Dear Dr. Middelburg,

We would first like to thank you and the three reviewers for the careful examination of our manuscript and the insightful comments. We have taken into account these comments in the revised manuscript.

Below is a response to the reviewers’ comments and the revised manuscript. Please do not hesitate to contact us should you have any additional questions or comments on our manuscript.

Sincerely,
Zuchuan Li

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Reviewer 1:

We thank the reviewer for his/her review of our manuscript. We disagree with his/her overall assessment. Below, we provide a response to the reviewer’s two points:

• The reviewer’s first comment states that our results “…show that this maximum constraint is consistent with past estimates of carbon export. As such, the analysis seems incomplete in failing to describe what new insight the current theoretical constraint provides”

As stated in the manuscript, our impetus for this study is to explain the recently reported field observations of an interesting relationship between export production proxies and mixed layer depths (Cassar et al., 2011; Eveleth et al., 2017; Tortell et al., 2015). Our theoretical considerations build on the qualitative description provided in these original studies.

We now further emphasize the key outcomes of our study in the introduction section of the manuscript, and enumerate them here: 1) the development of a mechanistic model of an upper bound on carbon export based on the metabolic balance of photosynthesis and respiration in the oceanic mixed layer, 2) using parameters available in the literature, the modeled upper bound envelopes field observations of export production estimated from $^{234}$Th and sediment traps and $O_2$/Ar-derived net community production, and 3) the model identifies regions of the Southern Ocean where carbon export is likely limited by light during part of the growing season. Our effort has significant implications for unraveling the influence of light and nutrients availability on carbon export production in the surface ocean (see Figure 5 of the revised manuscript), and for the development of models of export production based on satellite data products.

Numerous recent modeling efforts have used simplified models to explore patterns in field observations. As an example, we refer the reviewer to the recent study of Cael and Follows (2016). In their study, the authors elegantly use “what is arguably the simplest mechanistic model” to explain the observed dependence of carbon export efficiency on temperature.

• The reviewer’s second comment, related to the first, states that “…the mathematical posing an equation for maximum possible export includes extremely simplified assumptions such as first-order herbivory that is constant with depth…”

We, again, refer the reviewer to the multitude of recent modelling efforts which have used simplified equations for complex biogeochemical processes, including herbivory. Many recent studies use first-order kinetics for grazing losses and other assumptions (e.g., see Equation 1 in Cael and Follows, 2016; Cael et al., 2017; Dutkiewicz et al., 2001; Gong et al., 2015; Gong et al., 2017; Huisman et al., 2006; Taylor and Ferrari, 2011).
Most (if not all) of these recent studies also assume constant herbivory and biogeochemical properties with depth within the mixed layer (Cael and Follows, 2016; Cael et al., 2017; Dutkiewicz et al., 2001; Gong et al., 2015; Gong et al., 2017; Huisman et al., 2006; Siegel et al., 2014; Taylor and Ferrari, 2011). Nonetheless, we now further describe in the manuscript the limitations associated with Sverdrup’s assumption of homogeneously mixed organisms or constant loss rates with depth within the mixed layer.

Overall, the reviewer’s comments are unfounded in light of the fact that 1) many other recently published articles have used similar modeling approaches and equations, and 2) to the best of our knowledge, this is the first study to provide a theoretical constraint on an upper bound of carbon export fluxes as a function of light availability, mixed layer depth and temperature.

References


Cael B. B., K. Bisson, and M. J. Follows (2017), How have recent temperature changes affected the efficiency of ocean biological carbon export? Limnology and Oceanography Letters, DOI: 10.1002/lol2.10042


Reviewer 2:

We thank the reviewer for his/her careful review of our manuscript. Below, we provide a response to the reviewer’s comments which we think have significantly improved the quality of our manuscript:

Reviewer’s comment: “This is a nice, clearly written paper, based on an interesting idea and executed well. The paper could be improved by clarifying the significance of the study somewhat. It may be very difficult ever to test or ‘validate’ this model properly. Yet, it is conceptually useful in some ways, e.g. the discussion about f_{pt} and nutrient limitation. The authors might want to discuss further, or clarify the existing discussion of, what the reader is supposed to have learned about the ocean.”

Following the reviewer’s comment, we now describe at the end of the introduction some of the key outcomes of our study:

“Our study, we build upon Sverdrup (1953) and derive a mechanistic model of an upper bound on carbon export based on the metabolic balance of photosynthesis and respiration in the oceanic mixed layer, where the metabolic balance is derived from MLD, temperature, photosynthetically active radiation (PAR), phytoplankton maximum growth rate (\mu_{max}), and heterotrophic activity. Our approach is analogous to other efforts where mechanistic models were derived to predict proxies of carbon export (e.g., Dunne et al. (2005) and Cael and Follows (2016)). We compare our NCP’ model to observations, and use this model in conjunction with satellite export production estimates to identify regions in the world’s oceans where light may limit export production. Our key findings are that 1) using parameters available in the literature, the modeled upper bound envelopes field observations of export production estimated from 234Th and sediment traps and O₂/Ar-derived net community production, and 2) the model identifies regions of the Southern Ocean where carbon export is likely limited by light during part of the growing season.”

Reviewer’s comment: “There are several circumstances where the manuscript could be connected better to the literature. For instance, in line 30, there should be at least one
Following the reviewer’s recommendation, we now more explicitly make reference to the literature, including citations found in Boyd (2015). We agree with the reviewer that our effort is in the same vein as Dunne et al. (2005) and Cael and Follows (2016) and we now further emphasize the parallels in our approaches. The following references were added to the end of the first paragraph: “(Falkowski et al., 1998; Ito and Follows, 2005; Sigman and Boyle, 2000).” We also included references to Dunne et al. (2005) and Cael and Follows (2016) in the last paragraph of the introduction: “Our approach is analogous to other efforts where mechanistic models were derived to predict proxies of carbon export (e.g., Dunne et al. (2005) and Cael and Follows (2016)).”

Reviewer’s comment: “It is worth mentioning that not everyone loves the Sverdrup model (Behrenfeld, 2010), though using it in this context is a nice idea.”

We now refer to the competing models of “dilution recoupling hypothesis” or “disturbance recovery hypothesis” and “critical turbulence hypothesis” in the section on “caveats and limitations” and cite the relevant literature: “In our study, we used a model which builds on Sverdrup’s critical depth hypothesis. There are competing hypotheses to explain phytoplankton bloom phenology (timing and intensity), including the “dilution recoupling hypothesis” or “disturbance recovery hypothesis” (Behrenfeld, 2010; Boss and Behrenfeld, 2010) and “critical turbulence hypothesis” (Brody and Lozier, 2015; Huisman et al., 1999; Taylor and Ferrari, 2011). In the case of top-down control, any respiratory grazing loss not accounted for by our loss term would behave as a system not reaching its full light potential (NCP*). Conversely, any grazing loss associated with export (e.g., rapidly sinking fecal pellets and other zooplankton-mediated export pathways) would minimize respiratory losses thereby bringing NCP closer to its upper bound based on light-availability. These opposing effects are beyond the scope of this study, but could be modeled, especially as we learn more about their impacts on carbon fluxes through new efforts such as NASA’s EXPORTS program (Siegel et al., 2016). See also the point below on mixing vs. mixed layer depth.”

Reviewer’s comment: “Some readers might also take issue with the sentence starting on line 31 - it’s better to say ‘export production is frequently assumed to be a function of’ (e.g. Estapa et al, 2015), though the rest of the paragraph deals with this nicely.”

We have modified the sentence following the reviewer’s comment to: “export production is frequently assumed to be a function of”.

reference for this sentence (good references should be easy to find from the reference list in Boyd (2015) - same for the next sentence. Dunne et al (2005) and Cael and Follows (2016) develop mechanistic models to which this paper is very directly related, yet these models are mentioned only in passing.”
Reviewer’s comment: “It seems a bit ironic to compare this model, which is mechanistic, quite sophisticated, and carefully developed, with export data extrapolated using the Martin curve (an empirical parameterization) with a constant b-value. Granted, the model must be validated in some way, but the ‘comparison to observations’ subsection of the paper definitely appears to be its weak point.”

A study recently published shows that the fit of the Martin curve to observations is as good as more sophisticated parameterizations which account for the ballast effect (Gloege et al. 2017). However, we agree with the reviewer that using the Martin curve to extrapolate the carbon export observations to the base of the mixed layer introduces uncertainties. To circumvent this issue, we now also present a figure in the supplementary material which only includes biological carbon fluxes directly measured within the mixed layer:

**Figure S4.** Modeled upper bound on carbon export production compared to field observations as a function of mixed layer depth (MLD). Observations are based on O$_2$/Ar-derived net community production (NCP). To account for the effect of photosynthetically active radiation (PAR) on export production, both MLD and carbon fluxes are normalized to $-\log (1 - l_m(0))$ (see equations (19) and (21)). The thick gray line represents the upper bound fitted to the NCP data. Dash-lines represent the upper bounds calculated using parameters available in the literature (Table 2). A stoichiometric ratio of O$_2$/C=1.4 was used to convert NCP from O$_2$ to C units (Laws, 1991).

Reviewer’s comment: “Figures 3+4 are somewhat difficult to see/understand. The maps could be larger, and the axis limits could be chosen in a way to present the information more clearly.”

Following the reviewer’s comment, we have enlarged the maps, increased the resolution quality, and modified the axes scales.
The updated Figure 3 (Figure 4 in the revised manuscript) is shown below:

Figure 4. Modeled upper bound on carbon export production compared to field observations as a function of mixed layer depth (MLD) and sea surface temperature (SST). (A) The thick gray line represents the upper bound fitted to the net community production (NCP) data. Dash-lines represent the upper bounds calculated using...
parameters available in the literature (Table 2). (B) NCP as a function of SST with isopleths of constant upper bounds color coded for MLD. NCP observations are color coded with MLD. (C) Surface representing the envelope of the modeled upper bound of carbon export production as a function of SST and MLD. Bars represent field observations color coded with the ratio of NCP to the upper bound. Observations are based on $^{234}$Th and sediment traps estimates of carbon export production and O$_2$/Ar-derived NCP. A stoichiometric ratio of O$_2$/C=1.4 was used to convert NCP from O$_2$ to C units (Laws, 1991). To account for the effect of PAR on export production, both MLD and carbon fluxes are normalized to $-\log(1 - I_m(0))$ (see equations (19) and (21)). The temperature dependence of $r_{HR}$ was modeled as $r_{HR} = r_{HR}^0 \times e^{0.08\times T}$.

Reviewer’s comment: “Eq. 21 may be missing a normalizing constant - a proportionality (Eq. 20) is not the same as an equals sign. The values of Pt and Bt both merit a bit more discussion - both numbers have some associated uncertainty, do they not?”

Following the reviewer’s comment, we modified equations (20a) and (20b):

\[
\mu_{max} = \mu_{max}^0 \times e^{P_t \times T} \\
r_{HR} = r_{HR}^0 \times e^{B_t \times T}
\]

We also now elaborate on the uncertainties associated with both parameters. We modified the following paragraph in the section on caveats and limitations:

- $\mu_{max}$ and $r_{HR}$ are influenced by environmental factors other than temperature, including community structure (Chen and Laws, 2017), and may vary with depth within the mixed layer. For these reasons, the equations relating $\mu_{max}$ and $r_{HR}$ (i.e., $B_t$ and $P_t$) to temperature carry uncertainties (Bissinger et al., 2016; Edwards et al., 2016; Kremer et al., 2017; López-Urrutia and Morán, 2007; Rivkin and Legendre, 2001) which impacts our estimates of the upper bound on carbon export, especially in warmer regions. As in other recent studies (Cael and Follows, 2016; Cael et al., 2017; Dutkiewicz et al., 2001; Gong et al., 2015; Gong et al., 2017; Huisman et al., 2006; Taylor and Ferrari, 2011), we model heterotrophic respiration to vary in proportion to phytoplankton concentration. The model could be further improved by explicitly including the concentration of heterotrophs. See point above on the grazing effect on export with regards to $r_{HR}$.

Reviewer 3:

We thank the reviewer for his/her insightful review of our manuscript. Below, we provide a response to the reviewer’s comments which we think have significantly improved our manuscript.

Reviewer’s comment: “The paper would benefit from more motivation for the model at the start. The introduction is fairly short and general. The reader would be more eager to dive into all the details of the model if the need for this model and the questions that the authors hope to address with it were clearly laid out near the beginning of the paper.”
Figure 3 demonstrates that there are patterns in the observations that we should seek to explain, but this is only briefly introduced at the start of the paper. Figure 4 shows intuitive results, so here too the motivation to do the global analysis should be specifically stated."

Following the reviewer’s comment, we now discuss the relevance of the study at the end of the third paragraph in the introduction:

Likewise, the effects of light and nutrient on carbon fluxes are difficult to disentangle. For example, high-nutrient, low-chlorophyll regimes in the Southern Ocean have been attributed to iron limitation (Boyd et al., 2000), deep mixed layers and light limitation (Nelson and Smith, 1991; Mitchell and Holm-Hanse, 1991; Mitchell et al., 1991), or both (Sunda and Huntsman, 1997). To decompose the influence of light and nutrient availability on NCP, we define the upper bound on carbon export from the mixed layer (\(NCP^*\)) as the maximum export achievable should all limiting factors other than light (taking into account self-shading) be alleviated.

Reviewer’s comment: “A large proportion of export is potentially controlled by bloom dynamics as phytoplankton escape heterotrophic grazing control or not. The proposed model misses these dynamics by forcing heterotrophic respiration to be solely proportional to phytoplankton concentration, rather than also include heterotroph concentrations. Of course, this simplifies the model considerably. However, this simplification may render the results irrelevant since the model then does not approximate the real system closely enough. At the very least, the authors need to carefully argue that their model remains valid for the questions they wish to address despite this simplification of heterotrophic respiration. Such an argument is presently missing from the paper.”

We now better acknowledge this limitation in our revised manuscript, including in the section on caveats and limitations where we expand on grazing and heterotrophy. We now also cite additional papers where a similar approach has been used (e.g., Cael and Follows, 2016, Cael et al., 2017, Dutkiewicz et al., 2001, Gong et al., 2015, Gong et al., 2017, Huisman et al., 2006, and Taylor and Ferrari, 2011).

In the section on caveats and limitations, we added the following paragraph:

- \(\mu_{max}\) and \(r_{HR}\) are influenced by environmental factors other than temperature, including community structure (Chen and Laws, 2017), and may vary with depth within the mixed layer. For these reasons, the equations relating \(\mu_{max}\) and \(r_{HR}\) (i.e., \(B_t\) and \(P_t\)) to temperature carry uncertainties (Bissinger et al., 2008; Edwards et al., 2016; Kremer et al., 2017; López-Urrutia and Morán, 2007; Rivkin and Legendre, 2001) which impacts our estimates of the upper bound on carbon export, especially in warmer regions. As in other recent studies (Cael and Follows, 2016; Cael et al., 2017; Dutkiewicz et al., 2001; Gong et al., 2015; Gong et al., 2017; Huisman et al., 2006; Taylor and Ferrari, 2011), we model heterotrophic respiration to vary in proportion to phytoplankton concentration. The model could be further
improved by explicitly including the concentration of heterotrophs. See point above on the grazing effect on export with regards to $r_{HR}$.

Reviewer’s comment: “I would like to see more clarity about how the generalized conclusions of the model depend on choices for specific constants. For example, the discussion in the paragraph beginning on line 121 only holds where $kc$ is significant. As $kc$ goes toward zero, self-shading decreases and NPP will continuously increase as C increases. The text is not clear on whether the $kc$ required to cause the self-shading induced decrease in $dNCP/dC$ above a certain C is reasonable. The paper discusses specific values for some of these constants later in section 2.5, but it seems as though the values of these constants affect earlier conclusions as well.”

Because pure water and phytoplankton attenuate light, $K_{IW}$ and $k_c$ must be greater than zero. Over the range of $k_c$ values reported in the literature, the behavior of $dNCP/dC$ is not expected to change, as now clarified in the manuscript. Following the reviewer’s comment, we now also include a new table (Table 2) which shows the value or range of values (and references) associated with the constants used.

Reviewer’s comment: “The simplification in the last part of equation 15 appears to remove the dependence of average mixed layer irradiance on the depth of the mixed layer. Equation 16, based on this simplification, demonstrates that only the respiration term is now sensitive to the mixed layer depth (MLD cancels from the first term). This seems to run counter to all the previous arguments that MLD is important to integrated NPP values.”

This is an important point raised by the reviewer. We have now revised the approximation in Equation (15). Below, we show a figure showing the comparison of upper bounds derived using the original and approximated models. As can be seen, the difference in behavior is small. However, we now include this figure in the manuscript.
Figure 3. Upper bounds derived using the original and approximated models. The upper bound for the original model (equations (8-10)) is estimated through a non-linear optimization approach. The upper bound for the approximated model is calculated analytically from equation (19). The models use the constants listed in Table 2 and $I_m(0) = 0.9$. Decreasing $I_m(0)$ and increasing $r_{HR}$ results in greater discrepancies between the original and approximated models in regions with shallow mixed layers.

Reviewer’s comment: “Lines 51-56: The discussion of attribution of these patterns seems too limited. Low NCP at high temperatures could be primarily a function of a tendency toward increased stratification and nutrient limitation in warm waters. Additionally, deep mixed layers can bias the O$_2$/Ar method low if entrainment of deeper waters brings low oxygen into the mixed layer.”

In the section on caveats and limitations, we mention that the field observations harbor significant uncertainties. In the same bullet point, we now mention as an example that “deep mixed layers can bias the O$_2$/Ar method low if entrainment of deeper waters brings low oxygen into the mixed layer”.

On line 275 of the original manuscript, we now further elaborate on the low $f_{pl}$ in warm waters. These waters cannot reach their full export potential because of increased stratification and nutrient limitation (“The ultra-oligotrophic subtropical waters have a low export ratio, a strong biological pump efficiency with exhaustion of nutrients at the ocean surface, and therefore have not reached their full light potential (low $f_{pl}$) because of the strong stratification and nutrient limitation”).
Reviewer’s comment: “Line 82: “light” attenuation coefficient rather than “diffusion” attenuation coefficient?”

The term “light” attenuation coefficient has been replaced with “diffusion” attenuation coefficient.

Reviewer’s comment: “Lines 113-120 and following paragraph: This section is unclear in places. Figure 2 could be actively discussed to demonstrate why dNCP/dC asymptotes at $-\tau^*MLD$ through comparison of the production and respiration terms on the right side of Figure 2a where the production term becomes stable. I spent a long time thinking about this, so the authors could really lead the reader through these arguments better. The text implies in places that dNCP/dC always decreases with increasing C (lines 113-114), but this is only the case at C larger than $C^*$.”

As stated in our original manuscript, dNCP/dC systematically decreases with increasing C (this is because \(\frac{d^2NCP(0,MLD)}{dc^2}\) is smaller than zero (see equation 12)). However, dNCP/dC remains positive below $C^*$, and becomes negative above $C^*$. Following the reviewer’s comment, we now discuss the asymptote of \(\frac{dNCP(0,MLD)}{dc}\) using Figure 2: “Because increasing C decreases light availability due to self-shading, $NPP(0,MLD)$ saturates with increasing C. Thus, $NCP(0,MLD)$ will reach an asymptote of $\lim_{C\to\infty} \left(\frac{dNCP(0,MLD)}{dc}\right) = -\tau_{HR} \times MLD < 0$, because $HR(0,MLD)$ linearly increases with increasing C while $NPP(0,MLD)$ plateaus (Figure 2).”

Reviewer’s comment: “Lines 138-140: the statement here that integrated NCP is maximized when the MLD is below the compensation depth seems contrary to the schematic representation of the system in Figure 1a vs. 1b where the integrated NCP is maximized at the compensation depth.”

The compensation depth is a function of C. In Figure 1, C is assumed to be constant and MLD is allowed to vary (e.g., synoptic variability in MLD). In this case, depth-integrated NCP will be maximized when MLD deepens or shoals to the compensation depth. Conversely, in (equation 14), C is allowed to vary for a given MLD (e.g., stable water column with varying phytoplankton biomass), in which case, the compensation depth will respond and the depth-integrated NCP peaks when the mixed layer is slightly deeper than the compensation depth.

We amended the manuscript with the following sentence: “We note that in equation (14) the NCP profile ($NCP(z)$) varies with increasing $C$, which is different from what is conceptually presented in Figure 1. The depth-integrated NCP in Figure 1 maximizes at the compensation depth because the NCP profile ($NCP(z)$) is assumed to be invariant.”
Reviewer’s comment: “Line 163: Why the MLD should satisfy the given conditions are not clear here until Line 171, where the authors state that they have chosen not to consider other possibilities.”

Following the reviewer’s comment, we reorganized the sentences: “Equation (18) decreases with MLD. As $C^*$ is positive ($C^* \geq 0$) and cannot go to infinity ($C^* \leq C_{max}^*$), MLD should satisfy $MLD_{C_{max}} \leq MLD \leq \frac{\mu^*}{r_{HR} \times K_t}$, where $MLD_{C_{max}}$ represents the MLD corresponding to the maximum achievable autotroph’s biomass concentration ($C_{max}^*$) in the surface ocean. The $NCP^*$ model for $0 \leq MLD < MLD_{C_{max}}$ is not discussed here, because we do not have data with very shallow MLD to constrain and evaluate the model. The derivation of the model is however presented in the supplementary material.”

Reviewer’s comment: “Equations 20a and 20b: These are written as simple proportionalities here, but later treated as though the proportional sign is replaced with an equal sign. It seems like there should be an additional constant.”

Following the reviewer’s comment, we modified equations (20a) and (20b): $\mu_{max} = \mu_{max}^0 \times e^{P_r-T} \quad (20a)$

$r_{HR} = r_{HR}^0 \times e^{B_t-T} \quad (20b)$

Reviewer’s comment: “Section 2.5: Where specific values or ranges of values are chosen for model constants, it would be helpful to list these in the table defining notation.”

Following the reviewer’s comment, we added a table that includes the typical range of the parameters with references.

### Table 2. Value or range of values with references for the parameters used in the model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range or value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K^\mu$</td>
<td>0.09</td>
<td>(Werdell and Bailey, 2005)</td>
</tr>
<tr>
<td>$k_c$</td>
<td>0.03</td>
<td>(Werdell and Bailey, 2005)</td>
</tr>
<tr>
<td>Carbon to chlorophyll ratio</td>
<td>90</td>
<td>(Arrigo et al., 2008)</td>
</tr>
<tr>
<td>$k_{im}$</td>
<td>4.1 Einstein m$^{-2}$ d$^{-1}$</td>
<td>(Behrenfeld and Falkowski, 1997)</td>
</tr>
<tr>
<td>$P_t$</td>
<td>0.0663</td>
<td>(Eppley, 1972)</td>
</tr>
<tr>
<td>$B_t$</td>
<td>0.08</td>
<td>(Rivkin and Legendre, 2001; López-Urrutia et al., 2006)</td>
</tr>
<tr>
<td>$\mu_{max}$</td>
<td>1 d$^{-1}$, 1.2 d$^{-1}$</td>
<td>(Laws et al., 2000; Eppley, 1972)</td>
</tr>
<tr>
<td>$T_{HR}$</td>
<td>0.1 d$^{-1}$, 0.2 d$^{-1}$</td>
<td>(Laws et al., 2000; Mitchell et al., 1991)</td>
</tr>
</tbody>
</table>
Reviewer’s comment: “Line 196: It’s unclear why data could be below the theoretical line due to light limitation, when the theoretical line is specifically modeled to include light limitation.”

Following the reviewer’s comment, we have removed the reference to light limitation in the sentence. Now: “Conversely, points below the upper bound may be nutrient limited.”

Reviewer’s comment: “Model-data differences are difficult to clearly discern in Figure 3b. Perhaps it would be useful to directly plot model-data differences in a third panel. That the NCP* model performs poorly in warm deep mixed layers (as stated on lines 210-211) cannot be clearly seen in the figure.”

Following the reviewer’s comment, we added a panel in the original Figure 3 (now Figure 4) showing the upper bound as a function of SST with isopleths of constant upper bounds color coded for MLD.
Figure 4. Modeled upper bound on carbon export production compared to field observations as a function of mixed layer depth (MLD) and sea surface temperature (SST). (A) The thick gray line represents the upper bound fitted to the net community production (NCP) data. Dash-lines represent the upper bounds calculated using parameters available in the literature (Table 2). (B) NCP as a function of SST with isopleths of constant upper bounds color coded for MLD. NCP observations are color coded with MLD. (C) Surface representing the envelope of the modeled upper bound of carbon export production as a function of SST and MLD. Bars represent field observations color coded with the ratio of NCP to the upper bound. Observations are based on $^{234}$Th and sediment traps estimates of carbon export production and O$_2$/Ar-derived NCP. A stoichiometric ratio of O$_2$/C=1.4 was used to convert NCP from O$_2$ to C units (Laws, 1991). To account for the effect of PAR on export production, both MLD and carbon fluxes are normalized to $-\log(1 - I_m(0))$ (see equations (19) and (21)). The temperature dependence of $r_{HR}$ was modeled as $r_{HR} = r_{HR}^0 \times e^{0.08 \times T}$.

Reviewer’s comment: “Line 281: The text discusses discrepancies between predicted and observed NCP*. However, only NCP can be observed, not NCP*.”

We agree with the reviewer. The sentence has been modified to: “There are a multitude of uncertainties, simplifications, and approximations in our model and field observations. Among others:”
A mechanistic model of an upper bound on oceanic carbon export as a function of mixed layer depth and temperature

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Key points

1. A mechanistic model of an upper bound on carbon export is developed based on the metabolic balance of photosynthesis and respiration in the oceanic mixed layer

2. Using parameters available in the literature, the modeled upper bound envelopes field observations of export production estimated from $^{234}$Th and sediment traps and O$_2$/Ar-derived net community production

3. The model identifies regions of the Southern Ocean where carbon export is likely limited by light during part of the growing season
Abstract

Export production reflects the amount of organic matter transferred from the surface ocean to depth through biological processes. This export is in great part controlled by nutrient and light availability, which are conditioned by mixed layer depth (MLD). In this study, building on Sverdrup’s critical depth hypothesis, we derive a mechanistic model of an upper bound on carbon export based on the metabolic balance between photosynthesis and respiration as a function of MLD and temperature. We find that the upper bound is a positively skewed bell-shaped function of MLD. Specifically, the upper bound increases with deepening mixed layers down to a critical depth, beyond which a long tail of decreasing carbon export is associated with increasing heterotrophic activity and decreasing light availability. We also show that in cold regions the upper bound on carbon export decreases with increasing temperature when mixed layers are deep, but increases with temperature when mixed layers are shallow. A metaanalysis shows that our model envelopes field estimates of carbon export from the mixed layer. When compared to satellite export production estimates, our model indicates that export production in some regions of the Southern Ocean, most particularly the Subantarctic Zone, is likely limited by light for a significant portion of the growing season.

Key words: Export production, net community production, upper bound, mixed layer depth, temperature
1. Introduction

Photosynthesis in excess of respiration at the ocean surface leads to the production of organic matter, part of which is transported to the deep ocean through sinking and mixing (Volk and Hoffert, 1985). This biological process, known as export production (aka soft tissue biological carbon pump) lowers carbon dioxide ($CO_2$) concentrations at the ocean surface and facilitates the flux of $CO_2$ from the atmosphere into the ocean (Falkowski et al., 1998; Ito and Follows, 2005; Sigman and Boyle, 2000).

Export production is frequently assumed to be a function of net community production (NCP) which is defined as the balance between net primary production (NPP) and heterotrophic respiration (HR), or the difference between gross primary production (GPP) and community respiration (CR; HR plus autotrophic respiration (AR)) (the acronyms used in this study are presented in Table 1) (Li and Cassar, 2016):

\[ GPP = CO_2 + H_2O \frac{NCP}{NPP} \frac{HR}{AR} \text{ Organic matter} + O_2 \]  

(1)

\[ \text{Export production} = NCP - MLD \times \frac{d(POC + DOC)}{dt} \]  

(2)

where POC, DOC and MLD represent particulate organic carbon, dissolved organic carbon and mixed layer depth, respectively. If the organic carbon inventory (POC+DOC) in the mixed layer is at steady state, NCP is equal to export production (equation (2)). Without allochthonous sources of organic matter, if the organic matter inventory in the mixed layer decreases, NCP will be predicted to be transiently smaller than export production. Conversely, export may lag NPP (Henson et al., 2015; Stange et al., 2017), in which case NCP is expected to be greater than export production.
Net community production is in great part regulated by the availability of nutrients and light. Light availability exponentially decays with depth due to absorption by water and its constituents. The mixing of phytoplankton to depth therefore impacts phytoplankton physiology and productivity (Cullen and Lewis, 1988; Lewis et al., 1984), with the depth-integrated NPP expected to increase down to the euphotic depth. Respiration, on the other hand, is often modeled to be some function of organic matter concentration, which is expected to be constant with depth if homogenously mixed within the mixed layer. Temperature is also believed to be an important control on carbon export because respiration is more temperature-sensitive than photosynthesis (Laws et al., 2000; López-Urrutia et al., 2006; Rivkin and Legendre, 2001). Field observations confirm that NCP is generally lower at high temperatures and consistently low when mixed layers are deep. These patterns have been attributed to the balance between depth-integrated photosynthesis (controlled by the availability of nutrients and light) and respiration as a function of MLD and temperature (Cassar et al., 2011; Eveleth et al., 2016; Huang et al., 2012; Shadwick et al., 2015; Tortell et al., 2015). However, descriptions of the underlying mechanisms heretofore remain qualitative. Likewise, the effects of light and nutrient on carbon fluxes are difficult to disentangle. For example, high-nutrient, low-chlorophyll regimes in the Southern Ocean have been attributed to iron limitation (Boyd et al., 2000), deep mixed layers and light limitation (Nelson and Smith, 1991; Mitchell and Holm-Hansen, 1991; Mitchell et al., 1991), or both (Sunda and Huntsman, 1997). To decompose the influence of light and nutrient availability on NCP, we define the upper bound on carbon export \((NCP^*)\) from the mixed layer \((NCP^*)\) as the maximum export achievable should all limiting factors other than light (e.g., nutrient taking into account self-shading) be alleviated.
In his seminal paper, Sverdrup presented an elegant model to demonstrate that vernal phytoplankton blooms (i.e., organic matter accumulation at the ocean surface) may be driven by increased light availability when the MLD shoals above a critical depth ($Z_c$) (Sverdrup, 1953). In our study, we build upon Sverdrup (1953) and derive a mechanistic model of an upper bound on carbon export based on the metabolic balance of photosynthesis and respiration in the oceanic mixed layer, where the metabolic balance is derived from with respect to MLD, temperature, photosynthetically active radiation (PAR), phytoplankton maximum growth rate ($\mu_{\text{max}}$), and heterotrophic activity. Our approach is analogous to other efforts where mechanistic models were derived to predict proxies of carbon export (e.g., Dunne et al. (2005) and Cael and Follows (2016)). We compare our $NCP^*$ model to observations, and use this model in conjunction with satellite export production estimates to identify regions in the world’s oceans where light may limit export production. Our key findings are that 1) using parameters available in the literature, the modeled upper bound envelopes field observations of export production estimated from $^{234}$Th and sediment traps and $\text{O}_2$/Ar-derived NCP, and 2) the model identifies regions of the Southern Ocean where carbon export is likely limited by light during part of the growing season.

2. Model description and comparison to observations

2.1. Net community production and light availability

A conceptual representation of the metabolic balance between volumetric NCP, NPP, and HR profiles is presented in Figure 1(A). According to equation (1), the volumetric NCP flux at a given depth ($z$) in the mixed layer results from the difference between volumetric NPP and HR:

$$NCP(z) = NPP(z) - HR(z) \quad (3)$$

where $z$ increases with depth. $NPP(z)$ is a function of the autotroph’s intrinsic growth rate ($\mu$) times their biomass concentration ($C$). Assuming that the effect of nutrients and light on
photosynthetic rates abides by Michaelis-Menten kinetics, and neglecting the effect of
photoinhibition (Dutkiewicz et al., 2001; Huisman and Weissing, 1994), NPP(z) may be
expressed as follows:

\[
NPP(z) = \mu(z) \times C = \frac{N}{N + k_m^N} \times \frac{I(z)}{I(z) + k_m^l} \times \mu_{max} \times C \quad (4)
\]

where \(\mu_{max}\) is the maximum intrinsic growth rate of the autotrophic community; \(N\) and \(k_m^N\)
represent the nutrient concentration and half-saturation constant, respectively; and \(I\) and \(k_m^l\)
represent the irradiance level and half-saturation constant, respectively. \(\mu_{max}, N, k_m^N, k_m^l\) and \(C\)
are assumed to be well mixed within the mixed layer. The first two terms on the right-hand side of
equation (4) account for the effect of nutrient and light availability on autotrophic growth rates,
and they are hereafter defined as follows for simplicity:

\[
N_m = \frac{N}{N + k_m^N} \quad (5a)
\]

\[
l_m(z) = \frac{I(z)}{I(z) + k_m^l} \quad (5b)
\]

\(I(z)\) is modeled as an exponential decay of PAR just beneath the water surface \((I_0)\):

\[
I(z) = I_0 \times e^{-K_L \times z} \quad (6)
\]

where \(K_L\) is diffusion light attenuation coefficient which is assumed to be independent of depth in
the mixed layer.

As a first approximation, we assume that \(HR(z)\) is proportional to \(C\) as in previous studies
(Dutkiewicz et al., 2001; Huisman and Weissing, 1994; Rivkin and Legendre, 2001; Sverdrup,
1953; White et al., 1991):

\[
HR(z) = \tau_{HR} \times C \quad (7)
\]
where $r_{HR}$ represents the intrinsic heterotrophic respiration rate which is assumed to be dependent on temperature (see below), and independent of depth. In reality, $HR(z)$ is likely best modeled as a function of the concentration of labile organic matter — an additional term could be included to account for the relationship of total labile organic matter to $C$.

NCP integrated over the mixed layer ($NCP(0, MLD)$) can be derived from equations (3-7):

\[
NCP(0, MLD) = NPP(0, MLD) - HR(0, MLD)
\]

\[
= \int_0^{MLD} NPP(z)dz - \int_0^{MLD} HR(z)dz
\]

\[
= N_m \times I_m(0, MLD) \times \mu_{max} \times C - r_{HR} \times MLD \times C
\]  

The first term on the right side of equation (8) represents NPP integrated over the mixed layer ($NPP(0, MLD)$), which is equivalent to the product of $\int_0^{MLD} \mu(z)dz$ and $C$, where the former term is modeled to be a function of $\mu_{max}$ conditioned by nutrient and light availability within the mixed layer. $I_m(0, MLD)$ can be derived as follows:

\[
I_m(0, MLD) = \int_0^{MLD} I_m(z)dz = \frac{1}{K_l} \times ln \left( \frac{I_0 \times e^{-K_l \times MLD} + k_m^l}{I_0 + k_m^l} \right)
\]  

NCP integrated over the mixed layer (equation (8)) is a bell-shaped function of MLD as depicted in the schematic diagram of Figure 1(B).

2.2. Net community production and phytoplankton biomass concentration

As can be seen from equation (8), $NCP(0, MLD)$ is a direct function of $C$ because $NPP(0, MLD)$ and $HR(0, MLD)$ are proportional to $C$. $NCP(0, MLD)$ is also an indirect function of $C$ due its effect on light attenuation (i.e., $K_l$). The attenuation coefficient $K_l$ can be divided into water and non-water components ($K_l = K_{lw} + K_{lw}'$) (Baker and Smith, 1982; Smith and Baker, 1978a; Smith and Baker, 1978b), where $K_{lw}'$ is controlled by the concentrations of phytoplankton, colored dissolved organic matter (CDOM), and non-algal particles (NAP). In the open ocean where
CDOM and NAP co-vary with phytoplankton (Morel and Prieur, 1977), $K_t$ can be related to $C$ as follows:

$$K_t = K_t^w + k_c \times C$$ (10)

where $k_c$ is a function of the solar zenith angle, the specific absorption and backscattering coefficients of phytoplankton, and the relationship between phytoplankton, CDOM, and NAP. Because pure water and phytoplankton attenuate light, $K_t^w$ and $k_c$ should be greater than zero.

To calculate how $NCP(0, MLD)$ varies as a function of $C$, we examine its first ($\frac{dNCP(0, MLD)}{dC}$) and second ($\frac{d^2NCP(0, MLD)}{dC^2}$) derivatives with respect to $C$ based on equations (8) and (10):

$$\frac{dNCP(0, MLD)}{dC} = N_m \times \mu_{max} \times \frac{K_t^w \times I_m(0, MLD) + k_c \times C \times MLD \times I_m(MLD)}{K_t^w + k_c \times C} - r_{HR} \times MLD$$ (11)

$$\frac{d^2NCP(0, MLD)}{dC^2} = N_m \times k_c \times \frac{\mu_{max}}{K_t} \times \left\{ \frac{2 \times K_t^w}{K_t} \times (MLD \times I_m(MLD) - I_m(0, MLD)) - \frac{k_c \times C \times I_m(MLD)^2 \times MLD^2 \times k_m}{I_0 \times e^{-K_t \times MLD}} \right\}$$ (12)

when $MLD > 0, I_m(0, MLD) > MLD \times I_m(MLD)$:

$$I_m(0, MLD) = \int_0^{MLD} \frac{I_0 \times e^{-K_t \times x}}{I_0 \times e^{-K_t \times x} + k_m} \, dz$$

$$> \int_0^{MLD} \frac{I_0 \times e^{-K_t \times MLD}}{I_0 \times e^{-K_t \times MLD} + k_m} \, dz = MLD \times I_m(MLD)$$ (13)

The detailed derivation of equations (11-12) can be found in the supplementary material. Substituting the inequality (13) into equation (12) gives $\frac{d^2NCP(0, MLD)}{dC^2} < 0$, which suggests that $\frac{dNCP(0, MLD)}{dC}$ decreases with increasing $C$. Because increasing $C$ decreases light availability due to
shelf-shading, \(NPP(0, \text{MLD})\) saturate with increasing \(C\). Thus, \(NCP(0, \text{MLD})\) will reach an asymptote of \(\lim_{C \to \infty} \left( \frac{dNCP(0, \text{MLD})}{dc} \right) = -r_{HR} \times \text{MLD} < 0\), because \(HR(0, \text{MLD})\) linearly increases with increasing \(C\) while \(NPP(0, \text{MLD})\) plateaus (Figure 2), reaching an asymptote of \(\lim_{C \to \infty} \left( \frac{dNCP(0, \text{MLD})}{dc} \right) = -r_{HR} \times \text{MLD} < 0\) (Figure 2(B)). Additionally, because \(NCP(0, \text{MLD})\) must be nil when there is no autotrophic biomass \((NCP(0, \text{MLD}))|_{C=0} = 0\), \(\lim_{C \to 0} \left( \frac{dNCP(0, \text{MLD})}{dc} \right)\) must be larger greater than zero zero, otherwise the ecosystem would be net heterotrophic which is unachievable without an allochthonous source of organic matter. \(\lim_{C \to 0} \left( \frac{dNCP(0, \text{MLD})}{dc} \right) > 0\) and \(\lim_{C \to \infty} \left( \frac{dNCP(0, \text{MLD})}{dc} \right) = -r_{HR} \times \text{MLD} < 0\) suggest the existence of \(\frac{dNCP(0, \text{MLD})}{dc}|_{C=C^*} = 0\) where \(C^*\) corresponds to an autotrophic biomass concentration which maximizes \(NCP(0, \text{MLD})\) (i.e., \(NCP^*\)).

The dependence of \(NCP(0, \text{MLD})\) on \(C\) can be conceptually understood in the following way. Given a water column with sufficient nutrients, the critical depth \(Z_c\) and compensation depth \(Z_p\) are expected to shoal as \(C\) increases. When \(C\) is low, \(NCP(0, \text{MLD})\) increases with \(C\) because of its greater impact on \(NPP(0, \text{MLD})\) than on \(HR(0, \text{MLD})\). As \(C\) further increases, the increase in \(NPP(0, \text{MLD})\) with \(C\) slows because of light attenuation (i.e., \(K_t\)). There is therefore a \(C^*\) which maximizes the difference between \(NPP(0, \text{MLD})\) and \(HR(0, \text{MLD})\) leading to \(NCP^*\) (Figure 2).

Beyond this point \((C^*)\), further increasing \(C\) will cause self-shading and limit photosynthesis in the deep part of the mixed layer, as a result decreasing \(NCP(0, \text{MLD})\). Beyond a critical biomass \((C_c)\), the ecosystem becomes net heterotrophic. Without an allochthonous source of organic carbon, this is only transiently sustainable.

### 2.3. Mixed layer depth and compensation depth

By definition, if \(NCP(\text{MLD})\) is smaller than zero (i.e., net heterotrophy at the bottom of the mixed layer), the MLD must be deeper than \(Z_p\) \((\text{MLD} > Z_p)\) (and vice versa). To determine the
sign of $\text{NCP}(\text{MLD})$, we substitute inequality (13) into equation (11). According to the inequality presented in equation (13), $\frac{K_l^w \times I_m(0, \text{MLD}) + k_c \times C \times \text{MLD} \times I_m(\text{MLD})}{K_l^w + k_c \times C}$ in equation (11) must be larger than $\frac{K_l^w \times \text{MLD} \times I_m(\text{MLD}) + k_c \times C \times \text{MLD} \times I_m(\text{MLD})}{K_l^w + k_c \times C}$ (which is equal to $\text{MLD} \times I_m(\text{MLD})$). After simple rearrangements, the substitution of inequality (13) into equation (11) leads to:

$$\frac{\text{dNCP}(0, \text{MLD})}{\text{dC}} > \text{MLD} \times (N_m \times I_m(\text{MLD}) \times \mu_{\text{max}} - r_{\text{HR}}) = \frac{\text{MLD}}{C} \times \text{NCP}(\text{MLD})$$

(14)

The inequality in equation (14) in turn suggests that when $\text{NCP}(0, \text{MLD})$ is maximized ($\frac{\text{dNCP}(0, \text{MLD})}{\text{dC}} = 0$), $\text{NCP}(\text{MLD})$ is negative (net heterotrophic) and hence the MLD is deeper than $Z_p$ ($\text{MLD} > Z_p$). This counterintuitive result is attributable both to the uneven distribution of light availability in the water column (equation (13)) and to water which absorbs light but does not contribute to biomass accumulation. When the mixed layer is at the $Z_p$, a slight increase in $C$ will leads to negative $\text{NCP}(\text{MLD})$ due to decreasing light availability at the base of mixed layer, but will increase NCP higher in the water column because of the increase in biomass. The increase in NCP in the shallow parts of the mixed layer therefore overcompensates for the net heterotrophy at the bottom of the mixed layer, thus maximizing the depth-integrated NCP. If light were uniformly distributed in the water column (i.e., $I_m(0, \text{MLD}) = \text{MLD} \times I_m(\text{MLD})$) and if water did not attenuate light ($K_l^w = 0$ in equation (11)), $\text{MLD} = Z_p$ would maximize $\text{NCP}(0, \text{MLD})$, which is consistent with Huisman and Weissing (1994). We note that in equation (14) the NCP profile ($\text{NCP}(z)$) varies with increasing $C$, which is different from what is conceptually presented in Figure 1. The depth-integrated NCP in Figure 1 maximizes at the compensation depth because the NCP profile ($\text{NCP}(z)$) is assumed to be invariant.
2.4. An upper bound on carbon export

Equations (11-13) delineate the conditions for an upper bound on carbon export ($NCP^*$). In order to simplify the relationship of $NCP^*$ to MLD and temperature, we approximate $I_m(0, MLD)$:

$$I_m(0, MLD) = -\frac{1}{K_t} \times \ln \left( 1 + \frac{I_0}{I_0 + k_m^I} \times (e^{-K_t \times MLD} - 1) \right)$$

$$\approx I_m(0) \times \frac{1}{K_t} \times \frac{\exp(-K_t \times MLD)}{\exp(0)} - \frac{1}{K_t} \times \ln(1 - I_m(0))$$

$$\approx I_m(0) \times \frac{1}{K_t}$$

where $I_m(0) = \frac{I_0}{I_0 + k_m^I}$. Based on equation (15), $NCP(0, MLD)$ in equation (8) can be approximated as:

$$NCP(0, MLD) = C \times MLD \times \left( \frac{1}{K_t \times MLD} \times \mu^* - \tau_{HR} \right)$$

where $\mu^* = I_m(0) - \ln(1 - I_m(0)) \times N_m \times \mu_{max}$. To evaluate the approximation accuracy of equation (15), we compare the upper bounds estimated from equation (16) and the original model (equations (8-10)). Our comparison suggests that the approximation of equation (15) is accurate for the estimation of $NCP^*$ under most conditions (Figure 3).

We first need to derive the $C^*$ which maximizes $NCP(0, MLD)$ (i.e., $NCP^*$) in equation (16). $C^*$ can be solved from the first derivative of $NCP(0, MLD)$ in equation (16) with respect to $C$:

$$\frac{dNCP(0, MLD)}{dC} \bigg|_{NCP(0, MLD) = NCP^*} = \mu^* \times \frac{K_t^w}{(k_c \times C^* + K_t^w)^2} - MLD \times \tau_{HR} = 0$$

and therefore:

$$C^* = \frac{1}{k_c} \times \left[ -K_t^w + \sqrt{\frac{\mu^* \times K_t^w}{MLD \times \tau_{HR}}} \right]$$
Equation (18) decreases with MLD. As $C^*$ is positive ($C^* \geq 0$) and cannot go to infinity ($C^* \leq C_{max}^*$), MLD should satisfy $MLD_{C_{max}^*} < MLD \leq \frac{\mu^*}{r_{HR} \times \kappa I}$, where $MLD_{C_{max}^*}$ represents the MLD corresponding to the maximum achievable autotroph’s biomass concentration ($C_{max}^*$) in the surface ocean. The $NCP^*$ model for $0 \leq MLD < MLD_{C_{max}^*}$ is not discussed here, because we do not have data with very shallow MLD to constrain and evaluate the model. The derivation of the model can be found in the supplementary material. Substituting $C^*$ from equation (18) into equation (16):

$$\sqrt{NCP^*} = a_2 \times \frac{ln(1 - \mu_m(0))}{\mu_{max}} + a_1 \times \sqrt{MLD}$$

(19)

where $a_1 = -\sqrt{\frac{\kappa I \times r_{HR}}{k_c}}$ and $a_2 = \sqrt{\frac{N_m \times \mu_{max}}{k_c}}$. Constants $a_1$ and $a_2$ are functions of $r_{HR}$ and $\mu_{max}$, respectively, which are generally modeled to increase with temperature ($T$) (Eppley, 1972; Rivkin and Legendre, 2001):

$$\mu_{max} \propto \mu_{max}^0 \times e^{P_t \times T}$$

(20a)

$$r_{HR} \propto r_{HR}^0 \times e^{B_t \times T}$$

(20b)

where $P_t$ and $B_t$ are constants; and $\mu_{max}^0$ and $r_{HR}^0$ are maximum growth rate and heterotrophic respiration ratio for $T = 0 \, ^\circ C$, respectively. $P_t$ is commonly assumed to equal 0.0663 (Eppley, 1972). Substituting equations (20a) and (20b) into equation (19) yields:

$$\sqrt{NCP^*} = a_4 \times \sqrt{e^{P_t \times T}} \times \sqrt{-ln(1 - \mu_m(0))} + a_3 \times \sqrt{e^{B_t \times T}} \times \sqrt{MLD}$$

(21)

where $a_3 = -\sqrt{\frac{r_{HR}^0 \times \kappa I}{k_c}}$ and $a_4 = \sqrt{\frac{\mu_{max}^0 \times N_m}{k_c}}$. The $NCP^*$ model for $0 \leq MLD < MLD_{C_{max}^*}$ is not discussed here, because we do not have data with very shallow MLD to constrain and evaluate the model. The derivation of the model can be found in the supplementary material.

2.5. Comparison to observations
2.5.1 Data products

We assess the performance of our modeled upper bound on carbon export using a global dataset of MLD, PAR, sea surface temperature (SST), O$_2$/Ar-derived NCP, and export production derived from sediment traps and $^{234}$Th (see supplementary material). MLD was derived from global Argo profiles (Global Ocean Data Assimilation Experiment; http://www.usgodae.org/) and CTD casts (National Oceanographic Data Center; https://www.nodc.noaa.gov/). PAR was downloaded from the NASA ocean color website (https://oceancolor.gsfc.nasa.gov/). The NCP estimates are based on a compilation of O$_2$/Ar measurements from Li and Cassar (2016), Li et al. (2016), Shadwick et al. (2015), and Martin et al. (2013). The POC export production estimates were obtained from the recently compiled dataset of Mouw et al. (2016). These estimates were adjusted to reflect a flux at the base of mixed layer using the Martin curve of organic carbon attenuation with depth (Martin et al., 1987). The constants $k_c$ and $K_l^w$ in equation (10) were derived assuming a carbon to chlorophyll $a$ ratio of 90 (Arrigo et al., 2008) and an empirical linear relationship between $K_l$ and chlorophyll $a$ concentration (see Figure S3), calculated based on the NOMAD dataset (Werdell and Bailey, 2005). $k_m^l$ was set at 4.1 Einstein m$^{-2}$ d$^{-1}$ following Behrenfeld and Falkowski (1997). In our estimation of the upper bound on carbon export, we set $N_m$ to 1 in the NCP$^*$ calculations.

2.5.2 Results and discussion

Overall, we find that NCP$^*$ calculated using published parameters (Laws et al., 2000 Table 2) does a good job of enveloping carbon export observations reported in the literature (Figure 43(A)). Samples on the NCP$^*$ envelope (upper bound) are likely regulated by light availability. Conversely, points below the upper bound may be nutrient or in some cases light-limited. As expected, NCP$^*$ increases with $\mu_{max}$ and decreases with $r_{HR}$. Model parameters $a_1 = -1.80$ and $a_2 = 21.381.4.75$ (equation (19)) provide the best fit to the upper bound on O$_2$/Ar-NCP and as a
function of MLD. When compared to parameters available in the literature (Table 2), we find that the best fit to our modeled upper bound is using $\mu_{max}$ and $r_{HR}$ of 1.2 d$^{-1}$ and 0.2 d$^{-1}$, respectively. When accounting for the effect of $T$ on $\mu_{max}$ and $r_{HR}$, model constants $a_3 = -1.66 - 1.53$ and $a_4 = 20.4013.39$ (equation (21)) best fit the upper bound on $O_2$/Ar-NCP, SST and MLD observations.

Our results show that $NCP^*$ decreases faster with increasing MLD in warmer waters (Figures 43(B) and 4(C)), because the term $a_3 \times \sqrt{e^{B_t \times T}}$ in equation (21) is negative and negatively correlated to $T$. This temperature effect contributes to part of the relationship between export production and MLD in Figure 43(A). Interestingly, $NCP^*$ increases with $T$ in colder waters and shallow mixed layers (Figure 4(C)). This is because $NCP^*$ reflects the balance between productivity $(a_4 \times \sqrt{e^{P_t \times T}} \times \sqrt{-\ln(1 - I_m(0))I_m(0)})$ and heterotrophic respiration $(a_3 \times \sqrt{e^{B_t \times T}} \times \sqrt{MLD})$. In a shallow cold mixed layer, the change in productivity with $T$ $d \left( a_4 \times \sqrt{e^{P_t \times T}} \times \sqrt{-\ln(1 - I_m(0))I_m(0)} \right) / dT = \frac{P_t}{2} \times a_4 \times \sqrt{e^{P_t \times T}} \times \sqrt{-\ln(1 - I_m(0))I_m(0)}$ is greater than that of heterotrophic respiration $d \left( a_3 \times \sqrt{e^{B_t \times T}} \times \sqrt{MLD} \right) / dT = \frac{B_t}{2} \times a_3 \times \sqrt{e^{B_t \times T}} \times \sqrt{MLD})$. These results could explain part of the variability in the relationship between NCP and SST reported in previous studies (Li and Cassar, 2016). Our $NCP^*$ model does not perform as well in warmer deep mixed layers, where high variability in export ratio maxima have also been reported (Cael and Follows, 2016). This may stem from uncertainties in observations, the differing relationship between $T$, $\mu_{max}$, and $r_{HR}$ at high temperature, and/or violations of our assumptions (see caveats and limitations).
Several recent studies have explored the relationship of NCP to oceanic parameters based on various statistical approaches (Cassar et al., 2015; Chang et al., 2014; Huang et al., 2012; Li and Cassar, 2016; Li et al., 2016). Our model can shed some light into the mechanisms driving some of these patterns. To that end, we substitute equation (159) into equation (8):

\[ NCP(0, MLD) = C \times MLD \times \left( -\frac{N_m \times \mu_{max}}{K_i \times MLD} \times \ln \left( \frac{l_0 \times e^{-K_i \times MLD} + k_m^l}{l_0 + k_m^l} \right) - r_{HR} \right) \]  

(22)

Rearranging equation (22):

\[ NCP_B = \frac{NCP(0, MLD)}{C \times MLD} = -\frac{\ln \left( \frac{l_0 \times e^{-K_i \times MLD} + k_m^l}{l_0 + k_m^l} \right)}{l_0 \times (1 - e^{-K_i \times MLD})} \times N_m \times \mu_{max} \times PAR_{ML} - r_{HR} \]  

(23)

where \( NCP_B \) is the biomass-normalized volumetric NCP, \( PAR_{ML} \) is the average PAR in the mixed layer (\( PAR_{ML} = \frac{1-e^{-K_i \times MLD}}{K_i \times MLD} \times l_0 \)), and \(-\frac{\ln \left( \frac{l_0 \times e^{-K_i \times MLD} + k_m^l}{l_0 + k_m^l} \right)}{l_0 \times (1 - e^{-K_i \times MLD})} \) correspond to the slope and offset, respectively. The scatter in the relationship between chlorophyll-normalized volumetric NCP and \( PAR_{ML} \), as reported in previous studies (Bender et al., 2016), can likely be explained by the effect of temperature and the availability of nutrient and light (among other properties) on the slope and offset of equation (23). Equation (22) can also be reorganized to assess how environmental conditions may impact the export ratio (\( ef \)):

\[ ef = \frac{NCP(0, MLD)}{NPP(0, MLD)} = 1 - \frac{K_i \times MLD}{-\ln \left( \frac{l_0 \times e^{-K_i \times MLD} + k_m^l}{l_0 + k_m^l} \right)} \times \frac{1}{N_m \times \mu_{max}} \times \frac{r_{HR}}{r_{HR}} \]  

(24)

where \( \frac{r_{HR}}{\mu_{max}} \) is proportional to \( e^{(R_t-P_t)\times T} \). Equation (24) is consistent with multiple studies which predict decreasing \( ef \) with increasing temperature (Cael and Follows, 2016; Dunne et al., 2005; Henson et al., 2011; Laws et al., 2000; Li and Cassar, 2016). In fact, equation (5) of Cael and Follows (2016) can easily be derived from equation (24) (see supplementary material). Equation
(24) also highlights that a multitude of factors may confound the dependence of $e_f$ on temperature (including varying MLD, light attenuation, and availability of nutrient and light). This again may explain some of the conflicting observations recently reported in the literature (e.g., Maiti et al. (2013)), where the effect of temperature may be masked by changes in community composition (Britten et al., 2017; Henson et al., 2015). One therefore needs to account or correct for the multitude of confounding factors when predicting the effect of a given environmental condition (e.g., temperature, mineral ballast, and NPP) on the export ratio.

3. Spatial distribution of the upper bound on carbon export

We estimate the global distribution of the upper bound of carbon export using equation (19) and climatological monthly MLD and PAR. In general, $NCP^*$ is high in low latitudes and low in the North Atlantic and Antarctic Circumpolar Current (ACC) in the Southern Ocean (Figure 54(A)). As expected, this spatial pattern is controlled by MLD (see Figure S1). Satellite-derived estimates of NCP (Li and Cassar, 2016) are approximately 10% of global $NCP^*$, reflecting the high degree of nutrient limitation in the oceans. We also derive a global $NCP^*$ map using equation (21), and find that the global $NCP^*$ estimate is very sensitive to the temperature dependence of $r_{HR}$. For example, decreasing the $B_t$ in $r_{HR} = r_{HR}^0 \times e^{B_t(T \times T)}$ from 0.11 to 0.08 (as used in Rivkin and Legendre (2001) and López-Urrutia et al. (2006)) increases the global $NCP^*$ budget by a factor of 2.4. Large differences in $NCP^*$ in low-latitudes in great part explain this change. In light of the large uncertainties in the relationship between $r_{HR}$ and $T$ (Cael and Follows, 2016; López-Urrutia et al., 2006), we hereafter only discuss $NCP^*$ estimates derived from equation (19).

To estimate how close export production is to its upper bound, we calculate the ratio of export production to $NCP^*$ ($f_{pt}$). Low $f_{pt}$ regimes represent ecosystems likely regulated by nutrient availability (i.e., ecosystems that have not reached their full export potential based on MLD and
surface PAR). As expected, low latitude and subtropical regions have low $f_{pt}$ (Figure 54(B)). High $f_{pt}$ regimes represent ecosystems which have reached their full light potential, and are therefore less likely to respond to nutrient addition because of light limitation (e.g., North Atlantic and ACC (Figure 54(B))). In these regions, especially the subantarctic region, $f_{pt}$ is high in the spring (Figure 54(C)) and decreases in the summer (Figure 54(D)), suggesting that export production is likely co-limited by nutrient and light availability. This may in part explain the lower response to iron fertilization in the subantarctic region where substantial increases in surface chlorophyll were only observed in regions with shallower mixed layers (Boyd et al., 2007; Boyd et al., 2000; de Baar et al., 2005).

Also shown in Figure 54 are the biological pump efficiency and export ratio $ef$ (panels 54E and 54F, respectively). These various proxies reflect different components of the biological pump. Whereas $f_{pt}$ reflects the export potential based on current MLD and light availability, the biological pump efficiency reflects the potential as derived from nutrient distribution in the oceans, estimated from the extent of nutrient removal from the surface ocean (Sarmiento and Gruber, 2006) or the proportion of regenerated nutrients at depth (Ito and Follows, 2005). A revised estimate of the global biological pump efficiency, estimated based on the proportion of regenerated to total nutrients (preformed + regenerated) at depth is around 30-35% (Duteil et al., 2013). The $ef$ ratio on the other hand describes how much of production is exported as opposed to recycled in the surface (Dunne et al., 2005). The ultra-oligotrophic subtropical waters have a low export ratio, a strong biological pump efficiency with exhaustion of nutrients at the ocean surface, and therefore have not reached their full light potential (low $f_{pt}$) because of the strong stratification and nutrient limitation. The seasonal pattern of $f_{pt}$ in the subantarctic region suggests that the low biological
pump efficiency is the result of light limitation in the austral spring and nutrient (likely Fe) and light limitation in the austral summer.

4. Caveats and limitations

There are a multitude of uncertainties, simplifications, and approximations in our model and field observations may explain some of the discrepancies between the predicted and observed NCP*. Among others:

- In our study, we used a model which builds on Sverdrup’s critical depth hypothesis. There are competing hypotheses to explain phytoplankton bloom phenology (timing and intensity), including the “dilution recoupling hypothesis” or “disturbance recovery hypothesis” (Behrenfeld, 2010; Boss and Behrenfeld, 2010) and “critical turbulence hypothesis” (Brody and Lozier, 2015; Huisman et al., 1999; Taylor and Ferrari, 2011). In the case of top-down control, any respiratory grazing loss not accounted for by our loss term would behave as a system not reaching its full light potential (NCP*). Conversely, any grazing loss associated with export (e.g., rapidly sinking fecal pellets and other zooplankton-mediated export pathways) would minimize respiratory losses thereby bringing NCP closer to its upper bound based on light-availability. These opposing effects are beyond the scope of this study, but could be modeled, especially as we learn more about their impacts on carbon fluxes through new efforts such as NASA’s EXPORTS program (Siegel et al., 2016). See also the point below on mixing vs. mixed layer depth.

- Phytoplankton biomass concentration (C) may vary with depth in the mixed layer, especially for water columns experiencing varying degrees of turbulent mixing. In addition, MLD is not always the best proxy of light availability with mixing layer in some cases.
deviating from the mixed layer (Franks, 2015; Huisman et al., 1999). The factors defining the MLD also vary in different oceanic regions.

- For simplicity, we model the dependence of photosynthesis on irradiance assuming Michaelis-Menten kinetics, which does not account for photoinhibition. More accurate models can be found in other studies (Platt et al., 1980). Due to optional absorption, $K_I$ also varies with depth in the mixed layer. Additionally, the linear relationship between $K_I$ and $C$ is influenced by CDOM, NAP, and other environmental factors (e.g., solar zenith angle) (Gordon, 1989).

- $\mu_{max}$ and $T_{HR}$ are influenced by environmental factors other than temperature, including community structure (Chen and Laws, 2017), and may vary with depth within the mixed layer (Smetacek and Passow, 1990). For these reasons, the equations relating $\mu_{max}$ and $T_{HR}$ (i.e., $B_t$ and $P_t$) to temperature also carry significant uncertainties (Bissinger et al., 2008; Edwards et al., 2016; Kremer et al., 2017; López-Urrutia and Morán, 2007; Rivkin and Legendre, 2001) which impacts our estimates of the upper bound on carbon export, especially in warmer regions. As in other recent studies (Cael and Follows, 2016; Cael et al., 2017; Dutkiewicz et al., 2001; Gong et al., 2015; Gong et al., 2017; Huisman et al., 2006; Taylor and Ferrari, 2011), we model heterotrophic respiration to vary in proportion to phytoplankton concentration. The model could be further improved by explicitly including the concentration of heterotrophs. See point above on the grazing effect on export with regards to $T_{HR}$.

- NCP may underestimate export production when accompanied by a decrease in the inventory of organic matter in the mixed layer (see introduction and equation (2)).
Our field observations are limited, mostly focusing on the spring and summer seasons, and harbor significant uncertainties. For example, deep mixed layers can bias the O$_2$/Ar method low if entrainment of deeper waters brings low O$_2$ into the mixed layer. Descriptions of these uncertainties are presented in other studies (Bender et al., 2011; Cassar et al., 2014; Jonsson et al., 2013).

Finally, our study is only relevant to the mixed layer. It does not account for productivity below the mixed layer, which can be important in some regions such as the subtropical ocean.

5. Conclusions

In this study, we derived a mechanistic model of an upper bound on carbon export ($NCP^*$) based on the metabolic balance between photosynthesis and respiration of the plankton community. The upper bound is a positively skewed bell-shaped function of mixed layer depth (MLD). At low temperatures, the upper bound decreases with temperature if mixed layers are deep, but increases with temperature if mixed layers are shallow. We used this model to derive a global distribution of an upper bound on carbon export as a function of MLD and surface PAR, which shows high values in low latitudes and low values in high latitudes due to deep MLD. To examine how current export production compares to this upper bound in the world’s oceans, we calculated the ratio of satellite export production estimates to the upper bound derived by our model. High ratios of export production to $NCP^*$ in the North Atlantic and ACC indicate that export production in these regions is likely co-limited by nutrient and light availability. Overall, our results may explain differences in carbon export measured during past iron fertilization experiments (e.g., subantarctic and polar regions), inform future iron fertilization experiments, and help in the development of remotely-
sensed carbon export algorithms, and improve predictions of the response of marine ecosystems to a changing climate.

Acknowledgements

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Stange, P., Bach, L. T., Le Moigne, F. A. C., Taucher, J., Boxhammer, T., and Riebesell, U.: Quantifying the time lag between organic matter production and export in the surface ocean:


Figure 1. Schematic diagram of depth-profiles of net community production (NCP), net primary production (NPP), and heterotrophic respiration (HR). Yellow and black dots represent the compensation and critical depths, respectively.
Figure 2. Relationship between net primary production (NPP), heterotrophic respiration (HR), net community production (NCP), and phytoplankton biomass concentration (C) for a given mixed layer depth (MLD). Hatched area in panel A represents NCP. The yellow dot represents the maximal NCP (NCP*) obtainable for a given MLD, with the corresponding phytoplankton biomass concentration (C*) denoted with a cyan dot. NCP on the right of the yellow dot decreases with C due to self-shading. Black dot represents depth-integrated NCP =0 (i.e., NPP=HR), with the corresponding phytoplankton biomass concentration defined as critical biomass (C_c) and denoted with a blue dot. Ecosystems on the left and right of this threshold are net autotrophic and heterotrophic, respectively. The asymptote (dashed blue line) in panel B represents a system dominated by heterotrophic respiration (i.e., NCP \approx HR >> NPP).
Figure 3. Upper bounds derived using the original and approximated models. The upper bound for the original model (equations (8-10)) is estimated through a non-linear optimization approach. The upper bound for the approximated model is calculated analytically from equation (19). The models use the constants listed in Table 2 and $I_m(0) = 0.9$. Decreasing $I_m(0)$ and increasing $r_{HR}$ results in greater discrepancies between the original and approximated models in regions with shallow mixed layers.
Figure 4. Envelope of the modeled upper bound on carbon export production compared to field observations as a function of mixed layer depth (MLD) and sea surface temperature (SST).

(A) The thick gray line represents the upper bound fitted to the net community production (NCP) data. Dash-lines represent the upper bounds calculated using parameters available in the literature (Table 2). (B) NCP as a function of SST with isopleths of constant upper bounds color coded for MLD. NCP observations are color coded with MLD. (C) Surface representing the envelope of the modeled upper bound of carbon export production as a function of SST and MLD. Bars represent field observations color coded with the ratio of NCP to the upper bound.
Observations are based on $^{234}$Th and sediment traps estimates of carbon export production and O$_2$/Ar-derived NCP. A stoichiometric ratio of O$_2$/C=1.4 was used to convert NCP from O$_2$ to C units (Laws, 1991). To account for the effect of PAR on export production, both MLD and carbon fluxes are normalized to $-\log(1 - I_m(0))$ (see equations (19) and (21)). The temperature dependence of $r_{HR}$ was modeled as $r_{HR} = r_{HR}^0 \times e^{-0.08 \times T}$. 
Figure 5. (A) Modeled upper bound on carbon export derived from equation (19), (B-D) ratios of satellite export production estimates to the upper bound on carbon export, (E) biological pump efficiency calculated as the difference in nutrient concentrations between surface and depth, normalized to nutrient concentrations at depth (Sarmiento and Gruber, 2006) (nitrate concentration from World Ocean Atlas (https://www.nodc.noaa.gov/OC5/woa13/)), and (F) export ratio derived from Dunne et al. (2005). Annual represents annually-integrated value. Spring and summer represent average value in spring and summer, respectively. In the northern hemisphere, spring and summer seasons are defined as March-May and June-August, respectively. In the southern hemisphere, spring and summer seasons are defined as September-November and December-February, respectively.
Table 1. Model symbols, abbreviations, and units

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLD</td>
<td>Mixed layer depth</td>
<td>m</td>
</tr>
<tr>
<td>$MLD_{c_{max}}$</td>
<td>Maximum MLD corresponds to maximum achievable autotroph’s biomass concentration</td>
<td>m</td>
</tr>
<tr>
<td>z</td>
<td>Depth</td>
<td>m</td>
</tr>
<tr>
<td>$Z_{c}$</td>
<td>Critical depth</td>
<td>m</td>
</tr>
<tr>
<td>$Z_{p}$</td>
<td>Compensation depth</td>
<td>m</td>
</tr>
<tr>
<td>GPP(0,z)</td>
<td>Gross primary production</td>
<td>mmol C m$^{-2}$ d$^{-1}$</td>
</tr>
<tr>
<td>NPP(z)</td>
<td>Net primary production at depth z</td>
<td>mmol C m$^{-3}$ d$^{-1}$</td>
</tr>
<tr>
<td>NPP(0,z)</td>
<td>Net primary production above depth z</td>
<td>mmol C m$^{-3}$ d$^{-1}$</td>
</tr>
<tr>
<td>NCP(z)</td>
<td>Net community production at depth z</td>
<td>mmol C m$^{-3}$ d$^{-1}$</td>
</tr>
<tr>
<td>NCP(0,z)</td>
<td>Net community production above depth z</td>
<td>mmol C m$^{-3}$ d$^{-1}$</td>
</tr>
<tr>
<td>HR(z)</td>
<td>Heterotrophic respiration at depth z</td>
<td>mmol C m$^{-3}$ d$^{-1}$</td>
</tr>
<tr>
<td>HR(0,z)</td>
<td>Heterotrophic respiration above depth z</td>
<td>mmol C m$^{-3}$ d$^{-1}$</td>
</tr>
<tr>
<td>NCP*</td>
<td>The maximum NCP for a given MLD (upper bound on carbon export)</td>
<td>mmol C m$^{-3}$ d$^{-1}$</td>
</tr>
<tr>
<td>$NCP_{B}$</td>
<td>NCP normalized to autotroph’s biomass inventory in the mixed layer</td>
<td>d$^{-1}$</td>
</tr>
<tr>
<td>$ef$</td>
<td>Export ratio</td>
<td>unitless</td>
</tr>
<tr>
<td>$f_{pt}$</td>
<td>Ratio of satellite export production estimates to the upper bound on carbon export</td>
<td>unitless</td>
</tr>
<tr>
<td>N</td>
<td>Nutrient concentration</td>
<td>mmol m$^{-3}$</td>
</tr>
<tr>
<td>$k^N_{m}$</td>
<td>Half-saturation constant for nutrient concentration</td>
<td>mmol m$^{-3}$</td>
</tr>
<tr>
<td>$N_m$</td>
<td>Nutrient effect on phytoplankton grow $N_m = \frac{N}{N + k^N_{m}}$</td>
<td>unitless</td>
</tr>
<tr>
<td>PAR</td>
<td>Photosynthetically active radiation</td>
<td>Einstein m$^{-2}$ d$^{-1}$</td>
</tr>
<tr>
<td>$I_0$</td>
<td>Photosynthetically active radiation just beneath water surface</td>
<td>Einstein m$^{-2}$ d$^{-1}$</td>
</tr>
<tr>
<td>$I(z)$</td>
<td>Photosynthetically active radiation at depth z</td>
<td>Einstein m$^{-2}$ d$^{-1}$</td>
</tr>
<tr>
<td>$k^I_{m}$</td>
<td>Half-saturation constant for irradiance</td>
<td>Einstein m$^{-2}$ d$^{-1}$</td>
</tr>
<tr>
<td>$I_m(z)$</td>
<td>Light effect on phytoplankton grow at depth $z$, $I_m(z) = \frac{I(z)}{I(z) + k^I_{m}} = \frac{l_0 \times e^{-K_l z}}{l_0 \times e^{-K_l z} + k^I_{m}}$</td>
<td>unitless</td>
</tr>
<tr>
<td>$I_m(0,z)$</td>
<td>Integrated light effect on phytoplankton grow above depth $z$, $I_m(0,z) = -\frac{1}{K_l} \times ln \left( \frac{l_0 \times e^{-K_l z} + k^I_{m}}{l_0 + k^I_{m}} \right)$</td>
<td>unitless</td>
</tr>
<tr>
<td>$PAR_{ML}$</td>
<td>Average PAR in the mixed layer ($PAR_{ML} = \frac{1 - e^{-K_l \times MLD}}{K_l \times MLD} \times I_0$)</td>
<td>Einstein m$^{-2}$ d$^{-1}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Phytoplankton growth rate</td>
<td>d$^{-1}$</td>
</tr>
<tr>
<td>$\mu_{max}$</td>
<td>Maximum phytoplankton growth rate</td>
<td>d$^{-1}$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------------------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>$\mu_{max}^0$</td>
<td>Maximum phytoplankton growth rate for $T = 0 ^\circ C$</td>
<td>d$^{-1}$</td>
</tr>
<tr>
<td>$r_{HR}$</td>
<td>Heterotrophic respiration ratio</td>
<td>d$^{-1}$</td>
</tr>
<tr>
<td>$r_{HR}^0$</td>
<td>Heterotrophic respiration ratio for $T = 0 ^\circ C$</td>
<td>d$^{-1}$</td>
</tr>
<tr>
<td>$K_t$</td>
<td>Diffusion-Light attenuation coefficient ($K_t = K_t^w + K_t^{nw}$)</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$K_t^w$</td>
<td>Diffusion-Light attenuation coefficient due to water</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$K_t^{nw}$</td>
<td>Diffusion-Light attenuation coefficient due to optically active components</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$k_e$</td>
<td>Specific attenuation coefficient for irradiance</td>
<td>m$^2$ mmol$^{-1}$</td>
</tr>
<tr>
<td>$C$</td>
<td>Phytoplankton biomass concentration</td>
<td>mmol m$^{-3}$</td>
</tr>
<tr>
<td>$C^*$</td>
<td>Phytoplankton biomass concentration that maximizes NCP</td>
<td>mmol m$^{-3}$</td>
</tr>
<tr>
<td>$C_{max}^*$</td>
<td>Maximum achievable autotroph’s biomass concentration</td>
<td>mmol m$^{-3}$</td>
</tr>
<tr>
<td>POC</td>
<td>Particulate organic carbon</td>
<td>mmol m$^{-3}$</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
<td>mmol m$^{-3}$</td>
</tr>
<tr>
<td>CDOM</td>
<td>Colored dissolved organic matter</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>NAP</td>
<td>Non-algal particles</td>
<td>mmol m$^{-3}$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>$^\circ C$</td>
</tr>
<tr>
<td>$P_t$</td>
<td>Temperature dependence for phytoplankton growth rate</td>
<td>$^\circ C^{-1}$</td>
</tr>
<tr>
<td>$B_t$</td>
<td>Temperature dependence for heterotrophic respiration ratio</td>
<td>$^\circ C^{-1}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
<td>ppmv</td>
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### Table 2. Value or range of values with references for the parameters used in the model.

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<thead>
<tr>
<th>Parameter</th>
<th>Range or value</th>
<th>Reference</th>
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<tbody>
<tr>
<td>$K_f^w$</td>
<td>0.09</td>
<td>(Werdell and Bailey, 2005)</td>
</tr>
<tr>
<td>$k_t$</td>
<td>0.03</td>
<td>(Werdell and Bailey, 2005)</td>
</tr>
<tr>
<td>Carbon to chlorophyll ratio</td>
<td>90</td>
<td>(Arrigo et al., 2008)</td>
</tr>
<tr>
<td>$k_{lp}$</td>
<td>4.1 Einstein m$^{-2}$ d$^{-1}$</td>
<td>(Behrenfeld and Falkowski, 1997)</td>
</tr>
<tr>
<td>$P_t$</td>
<td>0.0663</td>
<td>(Eppley, 1972)</td>
</tr>
<tr>
<td>$B_t$</td>
<td>0.08</td>
<td>(Rivkin and Legendre, 2001; López-Urrutia et al., 2006)</td>
</tr>
<tr>
<td>$\mu_{max}$</td>
<td>1 d$^{-1}$, 1.2 d$^{-1}$</td>
<td>(Laws et al., 2000; Eppley, 1972)</td>
</tr>
<tr>
<td>$\tau_{HR}$</td>
<td>0.1 d$^{-1}$, 0.2 d$^{-1}$</td>
<td>(Laws et al., 2000; Mitchell et al., 1991)</td>
</tr>
</tbody>
</table>
Supplementary for: A mechanistic model of an upper bound on oceanic carbon export as a function of mixed layer depth and temperature

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1. Derivation of first and second derivatives of \(\text{NCP}(0,\text{MLD})\)

To explore how \(\text{NCP}(0,\text{MLD})\) varies with \(C\), we calculate its first and second derivatives with respect to \(C\).

Based on equations (8-10):

\[
\frac{d\text{NCP}(0,\text{MLD})}{dC} = -N_m \times \mu_{\text{max}} \times \ln\left(\frac{I_0 \times e^{-K_i \times \text{MLD}} + k_i^l}{I_0 + k_i^l}\right) \times C
\]

\[
\frac{d}{dC}\left\{-N_m \times \mu_{\text{max}} \times \ln\left(\frac{I_0 \times e^{-K_i \times \text{MLD}} + k_i^l}{I_0 + k_i^l}\right) \times C\right\} = -\frac{d(r_{HR} \times C \times \text{MLD})}{dC}
\]

\[
= -N_m \times \mu_{\text{max}} \times \left\{-K_i \times I_m(0,\text{MLD}) - C \times I_m(\text{MLD}) \times k_c \times \text{MLD}\right\} \times K_i
\]

\[
= N_m \times \mu_{\text{max}} \times K_i \times I_m(0,\text{MLD}) + k_c \times C \times I_m(\text{MLD}) \times \text{MLD} - k_c \times C \times K_i \times I_m(0,\text{MLD})
\]

\[
= N_m \times \mu_{\text{max}} \times \frac{K_i \times I_m(0,\text{MLD}) - k_c \times C \times I_m(0,\text{MLD}) + k_c \times C \times \text{MLD} \times I_m(\text{MLD})}{K_i}
\]

\[
= N_m \times \mu_{\text{max}} \times \frac{K_i^w \times I_m(0,\text{MLD}) + k_c \times C \times \text{MLD} \times I_m(\text{MLD})}{K_i} - r_{HR} \times \text{MLD}
\]

where \(I_m(\text{MLD}) = \frac{I_0 \times e^{-K_i \times \text{MLD}}}{I_0 \times e^{-K_i \times \text{MLD}} + k_i^l}\).

Based on equation (S1), the second derivative of \(\text{NCP}(0,\text{MLD})\) in equation (8) with respect to \(C\) may be expressed as follows:

\[
\frac{d^2 \text{NCP}(0,\text{MLD})}{dC^2} = N_m \times \mu_{\text{max}} \times \left(\frac{d}{dC} + \frac{d}{dC}\right)
\]

\[
\frac{d}{dC} \quad \text{and} \quad \frac{d}{dC} \quad \text{are derived as follows:}
\]
\[
\frac{dy}{dC} = -K_i^w \times \frac{l_0 + k_m^l}{l_0 \times e^{-K_i \times MLD} + k_m^l} \times \frac{l_0 \times e^{-K_i \times MLD}}{l_0 + k_m^l} \times (-k_c \times MLD) \times K_i^2 - \ln \left( \frac{l_0 \times e^{-K_i \times MLD} + k_m^l}{l_0 + k_m^l} \right) \times 2 \times K_i \times k_c
\]

\[
= -K_i^w \times \frac{-l_m(MLD) \times MLD \times K_i^2 + I_m(0, MLD) \times 2 \times K_i^2}{K_i^4}
\]

\[
= K_i^w \times \frac{l_m(MLD) \times MLD - 2 \times I_m(0, MLD) \times k_c}{K_i^2} \quad (S3)
\]

\[
\frac{dg}{dC}
\]

\[
= -k_c \times C \times MLD \times I_m(MLD) \times k_c + k_c \times MLD \times I_m(MLD) \times K_i
\]

\[
= \frac{k_c \times MLD \times I_m(MLD) \times K_i}{K_i^2}
\]

\[
+ \frac{l_0 \times e^{-K_i \times MLD} \times (-k_c \times MLD) \times \{l_0 \times e^{-K_i \times MLD} + k_m^l\} - l_0 \times e^{-K_i \times MLD} \times l_0 \times e^{-K_i \times MLD} \times (-k_c \times MLD) \times K_i}{(l_0 \times e^{-K_i \times MLD} + k_m^l)^2}
\]

\[
= \frac{k_c \times MLD \times I_m(MLD) \times K_i + k_c \times C \times MLD \times \frac{l_0 \times e^{-K_i \times MLD} \times (-k_c \times MLD) \times k_m^l}{l_0 \times e^{-K_i \times MLD} + k_m^l} \times K_i - k_c \times C \times MLD \times I_m(MLD)}{K_i^2}
\]

\[
= \frac{MLD \times I_m(MLD) \times K_i + k_c \times C \times MLD \times \frac{-l_m(MLD)^2 \times MLD \times k_m^l}{l_0 \times e^{-K_i \times MLD}} \times K_i - k_c \times C \times MLD \times I_m(MLD)}{K_i^2}
\]

\[
= \frac{MLD \times I_m(MLD) \times K_i - k_c \times C \times MLD \times I_m(MLD)}{K_i^2} \times k_c - \frac{k_c \times C \times MLD \times \frac{l_m(MLD)^2 \times MLD \times k_m^l}{l_0 \times e^{-K_i \times MLD}} \times K_i}{K_i^2} \times k_c
\]

\[
= \frac{MLD \times I_m(MLD) \times K_i^w}{K_i^2} \times k_c - \frac{MLD^2 \times C \times I_m(MLD)^2 \times k_m^l}{K_i \times l_0 \times e^{-K_i \times MLD}} \times k_c^2 \quad (S4)
\]

Substituting equations (S3-S4) into equation (S2) yields:

\[
\frac{d^2 NCP(0, MLD)}{dC^2}
\]

\[
= N_m \times \mu_{\text{max}} \times \left\{ K_i^w \times \frac{l_m(MLD) \times MLD - 2 \times I_m(0, MLD)}{K_i^2} \times k_c + \frac{MLD \times I_m(MLD) \times K_i^w}{K_i^2} \times k_c - \frac{MLD \times C \times I_m(MLD)^2 \times k_m^l}{K_i \times l_0 \times e^{-K_i \times MLD}} \times k_c \right\}
\]

\[
= N_m \times \frac{\mu_{\text{max}}}{K_i} \times k_c \times \left\{ \frac{2 \times K_i^w}{K_i} \times (l_m(MLD) \times MLD - I_m(0, MLD)) - \frac{MLD^2 \times C \times I_m(MLD)^2 \times k_m^l}{l_0 \times e^{-K_i \times MLD}} \times k_c \right\} \quad (S5)
\]

**2. NCP upper bound for shallow MLD**
When \(0 \leq \text{MLD} < \text{MLD}_{c_{\text{max}}}\) and \(\text{MLD} \to 0\), \(1 - \exp(-K_i \times \text{MLD})\) in equation (15) can be approximated using a second order of Taylor expansion:

\[
1 - \exp(-K_i \times \text{MLD}) \approx K_i \times \text{MLD} - \frac{1}{2} \times (K_i \times \text{MLD})^2 \quad (S6)
\]

From equation (S6), we may approximate equation (15):

\[
NCP(0, \text{MLD}) = C \times \text{MLD} \times \left(- \frac{1}{2} \times K_i \times \text{MLD} \times \mu^* + \mu^* - r_{HR}\right) \quad (S7)
\]

where the first derivative of equation (S7) with respective to \(C\) is:

\[
\frac{dNCP(0, \text{MLD})}{dC} = \text{MLD} \times \left(-K_i^{nw} \times \text{MLD} \times \mu^* - \frac{1}{2} \times K_i^{w} \times \text{MLD} \times \mu^* + \mu^* - r_{HR}\right) \quad (S8)
\]

when \(0 \leq \text{MLD} < \text{MLD}_{c_{\text{max}}}\), \(K_i^{nw}\) should satisfy \(K_i^{nw} \leq k_c \times C_{\text{max}} < -\frac{1}{2} \times K_i^{w} + \frac{\mu^*-r_{HR}}{\mu^*} \times \frac{1}{\text{MLD}}\), and equation (S8) should be greater than 0. \(NCP(0, \text{MLD})\) thus increases with \(C\) in the range of \(0 \leq \text{MLD} < \text{MLD}_{c_{\text{max}}}\), with an upper bound obtained at \(C_{\text{max}}^*\):

\[
NCP^* = \mu^* \times C_{\text{max}}^* \times \text{MLD} \times \left(- \frac{1}{2} \times (k_c \times C_{\text{max}}^* + K_i^{w}) \times \text{MLD} + \frac{\mu^* - r_{HR}}{\mu^*}\right) \quad (S9)
\]

Over this range, Equation (S9) states that \(NCP^*\) increases with \(\text{MLD}\), and as expected is nil when \(\text{MLD}\) equals 0.

3. An upper bound on export ratio

The export ratio ef (equation (24)) is written as follows:

\[
ef = \frac{NCP(0, \text{MLD})}{NPP(0, \text{MLD})} = 1 - \frac{K_i \times \text{MLD}}{-\ln \left(\frac{I_0 \times e^{-K_i \times \text{MLD}} + k_{I_m}}{I_0 + k_{I_m}}\right)} \times \frac{1}{N_m} \times \frac{r_{HR}}{\mu_{\text{max}}} \quad (S10)
\]

where \(\text{MLD}_{\text{opt}} = \frac{K_i \times \text{MLD}}{1 - e^{-K_i \times \text{MLD}}}\). The first derivative of \(\frac{d\ef}{d\text{MLD}}\) with respect to \(K_i \times \text{MLD}\) is expressed as:

\[
\frac{\partial \ef}{\partial C} = -\left(1 - \frac{\text{MLD} \times I_m(\text{MLD})}{I_m(0, \text{MLD})}\right) \times \frac{1}{K_i} \times k_c \times (1 - \ef) \quad (S11)
\]

Because \(e^{K_i \times \text{MLD}} > 1 + K_i \times \text{MLD}\) for \(K_i \times \text{MLD} > 0\), According to the inequality in equation (13), \(\frac{\partial \ef}{\partial C}\) in equation (S11) must be less than 0-zero. Therefore, minimum of \(\frac{d\ef}{d\text{MLD}}\) approximates to \(1\) maximizes when \(K_i \times \text{MLD} \to 0\) \((\ef = 1 - \frac{1}{I_m(0)} \times \frac{1}{N_m} \times \frac{r_{HR}}{\mu_{\text{max}}})\). Considering that in addition, the minimum values for the terms
\[
\frac{1}{N_m} \quad \text{and} \quad \frac{1}{\bar{L}_m(0)} \quad \text{in equation (S10) have the minimum of are} \quad 1. \quad \text{Therefore,} \quad e^f \quad \text{is maximized in the maximum of}\]

\[
\text{equation (S10) \ has with the maximum of} \quad e^f = 1 - \frac{r_{HR}}{\mu_{max}} = 1 - \alpha \times e^{(B_T-P_T)\times T}, \quad \text{where} \quad \alpha \quad \text{represents an constant,} \quad B_T = 0.11 \quad \text{and} \quad P_T = 0.0633 \quad \text{for the equation (5) of Cael and Follows (2016).}
\]

4. Dataset

To test the performance of our upper bound model, we compiled observations of net community production (Table S1) and carbon export in the world’s oceans.

4.1 O₂/Ar Net Community Production

The O₂/Ar method estimates NCP through a mass balance of biological O₂ in the mixed layer. Because Ar and O₂ have similar temperature dependencies and solubilities (Craig and Hayward, 1987), the saturation state of their ratio can partition oxygen concentration due to physical ([O₂]_{phys}) and biological processes ([O₂]_{biol}) (Cassar et al., 2011):

\[
[O₂]_{biol} = [O₂] - [O₂]_{phys} \approx [O₂] - \frac{[Ar]}{[Ar]_{sat}} [O₂]_{sat} = \frac{[Ar]}{[Ar]_{sat}} [O₂]_{sat} \Delta(O₂/Ar) \quad (S12)
\]

where \( \Delta(O₂/Ar) = \left[ \frac{([O₂]/[Ar])}{([O₂]/[Ar])_{sat}} - 1 \right] \) is the biological O₂ supersaturation. When ignoring vertical mixing and lateral advection, we can write the mass balance for [O₂]_{biol} in the mixed layer as follows (Cassar et al., 2011):

\[
MLD \frac{d[O₂]_{biol}}{dt} = NCP - k_{O₂} \frac{[Ar]}{[Ar]_{sat}} [O₂]_{sat} \Delta(O₂/Ar) \quad (S13)
\]

where \( k_{O₂} \) is the gas exchange velocity for O₂. At steady state (i.e., \( \frac{d[O₂]_{biol}}{dt} = 0 \)), equation (S13) reduces to (Cassar et al., 2011; Reuer et al., 2007):

\[
NCP = k_{O₂} [O₂]_{sat} \Delta(O₂/Ar) \quad (S14)
\]

where \( \frac{[Ar]}{[Ar]_{sat}} \) in equation (S13) is assumed to equal 1, which introduces an error of up to a couple percent in NCP estimates under most conditions (Cassar et al., 2011; Eveleth et al., 2014).

To derive NCP using equation (S14), we calculate \( k_{O₂} \) using daily NCEP wind speeds, MLD, the parameterization of Wanninkhof (1992), and a weighting technique to account for wind speed history following
(Reuer et al., 2007). Uncertainties and biases in O$_2$/Ar NCP estimates can be found in previous studies (Bender et al., 2011; Cassar et al., 2014; Jonsson et al., 2013).

### Table S1. O$_2$/Ar measurements included in this study.

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### 4.2 Sediment trap and $^{234}$Thorium POC export production

We also compared $NCP^*$ to sediment-trap and $^{234}$Th-derived POC export production estimates from the dataset recently compiled by Mouw et al. (2016). These observations were adjusted to reflect a flux at the base of the mixed layer using the Martin curve with $b = -0.86$ (Martin et al., 1987). Monthly climatological MLD were used.

### 4.3 Mixed layer depth

We derived MLD using Argo temperature-salinity profiling floats which were downloaded from [http://www.usgodae.org/](http://www.usgodae.org/). As real-time data (after 2008) have not been thoroughly checked, we only used profiles with temperature, salinity, and pressure with a quality flag of ‘1’ (‘good data’) or ‘2’ (‘probably good data’). To improve coverage, we also used the temperature and salinity profiles obtained by CTD casts in the World Ocean Database. These profiles were downloaded from the National Oceanographic Data Center (NODC) [https://www.nodc.noaa.gov/access/index.html](https://www.nodc.noaa.gov/access/index.html).
MLD is estimated as the depth at which the potential density ($\sigma_\theta$) exceeds a near-surface reference value at 10 m depth by $\Delta\sigma_\theta = 0.03 \text{ kg m}^{-3}$ (de Boyer Montegut et al., 2004; Dong et al., 2008). Estimates were averaged to daily $5^\circ \times 5^\circ$ grids, from which monthly climatologies were calculated (Figure S1).

Figure S1. Climatology of monthly mixed layer depth.

4.4 Satellite properties

To derive a global distribution of $\mathcal{NCP}^*$, we used monthly SST and PAR climatologies calculated based on MODIS-Aqua observations from 2002-2015 with a spatial resolution of $0.083^\circ \times 0.083^\circ$ (downloaded from NASA’s ocean color website (http://oceancolor.gsfc.nasa.gov/cms/)). We compared $\mathcal{NCP}^*$ to monthly and annual NCP climatologies as simulated by the algorithms developed by Li and Cassar (2016). This NCP dataset
represents the average of 11 satellite algorithms of export production for observations from 1997 to 2010 (Figure S2). More details can be found in Li and Cassar (2016).

Figure 2S. Average annual export production derived using 11 algorithms (see Li and Cassar (2016)).

4.5. Diffusion attenuation coefficient for photosynthetically active radiation

Constants $k_c$ and $K_t^w$ in equation (10) were derived using the NOMAD dataset (Werdell and Bailey, 2005), which includes chlorophyll a concentration and $K_t$ (Figure S3). NOMAD was downloaded from https://seabass.gsfc.nasa.gov/wiki/NOMAD. The regression in Figure S3 was converted to equation (10) using a carbon to chlorophyll ratio of 90 (Arrigo et al., 2008).
Figure S3. Attenuation coefficient for photosynthetically active radiation (PAR) as a function of chlorophyll a concentration based on the NOMAD dataset.
Figure S4. Modeled upper bound on carbon export production compared to field observations as a function of mixed layer depth (MLD). Observations are based on O\textsubscript{2}/Ar-derived net community production (NCP). To account for the effect of photosynthetically active radiation (PAR) on export production, both MLD and carbon fluxes are normalized to $-\log(1 - \mu_m(0))$ (see equations (19) and (21)). The thick gray line represents the upper bound fitted to the NCP data. Dash-lines represent the upper bounds calculated using parameters available in the literature (Table 2). A stoichiometric ratio of O\textsubscript{2}/C=1.4 was used to convert NCP from O\textsubscript{2} to C units (Laws, 1991).
References


