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## Feedbacks of CO<sub>2</sub> dependent dissolved organic carbon production on atmospheric CO<sub>2</sub> in an ocean biogeochemical model

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7983

#### Abstract

We use an ocean biogeochemical model to test whether a potential  $CO_2$  dependence of dissolved organic carbon (DOC) production may have an influence on marine carbon sequestration via particle aggregation and so may represent a potentially larger ocean

- sink for anthropogenic CO<sub>2</sub>. The hypothesis is based on mesocosm experiments that have shown enhanced carbon uptake by phytoplankton when more CO<sub>2</sub> is available, and where the extra carbon was probably directly routed into DOC instead of the particulate phase. Sensitivity experiments are carried out where phytoplankton exudation of DOC is systematically increased with and without a parallel rise in atmospheric CO<sub>2</sub>.
- <sup>10</sup> We find that under a fourfold increase of the DOC formation rate, there is a slight reduction of global particle export, which results in a shallower turnover of nutrients and carbon. As a consequence, a positive feedback loop develops, such that the ocean becomes a weak source of  $CO_2$  to the atmosphere. The effect is amplified under high  $CO_2$  conditions due to the decreased  $CO_2$  buffer capacity of the ocean, however, it is
- rather low compared to the total anthropogenic perturbation. The positive feedback is in contrast to a very similar study, where a slight stimulation of particle export was found. Therefore, we conclude that the sign of the feedback depends on the actual pathway the extra carbon is taking and on the overall background conditions of marine primary production and ocean circulation.

## 20 1 Introduction

The ocean has taken up nearly 1/3 of anthropogenic  $CO_2$  emissions since preindustrial times (Sabine et al., 2004), resulting in an overall pH drop of the global surface waters from 8.21 to 8.10 today (Doney et al., 2009). This decline of -0.1 pH units corresponds to a 30% increase in hydrogen ions in seawater. By the end of this century the surface search pH is expected to drap by an additional 0.2, 0.4 upits (Cettuge et al., 1009).

<sub>25</sub> face ocean pH is expected to drop by an additional 0.3–0.4 units (Gattuso et al., 1998;

Caldeira and Wicket, 2003), which my have severe consequences on marine organisms and the cycling of elements (Doney et al., 2009).

Model results have shown that in recent decades the oceanic sink for anthropogenic carbon reduced from 30 to 25% of the total emissions, while the airborne fraction

- <sup>5</sup> increased from about 40 to 45 % (Canadell et al., 2007). Consequently, it is presently unclear whether the ocean can continue its current rate of carbon uptake (Corbiere et al., 2007; Metzl et al., 1999; McKinley et al., 2011). A reduction in the efficiency of the ocean carbon sink, for example caused by reduced solubility of CO<sub>2</sub> in warming surface waters, would provide a positive feedback on the atmosphere and thus anthropogenic
- climate change (Friedlingstein et al., 2006). On the other hand, a continuing uptake of  $CO_2$  by the ocean (Roy et al., 2011) causes a further pH decline that will affect organisms that are sensitive to  $CO_2$  and/or pH changes, which in turn may also feed back on atmospheric  $CO_2$  and thus climate (Doney et al., 2009).
- The biological carbon pump describes the photosynthetic conversion of dissolved <sup>15</sup> inorganic carbon (DIC) at the sea surface into particulate organic matter, which sinks through the water column where it is partly or entirely remineralized. This pump sequesters carbon into the deep ocean, allowing CO<sub>2</sub> from the atmosphere to replace the carbon exported by particle flux (Volk and Hoffert, 1985). When transported (upwelled) back to the sea surface ,the CO<sub>2</sub> rich deep water masses act as a source of
- <sup>20</sup> CO<sub>2</sub> to the atmosphere. Marine phytoplankton have been documented to take up carbon and nitrogen in a fixed ratio, which in today's ocean equals 106:16 (6.6) (Redfield et al., 1963). However, elevated CO<sub>2</sub> levels have been found to affect phytoplankton by increasing DIC uptake during photosynthesis, and thus may raise C:N over the Redfield Ratio (Raven and Johnston, 1991; Riebesell et al., 1993; Hein and Sand-Jensen, 1997;
- <sup>25</sup> Gordillo et al., 2003; Hutchins et al., 2007). In mesocosm experiments under elevated CO<sub>2</sub> levels, natural communities of phytoplankton have shown to metabolize more carbon without increasing their nitrogen uptake (Riebesell et al., 2007). For example, a C:N uptake ratio of 8.0 was found under three times current atmospheric CO<sub>2</sub> conditions, significantly exceeding the classical Redfield Ratio. However, since the elevated C:N

7985

ratios were not immediately found in the particulate material, the fate of the excess carbon remains unknown. It was hypothesized that increased formation of dissolved organic carbon (DOC), which was rapidly transferred into transparent exopolymer particles (TEP), could explain the observed carbon loss (Riebesell et al., 2007). TEP par-

- ticles, mostly made of sugars, are known to be sticky and aid in particle aggregation (Passow, 2002; Engel et al., 2004). Therefore, it was proposed that an increased formation and thus concentration of DOC and TEP would intensify particle aggregation and sinking, so that the excess carbon would become sequestered in the deep ocean (Arrigo, 2007), providing a negative feedback on atmospheric *p*CO<sub>2</sub>.
- <sup>10</sup> The hypothesis of carbon overconsumption has been tested in ocean biogeochemical models, where it was found that carbon export (EP) and thereby air-sea CO<sub>2</sub> flux could indeed be increased via elevated C:N ratios of particulate organic matter (Schneider et al., 2004; Oschlies et al., 2008; Tagliabue et al., 2011). But compared to the total anthropogenic perturbation, the effect of an extra storage of carbon in the ocean
- 15 (34–70 GtC) on the atmospheric pCO<sub>2</sub> is rather marginal. However, according to the mesocosm study of Riebesell et al. (2007) the extra carbon was not immediately transferred to the sinking particles, but rather routed via DOC and TEP to the particle pool. Accordingly, the impact of a 25 % increase in NPP via DOC formation on particle export was estimated by Tagliabue et al. (2011), who found that in the absence of a change
- in the C:N ratio of particle fluxes, there is indeed a small stimulation of carbon export (+4%).

In the present study we will address the question of the impact of a  $CO_2$ -induced higher DOC exudation rate on particle flux via aggregation. Therefore, we use an ocean biogeochemical model, which includes particle aggregation under fixed element ratios,

<sup>25</sup> and where DOC formation will be coupled to the atmospheric  $pCO_2$ . Our study is similar to Tagliabue et al. (2011), but it differs in several aspects with regard to (1) the way the extra carbon is routed into DOC, (2) the sensitivity to atmospheric  $pCO_2$ , and (3) the CO<sub>2</sub> scenario which was used. Although reaching a very similar stimulation of DOC formation (approx. 20% of total carbon fixation via NPP), we find a reduction of particle export flux. This is in contrast to Tagliabue et al. (2011) and will be discussed in detail.

## 2 Model and experiments

#### 2.1 Model description

- <sup>5</sup> The PISCES model simulates the cycling of the major nutrients that control phytoplankton growth: silica, nitrate, ammonium, phosphate, and iron as well as dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and oxygen (Aumont et al., 2006). The model has two phytoplankton size classes (small and large), representing nanophytoplankton and diatoms, as well as two zooplankton size classes (small).
- and large), representing microzooplankton and mesozooplankton. For all species the C:N:P ratios are assumed constant (122:16:1; Anderson and Sarmiento, 1994), while the internal ratios of Fe:C, ChI:C, and Si:C of phytoplankton are predicted by the model. There are two size classes of detrital POC, small and large. The small size class sinks at a fixed rate of 2 mday<sup>-1</sup> while the large particles accelerate with depth from 50 to
- <sup>15</sup> 200 m day<sup>-1</sup> (Aumont and Bopp, 2006). In the model, dissolved organic carbon forms primarily from nanophytoplankton and diatom excretion, but also from zooplankton growth, zooplankton grazing on phytoplankton and POC and by the decay of POC. DOC is lost through particle aggregation, which occurs via turbulent shear and differential settling of particles. The detailed equations governing particle collision are given
- in Gehlen et al. (2006). Furthermore, DOC decays on a timescale from weeks to years. In order to simulate bacterial activity, degradation of DOC is dependent on temperature and nutrient availability (Aumont and Bopp, 2006).

The physical forcing fields to run the ocean biogeochemical model are obtained from the OPA 9.2 stand-alone ocean model. The model has a horizontal resolution of 2 de-

25 grees (lon × lat) at the poles and a finer resolution towards the tropics reaching 0.5 degrees in latitude at the equator. In the vertical it has 30 levels increasing from 10 m

thickness in the top 100 m to 500 m vertical extension at depth. The forcing fields to drive the ocean model are described in Aumont and Bopp (2006). We use a climatological 5-day forcing, repeating each year, so that ocean circulation exhibits seasonal, but no interannual or longer-term variability.

In the spinup and the control simulation atmospheric CO<sub>2</sub> is fixed at the preindustrial level of 284.6 ppm. The carbonate chemistry follows simplified OCMIP protocols (Aumont and Bopp, 2006).

## 2.2 Mean state

The Atlantic Meridional Overturning Circulation (AMOC; not shown) exhibits the typical pattern of a clockwise circulation in the upper 2500 m (NADW) and a counter clockwise flow below (AABW). The maximum of the NADW streamfunction lies at 40–45° N and amounts to 15.75 Sv (1 Sv =  $10^6$  m<sup>3</sup> s<sup>-1</sup>), which is in good agreement with observations (Schmitz and McCartney, 1993; Talley et al., 2003; Kanzow et al., 2010;). The boundary between NADW and AABW lies at 2500 m, which is shallower compared to 3000 m

- depth from observations (Tomczak and Godfrey, 2003) and other model studies (Lozier et al., 2010). The maximum strength of the Atlantic bottom water cell corresponds to 7.8Sv at 12° N, which also agrees well with observations and other models (Schmitz and McCartney, 1993; Lozier et al., 2010). The spatial distribution of temperature and salinity is well reproduced by the model as shown in a Taylor Diagram (Fig. 1), where
- <sup>20</sup> a normalized standard deviation of one and a correlation coefficient of R = 1 would indicate a perfect fit between model results and observational data. The agreement of T and S is at least as good as in typical IPCC simulations (Schneider et al., 2007). Nutrient and carbon (DIC) distributions are also well reproduced with correlation
- coefficients above R = 0.9, whereas oxygen and total alkalinity agree less well. The latter has already been shown to be difficult to reconcile in ocean biogeochemical models (Gehlen et al., 2007), probably due to large uncertainties in the sources and sinks of particulate inorganic carbon (CaCO<sub>3</sub>). Net primary production (NPP) shows the weakest match with R = 0.67), however, this is considerably better than in fully

7988

Discussion Paper | Discussion Paper

Discussion Paper

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

coupled models (Schneider et al., 2008). Interestingly, the distribution of the degree of calcite saturation Omega ( $CO_3^{2-}/CO_3^{2-}$  sat) has a high correlation (R = 0.98) and only a weak bias, while the depth of the calcite saturation horizon (CSH) matches less well (R = 0.83). This is probably caused by the large bias in the CSH, which is on the order of –20%, and the fact that a 2-D distribution has less degrees of freedom.

The fields of oxygen and apparent oxygen utilization (AOU) also exhibit correlations near R = 0.9, however, the distribution of oxygen minimum zones (OMZs; e.g., Stramma et al., 2008) is not very well reproduced (not shown). Generally the model oxygen concentrations are too high, corresponding to an overestimation of 15% on

- global average. Especially in the OMZs of the Atlantic and the Eastern Tropical Pacific oxygen concentrations are considerably too high. The overestimated upper water column oxygen values are a possibly caused by too weak downward mixing, whereas the high oxygen concentrations in the deep South Atlantic and Pacific are probably caused by too strong ventilation from the South. Only in the Atlantic from 60° N to 40° S below
   about 2000 m depth oxygen is by about 20–50 µmoll<sup>-1</sup> too low, most probably due to
- the too shallow overturning cell in the North Atlantic.

#### 2.3 Sensitivity experiments

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To assess the sensitivity of the ocean carbon sink to  $CO_2$ -induced changes in the DOC exudation rate of marine phytoplankton, we calculate a transfer function based on the increase of the C:N uptake ratio observed in the mesocosm studies by Riebesell et al. (2007). Therefore, we consider that in the pre-industrial control simulation,

- sell et al. (2007). Therefore, we consider that in the pre-industrial control simulation, our model has a net primary production (NPP) of around 30 GtCyr<sup>-1</sup>. DOC exudation by phytoplankton is set to 5 % of the model NPP, which means that 1.5GtCyr<sup>-1</sup> is exudated as DOC. In the mesocosm experiment of Riebesell et al. (2007) a C:N uptake ratio of 8.0 was found under almost 4 × preindustrial CO<sub>2</sub> concentrations (~ 3 × mod-
- ern  $pCO_2$ ), which corresponds to a 20% increase relative to a Redfield C:N ratio of 6.6. A 20% increase of our modeled NPP would amount to about 36 GtCyr<sup>-1</sup>, which can roughly be achieved by a quadrupling of modern DOC formation (~ 6GtCyr<sup>-1</sup>). 7989

Consequently, we run a standard CO<sub>2</sub> scenario with a 1 % CO<sub>2</sub> increase per year, reaching 4  $\times$  CO<sub>2</sub> after 140 yr, and directly link the DOC exudation rate to the rate of CO<sub>2</sub> increase, such that at the end of the simulation DOC formation from phytoplankton exudation amounts to 20 % of global NPP.

5 2.3.1 Control

The model was spun up over 6000 yr using the standard setup of the NEMO V3.2 model under the physical forcing fields explained above. This run was continued with constant preindustrial  $CO_2$  over 500 yr to serve as control simulation.

#### 2.3.2 CDOC

In this experiment, both the  $CO_2$  and DOC formation rate are increased by 1% every year for 140 yr. The quadrupled values are kept constant until the simulation reaches 500 yr. This experiment combines the affect of high DOC formation as well as high atmospheric  $CO_2$  levels on the carbon cycle.

## 2.3.3 CO<sub>2</sub>

In the CO<sub>2</sub> experiment, only the atmospheric CO<sub>2</sub> is increased by 1 % every year until it is quadrupled and then it is kept constant until the year 500. The aim of this experiment is to isolate the DOC affect at high CO<sub>2</sub> levels by calculating CDOC–CO<sub>2</sub>.

#### 2.3.4 DOC

In the DOC experiment, only the production of DOC is quadrupled by increasing the phytoplankton excretion rate by 1 % every year so that the excretion flux increases from 5 % to 20 % at the end of the 140 yr period, staying constant at this value until year 500. The purpose of this experiment is to isolate the DOC affects at low background  $CO_2$ (DOC–Control) and to compare this with the DOC effect under high  $CO_2$  (CDOC- $CO_2$ ),

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which in turn corresponds to the  $CO_2$  effect at high DOC formation (CDOC-DOC). All experiments are outlined in Table 1.

#### 3 Results

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# 3.1 Impact of CO<sub>2</sub>-sensitive DOC formation on ocean carbon and nutrient cycling

With a four times higher rate of DOC formation, the global inventory of DOC increases only marginally by about 2% to 43.8 GtC, independent of the atmospheric CO<sub>2</sub> values (Table 2). The highest accumulation of DOC is found in the subtropical gyres (Fig. 2a, b), where DOC degradation is nutrient limited (see discussion in Tagliabue et al., 2011).

- At the same time the global POC inventory decreases by about 4% to 1.04 GtC (Table 2), showing that in our model higher DOC formation and a slightly larger DOC inventory are at the expense of POC rather than fostering particle aggregation. Consequently, the global particle export flux reduces by roughly 5%, although regionally there are strongly enhanced POC-fluxes, for example in the low productive/low export
- <sup>15</sup> subtropical gyres (Fig. 2c, d). Especially in the Pacific on the borders of the subtropical gyres, an up to 5% amplified POC-flux reaches down into the deep ocean, although offset by up to 20% reduced POC-flux at higher latitudes (Fig. 2c). Interestingly, in the Atlantic a higher POC-flux is only found at the poleward sides of the subtropical gyres (Fig. 2d), probably due to the overall low NO<sub>3</sub> concentrations in the tropical surface
- waters. The changed DOC cycling also affects nutrient distributions with a tendency of shallow water nitrate accumulation, which reduces the vertical NO<sub>3</sub> gradient. Especially around and directly below the subtropical gyres NO<sub>3</sub> accumulates under higher DOC formation (Table 2, Fig. 2e, f). This shallower turnover of nitrogen stimulates global net primary production (NPP), which is amplified by about 10 % (+3GtCyr<sup>-1</sup>), proportion-
- <sup>25</sup> ally driven by both 10% increases in diatom and nanophytoplankton production (Table 2). Only about 1 GtC yr<sup>-1</sup> of the extra NPP is accounted for in the new production,

7991

showing that regenerated production, which according to Dugdale and Goering (1967) is based on  $NH_4$  uptake, is dominant. NPP stimulation due to the shallower carbon and nutrient turnover takes place mostly in the high productive regions of the North Atlantic, the eastern boundary upwelling regions of the tropical and subtropical Atlantic

- and Pacific. However, there is also a considerable increase of NPP on the borders of the subtropical gyres, fueled by the higher availability of nitrogen as shown in Fig. 3. In experiment CO<sub>2</sub>, the cycling of organic carbon and major nutrients remains largely unaffected, because organic matter turnover is not directly sensitive to CO<sub>2</sub>. However, in the experiment combining high DOC and CO<sub>2</sub> there is a slight positive CO<sub>2</sub> effect
- (+ 0.3 GtC yr<sup>-1</sup>) on NPP (Fig. 3e). This is probably due enhanced iron availability after reduced scavenging by particulate inorganic carbon (PIC) under ocean acidification. This effect will be explained in more detail in the discussion section. Interestingly, there is no stronger export in the high productive regions experiencing NPP stimulation, but rather a drop in EP (Fig. 4b, d). The strongest export increase under high DOM forma-
- tion can be found on the borders of the subtropical gyres and in the Western Pacific Warm Pool (WPWP), whereas EP remains largely unaffected by the pure CO<sub>2</sub> forcing (Fig. 4e).

#### 3.2 Ocean carbon storage

In both experiments in which  $CO_2$  is increased there is a flux of carbon from the atmosphere into the ocean, as can be expected due to the positive partial pressure difference (Fig. 5). However, in the experiments with elevated DOC formation by phytoplankton, there is a net loss of  $CO_2$  to the atmosphere, caused by the shallower turnover of nitrogen and carbon. When calculating the global cumulative net air-sea  $CO_2$  flux over the 500 model years, in experiment DOC this results in a net loss of 28 GtC to the

atmosphere, while under simultaneously elevated CO<sub>2</sub> concentrations this effect rises to 37 GtC, representing a positive feedback on atmospheric CO<sub>2</sub> (Table 2, Fig. 5). This amplification of carbon loss to the atmosphere at high CO<sub>2</sub> is caused by the reduced buffer capacity of the surface ocean.

Due to the spatial pattern of the sea-air partial pressure difference of CO<sub>2</sub> ( $\Delta \rho$ CO<sub>2</sub>), there is a constant exchange of carbon between atmosphere and ocean (Takahashi et al., 2002,2009). In general, the ocean takes up carbon from the atmosphere at intermediate to high northern latitudes and the southern mid-latitudes, while there is

- constant outgassing into the atmosphere primarily in the tropics, which is well repre-5 sented by our model simulation (Fig. 6 top; Mikaloff-Fletcher et al., 2007; Takahashi et al., 2009). At preindustrial times, the annual exchange was almost neutral with a small flux of about 0.4 GtCyr<sup>-1</sup> into the atmosphere, balancing the river input of carbon into the ocean (Takahashi et al., 2009). An increase of the atmospheric pCO2 due
- to anthropogenic emissions forces a stronger CO<sub>2</sub> flux into the ocean due to the more positive air-sea  $\Delta pCO_2$ . As shown in Fig. 5, assuming a CO<sub>2</sub>-related fourfold increase in DOC formation, the total uptake of anthropogenic carbon is reduced. The differences in carbon pathways between the experiments of high DOM formation (CDOC) and CO<sub>2</sub> only (CO<sub>2</sub>) is shown in Fig. 6 at the bottom, highlighting areas of stronger uptake and
- <sup>15</sup> outgassing in CDOC relative to CO<sub>2</sub>. Especially the equatorial borders of the subtropical gyres in the Pacific are characterized by increased carbon uptake by the ocean due to the higher NPP (Fig. 3) caused by higher nitrate availability (Fig. 2e). However, this extra carbon is quickly remineralized around and below the subtropical gyres and entrained as DIC into the equatorial current system, where it upwells near the equa-
- tor and then escapes back into the atmosphere. As this DIC transport is accompanied by NO3, its pathway can be tracked by the NO3 anomalies in Fig. 2e. At the same time the intermediate latitudes of both the Atlantic and Pacific become weaker carbon sinks (Fig. 6 bottom), probably due to the overall shallower carbon turnover resulting in a decreased buffer capacity. Consequently, the typical regions of preindustrial carbon
- uptake become reduced carbon sinks as marked by the horizontal hatches over blue 25 areas in Fig. 6 top, whereas the major outgassing region in the tropical Pacific is turning into a stronger carbon source, shown by vertical hatches over red background in Fig. 6 top.

#### 7993

#### Discussion

#### Feedbacks of extra carbon uptake on atmospheric CO<sub>2</sub>

In the present study we have used an ocean biogeochemical model to test the hypothesis that a higher DOC formation rate under elevated atmospheric CO<sub>2</sub> concentrations

- results in an intensification of (particulate) carbon export and thus CO<sub>2</sub> drawdown from the surface ocean due to aggregate formation (Arrigo, 2007). However, after quadrupling the DOC exudation rate of phytoplankton, we find a global reduction in particle export (-4%) despite an increase in NPP (+8%) and surface nitrate due to a shallower turnover of carbon and nutrients. Although the model allows for particle aggregation,
- and yields indeed higher POC export flux on the borders of the subtopical gyres where DOC accumulates, it obviously does not reach a critical concentration to strengthen particle export at the global scale (Figs. 2, 4). As a result, there is net outgassing of CO<sub>2</sub> from the ocean into the atmosphere, providing a positive feedback (Fig. 5). This finding is in contrast to two studies which directly route an above-Redfield carbon up-
- take into the pool of particulate organic carbon (POC) and thereby strengthen particle export and ocean CO<sub>2</sub> uptake (Schneider et al., 2004; Oschlies et al., 2008), and this difference highlights the importance of the actual pathway and thus fate that additional carbon uptake may take.
- Tagliabue et al. (2011) use a CO<sub>2</sub> sensitivity factor to route an additional amount of fixed carbon (up to +25%) via NPP directly into DOC. Although this is very similar to our approach, where the DOC formation rate (phytoplankton exudation) is increased from 5 to 20% of carbon fixation (NPP), they find a 4% stimulation of global carbon export (EP). Apart from potential effects of using different circulation fields, a major difference between the two studies is the overall amount of NPP, which is  $49 \, \text{GtCyr}^{-1}$  in Tagliabue
- et al. (2011) in contrast to 37 GtCyr<sup>-1</sup> in our study (Table 2). It is possible that by 25 linking CO<sub>2</sub>-dependent DOC formation to already higher background NPP, the critical threshold to yield higher particle aggregation and thus EP may have been surpassed. Furthermore, the sensitivity factor used by Tagliabue et al. (2011) prescribes a 25%

higher NPP at the end of their simulation period, whereas in our study NPP effectively increases only by 8 % (Table 2), representing a lower sensitivity. However, both studies have in common that they result in a reduction of the particle export efficiency (Laws et al., 2000), expressed as the pe-ratio (EP/NPP), on the order of 10 % (see Table 2

- <sup>5</sup> this study and Table 2 in Tagliabue et al., 2011). In the absence of DIC inventories or cumulative air-sea CO<sub>2</sub> exchange from the study by Tagliabue et al. (2011), a reduced pe-ratio can be expected to result in a net loss of CO<sub>2</sub> to the atmosphere (Schneider et al., 2008), even though EP may have been strengthened.
- A surprising result of our study is the slight apparent  $CO_2$  fertilization effect of NPP (+0.3 GtC yr<sup>-1</sup>) in the combined experiment (CDOC) relative to the DOC only experiment, which is is not found in the  $CO_2$  only experiment (Table 2, Fig. 3c, e). This NPP stimulation can be explained by a combination of higher nutrient and iron availability in the experiment CDOC. As it was explained before, the higher nutrient concentrations in the surface ocean are caused by the shallower turnover of organic matter. In addition to
- <sup>15</sup> this, reduced particle concentrations are lowering the scavenging of iron, which in turn increases iron availability up to 10% (not shown). In the combined experiment (CDOC) the total particle inventory is reduced by 7% (Table 2), whereas in the CO<sub>2</sub> and DOC experiment there is only a 3–4% reduction, caused by a lowering of either PIC (CO<sub>2</sub>) or small and large POC (DOC). A similar CO<sub>2</sub> fertilization does not appear in the CO<sub>2</sub>
- only experiment, as here the reduction in particle load is lower than in CDOC and not accompanied by a near surface accumulation of other nutrients such as NO<sub>3</sub> (Fig. 2). The weak iron fertilization effect under ocean acidification also explains why there is a clichtly explanated surged surged in the surgeriment CDOC relative to COC.

a slightly enhanced cumulative carbon uptake in the experiment CDOC relative to  $CO_2$  during the first 140 yr of the simulation, with a peak value of +5 GtC in year 70 (Fig. 5). This transient sink is due to a weakly enhanced carbon uptake in the low latitudes, as it

was explained above, which takes several decades to be entrained into the equatorial current system where this extra carbon outgasses again (Fig. 6). The finding that the net outgassing into the atmosphere only becomes active around and after the time

of stabilizing the atmospheric  $CO_2$  may also explain why in the study by Tagliabue et al. (2011) the DOC effect may have resulted in a potentially stronger carbon sink.

Since our model is lacking an atmospheric carbon reservoir, the feedback of the simulated net outgassing would in turn represent a positive feedback on the DOC formation, amplifying the response. Consequently, we assume that our model simulation slightly underestimates the feedbacks of enhanced DOC formation on the atmospheric CO<sub>2</sub>.

#### 4.2 Implications for future climate change

Since in our simulation a constant climatological circulation is used, we cannot directly quantify the impact of a stimulated DOC turnover on carbon fluxes in a future warming climate. However, a number of studies exist, which have investigated the impact of climate change on carbon and nutrient cycling in the ocean (Maier-Reimer, 1993, Maier-Reimer et al., 1996; Sarmiento and Le Quéré, 1996; Sarmiento et al., 1998; Sarmiento and Hughes, 1999; Matear and Hirst, 1999; Friedlingstein et al., 2001, 2006; Schnei-

- <sup>15</sup> der et al., 2003; Mckinley et al., 2004, 2006; Gangsto et al., 2008; Gruber et al., 2009; Steinacher et al., 2010; Arnosti et al., 2011). Based on these findings, we can estimate a potential feedback of a CO<sub>2</sub> sensitive DOC turnover under global warming. There is consensus that the surface ocean will warm and stratify. This is expected to cause a reduction of NPP due to lower nutrient input into the surface layer (e.g., Kirchman,
- et al., 2009; Prowe et al., 2009; Steinacher et al., 2010; Trabelsi and Rassoulzadegan, 2011), which would reduce the impact of NPP on DOC formation and thereby the positive feedback found in our study. However, due to an expansion of marine productivity into polar latitudes, mainly as a result of a retraction of sea-ice (Bopp et al., 2001), the DOC feedback would start operating here and thereby it would counteract
- the low latitude reduction of the positive feedback. Ocean warming is expected to stimulate bacterial activity and thereby the degradation of organic matter, also providing a positive feedback on the atmosphere (Kirchman et al., 2009; Engel et al., 2011). Accordingly, the DOC produced under higher CO<sub>2</sub> levels would be even more prone

to remineralization, which would amplify the positive feedback found in our study. The situation would be opposite in the high latitudes, where cooler surface waters prevail (Carlson et al., 1998; Laws et al., 2000), so that a stimulation of NPP might result in an overall more efficient carbon export. Apart from the temperature effect, there may also Discussion Paper

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- be a direct  $CO_2$  impact on bacterial degradation of organic matter (Piontek et al., 2010), which would further amplify the positive feedback of increased DOC turnover. To summarize, under combined future ocean warming, stratification, and ocean acidification a large number of mechanisms come into play, and may either amplify or dampen the positive feedback which was found in our study. Therefore, apart from potential effects
- of background conditions as discussed above, even the sign of the net response to be expected can not be estimated at present.

#### 5 Conclusion

In the present study we simulated a positive feedback of enhanced DOC formation in response to ocean acidification on atmospheric pCO<sub>2</sub>. Although allowing for particle

- aggregation, there is a shallower turnover of organic matter and nutrients resulting in a net outgassing of CO2 from the ocean, which does not confirm the hypothesis of higher particle aggregation and thus ocean carbon uptake by Arrigo (2007). A comparison with a very similar study (Tagliabue et al., 2011) highlights the importance of the actual pathway and thus fate the extra carbon takes in the ocean, as well as a potential
- impact of background conditions such as NPP, to decide whether a higher turnover of 20 DOC would result in a positive or negative feedback. Consequently, further research is needed to systematically analyze the pathway of CO<sub>2</sub>-stimulated extra carbon uptake in laboratory experiments and model studies.
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8003

Table 1. Overview of the experiments, which were initialized from a 6 000 yr spinup. The idealized scenarios for both CO<sub>2</sub> and DOC production follow a 1 % increase rate per year, resulting in a doubling after 70 yr and a quadrupling after 140 yr, respectively. Beyond the year 140 CO<sub>2</sub> and DOC formation are stabilized at the quadrupled value until the end of the simulation (model year 500).

Experiment	Atmospheric CO <sub>2</sub>	DOC production		
Control	preindustrial 284.6 ppm	constant 0.05		
CDOC	$1-4 \times CO_2 + $ stab.	1-4 × DOC+ stab.		
CO <sub>2</sub>	$1-4 \times CO_2 + $ stab.	constant 0.05		
DOC	preindustrial 284.6 ppm	1-4 × DOC+ stab.		

**Table 2.** Global values of key biogeochemical variables in the different experiments. Particle export (EP) is the flux of particulate organic matter across 100 m depth. The average surface nitrate concentrations are calculated for the top 100 m of the water column. All inventories quantify global standing stocks, whereby the opal inventory is expressed in carbon units, to be comparable with the other particle types.

Experiments	NPP (GtC)	NPP Diatoms (Gt C)	NPP Nanophyto. (Gt C)	EP (GtC)	surf. NO <sub>3</sub> (μmI <sup>-1</sup> )	DOC Inv. (Gt C)	DIC Inv. (Gt C)	POC Inv. (Gt C)	PIC Inv. (Gt C)	Opal Inv. (Gt C)
Control	36.6	6.83	29.8	7.44	5.85	43.3	35963	1.11	0.07	0.11
CDOC	39.7	7.50	32.2	7.10	6.16	43.9	37908	1.07	0.02	0.11
CO <sub>2</sub>	36.6	6.86	29.7	7.45	5.83	43.4	37945	1.11	0.02	0.11
DOC	39.5	7.40	32.1	7.12	6.15	43.8	35935	1.07	0.07	0.11

8005



**Fig. 1.** Taylor Diagram showing the agreement of the spatial distribution of physical and ocean biogeochemical variables from the model and observations. A perfect match between both would lie at the origin of the plot (1,1 point at the bottom). The color scale indicates the model-data bias, expressed as the ratio of global average values (model/data). 2-D variables are shown as squares and 3-D variables as circles. Data sources are as follows: oxygen (O<sub>2</sub>), silica (SI), apparent oxygen utilization (AOU), phosphate (PO<sub>4</sub>), nitrate (NO<sub>3</sub>), sea surface temperature (SST), sea surface salinity (SSS), temperature (TEMP), salinity (SALT) are from the World Ocean Atlas (Collier and Durack, 2006); depth of the calcite saturation horizon (CSH), degree of calcite saturation (Omega), total alkalinity (TALK) and dissolved inorganic carbon (DIC) are from Glodap data (Key et al., 2004), net primary production (NPP) is from Behrenfeld et al. (2006).

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**Fig. 2.** North-south transects across the Pacific at  $160^{\circ}$  W (A,C,E) and the Atlantic at  $25^{\circ}$  W (B,D,F) showing differences between the experiment CDOC and the control (CDOC-control) of DOC concentrations (A,B), POC-flux (C,D), and NO<sub>3</sub> concentrations (E,F). The contours in each plot indicate absolute values from the control run.





**Fig. 3.** Global Maps of NPP  $(gm^{-2}yr^{-1})$  and the effects of different mechanisms on NPP: (A) total NPP in the control run; (B) CDOC-Control, showing the combined effect of increased DOC formation and CO<sub>2</sub> on NPP; (C) CO<sub>2</sub>-Control, confirming that there is no direct effect of CO<sub>2</sub> on NPP; (D) CDOC-CO<sub>2</sub>, isolating the pure DOC effect on NPP at high CO<sub>2</sub>, (E) CDOC-DOC, highlighting a small positive impact of CO<sub>2</sub> on NPP under high DOM formation.

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**Fig. 4.** Global Maps of EP  $(gm^{-2}yr^{-1})$  and the effects of different mechanisms on EP: (A) total EP in the control run; (B) CDOC-Control, highlighting the full effect of increased DOC formation and CO<sub>2</sub> on EP; (C) CO<sub>2</sub>-Control, indicating a minor CO<sub>2</sub>-stimulated EP increase in the Southern Ocean, which does not contribute significantly to the global integral (Table 2); (D) CDOC-CO<sub>2</sub>, showing very similar values as in (B); (E) CDOC-DOC, showing that in contrast to NPP there is no effect of CO<sub>2</sub> on EP under high DOC formation.





**Fig. 5.** Cumulative global air-sea  $CO_2$  flux in all experiments. Note that the negative part of the vertical axis, which is indicating an oceanic  $CO_2$  source, is of a smaller scale than the positive part. The purple line shows the effect of high DOC formation at high  $CO_2$  (CDOC-CO<sub>2</sub>). Please note, that for the small  $CO_2$  sink in the first 140 yr as indicated by the purple line, the scale is given in purple on the left.

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**Fig. 6.** Sea-air  $CO_2$  flux cumulated over the 500 yr of the control simulation (top). Blue colors indicate  $CO_2$  uptake by the ocean, red colors show outgassing. The difference between cumulative  $CO_2$  fluxes in the CDOC experiment and the  $CO_2$  experiment (CDOC- $CO_2$ ) is shown at the bottom. Here blue colors mark regions of intensified sink or weakened ourgassing, while red colors highlight areas of weaker ocean uptake or stronger outgassing. A DOC-induced intensification of either sources or sinks is shown in the top panel by overlaid vertical hatches, whereas dampened sources/sinks are marked by horizontal hatches.

8011