Wednesday, September 13, 2017

Jack Middelburg
Editor
Biogeosciences

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

Division of Earth and Ocean Sciences
Nicholas School of the Environment
Duke University
email. zuchuan.li@duke.edu

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 dataproducts.

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.

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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:

"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 MLD, temperature, photosynthetically active radiation (PAR), phytoplankton maximum growth rate (μ_{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 O_2/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))."

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."

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

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:
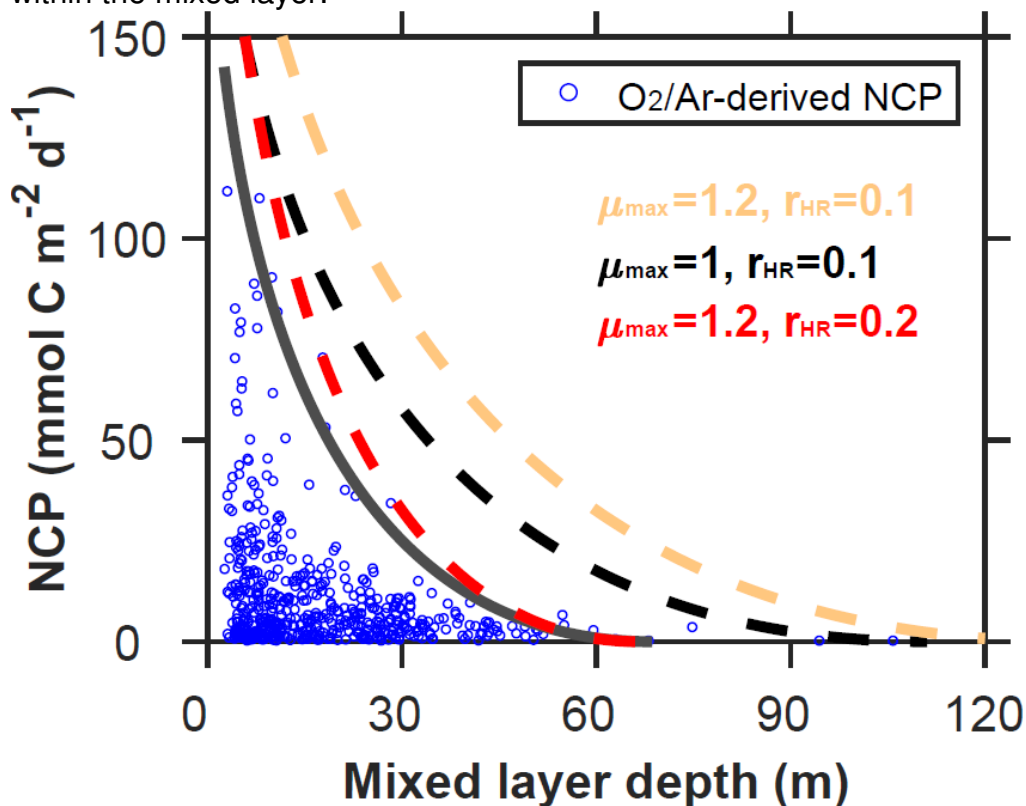

Figure S4. Modeled upper bound on carbon export production compared to field observations as a function of mixed layer depth (MLD). Observations are based on O_2/Ar-derived net community production (NCP). To account for the effect of photosynthetically active radiation (PAR) on export production, both MLD and carbon fluxes are normalized to $-log(1 - I_m(0))$ (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).

Gloege, L., McKinley, G. A., Mouw, C. B., and Ciochetto, A. B.: Global evaluation of particulate organic carbon flux parameterizations and implications for atmospheric pCO_2, Global Biogeochemical Cycles, 2017.

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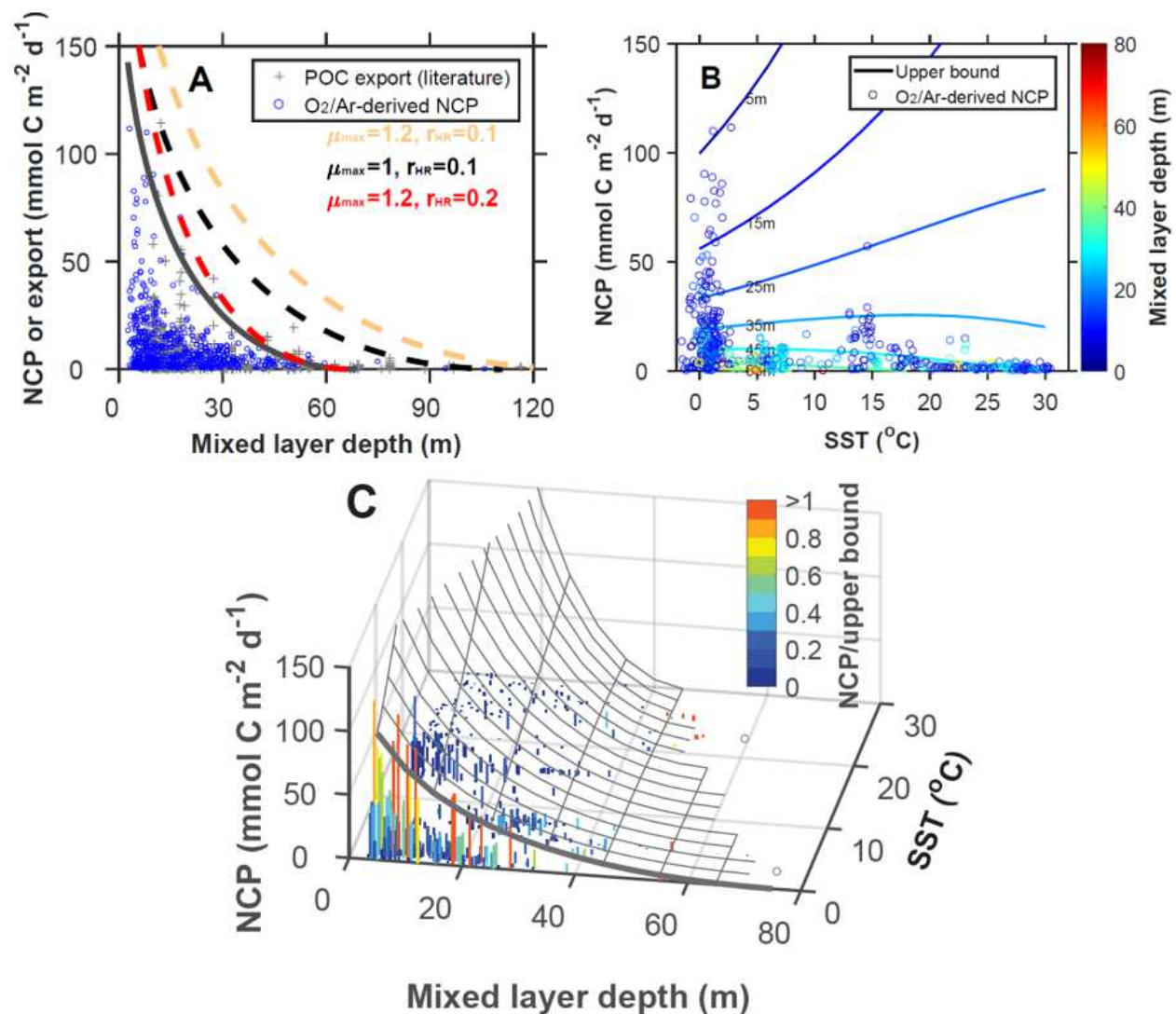The updated Figure 3 (Figure 4 in the revised manuscript) is shown below:

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):

$$\mu_{max} = \mu_{max}^0 \times e^{P_t \times T} \qquad (20a)$$
$$r_{HR} = r_{HR}^0 \times e^{B_t \times T} \qquad (20b)$$

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

- μ_{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 μ_{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 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.

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.

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:
- μ_{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 μ_{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, selfshading 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_I^w 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.
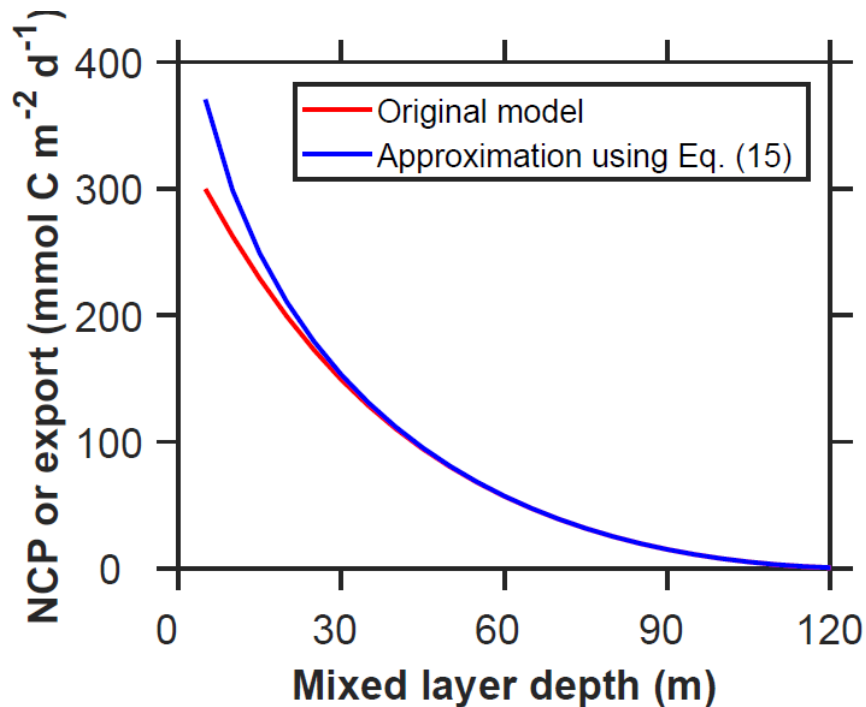
Figure 3. Upper bounds derived using the original and approximated models. The upper bound for the original model (equations (8-10)) is estimated through a non-linear optimization approach. The upper bound for the approximated model is calculated analytically from equation (19). The models use the constants 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 O_2 into the mixed layer".

On line 275 of the original manuscript, we now further elaborate on the low f_{pt} 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_{pt}) because of the strong stratification and nutrient limitation").

The term "light" attenuation coefficient has been replaced with "diffusion" attenuation coefficient.

As stated in our original manuscript, dNCP/dC systematically decreases with increasing C (this is because $\frac{d^2 NCP(0,MLD)}{dC^2}$ 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 $\lim_{C \to \infty} \left(\frac{dNCP(0,MLD)}{dC} \right) = -r_{HR} \times MLD < 0$, because $HR(0,MLD)$ linearly increases with increasing C while $NPP(0,MLD)$ plateaus (Figure 2)."

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."

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 $MLD_{C^*_{max}} \leq MLD \leq \frac{\mu^*}{r_{HR} \times K_I^w}$, 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."

Following the reviewer's comment, we modified equations (20a) and (20b):
$$\mu_{max} = \mu_{max}^0 \times e^{P_t \times T} \qquad (20a)$$
$$r_{HR} = r_{HR}^0 \times e^{B_t \times T} \qquad (20b)$$

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

Parameter	Range or value	Reference
K_I^w	0.09	(Werdell and Bailey, 2005)
k_c	0.03	(Werdell and Bailey, 2005)
Carbon to chlorophyll ratio	90	(Arrigo et al., 2008)
k_m^I	4.1 Einstein m^{-2} d^{-1}	(Behrenfeld and Falkowski, 1997)
P_t	0.0663	(Eppley, 1972)
B_t	0.08	(Rivkin and Legendre, 2001; López-Urrutia et al., 2006)
μ_{max}	1 d^{-1}, 1.2 d^{-1}	(Laws et al., 2000; Eppley, 1972)
r_{HR}	0.1 d^{-1}, 0.2 d^{-1}	(Laws et al., 2000; Mitchell et al., 1991)

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."

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

Zuchuan Li[*], Nicolas Cassar

Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University,

Durham, North Carolina, USA

[*] Corresponding author: Zuchuan Li (zuchuan.li@duke.edu)

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

21   **Abstract**

22   Export production reflects the amount of organic matter transferred from the surface ocean to depth

23   through biological processes. This export is in great part controlled by nutrient and light

24   availability, which are conditioned by mixed layer depth (MLD). In this study, building on

25   Sverdrup's critical depth hypothesis, we derive a mechanistic model of an upper bound on carbon

26   export based on the metabolic balance between photosynthesis and respiration as a function of

27   MLD and temperature. We find that the upper bound is a positively skewed bell-shaped function

28   of MLD. Specifically, the upper bound increases with deepening mixed layers down to a critical

29   depth, beyond which a long tail of decreasing carbon export is associated with increasing

30   heterotrophic activity and decreasing light availability. We also show that in cold regions the upper

31   bound on carbon export decreases with increasing temperature when mixed layers are deep, but

32   increases with temperature when mixed layers are shallow. A metaanalysis shows that our model

33   envelopes field estimates of carbon export from the mixed layer. When compared to satellite export

34   production estimates, our model indicates that export production in some regions of the Southern

35   Ocean, most particularly the Subantarctic Zone, is likely limited by light for a significant portion

36   of the growing season.

37   **Key words**: Export production, net community production, upper bound, mixed layer depth,

38   temperature

39

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):

$$CO_2 + H_2O \; \underbrace{\overset{GPP}{\underset{NPP}{\xrightarrow{NCP} \xleftarrow{HR}}}\xleftarrow{AR}} \; Organic\ matter + O_2 \qquad (1)$$
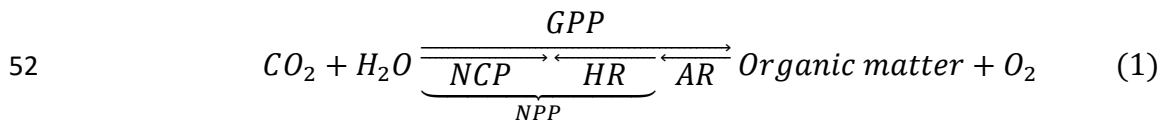
$$Export\ production = NCP - MLD \times \frac{d(POC + DOC)}{dt} \qquad (2)$$

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.

61   Net community production is in great part regulated by the availability of nutrients and light.

62   Light availability exponentially decays with depth due to absorption by water and its constituents.

63   The mixing of phytoplankton to depth therefore impacts phytoplankton physiology and

64   productivity (Cullen and Lewis, 1988; Lewis et al., 1984), with the depth-integrated NPP expected

65   to increase down to the euphotic depth. Respiration, on the other hand, is often modeled to be some

66   function of organic matter concentration, which is expected to be constant with depth if

67   homogenously mixed within the mixed layer. Temperature is also believed to be an important

68   control on carbon export because respiration is more temperature-sensitive than photosynthesis

69   (Laws et al., 2000; López-Urrutia et al., 2006; Rivkin and Legendre, 2001). Field observations

70   confirm that NCP is generally lower at high temperatures and consistently low when mixed layers

71   are deep. These patterns have been attributed to the balance between depth-integrated

72   photosynthesis (controlled by the availability of nutrients and light) and respiration as a function

73   of MLD and temperature (Cassar et al., 2011; Eveleth et al., 2016; Huang et al., 2012; Shadwick

74   et al., 2015; Tortell et al., 2015). However, descriptions of the underlying mechanisms heretofore

75   remain qualitative. Likewise, the effects of light and nutrient on carbon fluxes are difficult to

76   disentangle. For example, high-nutrient, low-chlorophyll regimes in the Southern Ocean have been

77   attributed to iron limitation (Boyd et al., 2000), deep mixed layers and light limitation (Nelson and

78   Smith, 1991; Mitchell and Holm-Hanse, 1991; Mitchell et al., 1991), or both (Sunda and Huntsman,

79   1997). To decompose the influence of light and nutrient availability on NCP, ~~W~~we define the

80   upper bound on carbon export ~~(NCP^*)~~ from the mixed layer (NCP^*) as the maximum export

81   achievable should all limiting factors other than light (~~e.g., nutrients~~taking into account self-

82   shading) be alleviated.

83   In his seminal paper, Sverdrup presented an elegant model to demonstrate that vernal

84   phytoplankton blooms (i.e., organic matter accumulation at the ocean surface) may be driven by

85   increased light availability when the MLD shoals above a critical depth (Z_c) (Sverdrup, 1953). In

86   our study, we build upon Sverdrup (1953) and derive a mechanistic model of an upper bound on

87   carbon export based on the metabolic balance of photosynthesis and respiration in the oceanic

88   mixed layer, where the metabolic balance is derived from ~~with respect to~~ MLD, temperature,

89   photosynthetically active radiation (PAR), phytoplankton maximum growth rate (μ_{max}), and

90   heterotrophic activity. Our approach is analogous to other efforts where mechanistic models were

91   derived to predict proxies of carbon export (e.g., Dunne et al. (2005) and Cael and Follows (2016)).

92   We compare our NCP^* model to observations, and use this model in conjunction with satellite

93   export production estimates to identify regions in the world's oceans where light may limit export

94   production. Our key findings are that 1) using parameters available in the literature, the modeled

95   upper bound envelopes field observations of export production estimated from [234]Th and sediment

96   traps and O$_2$/Ar-derived NCP, and 2) the model identifies regions of the Southern Ocean where

97   carbon export is likely limited by light during part of the growing season.

98   **2. Model description and comparison to observations**

99   **2.1. Net community production and light availability**

100   A conceptual representation of the metabolic balance between volumetric NCP, NPP, and HR

101   profiles is presented in Figure 1(A). According to equation (1), the volumetric NCP flux at a given

102   depth (z) in the mixed layer results from the difference between volumetric NPP and HR:

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

104   where z increases with depth. $NPP(z)$ is a function of the autotroph's intrinsic growth rate

105   (μ) times their biomass concentration (C). Assuming that the effect of nutrients and light on

106   photosynthetic rates abides by Michaelis-Menten kinetics, and neglecting the effect of

107   photoinhibition (Dutkiewicz et al., 2001; Huisman and Weissing, 1994), $NPP(z)$ may be

108   expressed as follows:

109    $$NPP(z) = \mu(z) \times C = \frac{N}{N + k_m^N} \times \frac{I(z)}{I(z) + k_m^I} \times \mu_{max} \times C \qquad (4)$$

110   where μ_{max} is the maximum intrinsic growth rate of the autotrophic community; N and k_m^N

111   represent the nutrient concentration and half-saturation constant, respectively; and I and k_m^I

112   represent the irradiance level and half-saturation constant, respectively. μ_{max}, N, k_m^N, k_m^I and C

113   are assumed to be well mixed within the mixed layer. The first two terms on the right-hand side of

114   equation (4) account for the effect of nutrient and light availability on autotrophic growth rates,

115   and they are hereafter defined as follows for simplicity:

116    $$N_m = \frac{N}{N + k_m^N} \qquad (5a)$$

117    $$I_m(z) = \frac{I(z)}{I(z) + k_m^I} \qquad (5b)$$

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

119    $$I(z) = I_0 \times e^{-K_I \times z} \qquad (6)$$

120   where K_I is ~~diffusion~~ light attenuation coefficient which is assumed to be independent of depth in

121   the mixed layer.

122   As a first approximation, we assume that $HR(z)$ is proportional to C as in previous studies

123   (Dutkiewicz et al., 2001; Huisman and Weissing, 1994; Rivkin and Legendre, 2001; Sverdrup,

124   1953; White et al., 1991):

125    $$HR(z) = r_{HR} \times C \qquad (7)$$

126   where r_{HR} represents the intrinsic heterotrophic respiration rate which is assumed to be dependent

127   on temperature (see below), and independent of depth. In reality, $HR(z)$ is likely best modeled as

128   a function of the concentration of labile organic matter — an additional term could be included to

129   account for the relationship of total labile organic matter to C.

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

131 $$NCP(0, MLD) = NPP(0, MLD) - HR(0, MLD)$$

132 $$= \int_0^{MLD} NPP(z)dz - \int_0^{MLD} HR(z)dz$$

133 $$= N_m \times I_m(0, MLD) \times \mu_{max} \times C - r_{HR} \times MLD \times C \qquad (8)$$

134   The first term on the right side of equation (8) represents NPP integrated over the mixed layer

135   ($NPP(0, MLD)$), which is equivalent to the product of $\int_0^{MLD} \mu(z)dz$ and C, where the former term

136   is modeled to be a function of μ_{max} conditioned by nutrient and light availability within the mixed

137   layer. $I_m(0, MLD)$ can be derived as follows:

138 $$I_m(0, MLD) = \int_0^{MLD} I_m(z)dz = -\frac{1}{K_I} \times ln\left(\frac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right) \qquad (9)$$

139   NCP integrated over the mixed layer (equation (8)) is a bell-shaped function of MLD as depicted

140   in the schematic diagram of Figure 1(B).

141 **2.2. Net community production and phytoplankton biomass concentration**

142   As can be seen from equation (8), $NCP(0, MLD)$ is a direct function of C because

143      $NPP(0, MLD)$ and $HR(0, MLD)$ are proportional to C. $NCP(0, MLD)$ is also an indirect function

144   of C due its effect on light attenuation (i.e., K_I). The attenuation coefficient K_I can be divided into

145   water and non-water components ($K_I = K_I^w + K_I^{nw}$) (Baker and Smith, 1982; Smith and Baker,

146   1978a; Smith and Baker, 1978b), where K_I^{nw} is controlled by the concentrations of phytoplankton,

147   colored dissolved organic matter (CDOM), and non-algal particles (NAP). In the open ocean where

148   CDOM and NAP co-vary with phytoplankton (Morel and Prieur, 1977), K_I can be related to C as

149   follows:

150
$$K_I = K_I^w + k_c \times C \quad (10)$$

151   where k_c is a function of the solar zenith angle, the specific absorption and backscattering

152   coefficients of phytoplankton, and the relationship between phytoplankton, CDOM, and NAP.

153   <u>Because pure water and phytoplankton attenuate light, K_I^w and k_c should be greater than zero.</u>

154   To calculate how $NCP(0, MLD)$ varies as a function of C, we examine its first $(\frac{dNCP(0,MLD)}{dC})$

155   and second $(\frac{d^2 NCP(0,MLD)}{dC^2})$ derivatives with respect to C based on equations (8) and (10):

156
$$\frac{dNCP(0, MLD)}{dC}$$

157
$$= N_m \times \mu_{max} \times \frac{K_I^w \times I_m(0, MLD) + k_c \times C \times MLD \times I_m(MLD)}{K_I^w + k_c \times C} - r_{HR} \times MLD \quad (11)$$

158
$$\frac{d^2 NCP(0, MLD)}{dC^2} = N_m \times k_c \times \frac{\mu_{max}}{K_I}$$

159
$$\times \left\{ \frac{2 \times K_I^w}{K_I} \times \left(MLD \times I_m(MLD) - I_m(0, MLD) \right) - \frac{k_c \times C \times I_m(MLD)^2 \times MLD^2 \times k_m^I}{I_0 \times e^{-K_I \times MLD}} \right\} \quad (12)$$

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

161
$$I_m(0, MLD) = \int_0^{MLD} \frac{I_0 \times e^{-K_I \times z}}{I_0 \times e^{-K_I \times z} + k_m^I} dz$$

162
$$> \int_0^{MLD} \frac{I_0 \times e^{-K_I \times MLD}}{I_0 \times e^{-K_I \times MLD} + k_m^I} dz = MLD \times I_m(MLD) \quad (13)$$

163   The detailed derivation of equations (11-12) can be found in the supplementary material.

164   Substituting the inequality (13) into equation (12) gives $\frac{d^2 NCP(0,MLD)}{dC^2} < 0$, which suggests that

165      $\frac{dNCP(0,MLD)}{dC}$ decreases with increasing C. <u>Because increasing C decreases light availability due to</u>

166   shelf-shading, $NPP(0, MLD)$ saturate with increasing C. Thus, $NCP(0, MLD)$ will reach an

167   asymptote of $\lim_{C \to \infty}\left(\frac{dNCP(0,MLD)}{dC}\right) = -r_{HR} \times MLD < 0$, because $HR(0, MLD)$ linearly increases

168   with increasing C while $NPP(0, MLD)$ plateaus (Figure 2). ~~reaching an asymptote of~~

169   ~~$\lim_{C \to \infty}\left(\frac{dNCP(0,MLD)}{dC}\right) = -r_{HR} \times MLD < 0$ (Figure 2(B)).~~. Additionally, because $NCP(0, MLD)$ must

170   be nil when there is no autotrophic biomass ($NCP(0, MLD)|_{C=0} = 0$), $\lim_{C \to 0}\left(\frac{dNCP(0,MLD)}{dC}\right)$ must be

171   ~~larger~~ greater than ~~zero0~~, otherwise the ecosystem would be net heterotrophic which is

172   unachievable without an allochthonous source of organic matter. $\lim_{C \to 0}\left(\frac{dNCP(0,MLD)}{dC}\right) > 0$ and

173     $\lim_{C \to \infty}\left(\frac{dNCP(0,MLD)}{dC}\right) = -r_{HR} \times MLD < 0$ suggest the existence of $\left.\frac{dNCP(0,MLD)}{dC}\right|_{C=C^*} = 0$ where C^*

174   corresponds to an autotrophic biomass concentration which maximizes $NCP(0, MLD)$ (i.e., NCP^*).

175   The dependence of $NCP(0, MLD)$ on C can be conceptually understood in the following way.

176   Given a water column with sufficient nutrients, the critical depth Z_c and compensation depth Z_p

177   are expected to shoal as C increases. When C is low, $NCP(0, MLD)$ increases with C because of

178   its greater impact on $NPP(0, MLD)$ than on $HR(0, MLD)$. As C further increases, the increase in

179     $NPP(0, MLD)$ with C slows because of light attenuation (i.e., K_I). There is therefore a C^* which

180   maximizes the difference between $NPP(0, MLD)$ and $HR(0, MLD)$ leading to NCP^* (Figure 2).

181   Beyond this point (C^*), further increasing C will cause self-shading and limit photosynthesis in the

182   deep part of the mixed layer, as a result decreasing $NCP(0, MLD)$. Beyond a critical biomass (C_c),

183   the ecosystem becomes net heterotrophic. Without an allochtonous source of organic carbon, this

184   is only transiently sustainable.

185   **2.3. Mixed layer depth and compensation depth**

186   By definition, if $NCP(MLD)$ is smaller than ~~0~~zero (i.e., net heterotrophy at the bottom of the

187   mixed layer), the MLD must be deeper than Z_p ($MLD > Z_p$) (and vice versa). To determine the

188   sign of $NCP(MLD)$, we substitute inequality (13) into equation (11). According to the inequality

189   presented in equation (13), $\frac{K_I^W \times I_m(0,MLD) + k_c \times C \times MLD \times I_m(MLD)}{K_I^W + k_c \times C}$ in equation (11) must be ~~larger~~ greater

190   than $\frac{K_I^W \times MLD \times I_m(MLD) + k_c \times C \times MLD \times I_m(MLD)}{K_I^W + k_c \times C}$ (which is equal to $MLD \times I_m(MLD)$). After simple

191   rearrangements, the substitution of inequality (13) into equation (11) leads to:

192    $$\frac{dNCP(0,MLD)}{dC}$$

193    $$> MLD \times (N_m \times I_m(MLD) \times \mu_{max} - r_{HR}) = \frac{MLD}{C} \times NCP(MLD) \qquad (14)$$

194   The inequality in equation (14) in turn suggests that when $NCP(0,MLD)$ is maximized

195   ($\frac{dNCP(0,MLD)}{dC} = 0$), $NCP(MLD)$ is negative (net heterotrophic) and hence the MLD is deeper than

196   Z_p ($MLD > Z_p$). This counterintuitive result is attributable both to the uneven distribution of light

197   availability in the water column (equation (13)) and to water which absorbs light but does not

198   contribute to biomass accumulation. When the mixed layer is at the Z_p, a slight increase in C will

199   leads to negative $NCP(MLD)$ due to decreasing light availability at the base of mixed layer, but

200   will increase NCP higher in the water column because of the increase in biomass. The increase in

201   NCP in the shallow parts of the mixed layer therefore overcompensates for the net heterotrophy at

202   the bottom of the mixed layer, thus maximizing the depth-integrated NCP. If light were uniformly

203   distributed in the water column (i.e., $I_m(0,MLD) = MLD \times I_m(MLD)$) and if water did not

204   attenuate light ($K_I^W = 0$ in equation (11)), $MLD = Z_p$ would maximize $NCP(0,MLD)$, which is

205   consistent with Huisman and Weissing (1994). We note that in equation (14) the NCP profile

206   ($NCP(z)$) varies with increasing C, which is different from what is conceptually presented in

207   Figure 1. The depth-integrated NCP in Figure 1 maximizes at the compensation depth because the

208   NCP profile ($NCP(z)$) 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 $I_m(0, MLD)$:

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

$$\approx \cancel{I_m(0)} \times \frac{\cancel{1 - e^{-K_I \times MLD}}}{\cancel{K_I}} - \frac{1}{K_I} \times ln(1 - I_m(0))$$

$$\approx \cancel{I_m(0)} \times \frac{\cancel{1}}{\cancel{K_I}} \qquad (15)$$

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:

$$NCP(0, MLD) = C \times MLD \times \left(\frac{1}{K_I \times MLD} \times \mu^* - r_{HR}\right) \qquad (16)$$

where $\mu^* = \cancel{I_m(0)} - ln(1 - I_m(0)) \times N_m \times \mu_{max}$. 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:

$$\left.\frac{dNCP(0, MLD)}{dC}\right|_{NCP(0,MLD)=NCP^*} = \mu^* \times \frac{K_I^w}{(k_c \times C^* + K_I^w)^2} - MLD \times r_{HR} = 0 \qquad (17)$$

and therefore:

$$C^* = \frac{1}{k_c} \times \left[-K_I^w + \sqrt{\frac{\mu^* \times K_I^w}{MLD \times r_{HR}}}\right] \qquad (18)$$

11

228 Equation (18) decreases with MLD. As C^* is positive ($C^* \geq 0$) and cannot go to infinity ($C^* \leq$

229 C_{max}^*), MLD should satisfy $MLD_{C_{max}^*} \leq MLD \leq \frac{\mu^*}{r_{HR} \times K_I^W}$, where $MLD_{C_{max}^*}$ represents the MLD

230 corresponding to the maximum achievable autotroph's biomass concentration (C_{max}^*) in the

231 surface ocean. The NCP^* model for $0 \leq MLD < MLD_{C_{max}^*}$ is not discussed here, because we do

232 not have data with very shallow MLD to constrain and evaluate the model. The derivation of the

233 model ~~can be found~~is however presented in the supplementary material. Substituting C^* from

234 equation (18) into equation (16):

235
$$\sqrt{NCP^*} = a_2 \times \sqrt{-ln(1 - I_m(0))\cancel{I_m(0)}} + a_1 \times \sqrt{MLD} \qquad (19)$$

236 where $a_1 = -\sqrt{\frac{K_I^W \times r_{HR}}{k_c}}$ and $a_2 = \sqrt{\frac{N_m \times \mu_{max}}{k_c}}$. Constants a_1 and a_2 are functions of r_{HR} and μ_{max},

237 respectively, which are generally modeled to increase with temperature (T) (Eppley, 1972; Rivkin

238 and Legendre, 2001):

239
$$\mu_{max} \cancel{\propto}= \mu_{max}^0 \times e^{P_t \times T} \qquad (20a)$$

240
$$r_{HR} \cancel{\propto}= r_{HR}^0 \times e^{B_t \times T} \qquad (20b)$$

241 where P_t and B_t are constants; and μ_{max}^0 and r_{HR}^0 are maximum growth rate and heterotrophic

242 respiration ratio for $T = 0$ °C, respectively. P_t is commonly assumed to equal 0.0663 (Eppley,

243 1972). Substituting equations (20a) and (20b) into equation (19) yields:

244
$$\sqrt{NCP^*} = a_4 \times \sqrt{e^{P_t \times T}} \times \sqrt{-ln(1 - I_m(0))\cancel{I_m(0)}} + a_3 \times \sqrt{e^{B_t \times T}} \times \sqrt{MLD} \qquad (21)$$

245 where $a_3 = -\sqrt{\frac{r_{HR}^0 \times K_I^W}{k_c}}$ 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~~

246 ~~discussed here, because we do not have data with very shallow MLD to constrain and evaluate the~~

247 ~~model. The derivation of the model can be found in the supplementary material.~~

248 **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_I^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_I and chlorophyll a concentration (see Figure S3), calculated based on the NOMAD dataset (Werdell and Bailey, 2005). k_m^I 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 ~~3~~4(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 μ_{max} and decreases with r_{HR}. Model parameters $a_1 = $ ~~−1.80~~ −1.78 and $a_2 = $ ~~21.38~~14.75 (equation (19)) provide the best fit to the upper bound on~~f~~ O_2/Ar-NCP ~~and~~ as a

13

272 function of MLD. When compared to parameters available in the literature (Table 2), ~~W~~we find

273 that the best fit to our modeled upper bound is using μ_{max} and r_{HR} of 1.2 d^{-1} and 0.2 d^{-1},

274 respectively. When accounting for the effect of T on μ_{max} and r_{HR}, model constants $a_3 =$

275 ~~-1.66~~ -1.53 and $a_4 = $ ~~20.40~~13.39 (equation (21)) best fit the upper bound on O$_2$/Ar-NCP, SST

276 and MLD observations.

277   Our results show that NCP^* decreases faster with increasing MLD in warmer waters (Figure~~s~~

278 4~~3~~(B) and 4(C)), because the term $a_3 \times \sqrt{e^{B_t \times T}}$ in equation (21) is negative and negatively

279 correlated to T. This temperature effect contributes to part of the relationship between export

280 production and MLD in Figure 4~~3~~(A). Interestingly, NCP^* increases with T in colder waters and

281 shallow mixed layers (Figure 4(C)). This is because NCP^* reflects the balance between

282 productivity ($a_4 \times \sqrt{e^{P_t \times T}} \times \sqrt{-ln\left(1 - I_m(0)\right)\cancel{I_m(0)}}$) and heterotrophic respiration ($a_3 \times$

283 $\sqrt{e^{B_t \times T}} \times \sqrt{MLD}$). In a shallow cold mixed layer, the change in productivity with T

284 ($\dfrac{d\left(a_4 \times \sqrt{e^{P_t \times T}} \times \sqrt{-ln\left(1 - I_m(0)\right)\cancel{I_m(0)}}\right)}{dT} = \dfrac{P_t}{2} \times a_4 \times \sqrt{e^{P_t \times T}} \times \sqrt{-ln\left(1 - I_m(0)\right)\cancel{I_m(0)}}$) is greater than

285 that of heterotrophic respiration ($\dfrac{d\left(a_3 \times \sqrt{e^{B_t \times T}} \times \sqrt{MLD}\right)}{dT} = \dfrac{B_t}{2} \times a_3 \times \sqrt{e^{B_t \times T}} \times \sqrt{MLD}$). These results

286 could explain part of the variability in the relationship between NCP and SST reported in previous

287 studies (Li and Cassar, 2016). Our NCP^* model does not perform as well in warmer deep mixed

288 layers, where high variability in export ratio maxima have also been reported (Cael and Follows,

289 2016). This may stem from uncertainties in observations, the differing relationship between T,

290 μ_{max} , and r_{HR} at high temperature, and/or violations of our assumptions (see caveats and

291 limitations).

292   Several recent studies have explored the relationship of NCP to oceanic parameters based on

293   various statistical approaches (Cassar et al., 2015; Chang et al., 2014; Huang et al., 2012; Li and

294   Cassar, 2016; Li et al., 2016). Our model can shed some light into the mechanisms driving some

295   of these patterns. To that end, we substitute equation (~~15~~9) into equation (8):

296
$$NCP(0, MLD) = C \times MLD \times \left(-\frac{N_m \times \mu_{max}}{K_I \times MLD} \times ln\left(\frac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right) - r_{HR} \right) \quad (22)$$

297   Rearranging equation (22):

298
$$NCP_B = \frac{NCP(0, MLD)}{C \times MLD} = -\frac{ln\left(\frac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right)}{I_0 \times (1 - e^{-K_I \times MLD})} \times N_m \times \mu_{max} \times PAR_{ML} - r_{HR} \quad (23)$$

299   where NCP_B is the biomass-normalized volumetric NCP, PAR_{ML} is the average PAR in the mixed

300   layer ($PAR_{ML} = \frac{1-e^{-K_I \times MLD}}{K_I \times MLD} \times I_0$), and $-\frac{ln\left(\frac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right)}{I_0 \times (1 - e^{-K_I \times MLD})} \frac{1}{I_0 + k_m^I} \times N_m \times \mu_{max}$ and $-r_{HR}$

301   correspond to the slope and offset, respectively. The scatter in the relationship between

302   chlorophyll-normalized volumetric NCP and PAR_{ML}, as reported in previous studies (Bender et

303   al., 2016), can likely be explained by the effect of temperature and the availability of nutrient and

304   light (among other properties) on the slope and offset of equation (23). Equation (22) can also be

305   reorganized to assess how environmental conditions may impact the export ratio (ef):

306
$$ef = \frac{NCP(0, MLD)}{NPP(0, MLD)} = 1 - \frac{K_I \times MLD}{-ln\left(\frac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right)} \times \frac{1}{N_m} \times \frac{r_{HR}}{\mu_{max}} \quad (24)$$

307   where $\frac{r_{HR}}{\mu_{max}}$ is proportional to $e^{(B_t - P_t) \times T}$. Equation (24) is consistent with multiple studies which

308   predict decreasing ef with increasing temperature (Cael and Follows, 2016; Dunne et al., 2005;

309   Henson et al., 2011; Laws et al., 2000; Li and Cassar, 2016). In fact, equation (5) of Cael and

310   Follows (2016) can easily be derived from equation (24) (see supplementary material). Equation

311   (24) also highlights that a multitude of factors may confound the dependence of ef on temperature

312   (including varying MLD, light attenuation, and availability of nutrient and light). This again may

313   explain some of the conflicting observations recently reported in the literature (e.g., Maiti et al.

314   (2013)), where the effect of temperature may be masked by changes in community composition

315   (Britten et al., 2017; Henson et al., 2015). One therefore needs to account or correct for the

316   multitude of confounding factors when predicting the effect of a given environmental condition

317   (e.g., temperature, mineral ballast, and NPP) on the export ratio.

318   **3. Spatial distribution of the upper bound on carbon export**

319   We estimate the global distribution of the upper bound of carbon export using equation (19)

320   and climatological monthly MLD and PAR. In general, NCP^* is high in low latitudes and low in

321   the North Atlantic and Antarctic Circumpolar Current (ACC) in the Southern Ocean (Figure

322   54(A)). As expected, this spatial pattern is controlled by MLD (see Figure S1). Satellite-derived

323   estimates of NCP (Li and Cassar, 2016) are approximately 10% of global NCP^* , reflecting the

324   high degree of nutrient limitation in the oceans. We also derive a global NCP^* map using equation

325   (21), and find that the global NCP^* estimate is very sensitive to the temperature dependence of

326   r_{HR}. For example, decreasing the B_t in $r_{HR} = r_{HR}^0 \times e^{B_t \times T}$ from 0.11 to 0.08 (as used in Rivkin

327   and Legendre (2001) and López-Urrutia et al. (2006)) increases the global NCP^* budget by a factor

328   of 2.4. Large differences in NCP^* in low-latitudes in great part explain this change. In light of the

329   large uncertainties in the relationship between r_{HR} and T (Cael and Follows, 2016; López-Urrutia

330   et al., 2006), we hereafter only discuss NCP^* estimates derived from equation (19).

331   To estimate how close export production is to its upper bound, we calculate the ratio of export

332   production to NCP^* (f_{pt}). Low f_{pt} regimes represent ecosystems likely regulated by nutrient

333   availability (i.e., ecosystems that have not reached their full export potential based on MLD and

334   surface PAR). As expected, low latitude and subtropical regions have low f_{pt} (Figure 54(B)). High

335   f_{pt} regimes represent ecosystems which have reached their full light potential, and are therefore

336   less likely to respond to nutrient addition because of light limitation (e.g., North Atlantic and ACC

337   (Figure 54(B))). In these regions, especially the subantarctic region, f_{pt} is high in the spring

338   (Figure 54(C)) and decreases in the summer (Figure 54(D)), suggesting that export production is

339   likely co-limited by nutrient and light availability. This may in part explain the lower response to

340   iron fertilization in the subantarctic region where substantial increases in surface chlorophyll were

341   only observed in regions with shallower mixed layers (Boyd et al., 2007; Boyd et al., 2000; de

342   Baar et al., 2005).

343   Also shown in Figure 54 are the biological pump efficiency and export ratio ef (panels 54E

344   and 54F, respectively). These various proxies reflect different components of the biological pump.

345   Whereas f_{pt} reflects the export potential based on current MLD and light availability, the

346   biological pump efficiency reflects the potential as derived from nutrient distribution in the oceans,

347   estimated from the extent of nutrient removal from the surface ocean (Sarmiento and Gruber, 2006)

348   or the proportion of regenerated nutrients at depth (Ito and Follows, 2005). A revised estimate of

349   the global biological pump efficiency, estimated based on the proportion of regenerated to total

350   nutrients (preformed + regenerated) at depth is around 30-35% (Duteil et al., 2013). The ef ratio

351   on the other hand describes how much of production is exported as opposed to recycled in the

352   surface (Dunne et al., 2005). The ultra-oligotrophic subtropical waters have a low export ratio, a

353   strong biological pump efficiency with exhaustion of nutrients at the ocean surface, and therefore

354   have not reached their full light potential (low f_{pt}) because of the strong stratification and nutrient

355   limitation. The seasonal pattern of f_{pt} in the subantarctic region suggests that the low biological

356 pump efficiency is the result of light limitation in the austral spring and nutrient (likely Fe) and

357 light limitation in the austral summer.

4. Caveats and limitations

359 ~~A~~ There are a multitude of uncertainties, simplifications, and approximations in our model and

360 field observations ~~may explain some of the discrepancies between the predicted and observed~~

361 ~~NCP*~~. Among others:

362 • In our study, we used a model which builds on Sverdrup's critical depth hypothesis. There

363 are competing hypotheses to explain phytoplankton bloom phenology (timing and

364 intensity), including the "dilution recoupling hypothesis" or "disturbance recovery

365 hypothesis" (Behrenfeld, 2010; Boss and Behrenfeld, 2010) and "critical turbulence

366 hypothesis" (Brody and Lozier, 2015; Huisman et al., 1999; Taylor and Ferrari, 2011). In

367 the case of top-down control, any respiratory grazing loss not accounted for by our loss

368 term would behave as a system not reaching its full light potential (NCP*). Conversely,

369 any grazing loss associated with export (e.g., rapidly sinking fecal pellets and other

370 zooplankton-mediated export pathways) would minimize respiratory losses thereby

371 bringing NCP closer to its upper bound based on light-availability. These opposing effects

372 are beyond the scope of this study, but could be modeled, especially as we learn more about

373 their impacts on carbon fluxes through new efforts such as NASA's EXPORTS program

374 (Siegel et al., 2016). See also the point below on mixing vs. mixed layer depth.

375 • Phytoplankton biomass concentration (C) may vary with depth in the mixed layer,

376 especially for water columns experiencing varying degrees of turbulent mixing. In addition,

377 MLD is not always the best proxy of light availability with mixing layer in some cases

378   deviating from the mixed layer (Franks, 2015; Huisman et al., 1999). The factors defining

379   the MLD also vary in different oceanic regions.

380   • For simplicity, we model the dependence of photosynthesis on irradiance assuming

381   Michaelis-Menten kinetics, which does not account for photoinhibition. More accurate

382   models can be found in other studies (Platt et al., 1980). Due to optional absorption, K_I

383   also varies with depth in the mixed layer. Additionally, the linear relationship between K_I

384   and C is influenced by CDOM, NAP, and other environmental factors (e.g., solar zenith

385   angle) (Gordon, 1989).

386   • μ_{max} and r_{HR} are influenced by environmental factors other than temperature, including

387   community structure (Chen and Laws, 2017), and may vary with depth within the mixed

388   layer (Smetacek and Passow, 1990). For these reasons, the equations relating μ_{max} and r_{HR}

389   (i.e., B_t and P_t) to temperature also carry significant uncertainties (Bissinger et al., 2008;

390   Edwards et al., 2016; Kremer et al., 2017; López-Urrutia and Morán, 2007; Rivkin and

391   Legendre, 2001) which impacts our estimates of the upper bound on carbon export,

392   especially in warmer regions. As in other recent studies (Cael and Follows, 2016; Cael et

393   al., 2017; Dutkiewicz et al., 2001; Gong et al., 2015; Gong et al., 2017; Huisman et al.,

394   2006; Taylor and Ferrari, 2011), we model heterotrophic respiration to vary in proportion

395   to phytoplankton concentration. The model could be further improved by explicitly

396   including the concentration of heterotrophs. See point above on the grazing effect on export

397   with regards to r_{HR}.

398   • NCP may underestimate export production when accompanied by a decrease in the

399   inventory of organic matter in the mixed layer (see introduction and equation (2)).

400   • Our field observations are limited, mostly focusing on the spring and summer seasons, and

401   harbor significant uncertainties. For example, deep mixed layers can bias the O_2/Ar method

402   low if entrainment of deeper waters brings low O_2 into the mixed layer. Descriptions of

403   these uncertainties are presented in other studies (Bender et al., 2011; Cassar et al., 2014;

404   Jonsson et al., 2013).

405   • Finally, our study is only relevant to the mixed layer. It does not account for productivity

406   below the mixed layer, which can be important in some regions such as the subtropical

407   ocean.

408   **5. Conclusions**

409   In this study, we derived a mechanistic model of an upper bound on carbon export (NCP^*) based

410   on the metabolic balance between photosynthesis and respiration of the plankton community. The

411   upper bound is a positively skewed bell-shaped function of mixed layer depth (MLD). At low

412   temperatures, the upper bound decreases with temperature if mixed layers are deep, but increases

413   with temperature if mixed layers are shallow. We used this model to derive a global distribution

414   of an upper bound on carbon export as a function of MLD and surface PAR, which shows high

415   values in low latitudes and low values in high latitudes due to deep MLD. To examine how current

416   export production compares to this upper bound in the world's oceans, we calculated the ratio of

417   satellite export production estimates to the upper bound derived by our model. High ratios of export

418   production to NCP^* in the North Atlantic and ACC indicate that export production in these regions

419   is likely co-limited by nutrient and light availability. Overall, our results may explain differences

420   in carbon export measured during past iron fertilization experiments (e.g., subantarctic and polar

421   regions), inform future iron fertilization experiments, and help in the development of remotely-

20

sensed carbon export algorithms, and improve predictions of the response of marine ecosystems
to a changing climate.

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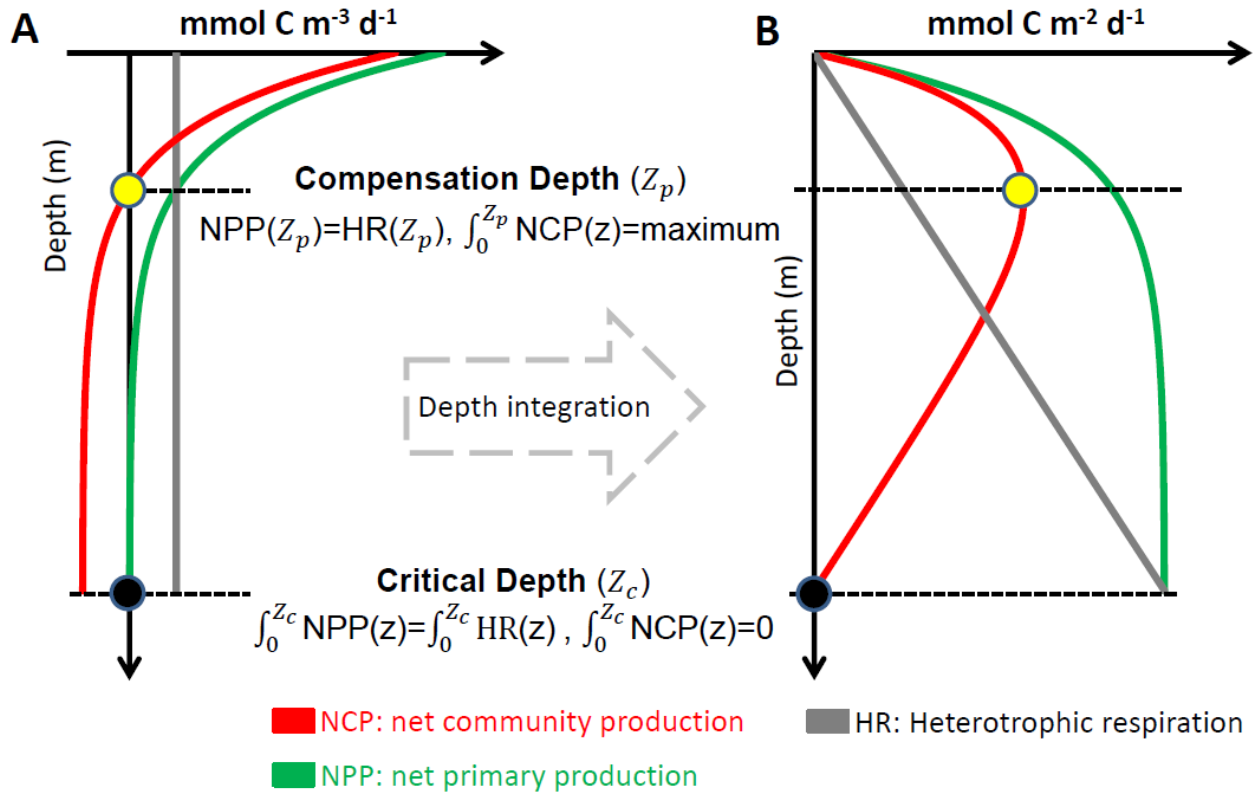
652

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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.
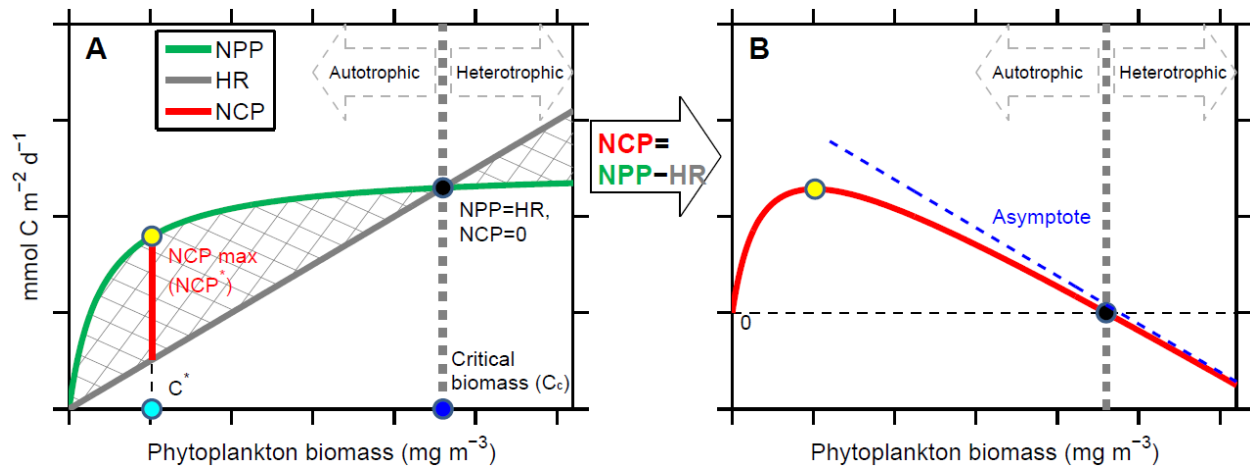
Figure 2. Relationship between net primary production (NPP), heterotrophic respiration (HR), net community production (NCP), and phytoplankton biomass concentration (C) for a given mixed layer depth (MLD). Hatched area in panel A represents NCP. The yellow dot represents the maximal NCP (NCP*) obtainable 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 $\gg$ NPP).
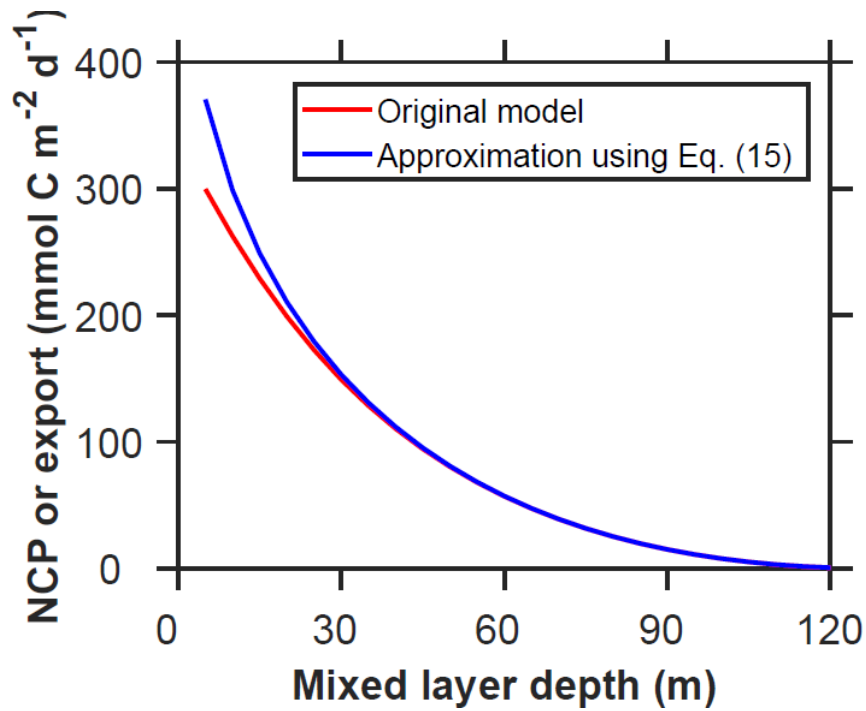
Figure 3. Upper bounds derived using the original and approximated models. The upper bound for the original model (equations (8-10)) is estimated through a non-linear optimization approach. The upper bound for the approximated model is calculated analytically from equation (19). The models use the constants 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.
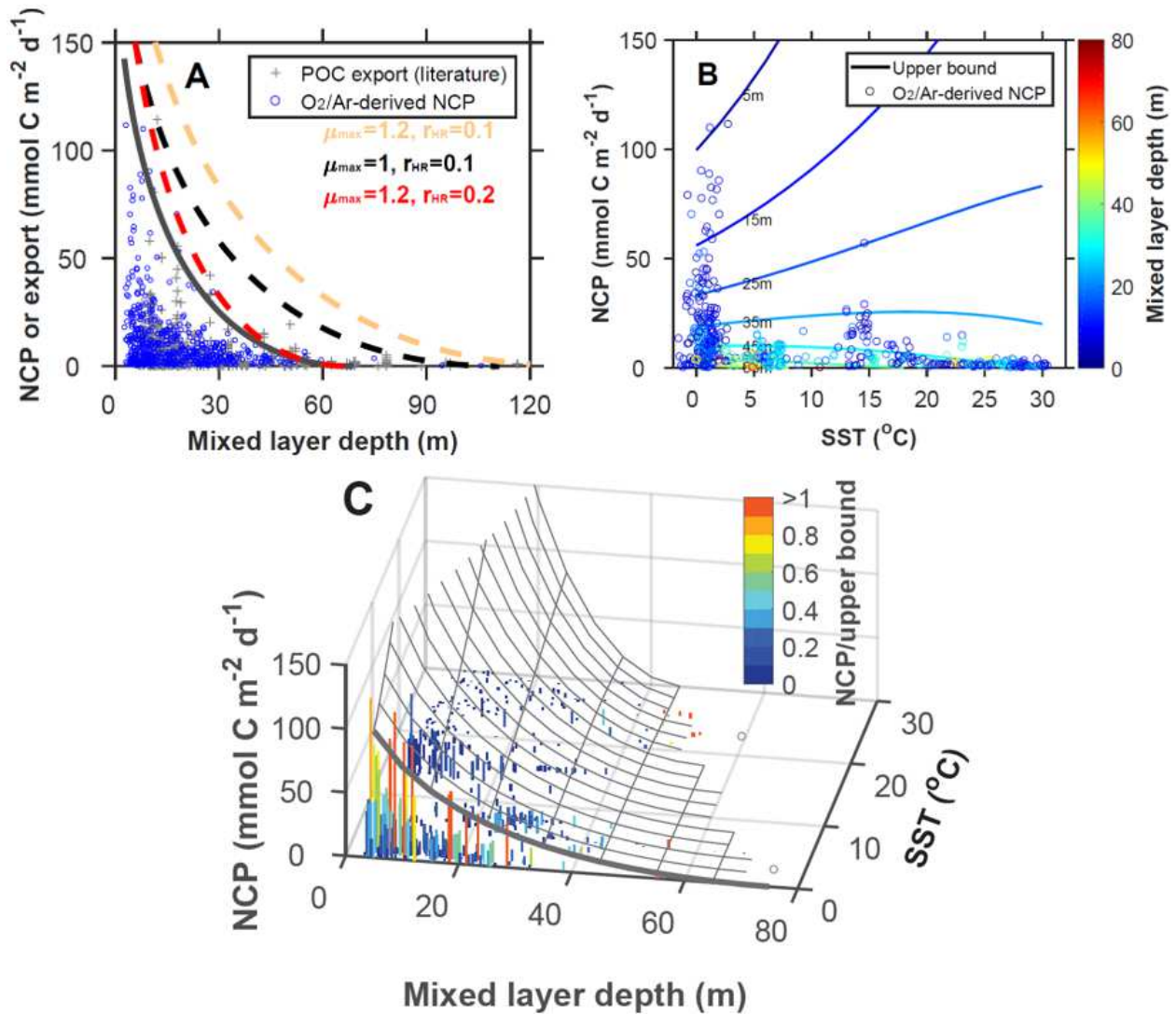
Figure 4. ~~Envelope of the m~~Modeled upper bound on carbon export production compared to field observations as a function of mixed layer depth (MLD) and sea surface temperature (SST). (A) The thick gray line represents the upper bound fitted to the net community production (NCP) data. Dash-lines represent 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

Symbol	Description	Units
MLD	Mixed layer depth	m
$MLD_{C^*_{max}}$	Maximum MLD corresponds to maximum achievable autotroph's biomass concentration	m
z	Depth	m
Z_c	Critical depth	m
Z_p	Compensation depth	m
GPP(0,z)	Gross primary production	mmol C m^{-2} d^{-1}
NPP(z)	Net primary production at depth z	mmol C m^{-3} d^{-1}
NPP(0,z)	Net primary production above depth z	mmol C m^{-2} d^{-1}
NCP(z)	Net community production at depth z	mmol C m^{-3} d^{-1}
NCP(0,z)	Net community production above depth z	mmol C m^{-2} d^{-1}
HR(z)	Heterotrophic respiration at depth z	mmol C m^{-3} d^{-1}
HR(0,z)	Heterotrophic respiration above depth z	mmol C m^{-2} d^{-1}
NCP^*	The maximum NCP for a given MLD (upper bound on carbon export)	mmol C m^{-2} d^{-1}
NCP_B	NCP normalized to autotroph's biomass inventory in the mixed layer	d^{-1}
ef	Export ratio	unitless
f_{pt}	Ratio of satellite export production estimates to the upper bound on carbon export	unitless
N	Nutrient concentration	mmol m^{-3}
k_m^N	Half-saturation constant for nutrient concentration	mmol m^{-3}
N_m	Nutrient effect on phytoplankton grow $N_m = \frac{N}{N+k_m^N}$	unitless
PAR	Photosynthetically active radiation	Einstein m^{-2} d^{-1}
I_0	Photosynthetically active radiation just beneath water surface	Einstein m^{-2} d^{-1}
$I(z)$	Photosynthetically active radiation at depth z	Einstein m^{-2} d^{-1}
k_m^I	Half-saturation constant for irradiance	Einstein m^{-2} d^{-1}
$I_m(z)$	Light effect on phytoplankton grow at depth z, $I_m(z) = \frac{I(z)}{I(z)+k_m^I} = \frac{I_0 \times e^{-K_I \times z}}{I_0 \times e^{-K_I \times z}+k_m^I}$	unitless
$I_m(0,z)$	Integrated light effect on phytoplankton grow above depth z, $I_m(0,z) = -\frac{1}{K_I} \times ln\left(\frac{I_0 \times e^{-K_I \times z}+k_m^I}{I_0+k_m^I}\right)$	unitless
PAR_{ML}	Average PAR in the mixed layer ($PAR_{ML} = \frac{1-e^{-K_I \times MLD}}{K_I \times MLD} \times I_0$)	Einstein m^{-2} d^{-1}
μ	Phytoplankton growth rate	d^{-1}
μ_{max}	Maximum phytoplankton growth rate	d^{-1}

μ_{max}^0	Maximum phytoplankton growth rate for $T = 0$ °C	d^{-1}
r_{HR}	Heterotrophic respiration ratio	d^{-1}
r_{HR}^0	Heterotrophic respiration ratio for $T = 0$ °C	d^{-1}
K_I	~~Diffusion~~ Light attenuation coefficient ($K_I = K_I^w + K_I^{nw}$)	m^{-1}
K_I^w	~~Diffusion~~ Light attenuation coefficient due to water	m^{-1}
K_I^{nw}	~~Diffusion~~ Light attenuation coefficient due to optically active components	m^{-1}
k_c	Specific attenuation coefficient for irradiance	m^2 mmol^{-1}
C	Phytoplankton biomass concentration	mmol m^{-3}
C^*	Phytoplankton biomass concentration that maximizes NCP	mmol m^{-3}
C_{max}^*	Maximum achievable autotroph's biomass concentration	mmol m^{-3}
POC	Particulate organic carbon	mmol m^{-3}
DOC	Dissolved organic carbon	mmol m^{-3}
CDOM	Colored dissolved organic matter	m^{-1}
NAP	Non-algal particles	mmol m^{-3}
T	Temperature	°C
P_t	Temperature dependence for phytoplankton grow rate	°C^{-1}
B_t	Temperature dependence for heterotrophic respiration ratio	°C^{-1}
CO_2	Carbon dioxide	ppmv

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

Parameter	Range or value	Reference
K_I^w	0.09	(Werdell and Bailey, 2005)
k_c	0.03	(Werdell and Bailey, 2005)
Carbon to chlorophyll ratio	90	(Arrigo et al., 2008)
k_m^I	4.1 Einstein m^{-2} d^{-1}	(Behrenfeld and Falkowski, 1997)
P_t	0.0663	(Eppley, 1972)
B_t	0.08	(Rivkin and Legendre, 2001; López-Urrutia et al., 2006)
μ_{max}	1 d^{-1}, 1.2 d^{-1}	(Laws et al., 2000; Eppley, 1972)
r_{HR}	0.1 d^{-1}, 0.2 d^{-1}	(Laws et al., 2000; Mitchell et al., 1991)

Supplementary for: **A mechanistic model of an upper bound on oceanic carbon export as a function of mixed layer depth and temperature**

Zuchuan Li[*], Nicolas Cassar

Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, North

Carolina, USA

[*] Corresponding to: zuchuan.li@duke.edu

1. Derivation of first and second derivatives of $NCP(0, MLD)$

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

Based on equations (8-10):

$$\frac{dNCP(0, MLD)}{dC}$$

$$= \frac{d\left\{-N_m \times \mu_{max} \times \dfrac{\ln\left(\dfrac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right) \times C}{K_I}\right\}}{dC} - \frac{d\{r_{HR} \times C \times MLD\}}{dC}$$

$$= -N_m \times \mu_{max}$$

$$\times \frac{\left\{\ln\left(\dfrac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right) - C \times \dfrac{I_0 + k_m^I}{I_0 \times e^{-K_I \times MLD} + k_m^I} \times \dfrac{I_0 \times e^{-K_I \times MLD}}{I_0 + k_m^I} \times k_c \times MLD\right\} \times K_I - k_c \times C \times \ln\left(\dfrac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right)}{K_I{}^2}$$

$$- r_{HR} \times MLD$$

$$= -N_m \times \mu_{max} \times \frac{\{-K_I \times I_m(0, MLD) - C \times I_m(MLD) \times k_c \times MLD\} \times K_I + k_c \times C \times K_I \times I_m(0, MLD)}{K_I{}^2} - r_{HR} \times MLD$$

$$= N_m \times \mu_{max} \times \frac{K_I \times I_m(0, MLD) + k_c \times C \times I_m(MLD) \times MLD - k_c \times C \times I_m(0, MLD)}{K_I} - r_{HR} \times MLD$$

$$= N_m \times \mu_{max} \times \frac{K_I \times I_m(0, MLD) - k_c \times C \times I_m(0, MLD) + k_c \times C \times MLD \times I_m(MLD)}{K_I} - r_{HR} \times MLD$$

$$= N_m \times \mu_{max} \times \frac{K_I^w \times I_m(0, MLD) + k_c \times C \times MLD \times I_m(MLD)}{K_I^w + k_c \times C} - r_{HR} \times MLD \qquad (S1)$$

where $I_m(MLD) = \dfrac{I_0 \times e^{-K_I \times MLD}}{I_0 \times e^{-K_I \times MLD} + k_m^I}$.

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

$$\frac{d^2 NCP(0, MLD)}{dC^2} = N_m \times \mu_{max} \times \left\{\frac{dy}{dC} + \frac{dg}{dC}\right\} \qquad (S2)$$

where $y = \dfrac{K_I^w \times I_m(0, MLD)}{K_I} = -\dfrac{K_I^w \times \ln\left(\dfrac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right)}{K_I{}^2}$ and $g = \dfrac{k_c \times C \times MLD \times I_m(MLD)}{K_I}$.

$\dfrac{dy}{dC}$ and $\dfrac{dg}{dC}$ are derived as follows:

$$\frac{dy}{dC} = -K_I^w \times \frac{\frac{I_0 + k_m^I}{I_0 \times e^{-K_I \times MLD} + k_m^I} \times \frac{I_0 \times e^{-K_I \times MLD}}{I_0 + k_m^I} \times (-k_c \times MLD) \times K_I^2 - ln\left(\frac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I}\right) \times 2 \times K_I \times k_c}{K_I^4}$$

$$= -K_I^w \times \frac{-I_m(MLD) \times MLD \times K_I^2 + I_m(0, MLD) \times 2 \times K_I^2}{K_I^4} \times k_c$$

$$= K_I^w \times \frac{I_m(MLD) \times MLD - 2 \times I_m(0, MLD)}{K_I^2} \times k_c \qquad (S3)$$

$$\frac{dg}{dC}$$

$$= \frac{-k_c \times C \times MLD \times I_m(MLD) \times k_c + k_c \times MLD \times I_m(MLD) \times K_I}{K_I^2}$$

$$+ \frac{k_c \times C \times MLD \times \frac{I_0 \times e^{-K_I \times MLD} \times (-k_c \times MLD) \times \{I_0 \times e^{-K_I \times MLD} + k_m^I\} - I_0 \times e^{-K_I \times MLD} \times I_0 \times e^{-K_I \times MLD} \times (-k_c \times MLD)}{\{I_0 \times e^{-K_I \times MLD} + k_m^I\}^2} \times K_I}{K_I^2}$$

$$= \frac{k_c \times MLD \times I_m(MLD) \times K_I + k_c \times C \times MLD \times \frac{I_0 \times e^{-K_I \times MLD} \times (-k_c \times MLD) \times k_m^I}{\{I_0 \times e^{-K_I \times MLD} + k_m^I\}^2} \times K_I - k_c^2 \times C \times MLD \times I_m(MLD)}{K_I^2}$$

$$= \frac{k_c \times MLD \times I_m(MLD) \times K_I + k_c \times C \times MLD \times \frac{I_m(MLD)^2 \times (-k_c \times MLD) \times k_m^I}{I_0 \times e^{-K_I \times MLD}} \times K_I - k_c^2 \times C \times MLD \times I_m(MLD)}{K_I^2}$$

$$= \frac{MLD \times I_m(MLD) \times K_I + k_c \times C \times MLD \times \frac{-I_m(MLD)^2 \times MLD \times k_m^I}{I_0 \times e^{-K_I \times MLD}} \times K_I - k_c \times C \times MLD \times I_m(MLD)}{K_I^2} \times k_c$$

$$= \frac{MLD \times I_m(MLD) \times K_I - k_c \times C \times MLD \times I_m(MLD)}{K_I^2} \times k_c - \frac{k_c \times C \times MLD \times \frac{I_m(MLD)^2 \times MLD \times k_m^I}{I_0 \times e^{-K_I \times MLD}} \times K_I}{K_I^2} \times k_c$$

$$= \frac{MLD \times I_m(MLD) \times K_I^w}{K_I^2} \times k_c - \frac{MLD^2 \times C \times I_m(MLD)^2 \times k_m^I}{K_I \times I_0 \times e^{-K_I \times MLD}} \times k_c^2 \quad (S4)$$

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

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

$$= N_m \times \mu_{max} \times \left\{ K_I^w \times \frac{I_m(MLD) \times MLD - 2 \times I_m(0, MLD)}{K_I^2} \times k_c + \frac{MLD \times I_m(MLD) \times K_I^w}{K_I^2} \times k_c - \frac{MLD^2 \times C \times I_m(MLD)^2 \times k_m^I}{K_I \times I_0 \times e^{-K_I \times MLD}} \right.$$

$$\left. \times k_c^2 \right\}$$

$$= N_m \times \frac{\mu_{max}}{K_I} \times k_c \times \left\{ \frac{2 \times K_I^w}{K_I} \times \left(I_m(MLD) \times MLD - I_m(0, MLD) \right) - \frac{MLD^2 \times C \times I_m(MLD)^2 \times k_m^I}{I_0 \times e^{-K_I \times MLD}} \times k_c \right\} \quad (S5)$$

2. NCP upper bound for shallow MLD

When $0 \leq MLD < MLD_{C_{max}^*}$ and $MLD \to 0$, $1 - \exp(-K_I \times MLD)$ in equation (15) can be approximated using a second order of Taylor expansion:

$$1 - \exp(-K_I \times MLD) \approx K_I \times MLD - \frac{1}{2} \times (K_I \times MLD)^2 \qquad (S6)$$

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

$$NCP(0, MLD) = C \times MLD \times \left(-\frac{1}{2} \times K_I \times MLD \times \mu^* + \mu^* - r_{HR} \right) \qquad (S7)$$

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

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

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

$$NCP^* = \mu^* \times C_{max}^* \times MLD \times \left(-\frac{1}{2} \times (k_c \times C_{max}^* + K_I^w) \times MLD + \frac{\mu^* - r_{HR}}{\mu^*} \right) \qquad (S9)$$

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

3. An upper bound on export ratio

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

$$ef = \frac{NCP(0, MLD)}{NPP(0, MLD)} = 1 - \frac{K_I \times MLD}{-ln\left(\frac{I_0 \times e^{-K_I \times MLD} + k_m^I}{I_0 + k_m^I} \right)} \times \frac{1}{N_m} \times \frac{r_{HR}}{\mu_{max}} \qquad (S10)$$

~~where $MLD_{opt} = \frac{K_I \times MLD}{1 - e^{-K_I \times MLD}}$.~~ The first derivative of ef ~~MLD_{opt}~~ with respect to ~~$K_I \times MLD$~~ C is expressed as:

$$\frac{\partial ef}{\partial C} = -\left(1 - \frac{MLD \times I_m(MLD)}{I_m(0, MLD)} \right) \times \frac{1}{K_I} \times k_c \times (1 - ef) \qquad (S11)$$

~~Because $e^{K_I \times MLD} > 1 + K_I \times MLD$ for $K_I \times MLD > 0$,~~ According to the inequality in equation (13), $\frac{\partial ef}{\partial C}$ in equation (S11) must be less than ~~0~~ zero. The~~refore, minimum of ef~~ MLD_{opt} ~~approximates to 1~~ maximizes when ~~$K_I \times MLD$~~ $C \to 0$ ($ef = 1 - \frac{1}{I_m(0)} \times \frac{1}{N_m} \times \frac{r_{HR}}{\mu_{max}}$). Considering that ~~In addition,~~ the minimum values for the terms

$\frac{1}{N_m}$ and $\frac{1}{I_m(0)}$ ~~in equation (S10) have the minimum of~~ are 1~~. Therefore~~, ef is maximized in ~~the maximum of~~

equation (S10) ~~is~~ ~~has~~ with ~~the maximum of~~ $ef^* = 1 - \frac{r_{HR}}{\mu_{max}} = 1 - \alpha \times e^{(B_T - P_T) \times T}$, where α represents an

constant, $B_T = 0.11$ and $P_T = 0.0633$ 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 O_2/Ar method estimates NCP through a mass balance of biological O_2 in the mixed layer. Because Ar

and O_2 have similar temperature dependencies and solubilities (Craig and Hayward, 1987), the saturation state of

their ratio can partition oxygen concentration due to physical ($[O_2]_{phys}$) and biological processes ($[O_2]_{biol}$)

(Cassar et al., 2011):

$$[O_2]_{biol} = [O_2] - [O_2]_{phys} \approx [O_2] - \frac{[Ar]}{[Ar]_{sat}} [O_2]_{sat} = \frac{[Ar]}{[Ar]_{sat}} [O_2]_{sat} \Delta(O_2/Ar) \qquad (S12)$$

where $\Delta(O_2/Ar) = \left[\frac{([O_2]/[Ar])}{([O_2]/[Ar])_{sat}} - 1 \right]$ is the biological O_2 supersatulation. When ignoring vertical mixing and

lateral advection, we can write the mass balance for $[O_2]_{biol}$ in the mixed layer as follows (Cassar et al., 2011):

$$MLD \frac{d[O_2]_{biol}}{dt} = NCP - k_{O_2} \frac{[Ar]}{[Ar]_{sat}} [O_2]_{sat} \Delta(O_2/Ar) \qquad (S13)$$

where k_{O_2} is the gas exchange velocity for O_2. At steady state (i.e., $\frac{d[O_2]_{biol}}{dt} = 0$), equation (S13) reduces to

(Cassar et al., 2011; Reuer et al., 2007):

$$NCP = k_{O_2}[O_2]_{sat}\Delta(O_2/Ar) \qquad (S14)$$

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_{O_2} 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 O₂/Ar NCP estimates can be found in previous studies (Bender et al., 2011; Cassar et al., 2014; Jonsson et al., 2013).

Table S1. O₂/Ar measurements included in this study.

Citation	Cruise	Start date	End date	Location
(Reuer et al., 2007)	A0103	10/30/2001	12/10/2001	South of Australia
	SOFEXR	01/07/2002	02/12/2002	South of New Zealand
	SOFEXM	01/20/2002	02/24/2002	South of New Zealand
	NBP0305	10/28/2003	11/13/2003	South of New Zealand
	ANTXXI/2	11/18/2003	01/15/2004	South of South Africa
	NBP0305A	12/20/2003	12/29/2003	South of New Zealand
(Cassar et al., 2007)	AA2006	12/03/2005	02/09/2006	South of Australia
(Juranek et al., 2010)	AMT16	05/22/2005	06/28/2005	Atlantic
	AMT17	10/18/2005	11/25/2005	Atlantic
(Stanley et al., 2010)	EUC-Fe	07/19/2006	08/31/2006	Equatorial Pacific
(Tortell et al., 2011)	CORSACS II	11/03/2006	12/11/2006	South of New Zealand
(Cassar et al., 2011)	SAZ-SENSE	01/19/2007	02/19/2007	South of Australia
(Huang et al., 2012)	LMG0801	01/07/2008	01/29/2008	Drake Passage
(Hamme et al., 2012)	GASEX	03/02/2008	04/11/2008	South of Atlantic
(Martin et al., 2013)	LOHAFEX	01/26/2009	03/06/2009	South of Atlantic
(Shadwick et al., 2015)	AA1203	01/08/2012	02/10/2012	South of Australia
(Eveleth et al., 2016)	LMG1201	12/30/2011	02/07/2012	Drake Passage
	LMG1301	01/05/2013	02/03/2013	Drake Passage
	LMG1401	01/01/2014	02/01/2014	Drake Passage
(Huang et al., unpublished)	LMG0901	01/06/2009	02/01/2009	Drake Passage
	LMG1001	01/01/2010	02/07/2010	Drake Passage
	LMG1101	01/02/2011	02/06/2011	Drake Passage

4.2 Sediment trap and ²³⁴Thorium POC export production

We also compared NCP^* to sediment-trap and ²³⁴Th-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/. 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.

MLD is estimated as the depth at which the potential density (σ_θ) exceeds a near-surface reference value at 10 m depth by $\Delta\sigma_\theta = 0.03$ kg m^{-3} (de Boyer Montegut et al., 2004; Dong et al., 2008). Estimates were averaged to daily $5° \times 5°$ grids, from which monthly climatologies were calculated (Figure S1).
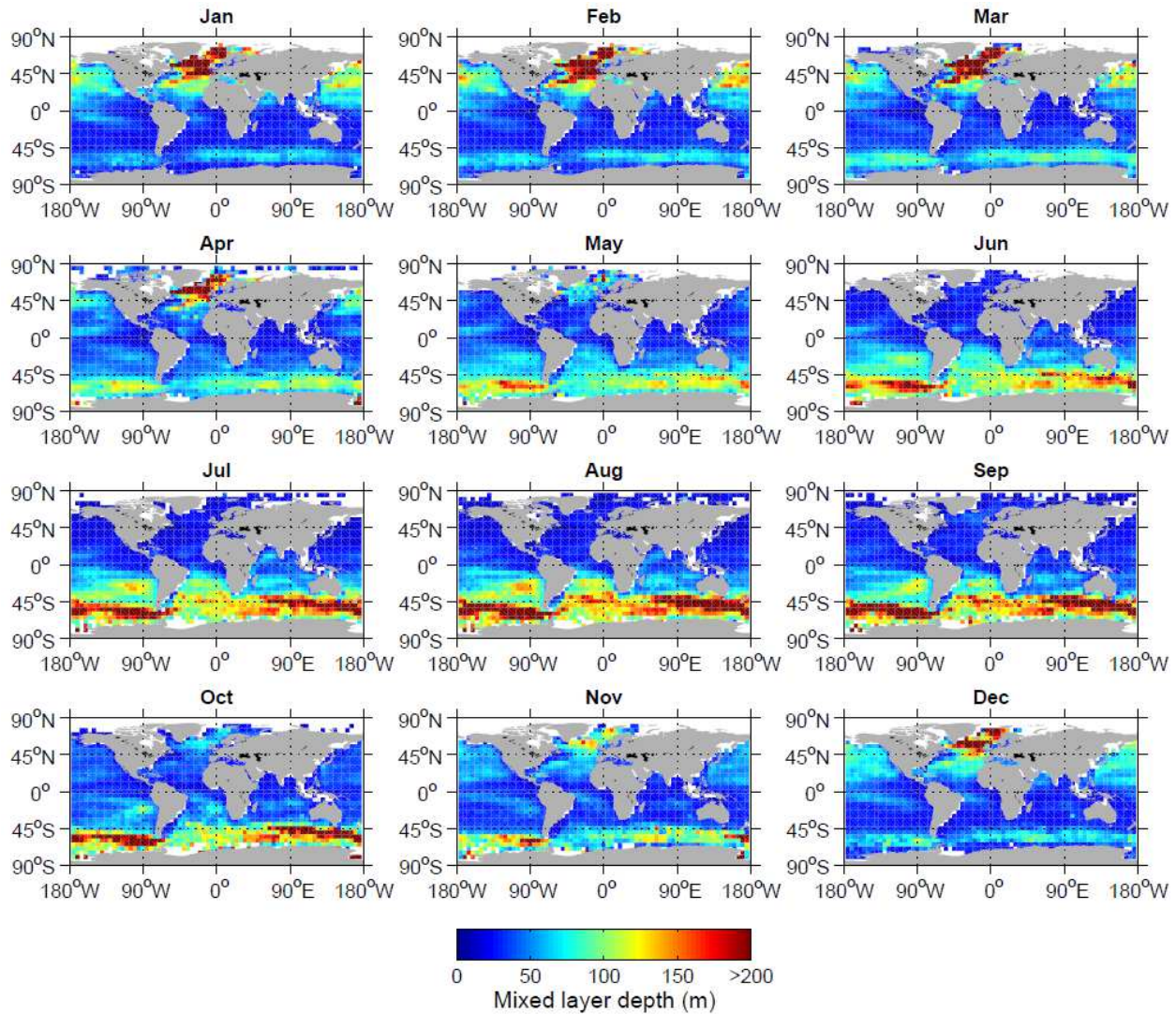

Figure S1. Climatology of monthly mixed layer depth.

4.4 Satellite properties

To derive a global distribution of NCP^*, we used monthly SST and PAR climatologies calculated based on MODIS-Aqua observations from 2002-2015 with a spatial resolution of $0.083° \times 0.083°$ (downloaded from NASA's ocean color website (http://oceancolor.gsfc.nasa.gov/cms/)). We compared 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).
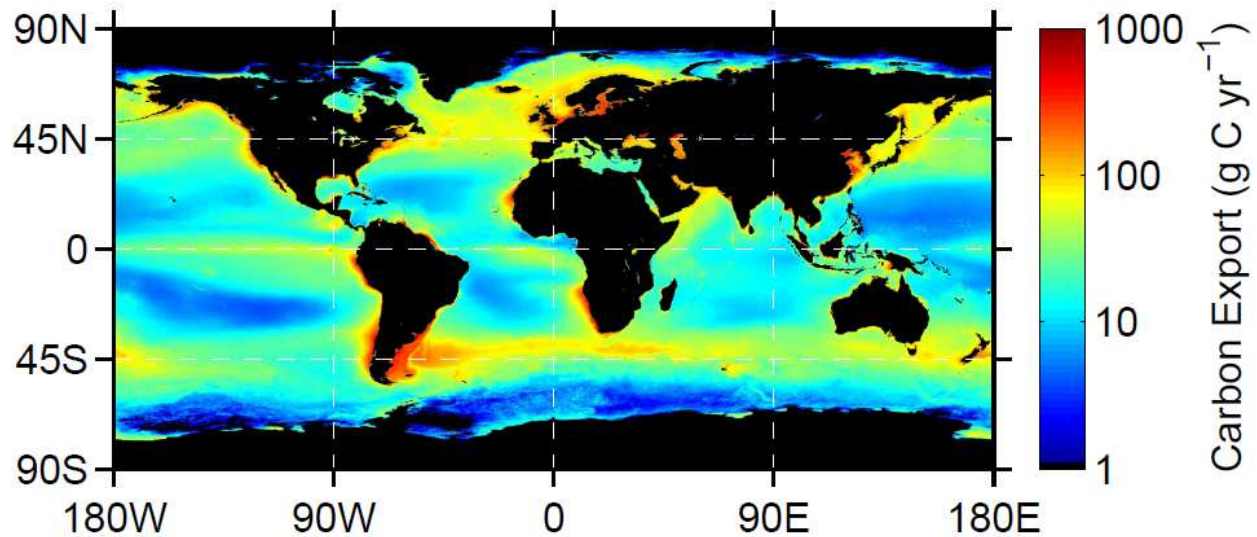

Figure 2S. Average annual export production derived using 11 algorithms (see Li and Cassar (2016)).

4.5. Diffusion attenuation coefficient for photosynthetically active radiation

Constants k_c and K_I^w in equation (10) were derived using the NOMAD dataset (Werdell and Bailey, 2005), which includes chlorophyll a concentration and K_I (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).
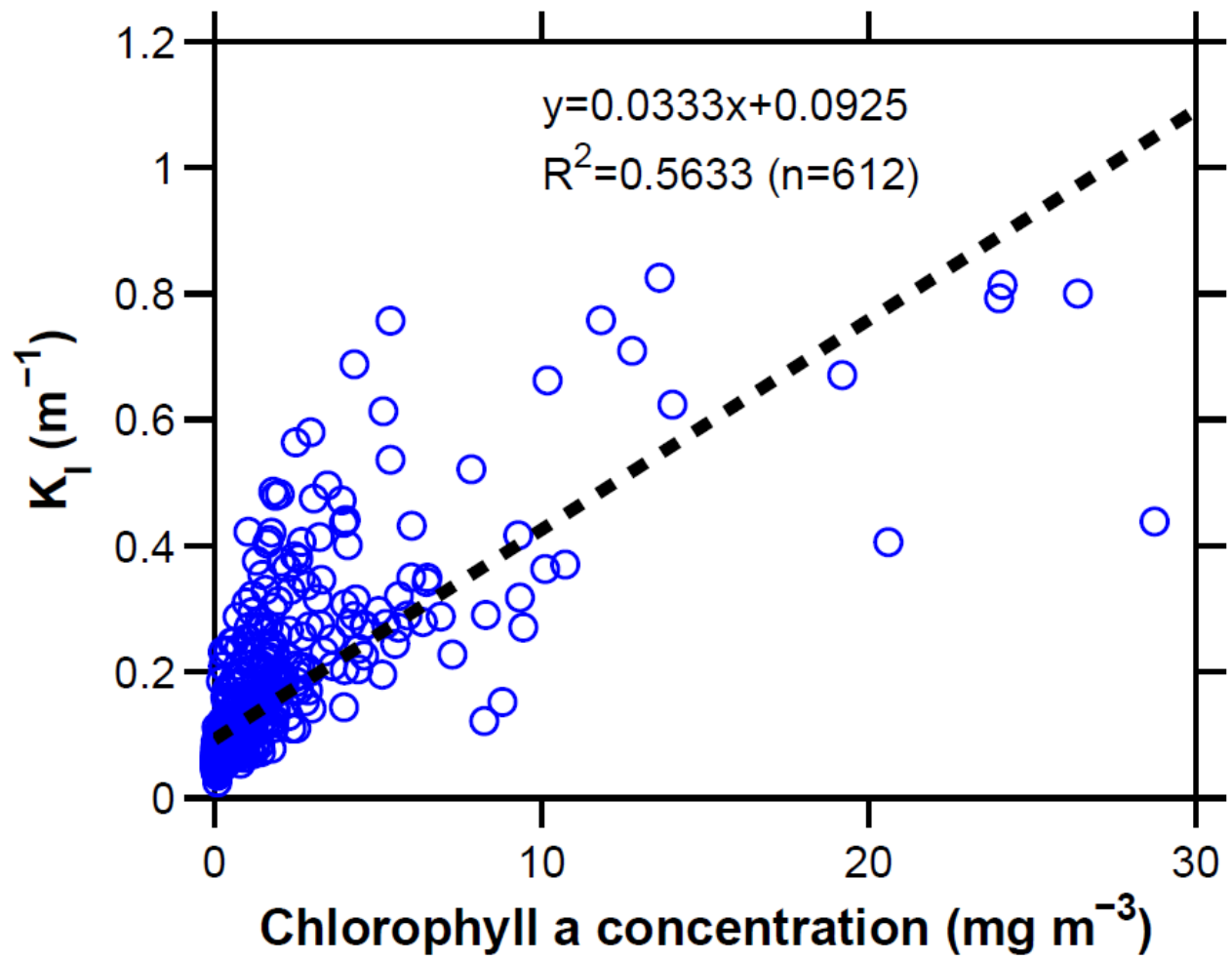
Figure S3. Attenuation coefficient for photosynthetically active radiation (PAR) as a function of chlorophyll a concentration based on the NOMAD dataset.
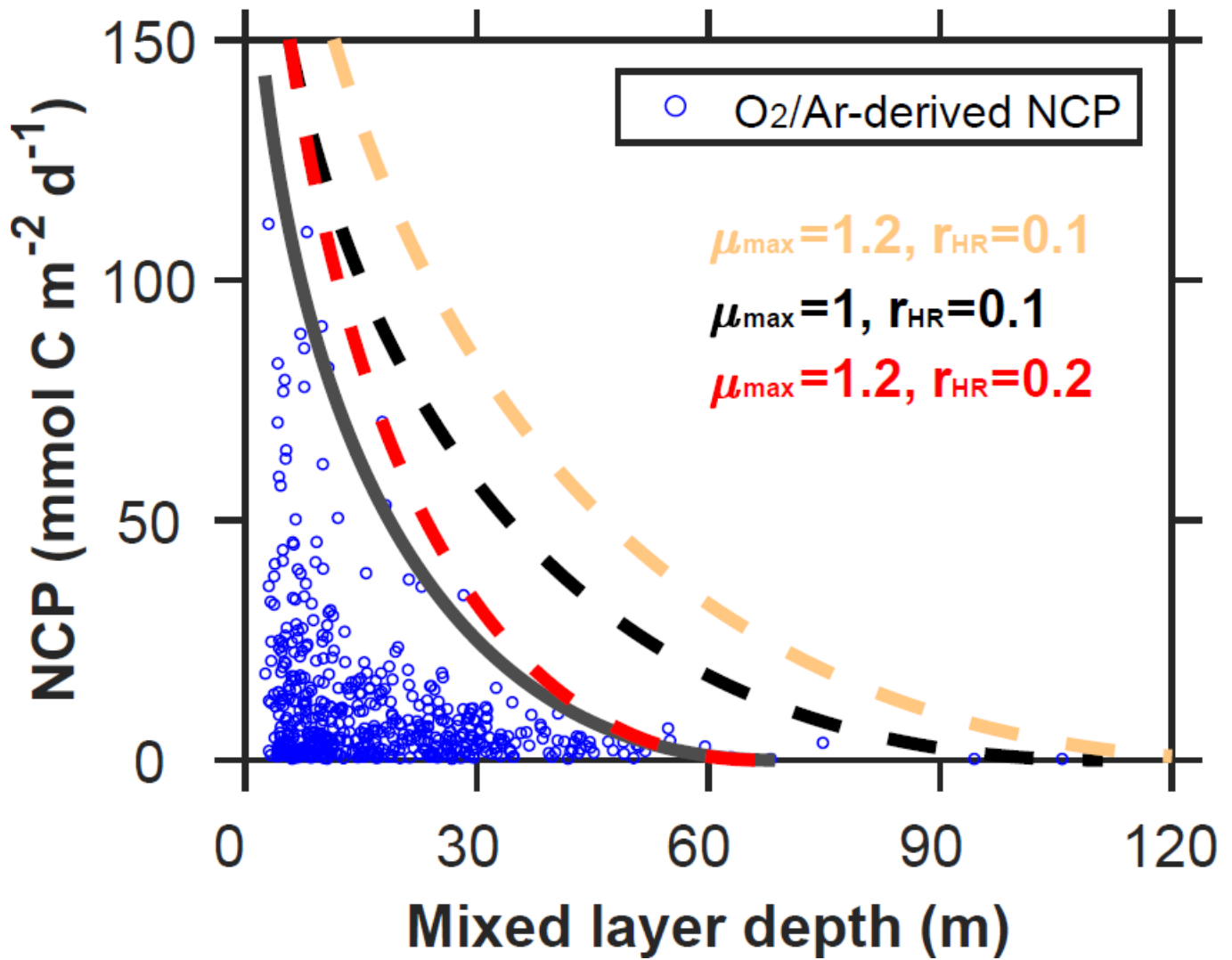
Figure S4. Modeled upper bound on carbon export production compared to field observations as a function of mixed layer depth (MLD). Observations are based on O_2/Ar-derived net community production (NCP). To account for the effect of photosynthetically active radiation (PAR) on export production, both MLD and carbon fluxes are normalized to $-log(1 - I_m(0))$ (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).

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