close to detection limit at the beginning of the experiment ( $0.11 \mu\text{mol kg}^{-1}$  for nitrate,  $0.13 \mu\text{mol kg}^{-1}$  for phosphate). Concentration of ammonia was  $0.7 \mu\text{mol kg}^{-1}$  (Schulz et al., 2013). Additionally, there were  $5.5 \mu\text{mol kg}^{-1}$  of dissolved

organic nitrogen,  $0.20 \mu\text{mol kg}^{-1}$  of dissolved organic phosphorus (Schulz et al., 2013) and  $75 \mu\text{mol kg}^{-1}$  of dissolved organic carbon (Engel et al., 2013). A post-bloom situation in the fjord at the start of the experiment was identified.

Despite relatively low nutrient concentrations chlorophyll *a* increased steadily from  $0.2 \mu\text{g L}^{-1}$  at day  $t_3$  to  $1.4 \mu\text{g L}^{-1}$  at days  $t_6$ – $t_8$  (Fig. 2; Schulz et al., 2013). After day  $t_8$  chlorophyll *a* declined reaching minimum concentrations on day  $t_{13}$ . Addition of mineral nutrients on day  $t_{13}$  stimulated phytoplankton biomass with Chl *a* peaking on day  $t_{19}$  at  $2 \mu\text{g L}^{-1}$  in the highest  $\text{CO}_2$  treatment and a minimum of  $1 \mu\text{g L}^{-1}$  in one of the control mesocosms



**Fig. 5.** (A) Net community production for the total period of the experiment; (B) net community production in every phase of the experiment. Horizontal dashed line on both figures shows the border between heterotrophic (below 0) and autotrophic (above 0) systems. Line colours and numbers in a legend are as described for Fig. 2.

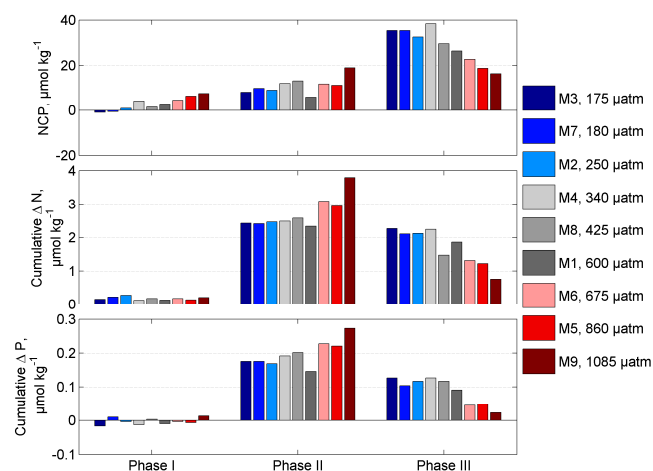
(Schulz et al., 2013). After the second minimum on day  $t_{21}$ , chlorophyll *a* increased in low and intermediate  $\text{CO}_2$  treatments, peaking on day  $t_{27}$  with values of  $2.5\text{--}3.7\ \mu\text{g L}^{-1}$ . In the high  $\text{CO}_2$  treatment, chlorophyll *a* concentration increased gradually towards the end of the experiment, yet did not exceed  $2\ \mu\text{g L}^{-1}$ . The phytoplankton community was composed predominantly of haptophytes in phase I, prasinophytes, dinoflagellates, and cryptophytes in phase II, haptophytes, prasinophytes, dinoflagellates and chlorophytes in phase III (Schulz et al., 2013). There was also significant plankton wall growth that built up during the experiment (Czerny et al., 2013c).

Cumulative NCP was similar in all mesocosms, reaching  $50.0 \pm 5.0\ \mu\text{mol kg}^{-1}$  by day  $t_{27}$  (Fig. 5a). In phase I, NCP was positive in the high and intermediate  $\text{CO}_2$  treatments accounting for  $6.1 \pm 1.5$  and  $2.8 \pm 1.4\ \mu\text{mol kg}^{-1}$ , respectively (Figs. 5b, 6), indicating a net autotrophic system. NCP in mesocosms with low  $\text{CO}_2$  treatments was close to zero ( $-0.2 \pm 0.9\ \mu\text{mol kg}^{-1}$ ), indicating that autotrophic and heterotrophic processes were in balance. In

phase II, NCP was positive and higher than in phase I in all mesocosms. The highest NCP was in the high  $\text{CO}_2$  treatments, on average  $13.9 \pm 4.3\ \mu\text{mol kg}^{-1}$  with the intermediate and low  $\text{CO}_2$  treatments having  $10.3 \pm 3.9$  and  $8.9 \pm 0.9\ \mu\text{mol kg}^{-1}$ , respectively. In phase III NCP was highest of all the phases for all scenarios. The highest NCP was in the low ( $34.4 \pm 1.7\ \mu\text{mol kg}^{-1}$ ) and intermediate  $\text{CO}_2$  treatments ( $31.4 \pm 6.2\ \mu\text{mol kg}^{-1}$ ), while in the high  $\text{CO}_2$  treatments NCP was  $19.2 \pm 3.2\ \mu\text{mol kg}^{-1}$ . NCP showed a significant positive linear relationship with increasing  $p\text{CO}_2$  levels in phase I ( $p < 0.001$ ) (Table 2), but significant negative linear relationship with increasing  $p\text{CO}_2$  levels in phase III ( $p < 0.001$ ).

Due to the very low concentrations of inorganic nutrients in phase I, around the limit of detection (Fig. 6) calculations of stoichiometric uptake rates provided unreasonable values. Therefore, we evaluated the cumulative changes in inorganic nutrients, C:N and C:P uptake ratios for phase II, III and phase II+III only. By the end of phase II, the cumulative change in





**Fig. 6.** Net community production, cumulative change in inorganic nitrogen ( $\Delta N$ ) and cumulative change in inorganic phosphorus ( $\Delta P$ ) on the last day of every experimental phase for 9 mesocosms.

inorganic nitrogen was on average  $2.43 \pm 0.03 \mu\text{mol kg}^{-1}$  in the low,  $2.47 \pm 0.13 \mu\text{mol kg}^{-1}$  in the intermediate and  $3.27 \pm 0.50 \mu\text{mol kg}^{-1}$  in the high  $\text{CO}_2$  treatments (Fig. 6). The cumulative change in inorganic phosphorus was  $0.17 \pm 0.04 \mu\text{mol kg}^{-1}$  in the low,  $0.18 \pm 0.03 \mu\text{mol kg}^{-1}$  in the intermediate and  $0.24 \pm 0.03 \mu\text{mol kg}^{-1}$  in the high  $\text{CO}_2$  treatments. In phase III, the cumulative change in inorganic nitrogen was on average  $2.16 \pm 0.09 \mu\text{mol kg}^{-1}$  in the low,  $1.86 \pm 0.38 \mu\text{mol kg}^{-1}$  in the intermediate and  $1.09 \pm 0.30 \mu\text{mol kg}^{-1}$  in the high  $\text{CO}_2$  treatments. The corresponding change in inorganic phosphorus was  $0.12 \pm 0.01 \mu\text{mol kg}^{-1}$  in the low,  $0.11 \pm 0.02 \mu\text{mol kg}^{-1}$  in the intermediate and only  $0.04 \pm 0.02 \mu\text{mol kg}^{-1}$  in the high  $\text{CO}_2$  treatments (Fig. 6). In contrast to phase II, the amount of inorganic nitrogen and phosphorus consumed by the community in phase III was lower at high  $\text{CO}_2$  in comparison to intermediate and low  $\text{CO}_2$  levels. This was primarily due to the high nutrient consumption in phase II that resulted in rapid nutrient depletion under high  $\text{CO}_2$  in phase III.

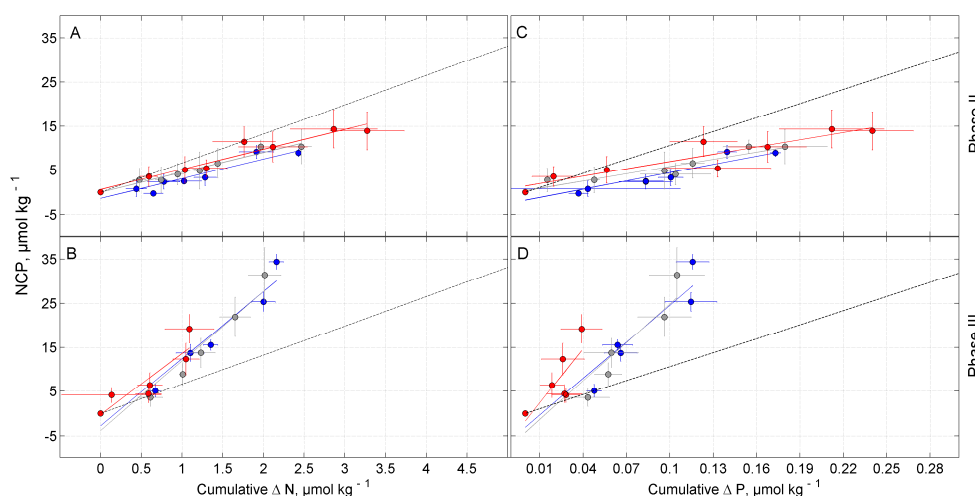
In phase II C:N and C:P uptake ratios were similar in all mesocosms and lower than respective Redfield ratios. (Tables 3, 4 and Fig. 7) In phase III, C:N and C:P were higher than respective Redfield ratios, probably due to very low concentrations of inorganic nutrients available at the end of phase III (Fig. 7b, d). C:N and C:P were slightly lower in the high  $\text{CO}_2$  in comparison to the intermediate and low  $\text{CO}_2$  treatments (Fig. 7b, Table 3). Combining phase II and III, C:N and C:P uptake ratios were close to the respective Redfield ratios and C:N uptake ratios decreased with increasing  $p\text{CO}_2$  from  $8.9 \pm 0.6$  in the low and  $8.7 \pm 1.1$  in the intermediate to  $6.6 \pm 0.8$  in the high  $p\text{CO}_2$  treatments (Table 3). In a similar manner, C:P uptake ratios also decreased with increasing  $p\text{CO}_2$  from  $136.3 \pm 18.3$  in the low and  $127.3 \pm 16.4$  in the intermediate to  $92.8 \pm 14.4$  in the

high  $p\text{CO}_2$  treatments (Table 4). This trend, based on averages, was confirmed by linear regression analyses taking into account individual  $\text{CO}_2$  levels in each mesocosm, and was found to be statistically significant (Table 2).

#### 4 Discussion

NCP increased with increasing  $p\text{CO}_2$  in phase I, which was consistent with the higher growth of small-sized phytoplankton ( $0.8\text{--}2.0 \mu\text{m}$ ) stimulated by elevated  $\text{CO}_2$  (Brussaard et al., 2013). The inherited fjord water had low autotrophic production. The initial concentrations of inorganic nutrients in the mesocosms on  $t_0$ , suggested Si limitation for Si-consuming phytoplankton, and N deficient for the other phytoplankton. Such a situation may have promoted the growth of pico- and nanophytoplankton with low or absent silicate demand and they could have had a competitive advantage under low nutrient concentration during phase I. Remineralization of inorganic nutrients from organic matter indicates that in a post-bloom situation in Kongsfjorden at the very start of the experiment only very slightly net-heterotrophic (Rokkan Iversen and Seuthe, 2011; de Kluijver et al., 2013). Mixotrophy could also have contributed to the phase I balance. Large zooplankton abundance was high (Niehoff et al., 2013) and would have contributed to the remineralization of organic matter. Balanced to moderately positive NCP in phase I was fuelled by phosphate remineralized from organic matter and most importantly ammonia as an N source (Schulz et al., 2013). In mesocosms with intermediate and high  $p\text{CO}_2$ , NCP was positive, indicating that production rates were higher than respiration rates, and most likely the phytoplankton were mildly stimulated by elevated  $\text{CO}_2$  (Engel et al., 2013). However, the effect size is small and positive NCP could also be caused by relatively low respiration rates in the high  $\text{CO}_2$  treatments, as there was increased sedimentation of freshly produced organic matter with increasing  $\text{CO}_2$  (de Kluijver et al., 2013). Zooplankton grazing decreased from low to high  $p\text{CO}_2$  treatment (de Kluijver et al., 2013) and thus could also contribute to the NCP increase with increasing  $p\text{CO}_2$ . However, the dominant cause of the high NCP to increased  $\text{CO}_2$  was higher exudation of DOC (dissolved organic carbon; Engel et al., 2013; Czerny et al. 2013c).

Phytoplankton growth in phase I was terminated by viral infection (Brussaard et al., 2013), but after nutrient addition at the beginning of phase II, phytoplankton numbers started to rise showing increasing growth rates with higher  $p\text{CO}_2$  (Brussaard et al., 2013; Schulz et al., 2013). Following phytoplankton growth, NCP was positive in phase II, indicating net autotrophy in all mesocosms. Higher rates of NCP with increasing  $p\text{CO}_2$  show that small-sized phytoplankton, which was dominant in phase II (Brussaard et al., 2013; Schulz et al., 2013), fixed more dissolved inorganic carbon at higher  $\text{CO}_2$  levels. Along with inorganic carbon



**Fig. 7.** Ratios of net community production to a cumulative change in inorganic nitrogen (**A**) and phosphorus (**C**) in phase II and phase III (**B**, **D**) (C:N and C:P uptake ratios). Data and slopes are averaged for low (blue), intermediate (grey) and high (red)  $p\text{CO}_2$  treatment. Error bars are 1 standard deviation. Slopes were calculated with linear regression analysis (see Methods section for details). Slopes of linear regression analysis and statistics of the  $F$  test are shown in Table 3 for C:N uptake ratio and in Table 4 for C:P uptake ratio. Dashed black lines are the Redfield C:N and C:P elemental ratios.

there was also greater utilization of inorganic nutrients in the high  $p\text{CO}_2$  treatments (Schulz et al., 2013). Increased NCP at high  $\text{CO}_2$  was reflected by high concentrations of particulate organic carbon (POC) (Schulz et al., 2013). Nutrient addition also stimulated the production of DOC, which increased with increasing  $p\text{CO}_2$  (Engel et al., 2013). Concentrations of DOC, however, did not change significantly after nutrient addition, indicating higher DOC consumption by bacteria with increasing  $p\text{CO}_2$  (Engel et al., 2013). Like phytoplankton, bacteria require inorganic nutrients to grow and to increase their biomass (Thingstad et al., 2008), thus higher abundance of both phytoplankton and bacteria in mesocosms with high  $p\text{CO}_2$  results in an increased demand for mineral nutrients. Phytoplankton growth in phase II was again terminated by viral infection (Brussaard et al., 2013).

NCP rates in phase III were the highest of the phases of the experiment. There was a greater abundance of large phytoplankton during the bloom in phase III than in earlier phases (Brussaard et al., 2013). The negative effect of elevated  $\text{CO}_2$  on phytoplankton growth and NCP rates in phase III should not be interpreted as a  $\text{CO}_2$ -response but was due to nutrient limitation following the high biomass accumulation in phase II. Production of dissolved organics (and increased wall growth) was probably also high during phase III when inorganic nutrients became limiting (Czerny et al., 2013c).

NCP in this investigation was similar to the NCP calculated from  $^{13}\text{C}$  labelling (de Kluijver et al., 2013) and to NCP based on changes in dissolved oxygen concentration during light/dark incubations (see comparison analysis by Tanaka et al., 2013). However, NCP estimates did not agree very well with primary production (PP) of POC and DOC based on 24 h  $^{14}\text{C}$  incubations, reported in Engel et al. (2013). The

mismatch between PP and NCP is a result of the different methodological approaches to determine net carbon uptake. The  $^{14}\text{C}$  method measures “new production” over periods of hours, whereas the integrated NCP measures the whole system carbon balance. Most importantly, the PP data of Engel et al. (2013) are derived from single depth incubations (1m) and received about 60% of incoming light, whereas NCP data captured productivity over the whole mesocosm water column. Moreover, water for the incubations in the study of Engel et al. (2013) was sampled in the mesocosms and pre-filtered using 200  $\mu\text{m}$  meshes. This may have led to over-estimation of phytoplankton productivity in the  $^{14}\text{C}$  incubations as grazing by larger zooplankton was excluded.

Stoichiometric uptake ratios, C:N and C:P, evaluated in this study were lower than the respective Redfield ratios in phase II and higher than the respective Redfield ratio in phase III. The phase separation reflects the different biogeochemical demands of the dominant plankton functional types (PFT) and the different life stage biogeochemical requirements. Another source of control on community stoichiometry would have been the nutrient requirements of bacteria, which significantly increased in biomass during the course of the experiment (Brussaard et al., 2013). An efficient recycling system with high bacterial abundance is typical for Kongsfjorden for the post-bloom time of the year (Rokkan-Iversen and Seuthe, 2011). However, a  $p\text{CO}_2$ -sensitive effect on bacterial respiration was not observed during the experiment (Motegi et al., 2013). Tanaka et al. (2013) also described no  $p\text{CO}_2$  effect on community respiration. These findings imply that the role of bacterioplankton as competitor for mineral nutrients could be strengthened in the Arctic Ocean (Thingstad et al., 2008),

while their role in recycling organic matter into inorganic carbon and nutrients could remain unchanged.

The complexity of the results from this experiment challenges any delivery of any simple mathematical representations of the Arctic pelagic ecosystem NCP and nutrient uptake response to a high CO<sub>2</sub> world. Further work is required on Arctic plankton to investigate individual PFT responses and changes to species interaction under ocean acidification. This experiment identifies the importance of studying collectively the interactions of autotrophic, mixotrophic and heterotrophic components if we are to untangle the complexities of future marine ecosystem change. Experiments are also required over all seasons and it should be emphasized that the experiment was performed after the first natural spring bloom had passed and thus the nutrient perturbation, although potentially simulating fresh nutrient supply from, for example, a storm event, was likely to generate responses which cannot readily be applied to the entire growth season. It is important to keep this in mind if extrapolating these results to future changes in the Arctic Ocean.

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