Appendix 1

Here we describe the dynamics of primary producers A, heterotrophic consumers H, the detritus they supply D, and the O_2 and DIC they exchange within the surface mixed layer (Fig. S1). Changes in autotrophic biomass B_A (mol C m^{-3}) reflects a balance between the photosynthetic rate $\mathbb{P}$ (s^{-1}) and the mortality rate m_A (s^{-1}; eq. 1). Note that $\mathbb{P}B_A$ is inclusive of any autotrophic respiratory or excretory carbon loss, equivalent to net primary carbon production (NPP). Similarly, heterotrophic biomass B_H is balanced by the consumption of detritus (defined by the uptake rate k and the anabolic yield y) and mortality m_H (eq. 2). The detritus pool draws directly from the mortality of both the primary producers and heterotrophic consumers, and is subsequently consumed by heterotrophs (eq. 3). The detritus can also be exported through sinking $\frac{wB_D}{h}$, where w is the sinking rate (m s^{-1}) and h is the mixed layer thickness (m). An external source of particles is supplied by advection or mixing $\nabla\cdot(\mathbf{u}B)$ (mol m^{-3} s^{-1}). As will become clear, the choice between a linear or quadratic mortality has no effect at steady state.

$$\frac{\partial B_A}{\partial t} = \mathbb{P}B_A - m_A B_A^2 - \nabla\cdot(\mathbf{u}B_A) \tag{1}$$

$$\frac{\partial B_H}{\partial t} = kB_H B_D y - m_H B_H^2 - \nabla\cdot(\mathbf{u}B_H) \tag{2}$$

$$\frac{\partial B_D}{\partial t} = m_A B_A^2 + m_H B_H^2 - kB_H B_D - \frac{wB_D}{h} - \nabla\cdot(\mathbf{u}B_D) \tag{3}$$

DIC is consumed by photosynthesis and produced by the respiration of detritus at a rate scaled by the yield $1-y$ (eq. 4). In addition to advection and mixing, DIC can also be outgassed to the atmosphere at a rate $\frac{F_{DIC}}{h}$ (mol C m^{-3} s^{-1}).

$$\frac{\partial B_{DIC}}{\partial t} = -\mathbb{P}B_A + kB_H B_D(1-y) - \nabla\cdot(\mathbf{u}B_{DIC}) - \frac{F_{DIC}}{h} \tag{4}$$

Similarly, oxygen is produced by primary producers and consumed by heterotrophs, but at rates dependent on the stoichiometry of oxygen to DIC associated with photosynthesis and respiration (eq. 5). We refer to these stoichiometric ratios as the photosynthetic quotient (PQ) and the respiratory quotient (RQ), respectively, with consistent units of mol O_2 produced [mol DIC consumed]$^{-1}$. As in the case of DIC, a supply of oxygen from advection, mixing and exchange with the atmosphere closes the budget.

$$\frac{\partial B_{O_2}}{\partial t} = \mathbb{P}B_A PQ - kB_H B_D(1-y)RQ - \nabla\cdot(\mathbf{u}B_{O_2}) - \frac{F_{O_2}}{h} \tag{5}$$

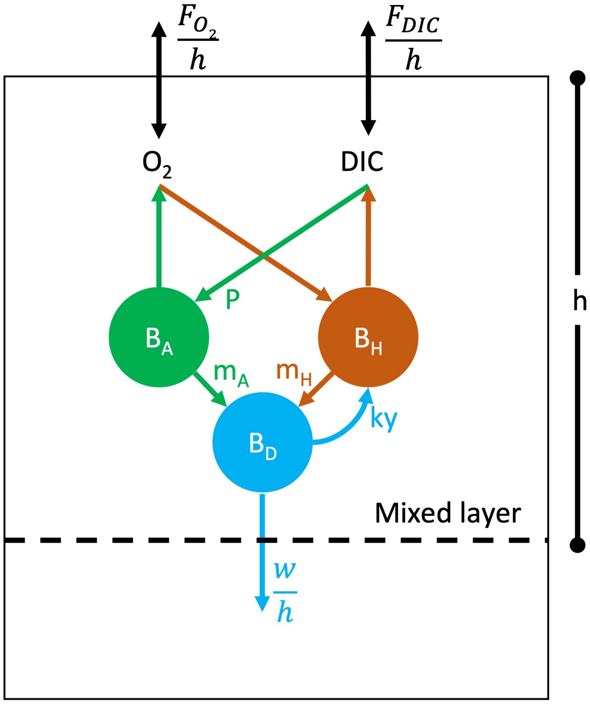

Fig. S1 - Autotrophic and heterotrophic biomass (B_A and B_H, respectively) exchange oxygen and DIC within a mixed layer of thickness h. At steady state, growth is balanced by mortality of B_A and B_H into the detritus pool (B_D) at rates m_A and m_H. The detritus is consumed by heterotrophs at rate k and sinks at rate w, which is balanced by an efflux of DIC ($F_{DIC} = -wB_D$). Oxygen exchanges with the atmosphere at a flux F_{O_2} and is coupled to the carbon flux through the balance of photosynthesis and respiration by the stoichiometric ratios PQ and RQ.

To evaluate the contribution of advection and mixing to the dynamics of particles and gasses, we consider the vector components of the total divergence individually:

$$\nabla \cdot (\mathbf{u}B) = -(u\frac{\partial B}{\partial x} + v\frac{\partial B}{\partial y} + w\frac{\partial B}{\partial z}) + K_z\frac{\partial^2 B}{\partial z^2} \tag{6}$$

where K_z is the eddy diffusivity coefficient (m^2 s^{-1}). Mesoscale (order 100 km) gradients in mixed layer microbial biomass, oxygen, and DIC are modest (with a slope of less than 10% of the mean at a 100 km spatial resolution) within the subtropical gyres, and geostrophic transport velocities are on the order of 0.1 m s^{-1}. If we consider a time scale of one day, the resulting supply is less than 1% of biological production and consumption rates, and we can reasonably discount their contributions. The vertical contribution to the total divergence would be even smaller, since particles and gas concentrations are approximately constant within a well mixed layer. A reasonable estimate for K_z is on the order 10^{-5} m^2 s^{-1}, which also translates to a vanishingly small component compared with biological rates. For a stable mixed layer (in the absence of substantial entrainment events), a steady state (i.e., $\frac{\partial B}{\partial t} = 0$) is reached at a time scale of days to weeks, compensating for diurnal fluctuations in the mixed layer depth h.

In this scenario, the growth of primary producers and heterotrophic consumers is strictly balanced by their morality losses to the detritus pool (eq. 7 and 8).

$$\mathbb{P}B_A = m_A B_A^2 \tag{7}$$

$$kB_H B_D y = m_H B_H^2 \tag{8}$$

By substitution (eq. 3), one finds that the export of carbon is what remains of the net primary production after any heterotrophic respiratory losses, also known as net community production (NCP).

$$\frac{wB_D}{h} = \mathbb{P}B_A - kB_H B_D(1-y) \tag{9}$$

To close the carbon budget, the exchange of DIC with the atmosphere is set by this export rate. A positive export flux ($wB_D > 0$) indicates outgassing of DIC to the atmosphere ($F_{DIC} < 0$; mol m^{-2} s^{-1}).

$$F_{DIC} = -wB_D \tag{10}$$

However, when we consider the exchange of oxygen with the atmosphere, we need also to take account of PQ and RQ:

$$F_{O_2} = wB_D RQ + \mathbb{P}B_A(PQ - RQ)h \tag{11}$$

Notice that if these stoichiometries are identical ($PQ = RQ$), the oxygen flux is simply equal to the stoichiometric equivalent of the DIC flux, but opposite in sign, indicating the outgassing of oxygen associated with non-negative particle export. Equation 11 can be restated in terms of the export ratio ($E = \frac{\frac{wB_D}{h}}{\mathbb{P}B_A}$):

$$E = \frac{RQ - PQ}{RQ} + \frac{\frac{F_{O_2}}{h}}{\mathbb{P}B_A RQ} \tag{12}$$

In the main text, we interpret $\frac{F_{O_2}}{h}$ to be equivalent to net community oxygen production (NCP_{O_2}), and $\mathbb{P}B_A PQ$ to be equivalent to net primary oxygen production (NPP_{O_2}). Rearranging from Equation 12:

$$E = 1 - \frac{PQ}{RQ} + \frac{NCP_{O_2}}{NPP_{O_2}} \tag{13}$$

from which we can identify two important limits. In the first limit, we assume that the oxygen to dissolved inorganic carbon stoichiometry of photosynthesis is counterbalanced by respiration $PQ = RQ$. At this limit we find the standard interpretation of the link between NCP_{O_2} and export:

$$E = \frac{\frac{F_{O_2}}{h}}{\mathbb{P}B_A RQ} \tag{14}$$

However, in the second limit, NCP_{O_2} is small relative to NPP_{O_2} rates ($F_{O_2} \to 0$). Eliminating this term, the export ratio is then solely a function of the ratio of the photosynthetic and respiratory stoichiometries,

$$E = 1 - \frac{PQ}{RQ} \tag{15}$$

Appendix 2

Both PQ and RQ are stoichiometrically constrained with respect to the redox state of organic matter transformations. In the following sections, we will derive the relationships between (A) RQ, the nominal oxidation state of carbon substrates for aerobic respiration, and the Gibbs energy of combustion, and (B) PQ, the oxidation state of nitrogen, and the elemental stoichiometry of autotrophic biomass,

Respiration of organic carbon

Aerobic respiration combines molecular oxygen with an organic carbon substrate, yielding CO_2 and water. The stoichiometry of O_2 to CO_2 in the complete oxidation reaction RQ is dependent on the nominal carbon oxidation state of

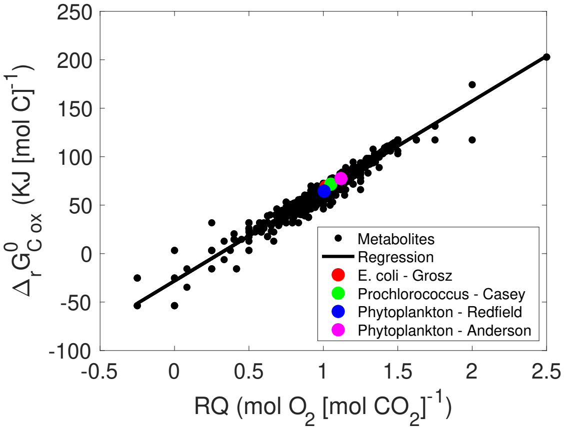

Fig. S2 - Calculated Gibbs energy of carbon oxidation (ΔG^0_{Cox}) versus RQ for a database of metabolites (*38*)(black markers) and several microbial biomass compositions (*38–40*)(colored markers). ΔG^0_{Cox} values were calculated according to (*37*) from C^* for each molecular formula.

the substrate. For most organic carbon sources, the stoichiometry of complete oxidation is given by

$$\begin{aligned}
&C_aH_bO_cN_dP_eS_f^z + (\frac{2a+4e+n-c}{2})O_2 <=> \\
&aCO_2 + dNH_3 + eHPO_4^{2-} + fHS^- + nH_2O \\
&+ (4a+b-2c-3d+5e-2f-z)e^-
\end{aligned}$$

where $n = \frac{b-f-3d-e}{2}$. The molar ratio of oxygen to CO_2 simplifies to:

$$RQ = \frac{c-n-4e}{2a} - 1$$

Reduced substrates require more oxygen and result in a higher energy yield of combustion $\Delta_r G_C^{'}$ than oxidized ones. The standard Gibbs free energy for combustion (complete aerobic oxidation) is reasonably well predicted by a linear relationship with the average oxidation state of carbon $C^* = \frac{4a+b-2c-3d+5e-2f-z}{a} + 4$, approximated by $\Delta G^0_{Cox} = 60.3 - 28.5C^*$ (*37*). This parameterization is specified at standard temperature (298°K) and pressure (1 atm), and does not account for nitrile or phosphono bonds of the substrate. However, there is a close correspondence between the predicted ΔG^0_{Cox} and RQ ($R^2 = 0.95$; Fig. S2).

Photosynthetic growth

Primary producer biomass is synthesized by the reverse (anabolic) reaction - the reduction of DIC to cellular biomass coupled to the oxidation of water. Although the stoichiometry of DIC consumption to oxygen production depends on both the molecular formula of biomass and the nitrogen, phosphorus, and sulfur sources, the redox state of biomass is reasonably constant and the nitrogen source mostly determines PQ. If we assume an average molecular formula of cells $CH_{1.77}O_{0.49}N_{0.14}$, growth on ammonia as a sole nitrogen source has a corresponding PQ of -1.09 mol O_2 [mol DIC]$^{-1}$:

$$aCO_2 + dNH_3 + nH_2O => C_aH_bO_cN_d + \frac{n + 2a - c}{2}O_2 \tag{16}$$

where $n = \frac{b-3d}{2}$. Considering the extra reductant needed, growth on nitrate as a sole nitrogen source has a corresponding PQ of -1.41 mol O_2 [mol DIC]$^{-1}$:

$$aCO_2 + dNO_3^- + nH_2O => C_aH_bO_cN_d + \frac{n + 2a + 3d - c}{2}O_2 \tag{17}$$

where $n = \frac{b}{2}$. These are reasonable upper and lower bounds on PQ (*27*), since ammonia and nitrate are the most reduced and most oxidized nitrogen sources for phytoplankton growth, respectively (excluding cyanate, which is probably a small component of nitrogen uptake by phytoplankton). The fraction of total nitrogen uptake supplied as nitrate, known as the f-ratio f (*41*), is then a reasonable approximation of PQ

$$PQ = -1.09 - 0.32f \tag{18}$$

Interestingly, f is also interpreted to be equal to the export ratio E at steady state (*41*). Thus, in the limit given by eq. 15, we can infer

$$RQ = \frac{-1.09 - 0.32f}{f - 1} \tag{19}$$

Combining Eq. 18 and Eq. 19, we can plot both PQ and RQ in the same E coordinates under the $F_{O_2} = 0$ limit (Eq. 15; Fig. S3). By comparison with RQ values associated with a selection of organic carbon substrates (horizonal lines in Fig. S3), a heterotrophic diet of exclusively lipids would maintain $E = 0.19$ under this scenario. Given that lipids are the most reduced macromolecular component of biomass, it is unlikely that one might continuously observe $F_{O_2} = 0$ at E above this level, and $RQ = -2$ mol O_2 [mol DIC]$^{-1}$ serves as a theoretical upper boundary on the carbon export that can be supported at $F_{O_2} = 0$. At the oligotrophic time-series Station ALOHA, the annual average of E is 0.122 (*30*) (vertical line in Fig. S3), which corresponds to an RQ value of 1.3 mol O_2 [mol DIC]$^{-1}$. RQ values of microbial biomass (Fig. S2) fall within the range $\{1.01,1.12\}$ mol O_2 [mol DIC]$^{-1}$; thus, the redox state of the respired detritus must be more reduced than the biomass it derives from. Conserving electrons, this leads to the expectation that as detritus ages or sinks, it becomes more oxidized.

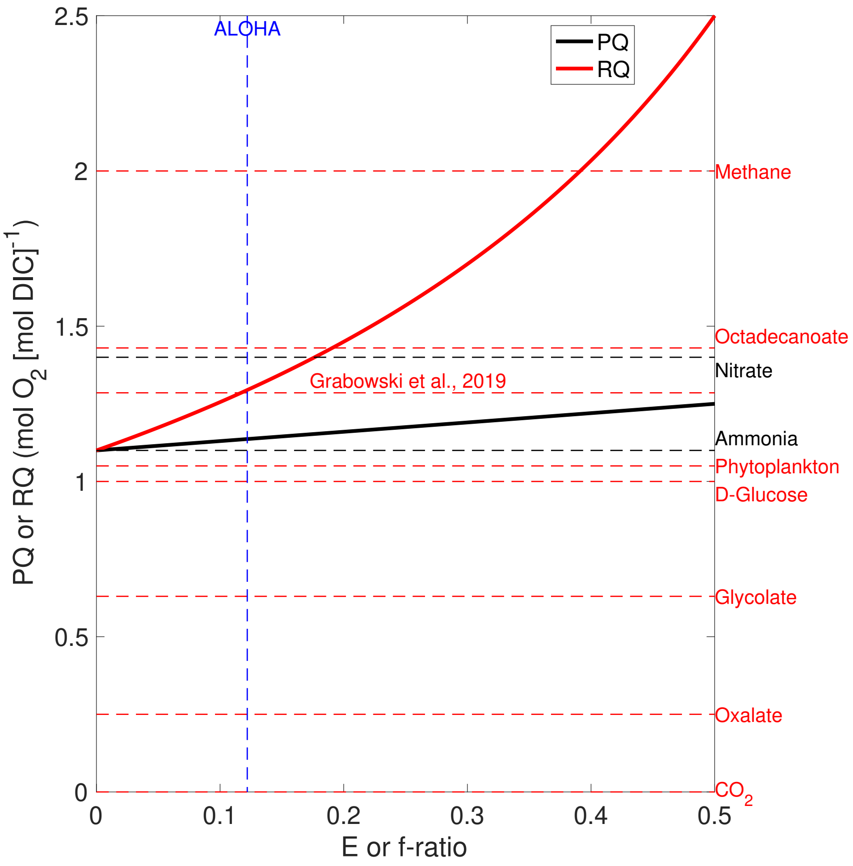

Fig. S3 - Oxygen to DIC stoichiometry of hetrotrophy (RQ; red solid line) and autotrophy (PQ; black solid line) as a function of the export ratio E, or, equivalently, the f-ratio, for the limit $F_{O_2} = 0$. RQ values associated with the oxidation of a selection of substrates spanning the carbon redox range are indicated (horizontal red dashed lines). Phytoplankton biomass is based on an average macromolecular composition (*40*). The RQ value associated with the remineralization of sinking particles at Station ALOHA determined by elemental analysis (*2*) is also shown. PQ values associated with primary production supported entirely by ammonia and nitrate are indicated (horizontal black dashed lines). For reference, the annual mean E ratios measured at Station ALOHA is indicated (vertical blue dashed lines).