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 $NCP(0, MLD)$

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):

$$\frac{dNCP(0, MLD)}{dC} = \frac{d}{dC}\left\{-N_m \times \mu_{max} \times \ln\left(\frac{l_0 \times e^{-K_I \times MLD}}{l_0 + k^l_m} + k^l_m\right) \times \mathcal{L}\right\} - \frac{d{r_{HR}} \times C \times MLD}{dC}$$

$$= -N_m \times \mu_{max} \times \ln\left(\frac{l_0 \times e^{-K_I \times MLD} + k^l_m}{l_0 + k^l_m}\right) - C \times \ln\left(\frac{l_0 \times e^{-K_I \times MLD}}{l_0 + k^l_m}\right) \times K_I$$

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

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

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

where $y = \frac{k^w_I \times l_m(0, MLD)}{K_I} = - \frac{k^w_I \times \ln\left(\frac{l_0 \times e^{-K_I \times MLD} + k^l_m}{l_0 + k^l_m}\right)}{K_I^2}$ and $g = \frac{k_c \times C \times MLD \times l_m(0, MLD)}{K_I^2}$. $\frac{dy}{dC}$ and $\frac{dg}{dC}$ are derived as follows:
\[
\frac{dy}{dC} = -K_i^w \times \frac{l_0 + k_m^i}{l_0 \times e^{-K_i \times MLD} + k_m^i} \times \frac{l_0 \times e^{-K_i \times MLD}}{l_0 + k_m^i} \times \left(-k_c \times MLD\right) \times K_i^2 - \ln \left(\frac{l_0 \times e^{-K_i \times MLD} + k_m^i}{l_0 + k_m^i}\right) \times 2 \times K_i \times k_c
\]

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

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

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

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

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

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

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

Substituting equations (S3-S4) into equation (S2) yields:
\[
\frac{d^2 NCP(0, MLD)}{dC^2} = N_m \times \mu_{max} \times \left\{ K_i^{nw} \times \frac{I_m(MLD) \times MLD - 2 \times I_m(0, MLD)}{K_i} \times k_c + \frac{MLD \times I_m(MLD) \times K_i^{nw}}{K_i} \times k_c \\
- \frac{MLD^2 \times C \times I_m(MLD)^2 \times k_m^l}{K_i \times I_0 \times e^{-K_i \times MLD} \times k_c^2} \right\}
\]
\[
= N_m \times \frac{\mu_{max}}{K_i} \times k_c \times \left\{ 2 \times \frac{K_i^{nw}}{K_i} \times \left( I_m(MLD) \times MLD - I_m(0, MLD) \right) - \frac{MLD^2 \times C \times I_m(MLD)^2 \times k_m^l}{I_0 \times e^{-K_i \times MLD}} \times k_c \right\} \quad (S5)
\]

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:

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

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

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

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

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

when \(0 \leq MLD < MLD_{c_{max}}\), \(K_i^{nw}\) should satisfy \(K_i^{nw} \leq k_c \times C_{max}^* < -\frac{1}{2} \times K_i^{nw} + \frac{\mu^* - r_{HR}}{\mu^*} \times \frac{1}{MLD^*}\), 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 \(C_{max}^*\):

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

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 $e_f$ (equation (24)) is written as follows:

$$
e_f = \frac{NCP(0, MLD)}{NPP(0, MLD)} = 1 - MLD_{opt} \times \frac{1}{N_m} \times \frac{1}{I_m(0)} \times \frac{r_H}{\mu_{max}}$$  \hspace{1cm} (S10)

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

$$
\frac{dMLD_{opt}}{d(K_I \times MLD)} = \frac{1 - \frac{1}{e^{K_I \times MLD}}}{(1 - e^{-K_I \times MLD})^2}
$$  \hspace{1cm} (S11)

Because $e^{K_I \times MLD} > 1 + K_I \times MLD$ for $K_I \times MLD > 0$, equation (S11) should be greater than 0 ($\frac{dMLD_{opt}}{d(K_I \times MLD)} > 0$). The minimum of $MLD_{opt}$ approximates to 1 when $K_I \times MLD \to 0$. In addition, terms $\frac{1}{N_m}$ and $\frac{1}{I_m(0)}$ in equation (S10) have the minimum of 1. Therefore, equation (S10) has the maximum of

$$e_f^* = 1 - \frac{r_H}{\mu_{max}} = 1 - \alpha \times e^{(B_T - P_T) \times T},$$

where $\alpha$ 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 O$_2$/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]:

$$[O_2]_{biol} = [O_2] - [O_2]_{phys} \approx [O_2] - \frac{[Ar]}{[Ar]_{sat}}[O_2]_{sat} = \frac{[Ar]}{[Ar]_{sat}}[O_2]_{sat} \Delta(O_2/Ar)$$  \hspace{1cm} (S12)
where $\Delta(O_2/Ar) = \frac{([O_2]/[Ar]) - 1}{([O_2]/[Ar])_{sat}}$ is the biological $O_2$ supersaturation. 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]:

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

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]:

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

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 $O_2/Ar$ 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 $b = -0.86$ [J H 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 $\Delta \sigma_\theta = 0.03$ 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).
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 $0.083\degree \times 0.083\degree$ (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.
References


Eveleth, R., N. Cassar, R. M. Sherrell, H. Ducklow, M. Meredith, H. Venables, Y. Lin, and Z. Li (2016), Ice melt influence on summertime net community production along the Western Antarctic Peninsula, *Deep Sea Research Part II.*


Li, Z., and N. Cassar (2016), Satellite estimates of net community production based on O2/Ar observations and comparison to other estimates, *Global Biogeochem Cy*, 30(5), 735-752.


