Response to review

Dear Editor

We are grateful for all the constructive comments and suggestions by the reviewers, which have improved the manuscript a lot. Below we have placed all our original responses plus additional comments and changes made to the manuscript. Additional text put in the manuscript is marked in red.

On behalf of all the authors

Sincerely,

Kristian Spilling

Reviewer #1, Comment #1

The main results show that elevated CO2 conditions increased total particulate carbon and the DOC pool due to a decrease in respiration and bacterial production at elevated CO2 concentrations. I think that this is a very interesting result that needs to be discussed more deeply in the manuscript. I refer the authors to Hopkinson et al. 2010 and Teira et al. 2012 for information about decreases in phyto and bacterial respiration under high CO2 concentrations. Sobrino et al. 2014 can be also used as a reference related to downregulation of phytoplankton metabolism under high CO2, which might be an appropriate topic for the discussion of the manuscript.

Author response:

A good point and we will expand the discussion on this topic relating the decrease in respiration to possible downregulation of metabolism.

Additional comments and Changes made:

We did cover the reduced respiration and bacterial production in the Spilling et al 2016 paper and we do not want to be too repetitive, but we did expand on this in order to cover all relevant topics. We included the references suggested by the reviewer and expanded on the discussion around changes in the metabolism and possible impact on carbon concentrating mechanisms.

Reviewer #1, Comment #2

Regarding the data analysis, I like the idea of using estimated instead raw data to make comparisons between variables or when observed values are not available. However the authors should also provide more information to complement or justify the usage of estimated vs. measured data. For example when comparing NPP14C and NPPe the authors only say that results "agree reasonably well" which is a very general contention for this paper. In addition, during Phase III, total respiration was not measured and the authors estimated TR based on the NPPe TR-1 and BP TR-1 ratios during Phase II. Information about their correlations during Phase II would be desirable to justify the estimation carried out during Phase III.

Author response:

We will make changes to the estimated variables according to the suggestions of reviewer #2 (see comments below). We will be more specific when comparing different variables and also provide a better justification for the estimates of TR in Phase III. This was done using two methods as to give a range rather than specific number for the TR estimate.

Change made:

This was also a topic covered by reviewer #2 and we have followed those recommendations to make the distinction between the different properties easier to follow. For the comparison (referring to the statement "agree reasonably well") has now been removed. The details regarding the changes made can be found below under the comments made by reviewer #2.

Regarding the estimations carried out in Phase III, we are aware that this is highly uncertain, but this is also why we did it using two different ways and this can be seen as a much wider span in the estimate presented in Fig 5.

Reviewer #1; Comment #3

Finally, a specific equation for the estimation of bacterial respiration would be nice to see in the Methods.

Author response:

This equation will be added

Changes made:

We added the equation in parenthesis as it can also be deduced from the following equation: Eq 10

The added text: …(BR $\leq$ BB/TB)…

Reviewer #1; Minor comments

Minor issues: - Line 234 days - Line 269 correlated to?? - Line 410. Revise sentence " The initial increase in the: : :." - Line 425 during - Fig. 1 filtration - Fig. 2. What about using similar units in the Y axis and legend (i.e. uatm??)

Author response:

Appropriate changes will be made

Changes made:

All the changes were made with the exception of the comment to Fig 2. The legend has units µatm as these are the treatments. The flux has been measured in mmol m-2 d-1.

Reviewer #2, Comment #1

Although I am convinced of the scientific relevance of this study, I am not convinced considering this budgeting exercice as a separate manuscript is highly relevant. Spilling et al. under revision in this special issue already reports on decreasing respiration rates at high CO2, causing higher Chla, TPC and DOC concentrations in the high CO2 treatments. The added value of the present manuscript is to estimate plankton rates that have not been directly measured (NPPe, but see later comment on this term; GPPi, but again see later comment; BR; DOC production). I would definitely recommend merging the two Spilling et al. papers to provide a more comprehensive overview of what happened during this experiment.

If this suggestion is not followed, this manuscript, in my opinion, needs major revisions in order to improve its clarity and to discuss and criticise more deeply what has been found.

Author response:

We do understand this point as having one manuscript was the original idea. During the writing process, however, we decided to present the budgeting exercise on its own in order to keep a more focused paper on respiration and primary production. The present manuscript was submitted as a synthesis paper and additionally presents data from many of the other papers submitted to the special issue, including bacterial production, DOC and a budget for the DIC based on atmospheric exchange. We are confident that following the referees' comments and suggestions will considerably improve our manuscript and justify separate publication.

Changes made:

We have taken the second approach and made a major revision, where we e.g. have reformulated some of the terms according the reviewer’s suggestion (see comments below)

Reviewer #2, Comment #2

Estimates of DOC, TPC and DIC pools in mol C m-2: I was wondering for quite a while how these initial pools have been calculated and how the authors could provide an error estimate on a single sampling. I saw in the other Spilling et al. that these pools were actually averages of 3 sampling dates at the start of each phase. This must be clarified in the present manuscript. Also, how were integrated pools estimated: it is mentioned (and only for DIC, L136) in the ms that volumetric concentrations in per kg were converted using seawater density. Obviously, they were further multiplied by the considered depth. Please clarify.

Author response:

The reviewer is correct, the error estimates where made from consecutive measurements, and this will be mentioned in the materials and methods and table legends (Tables 1-3). We will also add the information that the depth and area of the mesocosms were used to calculate all pools and fluxes in m-2 units.

Changes made:

We made a new paragraph under section '2.4. Data treatment', where these issues have been addressed (inserted below). Part of this paragraph was mover up from the last paragraph of this section for improving the readability.

"Based on the primary variables the experiment where divided into three distinct phases: Phase I: *t0-t16*; Phase II: *t17-t30* and Phase III: *t31-t43*, where e.g. Chlorophyll *a* (Chl *a*) concentration was relatively high during Phase I, decreased during Phase II and remained low during Phase III (Paul et al. 2015). Measurements of pools and rates were average for the two first sampling points of each experimental phase (n = 2) and where normalized to m^2 knowing the total depth and volume of the mesocosms. The three different phases of the experiments were of different length (16, 14 and 13 days respectively). For fluxes and biological rates we used the average for the whole periods normalized to days (day^{-1}) All error estimates were calculated as standard error (SE), with n = 16, n = 14 and n = 13 for Phases I – III respectively. SE for estimated rates were calculated from the square root of the sum of variance for all the variables (Eq 6-11 below) The primary papers present detailed statistical analyses and we only refer to those here. "

Reviewer #2, Comment #3

Estimates of DOC, DIC and TPC rates of change: no information is provided on how these rates have been calculated. I believe these were calculated through linear regressions of each stock evolution during the considered phase. This must be clarified. Looking at Table 1 of the other Spilling et al., there are some discrepancies with rates presented here (e.g. Exp TPC of 7.4 in the first mesocosm compared to 6.6 in this paper, but this is also the case for other rates). Looking at the important errors associated with these rate estimates, it does seem like many slopes are not significantly different from 0. Please comment. In that case, how is it possible to compare these rates between the different mesocosms. Were these differences actually tested?

Author response:

This is a good point. It was calculated based on the difference between the start of each period, and using the average of the first two sampling days as the initial value for each period. So they are not slopes per se. There is no statistical testing of the differences in this paper, but we have explained that this was done in the paper where the original data is presented (and here linear regressions were used e.g. Paul et al 2015).

The discrepancy between the table in this paper with the other Spilling et al. paper is that here we did not include the time before the start of the CO2 treatment (this will be changed also in the other Spilling et al paper), i.e. discarding the Exp TPC data from day T-1.

Changes made:

How these rates were calculated is now described in the new paragraph under section 2.4. Data treatment. Please see our response to the previous comment.

Changes to the Spilling et al. (2016) paper have been made.

Reviewer #2, Comment #4

Estimates of NPPe and GPPi: Based on observed variations of TPC, DOC and DIC, the authors further calculated biological carbon fluxes. Net primary production measured by the 14C method (over 24h incubations) were compared to, what the authors refer to as NPPe being the missing process closing the organic budget: NPPe = Export + net variation in TPC + net variation in DOC). As the authors correctly mention, NPPe does incorporate total respiration and not only autotrophic respiration, as does the 14C method (this is actually clearly doubtful considering the long incubations that have been performed)). Anyway, this is incorrect to refer to this process as Net Primary production, this is misleading and you really should consider using the proper term: Net Community Production, and as it is based on an organic budget, you should use NCPo. The authors further use an inorganic budget (based on DIC net fluxes, and estimated CO2 fluxes) to estimate Gross Primary Production. I would strongly recommend for clarity to reconsider this part and to calculate NCPi, being the Net Community Production based on the inorganic budget. This is, I believe, what is shown in Fig. 3 and termed as Biological release or uptake. The authors have thus two estimates of the plankton community metabolism that do provide different outputs. While it seems like the inorganic budget shows that the community was heterotrophic in ambient mesocosms (Biological release of DIC), the organic budget suggests the opposite for all phases. This must be discussed. The paper as it stands is highly confusing with respect to this metabolic aspect. i.e. In the abstract is mentioned that during phase 1, the community under ambient and high CO2 treatments was autotrophic (i.e. more production than respiration, with capacity to export to the sediment traps and export to the DOC pool). However, it is clearly stated that the community was heterotrophic during the entire experiment under ambient CO2 conditions. Again, this must be clarified.

Author response:

We were a bit back and forth on how to best present the different variables when the manuscript was being written, and we ended up using the estimated net and gross production. The reviewer has a good point suggesting a better distinction between measured primary production and the estimated community production. We will change the NPPe to Net Community Production, organic budget (NCPo) and furthermore add the Net Community Production, inorganic budget (NCPi) as the reviewer suggests.

We will carefully go through the suggested points for clarification and discuss more in detail the discrepancy between the organic and inorganic carbon budget.

Changes made:

We changed the NPPe to become NCPo as suggested, and furthermore introduced the net community production based on inorganic carbon budget NCPi (Eq 6). This change was done throughout the manuscript including tables and figure legends.

We added a paragraph discussing the difference between NCPo and NCPi. They are different as the reviewer pointed out, but overall both give the same picture that NCP was higher in high CO2 treatments. Because of this we decided to change around a bit on the order of the Results and Discussion chapter, and placed the Biological rates after the presentation of the different carbon pools.

The new paragraph reads:

"The results of the DIC pool and atmospheric exchange of CO_2 provides another way of estimating the net community production based on inorganic carbon (NCP_i). There was some discrepancy between the NCP_o and NCP_i as the latter suggested net heterotrophy in the ambient CO_2 whereas the high CO_2 treatments were net autotrophic during all three phases of the experiment (Fig. 3). For the NCPo there was no indication of net heterotrophy at ambient CO_2 concentration. In terms of the absolute numbers, the NCPi estimate is probably more uncertain than NCP_o. Calculating the CO_2 atmospheric exchange from the measurements of a tracer gas involves several steps, each adding uncertainty to the calculation. However, both estimations (NCPi and NCPo) indicate that increased CO_2 concentrations lead to higher overall community production, supporting our overall conclusion. "

Reviewer #2, Comment #5

Comparison between the inorganic and organic budget: I already mentioned this, but I would like to insist on the fact that this paper reports on budgets based on both inorganic and organic constituents. Since they do not really agree, this must be deeply discussed. A recommendation on which type of budget is the most relevant and associated with the lowest uncertainties should be further proposed.

Author response:

This comment relates to comment #4 above and our reply to that. We will make the distinction between the organic and inorganic carbon budget as suggested and expand on this in the discussion.

Changes made

Please see our reply to Comment #4 above.

Reviewer #2, Comment #6

CO2 effects on estimated rates: I do not see how differences between estimated rates between low and high CO2 treatments have been tested. It is mentioned on L345 that "an effect of the different CO2 treatments was noticeable in the NPPe but not in the NPP14C", how was it tested?

Author response:

It was not tested statistically, and the term 'noticeable' refers to visual inspection of the data. We will however make a statistical test to strengthen this conclusion.

Changes made:

We added linear regression test to further underline this point and the line now reads:

There was no consistent difference between CO_2 treatments for NPP_{14C} ($p > 0.1$), but NCP_o increased with increasing CO_2 enrichment during Phase II (Phase II; linear regression $p = 0.003$; $R^2 = 0.91$).

Reviewer #2, Comment #7

Comparison between NPP14C and NPPe: as correctly stated by the authors, NPP14C rates should provide equal or higher estimates than NPPe (NCPo, see above). This is not the case and attributed (on top of potential errors in one control mesocosm) to "changed parameterisation during in

incubation in small volumes". Based on my experience, we usually observe higher rates in small incubations vs large ones, not really in accordance with the lower rates of NPP14C during phase 1. Alternatively, this offset could be attributed to errors associated with NPPe estimates, since the TPC pool was clearly underestimated. Could you comment on this?

Author response:

We do not have a good explanation for the discrepancy between NPPe and NPP14C, but underestimating of NPP14C seems more plausible as this are incubations in small volumes involving more steps than bulk measurements of TPC. Another possible explanation, suggested by the reviewer, is that the discrepancy could be due to an overestimation of NPPe. That would indicate an overestimation of either ΔTPC, ΔDOC or exported TPC (or a combination of these variables). TPC is not likely to be overestimated considering the methodology used, as measuring TPC has a relatively small uncertainty and would miss the <0.7 µm fraction. With this assumption, exported TPC would have been substantially overestimated. ΔTPC or ΔDOC would only be overestimated in the case when there is an underestimate at the start point, an overestimate at the end point or both an underestimate and overestimate increasing the difference between experimental phases in TPC or DOC. The discrepancy between NPPe and NPP14C during Phase I is so consistent for all treatments that we have hard time believing that we would have this consistent overestimation of ΔTPC or ΔDOC in all mesocosm bags.

Concerning the statement that: 'the TPC pool was clearly underestimated', we assume that you refer to the difference between the TPC pool and what was found in the bacterial and virus fraction based on flow cytometry. The small bacterial/virus not caught on the GFF filter did not contribute to the NPPe estimate. Defining the TPC as the >0.7 µm fraction, it is not obvious that TPC is underestimated.

Reviewer #2, Comment #8

Estimates of biological pools: I do not really get what is the added value of calculating and presenting pools of meso- and microzooplankton, micro- and nanophytoplankton, picophytoplankton, bacteria and viruses. I would guess that these informations are already available in other manuscripts from the special issue. Is this not the case? This makes a small paragraph of the Results and Discussion and, apart from showing that measured TPC is much much lower than the cumulated stocks of these biological compartments, I do not see what valuable information it brings.

Author response:

There is no paper presenting all of the organism groups together, and this being a synthesis paper we wanted to present these different pools. We agree that this data is not well incorporated into the story and we will expand on this in the discussion, trying to better link the relative contribution of the different groups to the fluxes presented.

Changes made:

We expanded on the community section (3.1.), relating the different plankton groups to the prevailing nutrient regime primarily driven by recycling. We also added a new paragraph about the virus fraction that was missing in the original manuscript.:

"Although there are some uncertainty in the carbon estimate (Jover et al. 2014), virus make up (due to their numerical dominance) a significant fraction of the pelagic carbon pool. Of the different plankton fractions the virioplankton have been the least studied, but their role in the pelagic ecosystem is ecologically important (Suttle 2007 NMR, Brussaard et al. 2008 ISMEJ; Mojica et al., 2016 ISMEJ). Viral lysis rates were equivalent to the grazing rates for phytoplankton and for bacteria in the current study (Crawfurd et al., 2015). As mortality agents they are drivers of the regenerative microbial food web, viruses (Suttle 2007, Brussaard et al. 2008). Overall, the structure of the plankton community reflected the nutrient status of the system. The increasing N-limitation favoring development of smaller cells, and increasing dependence of the primary producers on regenerated nutrients. "

Reviewer #2, Comment #9

Estimates of variability: I would recommend the authors to mention the sample size each time SE are provided. Furthermore, I do not really see (as this is not explained) how SEs have been calculated for estimated rates (error propagation). e.g. as NPPe rates are based on DOC net fluxes, therefore the associated errors should be at least equal to the errors associated with DOC net fluxes right? This is not the case, and this must be clarified further.

Author response:

We agree that the error estimates needs to be better explained. In the case of NPPe the SE was calculated from the square root of the sum of variance of the three parameters used to calculate the NPPe: DOC TPC and Exported TPC. We will include the sample size as suggested.

Changes made:

We added the sample size (n =) for each SE in the text and tables. We also added the way SE was determined for the biological rates as described above in the materials and methods chapter and also in the table legend.

Reviewer #2, Comment #10

Minor issues: Abstract: L57: did not transfer, please correct L58: revealed a clear effect of increasing CO2 on carbon production. I don't think this is correct. Carbon production does not seem impacted, while carbon loss is.

Author response:

This will be corrected.

Changes made:

L57 Corrected as suggested by the reviewer

L58 changed to: revealed a clear effect of increasing CO2 on the carbon budget

Reviewer #2, Comment #11

Materials and Methods: L104: I understood that more mesocosms were initially deployed, I do not see why this is not mentioned here. Everyone must also know how hard such experiment is. L159: Grossart et al. (2006), please correct L185: according to: , please correct L194: Cherny et al. (2013b), please correct. L205: organic carbon pool, please add dissolved + particulate for clarity L207: Direct measurements using : : :, please correct

Author response:

We will refer to the Paul et al. (2015) paper where the initial deployments are mentioned and the overall methods are described in more detail and incorporate the suggested corrections.

Changes made:

We added the text: "… (nine KOSMOS units were originally deployed but three were lost due to leaks). A more detailed description of the set-up can be found in Paul et al. (2015)."

The rest of the changes were made according to the reviewer's suggestions

Reviewer #2, Comment #12

Results and Discussion: L265: While some indication on temporal evolution is provided for the other measured variables, this is not the case for bacterial biomass, please add this information. L280: Spilling et al. 2016), please correct L286: in e.g., please remove e.g. L287: have pointed at, please correct L297: p<= 0.01 I believe, please correct. L325: (Paul et al. 2015 (a or b)), please correct and clarify L353: Spilling et al. 2016), please correct

Author response:

This will be added and corrections will be made.

Changes made:

There was temporal development of the bacterial community and this information was added:

"Overall, the bacterial numbers largely followed the phytoplankton biomass with an initial increase then decrease during Phase I; increase during Phase II and slight decrease during Phase III (Crawfurd et al., 2016)."

All the other corrections were made according to the reviewer's suggestions

Reviewer #2, Comment #13

Figures Fig. 3. As mentioned earlier, for clarity, Biological release or uptake should be referred to as NCPi (based on the inorganic budget). Values are not in mol C m-2 but in mol C m-2 d-1 I think, please correct.

Author response:

The reviewer is right and this will be corrected.

Changes made:

This was corrected in Fig 3 and we also adopted the NCPi parameter instead of the biological release/uptake.

Effects of ocean acidification on pelagic carbon fluxes in a mesocosm experiment

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Running title: Modified pelagic carbon fluxes

Key words: Carbon fluxes, carbon budget, gross primary production, respiration, bacterial production, sinking carbon flux, CO_2 exchange with atmosphere

Abstract

About a quarter of anthropogenic CO_2 emissions are currently taken up by the oceans decreasing seawater pH. We performed a mesocosm experiment in the Baltic Sea in order to investigate the consequences of increasing CO_2 levels on pelagic carbon fluxes. A gradient of different CO_2 scenarios, ranging from ambient (~370 µatm) to high (~1200 µatm), were set up in mesocosm bags (~55 m^3). We determined standing stocks and temporal changes of total particulate carbon (TPC), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and particulate organic carbon (POC) of specific plankton groups. We also measured carbon flux via CO_2 exchange with the atmosphere and sedimentation (export); and biological rate measurements of primary production, bacterial production and total respiration. The experiment lasted for 44 days and was divided into three different phases (I: *t0-t16*; II: *t17-t30*; III: *t31-t43*). Pools of TPC, DOC and DIC were approximately 420, 7200 and 25200 mmol C m^{-2} at the start of the experiment, and the initial CO_2 additions increased the DIC pool by ~7% in the highest CO_2 treatment. Overall, there was a decrease in TPC and increase of DOC over the course of the experiment. The decrease in TPC was lower, and increase in DOC higher, in treatments with added CO_2. During Phase I the estimated gross primary production (GPP) was ~100 mmol C fixed m^{-2} d^{-1}; from which 75-95% were respired, ~1% ended up in the TPC (including export) and 5-25% added to the DOC pool. During Phase II, the respiration loss increased to ~100% of GPP at the ambient CO_2 concentration, whereas respiration was lower (85-95% of GPP) in the highest CO_2 treatment. Bacterial production was ~30% lower, on average, at the highest CO_2 concentration compared with the controls during Phases II and III. This resulted in a higher accumulation DOC standing stock and lower reduction in TPC in the elevated CO_2 treatments at the end of Phase II extending throughout Phase III. The "extra" organic carbon at high CO_2 remained fixed in an increasing biomass of small-sized plankton and in the DOC pool, and did not transfer~~transferred~~ into large, sinking aggregates. Our results revealed a clear effect of increasing CO_2 on the carbon budget~~production~~ and mineralization, in particular under nutrient limited conditions. Lower carbon loss processes (respiration and bacterial remineralization) at elevated CO_2 levels resulted in higher TPC and DOC pools compared with the ambient CO_2 concentration. These results highlight the importance to address not only net changes in carbon standing stocks, but also carbon fluxes and budgets to better disentangle the effects of ocean acidification.

1 Introduction

Combustion of fossil fuels and change in land use, have caused increasing atmospheric concentrations of carbon dioxide (CO_2). Ca. 25% of the anthropogenic CO_2 is absorbed by the oceans, thereby decreasing surface water pH, a process termed ocean acidification (Le Quéré et al., 2009). Ocean acidification and its alterations of aquatic ecosystems have received considerable attention during the past decade, but there are many open questions, in particular related to consequences for planktonic mediated carbon fluxes.

Some studies on ocean acidification have reported increased carbon fixation (Egge et al., 2009; Engel et al., 2013), bacterial production (Grossart et al., 2006) and bacterial degradation of polysaccharides (Piontek et al., 2010) at enhanced CO_2 levels, with potential consequences for carbon fluxes within pelagic ecosystems and export to the deep ocean, i.e. the biological carbon pump. Increasing carbon fixation in a high CO_2 environment can translate into an enhanced sequestration of carbon (Riebesell et al., 2007), but this depends on numerous environmental factors including phytoplankton community composition, aggregate formation and nutrient availability. For example, if the community shifts towards smaller cell sizes and/or enhanced cycling of organic matter carbon, export from the upper water layers may decrease (Czerny et al., 2013a).

The effect of ocean acidification has mostly been studied in marine ecosystems under high phytoplankton biomass. Brackish water has lower buffering capacity than ocean water and the pH fluctuates more. The limited number of studies of ocean acidification in brackish water and indications that ocean acidification effects are greatest under nutrient limitation (De Kluijver et al., 2010), motivated this mesocosm study in the Baltic Sea during low nutrient, summer months.

The Baltic Sea is functionally much like a large estuary, with a salinity gradient ranging from approximately 20 in the South-West to <3 in the Northernmost Bothnian Bay. It is an almost landlocked body of water with a large population in its vicinity (~80 million). Human activities (e.g. agriculture, shipping and fishing) cause a number of environmental problems such as eutrophication and pollution. As a coastal sea projected to change rapidly due to interaction of direct and indirect anthropogenic pressures, the Baltic Sea can be seen as a model ecosystem to study global change scenarios (Niiranen et al., 2013).

Most primary data from this experiment are published in several papers of this Special Issue (Riebesell et al., 2015). The aim of the present paper is to provide an overarching synthesis of

all information related to carbon standing stocks and fluxes. This enabled us to calculate carbon budgets in relation to different CO_2 levels.

2 Materials and methods

2.1. Experimental set-up

Six Kiel Off-Shore Mesocosms for future Ocean Simulations (KOSMOS; with a volume of ca. 55 m^3) were moored at Storfjärden, on the south west coast of Finland (59° 51.5' N; 23° 15.5' E) on 12 June 2012 (nine KOSMOS units were originally deployed but three were lost due to leaks). A more detailed description of the set-up can be found in Paul et al. (2015).

The mesocosms extended from the surface down to 19 m depth and had a conical bottom end, which enabled quantitative collection of the settling material. Different CO_2 levels in the bags were achieved by adding filtered (50 µm), CO_2-saturated seawater. The CO_2 enriched water was evenly distributed over the upper 17 m of the water columns and added in 4 consecutive time steps (*t0 – t3*). Two controls and four treatments were used, and for the controls, filtered seawater (without additional CO_2 enrichment) was added. The CO_2 fugacity gradient after all additions ranged from ambient (average throughout the experiment: ~370 µatm fCO_2) in the two control mesocosms (M1 and M5), up to ~1200 µatm fCO_2 in the highest treatment (M8). We used the average fCO_2 throughout this experiment (from *t1 – t43*) to denote the different treatments: 365 (M1), 368 (M5), 497 (M7), 821 (M6), 1007 (M3) and 1231 (M8) µatm fCO_2. On *t15*, additional CO_2–saturated seawater was added to the upper 7 m in the same manner as the initial enrichment, to counteract outgassing of CO_2.

We sampled the mesocosm every morning, but some variables were determined only every second day. Depth-integrated water samples (0 – 17 m) were taken by using integrating water samplers (IWS, HYDRO-BIOS, Kiel). The water was collected into plastic carboys (10 L) and taken to the laboratory for sub-sampling and subsequent determination of carbon stocks.

2.2. Primary variables

For more detailed descriptions of the primary variables and the different methods used during this CO_2 mesocosm campaign, we refer to other papers in this joint volume: i.e. total particulate carbon (TPC), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) are described by Paul et al. (2015~~2015b~~); micro and nanophytoplankton enumeration by Bermúdez et al. (2016); picophytoplankton, heterotrophic prokaryotes and viruses by Crawfurd et al. (2016); zooplankton community by Lischka et al. (2015); primary production and respiration by Spilling et al. (2016); bacterial production (BP) by Hornick et al. (2016); and sedimentation by Boxhammer et al. (2016~~2015~~); and Paul et al. (2015~~2015b~~).

Briefly, samples for TPC (500 mL) were GF/F filtered and determined using an elemental analyser (EuroAE). DOC was measured using the high temperature combustion method (Shimadzu TOC –VCPN) following Badr et al. (2003). DIC was determined by infrared absorption (LI-COR LI-7000 on an AIRICA system). The DIC concentrations were converted from µmol kg^{-1} to µmol L^{-1}~~mmol m^{-2}~~ using the average seawater density of 1.0038 kg L^{-1} throughout the experiment. Settling particles were quantitatively collected every other day from sediment traps at the bottom of the mesocosm units and the TPC determined from the processed samples (Boxhammer et al., 2016) as described above.

Mesozooplankton was collected by net hauls (100 µm mesh size), fixed (ethanol) and counted in a stereomicroscope.~~stereomicroscopy in combination with a Folsom plankton splitter.~~ Zooplankton carbon biomass (CB) was calculated using the displacement volume (DV) and the equation of Wiebe (1988): (log DV + 1.429)/0.82 = log CB. Micro and nanoplankton (zoo- and phytoplankton) CB was determined from microscopic counts of fixed (acidic Lugol's iodine solution) samples, and the cellular bio-volumes were determined according to Olenina et al. (2006) and converted to POC by the equations provided by Menden-Deuer and Lessard (2000).

Picophytoplankton were counted using flow cytometry and converted to CB by size fractionation (Veldhuis and Kraay, 2004) and cellular carbon conversion factors (0.2 pg C $µm^{-3}$ (Waterbury et al., 1986). Prokaryotes and viruses were determined according to Marie et al. (1999) and Brussaard (2004), respectively. All heterotrophic prokaryotes, hereafter termed bacteria, and viruses were converted to CB assuming 12.5 fg C $cell^{-1}$ (Heinänen and Kuparinen, 1991) and 0.055 fg C $virus^{-1}$ (Steward et al., 2007), respectively.

The respiration rate was calculated from the difference between the O_2 concentration (measured with a Fibox 3, PreSens) before and after a 48 h incubation period in a dark, climate controlled room set to the average temperature observed in the mesocosms.

Bacterial protein production (BPP) was determined by ^{14}C-leucine (^{14}C-Leu) incorporation (Simon and Azam, 1989) according to (Grossart et al. (,, 2006). The amount of incorporated ^{14}C-Leu was converted into BPP by using an intracellular isotope dilution factor of 2. A conversion factor of 0.86 was used to convert the produced protein into carbon (Simon and Azam, 1989).

Net primary production (NPP) was measured using radio-labeled $NaH^{14}CO_3$ (Steeman-Nielsen, 1952). Samples were incubated for 24 h in duplicate, 8 ml vials moored on small incubation platforms at 2, 4, 6, 8 and 10 m depth next to the mesocosms. The areal primary production was calculated based on a simple linear model of the production measurements from the different depths (Spilling et al., 2016).

2.3. Gas exchange

In order to calculate the CO_2 gas exchange with the atmosphere (CO_{2flux}),, we used N_2O as tracer gas, and this was added to mesocosm M5 and M8 (control and high CO_2 treatment) according to Czerny et al. (2013b). The N_2O concentration was determined every second day using gas chromatography. Using the N_2O measurements, the fluxes across the water surface (F_{N2O}) was calculated according to:

$$F_{N2O} = I_{t1} - I_{t2} / (A * \Delta t) \quad (12)$$

where I_{t1} and I_{t2} is the bulk N_2O concentration at time: t_1 and t_2; A is the surface area and Δt is the time difference between t_1 and t_2.

The flux velocity was then calculated by:

$$K_{N2O} = F_{N2O} / (C_{N2Ow} - (C_{N2O\,aw}) \quad (23)$$

where C_{N2Ow} is the bulk N_2O concentration in the water at a given time point, and C_{N2Oaw} is the equilibrium concentration for N_2O (Weiss and Price, 1980).

The flux velocity for CO_2 was calculated from the flux velocity of N_2O according to:

$$k_{CO2} = k_{N2O} / (Sc_{CO2}/Sc_{N2O})^{0.5} \quad (34)$$

where Sc_{CO2} and Sc_{N2O} are the Schmidt numbers for CO_2 and N_2O, respectively. The CO_2flux across the water surface was calculated according to:

$$F_{CO2} = k_{CO2} (C_{CO2w} – C_{CO2aw}) \quad (45)$$

where C_{CO2w} is the water concentration of CO_2 and C_{CO2aw} is the equilibrium concentration of CO_2. CO_2 is preferentially taken up by phytoplankton at the surface, where also the atmospheric exchange takes place. For this reason, we used the calculated CO_2 concentration (based on the integrated CO_2 concentration and pH in the surface) from the upper 5 m as the input for equation 5.

In contrast to N_2O, the CO_2 flux can be chemically enhanced by hydration reactions of CO_2 with hydroxide ions and water molecules in the boundary layer (Wanninkhof and Knox, 1996). Using the method outlined in (Czerny et al. (., 2013b) we found an enhancement of up to 12% on warm days and this was included into our flux calculations.

2.4. Data treatment

The primary data generated in this study comprise of carbon standing stock measurements of TPC, DOC, DIC, as well as carbon estimates of meso- and microzooplankton, micro-, nano- and picophytoplankton, bacteria and viruses. Flux measurements of atmospheric CO_2 exchange and sedimentation of TPC, as well as the biological rates of net primary production (NPP_{14C}), bacterial production (BP) and total respiration (TR) enabled us to make a closed carbon budget.

Based on the primary variables (Chl *a* and temperature), the experiment where divided into three distinct phases: Phase I: *t0-t16*; Phase II: *t17-t30* and Phase III: *t31-t43*, where e.g. Chlorophyll *a* (Chl *a*) concentration was relatively high during Phase I, decreased during Phase II and remained low during Phase III (Paul et al. 2015). Measurements of pools and rates were average for the two first sampling points of each experimental phase (n = 2) and where normalized to m^2 knowing the total depth (17 m, excluding the sedimentation funnel) of the mesocosms. For fluxes and biological rates we used the average for the whole periods normalized to days (day^{-1}). The rates of change (ΔTPC, ΔDOC and ΔDIC) were the difference between the start and end of each phase. All error estimates were calculated as

standard error (SE). The three different phases of the experiments were of different length with n = 16, n = 14 and n = 13 for Phases I – III respectively. SE for estimated rates were calculated from the square root of the sum of variance for all the variables (Eq 5-10 below) The primary papers mentioned above (section 2.2.) present detailed statistical analyses and we only refer to those here.

NPP was measured directly and we additionally estimated the net community production (NCP). This was done ~~(NPP_e) from the total change~~ in two different ways from the organic (NCP_o), dissolved plus particulate and inorganic (NCP_i) fractions of carbon. NCP_o was calculated from changes in the organic fraction ~~pool~~ plus the exported TPC (EXP_{TPC}) according to:

$$NCP_o\ ~~NPP_e~~ = EXP_{TPC} + \Delta TPC + \Delta DOC \quad (5~~6~~)$$

Direct~~Comparing direct~~ measurements using ^{14}C isotope incubations should in principal provide a higher value than summing up the difference in overall carbon balance (our NCP_o ~~NPP_e~~), as the latter would incorporate total respiration and not only autotrophic respiration. NCP_i was calculated through changes in the dissolved inorganic carbon pool, corrected for CO_2 gas exchange with the atmosphere (CO2flux) according to:

$$NCP_i = CO_{2flux} - \Delta DIC \quad (6)$$

In order to close the budget we estimated gross primary production (GPP) and DOC production (DOC_{prod}). GPP is defined as the photosynthetically fixed carbon without any loss processes (i.e. NPP + autotrophic respiration). GPP can be estimated based on changes in organic (GPP_o) or inorganic (GPP_i) carbon pools, and we used these two different approaches providing a GPP range:

$$GPP_o = NCP_o\ ~~NPP_e~~ + TR \quad (7)$$

$$GPP_i = TR + CO_{2flux} - \Delta DIC \quad (8)$$

During Phase III, TR was not measured and we estimated TR based on the ratios bwteeen NCP_o ~~NPP_e TR^{-1}~~ and BP to TR^{-1} ~~ratios~~ during Phase II. The minimum production of DOC (DOC_{minp}) in the system was calculated assuming bacterial carbon uptake was taken from the DOC pool according to:

$$DOC_{minp} = \Delta DOC + BP \quad (9)$$

However, this could underestimate DOC_{prod} as a fraction of bacterial DOC uptake is respired. Without direct measurement of (heterotrophic prokaryote) bacterial respiration, (BR), we estimated BR from TR. The share of active bacteria contributing to bacterial production is typically in the range of 10-30% of the total bacterial community (Lignell et al., 2013). We used the fraction of bacterial biomass (BB) of total biomass (TB) as the maximum limit of BR (BR $\leq$ BB/TB),~~,~~ and hence calculated max DOC production (DOC_{maxp}) according to:

$$DOC_{maxp} = \Delta DOC + BP + (BB * TR / TB) \quad (10)$$

We assumed that carbon synthesized by bacteria added to the TPC pool.~~, thus aggregation of DOC equaled BP.~~

There are a number of uncertainties in these calculations, but this budgeting exercise provides an order-of-magnitude estimate of the flow of carbon within the system and enables comparison between the treatments. The average of the two controls (M1 and M5) and two highest CO_2 treatments (M3 and M8) were used to illustrate CO_2 effects. ~~The three different phases of the experiments (I, II and III) were of different length (16, 14 and 13 day respectively). We used the average carbon pools from the whole period, but normalized fluxes and biological rates to day^{-1}. All error estimates were calculated as standard error (SE). The primary papers present detailed statistical analyses and we only refer to those here.~~

3. Results and discussion

3.1 Change in plankton community, from large to small forms over time

The overall size structure of the plankton community decreased over the course of the experiment. Fig 1 illustrates the carbon content in different plankton groups in the control mesocoms. During Phase I, the phytoplankton abundances~~concentration~~ increased at first in all treatments before starting to decrease at the end of Phase I (Paul et al., 2015~~2015b~~). At the start of Phase II (t17), the phytoplankton biomass was higher than at the start of the experiment (~130 mmol C m^{-2} in the controls) but decreased throughout Phase II and III. The fraction of picophytoplankton increased in all treatments, but some groups of picophytoplankton increased more in the high CO_2 treatments (Crawfurd et al., 2016).

Nitrogen was the limiting nutrient throughout~~during~~ the entire experiment (Paul et al., 2015~~2015b~~), and primary producers are generally N-limited in the main sub-basins of the Baltic Sea (Tamminen and Andersen, 2007). The surface to~~:~~ volume ratio increases with decreasing cell size, and consequently small cells have higher nutrient affinity, and are better competitors for scarce nutrient sources than large cells (Reynolds, 2006). The prevailing N-limitation was likely the reason for the decreasing size structure of the phytoplankton community.

Micro and mesozooplankton standing stock was approximately half of the phytoplankton biomass initially, but decreased rapidly in the control treatments during Phase I (Fig 1).~~.~~ In the CO_2 enriched treatments the zooplankton biomass also decreased but not to the same extent as in the control treatments (Spilling et al., 2016). Overall, smaller species benefitted from the extra CO_2 addition, but there was no significant negative effect of high CO_2 on the mesozooplankton community (Lischka et al., 2015).

Bacterial biomass was the main fraction of the plankton carbon throughout the experiment. The bacterial numbers largely followed the phytoplankton biomass with an initial increase then decrease during Phase I; increase during Phase II and slight decrease during Phase III (Crawfurd et al., 2016). The bacterial community was controlled by mineral nutrient limitation, bacterial grazing and viral lysis (Crawfurd et al., 2016), and bacterial~~). Bacterial~~ growth is typically limited by N or a combination of N and C in the study area (Lignell et al., 2008; Lignell et al., 2013~~).),~~

The bacterial carbon pool was higher than the measured TPC. Part of the bacteria must have passed the GFF filters (0.7 µm), and assuming pico- to mesoplankton was part of the TPC, >50% of the bacterial carbon was not contributing to the measured TPC. The conversion factor from cells to carbon is positively correlated to cell size, and there is consequently uncertainty related to the absolute carbon content of the bacterial pool (we used a constant conversion factor). However, bacteria is known to be the dominating carbon share in the Baltic Sea during the N-limited summer months (Lignell et al., 2013), and its relative dominance is in line with this.

Although there are some uncertainty in the carbon estimate (Jover et al. 2014), virus make up (due to their numerical dominance) a significant fraction of the pelagic carbon pool. Of the different plankton fractions the virioplankton have been the least studied, but their role in the pelagic ecosystem is ecologically important (Suttle, 2007; Brussaard et al., 2008; Mojica et

al., 2016). Viral lysis rates were equivalent to the grazing rates for phytoplankton and for bacteria in the current study (Crawfurd et al., 2015). As mortality agents, viruses are key drivers of the regenerative microbial food web (Suttle, 2007; Brussaard et al., 2008). Overall, the structure of the plankton community reflected the nutrient status of the system. The increasing N-limitation favoring development of smaller cells, and increasing dependence of the primary producers on regenerated nutrients.

3.2. The DIC pool and atmospheric exchange of CO_2

The DIC pool was the largest carbon pool: 3-4 fold higher than the DOC pool and roughly 60-fold higher than the TPC pool (Tables 1-3). After the addition of CO_2, the DIC pool was ~7% higher in the highest CO_2 treatment compared to the control mesocosms (Table 1). The gas exchange with the atmosphere was the most apparent flux affected by CO_2 addition (Tables 1-3). Seawater in the mesocosms with added CO_2 were supersaturated, hence CO_2 outgassed throughout the experiment. The control mesocosms were initially undersaturated, hence ingassing occurred during Phases I and II (Fig 2). In the first part of Phase III, the control mesocosms reached equilibrium with the atmospheric fCO_2 (Fig. 2). The gas exchange had direct effects on the DIC concentration in the mesocosms (Fig. 3). From the measured gas exchange and change in DIC it is possible to calculate the biologically mediated carbon flux. In the mesocosms with ambient CO_2 concentration, the flux measurements indicated net heterotrophy throughout the experiment. The opposite pattern, net autotrophy, was indicated in the two mesocosms with the highest CO_2 addition (Fig 3; see also section 3.7.).

3.3. ~~The DOC pool, DOC production and remineralization~~

~~The DOC pool increased throughout the experiment in all mesocosm bags, but more in the treatments with elevated CO_2 concentration. The initial DOC standing stock in all treatments was approximately 7200 mmol C m^{-3}. At the end of the experiment, the DOC pool was ~2% higher in the~~ two highest CO_2 treatments compared to the controls (Fig. 4), and there is statistical support for this difference between CO_2 treatments (Phase III, $p = 0.05$) (Paul et al., 2015). Interestingly, the data does not point to a substantially higher release of DOC at high CO_2 (Figs 4 and 5). ~~The bacterial production was notably lower during Phases II and III in the high CO_2 treatments (Hornick et al., 2016), and of similar magnitude as the rate of change~~

~~in DOC pool (Table 2 and 3), indicating reduced bacterial uptake and remineralization of DOC. The combined results suggest that the increase in the DOC pool at high CO_2 was related to reduced DOC loss (uptake by bacteria), rather than increased release of DOC by the plankton community, at elevated CO_2 concentration.~~

~~The Baltic Sea is affected by large inflow of freshwater containing high concentrations of refractory DOC such as humic substances, and the concentration in Gulf of Finland is typically 400-500 µmol C L^{-1} (Hoikkala et al., 2015). The large pool of DOC and turn over times of ~200 days (Tables 1-3) is most likely a reflection of the relatively low fraction of labile DOC, but bacterial limitation of mineral nutrients can also increase turn over times (Thingstad et al., 1997).~~

~~The DOC pool has been demonstrated to aggregate into transparent exopolymeric particles (TEP) under certain circumstances, which can increase sedimentation at high CO_2 levels (Riebesell et al., 2007). We did not have any direct measurements of TEP, but any CO_2 effect on its formation is highly dependent on the plankton community and its physiological status (MacGilchrist et al., 2014).~~ No observed effect of CO_2 treatment on carbon export suggests that we did not have a community where the TEP production was any different between the treatments used.

3.4. ~~The TPC pool and export of carbon~~

~~There was a positive effect of elevated CO_2 on TPC relative to the controls. At the start of the experiment, the measured TPC concentration in the enclosed water columns was 400-500 mmol C m^{-3} (Table 1). The TPC pool decreased over time but less in the high CO_2 treatment and at the end of the experiment, the standing stock of TPC was ~6% higher (Phase III, p = 0.01; Paul et al. (2015) in the high CO_2 treatment (Fig. 4).~~

~~The export of TPC was not dependent on the CO_2 concentration but varied temporally. The largest flux of TPC out of the mesocosms occurred during Phase I with ~6 mmol C m^{-3} d^{-1}. It decreased to ~3 mmol C m^{-3} d^{-1} during Phase II and was ~2 mmol C m^{-3} d^{-1} during Phase III (Table 1-3). The exported carbon as percent of average TPC standing stock similarly decreased from ~1.3% during Phase I to 0.3-0.5% during Phase III.~~ The initial increase in the autotrophic biomass was the likely reason for relatively more of the carbon settling in the mesocosms in the beginning of the experiment whereas the decreasing carbon export was most likely caused by the shift towards a plankton community depending on recycled

nitrogen. This reduced the overall suspended TPC and also the average plankton size in the community.

3.5. Biological rates: respiration

Total respiration (TR) was always lower in the CO_2 enriched treatments (Tables 1-3). The average TR was 83 mmol C m^{-2} d^{-1} during Phase I, and initially without any detectable treatment effect. The respiration rate started to be lower in the high CO_2 treatments, compared with the controls, in the beginning of Phase II. At the end of Phase II there was a significant difference ($p = 0.02$; Spilling et al., 2016) between the treatments (Table 2),~~,~~ and 40% lower respiration rate in the highest CO_2 treatment compared with the controls (Spilling et al., 2016~~Table 2~~).

Cytosol pH is close to neutral in most organisms, and reduced energetic cost for internal pH regulation (e.g. transport of H^+) and at lower external pH levels could be one factor reducing respiration (Smith and Raven, 1979). Hopkinson et al. (2010) found indirect evidence for decreased respiration and also proposed that increased CO_2 concentration (i.e. decreased pH) reduced metabolic cost of remaining intracellular homeostasis. Mitochondrial respiration~~Respiration rate~~ in plant foliage decreases in high CO_2 environments, possibly affected by respiratory enzymes or other metabolic processes (Amthor, 1991; Puhe and Ulrich, 2012). Most inorganic carbon in water is in the form of bicarbonate (HCO_3^-) at relevant pH, and many aquatic autotrophs have developed carbon concentrating mechanisms (CCMs) (e.g. Singh et al., 2014) that could reduce the cost of growth (Raven, 1991). There are some studies that have pointed to savings of metabolic energy due to down-regulation of carbon concentrating mechanisms (Hopkinson et al., 2010) or overall photosynthetic apparatus (Sobrino et al., 2014) in phytoplankton at high CO_2 concentrations. Yet, other studies of the total plankton community have~~), and similar processes could take place in e.g. phytoplankton. Yet, previous studies of plankton has~~ pointed at no effect or increased respiration at elevated CO_2 concentration (Li and Gao, 2012; Tanaka et al., 2013), and the metabolic changes behind reduced respiration, remains an open question. Membrane transport of H+ is sensitive to changes in external pH, but the physiological impacts of increasing H+ needs further study to better address effects of ocean acidification (Taylor et al., 2012). An important aspect is also to consider the microenvironment surrounding plankton; exchange of nutrients and gases takes place through the boundary layer, which

might have very different pH properties than bulk water measurements (Flynn et al., 2012).~~is an open question. However, there does seem to have been a connection between respiration and bacterial activity in the high CO_2 treatments.~~

3.~~6~~3. Biological rates: bacterial production

Bacterial production (BP) became lower in the high CO_2 treatment in the latter part of the experiment. During Phase I, BP ranged from 27 to 46 mmol C m^{-2} d^{-1} (Table 1). The difference in BP between treatments became apparent in Phases II and III of the experiment. The average BP was 18% and 24% higher in the controls compared to the highest CO_2 treatments during Phases II and III, respectively (Tables 2 and 3). Statistical support ($p \leq 0.01$) for a treatment effect during parts of the experiment is presented in Hornick et al. (2016).

The lower bacterial production accounted for ~40% of the reduced respiration during Phase II, and the reduced respiration described above could at least partly be explained by the lower bacterial activity. This~~this~~ raises an interesting question: what was the mechanism behind the reduced bacterial production/respiration~~activity~~ in the high CO_2 treatment? There are examples of decreased bacterial production ~~at high CO_2 concentration~~ (Motegi et al 2013) and respiration (Teira et al., 2012) at elevated CO_2 concentration. However,~~), but~~ most previous studies have reported no change (Allgaier et al., 2008) or a higher bacterial production at elevated CO_2 concentration (Grossart et al., 2006; Piontek et al., 2010; Endres et al., 2014). The latter was also supported by the recent study of Bunse et al. (2016), describing up-regulation of bacterial genes related to respiration, membrane transport and protein metabolism at elevated CO_2 concentration; albeit~~however~~, this effect was not evident when inorganic nutrients had been added (high Chl *a* treatment).

In this study, the reason for the lower bacterial activity in the high CO_2 treatments could be due to either limitation and/or inhibition of bacterial growth or driven by difference in loss processes. ~~Increased loss processes could also have affected BP.~~ Bacterial grazing and viral lysis was higher in the high CO_2 treatments during periods of the experiment (Crawfurd et al., 2016), and would at least partly be the reason for the reduced bacterial production at high CO_2 concentration.

N-limitation increased during the experiment (Paul et al., 2015~~2015b~~), and mineral nutrient limitation of bacteria can lead to accumulation of DOC, i.e. reduced bacterial uptake

(Thingstad et al., 1997), similar to our results. Bacterial N limitation is common in the area during summer (Lignell et al., 2013), however, this N-limitation was not apparently different in the controls (Paul et al., 2015~~2015b~~), and CO_2 did not affect N-fixation (Paul et al., 2016~~2015a~~). In a scenario where the competition for N is fierce, the balance between ~~the~~ bacteria and similar sized picophytoplankton could be tilted in favor of phytoplankton if they gain an advantage by having easier access to carbon, i.e. CO_2 (Hornick et al., 2016).

We have not found evidence in the literature that bacterial production will be suppressed in the observed pH range inside the mesocosms, varying from approximately pH 8.1 in the control to pH 7.6 in the highest fCO_2 treatment (Paul et al., 2015), although enzyme activity seems~~but enzymes seem~~ to be affected even by moderate pH changes. For example, some studies report on an increase in protein degrading enzyme leucine aminopeptidase activities at reduced pH (Grossart et al., 2006; Piontek et al., 2010; Endres et al., 2014), whereas others indicate a reduced activity of this enzyme (Yamada and Suzumura, 2010). A range of other factors affects this enzyme, for example the nitrogen source and salinity (Stepanauskas et al., 1999), and any potential interaction effects with decreasing pH are not yet resolved. Any pH-induced changes in bacterial enzymatic activity could potentially affect bacterial production.

3.~~7~~4. Biological rates: primary production

There was an effect of CO_2 concentration on the~~The estimated~~ net community~~primary~~ production based on the organic carbon fraction (NCP_o). NCP_o was~~(NPP_e) indicated~~ higher ~~primary productivity~~ during Phase I than during the rest of the experiments and during this initial phase without any apparent CO_2 effect.~~.~~ There was no consistent difference between CO_2 treatments for NPP_{14C} ($p > 0.1$),~~.~~ but NCP_o~~NPP_e~~ increased with increasing CO_2 enrichment during Phase II (Phase II; linear regression $p = 0.003$; $R^2 = 0.91$).~~.~~ This was caused by the different development in the TPC and DOC pools. The pattern of gross primary production (GPP) was similar to NCP_o~~NPP_e~~ during Phases I and II. During Phase III there were no respiration or NPP_{14C} measurements and the estimated GPP is more uncertain. The NCP_o~~NPP_e~~ and GPP indicated a smaller difference between treatments during Phase III compared with Phase II.

The ~~two~~ measures of NPP_{14C} and NCP_o~~NPP~~ were of a similar magnitude (Tables 1-3). During Phase I, $NPP_{14C} < NCP_o$~~NPP_e~~ (Table 1), this relationship reversed for most treatments during Phase II, with the exception of the highest CO_2 levels (Table 2). The difference between

~~Interestingly, an effect of the different CO_2 treatments was noticeable in the NPP_e but not in~~ NPP_{14C} and NCP_o suggests~~, suggesting~~ that observed reduction in respiration at~~the effect of~~ elevated CO_2 ~~concentration~~ could be mainly~~refer to~~ heterotrophic respiration. However, in terms of the $NPP_{14C} < NCP_o$~~NPP_e~~, the uncertainty seems to be higher than the potential signal of heterotrophic respiration. This would also indicate that the NPP_{14C} during Phase I have~~has~~ been underestimated, in particular for the control mesocosm M1. During Phase II, the NPP_{14C} was higher than NCP_o~~NPP_e~~, except for the two highest CO_2 treatments, more in line with our assumption of $NPP_{14C} > NCP_o$~~NPP_e~~. The systematic offset in NPP_{14C} during Phase I could be due to changed parameterization during incubation in small volumes (8 mL, Spilling et al.~~,~~ 2016), for example increased loss due to grazing~~. Overall, however, the results suggest that the measured NPP_{14C} and estimated NPP_e agree reasonably well~~.

The results of the DIC pool and atmospheric exchange of CO_2 provides another way of estimating the net community production based on inorganic carbon (NCP_i). There was some discrepancy between the NCP_o and NCP_i as the latter suggested net heterotrophy in the ambient CO_2 whereas the high CO_2 treatments were net autotrophic during all three phases of the experiment (Fig. 3). For the NCPo there was no indication of net heterotrophy at ambient CO_2 concentration. In terms of the absolute numbers, the NCPi estimate is probably more uncertain than NCP_o. Calculating the CO_2 atmospheric exchange from the measurements of a tracer gas involves several calculation steps (Eq 1-4), each adding uncertainty to the calculation. However, both estimations (NCPi and NCPo) indicate that increased CO_2 concentrations lead to higher overall community production, supporting our overall conclusion.

~~**3.5. The DIC pool and atmospheric exchange of CO_2**~~

~~The DIC pool was the largest carbon pool: 3-4 fold higher than the DOC pool and roughly 60-fold higher than the TPC pool (Tables 1-3). After the addition of CO_2, the DIC pool was ~7% higher in the highest CO_2 treatment compared to the control mesocosms (Table 1). The gas exchange with the atmosphere was the most apparent flux affected by CO_2 addition (Tables 1-3). Seawater in the mesocosms with added CO_2 were supersaturated, hence CO_2 outgassed throughout the experiment. The control mesocosms were initially undersaturated, hence ingassing occurred during Phases I and II (Fig 2). In the first part of Phase III, the control mesocosms reached equilibrium with the atmospheric fCO_2 (Fig. 2).~~

~~Using the direct flux measurements and the net change in the DIC pool, we calculated the net uptake or release of carbon by biological activity. Comparing the controls to the mesocosm with the highest CO_2 addition (Fig. 3), the CO_2 addition had an effect on the biologically mediated carbon flux. In the mesocosm with an ambient CO_2 concentration, the flux measurements indicated net heterotrophy throughout the experiment. The opposite pattern, net autotrophy, was indicated in the mesocosm with the highest CO_2 addition (Fig 3).~~

~~3.6.~~ The DOC pool, DOC production and remineralization

The DOC pool increased throughout the experiment in all mesocosm bags, but more in the treatments with elevated CO_2 concentration. The initial DOC standing stock in all treatments was approximately 7200 mmol C m^{-2}. At the end of the experiment, the DOC pool was ~2% higher in the ~~high CO_2 treatments compared to the controls (Fig. 4), and there is statistical support for these treatments being different (Phase III, p = 0.05) (Paul et al., 2015b). Interestingly, the data does not point to a substantially higher release of DOC at high CO_2 (Fig 5).~~ The bacterial production was notably lower during Phases II and III in the high CO_2 treatments (Hornick et al., 2016), and of similar magnitude as the rate of change in DOC pool (Table 2 and 3), indicating reduced bacterial uptake and remineralization of DOC. The combined results suggest that the increase in the DOC pool at high CO_2 was related to reduced DOC loss (uptake by bacteria), rather than increased release of DOC by the plankton community, at elevated CO_2 concentration.

The Baltic Sea is affected by large inflow of freshwater containing high concentrations of refractory DOC such as humic substances, and the concentration in Gulf of Finland is typically 400-500 µmol C L^{-1} (Hoikkala et al., 2015). The large pool of DOC and turn over times of ~200 days (Tables 1-3) is most likely a reflection of the relatively low fraction of labile DOC, but bacterial limitation of mineral nutrients can also increase turn over times (Thingstad et al., 1997).

The DOC pool has been demonstrated to aggregate into transparent exopolymeric particles (TEP) under certain circumstances, which can increase sedimentation at high CO_2 levels (Riebesell et al., 2007). We did not have any direct measurements of TEP, but any CO_2 effect on its formation is highly dependent on the plankton community and its physiological status (MacGilchrist et al., 2014). ~~No effect of CO_2 treatment on carbon export suggests that we did~~

~~not have a community where the TEP production was any different between the treatments used.~~

~~3.7~~ The TPC pool and export of carbon

There was a positive effect of elevated CO_2 on TPC relative to the controls. At the start of the experiment, the measured TPC concentration in the enclosed water columns was 400-500 mmol C m^{-2} (Table 1). The TPC pool decreased over time but less in the high CO_2 treatment and at the end of the experiment, the standing stock of TPC was ~6% higher (Phase III, p = 0.01; Paul et al. ~~(2015b)~~) in the high CO_2 treatment (Fig. 4).

The export of TPC was not dependent on the CO_2 concentration but varied temporally. The largest flux of TPC out of the mesocosms occurred during Phase I with ~6 mmol C m^{-2} d^{-1}. It decreased to ~3 mmol C m^{-2} d^{-1} during Phase II and was ~2 mmol C m^{-2} d^{-1} during Phase III (Table 1-3). The exported carbon as percent of average TPC standing stock similarly decreased from ~1.3% during Phase I to 0.3-0.5% during Phase III. ~~The initial increase in the autotrophic biomass associated with relatively more of the carbon settling in the mesocosms. The decreasing carbon export was most likely caused by the shift towards a plankton community depending on recycled nitrogen, reducing the overall TPC and also the size structure of the plankton community.~~

3.8 Budget

A carbon budget for the two control mesocosms and two highest CO_2 additions is presented in Fig. 5. During Phase I the estimated gross primary production (GPP) was ~100 mmol C fixed m^{-2} d^{-1}; from which 75-95% were respired, ~1% ended up in the TPC (including export) and 5-25% added to the DOC pool. The main difference between CO_2 treatments became apparent during Phase II when the NCP_0~~NPP_e~~ was higher in the elevated CO_2 treatments. The respiration loss increased to ~100% of GPP at the ambient CO_2 concentration, whereas respiration was lower (85-95% of GPP) in the highest CO_2 treatment. Bacterial production was ~30% lower, on average, at the highest CO_2 concentration compared with the controls during Phase II. The share of NCP_0~~NPP_e~~ of GPP ranged from 2% to 20% and the minimum flux to the DOC pool was 11% to 18% of TPC.

The overall budget was calculated by using the direct measurements of changes in standing stocks and fluxes of export, respiration and bacterial production rates. The most robust data are the direct measurements of carbon standing stocks and their development (e.g. ΔTPC).~~differences.~~ These are based on well-established analytical methods with relatively low standard error (SE) of the carbon pools. However, the dynamic nature of these pools made the relative SE for the rate of change much higher, reflecting that the rate of change varied considerably within the different phases.

The rate parameters, calculated based on conversion factors, have greater uncertainty, although their SEs were relatively low, caused by uncertainty in the conversion steps. For example, the respiratory quotient (RQ) was set to one, which is a good estimate for carbohydrate oxidation. For lipids and proteins the RQ is close to 0.7, but in a natural environment RQ is often >1 (Berggren et al., 2012), and is affected by physiological state e.g. nutrient limitation (Romero-Kutzner et al., 2015). Any temporal variability in the conversion factors would directly change the overall budget calculations, e.g. RQ affecting total respiration and gross primary production estimates. However, the budget provides an order-of-magnitude estimate of the carbon flow within the system. Some of the parameters such as GPP were~~was~~ estimated using different approaches, providing a more robust comparison of the different treatments.

The primary effect of increasing CO_2 concentration was the higher standing stocks of TPC and DOC compared with ambient CO_2 concentration. The increasing DOC pool and relatively higher TPC pool were driven by reduced respiration and bacterial production at elevated CO_2 concentration. Decreasing respiration rate reduced the recycling of organic carbon back to the DIC pool. The lower respiration and bacterial production also indicates reduced remineralization of DOC. These two effects caused the higher TPC and DOC pools in the elevated CO_2 treatments. The results highlight the importance of looking beyond net changes in carbon standing stocks to understand how carbon fluxes are affected under increasing ocean acidification.

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Table 1. The standing stock of total particular carbon (TPC_{pool}), dissolved organic carbon (DOC_{pool}) and dissolved inorganic carbon (DIC_{pool}) at the start of Phase I in mmol C m^{-2} ± SE (n = 2). The DOC_{pool} was missing some initial measurements and is the average for all mesocosms assuming that the DOC concentration was similar at the onset of the experiment. The net change in TPC (ΔTPC), DOC (ΔDOC) and DIC (ΔDIC) are average changes in the standing stocks during Phase I in mmol C m^{-2} d^{-1} ± SE (n = 2). Flux measurements of atmospheric gas exchange (CO_{2flux}) and exported carbon (EXP_{TPC}) plus biological rates: total respiration (TR), bacterial (BP) and net primary production ~~(BP), measured~~ (NPP_{14C}) and net community production estimated based on organic carbon pools (NCP_0~~(NPP_e)~~) net primary production, are all average for Phase I in mmol C m^{-2} d^{-1} ± SE (n = 16). SE for NCPo was calculated from the square root of the sum of variance of the three variables used in Eq 6. The NCP_0~~NPP_e~~ was calculated from the net change in carbon pools plus carbon export, whereas NPP_{14C} was measured carbon fixation using radiolabeled ^{14}C over a 24 h incubation period *in situ*. TR was measured as O_2 consumption and for comparison with carbon fixation we used a respiratory quotient (RQ) of 1. A total budget of carbon fluxes for ambient and high CO_2 treatments is presented in Fig 5.

Phase I (*t0-t16*)						
CO_2 treatment (µatm fCO_2)	**365**	**368**	**497**	**821**	**1007**	**1231**
Mesocosm number	**M1**	**M5**	**M7**	**M6**	**M3**	**M8**
TPC_{pool}	417 ± 38	425 ± 39	472 ± 48	458 ± 38	431 ± 48	446 ± 57
DOC_{pool}	7172 ± 87	7172 ± 87	7172 ± 87	7172 ± 87	7172 ± 87	7172 ± 87
DIC_{pool}	25158 ± 9	25182 ± 10	25628 ± 8	26295 ± 22	26637 ± 36	26953 ± 48
ΔTPC	-4.6 ± 15	-5.2 ± 13	-8.3 ± 13	-8.2 ± 17	-7.0 ± 13	-6.3 ± 20
ΔDOC	15.5 ± 58	18.3 ± 30	18.5 ± 33	25.0 ± 36	18. 5 ± 73	18.1 ± 63
ΔDIC	5.5 ± 5.2	6.9 ± 9.2	-6.1 ± 11	-24 ± 14	-32 ± 20	-49 ± 42
CO_{2flux}	4.4 ± 0.2	4.8 ± 0.3	-0.8 ± 0.5	-11 ± 1.0	-17 ± 1.4	-23 ± 2.0
EXP_{TPC}	6.6 ± 0.10	5.6 ± 0.04	5.4 ± 0.07	6.0 ± 0.07	5.6 ± 0.06	6.0 ± 0.05
TR	107 ± 9	82 ± 7	81 ± 6	80 ± 8	75 ± 8	74 ± 8
BP	27 ± 8	41 ± 6	43 ± 8	41 ± 4	36 ± 5	46 ± 9
NPP_{14c}	4.8 ± 0.8	11.4 ± 2.1	14.9 ± 3.6	12.3 ± 2.3	11.3 ± 2.4	14.5 ± 2.7
NCP_0~~NPP_e~~	17.4 ± 33	18.7 ± 20	15.6 ± 30	22.8 ± 28	17.1 ± 25	17.8 ± 28

Table 2. The standing stock of total particular carbon (TPC_{pool}), dissolved organic carbon (DOC_{pool}) and dissolved inorganic carbon (DIC_{pool}) at the start of Phase II in mmol C m^{-2} ± SE (n = 2).~~.~~ The net change in TPC (ΔTPC), DOC (ΔDOC) and DIC (ΔDIC) are average changes in the standing stocks during Phase II in mmol C m^{-2} d^{-1} ± SE (n = 2).~~.~~ Flux measurements of atmospheric gas exchange (CO_{2flux}) and exported carbon (EXP_{TPC}) plus biological rates: total respiration (TR), bacterial production (BP), measured (NPP_{14C}) and ~~estimated (NPP_e)~~ net community~~primary~~ production estimated based on organic carbon pools (NCP_0),~~,~~ are all average for Phase II in mmol C m^{-2} d^{-1} ± SE (n = 14).~~.~~ See Table 1 legend for further details.

Phase II (*t17-t30*)

CO_2 treatment (µatm *f*CO_2)	**365**	**368**	**497**	**821**	**1007**	**1231**
Mesocosm number	**M1**	**M5**	**M7**	**M6**	**M3**	**M8**
TPC_{pool}	339 ± 14	337 ± 20	331 ± 22	318 ± 9	312 ± 12	339 ± 23
DOC_{pool}	7435 ± 38	7483 ± 37	7487 ± 43	7597 ± 37	7487 ± 61	7479 ± 37
DIC_{pool}	25247 ± 34	25269 ± 34	25639 ± 8	26177 ± 25	26413 ± 28	26757 ± 45
ΔTPC	-2.4 ± 5	-2.3 ± 8	-1.6 ± 14	0.3 ± 6	2.8 ± 4	3.2 ± 8
ΔDOC	-0.6 ± 39	2.4 ± 30	3.6 ± 40	8.4 ± 31	11.3 ± 58	9.1 ± 36
ΔDIC	22.4 ± 12	17.6 ± 8.1	-0.4 ± 4.5	-10.5 ± 16	-14.2 ± 10	-23.1 ± 13
CO_{2flux}	1.7 ± 0.3	1.2 ± 0.3	-2.6 ± 0.3	-10 ± 0.5	-14 ± 0.6	-19 ± 1.0
EXP_{TPC}	3.3 ± 0.08	2.6 ± 0.06	2.5 ± 0.08	2.6 ± 0.06	2.8 ± 0.07	2.9 ± 0.06
TR	140 ± 7	127 ± 5	103 ± 3	103 ± 4	101 ± 5	86 ± 4
BP	66 ± 17	57 ± 8	61 ± 7	57 ± 7	43 ± 6	47 ± 6
NPP_{14c}	3.8 ± 0.6	11.2 ± 1.9	10.8 ± 2.0	14.3 ± 2.8	10.4 ± 2.1	12.0 ± 2.5
NCP_0~~NPP_e~~	0.3 ± 20	2.7 ± 15	4.5 ± 22	11.4 ± 16	16.9 ± 19	15.2 ± 16

Table 3. The standing stock of total particular carbon (TPC_{pool}), dissolved organic carbon (DOC_{pool}) and dissolved inorganic carbon (DIC_{pool}) at the start of Phase III in mmol C m^{-2} ± SE (n = 2).~~.~~ The net change in TPC (ΔTPC), DOC (ΔDOC) and DIC (ΔDIC) are average changes in the standing stocks during Phase III in mmol C m^{-2} d^{-1} ± SE (n = 2).~~.~~ Flux measurements of atmospheric gas exchange (CO_{2flux}) and exported carbon (EXP_{TPC}) plus biological rates: total respiration (TR), bacterial production (BP), measured (NPP_{14C}) and ~~estimated (NPP_e)~~ net community~~primary~~ production estimated based on organic carbon pools (NCP_0),~~.~~ are all average for Phase III in mmol C m^{-2} d^{-1} ± SE (n = 13).~~.~~ See Table 1 legend for further details. During Phase III we did not have direct measurements of net primary production (NPP_{14C}) or total respiration (TR).

Phase III (*t31-t43*)

CO_2 treatment (µatm *f*CO_2)	**365**	**368**	**497**	**821**	**1007**	**1231**
Mesocosm number	**M1**	**M5**	**M7**	**M6**	**M3**	**M8**
TPC_{pool}	306 ± 12	304 ± 20	309 ± 20	323 ± 2	351 ± 13	384 ± 16
DOC_{pool}	7426 ± 16	7469 ± 20	7485 ± 92	7553 ± 20	7593 ± 30	7562 ± 38
DIC_{pool}	25557 ± 9	25545 ± 10	25648 ± 13	26030 ± 19	26197 ± 31	26371 ± 32
ΔTPC	-3.8 ± 10	0.3 ± 7	3.3 ± 14	3.3 ± 10	-1.4 ± 8	-4.8 ± 8
ΔDOC	9.8 ± 5	8.8 ± 7	8.9 ± 43	9.2 ± 10	5.7 ± 17	16.3 ± 20
ΔDIC	4.3 ± 3.9	5.5 ± 8.7	6.2 ± 11	-12.3 ± 7.2	-16.3 ± 14	-20.1 ± 14
CO_{2flux}	-0.3 ± 0.7	-0.8 ± 0.6	-3.0 ± 0.5	-7.3 ± 0.5	-9.4 ± 0.6	-13 ± 0.6
EXP_{TPC}	1.5 ± 0.07	1.4 ± 0.05	0.4 ± 0.07	1.9 ± 0.05	1.6 ± 0.04	1.7 ± 0.05
BP	31 ± 6.8	37 ± 1.4	38 ± 1.4	27 ± 2.1	17 ± 3.8	28 ± 2.3
NCP_0~~NPP_e~~	7.6 ± 16	10.5 ± 13	12.7 ± 20	14.3 ± 13	6.0 ± 10	13.2 ± 14

Figure legends

Fig. 1. The different fractions of carbon in the control mesocosms (M1 and M5) at the start of Phase I (t0), II (t17) and III (t31) in mmol C m^{-2} ± SE (n = 2).~~.~~ The differences between the controls and elevated CO_2 concentration are discussed in the text. The size of the boxes indicates the relative size of the carbon standing stocks.

Fig 2. The calculated exchange of CO_2 between the mesocosms and the atmosphere. Positive values indicate net influx (ingassing) and negative values net outflux (outgassing) from the mesocosms. The flux was based on measurements of N_2O as a tracer gas and calculated using equations 2-5.

Fig 3. Change in dissolved inorganic carbon (DIC) pool and the atmospheric CO_2 exchange (Fig. 2). All values are average mmol C m^{-2} d^{-1} ± SE for the three different phases (n = 16, 14 and 13 for Phases I – III respectively) in the control mesocosms (M1 + M5) and high CO_2 mesocosms (M3 + M8).~~.~~ Black, solid arrows indicated measured fluxes. Grey, dashed arrows are estimated by closing the budget, and indicate the net community production based on inorganic carbon budget (NCP_i), which equals biological uptake or release of CO_2.

Fig 4. Standing stocks of total particulate carbon (TPC) and dissolved carbon (DOC) at the last day of the experiment (*t43*), plus the sum of exported TPC throughout the experiment; all values are in mmol C m^{-2} ± SE (n = 2).~~.~~ The values are averages of the two controls (M1 and M5) and the two highest CO_2 treatments (M3 and M8). Red circles indicate statistically significant higher standing stocks in the high CO_2 treatments (further details in text). The size of the boxes indicates the relative size of the carbon standing stocks and export.

Fig 5. Average carbon standing stocks and flow in the control mesocosms (M1 + M5) and high CO_2 mesocosms (M3 + M8) during the three phases of the experiment. All carbon stocks (squares): dissolved inorganic carbon (DIC), total particulate carbon (TPC) and dissolved organic carbon (DOC), are average from the start of the period in mmol C m^{-2} ± SE (n = 2).~~.~~ Fluxes (arrows) and net changes (Δ) are averages for the whole phase in mmol C m^{-2} d^{-1} ± SE (n = 2) . Black, solid arrows indicated measured fluxes (Tables 1-3): total respiration (TR), bacterial production (BP), exported TPC (EXP_{TPC}). Grey, dashed arrows are estimated by closing the budget: gross primary production (GPP) using equations 7 and 8; DOC production (DOC_{prod}) using equations 9 and 10. Bacterial respiration was calculated using

equation 10 and is a share of TR (indicated by the parenthesis). Aggregation was assumed to equal BP. Red circles indicate statistically higher values compared with the other CO_2 treatment ($p < 0.05$, tests presented in the primary papers described in section 2.2.). The size of the boxes indicates the relative size of the carbon standing stocks.

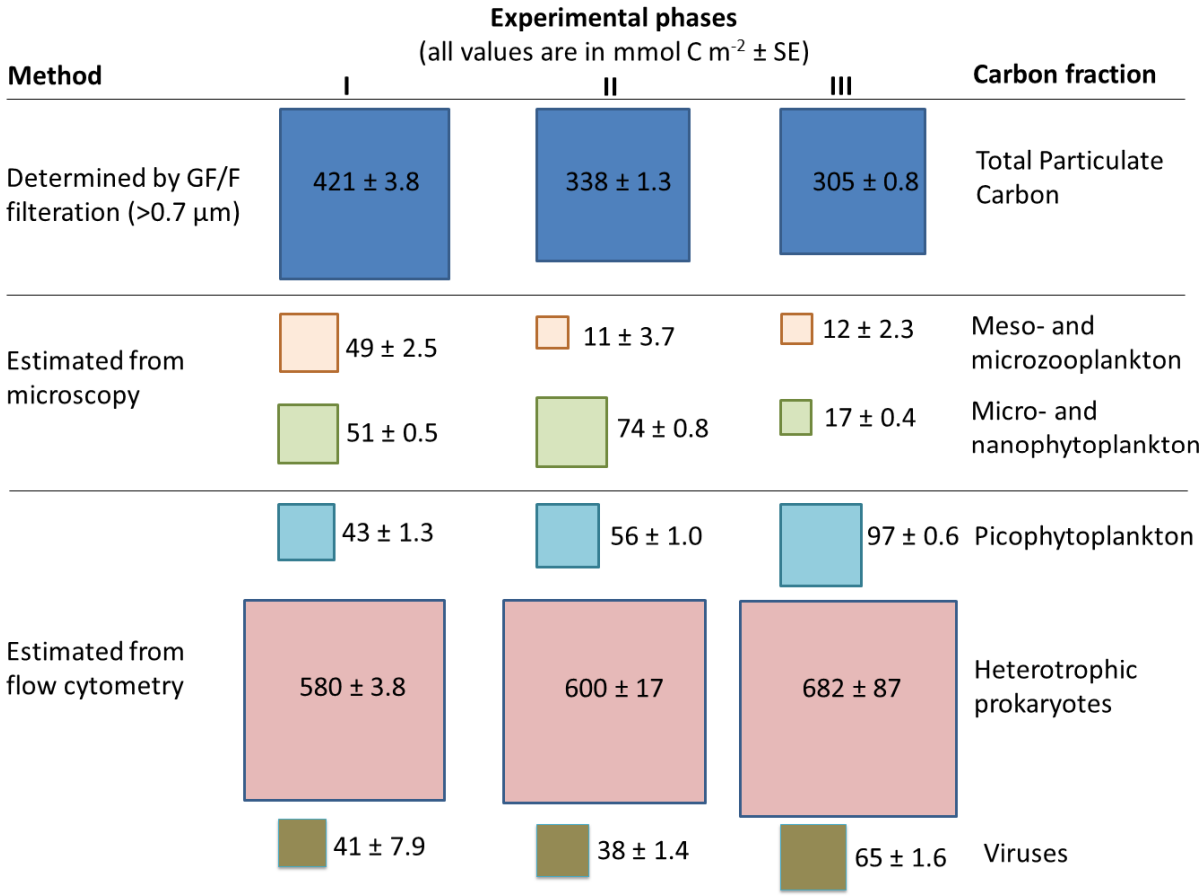
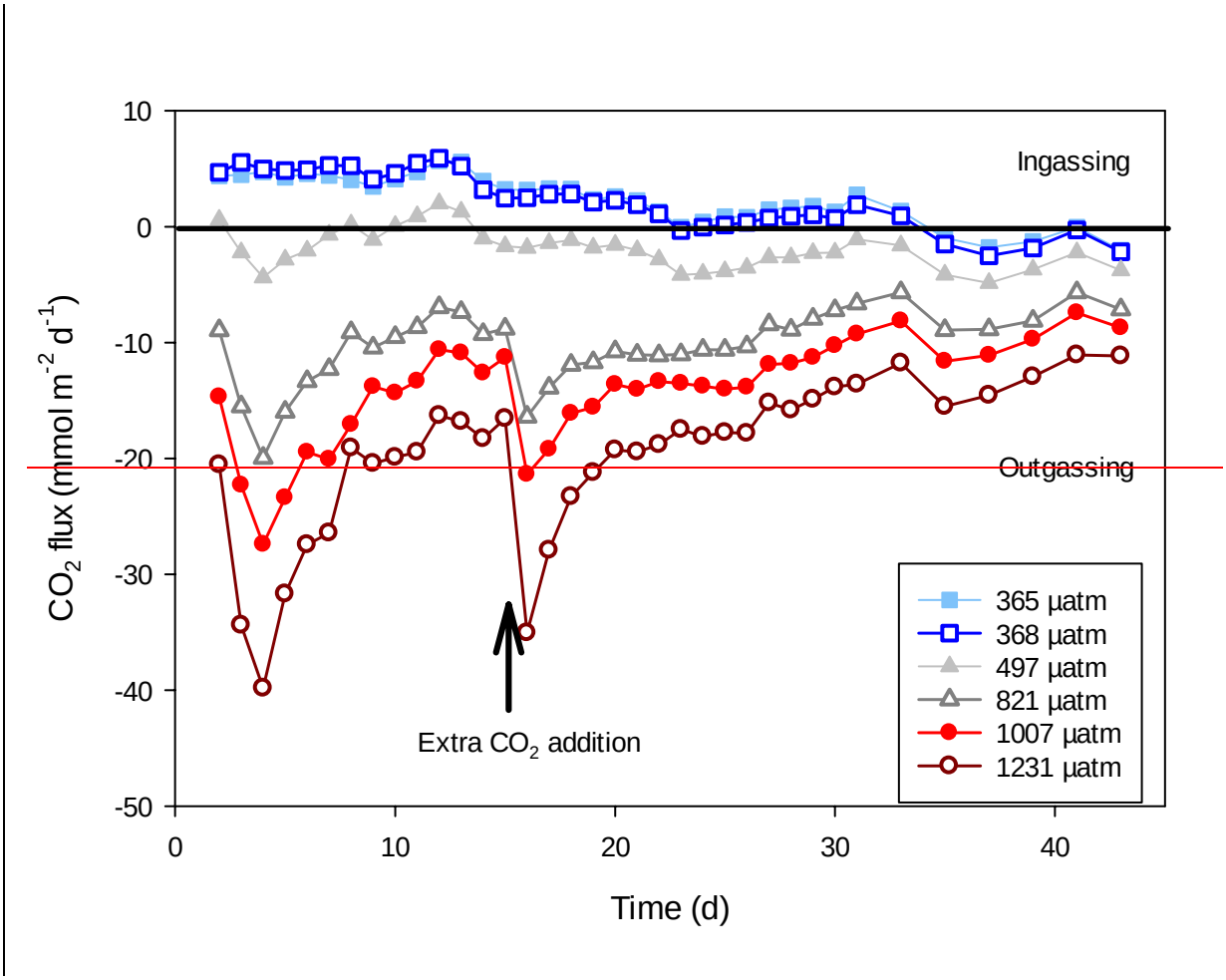

Experimental phases
(all values are in mmol C m-2 ± SE)
Method
I
II
III
Carbon fraction
Determined by GF/F filteration (>0.7 µm)
421 ± 3.8
338 ± 1.3
305 ± 0.8
Total Particulate Carbon
Estimated from microscopy
49 ± 2.5
11 ± 3.7
12 ± 2.3
Meso- and microzooplankton
51 ± 0.5
74 ± 0.8
17 ± 0.4
Micro- and nanophytoplankton
Estimated from flow cytometry
43 ± 1.3
56 ± 1.0
97 ± 0.6
Picophytoplankton
580 ± 3.8
600 ± 17
682 ± 87
Heterotrophic prokaryotes
41 ± 7.9
38 ± 1.4
65 ± 1.6
Viruses

Fig 1


10
0
-10
-20
-30
-40
-50
0
10
20
30
40
Time (d)
CO2 flux (mmol m-2 d-1)
Ingassing
Outgassing
Extra CO2 addition
365 µatm
368 µatm
497 µatm
821 µatm
1007 µatm
1231 µatm

1

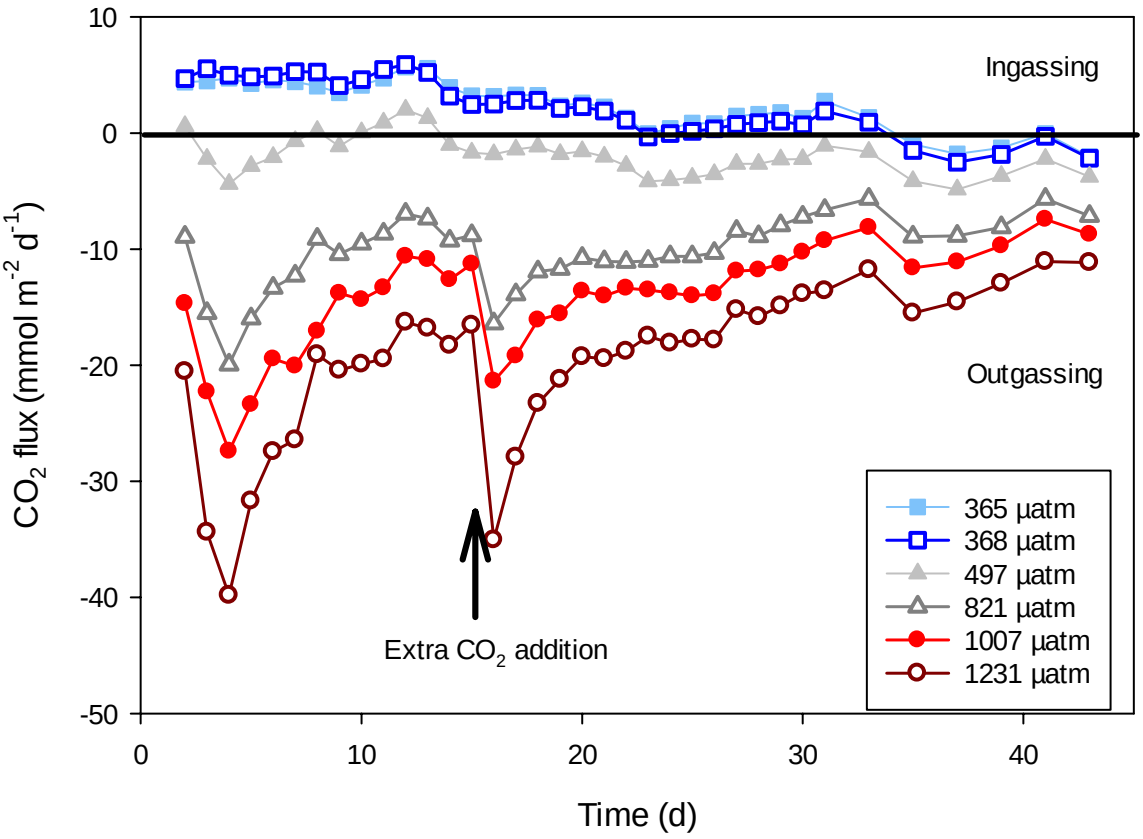
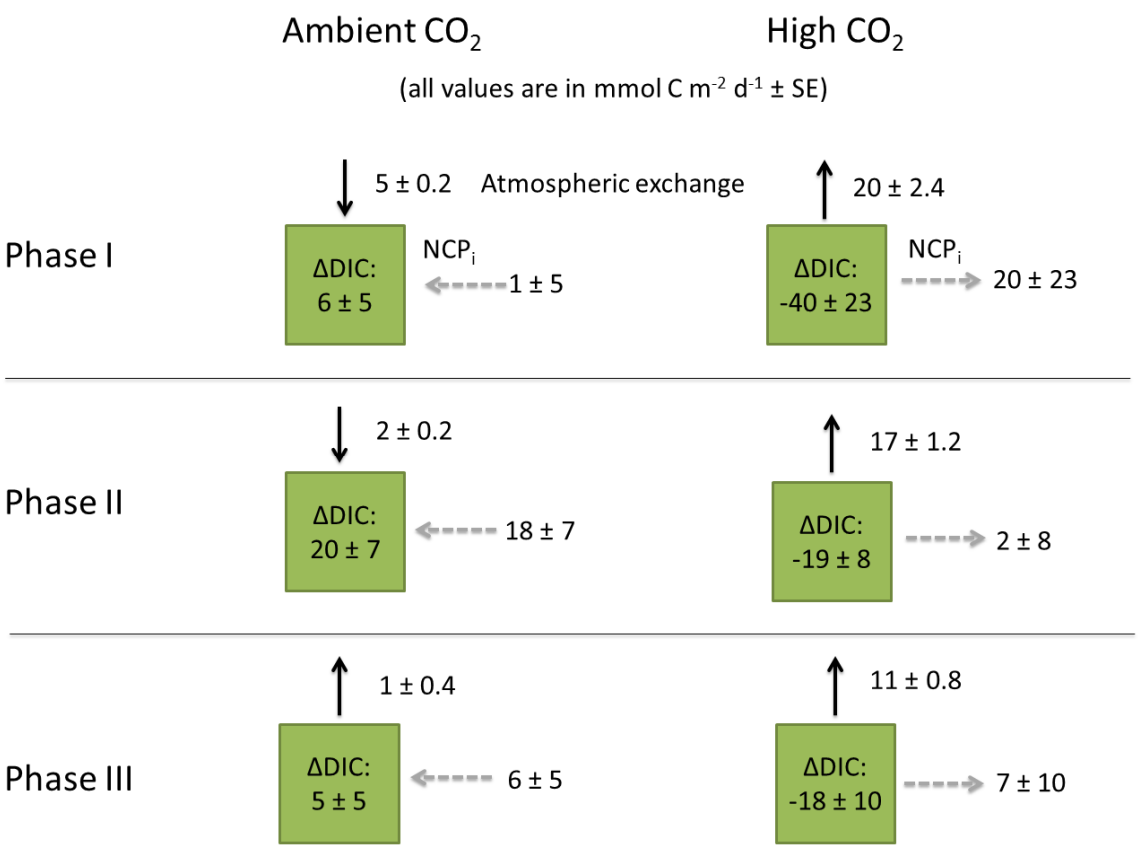

10
0
-10
-20
-30
-40
-50
0
10
20
30
40
Time (d)
CO2 flux (mmol m-2 d-1)
Ingassing
Outgassing
Extra CO2 addition
365 µatm
368 µatm
497 µatm
821 µatm
1007 µatm
1231 µatm

Fig 2


Ambient CO_2
High CO_2
(all values are in mmol C m^{-2} d^{-1} ± SE)
Phase I
5 ± 0.2
Atmospheric exchange
20 ± 2.4
ΔDIC: 6 ± 5
NCP_i
1 ± 5
ΔDIC: -40 ± 23
NCP_i
20 ± 23
Phase II
2 ± 0.2
17 ± 1.2
ΔDIC: 20 ± 7
18 ± 7
ΔDIC: -19 ± 8
2 ± 8
Phase III
1 ± 0.4
11 ± 0.8
ΔDIC: 5 ± 5
6 ± 5
ΔDIC: -18 ± 10
7 ± 10

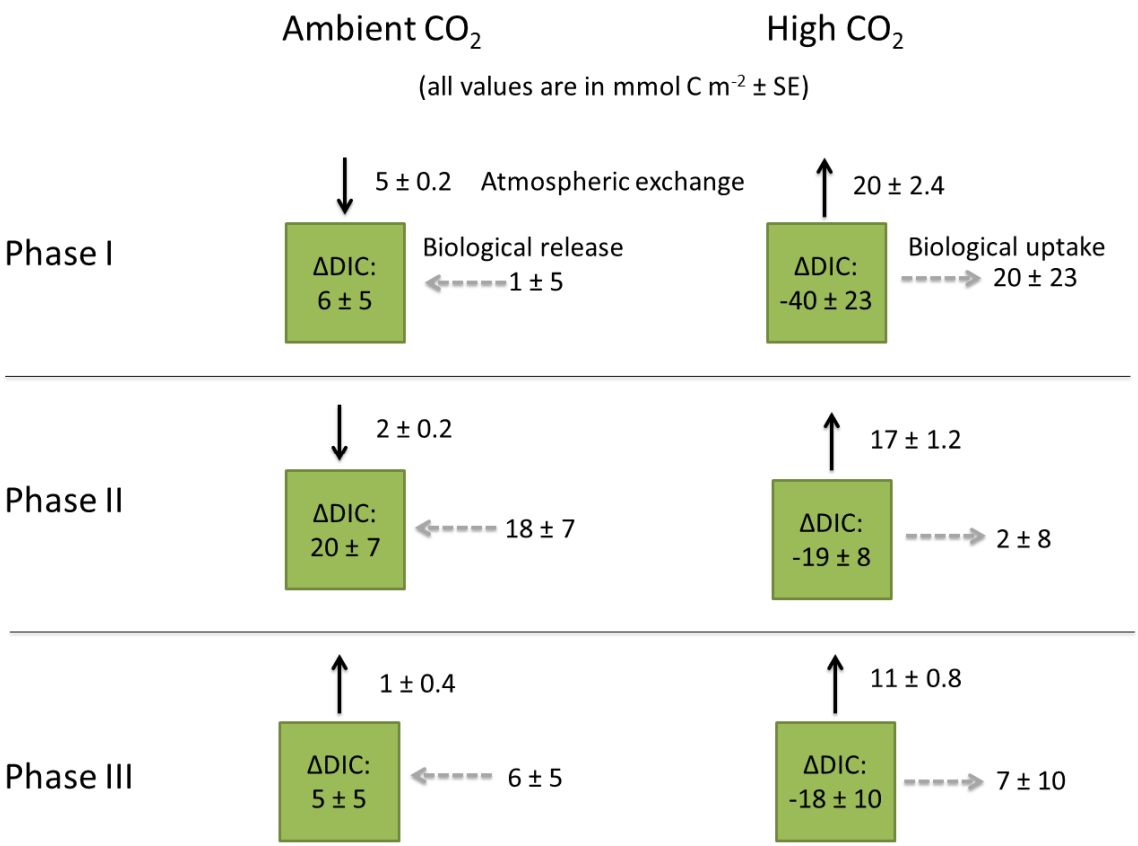

Ambient CO_2
High CO_2
(all values are in mmol C m^{-2} ± SE)
Phase I
5 ± 0.2
Atmospheric exchange
20 ± 2.4
ΔDIC:
6 ± 5
Biological release
1 ± 5
ΔDIC:
-40 ± 23
Biological uptake
20 ± 23
Phase II
2 ± 0.2
17 ± 1.2
ΔDIC:
20 ± 7
18 ± 7
ΔDIC:
-19 ± 8
2 ± 8
Phase III
1 ± 0.4
11 ± 0.8
ΔDIC:
5 ± 5
6 ± 5
ΔDIC:
-18 ± 10
7 ± 10

Fig 3

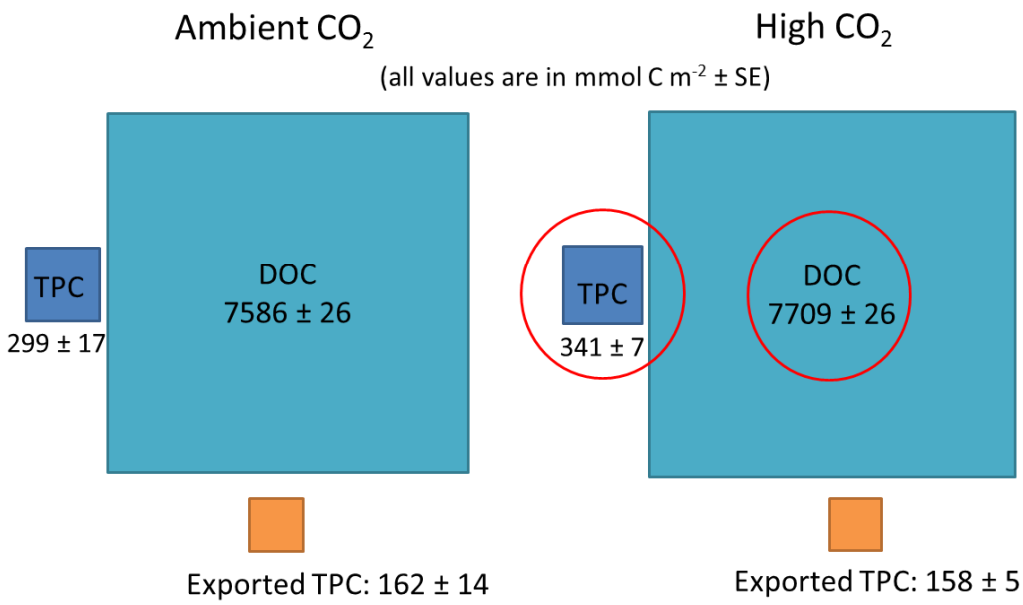

Ambient CO_2
High CO_2
(all values are in mmol C m^{-2} ± SE)
TPC
299 ± 17
DOC
7586 ± 26
TPC
341 ± 7
DOC
7709 ± 26
Exported TPC: 162 ± 14
Exported TPC: 158 ± 5

Fig 4

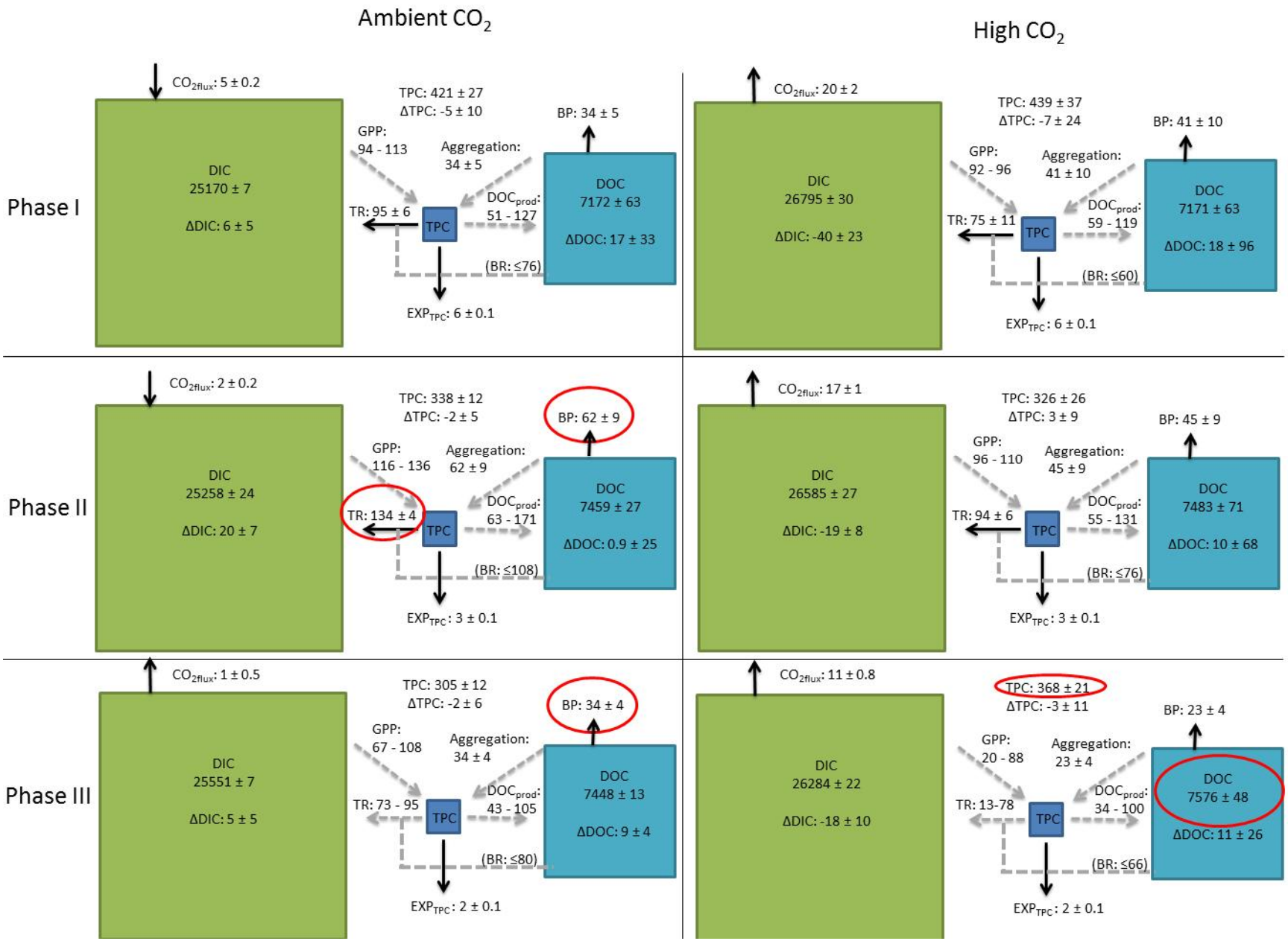

Ambient CO_2
High CO_2
Phase I
Phase II
Phase III
CO_{2flux}: 5 ± 0.2
DIC
25170 ± 7
ΔDIC: 6 ± 5
TPC: 421 ± 27
ΔTPC: -5 ± 10
GPP:
94 - 113
Aggregation:
34 ± 5
TR: 95 ± 6
TPC
DOC_{prod}:
51 - 127
(BR: ≤76)
EXP_{TPC}: 6 ± 0.1
BP: 34 ± 5
DOC
7172 ± 63
ΔDOC: 17 ± 33
CO_{2flux}: 20 ± 2
DIC
26795 ± 30
ΔDIC: -40 ± 23
TPC: 439 ± 37
ΔTPC: -7 ± 24
GPP:
92 - 96
Aggregation:
41 ± 10
TR: 75 ± 11
TPC
DOC_{prod}:
59 - 119
(BR: ≤60)
EXP_{TPC}: 6 ± 0.1
BP: 41 ± 10
DOC
7171 ± 63
ΔDOC: 18 ± 96
CO_{2flux}: 2 ± 0.2
DIC
25258 ± 24
ΔDIC: 20 ± 7
TPC: 338 ± 12
ΔTPC: -2 ± 5
GPP:
116 - 136
Aggregation:
62 ± 9
TR: 134 ± 4
TPC
DOC_{prod}:
63 - 171
(BR: ≤108)
EXP_{TPC}: 3 ± 0.1
BP: 62 ± 9
DOC
7459 ± 27
ΔDOC: 0.9 ± 25
CO_{2flux}: 17 ± 1
DIC
26585 ± 27
ΔDIC: -19 ± 8
TPC: 326 ± 26
ΔTPC: 3 ± 9
GPP:
96 - 110
Aggregation:
45 ± 9
TR: 94 ± 6
TPC
DOC_{prod}:
55 - 131
(BR: ≤76)
EXP_{TPC}: 3 ± 0.1
BP: 45 ± 9
DOC
7483 ± 71
ΔDOC: 10 ± 68
CO_{2flux}: 1 ± 0.5
DIC
25551 ± 7
ΔDIC: 5 ± 5
TPC: 305 ± 12
ΔTPC: -2 ± 6
GPP:
67 - 108
Aggregation:
34 ± 4
TR: 73 - 95
TPC
DOC_{prod}:
43 - 105
(BR: ≤80)
EXP_{TPC}: 2 ± 0.1
BP: 34 ± 4
DOC
7448 ± 13
ΔDOC: 9 ± 4
CO_{2flux}: 11 ± 0.8
DIC
26284 ± 22
ΔDIC: -18 ± 10
TPC: 368 ± 21
ΔTPC: -3 ± 11
GPP:
20 - 88
Aggregation:
23 ± 4
TR: 13-78
TPC
DOC_{prod}:
34 - 100
(BR: ≤66)
EXP_{TPC}: 2 ± 0.1
BP: 23 ± 4
DOC
7576 ± 48
ΔDOC: 11 ± 26

Fig 5