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CO_2 increases ^{14}C primary production in an Arctic plankton community

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Abstract. Responses to ocean acidification in plankton communities were studied during a CO_2-enrichment experiment in the Arctic Ocean, accomplished from June to July 2010 in Kongsfjorden, Svalbard (78°56′2″ N, 11°53′6″ E). Enclosed in 9 mesocosms (volume: 43.9–47.6 m^3), plankton was exposed to CO_2 concentrations, ranging from glacial to projected mid-next-century levels. Fertilization with inorganic nutrients at day 13 of the experiment supported the accumulation of phytoplankton biomass, as indicated by two periods of high chl *a* concentration.

This study tested for CO_2 sensitivities in primary production (PP) of particulate organic carbon (PP_{POC}) and of dissolved organic carbon (PP_{DOC}). Therefore, ^{14}C-bottle incubations (24 h) of mesocosm samples were performed at 1 m depth receiving about 60 % of incoming radiation. PP for all mesocosms averaged 8.06 ± 3.64 µmol C L^{-1} d^{-1} and was slightly higher than in the outside fjord system. Comparison between mesocosms revealed significantly higher PP_{POC} at elevated compared to low pCO_2 after nutrient addition. PP_{DOC} was significantly higher in CO_2-enriched mesocosms before as well as after nutrient addition, suggesting that CO_2 had a direct influence on DOC production. DOC concentrations inside the mesocosms increased before nutrient addition and more in high CO_2 mesocosms. After addition of nutrients, however, further DOC accumulation was negligible and not significantly different between treatments, indicating rapid utilization of freshly produced DOC. Bacterial biomass production (BP) was coupled to PP in all treatments, indicating that 3.5 ± 1.9 % of PP or 21.6 ± 12.5 % of PP_{DOC} provided on average sufficient carbon for synthesis of bacterial biomass. During the later course of the bloom, the response of ^{14}C-based PP rates to CO_2 enrichment differed from net community production (NCP) rates that were also determined during this mesocosm campaign. We conclude that the enhanced release of labile DOC during autotrophic production at high CO_2 exceedingly stimulated activities of heterotrophic microorganisms. As a consequence, increased PP induced less NCP, as suggested earlier for carbon-limited microbial systems in the Arctic.

1 Introduction

The Arctic Ocean is predicted to be among the most affected marine ecosystems with respect to consequences of anthropogenic emissions of carbon dioxide (CO_2), such as ocean acidification and warming. Temperature increase in the Arctic is about twice as fast as the global rate, yielding an average of 1–2 °C yr^{-1} (Anisimov et al., 2007). Warming accelerates the melting of sea ice and Greenland's glaciers. Satellite data revealed that the loss of Arctic sea ice has tripled over the last 10 yr (Comiso et al., 2008). Freshening of seawater due to ice melt along with an enhanced uptake of CO_2 due to shrinking sea-ice coverage is predicted to amplify CO_2-induced acidification of Arctic seawater (Steinacher et al., 2009), with so far unknown consequences on the pelagic ecosystem dynamics and productivity.

The Kongsfjorden is part of the Arctic archipelago Svalbard and situated on the west coast of Spitsbergen. It is a relatively well-studied system, compared to other areas in the Arctic, as several research stations are located in the village of Ny-Ålesund. A review by Hop et al. (2002) provides a compilation of current knowledge obtained for the Kongsfjorden ecosystem. For the phytoplankton community, a total of 148 taxa have been reported and showed the numerical dominance of diatoms and dinoflagellates (Eilertsen et al., 1989; Hasle and Heimdal, 1998; Keck et al., 1999; Wiktor, 1999). Primary production in Kongsfjorden was determined during several field studies, focusing mainly on the spring period (Piwosz et al., 2009; Rokkan and Seuthe, 2011; Hodal et al., 2011), when availability of nutrients and light after the polar night support a substantial fraction of annual productivity (Sakshaug, 2004).

Phytoplankton primary production is based on CO_2 as the main substrate, and since the CO_2-binding enzyme RubisCO has a low affinity for its substrate (Badger et al., 1998), an increase in seawater pCO_2 was hypothesized to stimulate primary production (Riebesell et al., 2000; Schippers et al., 2004; Rost et al., 2008). The impact of increased pCO_2 on primary production has been investigated theoretically as well as experimentally. Some authors report small, if any, effects (Clark and Flynn, 2000; Tortell et al., 2002), whereas others document a clear increase in primary production with increasing pCO_2 (Hein and Sand-Jensen, 1997; Schippers et al., 2004; Riebesell et al., 2007). The effect of seawater carbonate chemistry on photosynthesis rates thereby strongly depends on the presence and characteristics of cellular CO_2-concentrating mechanisms (CCMs; Rost et al., 2003, Giordano et al., 2005). Phytoplankton species that are able to enhance their CO_2 supply by CCMs (Raven, 1991) may exhibit no or minimal sensitivity to CO_2 enrichment (Raven and Johnson, 1991; Rost et al., 2003; Giordano et al., 2005). Others, such as the coccolithophore *Emiliania huxleyi*, respond to CO_2 enrichment with an increase in primary production (Rost and Riebesell, 2004). This suggests that the efficiency and regulation of CCMs differ among phytoplankton functional groups and species. Moreover, the capability of the phytoplankton cell to express a CCM relies on the availability of light and nutrients (Young and Beardall, 2005; Beardall et al., 2005), and may thus be restrained under sub-optimal conditions. Changes in CO_2 availability might therefore affect competition and succession of phytoplankton species (Burkhardt et al., 2001; Rost et al., 2003; Tortell et al., 2002).

Effects of elevated pCO_2 on phytoplankton are of major interest for understanding global biogeochemical cycles, since primary production mediates the transformation of CO_2 into organic carbon with variable stoichiometric relationships to other major elements, for example phosphorus (P) and nitrogen (N). If CO_2 assimilation is decoupled from other major elements, changes in the stoichiometric composition of organic material and altered biogeochemical pathways through the microbial food web are potential consequences. A particular increase in C assimilation relative to the uptake of N and P and compared to Redfield stoichiometry of 106C : 16N : 1P is referred to as *carbon overconsumption* (Toggweiler, 1993). This imbalance in carbon and nutrient assimilation has been related to nutrient limitation of the cell (Wood and van Valen, 1990; Engel et al., 2002; Schartau et al., 2007) and also to enhanced CO_2 concentration (Engel, 2002; Riebesell et al., 2007; Kim et al., 2011; Borchard and Engel, 2012). Carbon overconsumption is often accompanied by a release of dissolved organic carbon (DOC) from the cell, either by passive (leakage) or active processes (exudation) (Fogg, 1966; Bjørnsen, 1988; Engel et al., 2004a, b; López-Sandoval et al., 2011). The extracellular release of DOC is a normal function of algal cells (Fogg, 1966) and represents with $\sim$ 3–40 % (percentage of extracellular release, PER) a significant fraction of primary production (Myklestad, 1977; Mague et al., 1980; Baines and Pace, 1991). Factors influencing primary production, such as light and temperature, were shown to also affect the production of DOC (Zlotnik and Dubinsky, 1989; Baines and Pace, 1991; Engel et al., 2011).

Release from phytoplankton cells is the major source of labile and semi-labile DOC in the ocean and drives the microbial loop (Azam et al., 1983), whereby DOC is either transferred to higher trophic levels or respired back to CO_2 (Ducklow et al., 1986). Microbial respiration represents an important loss for DOC globally (Williams, 2000; Hansell et al., 2009). Under a "malfunctioning" of the microbial loop, DOC accumulates (Thingstad et al., 1997) and may be subject to abiotic aggregation into gel particles, such as transparent exopolymer particles (TEP) (Alldredge et al., 1995). TEP formation thereby represents a repartitioning of dissolved organic carbon into particulate organic carbon (POC) without loss of mass (Engel et al., 2004b). An increase in TEP-C may raise C : N or C : P ratios in particulate organic matter, potentially providing an enhanced sinking flux of carbon to depth (Schneider et al., 2004).

In Arctic ecosystems, heterotrophic microbes are often limited by the amount of labile DOC (Kirchman et al., 2009) and co-limited by nutrients (Cuevas et al., 2011). An increased input of labile DOC (glucose) was rapidly consumed by bacteria and other osmotrophs during an earlier mesocosm study at Svalbard, resulting in enhanced competition for inorganic nutrients between phyto- and bacterioplankton, and in an overall reduction of autotrophic productivity of the system (Thingstad et al., 2008). A hypothesis that came out of the study of Thingstad et al. (2008) was that stimulation of the microbial loop in Arctic waters by increased DOC release under high pCO_2 may result in a counterintuitive carbon cycling (i.e., "more organic carbon gives less organic carbon") and not necessarily enhance carbon export to the deep sea.

In order to address potential consequences of the ongoing seawater pCO_2 increase in Arctic pelagic ecosystems, a mesocosm study was conducted in the framework of the European Project on Ocean Acidification (EPOCA).

Several methods were applied during this mesocosm study to investigate the sensitivity of plankton productivity to CO_2 perturbation, including in vitro O_2 measurements at 4 m depth outside the mesocosms (Tanaka et al., 2013), as well as changes in dissolved inorganic carbon (DIC) concentration (Silyakova et al., 2012) and uptake of ^{13}C-labelled DIC inside the mesocosms (de Kluijver et al., 2012).

Here, we report on sensitivities in primary production to increasing pCO_2, for both the production of POC and of DOC based on the classical Steemann Nielsen in vitro ^{14}C-tracer approach (Steemann Nielsen, 1952). Bottle incubations outside of the mesocosms were performed at 1 m depth, equivalent to approximately 60 % of incoming light, and over a period of 24 h.

The ^{14}C-tracer approach has the advantage of being highly sensitive, and thus ideally suited for fieldwork, when there is low photosynthetic activity. One drawback of this method, however, is that C-uptake rates cannot be attributed precisely to either net or gross primary production (Peterson, 1980; Dring and Jewson, 1982). Short-term incubations are expected to provide gross rates of C-fixation, whereas longer incubations tend to measure net production, depending, however, on the metabolic activity of the microbial community included.

Primary production was compared to changes in the concentration of DOC and to the production of bacterial biomass in order to infer the fate of freshly produced organic compounds at different pCO_2 in this Arctic ecosystem.

2 Material and methods

2.1 Sampling and incubation

The mesocosm experiment was conducted in Kongsfjorden, northern Spitsbergen (78°56′2″ N, 11°53′6″ E) from June to July 2010 as a part of the European Project on Ocean Acidification (EPOCA). Detailed information about the set-up of the experiment, the CO_2-perturbation of seawater within the mesocosms and sampling procedures is given elsewhere in this issue (Riebesell et al., 2012; Schulz et al., 2013; Czerny et al., 2012; Bellerby et al., 2012; Silyakova et al., 2012). Briefly, nine mesocosms were deployed close to the coast of Spitsbergen near Ny-Ålesund on 28 May 2010 (day 10). All mesocosms enclosed nutrient-poor, post-bloom fjord water. The CO_2 manipulation was carried out between 3 and 6 June (day −1 to day 4) by the addition of different quantities of pre-filtered (55 µm), CO_2-enriched natural water from the fjord (Fig. 1). Two untreated mesocosms served as controls, while seven mesocosms were manipulated to establish elevated pCO_2 in a range of ∼ 170–1100 µatm. Time-averaged (day 5–day 27) pCO_2 levels in the different mesocosms were 178 µatm (control M3), 180 µatm (control M7), 255 µatm (M2), 345 µatm (M4), 435 µatm (M8), 611 µatm (M1), 701 µatm (M6), 892 µatm (M5), and 1136 µatm (M9).

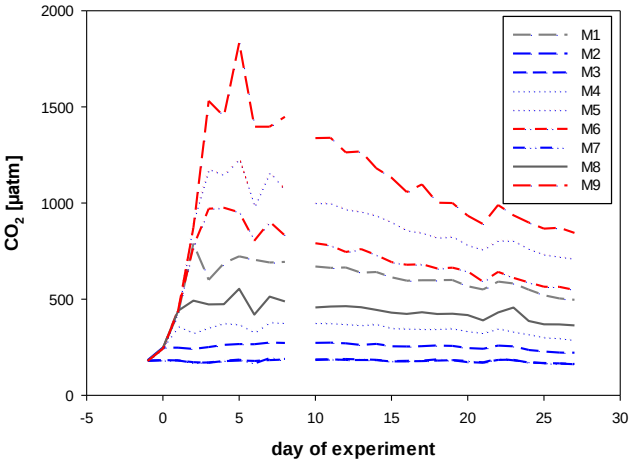

Fig. 1. Development of pCO_2 (µatm) in the nine mesocosms during the course of the Svalbard experiment.

For comparison, mesocosms were grouped into low (M3, M7, M2), medium (M4, M8, M1) and high (M6, M5, M9) pCO_2.

Ten days after CO_2 enrichment, nutrients were added to yield concentrations of 5 µmol L^{-1} NO_3, 0.32 µmol L^{-1} PO_4, and 2.5 µmol L^{-1} Si to induce the development of a phytoplankton bloom. Nutrient concentrations were determined on a segmented flow analyzer (SEAL QuAAtro) equipped with an autosampler generally following the methods of Hansen and Koroleff (1999) as well as Kerouel and Aminot (1997). For more information on nutrients, see Schulz et al. (2013).

Sampling of seawater from the mesocosms was conducted with a depth-integrated water sampler (Hydro-Bios). The sampler is equipped with a motor and continuously collects water (5 L volume) while being lowered from surface to 12 m depth. Samples were collected in the morning (09:00 a.m.–11:00 a.m. local time).

2.2 ^{14}C primary production

^{14}C primary production was determined according to Steemann Nielsen (1952) and Gargas (1975). Polycarbonate bottles (Nunc EasYFlask, 75 cm^2) were filled with 260 mL prefiltered (mesh size 200 µm) sample and spiked with 50 µL of an ∼ 8 µCi $NaH^{14}CO_3^-$ solution (Perkin Elmer, Norway). For determination of added activity, 200 µL were removed immediately after spiking, transferred to a 5 mL scintillation vial. Then, 200 µL of 2N NaOH and 4 mL scintillation cocktail (Ultima Gold AB) were added.

Triplicate light and one dark incubation were performed for each of the nine mesocosms and for the fjord on days −1, 2, 5, 7, 10, 12, 14, 16, 18, 20, 22, 24, 26, and 28 of the experiment. Dark incubation was conducted with black taped bottles. All samples were incubated for 24 h. The incubation length was chosen for two reasons. First, we expected an overall low productivity of the Arctic phytoplankton

community at low temperatures, low biomass density, and low nutrient concentrations at the start of the experiment. Under these conditions, short-term incubations of only a few hours may underestimate primary production, because carbon assimilation by algal cells may be too low to discriminate against ^{14}C adsorption as determined in blank dark incubation. Moreover, release of freshly assimilated carbon into the pool of dissolved organic matter has a time scale of several hours, because of equilibration of the tracer and because metabolic processes of organic carbon exudation follow those of carbon fixation inside the cell. Another reason was to cover the daily photoperiod for the cells. Since the experiment was conducted at high latitude (78°56′ N) and around the time of summer solstice, light availability was high ($> 100\,\mu mol\,photons\,m^{-2}\,s^{-1}$) even during the middle of the night (Schulz et al., 2013), and supported autotrophic production over a 24 h period. Other studies in the Svalbard area therefore also used 24 h incubations for measurements of primary production when working with the ^{14}C-tracer (Iversen and Seuthe, 2011; Hodal et al., 2011).

Incubations were performed close to the marine lab at 1 m depth, receiving about 60 % of the incoming photosynthetically active radiation (PAR) during most time of the study. For comparison, in vitro O_2- measurements were performed at 4 m depth, equivalent to 20 % PAR, whereas productivity estimates directly in the mesocosms obtained from DIC changes (Silyakova et al., 2012) or ^{13}C incorporation (de Kluijver et al., 2012) yielded integrated values over a 12 m water column that received 100–17 % of incoming light, with a median value of 23 % (see Fig. 2). Hence, ^{14}C primary production rates were obtained at a relatively high light level. This level was chosen to ensure that (i) cells would not become light-limited in the course of the study, and (ii) cell would receive enough light for determinable exudation of DOC, since exudation in marine phytoplankton has been reported to increase with light availability (Zlotnik and Dubinsky, 1989).

Incubations were stopped by filtration of a 50 or 100 mL sub-sample onto 0.4 µm polycarbonate filters (Nuclepore). Primary production of POC (PP_{POC}) was determined from material collected on the filter, while the filtrate was used to determine primary production of DOC (PP_{DOC}). After removing the vials collecting the filtrate of the associated filter, all filters were rinsed with 10 mL sterile filtered (< 0.2 µm) seawater, and then acidified with 250 µL 2N HCl in order to remove inorganic carbon (Descy et al., 2002). Filters were transferred into 5 mL scintillation vials, 200 µL of 2N NaOH, and 4 mL scintillation cocktail (Ultima Gold AB) were added. For determination of PP_{DOC}, 4 mL of filtrate were transferred to 20 mL scintillation vials, acidified (100 µL 1N HCl) and left open in the fume hood to remove inorganic carbon. Then, 800 µL of 2N NaOH and 15 mL scintillation cocktail were added. All samples were counted the following day in a liquid scintillation analyzer (Packard Tri-Carb, model 1900 A).

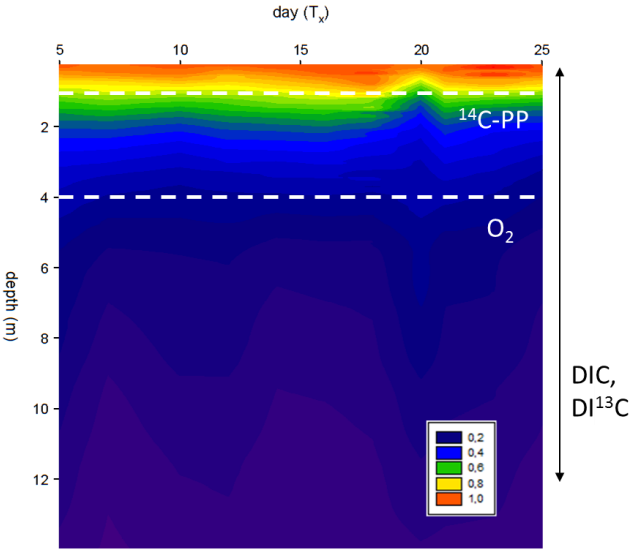

Fig. 2. Fraction of surface light received at different depths in the mesocosms in the course of the study as exemplified for M1. For comparison, bottle incubations were performed at 1 m depth (^{14}C incubations) and at 4 m depth (O_2, Tanaka et al., 2013), while changes in DIC concentration were calculated from depth-integrated water sampling (0–12 m; de Kluijver et al., 2012; Silyakova et al., 2012).

Primary production of organic carbon was calculated from scintillation data according to Gargas (1975):

$$C_{org}(\mu mol\,L^{-1}\,d^{-1}) = \frac{a_2 \cdot DI^{12}C \cdot 1.05 \cdot k_1 \cdot k_2}{a_1}, \quad (1)$$

where a_1 and a_2 are the activities (DPM) (disintegrations per minute) of the added solution and of the sample corrected for dark samples, respectively, and $DI^{12}C$ is the concentration ($\mu mol\,L^{-1}$) of dissolved inorganic carbon (DIC) in the sample. The value 1.05 is a correction factor for the discrimination between ^{12}C and ^{14}C, as the uptake of the ^{14}C isotope is 5 % slower than the uptake of ^{12}C, k_1 is a correction factor for subsampling (bottle volume/filtered volume) and k_2 is the incubation time (d^{-1}).

Total primary production (PP; $\mu mol\,C\,L^{-1}\,d^{-1}$) was derived from the sum of the production of PP_{POC} and PP_{DOC} according to

$$PP = PP_{POC} + PP_{DOC}. \quad (2)$$

The percentage of extracellular release (PER) was calculated as

$$PER\ (\%) = (PP_{DOC}/PP) \times 100. \quad (3)$$

Based on ^{14}C primary production, the cumulative production of POC and DOC was calculated from the sum of daily production. Values for days between measurements were calculated by linear interpolation of adjacent data points.

Primary production estimates obtained with the ^{14}C-method at 1 m depth exceeded O_2 gross community production (GCP) determined at 4 m depth by a factor of ~ 2 (Tanaka et al., 2013), and O_2- and ΔDIC-based net community production (NCP) by a factor of 3–4 (Silyakova et al., 2012). These discrepancies were mainly due to the different amount of light that cells received during the various measurements, and are comparable to differences observed for polar phytoplankton along comparable depth and light gradients (Yun et al., 2012).

2.3 Light and temperature during the ^{14}C incubations

PAR, for practical reasons defined as radiation in the wavelength range 400–700 nm, and temperature were determined at the incubation site in the afternoon (between 03:00 and 04:00 p.m.) from day 7 onwards by the use of a CTD-mounted LICOR spherical quantum sensor (LI-193).

Seawater temperature increased during the mesocosm study from 2.0 °C at the beginning of June to 5.2 °C at the end of the study. No temperature differences were observed among the nine mesocosms, and between the mesocosms and the fjord. At the site and depth of ^{14}C incubations, temperature was on average 1–1.5 °C higher than at the location of mesocosm deployment.

PAR ranged between 130 and 800 µmol photons m^{-2} s^{-1} at the incubation site (1 m), representing cloudy and clear sky, respectively, and corresponded to approximately 60 % of surface light for most time (range: 45–85 %) (Fig. 2). PAR at the incubation site was not significantly different from the 1 m depth horizon in the fjord at the mesocosm site ($p = 0.09$).

2.4 Chlorophyll *a*

Concentration of chlorophyll *a* (chl *a*) in the mesocosms and in the fjord was determined from 500 mL seawater filtered onto glass fiber filters (Whatman GF/F 25 mm, pre-combusted 450 °C for 5 h) by low vacuum filtration (< 200 mbar) and stored frozen at −20 °C. Chl *a* was determined fluorometrically according to Welschmeyer (1994) using a Turner fluorometer 10-AU (Turner BioSystems, CA, USA).

2.5 Dissolved organic carbon (DOC)

Samples for dissolved organic carbon (DOC) were collected in combusted glass ampoules after filtration through combusted GF/F filters. Samples of 20 mL were acidified with 100 µL of 85 % phosphoric acid and stored at 4 °C in the dark until analysis. DOC samples were analysed using the high-temperature combustion method (TOC-VCSH, Shimadzu) (Qian and Mopper, 1996). A multi-point calibration curve was constituted for each day of measurement using potassium hydrogen phthalate standard, which was prepared in Milli-Q water. Additionally, two reference seawater standards (Hansell laboratory, RSMAS, University of Miami) were used to determine the instrument blank. Each sample was measured in quadruplets.

Considerable day-to-day variations of DOC concentrations of up to 30 % were observed on some days in all mesocosms and in the fjord samples. These variations may partly be attributed to contamination of samples during sample collection and transport as well as during instrument deployment inside the mesocosms. We assume that this methodological error occurred randomly and was not discriminating between CO_2 treatments. Thus, although the absolute concentration of DOC may have been defective on individual days, averaged and time-averaged differences in DOC concentration between treatments should be reliable.

In order to identify treatment related differences, we calculated mean deviations of DOC concentration (MD-DOC) in the mesocosms. We did not include fjord samples in this analysis, because temporal variations of DOC concentration in the fjord may have been due to processes other than biological activity, such as glacial melting and terrestrial meltwater run-off. The latter was at times indicated in the area of mesocosm deployment by a brownish color of surface water.

2.6 Bacterial secondary production

Bacterial production (BP) was estimated from the uptake of ^{14}C leucine during < 24 h incubations in 2 mL vials at 2 °C in the dark. Duplicate incubations revealed an analytical error ≤ 10 %. Rates of ^{14}C leucine incorporation were converted into BP applying a conversion factor of 1.5 kg C mol^{-1} leucine (Ducklow et al., 1999). For more information see Piontek et al. (2013).

2.7 Data treatment

Differences in data as revealed by statistical tests (t-test, ANOVA, Kolmogorov–Smirnov test) were accepted as significant for $p < 0.05$. Average values for total concentrations are given by their arithmetic mean, averages for ratios by their geometric mean.

For identifying differences between the pCO_2 treatments, absolute deviations (AD) were calculated for each mesocosm for PP_{POC}, PP_{DOC} and DOC. Therefore, the arithmetic mean of all mesocosm observations per time-point was subtracted from each mesocosm observation at that time-point. The mean deviation (MD) represents the arithmetic mean of AD for a specific time interval, and is expressed in a relative value (%). Three time intervals were considered: total period of CO_2 treatment (day 5–day 28), before nutrient addition (day 5–day 12), and after nutrient addition (day 14–day 28). MD values thus illustrate how one mesocosm deviates from the mean development in all mesocosms, i.e., the anomaly of a mesocosm.

Table 1. Time averaged (day 5–day 28) rates (µmol C L^{-1} d^{-1}) of total primary production (PP), primary POC production (PP_{POC}), and primary DOC production (PP_{DOC}), based on ^{14}C bottle incubations, as well as ratios of PP normalized to chlorophyll *a* concentration (µmol C µg^{-1} chl *a* d^{-1}). Averages (Avg.) and standard deviations (SD) were calculated from $n = 12$ observations for each mesocosm and for the fjord, respectively.

	mesocosm	3	7	2	4	8	1	6	5	9	fjord
	Avg. pCO_2 (µatm)	178	180	255	345	435	611	701	892	1136	167
PP	Avg.	8.7	4.2	7.3	4.6	10.1	7.4	9.8	9.5	11.0	6.5
	SD	2.5	1.9	1.8	1.7	4.3	3.3	3.2	3.2	3.7	2.5
PP_{POC}	Avg.	7.2	3.5	6.2	3.8	8.7	6.2	8.5	8.2	9.4	5.8
	SD	2.3	1.7	1.8	1.7	4.3	3.2	3.1	2.9	3.5	2.5
PP_{DOC}	Avg.	1.6	0.85	1.3	0.85	1.6	1.2	1.4	1.4	1.8	0.79
	SD	0.75	0.39	0.35	0.45	0.47	0.44	0.49	0.67	0.78	0.38
[PP] : [chl *a*]	Avg.	8.3	3.9	7.1	4.3	9.3	6.6	9.3	9.0	10.3	6.0
	SD	2.9	2.1	2.1	2.0	4.8	3.4	4.1	3.9	4.7	2.5

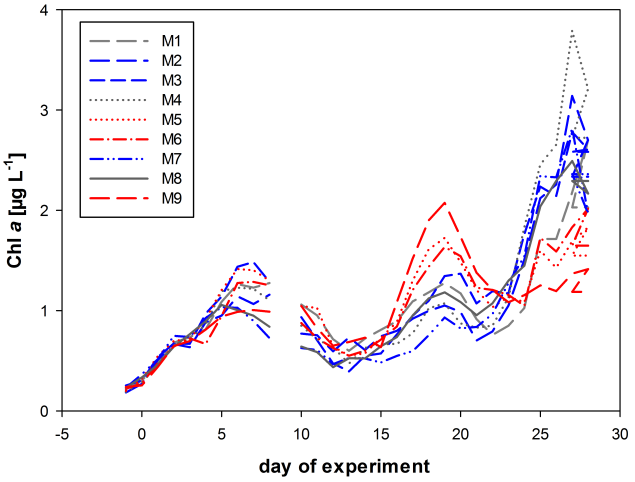

Fig. 3. Biomass changes of the phytoplankton community in the nine mesocosms as indicated by chlorophyll *a* (chl *a*) concentration.

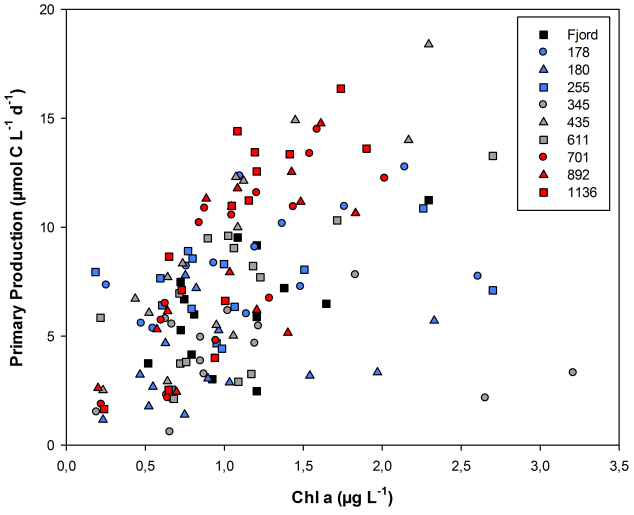

Fig. 4. Total primary production ($PP_{POC} + PP_{DOC}$), as determined for each of the nine mesocosms and for the fjord during the mesocosm study, was not related to chl *a* concentration. Red symbols: high pCO_2 mesocosms (M5, M6, M9), grey symbols: medium pCO_2 mesocosms (M1, M4, M8), blue symbols: low pCO_2 mesocosms (M2, M3, M7), black symbols: fjord.

Calculations, statistical tests and illustration of the data were performed with the software packages Microsoft Office Excel 2010 and SigmaPlot 12.0 (SYSTAT).

3 Results

3.1 Bloom development

Changes in chl *a* concentration (range: ∼ 1–3 µg L^{-1}) during the study indicated the development of one smaller phytoplankton bloom before day 13, i.e., before addition of nutrients to the mesocosms, as well as two bloom phases thereafter (Fig. 3). Thereby, the bloom directly following nutrient addition (day 14–day 22) developed faster and more pronounced in the high pCO_2 mesocosms, while the second bloom phase after day 23 was characterized by higher chl *a* concentrations in the lower pCO_2 mesocosms. For more information on phytoplankton bloom development and nutrient uptake, see Brussaard et al. (2013) and Schulz et al. (2013).

3.2 Primary production of organic carbon

Primary production (PP) during the time of the experiment (day 5–day 28) averaged 8.1 ± 3.6 µmol C L^{-1} d^{-1} in all mesocosm samples and was slightly higher than in the fjord samples with 6.5 ± 2.5 µmol C L^{-1} d^{-1} (Table 1). PP varied significantly between mesocosm samples (ANOVA; $p < 0.001$), with highest rates observed in the high CO_2 mesocosm (M9: 1136 µatm) and lowest rates in the low CO_2 mesocosm (M7: 180 µatm).

PP in the mesocosms, as well as in the fjord samples, was not significantly related to chl *a* concentration (Fig. 4). Yet, [PP] : [chl *a*] (µmol C d^{-1} : µg chl *a*) ratios were significantly different between mesocosms (ANOVA, $p < 0.05$), yielding highest time-averaged [PP] : [chl *a*] ratios (range: 9.5–11.0 µmol C $µg^{-1}$ chl *a* d^{-1}) for the high pCO_2 mesocosms (1136, 892, and 701 µatm) as well as for the medium CO_2 mesocosm (435 µatm) (Table 1). Lowest time-averaged [PP] : [chl *a*] ratios (range: 4.2–4.6 µmol C $µg^{-1}$ chl *a* d^{-1}) were determined for the low CO_2 mesocosm M7 (180 µatm) and for the medium CO_2 mesocosm M4 (345µatm). In all other mesocosms and the fjord, [PP] : [chl *a*] ranged between 6.5 and 8.7 µmol C $µg^{-1}$ chl *a* d^{-1}. PP in all samples was not directly related to PAR measured at the incubation site (1 m depth) (data not shown).

We observed that PP_{POC} on the first day of incubation (day −1), i.e., after first salt addition but before pCO_2 perturbation, was not equal among samples that were collected from the mesocosms. While mesocosms 1–3 had a similarly high primary production of POC (PP_{POC}) in range of 4.1–6.1 µmol C L^{-1} d^{-1}, comparable to PP_{POC} observed in the fjord, mesocosm 4–9 clearly showed lower productivity. This difference in the initial conditions between mesocosms disappeared during the following days and was already absent at day 2 (Table 2).

Time-averaged (day 5–day 28) PP_{POC} in mesocosm samples ranged from 3.5 ± 1.7 µmol C L^{-1} d^{-1} (M7: 180 µatm) to 9.4 ± 3.5 µmol C L^{-1} d^{-1} (M9: 1136 µatm) and encompassed PP_{POC} observed in the fjord (5.8 ± 2.5 µmol C L^{-1} d^{-1}; Table 1). PP_{POC} rates determined during this study (Tables 1 and 2) compare well to other measurements at the same site; for example Hodal et al. (2011) determined PP_{POC} rates from 4–8 µmol C L^{-1} d^{-1} for a phytoplankton community with about 1 µg chl *a* L^{-1} incubated directly beneath the surface (0 m) in May in 2002.

The average rate of primary production of DOC (PP_{DOC}) during this study varied between 0.85 ± 0.39 µmol C L^{-1} d^{-1} (M7: 180 µatm) and 1.8 ± 0.78 µmol C L^{-1} d^{-1} (M9: 1136 µatm) for the mesocosms, and was slightly higher than for the fjord with 0.79 ± 0.38 µmol C L^{-1} d^{-1}.

PP_{POC} as well as PP_{DOC} increased with increasing phytoplankton biomass after nutrient addition on day 13 (Tables 2, 3). Response of PP_{POC} to nutrient addition was clearly faster in the high pCO_2 mesocosms; i.e., between day 12 and day 16, PP_{POC} increased by 74 % in the high CO_2 mesocosms, by 48 % in the medium, and by only 21 % in the low CO_2 mesocosms.

For the total period of the experiment (day 5–day 28), a cumulative PP_{POC} between 84 and 174 µmol C L^{-1} was obtained for the three lowest, between 94 and 203 µmol C L^{-1} for the three medium, and between 196 and 222 µmol C L^{-1} for the three highest pCO_2 mesocosms. For comparison, cumulative PP_{POC} in the fjord was 138 µmol C L^{-1} and therewith in the range of data observed in mesocosms with a similarly low pCO_2. Cumulative PP_{POC} of the autotrophic community clearly increased with CO_2 concentration ($p < 0.01$), while the variability between mesocosms decreased. Hence, highest variability of cumulative POC production was observed at the lower end of the pCO_2 range (Fig. 5a). The difference in cumulative PP_{POC} between low and high CO_2 treatments covered a relatively broad range, i.e., 29 µmol C L^{-1} comparing M3 (178 µatm) and M5 (892 µatm), or 138 µmol C L^{-1} comparing M7 (180 µatm) and M9 (1136 µatm). Thus, the applied pCO_2 induced an increase in PP_{POC} by 10–60 %.

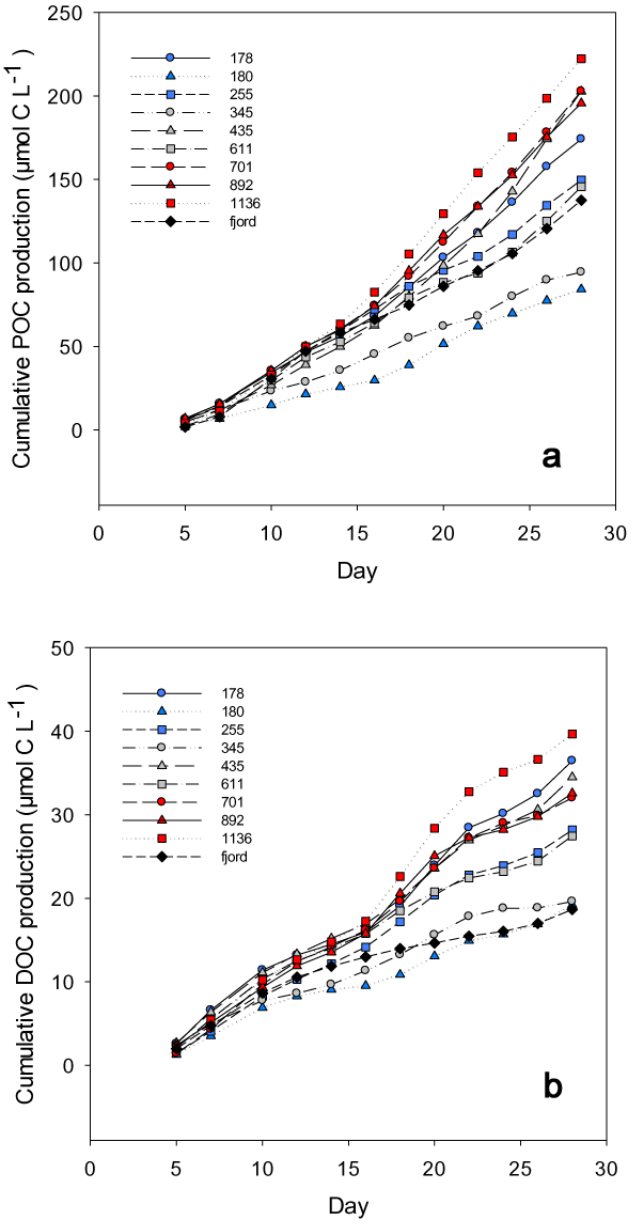

Fig. 5. Cumulative primary production of POC **(a)** and of DOC **(b)** as determined from ^{14}C-bottle incubations for the different mesocosms and for the fjord. Values for pCO_2 are the arithmetic mean of data over the full period of observation (day 5–day 27).

Table 2. Production (µmol L^{-1} d^{-1}) of particulate organic carbon (POC), based on ^{14}C bottle incubations. Averages (Avg.) and standard deviations (SD) were calculated from on triplicate measurements of 24 h incubations.

	Mesocosm	3	7	2	4	8	1	6	5	9	Fjord
	Avg. pCO_2 (µatm)	178	180	255	345	435	611	701	892	1136	167
Day											
−1	Avg.	6.08	0.29	5.95	1.09	1.45	4.07	1.55	1.59	1.27	6.53
	SD	0.45	0.01	0.61	0.04	0.07	1.14	0.52	0.04	0.35	2.38
2	Avg.	2.05	0.92	2.05	0.32	2.15	1.91	1.82	2.04	2.01	2.54
	SD	0.37	0.06	0.17	0.02	0.34	0.01	0.02	0.02	0.09	0.27
5	Avg.	4.31	2.00	3.75	3.13	3.25	1.52	3.86	4.64	2.61	1.16
	SD	0.33	0.44	0.47	0.11	0.04	0.34	0.17	0.37	0.72	2.00
7	Avg.	4.95	1.72	4.58	4.33	3.60	5.67	4.78	3.95	4.65	5.04
	SD	0.72	0.29	0.37	0.30	0.18	0.15	0.19	0.12	0.48	0.36
10	Avg.	7.47	3.76	7.89	3.14	6.45	7.87	9.22	9.34	9.77	10.08
	SD	1.04	0.26	1.00	0.30	2.51	0.58	1.34	0.82	0.59	0.45
12	Avg.	4.67	2.75	6.65	2.15	5.75	5.93	5.39	5.18	7.42	6.48
	SD	0.32	0.11	0.50	0.04	0.70	2.73	0.11	0.47	0.14	0.25
14	Avg.	4.98	1.48	5.52	4.86	5.15	3.30	5.08	4.64	6.22	4.69
	SD	0.59	0.25	0.30	0.49	0.57	0.61	0.54	0.23	0.44	0.35
16	Avg.	7.13	2.50	7.46	4.80	7.50	8.18	8.88	9.74	12.84	3.23
	SD	0.64	0.39	0.19	0.39	1.05	0.58	0.73	1.88	2.15	0.48
18	Avg.	10.32	6.65	6.37	5.01	10.03	6.80	8.81	11.53	9.85	5.41
	SD	0.19	0.32	0.46	0.25	3.04	0.58	7.64	0.44	8.58	0.71
20	Avg.	7.34	6.11	3.16	2.03	8.41	2.39	11.54	9.94	14.34	5.78
	SD	2.04	0.32	0.74	0.39	0.34	0.63	0.74	3.12	0.92	0.25
22	Avg.	7.39	4.52	5.12	3.97	10.55	3.05	9.79	6.98	10.23	3.57
	SD	1.42	1.86	0.67	0.55	3.84	0.58	2.36	1.06	2.18	0.61
24	Avg.	10.95	3.18	8.05	7.82	14.92	9.61	10.55	11.79	11.24	6.69
	SD	1.49	0.59	1.64	1.62	0.73	1.56	0.38	1.68	0.30	0.34
26	Avg.	10.39	4.48	9.31	2.10	16.49	9.04	13.60	10.97	11.89	8.23
	SD	0.39	0.40	0.95	0.60	1.73	1.32	0.65	1.05	0.24	0.66
28	Avg.	6.17	2.25	5.94	2.60	12.05	11.56	11.04	9.43	11.92	8.85
	SD	0.25	0.27	0.86	0.22	2.03	0.55	0.28	1.22	1.77	0.30

The cumulative production (day 5–day 28) of DOC was estimated in a similar way and ranged between 19 and 36 µmol C L^{-1} in the low, 20–34 µmol C L^{-1} in the medium, and 32–40 µmol C L^{-1} in the high pCO_2 mesocosms (Fig. 5b). Cumulative PP_{DOC} in the fjord, was estimated to 19 µmol C L^{-1}, and thus at the lower end of values observed in the mesocosms. Similar to cumulative PP_{POC}, cumulative PP_{DOC} increased significantly with CO_2 concentration ($p < 0.05$). Maximum difference in cumulative PP_{DOC} was observed between M7 (180 µatm) and M9 (1136 µatm) with 21 µmol C L^{-1}, equivalent to an increase by about 50 %. However, variability of cumulative PP_{DOC} was high at the lower pCO_2 range also. The low pCO_2 mesocosm M3 (178 µatm) even yielded about 11 % higher cumulative PP_{DOC} than the high CO_2 treatments M5 (892 µatm) and M6 (701 µatm).

PP_{DOC} generally increased after nutrient addition, following the course of PP (Table 1). The percentage of extracellular organic carbon release (PER), however, decreased immediately after nutrient addition in all mesocosms (Fig. 6). Until day 12 PER ranged between 21 and 23 %. After nutrient addition, PER was 18 ± 6 % in the three low pCO_2 mesocosms and decreased with increasing pCO_2 to 14 ± 5 % in the three high CO_2 mesocosms. Thus, nutrient addition suppressed exudation at higher pCO_2 more than at low pCO_2 (t-test, $p < 0.05$), suggesting in turn that a higher proportion of PP was used for POC production at high pCO_2. However, due to absolute higher PP, the total amount of DOC released by autotrophs was still higher at high CO_2 despite of lower PER.

In the fjord, PER was 14 ± 8 % until day 12, and also decreased – not impacted by nutrient addition – to 11 % by day 14. This suggests that nutrient addition was not the sole factor responsible for the PER decrease after day 12. Another factor that has often been reported to increase exudation of organic carbon is light (Zlotnik and Dubinsky, 1989). During this study, we also observed a moderate increase in PER with light intensity (Fig. 7, $p < 0.05$). Following this argument, light was likely not responsible for the reduction of PER observed on day 14, because PAR at that

Table 3. Production (µmol C L^{-1} d^{-1}) of dissolved organic carbon (DOC), based on ^{14}C bottle incubations. Averages (Avg.) and standard deviations (SD) were calculated from on triplicate measurements of 24 h incubations.

	Mesocosm	3	7	2	4	8	1	6	5	9	Fjord
	Avg. pCO_2 (µatm)	178	180	255	345	435	611	701	892	1136	167
Day											
−1	Avg.	1.25	0.87	1.99	0.42	1.06	1.76	0.32	1.03	0.38	0.95
	SD	0.49	0.42	0.20	0.05	0.05	0.60	0.45	0.84	0.23	0.23
2	Avg.	0.05	0.48	0.49	0.27	0.77	0.22	0.34	0.39	0.52	0.48
	SD	0.03	0.07	0.21	0.14	0.51	0.05	0.11	0.00	0.02	0.08
5	Avg.	1.71	0.87	0.93	1.53	1.77	1.39	0.93	1.56	1.39	1.32
	SD	0.42	0.57	0.81	0.23	0.29	0.15	0.85	0.06	0.13	0.24
7	Avg.	2.32	1.33	1.76	1.13	1.91	2.03	1.96	1.20	1.97	1.45
	SD	0.68	0.46	0.11	0.98	0.17	1.82	0.35	1.10	0.29	0.09
10	Avg.	0.89	0.92	1.02	0.72	1.26	1.18	1.65	1.61	1.21	1.16
	SD	0.35	0.34	0.22	0.27	1.06	0.34	0.33	1.40	0.34	1.10
12	Avg.	0.91	0.48	1.00	0.14	0.96	1.04	1.11	0.97	1.23	0.73
	SD	0.26	0.15	0.18	0.12	0.12	0.82	0.40	0.15	0.14	0.07
14	Avg.	0.38	0.29	0.89	0.93	0.92	0.44	0.65	0.67	0.90	0.60
	SD	0.33	0.26	0.31	0.32	0.42	0.13	0.41	0.38	0.25	0.02
16	Avg.	1.09	0.17	1.10	0.75	0.84	1.32	1.33	1.58	1.59	0.52
	SD	0.29	0.13	0.51	0.55	0.33	0.35	0.17	0.52	0.55	0.49
18	Avg.	2.03	1.14	1.93	1.15	2.11	1.41	2.12	3.23	3.76	0.46
	SD	0.57	0.35	0.06	0.28	0.68	0.13	0.96	0.37	0.72	0.33
20	Avg.	2.84	1.11	1.26	1.23	1.59	0.88	1.85	1.23	2.03	0.23
	SD	1.32	0.09	0.83	0.43	0.16	0.76	0.24	1.23	0.55	0.23
22	Avg.	1.70	0.75	1.14	0.98	1.77	0.77	1.79	0.96	2.33	0.58
	SD	0.13	0.26	0.15	0.17	0.45	0.41	0.54	0.83	0.48	0.38
24	Avg.	1.25	0.87	1.99	0.42	1.06	1.76	0.32	1.03	0.38	0.95
	SD	0.49	0.42	0.20	0.05	0.05	0.60	0.45	0.84	0.23	0.23
26	Avg.	0.05	0.48	0.49	0.27	0.77	0.22	0.34	0.39	0.52	0.48
	SD	0.03	0.07	0.21	0.14	0.51	0.05	0.11	0.00	0.02	0.08
28	Avg.	1.71	0.87	0.93	1.53	1.77	1.39	0.93	1.56	1.39	1.32
	SD	0.42	0.57	0.81	0.23	0.29	0.15	0.85	0.06	0.13	0.24

day was 325 ± 164 µmol photons m^{-2} s^{-1} and rather above than below the PAR of previous days. Temperature has also been suggested to affect exudation, yielding higher PER at higher temperatures (Zlotnik and Dubinsky, 1989; Moran et al., 2006; Engel et al., 2011). However, since temperature increased in the course of the mesocosms study, this also would favor rather than suppress PER. We do not know if the decreases in PER in fjord and in mesocosms samples around day 14 were related, or just coincided. Therefore, we cannot exclude a potential co-effect on PER besides nutrient availability.

Mean deviations (MD) of PP_{POC} were positive for the three highest CO_2 mesocosms during all periods (Fig. 8a–c). This was most pronounced for the period after nutrient addition, when MD of PP_{POC} in the high pCO_2 mesocosm (974 µatm) was 44 % higher than average. For the total period, a significant positive relationship was observed between MD-PP_{POC} and average pCO_2 ($p < 0.05$) (Fig. 8a). This relationship was not seen during the time before nutrient addition, but clearly observed thereafter ($p < 0.01$) (Fig. 8b, c). Again, relatively large differences were determined among the low CO_2 mesocosms, where MD-PP_{POC} ranged from −49 % to +6 %.

For PP_{DOC}, the relationships of MD to average pCO_2 during the respective periods were significant before as well as after nutrient addition (Fig. 9a–c). Largest negative values for MD-PP_{DOC} were observed for the period after nutrient addition for the fjord (−57 %) and for the low pCO_2 mesocosm M7 (−41 %). Largest positive values for MD-PP_{DOC} again were determined in samples of the high pCO_2 mesocosm M9 (+40 %).

3.3 DOC concentration

Average DOC concentration in the mesocosm at day −1 was 76 ± 3 µmol C L^{-1}, and slightly higher than observed in the fjord at that day (71 µmol C L^{-1}). DOC concentrations were thus lower than the annual range of 100–244 µmol C L^{-1} determined for the Kongsfjorden by Iversen and Seuthe (2011), but comparable to data received for the Arctic Ocean by

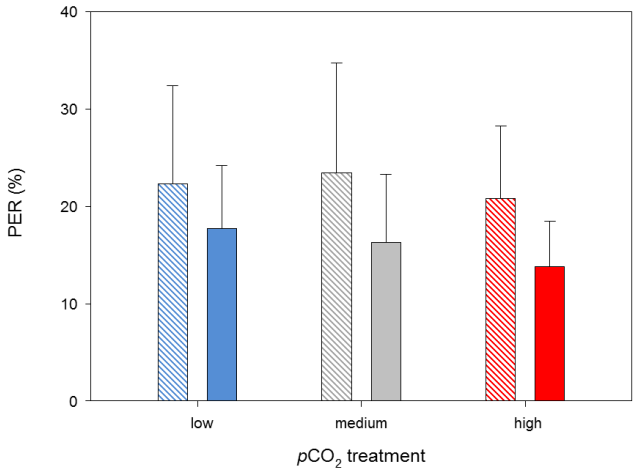

Fig. 6. Exudation of DOC calculated as percentage of extracellular release (PER) and averaged for grouped treatments (low, medium, high pCO_2) for the time before nutrient addition (hatched bars, day 5–day 12, $n = 12$), and after nutrient addition (solid bars, day 14–day 28; $n = 21$). For color information see Fig. 3. PER was not significantly different before nutrient addition, but decreased thereafter with increasing pCO_2 (t-test, $p < 0.05$).

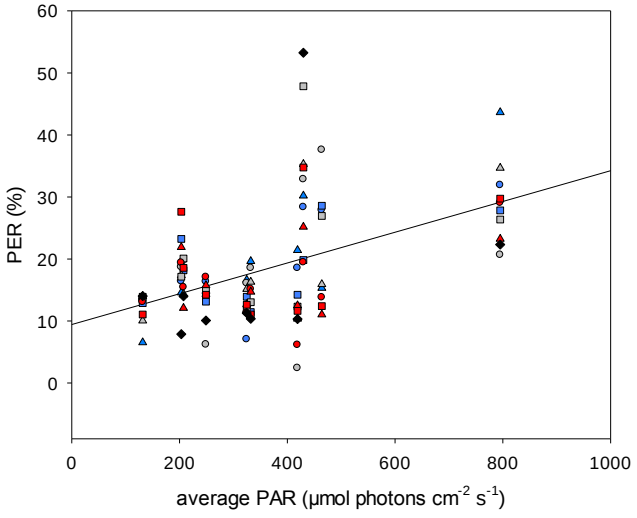

Fig. 7. PER during the total period of observation (day 5–day 28) increased with average PAR received during the 24 h bottle incubations. For color information see Fig. 3.

Cuevas et al. (2011), i.e., 61–84 µmol L^{-1}, and by Myklestad and Boersheim (2007), i.e., 87 ± 16 µmol C L^{-1}.

DOC concentration increased significantly between day 4 and day 13 in all mesocosms, yielding a rate of 1.6 ± 5.4 µmol C L^{-1} d^{-1} ($p < 0.01$) (Fig. 10), equivalent to 15 ± 5.4 µmol C L^{-1} for this period. DOC accumulation before nutrient addition was thus comparable to cumulative PP_{DOC} (range day 12: 8–13 µmol C L^{-1}). For the period after nutrient addition, no further accumulation of DOC was observed, and values averaged 91 ± 7 µmol C L^{-1}. The absence of DOC accumulation during the bloom periods was in contrast to the potential production of DOC by PP_{DOC}, which was estimated for that period to amount to 11–27 µmol C L^{-1}.

For the mesocosms, a positive correlation between MD-DOC and average pCO_2 was observed only for the period before nutrient addition ($p < 0.05$) (Fig. 11), and in accordance with increasing PP_{DOC} at higher pCO_2 observed during this period (Fig. 9b). After nutrient addition, no significant difference in MD-DOC between mesocosms was observed, despite CO_2-related differences in carbon exudation.

3.4 Primary vs. bacterial production

Primary produced organic compounds directly fuel the heterotrophic food web, amongst which bacteria are the main consumers. Bacterial production (BP) during this study ranged between 0.04 and 0.54 µmol C L^{-1} d^{-1} in the mesocosms, and between 0.10 and 0.84 µmol C L^{-1} d^{-1} in the fjord samples. Detailed information is given in Piontek et al. (2013). BP was directly related to PP considering the entire duration of the experiment (day 5–day 28) and all mesocosms ($n = 108$, $r^2 = 0.28$, $p < 0.001$) (Fig. 12).

Assuming that bacteria preferentially consume dissolved organic compounds, we calculated the ratio of BP : PP_{DOC} Here, values ranged between 20 % and 50 % in the mesocosms (Fig. 13a), and were lower than in the fjord water outside the mesocosms.

Related to the total amount of organic carbon produced, the fraction of BP was much smaller. Averaged over all mesocosms, BP : PP was 3.5 ± 1.9 %, and lower than in the fjord at the same time (6.5 ± 4.0 %). BP : PP_{DOC} as well as BP : PP did not differ significantly between mesocosms, nor over time (ANOVA; $p > 0.1$), and no significant influence of nutrient addition at day 13 was determined either (t-test; $p > 0.1$). However, lowest ratios were observed at highest pCO_2 (Fig. 13b).

4 Discussion

4.1 Temporal variability of primary production during the experiment

The experiment started at a time when the natural autotrophic community in the Kongsfjorden experienced low nutrient concentrations (Schulz et al., 2013). Until the day of nutrient addition (day 13), PP_{POC} and PP_{DOC} in the mesocosms were low and similar to rates determined in the fjord. During this time, CO_2-related differences were identified for PP_{DOC} but not for PP_{POC}. Higher exudation of $DO^{14}C$ at higher pCO_2 was in good accordance with higher accumulation of DOC.

Addition of nutrients to the mesocosms on day 13 initiated phytoplankton bloom developments with a faster and more pronounced immediate response of the autotrophic community at high pCO_2 (Fig. 3; see also Schulz et al., 2013). In

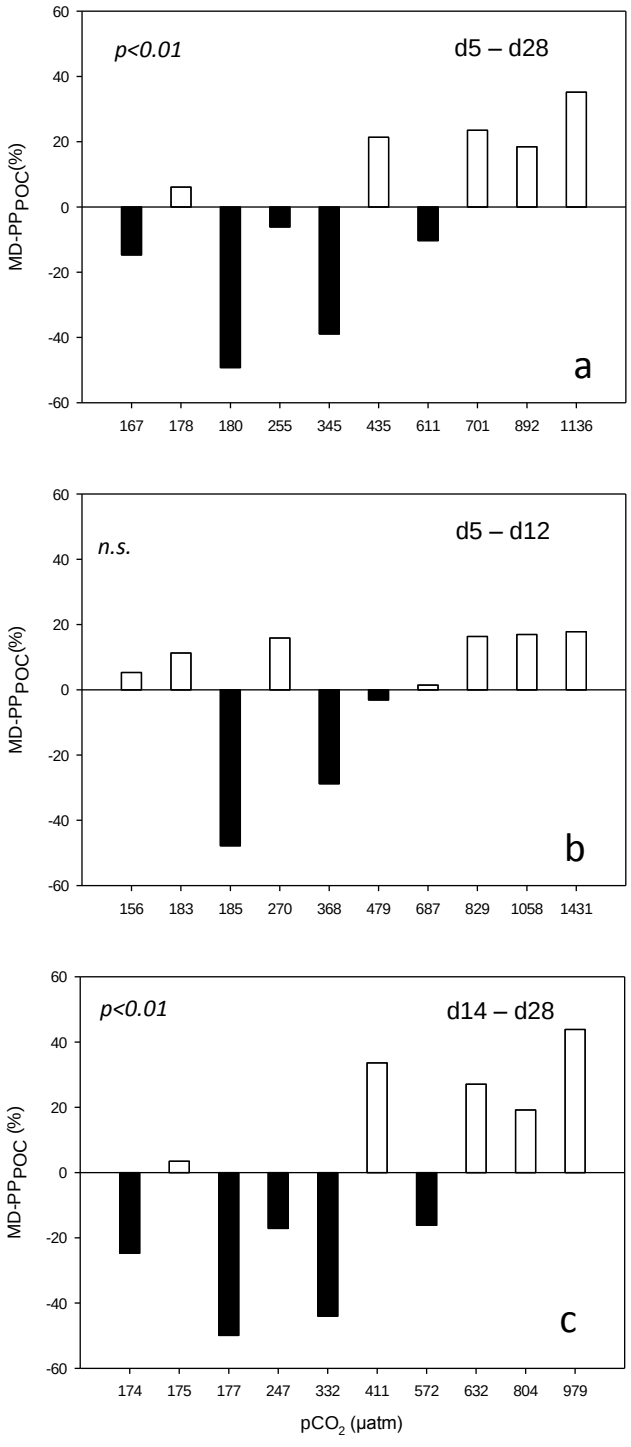

Fig. 8. Mean deviations of PP_{POC} (MD-PP_{POC}, %) for the nine mesocosms and for the fjord (left bar) calculated for **(a)** the total period of observation (day 5–day 28; $n = 12$), **(b)** the period before nutrient addition (day 5–day 12; $n = 4$), and **(c)** the period after nutrient addition (day 14–day 28; $n = 8$). Significance of relation between MD-PP_{POC} and average pCO_2 at the time of observation was calculated by linear regression.

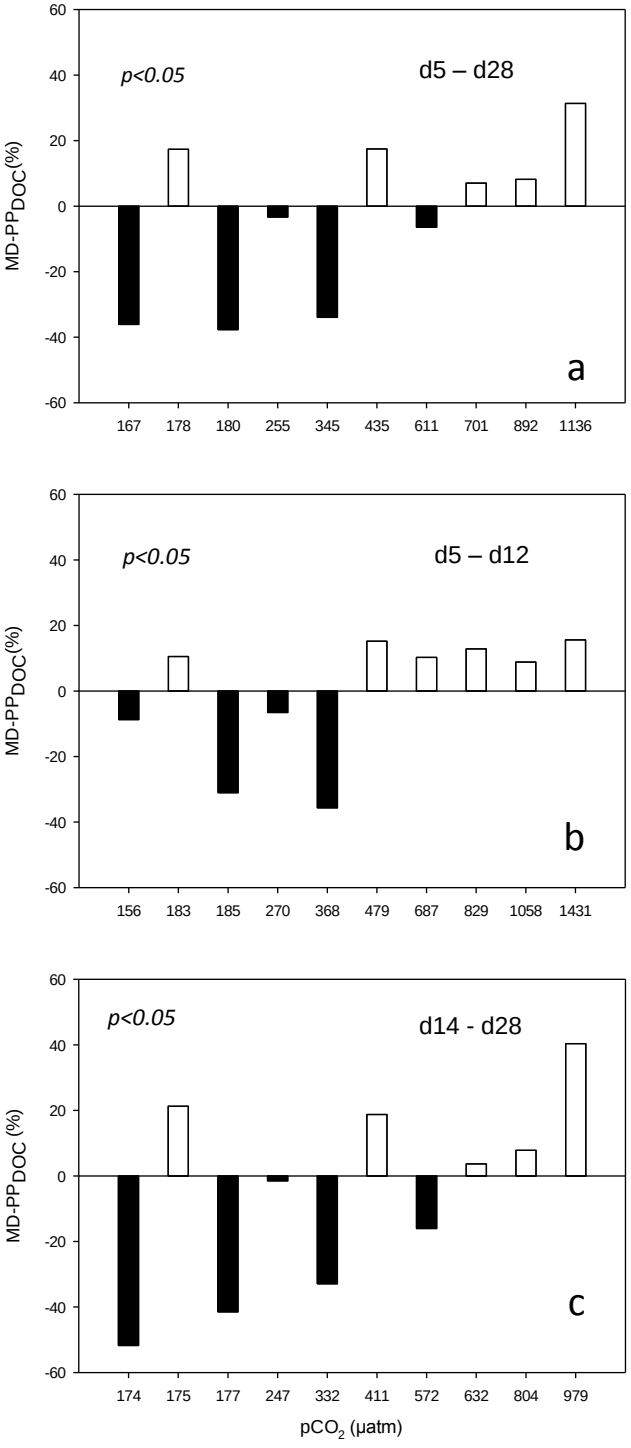

Fig. 9. Mean deviations of PP_{DOC} (MD-PP_{DOC}, %) for the nine mesocosms and for the fjord (left bar) calculated for **(a)** the total period of observation (day 5–day 28; $n = 12$), **(b)** the period before nutrient addition (day 5–day 12; $n = 4$), and **(c)** the period after nutrient addition (day 13-day 27; $n = 8$). Significance of relationship between MD-PP_{DOC} and average pCO_2 at the time of observation was calculated by linear regression.

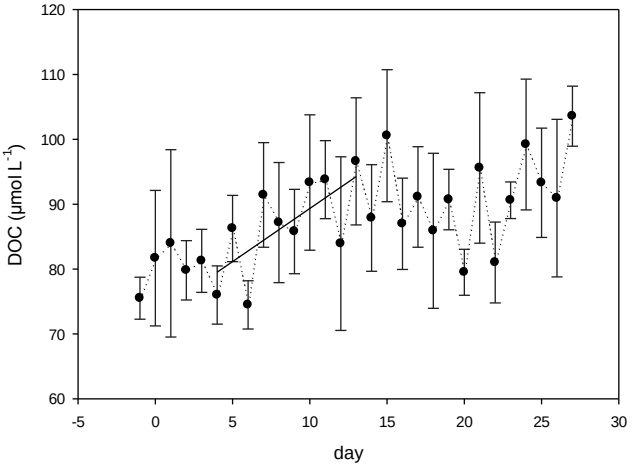

Fig. 10. Average concentration of dissolved organic carbon (DOC) in the course of the mesocosm experiment as determined from depth-integrated samples of the nine mesocosms. Error bars give ±1SD. Between days 4 and 13 (nutrient addition), DOC increased significantly over time ($r^2 = 0.45$, $n = 10$, $p = 0.01$), whereas no significant increase of DOC concentration was observed afterwards.

accordance, higher values for PP_{POC} and PP_{DOC} were determined for the high pCO_2 mesocosms, also.

A positive response of primary production (PP_{POC}) to increasing seawater pCO_2 has been observed during earlier mesocosm experiments (Egge et al., 2009), as well as during laboratory studies for a variety of phytoplankton species and at different light and temperature conditions (Hein and Sand-Jensen, 1997; Schippers et al., 2004; Rost et al., 2008). A stimulation of photosynthesis by increasing pCO_2 is attributed to the Michaelis–Menten type relationship between photosynthesis rate and CO_2 concentration, showing high sensitivity of photosynthesis to changes in CO_2 at lower CO_2 concentration and little changes at high and saturating pCO_2. During this study, larger differences of primary production rates were observed among the low pCO_2 mesocosms and may be explained by differences in the CO_2 affinity (K_m value) between phytoplankton species (Reinfelder, 2011). Hence, the natural variability in species composition and physiology of the phytoplankton community likely translated into larger differences of primary production rates among the low pCO_2 mesocosms.

Overall, the temporal development of primary production of phytoplankton sampled from the mesocosms and the stimulation of PP_{POC} and PP_{DOC} by increasing pCO_2 met well with our expectations and earlier findings.

4.2 Primary production vs. net community production

While ^{14}C primary production increased with pCO_2 during all phases of the experiment, net community production (NCP) determined by in vitro O_2 measurements as well as by cumulative changes of DIC concentration inside the

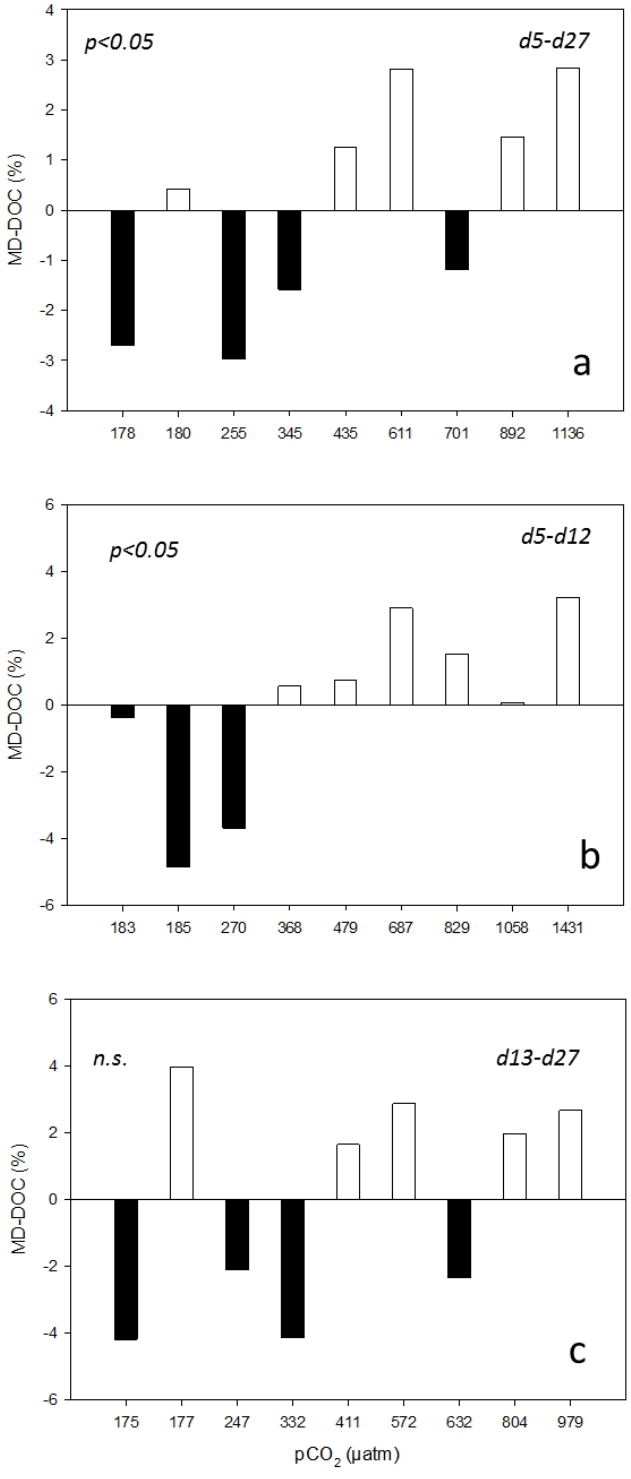

Fig. 11. Mean deviations of DOC concentrations (MD_{DOC}, %) for the nine mesocosms, for **(a)** the total period of observation (day 4–day 27; $n = 24$), **(b)** the period before nutrient addition (day 4–day 12; $n = 10$), and **(c)** the period after nutrient addition (day 13–day 27; $n = 14$). Significance of relation between MD_{DOC} and average pCO_2 at the time of observation was calculated by linear regression. Fjord samples were not included.

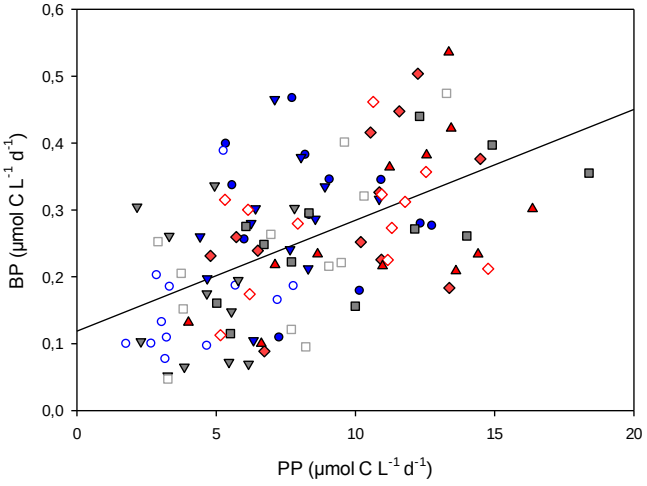

Fig. 12. Relationship between bacterial biomass production (BP) and primary production (PP) in the mesocosm samples was highly significant ($p < 0.001$, $n = 108$) for the total period of the experiment (day 4–day 28).

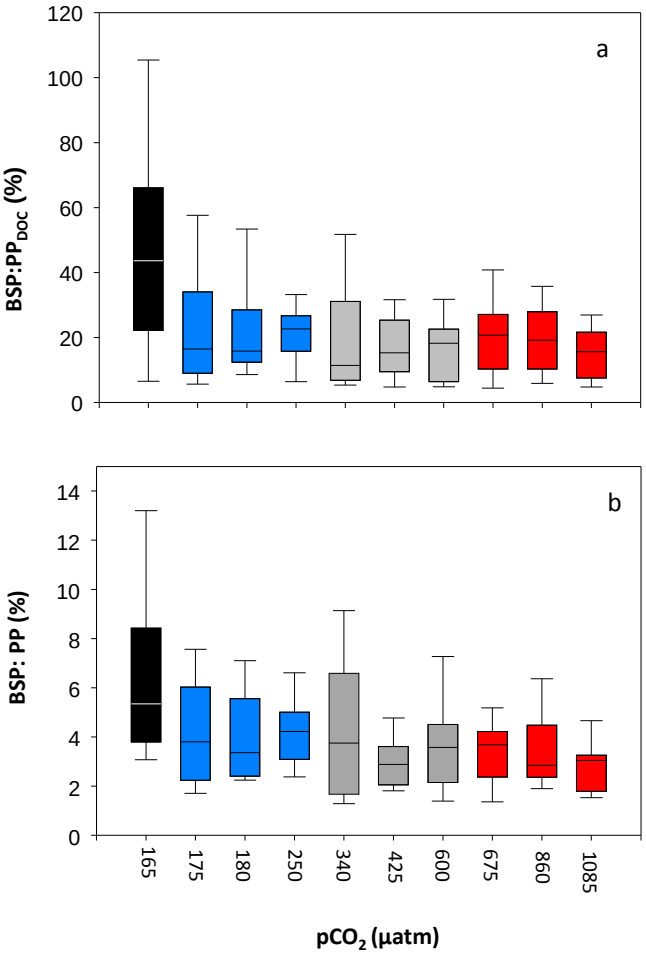

Fig. 13. Box and whisker plots of the ratio of bacterial biomass production (BP) to **(a)** primary production of DOC (PP_{DOC}) and to **(b)** total primary production ($PP = PP_{POC} + PP_{DOC}$) as derived from dark and light bottle incubations. Average values (day 5–day 28) for pCO_2 are shown.

mesocosms was highest at low CO_2 concentration during the later phase of the experiment, i.e., after day 21 (Tanaka et al., 2013; Silyakova et al., 2012). A different or even anti-correlated response of PP and NCP to increasing pCO_2 would have important implications for carbon and oxygen cycling in the surface ocean. We therefore will try to find some explanations for the apparent discrepancies.

First, the observed differences between PP and NCP may be due to methodological constraints. It has to be emphasized that the ^{14}C technique gives an estimate for the assimilation of carbon into POC and DOC that is lower than gross but higher than net production. Even under high heterotrophic activities, ^{14}C primary production rates cannot become negative, as respiration of abundant organic matter by heterotrophic organisms cannot be accounted for. Respiration, however, is included in NCP measurement based on O_2 or DIC, and negative NCP was determined on some days during this study (Tanaka et al., 2013), suggesting that "older" and previously abundant organic matter was respired by the plankton community. Thus, in vitro ^{14}C-PP measurements are biased towards autotrophic production, while NCP measurements rather estimate the net productivity of the auto- and heterotrophic community. This general difference was even amplified in this study, because our ^{14}C incubations were performed at high light (1 m) and excluded larger zooplankton (> 200 µm), while in vitro O_2 and ΔDIC measurements also included lower light levels (4 m and whole mesocosm) without pre-filtering.

Discrepancies between ^{14}C-PP and NCP were primarily observed during the second bloom phase after nutrient addition. Until day 21, highest cumulative NCP as estimated from ΔDIC was determined for the high pCO_2 mesocosms (Silyakova et al., 2012; this study), in accordance with higher ^{14}C-PP. Thus, a potential cause for the discrepancy between ^{14}C-PP and NCP estimates likely involved the response of the heterotrophic community and evolved during the experiment.

We suggest that heterotrophic microbes were primarily responsible for differences in the response of PP and NCP to CO_2. During this study, heterotrophic activity was closely coupled to PP, as derived from bacterial production and from hydrolytic enzyme activities (Fig. 11; see also Piontek et al., 2013). Prior to the experiment, bacterial growth was limited by the availability of labile organic carbon and co-limited by nitrogen (Piontek et al., 2013). It can therefore be assumed that bacteria directly responded to the release of labile organic carbon by phytoplankton. Nutrient addition at day 13 then not only provided substrate for autotrophic cells but likely fueled the growing community of heterotrophic bacteria also.

After nutrient addition, values of PER decreased in all mesocosms. Nutrient limitation has been shown earlier to increase PER in marine phytoplankton (Myklestad, 1977; Obernosterer and Herndl, 1995; Lopez-Sandoval et al., 2011). A reduction of PER in response to the elimination of nutrient limitation as observed during this study supports the idea of exudation being a discharge mechanisms for excess photosynthates (Wood and van Valen, 1990; Schartau et al., 2007). Nevertheless, as PP was higher at high CO_2, the absolute rates of PP_{DOC} were still higher in the high CO_2 mesocosm samples. The observation that PP_{DOC} increased with pCO_2 after nutrient addition, but DOC concentration did not (Figs. 5b and 10), suggests that the growing community of heterotrophic bacteria consumed DOC to a larger extent at high pCO_2.

Higher PP_{POC} in the high pCO_2 mesocosms translated into higher phytoplankton biomass directly after addition and before re-depletion of nutrients. This is in accordance with our expectation, as the utilization of photosynthetic products for biomass synthesis by heterotrophic as well as by autotrophic cells depends on the availability of nitrogen and phosphorus. Data on cell abundance as determined by flow cytometry suggest that particularly fast-growing picoautotrophic cells benefitted from nutrient addition at high pCO_2 (Brussaard et al., 2012).

However, with regard to the entire study period, the maximum yield of phytoplankton biomass in the low pCO_2 mesocosms exceeded the maximum biomass yield in the high CO_2 treatments, despite higher PP_{POC} in the latter. This apparent difference between autotrophic POC production and accumulation of phytoplankton biomass at high CO_2 may be explained by either one, or a combination of the following processes: (i) enhanced settling loss of phytoplankton biomass from the water column, (ii) enhanced solubilization and remineralization of phytoplankton cells, or (iii) increased nutrient competition between auto- and heterotrophic microorganisms. (i) It has been suggested that under nutrient limiting conditions phytoplankton produce more exopolymer carbohydrates at high pCO_2 (Engel, 2002; Borchard and Engel, 2012). Since exopolymer carbohydrates are important agents in coagulation processes and enhance aggregate formation, a higher export of organic matter may be inferred. However, higher export fluxes and therewith a higher loss of organic matter from the water column in the high pCO_2 bags were not directly observed during this study (Czerny et al., 2012). (ii) Recent studies suggest that bacterial processes such as organic matter solubilization and hydrolysis by extracellular enzymes are enhanced by ocean acidification (Grossart et al., 2006; Piontek et al., 2010, 2013; Yamada and Suzumura, 2010; Endres et al., 2013). Higher activities of hydrolytic enzymes were observed at reduced pH also during side-experiments of this study (Piontek et al., 2013), and may have resulted in faster degradation of organic matter, including autotrophic biomass. (iii) It is well known that the release of organic substrates from phytoplankton fuels the microbial food web (Azam and Hodson, 1977; Azam et al., 1983). The higher production and release of DOC at high pCO_2 likely enhanced the utilization of organic carbon, oxygen and nutrients by marine bacteria also during this study. The higher demand for nitrogen and phosphorus in marine bacteria potentially exacerbated competition between phyto- and bacterioplankton for inorganic nutrients and curtailed autotrophic growth. During this study, nutrient consumption directly after nutrient addition was faster in the high pCO_2 mesocosms. Although more autotrophic biomass, as indicated from chl *a*, was observed at higher pCO_2 initially, a much stronger phytoplankton bloom developed later during the experiment at low pCO_2 (Schulz et al., 2012). As a consequence the peak ratios of chl *a* to particulate organic nitrogen ([chl *a*] : [PON]) achieved during this study were smaller at high pCO_2 than at medium and low pCO_2 (data Schulz et al., 2012). This supports the idea that a higher amount of nutrients were partitioned into the heterotrophic food web under high pCO_2.

5 Conclusion

Increasing CO_2 concentration can enhance the primary production of organic carbon by Arctic phytoplankton. Due to higher primary production, the amount of DOC released by phytoplankton at high pCO_2 may also increase. However, as activities of Arctic bacterioplankton seem closely coupled to primary production, bacteria will efficiently counteract a surplus of labile organic carbon during bloom and post-bloom situations. The stimulation of bacterial activities, further supported by acceleration of extracellular enzyme activities, would exacerbate the competition between phyto- and bacterioplankton for inorganic nutrients.

As a consequence, net community production may decrease at high pCO_2 despite higher primary production of organic carbon. Such a counterintuitive cycling of carbon (i.e., higher autotrophic carbon fixation leads to less net production of the whole community) has been hypothesized for Arctic systems previously (Thingstad et al., 2008).

The Arctic Ocean at present is a net sink for atmospheric CO_2 on an annual scale (Arrigo et al., 2010), and an increase in primary production and biological CO_2 draw-down associated with the ongoing sea-ice loss have been predicted (Arrigo et al., 2008). This study reveals that primary production may increase in the wake of ocean acidification. However, the heterotrophic microbial community has a strong potential to diminish air–sea carbon fluxes and needs to be considered when estimating the response of the Arctic Ocean to future environmental changes.

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