



The biological pump in a high CO₂ world

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ABSTRACT: The vertical separation of organic matter formation from respiration can lead to net carbon sequestration within the ocean's interior, making the biological pump an important component of the global carbon cycle. Understanding the response of the biological pump to the changing environment is a prerequisite to predicting future atmospheric carbon dioxide concentrations. Will the biological pump weaken or strengthen? Currently the ocean science community is unable to confidently answer this question. Carbon flux at approximately 1000 m depth, the sequestration flux, determines the removal of carbon from the atmosphere on time scales ≥ 100 yr. The sequestration flux depends upon: (1) input rates of nutrients allochthonous to the ocean, (2) the export flux at the base of the euphotic zone, (3) the deviation of carbon fixation and remineralization from Redfield stoichiometry, and (4) the flux attenuation in the upper 1000 m. The biological response to increasing temperature, ocean stratification, nutrient availability and ocean acidification is frequently taxa- and ecosystem-specific and the results of synergistic effects are challenging to predict. Consequently, the use of global averages and steady state assumptions (e.g. Redfield stoichiometry, mesopelagic nutrient inventory) for predictive models is often insufficient. Our ability to predict sequestration flux additionally suffers from a lack of understanding of mesopelagic food web functioning and flux attenuation. However, regional specific investigations show great promise, suggesting that in the near future predictions of changes to the biological pump will have to be regionally and ecosystem specific, with the ultimate goal of integrating to global scales.

KEY WORDS: Biological pump · Climate change · Ocean acidification · Rising temperature · Marine carbon cycle · Carbon sequestration · Export flux · Sequestration flux

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INTRODUCTION

Concerns regarding the increase of atmospheric partial pressure of carbon dioxide (pCO₂) have focused attention on the biological carbon pump, because the ocean sequesters one-fourth to one-third of the carbon released by human activities (e.g. fossil fuel oxidation, deforestation and cement manufacturing) each year (Sabine et al. 2004, Sabine & Tanhua 2010). The term biological carbon pump refers to the suite of biologically mediated processes responsible for transporting carbon against a concentration gradient from the upper ocean to the deep

ocean. According to our best estimates, approximately two-thirds of the vertical gradient in carbon in the ocean is attributed to the biological pump with the rest due to the solubility pump, but estimates of the relative activity of the different pumps are poorly constrained (Gruber & Sarmiento 2002, Reid et al. 2009). The questions of (1) whether the ocean will continue to take up carbon, (2) at which rate, (3) for how long the exported carbon will remain removed from the atmosphere, and (4) how the biological pump will respond to the consequences of increased carbon input combined with warming have become central both for scientists and politicians. In this

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review article we will explore potential impacts of predicted changes in the global temperature and carbonate system on the ability of the biological pump to sequester carbon and highlight exciting new research directions attempting to address these questions.

THE BIOLOGICAL CARBON PUMP AND ITS CONTROLS

Components of the biological pump

The term biological carbon pump describes the combination of biologically driven processes that spatially separate particulate and dissolved organic matter production from remineralization (organic carbon pump), and the biologically mediated carbon incorporation in calcium carbonate shells from their dissolution (calcium carbonate pump). The organic carbon pump exports about 10 times more carbon than the calcium carbonate pump (Sarmiento et al. 2002).

Photosynthetic production of organic matter is confined to the surface waters, whereas respiration occurs throughout the water column. Photosynthesis converts CO_2 , thereby drawing down dissolved inorganic carbon (DIC), to organic matter. The subsequent export of particulate organic matter (POM) via gravitational flux, of dissolved organic matter (DOM) via mixing and advection, and the active transport of carbon via vertically migrating zooplankton removes the organic matter to deeper regions where it accu-

mulates or is respired (Fig. 1). The effect of the biological pump on carbon storage in the ocean interior can be partitioned into short-term (months to decades) and long-term (centuries to millennia) storage. The depth of remineralization or the remineralization length scale (RLS) of the exported carbon determines the extent to which carbon can be effectively removed through exchange with the atmosphere.

Here we define the vertical export of organic matter from the base of the euphotic zone (~100 m; 1% light level) or from the mixed layer depth as export flux. Photosynthesis sets the upper limit for export flux, however, a greater portion of organic matter produced via photosynthesis is recycled within the euphotic zone of the ocean (regenerated production), thereby escaping export (Buesseler 1998). New production *sensu* Dugdale & Goering (1967) is defined as production that is supported by input of new nitrogen (nitrate) into the euphotic zone via convective mixing, upwelling, atmospheric deposition, nitrogen fixation or horizontal advection. On an annual average, new production is often considered to be equivalent to the export flux at the base of the surface ocean (Jenkins & Goldman 1985).

Long-term sequestration of carbon, as stipulated by the International Panel of Climate Change (IPCC 2007), requires removal from the atmosphere for over 100 yr. This criterion is met after carbon is transported below 1000 m on average (Primeau 2005) and coincides with the nitrate maximum, the base of the mesopelagic zone, and the greatest extent of vertically migrating zooplankton. In this review we consider removal of carbon by the biological pump to

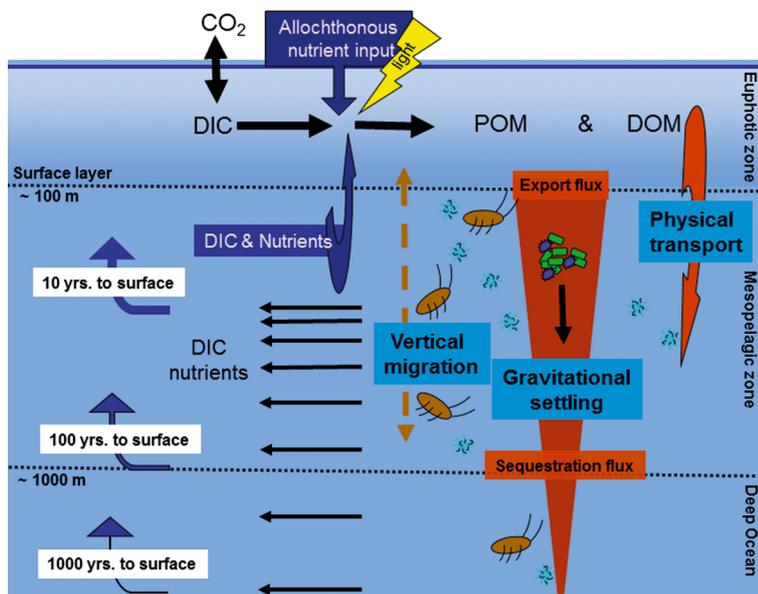


Fig. 1. Schematic of the biological carbon pump. Organic matter formed within the euphotic zone is transported to depth by (1) vertical migrating zooplankton (brown ovals with antennae), (2) gravitational settling of marine snow (green clusters with black bacteria) or (3) physical transport of dissolved organic matter (DOM). The sinking flux of aggregates (symbolized by green cells and blue transparent exopolymer particles) decreases with depth as organic matter is remineralized (turned into its inorganic form). The average time until the dissolved inorganic carbon (DIC) and nutrients are returned back to the surface depends on the depth of remineralization, the remineralization length scale (RLS). Sedimentation out of the surface layer (euphotic zone or mixed layer depth, whichever is deeper) is termed export flux, whereas the sedimentation out of the mesopelagic is called sequestration flux. The carbon sequestration flux determines the storage of carbon within the ocean for 100 yr or more

≥ 1000 m as the sequestration flux sensu Lampitt et al. (2008) (Fig. 1), but caution that the actual depth of the sequestration flux varies regionally depending on ventilation depth. The magnitude and change to the sequestration flux is a critical variable to constrain in order to assess long-term carbon storage and efficiency of the biological pump.

The sequestration flux of carbon at the base of the mesopelagic zone is smaller than export flux and constitutes between 6 and 25% of new production as estimated from deep-moored trap fluxes (Berelson 2001a, Francois et al. 2002). The reduction in flux between the base of the euphotic and mesopelagic zone is referred to as flux attenuation and is caused by intense biological remineralization (conversion of organic carbon to inorganic carbon) and solubilization (conversion of particulate matter to dissolved matter) within the mesopelagic (100 to 1000 m) during downward transport (Martin et al. 1987, Karl et al. 1988, Steinberg et al. 2008a). These biological processes in the mesopelagic zone reduce export flux by ~90% within the upper 1000 m (Nelson et al. 2002, Fasham 2003).

Two schools of thought exist when referring to the efficiency of the biological pump (De La Rocha & Passow 2012). The efficiency of nutrient utilization in the euphotic zone, e.g. the ratio between export flux and primary production, may be meant. In this review we use the alternative, defining the efficiency of the biological pump as the ratio between sequestration flux and export flux.

How the biological pump varies in the face of increased CO_2 and temperature and decreased pH is of critical importance for assessing the role the ocean plays in the oceanic carbon cycle. Here, we provide a summary of several potential scenarios that describe how small changes in the nutrient stoichiometry during production or remineralization of organic matter coupled with changes in allochthonous nutrient inputs and shifts in flux attenuation may affect carbon sequestration via the biological pump.

POM flux

A variety of drivers, such as adherence to or departure from Redfield stoichiometry of organic matter and an increase or decrease in flux attenuation, can result in various scenarios that affect both sequestration flux and nutrient inventories in the mesopelagic zone (Fig. 2).

- Scenario 1: Assuming Redfield stoichiometry and that new production is driven solely by the entrain-

ment of nutrients from depth, equivalent amounts of CO_2 to support the consumption of those inorganic nutrients (i.e. nitrate, phosphate) are also brought to the surface. In such a scenario the export flux of POM returns the C, N and P to depth in amounts equal to the original vertical supply with no net flux of carbon to depth over an annual cycle (Michaels et al. 2001, Hopkinson & Vallino 2005; Fig. 2a).

- Scenario 2: Under assumptions of Redfield stoichiometry and steady state of mesopelagic nutrient inventories, decreased delivery of nutrients into the euphotic zone from below, due to increased stratification, leads to decreased new production and export flux but has no impact on sequestration flux, which remains negligible as in the first scenario (Fig. 2b)
- Scenario 3: Allochthonous input of nutrients (nitrogen, iron, phosphorous) from aeolian or fluvial inputs or due to nitrogen fixation to the ocean can result in an increased sequestration flux, independent of the export flux, if steady states of mesopelagic nutrient inventories and Redfield stoichiometry are maintained (Fig. 2c). Data on sedimentation rates of POM below 1000 m (from traps or ^{234}Th determinations) indicate that in today's ocean some fraction of organic matter is indeed transported to great depths supporting the idea of increased allochthonous nutrient inputs (Gruber & Sarmiento 1997, Gruber 2005).

The above 3 scenarios are constrained by Redfield stoichiometry and based on the tight coupling between essential nutrients (nitrogen, phosphorus) and carbon during photosynthesis and respiration.

- Scenario 4: Any mechanism that relaxes the C: N: P stoichiometry and results in the production or accumulation of C-rich organic matter has the potential to change the amount of carbon export- and sequestration flux (Fig. 2d). A longer RLS for carbon compared to nitrogen results in the preferential transport of organic carbon to depths (Michaels et al. 2001). This could increase the sequestration flux of carbon without necessarily impacting nutrient inventories within the mesopelagic zone. Experimental and field data support the preferential remineralization of nutrients over carbon (Anderson & Sarmiento 1994, Michaels et al. 2001, Boyd & Trull 2007); however, the effect is small and spatially and temporally variable, making it difficult to quantify on a global scale using current techniques
- Scenarios 5 and 6: Alternatively a change in flux attenuation has the potential to impact the sequestration flux, without deviating from the Redfield stoichiometry and without changes in allochtho-

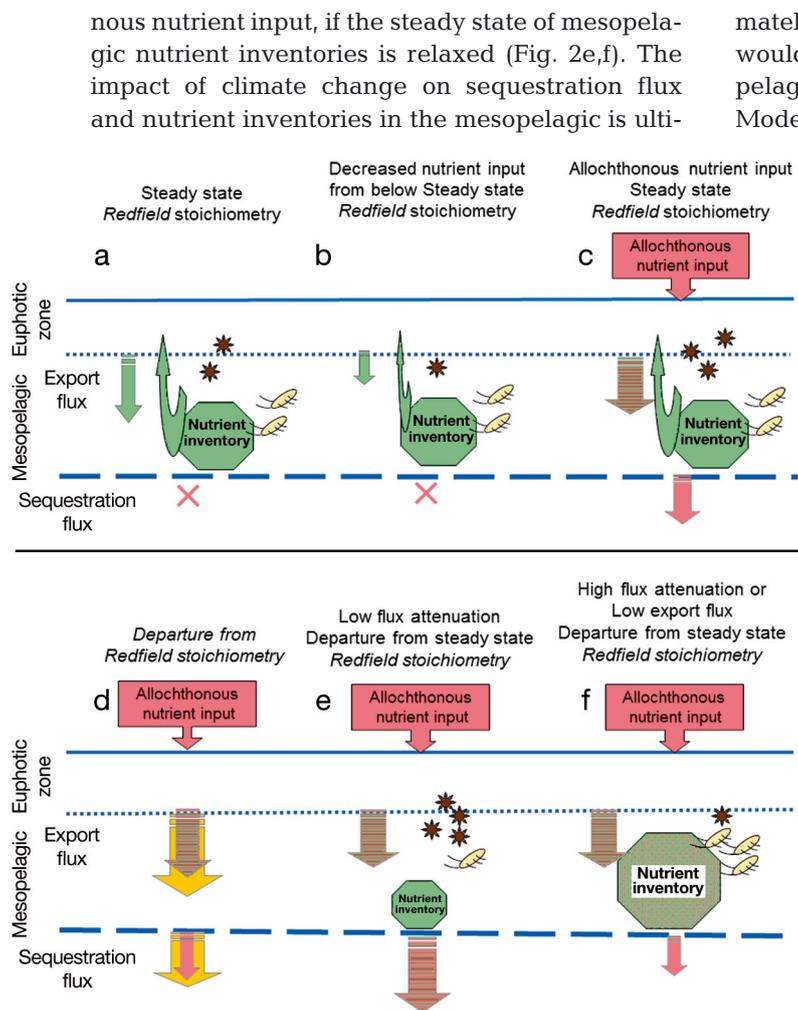


Fig. 2. Six scenarios highlighting processes that impact sequestration flux (see 'POM flux'). Under steady state conditions (nutrient inventory of the upper 1000 m of the ocean (symbolized in green) remains constant on an annual basis), and assuming Redfield stoichiometry, (a–c) sequestration flux (flux through 1000 m) equals allochthonous (red) nutrient input. Under the same assumptions, the export flux at the base of the euphotic zone depends on mixing of nutrients into the euphotic zone from depths and allochthonous nutrient input. (d) A deviation from Redfield stoichiometry during production or remineralization of organic matter allows for the preferential sedimentation of carbon over limiting nutrients (carbon in excess to that associated with nutrients in yellow), potentially having an impact on both export and sequestration flux. (e,f) The relaxation of the steady state condition allows for a change in the nutrient inventory of the upper 1000 m, thus decoupling sequestration flux from allochthonous nutrient input. (e) Low flux attenuation results in increased sequestration flux, supported by organic matter generated from nutrients from the upper 1000 m. (f) Inefficient nutrient utilization within the euphotic zone, or high flux attenuation, both result in a sequestration flux smaller than the allochthonous nutrient input and an increase in the nutrient inventory of the upper 1000 m. Brown stars symbolize sinking marine snow, ovals with antenna heterotrophs and the relative abundance of both denotes the food supply vs. respiration, e.g. flux attenuation. The size and color of green polygons symbolizes the relative size and origin of the limiting nutrient within the upper 1000 m. Red denotes allochthonous nutrients, green stands for nutrients from the upper 1000 m of the ocean. Down arrows denote flux out of the upper layer (export flux) or out of the mesopelagic (sequestration flux). Color of arrows denotes the origin of the exported limiting nutrient as specified above

nous nutrient input, if the steady state of mesopelagic nutrient inventories is relaxed (Fig. 2e,f). The impact of climate change on sequestration flux and nutrient inventories in the mesopelagic is ultimately dependent upon the RLS. A shallow RLS would increase nutrient inventories within the mesopelagic zone and reduce sequestration flux (Fig. 2f). Modeling experiments indicate that if the RLS was to

increase by 24 m globally, carbon sequestration flux would increase enough to reduce atmospheric CO₂ by 1 to 27 ppm (Kwon et al. 2009). But, is such a decrease in flux attenuation and the associated increase of the sequestration flux potentially possible on time scales of 100s of years?

The upper 1000 m of the ocean contain about 8.06×10^{15} mol of nitrate + nitrite (World Ocean Atlas 2005) whereas annual POC flux through 1000 m (sequestration flux) is estimated as $0.07 \text{ Pmol yr}^{-1}$ ($0.86 \text{ Pg C yr}^{-1}$; Jahnke 1996, Dunne et al. 2007). Under Redfield conditions this mesopelagic nitrogen inventory could support the annual sequestration flux of POC for almost 750 yr assuming the sequestration flux remained constant. A doubling of the annual sequestration flux based on the mesopelagic nutrient inventory would reduce the mesopelagic nutrient reservoir by only 23% over the next 100 yr. This decrease in the global mesopelagic nutrient inventories would be difficult to resolve with current methods on times scales of a few decades. Either, a decrease in flux attenuation and the resulting increase in sequestration flux (Fig. 2e), or an increase in flux attenuation resulting in a concomitant decrease in sequestration flux (Fig. 2f), may result from changing ecosystem structure and function.

These theoretical considerations illustrate that sequestration flux may be primarily dependent on flux attenuation of organic matter in the mesopelagic. Flux attenuation of sinking organic particles and their RLS are determined by the sinking velocity of particles and their loss rates (De La Rocha & Passow 2007).

DOM flux

Research over the past 2 decades has demonstrated significant contribution of dissolved or suspended organic matter to export flux in some regions of the global ocean (Copin-Montégut & Avril 1993, Carlson et al. 1994, Hansell et al. 2009). Vertical transport of DOM can contribute up to 20% to the bio-

logical pump (Hansell 2002), but as a dissolved phase it can only be exported to depth during isopycnal exchange or convective overturn of the host water mass (Carlson et al. 1994, Hansell & Carlson 2001, Kähler & Koeve 2001, Hansell et al. 2002, Hopkinson & Vallino 2005, Carlson et al. 2010) or trapped within aggregates (Noji et al. 1999, Antia 2005). The abiotic formation of transparent exopolymer particles (TEP) from DOM is another potential pathway for the export of dissolved organic matter, because TEP contribute significantly to sinking aggregates. Export of DOM via mixing processes requires that it resists degradation in the surface waters until it can be entrained to depth. Only the forms of DOM that survive in surface waters for weeks to months can be effectively exported (Carlson 2002).

These differences in the transport mechanisms of POM and DOM mean that potential changes in the partitioning of organic carbon between the dissolved and the particulate pools are of particular interest. Any increase in the fraction of photosynthate that is DOM or an increase in heterotrophic activity compared to autotrophy would shift the balance between the DOM and POM pumps.

Active zooplankton pump

Zooplankton that feed in the ocean's surface layer migrate to depths of 300 to 800 m where they respire and defecate, actively transporting carbon to depths (active zooplankton pump). Active vertical transport by migrating zooplankton to below the euphotic zone is estimated as 4 to 34% on average of POC flux at those depths (Ducklow et al. 2001, Steinberg et al. 2002), but the transport to 1000 m has, to our knowledge, not been estimated. Changes in the populations of vertically migrating zooplankton due to environmental change could affect the contribution of this component of the organic carbon pump.

ENVIRONMENTAL CHANGE AND RESPONSE OF THE BIOLOGICAL PUMP

Environmental changes

Rising atmospheric $p\text{CO}_2$ is reflected in the global mean surface ocean with oceanic $p\text{CO}_2$ rising at nearly the same rate as atmospheric $p\text{CO}_2$. The increased anthropogenic CO_2 induces change in the carbonate system, whereby DIC increases and the subsequent shift in speciation between bicarbonate

(HCO_3^-) and carbonate (CO_3^{2-}) ions and CO_2 (including CO_2 plus H_2CO_3) results in the release of protons. The increase in proton concentration, while total alkalinity (TA) remains roughly constant, results in a decrease in pH (i.e. ocean acidification; Caldeira & Wickett 2003, Orr et al. 2005).

The global increase in the average air temperature (Kerr 1995a, Vinnikov & Grody 2003) due to the trapping of infrared radiation (i.e. greenhouse effect; Harries et al. 2001) leads to rising temperatures in the surface ocean (Levitus et al. 2000). This increase is observed despite the partial off-set by the inadvertent release of additional aerosols (Kerr 1995b, Kaufmann et al. 2011). The increase in water temperatures of the surface ocean can directly affect the stratification of the ocean, physiological rate processes, and planktonic community structure. Stratification of the surface ocean can locally be intensified by predicted changes in precipitation patterns and the melting of sea ice (Reid et al. 2009). The resulting changes in mixing regimes as well as possible changes in allochthonous nutrient inputs affect nutrient and light availability and nutrient stoichiometry.

In the following sections we will explore how the direct and indirect effects of changes in the carbonate chemistry, temperature, water column stratification and nutrient regime may impact the different components of the biological pump focusing on the sequestration flux.

Factors that potentially affect export flux

Nutrient availability

Changes in weather and wind patterns are anticipated to increase dust deposition to the ocean (Mahowald et al. 1999) and ocean acidification is predicted to increase biological availability of iron (Millero et al. 2009, Hoffmann et al. 2012 this issue). Both these factors may partially relieve iron limitation of primary production especially in the HNLC (high nutrient, low chlorophyll) areas of the ocean (Breitbarth et al. 2010). Increased iron availability will likely alter export flux, but the magnitude and duration of this effect and how it impacts sequestration flux remain unknown. As iron limitation is relieved, primary production will subsequently be limited by another resource.

Globally, anthropogenic nitrogen inputs into the biosphere have increased by a factor of 3 to 4 since 1860, increasing oceanic nitrogen supply. This allochthonous input can potentially induce an imbal-

ance between nitrogen and phosphorus (Peñuelas et al. 2012). The anthropogenic inputs of nitrogen to the ocean via enhanced riverine effluent (Smith et al. 2003) and as atmospheric fixed nitrogen have already contributed to measurably higher algal production in some coastal areas (Duce et al. 2008). Additionally several laboratory studies have demonstrated increased nitrogen fixation under ocean acidification simulations leading to speculation that some of the nitrogen-limited regions of the ocean could experience increases in new production in the future (Barcelos e Ramos et al. 2007, Hutchins et al. 2009, Kranz et al. 2010, Liu et al. 2010). Increased temperature can further promote the growth of nitrogen fixers, if nutrients, especially phosphorus and iron, are available (Langlois et al. 2008, Stal 2009), suggesting the possibility of a geographic expansion of nitrogen fixation. Nitrogen fixation supplies up to 50% of nitrogen for export flux at station ALOHA (near Hawaii) and has increased through the turn of the century (Michaels et al. 2001). However, for elevated nitrogen fixation to be sustained, demand for phosphate must be met and that source remains unclear in the face of increased ocean stratification.

The balance between nitrogen fixation and denitrification must be considered as this balance constrains the net input of nitrogen into the system. Increased stratification, for example, is predicted to reduce ventilation of the surface ocean, thereby leading to a decrease in oxygen concentrations in the ocean interior (Bopp et al. 2002). Expansion of the suboxic habitats of denitrifying bacteria may enhance global denitrification rates (Deutsch & Weber 2012). However, ecosystem responses to such changes in nitrogen sinks and sources may result in further feedbacks to the marine nitrogen cycle and the biological pump, which are only beginning to reveal themselves (Weber & Deutsch 2010, Deutsch & Weber 2012). Nitrification rates are also sensitive to ocean acidification with rates decreasing at several open ocean sites (Beman et al. 2011) but increasing at an estuarine site (Fulweiler et al. 2011).

Increased stratification of the surface ocean restricts nutrient delivery into the euphotic zone from below. For example, reduced availability of nitrate for primary production due to a shoaling of the thermocline between 1909 and 2002 has been inferred for large parts of the ocean from a temperature–nitrate relationship (Kamykowski & Zentara 2005). A significant decrease in global marine photosynthesis attributed to rising temperatures and increased stratification has also been postulated from global data sets combining Secchi depths, transmissometer and satellite informa-

tion (Boyce et al. 2010), indicating a negative relationship between primary production and surface temperature observed *in situ* during the last decade (Behrenfeld et al. 2006). These latter studies suggest that export flux is decreasing globally because nutrients from the mesopelagic are not made available for primary production due to their reduced entrainment into the euphotic zone. However, these findings remain controversial (Mackas 2011, Rykaczewski & Dunne 2011) with contrasting results showing increases in phytoplankton biomass in several oceanic biomes for the past several decades (McQuatters-Gollop et al. 2011). Lomas et al. (2010) demonstrated that primary production and carbon export flux in the oligotrophic Sargasso Sea has increased over 50% since 1996 despite increased stratification. However, they found that the attenuation of export flux in the upper mesopelagic zone had also doubled, partially due to increased zooplankton biomass, so that flux at 300 m remained largely unchanged. This study reiterates the potential importance of mesopelagic food web structure and its link to export flux out of the euphotic zone (Michaels & Silver 1988, Steinberg et al. 2008a). Changes in export flux may not necessarily translate to a change in sequestration flux (Fig. 2).

Light field

Stratification may lead to photoinhibition in the surface layer of some regions (oligotrophic gyres), but the deeper penetration of light due to a nutrient- and phytoplankton-poor surface layer may compensate for the lack of primary production at the surface. In other regions, for example in parts of the Southern Ocean where deep mixing prevails, light limitation may be relieved. Relief of light limitation would allow for more efficient use of the nutrients available within the euphotic zone and initially could lead to increased export flux. However, this increased flux could only be sustained until the system became limited by another factor such as nutrient availability. Regionally specific information on the timescales of depth penetration of increased temperatures is required for a more accurate evaluation of the consequences of a changed light field for export flux.

Temperature

Rising temperatures generally increase metabolic processes including phytoplankton growth and microbial respiration (Sarmiento et al. 2010). Several

mesocosm simulation experiments have examined the potential impacts of rising temperatures alone (Sommer & Lengfellner 2008, Lassen et al. 2010, Taucher et al. 2012), or in combination with perturbations of $p\text{CO}_2$ (Kim et al. 2011), light (Lewandowska & Sommer 2010), nutrients (Wohlers-Zöllner et al. 2011) or grazing (Sommer & Lewandowska 2011), on phytoplankton blooms. All of these studies observed an early onset and peak of the spring phytoplankton blooms, which has also been observed *in situ* (Edwards & Richardson 2004). Peak biomass was generally (Wohlers et al. 2009, Lassen et al. 2010, Lewandowska & Sommer 2010, Kim et al. 2011, Sommer & Lewandowska 2011), although not always (Taucher et al. 2012), smaller at elevated temperatures. Shifts in phytoplankton community composition at elevated temperatures especially towards smaller cells have been documented in several studies (Lassen et al. 2010, Lewandowska & Sommer 2010, Sommer & Lewandowska 2011). Diminished bloom biomass and smaller average cell sizes at elevated temperatures have also been observed *in situ* (Richardson & Schoeman 2004, Behrenfeld et al. 2006, Morán et al. 2010). Paleoproxy analysis of phytoplankton cell size supports the idea that body size decreases as temperature increases (Falkowski & Oliver 2007). The reduction in plankton cell size could arguably result in decreased export flux; however, other studies have challenged this argument suggesting that small cells are also incorporated into sinking aggregates in proportion to their abundance (Richardson & Jackson 2007).

The relative effect of temperature increase on microbial respiration compared to that of phytoplankton production may have a larger impact on export production (Harris et al. 2006, López-Urrutia et al. 2006, Sarmiento et al. 2010) compared to absolute changes in primary production. One anticipated effect of global warming deduced from experiments, ecological theory and long term *in situ* observations is the expansion of oligotrophic areas of the ocean and the strengthening of the relative contribution of heterotrophy associated with a reduced export flux, although the evidence of this outcome is equivocal (Sarmiento et al. 2010).

Inorganic carbon speciation and availability

Culture experiments have revealed that many phytoplankton species grow well over a large range of pH (Hinga 2002, Berge et al. 2010, Liu et al. 2010, Joint et al. 2011) especially when the pH change was

caused by TA perturbations. However, truly oceanic species growing *in situ* are not exposed to large fluctuations in pH and may be more sensitive to such changes. The effect of increased surface water CO_2 concentrations due to ocean acidification (DIC perturbation) on phytoplankton taxonomic groups is highly variable (Rost et al. 2008). The CO_2 specificity of the carboxylating enzyme ribulose biphosphate carboxylase/oxygenase (Rubisco) is relatively high in diatoms compared to coccolithophores or dinoflagellates (Raven 1991). Kinetic carbon uptake studies suggest that at present day $p\text{CO}_2$ levels the photosynthetic carbon fixation rates of diatoms are close to their maximal rates (CO_2 saturation at present day levels), whereas coccolithophores have a low affinity for inorganic carbon and appear carbon limited under present day conditions (Rost & Riebesell 2004). Such physiological differences between taxa or species may lead to shifts in phytoplankton composition (Boyd et al. 2010). Shifts in phytoplankton composition are important to consider when assessing how increased DIC content affects new production and aggregation, and these are likely one of the main factors explaining ambiguous or contrasting results from mesocosm experiments (i.e. Kim et al. 2006, Egge et al. 2009, Riebesell et al. 2008).

Role of phytoplankton

The efficiency with which phytoplankton are exported is thought to be dependent on species composition, and shifts in dominant phytoplankton taxa will have consequences for export because of their different life strategies. The export of carbon fixed by small cells like picoplankton, which compared to diatoms have a higher surface area to volume ratio and potentially release a greater percentage of fixed carbon as DOM (Karl et al. 1998), will depend more on transport via the DOM-pump. Diatoms, in contrast, are very efficient in transporting carbon to depths by forming large, rapidly sinking aggregates (Smetacek 1985, 1998) and a decrease in diatom abundance due to increased stratification is expected to lead to a decrease in carbon flux (Bopp et al. 2005). *Phaeocystis* spp. provide non-sinking, carbon-rich mucus that requires attachment to heavy particles or physical processes prior to export (Passow & Wassman 1994, Wassman et al. 1995), whereas dinoflagellates rarely aggregate directly (Alldredge et al. 1998). Coccolithophores play a prominent role in the hard tissue pump and their coccoliths may be central for aggregation and ballasting (see 'The calcium

carbonate pump' below). However, the argument has been made that all phytoplankton, including picoplankton cells, contribute equally to flux (Richardson & Jackson 2007) and increased export flux concomitant with higher phytoplankton stocks dominated by picoplankton support this suggestion (Lomas et al. 2010).

Shifts in phytoplankton composition due to ocean acidification (Tortell et al. 2002, Rochelle-Newall et al. 2004, Low-Décarie et al. 2011, Meakin & Wyman 2011) or increased temperatures (Hare et al. 2007) are commonly observed experimentally. The impact of ocean acidification on the calcifying coccolithophores has received special attention. Ocean acidification makes calcification more difficult, but increased $p\text{CO}_2$ appears to facilitate primary production for this group with variable outcome for the growth success of the species (Zondervan 2007, Iglesias-Rodriguez et al. 2008, Bach et al. 2011). Inclusion of other factors for an evaluation of the competitiveness of coccolithophores in the future ocean (Irie et al. 2010, Xu et al. 2011) makes predictions even less robust at present. The degree of water column stability exerts an additional strong selective pressure on phytoplankton composition (Falkowski & Oliver 2007). A shift towards a phytoplankton community dominated by smaller cells (picoplankton) adapted to be more competitive at low nutrient concentrations and input may be expected (Bopp et al. 2005, Lomas et al. 2010, Morán et al. 2010). Phytoplankton species that utilize organic nitrogen or phosphorus (Benner & Passow 2010) may gain a competitive advantage under increase stratification. Modified speciation of trace elements (Miller et al. 2009) promoting or inhibiting (e.g. iron versus copper) growth of phytoplankton may cause further shifts in phytoplankton composition.

The interactive and synergistic effects of these different environmental stressors and the results for the competitive ability of individual species are extremely complex and difficult to predict (Feng et al. 2009, Boyd et al. 2010, Low-Décarie et al. 2011). However, shifts in phytoplankton composition appear likely and are becoming apparent: Coccolithophores appear to have expanded their geographic range (Merico et al. 2003, Cubillos et al. 2007) and a shift towards *Prochlorococcus* and *Trichodesmium* due to increased stratification has become visible in the North Atlantic (Lomas et al. 2010) and Pacific Subtropical Gyre (Karl et al. 2001). A regime shift in phytoplankton abundance, composition and seasonal cycle due to changed river discharge has been documented in the Adriatic (Mari et al. 2012).

Role of aggregation

The importance of marine snow for carbon sequestration lies in its rapid sinking velocities. Marine snow is formed from feeding structures or via aggregation of small component particles (Alldredge & Silver 1988). Aggregation, especially of diatoms, plays a critical role for the rapid transfer of algal carbon to depth (Alldredge & Jackson 1995, Boyd & Newton 1995, Buesseler 1998, Boyd & Newton 1999). However, on varying regional or temporal scales the contribution of sinking feces (Wilson et al. 2008) or feeding structures (Noji et al. 1997, Passow et al. 2001, Robison et al. 2005) may be large. Fecal pellet flux may vary between <5 and up to 100% of sinking flux, and zooplankton species may dramatically affect the amount of primary production consumed, the composition and sedimentation rate of sinking particles and the flux of organic carbon to the deep ocean (Ducklow et al. 2001, Steinberg et al. 2008a).

Aggregation rates are a function of particle numbers and sizes (Jackson & Burd 1998, Burd & Jackson 2009), implying that the marine snow sized aggregates that sink rapidly only form during times of high particle concentrations, especially during large blooms (Jackson 2005). The suggested reduction of large phytoplankton blooms (see 'Role of phytoplankton' above) could potentially result in a decrease of aggregation events. Few studies have investigated the dependence of aggregation rate on temperature or ocean acidification directly. Increased aggregation rate at elevated temperatures was detected during one experimental study, possibly due to increased abundance of transparent exopolymer particles (TEP), but degradation of aggregates was also enhanced, with the net result of increased or decreased sedimentation of aggregates dependent upon temperature (Piontek et al. 2009).

A reduced availability of bio-minerals due to decreased production may negatively impact sinking velocity of aggregates. Calcifying coccolithophores aggregated more rapidly than their non-calcifying counterparts (Engel et al. 2009b), in agreement with the concept that the presence of minerals promotes aggregation (Passow & De La Rocha 2006, De La Rocha et al. 2008). Experimental evidence suggests that the sinking velocities of coccolithophore aggregates decreased under ocean acidification conditions (Biermann & Engel 2010).

TEP are an essential component of aggregates, having impacts on both their formation (Alldredge et al. 1993, Alldredge & Jackson 1995) and sinking velocity (Engel & Schartau 1999, Azetsu-Scott & Passow 2004). Ocean acidification and increased tempera-

tures are hypothesized to increase TEP production (Engel et al. 2004), which in turn is thought to result in increased aggregation and sedimentation rates (Arrigo 2007, Riebesell et al. 2007). However, stickiness of TEP may decrease due to ocean acidification (Mari 2008), challenging this assumption. To date the impact of ocean acidification and temperature on TEP production and thus aggregation and flux remain equivocal. Increased TEP production by phytoplankton under ocean acidification conditions has been demonstrated in one mesocosm experiment (Engel et al. 2004), but results were contradictory in another two (Schulz et al. 2008, Egge et al. 2009). These contrasting results indicate that additional factors, such as total alkalinity (Mari 2008, Passow 2012) or nutrient stoichiometry (Corzo et al. 2000, Staats et al. 2000, Passow 2002, Beauvais et al. 2006), must be carefully considered in future experiments that test the role of ocean acidification and TEP in aggregation.

Based on the correlation between sinking POC and minerals (calcium carbonate, opal, lithogenic minerals) in deep sediment traps (Armstrong et al. 2001, Francois et al. 2002, Klaas & Archer 2002), mineral ballasting has been proposed as an important mechanism controlling POM flux. Model results based on the 'Ballast Hypothesis' suggest a weakening of the biological pump in the future (Bopp et al. 2005, Gehlen et al. 2006) due to the expected decrease in ballasting by coccoliths (Zondervan et al. 2001, Beaufort et al. 2007). Depending on the relative contribution of minerals, some ballasting does occur, and increased aggregation and sinking velocities may be expected in some coastal systems that experience increased dust input or river run off. Laboratory-made aggregates or feces ballasted with diatom frustules or coccoliths effectively increased settling velocities of aggregates in laboratory experiments (Ploug et al. 2008a,b), but *in situ* data from the Mediterranean suggest that mineral ballasting did not drive sinking velocity (Lee et al. 2009b). Furthermore, controlled laboratory experiments show that as a result of decreasing aggregate size coincident with increasing density the effect of scavenged minerals on aggregate sinking velocity is more complex than originally conceived (Hamm 2002, Passow & De La Rocha 2006).

Altering elemental stoichiometry of organic matter

Considering stoichiometry of POM

Organic matter production and remineralization operate with approximately Redfield stoichiometry of

106C:16N:1P. Although the bulk particulate organic matter measured in the upper water column over vast geographical ranges does not deviate significantly from the canonical Redfield molar ratio, laboratory studies have demonstrated that elemental ratios in phytoplankton can be highly plastic, with elemental allocation varying as a function of growth rates and nutrient stress (Goldman et al. 1979, Geider & La Roche 2002). Whereas the ratios of recycled nutrients suggest remineralization according to Redfield (e.g. Anderson & Sarmiento 1994), the POC:PON ratios of sinking particles increase with depths, indicating preferential remineralization of nitrogen over carbon (Schneider et al. 2003). Deutsch & Weber (2012) suggest that the variability of nutrient stoichiometry is not random and that it may depart systematically from Redfield on regional scales, but that circulation patterns obfuscate the regional signatures leading to a globally homogenous (Redfield) nutrient ratio.

Assuming that remineralization of carbon and the limiting nutrient is vertically decoupled so that remineralization of carbon occurs deeper than that of nitrogen, a net export of carbon in the absence of an input of allochthonous nutrients is possible (Michaels et al. 2001, Schneider et al. 2004; Fig 2d). Thus, if conditions prevail that allow organic matter to be fixed into carbon-rich exportable POM (C:N > 6.6), or if there is preferential loss of N and P relative to C as sinking particles are remineralized, than net sequestration of C into the interior can occur (Michaels et al. 2001).

Enhanced photosynthesis in the absence of increased nutrient supply may be expected under ocean acidification conditions (Doney et al. 2009) and the production of C-rich POM (Burkhardt & Riebesell 1997, Wolf-Gladrow et al. 1999) under high CO₂ conditions has been postulated based on experimental evidence. Variable stoichiometry based on uptake ratios was observed in a mesocosm experiment simulating different ocean acidification scenarios (Riebesell et al. 2007, Bellerby et al. 2008) but was not reflected in the respective pools of particulate or dissolved organic matter (Riebesell et al. 2008, Schulz et al. 2008). Additionally, there is a paucity of experimental evidence supporting a systematic increase of the C:N ratio in POM due to ocean acidification or temperature in mesocosm (Kim et al. 2011, Wohlers-Zöllner et al. 2011) or laboratory culture experiments (Burkhardt et al. 1999, Hutchins et al. 2009). This issue may be critically dependent on taxa (Riebesell & Tortell 2011) or on the nutrient availability and temperature conditions associated with the ocean acidification perturbation.

Deviations from the Redfield ratio during production or remineralization are difficult to determine *in situ* because of the high spatial and temporal variability in the C:N ratio of organic matter, the homogenizing effect of circulation patterns, and the synergistic effects of different biological processes. Sedimentary denitrification, for example, masks the signature of organic matter remineralization during sedimentation (Deutsch & Weber 2012). Nevertheless, indications of preferential remineralization of nitrogen during sedimentation are observed (see overview in Boyd & Trull 2007) and oceanic nutrient ratios are found to be dynamic on decadal to geological scales (Finkel et al. 2010, Deutsch & Weber 2012).

Considering stoichiometry of DOM

In contrast to POM, the production of DOM can more easily be decoupled from nutrient supply (Hopkinson & Vallino 2005). When phytoplankton deplete ambient nutrient stores (including upwelled CO₂), some continue to fix C as an energy dissipation mechanism and release it as C-rich DOM in vast excess of Redfield stoichiometry (Williams 1995, Hopkinson & Vallino 2005, Conan et al. 2007, Wetz & Wheeler 2007). This surplus fixation of carbon is called carbon overconsumption (Sambrotto et al. 1993, Williams 1995, Carlson 2002, Conan et al. 2007) and in the short term produces 'new' organic carbon in the sense that it allows organic matter production by phytoplankton to exceed the CO₂ supplied to the surface waters by vertical exchange. Accumulation of nitrogen-rich but phosphorus-poor DOM in the surface layer of the North Pacific Subtropical Gyre between 1993 and 1999, possibly due to increased nitrogen fixation and as a result of a shift in autotrophic community structure, gives evidence for the multi-year storage of carbon as dissolved organic matter (Church et al. 2002).

DOM released by phytoplankton varies with species, growth stage and environmental conditions (Nagata 2000, Carlson 2002), but if under ocean acidification conditions or increased temperature exuded DOM is on average more carbon rich and less bioavailable to heterotrophs, this may represent a highly efficient C sequestration mechanism with global implications for the operation of the biological pump assuming convective overturn or isopycnal exchange is deep enough (Hopkinson & Vallino 2005). Experimental evidence on increased C:N ratios of DOM due to temperature or ocean acidifica-

tion effects is scarce and often equivocal (Wohlers-Zöllner et al. 2011, Taucher et al. 2012). Nonetheless accumulation of C-rich DOM represents a potentially important shift in carbon storage away from particle export to sequestration in a suspended/dissolved form as proposed in the microbial carbon pump (Jiao et al. 2010, see below).

The role of DOM in carbon storage or export is ultimately dependent upon its bioavailability to heterotrophic bacterioplankton. If DOM becomes resistant to extant microbial remineralization then it is potentially available for export (Carlson 2002). Initial studies of the effects of ocean acidification have demonstrated shifts in chemical composition (i.e. variability in the mol fraction of neutral sugars and amino acids) and changes in some exoenzyme activities (Grossart et al. 2006, Arnosti et al. 2011, Engel et al. 2011, Wohlers-Zöllner et al. 2011), but the overall impact on DOM bioavailability is currently under investigation. Changes in the C:N ratio of organic matter production or utilization are supported by experimental and geological observations. However an understanding of remineralization and physical transport processes are required to estimate their potential global impact on sequestration flux.

Recently the production of refractory DOM (rDOM) via heterotrophic microbial processes has been proposed to result in the production of C-rich DOM that can persist for hundreds to thousands of years (microbial carbon pump, MCP; Jiao et al. 2010). Several studies have shown that heterotrophic bacterial biomarkers are observed in this rDOM pool lending support to the MCP (Benner 2002, Benner & Kaiser 2003). However, the bioavailability of DOM to marine microbes is controlled by a number of factors such as the inorganic nutrient availability, molecular composition of DOM and the extant microbial community (Carlson et al. 2004). Little is known regarding the impact of ocean acidification, warming or increased stratification on this proposed shunt (Jiao & Azam 2011). Study of the oceanic MCP and its impact on carbon export and sequestration in the face of a high CO₂ world and ocean warming is currently an active research area in microbial oceanography.

Flux attenuation

Role of food webs

Direct predictions of potential global changes in sequestration flux require a better understanding of particle processing in the mesopelagic. Gravitational

settling of particles, which dominates the export of organic matter from the euphotic zone, accounts for up to 80% of the carbon reaching the deep sea (Hansell 2002, Hopkinson & Vallino 2005). Size distribution and sinking velocity of marine snow, as well as its repackaging, destruction and respiration, are regulated by food web structure within the water column (Michaels & Silver 1988, Peinert et al. 1989, Boyd & Newton 1999, Boyd et al. 1999, Steinberg & Hansell 2010). Particle transformations determine the RLS and thus the efficiency with which organic matter is transported to depth. The formation or potential reduction of fast sinking POM (i.e. marine snow) is of particular interest in this context as only large, marine snow sized (>0.5 mm) feeding structures, aggregates, or feces sink at velocities (>50 to 100 m d^{-1}) great enough to potentially escape remineralization within the upper 1000 m (Asper 1987, Alldredge & Gotschalk 1988, Knauer 1991, Berelson 2001b, Armstrong et al. 2009). The magnitude of flux attenuation varies regionally and temporally because there is significant variability in food web structure and processing over geographic and temporal scales (Boyd & Trull 2007). Below we discuss some of the expected changes to euphotic and mesopelagic food webs and explore their potential to alter sequestration flux of POC.

Increased temperatures may enhance bacterial respiration in relation to primary production (López-Urrutia et al. 2006, Sarmiento et al. 2010) resulting in reduced export flux (Wohlers et al. 2009, Kritzberg et al. 2010, Vaquer-Sunyer et al. 2010). Rose & Caron (2007) demonstrated that as temperatures increased in microcosm experiments microzooplankton growth rates became greater than phytoplankton growth rates. Using their temperature relationships, they calculated that the maximal growth of herbivorous microplankton at 0°C is 60% that of phytoplankton, whereas at 15°C it is 110%, implying a reduction of large sedimentation events in a warmer ocean, especially if grazers generate fecal pellets that are recycled within the surface ocean.

An increase in ocean temperature may also result in a reduction in bloom biomass. If true, this could affect export flux as well as flux attenuation in the mesopelagic. For example, the fraction of sinking organic carbon that escapes remineralization in the euphotic and mesopelagic zone is greater during pulsed sedimentation events after phytoplankton blooms compared to periods of more continuous but lower sedimentation rates typical for recycling-type systems (Ducklow et al. 2001). The argument is that the mesopelagic community acclimates and opti-

mizes its growth response under more constant flux conditions and, thus, increases flux attenuation and reduces sequestration flux.

Particle transformation due to zooplankton activity

Zooplankton utilize, repackage, and physically disrupt aggregates, thus transforming sinking POM, with various functional groups of zooplankton impacting sinking flux differently. For example, while large salp pellets sink rapidly (Bruland & Silver 1981), copepod fecal pellets are generally recycled within hundreds of meters of their release (Lampitt et al. 1990, Noji 1991, Noji et al. 1991). Abandoned larvacean houses may dominate sinking flux by scavenging other particles on their way (Passow et al. 2001), while a swarm of euphausiids may fragment marine snow (Goldthwait et al. 2004, Dilling 1997, Dilling et al. 1998, 2004), thereby affecting its sinking velocity and potentially but not necessarily its remineralization (Goldthwait et al. 2005). Fractionation of particles due to sloppy feeding (Goldthwait et al. 2005) or swimming activity of zooplankton (Dilling et al. 1998, Goldthwait et al. 2004) as well as solubilization of POM to DOM due to the hydrolytic enzymes produced by attached bacteria (Smith et al. 1992, Grossart & Simon 1998, Ploug & Grossart 2000) effectively convert rapidly sinking particles to suspended organic matter. Zooplankton also consume marine snow (Steinberg 1995, Green & Dagg 1997, Dilling et al. 2004, Koski et al. 2005, 2007), feces (Lampitt et al. 1990, Noji et al. 1991, Poulsen & Kiørboe 2005) and appendicularian houses (Alldredge 1976), potentially recycling the majority of the fixed carbon back to DIC.

Consequently, shifts in zooplankton composition can have an impact on sequestration flux. For example, a shift from euphausiids that fragment and eat marine snow to salps that produce rapidly sinking feces in Antarctic waters has appreciable ramifications for carbon cycling, including an increased sequestration flux (Loeb et al. 1997, Atkinson et al. 2004). In the Northern Bering Sea a decreased carbon supply to the benthos is causing simultaneous shifts in top predator distributions, suggesting that the whole ecosystems structure is adjusting as export is changing (Grebmeier et al. 2006, Grebmeier 2012). Increases in export flux of more degraded, biogenic material are expected in the Northern Barent Sea in the future (Wassmann et al. 2008). Such changes in ecosystem structure and functioning and thus carbon cycling are especially evident in high latitude areas, which are the most sensitive regions to change and

where the retreat of the sea ice adds an additional critical component (Wassmann 2011, Wassmann et al. 2011). The complexity of the role that marine food webs play for flux attenuation and their high spatial and temporal variability (Noji 1991, Silver & Gowing 1991, Gage 2003, Boyd & Trull 2007, Buesseler et al. 2007, Smith et al. 2008) prevents global generalizations, and effects and consequences to change will most likely have to be determined on a regional and seasonal basis before global predictions become possible. However, shifts in food webs, especially of the upper ocean, are evident in many regions including the Bristol Channel (Henderson et al. 2011) and the Irish Sea (Lynam et al. 2011), although causes are often unclear (Richardson & Gibbons 2008) and responses may be very spatially variable as observed in the NE Atlantic (McGinty et al. 2011).

Changes within the mesopelagic food webs will likely control flux attenuation between export flux and sequestration flux. Changes in any part of the mesopelagic food web, which is highly adapted to the flux of particles sustaining it, will be reflected in the type and quantity of sequestration flux. The coupling or decoupling between a sedimentation event of rapidly sinking marine snow and the mesopelagic predators will determine sequestration flux; their synchronization will result in high flux attenuation, and their decoupling in a large flux event. Spatial migration (pole wards or to greater depths) due to warming as observed for copepods in the Atlantic (Beaugrand et al. 2002) as well as temporal shifts (e.g. seasonal or ontogenetic delays) of events like the timing of the phytoplankton bloom are expected to uncouple trophic interactions (Edwards & Richardson 2004), with unforeseeable consequences for the biological pump. Accelerated bloom build-up and a forward shift of the bloom peak by $\sim 2 \text{ d } ^\circ\text{C}^{-1}$ due to more rapid growth, as well as the amplification of microbial degradation and grazing (see 'Role of food webs' above) are anticipated to impact particle–food web interactions in the mesopelagic. Large changes within marine ecosystems have been observed in many parts of the ocean (e.g. Reid et al. 2009, Philippart et al. 2011), but the consequences for sequestration flux have rarely been assessed and will be a major emphasis in refining our understanding of the biological pump in the next decade.

To complicate matters, direct environmental changes to the mesopelagic have to be considered as well. The expected combination of decreased oxygen and increased pCO_2 in increasingly larger areas of the ocean interior may make respiration a challenge for many marine heterotrophs living at these depths

(Brewer & Peltzer 2009). The resulting decreased activity of such heterotrophs would shift remineralization to organisms less sensitive to O_2 . Direct impacts of ocean acidification and elevated temperature are also anticipated in some organisms, e.g. for aragonite-precipitating pteropods (Fabry 2008, Lischka et al. 2011). Environmental conditions in the Canada Basin are already at levels expected to inhibit development and growth of pteropods there (McLaughlin et al. 2011). Direct responses of ocean acidification on adult non-calcifying zooplankton have rarely been measured, but those that do exist show only subtle change in survival, growth and physiology (Hauton et al. 2009). However, planktonic larval stages of benthic organisms indicate that potentially the success of larval development of many organisms could be appreciably reduced (Dupont et al. 2008), but different organisms do not respond uniformly (Hendriks et al. 2010).

The complex interactions within marine food webs and the microbial loop, which drive both sinking velocity and degradation rate of organic matter (Noji 1991, Silver & Gowing 1991, Neuer et al. 2002, Gage 2003, Boyd & Trull 2007, Buesseler et al. 2007, Smith et al. 2008), are expected to change as ecosystems shift.

Microbial impact on flux attenuation

Cho & Azam (1990) reported that the bacterial carbon demand in the mesopelagic zone of the North Pacific was equivalent to the sinking POC flux, indicating that mechanisms responsible for the transformation of sinking POM to suspended matter or DOM could support the free-living mesopelagic bacterioplankton. Uncoupled solubilization, i.e. the solubilization of POM via the production of hydrolytic enzymes and the subsequent release of DOM to the surrounding environment, was proposed as a possible mechanism to help support the mesopelagic bacterial carbon demand (Smith et al. 1992, Azam 1998, Grossart & Simon 1998, Azam & Long 2001, Kiørboe et al. 2001). Further work by Ploug & Grossart (2000) demonstrated that the O_2 exchange across surfaces of a sinking particle results in a larger percentage of microbial remineralization (compared to solubilization) than had been previously estimated (Ducklow et al. 1985, Karl et al. 1988) and helps to explain POC flux attenuation in the open sea. Both microbial remineralization and/or solubilization of sinking particles are important for the attenuation of POC flux in the mesopelagic.

If enhanced microbial utilization of organic matter were true for the mesopelagic bacterial community, a decrease in sequestration flux would be expected. However, the relative contributions of zooplankton and heterotrophic bacteria to the attenuation of particles and to the recycling of organic carbon remains under considerable debate. Steinberg et al. (2008b) reported that either zooplankton processes or bacterial processes could account for more than 100% of the POC flux at 2 oligotrophic and highly productive stations in the North Pacific. This discrepancy reveals that our understanding of mesopelagic biological processes or constraining these processes by measured flux estimates is still somewhat rudimentary but progress continues. Reports indicate that microbial contribution to flux attenuation may increase with depth, dominating in the lower mesopelagic and below (Steinberg et al. 2008b, Anderson & Tang 2010, Burd et al. 2010, Robinson et al. 2010). Zooplankton preferentially feed on large, fast settling particles (Bathmann et al. 1987, Lampitt et al. 1990), whereas attached Bacteria and Archaea appear to affect all size classes via solubilization or remineralization (Stemmann et al. 2004).

The few investigations that address potential impacts of environmental changes on bacterial activity and composition have indicated that while some changes are apparent, the signal is often obfuscated by factors such as fast turnover time of DOM and the complexity of shifts in the composition of both DOM and bacterioplankton (Weinbauer et al. 2011). Three mesocosm studies implied minor effects of ocean acidification on bacterial abundance (Rochelle-Newall et al. 2004, Grossart et al. 2006, Allgaier et al. 2008), but clearer shifts in bacterial community structure (Allgaier et al. 2008, Arnosti et al. 2011). Hydrolysis rates of complex polysaccharides exhibited treatment-specific effects in some cases (Arnosti et al. 2011). For example, glucosidase activity appears accelerated at higher hydrogen ion concentrations (Piontek et al. 2010), although the effect is not always visible (Grossart et al. 2006). Association with minerals are hypothesized to protect organic matter from degradation (Lee et al. 2009a), and a laboratory experiment comparing degradation of calcified and naked coccolithophores partially supported this possibility (Engel et al. 2009a). However the consequences of reduced occurrence of biomineral-forming phytoplankton in combination with degradation of organic matter during transit needs further study.

The most pressing question is thus whether the microbial population will be able to respire most of the DOM created under changed conditions. This

question is important, as the remineralization of exported DOC accounts for up to half the oxygen utilized in the mesopelagic zone (Carlson et al. 1994, Doval & Hansell 2000, Hansell et al. 2002). Studies have indicated that DOM which is persistent at one geographical location or depth horizon can be bioavailable at another (Carlson et al. 2004, 2011). DeLong et al. (2006) identified a greater number of genes putatively involved in polysaccharide degradation in deep microbial populations compared to those found in the surface populations with some piezophiles capable of degrading complex organic matter due to modifications in their gene structure and protein regulation (Vezi et al. 2005, Lauro & Bartlett 2008). These studies suggest that the deep populations of prokaryotes are better adapted to utilizing recalcitrant polysaccharides. Whether this would be altered under future climate scenarios remains unclear.

The calcium carbonate pump

In contrast to the organic matter pump, which is based on the conversion of DIC to organic carbon, the calcium carbonate pump removes carbon from surface waters in its particulate inorganic forms. Production of calcium carbonate frustules by autotrophic or heterotrophic organisms incorporates carbon in shells or exoskeletons, which sink before dissolution or burial. Under ocean acidification conditions, calcification of coccolithophores has been proposed to typically decrease, although a large variability exists even between strains of the same species (Zondervan 2007, Langer et al. 2009) and coccolithophores are to some extent able to compensate for reduced pH during growth (Fukuda et al. 2011). Interaction effects of temperature, UV and pH challenge our ability to predict future patterns for even the most well studied groups, e.g. *Emiliana huxleyi* (Xu et al. 2011), and this currently an area of active research. Experimental (Feng et al. 2009), and *in situ* (Merico et al. 2003, Cubillos et al. 2007) data on mixed populations and palaeo-reconstructions do not indicate a reduction in abundance of *E. huxleyi* in the near future. However, palaeo-reconstruction indicates that the mass of individual coccoliths decreased at times of low CO_3^{2-} on geological timescales (Beaufort et al. 2011). Assuming that production of POC and PIC remains the same, elevated temperatures that result in increased POC respiration would result in a larger PIC to POC ratio (rain-ratio), potentially supporting increased sinking velocities and flux rates.

Production of calcium carbonate by organisms affects the carbonate system in a way that may seem counter intuitive. In contrast to photosynthesis, calcification alters TA, thereby shifting the equilibrium between carbonate, bicarbonate and CO_2 in the ocean. As a consequence the ability of the water to take up dissolved CO_2 decreases, despite carbon being simultaneously removed from the DIC pool (Table 1). The reduction of the capacity of the surface ocean to take up CO_2 due to calcification explains why this calcium carbonate pump is also sometimes referred to as the carbonate counter pump. The removal of $50 \mu\text{mol carbon kg}^{-1}$ as PIC simultaneously increases CO_2 from $16.6 \mu\text{mol kg}^{-1}$ to $20.9 \mu\text{mol kg}^{-1}$ (at 15°C , 35‰), whereas a removal of the same amount by photosynthesis lowers CO_2 to $12.6 \mu\text{mol kg}^{-1}$ (Table 1). Thus, the sequestration of carbon in surface water by non-calcifying phytoplankton is appreciably higher (per mol organic matter produced) compared to that of calcifying phytoplankton. If ocean acidification results in a reduction of calcifying phytoplankton, the counter-intuitive consequence will be an increased capacity of the surface ocean to store CO_2 (Reid et al. 2009). In contrast, the simultaneous reduction in sinking velocity due to the lack of ballasting with calcium carbonate has been suggested to decrease export and thereby the ability of the ocean to take up CO_2 via the organic carbon pump (Armstrong et al. 2001). However, the importance of minerals for ballasting of sinking flux has also been challenged (Passow 2004, Lee et al. 2009b).

On timescales of millennia the carbonate minerals deposited in sediments during the past 100 000 yr will act as a buffer, as their eventual dissolution will increase the TA, resupplying the water with CO_3^{2-} and readjusting the pH. However, as this process is slow compared to the current rate of pCO_2 increase, it is fairly irrelevant with respect to changes expected within the coming 100 yr.

DELIBERATE PERTURBATION OF THE BIOLOGICAL PUMP

Several geo-engineering schemes have been proposed to increase carbon sequestration via the biological pump. An overview of the state of the art is given by Lampitt et al. (2008). Briefly, iron fertilization of the HNLC regions of the ocean is the most publicized proposal, and the only one that has been tested in *in situ* experiments. However, these experiments mainly focused on biological response and export flux (Boyd et al. 2007, Boyd 2008) and did not assess if fertilization had an impact on sequestration flux. Iron fertilization of areas with residual phosphate but deficient in nitrate and iron has also been proposed to enhance nitrogen fixation and thus input of allochthonous nutrients. Natural feedbacks to ocean acidification and increasing temperatures may have a similar effect. Piping a nutrient mix, especially macronutrients, from land to beyond the edge of the continental shelf is another suggested approach thought to result in carbon sequestration. The cost for such a scheme may be prohibitive, but as for the other 3 ideas, no detailed cost–benefit analysis has been made. The fourth suggested manipulation uses wave energy to induce artificial upwelling by pumping deep water to the surface. Comprehensive experiments are currently still lacking for this approach as well, but calculations suggest that the efficiency may be very low (Oschlies et al. 2010), and of course DIC will also be brought to the surface as well via this mechanism. Currently, the practicality of utilizing deep, cold sea water to run air conditioning systems (SWAC) is being explored as a source of renewable energy (Elsafty & Saeid 2009). Studying the effect of this nutrient-rich water after its return to the ocean to a shallower depth than its origin may provide insight into the fertilization approaches as a geoengineering scheme.

Table 1. Effect of removal of inorganic carbon due to calcification or photosynthesis (35‰, 15°C , no nutrients) on the carbonate chemistry of seawater. The fixation of $50 \mu\text{mol C kg}^{-1}$ seawater in organic matter (photosynthesis) has a significantly different result for seawater chemistry than the equivalent incorporation of carbon in carbonate, because calcification uses 2 mol total alkalinity (TA) for every mol of dissolved inorganic carbon (DIC). Whereas a decrease in carbon dioxide concentration during photosynthesis allows the water to take up more CO_2 , its increase during calcification leads to relative out-gassing. pH measured as total scale

	DIC ($\mu\text{mol kg}^{-1}$)	TA ($\mu\text{mol kg}^{-1}$)	pH _T	pCO ₂ (μatm)	CO ₂ ($\mu\text{mol kg}^{-1}$)	HCO ₃ ⁻ ($\mu\text{mol kg}^{-1}$)	CO ₃ ²⁻ ($\mu\text{mol kg}^{-1}$)
Start	2100	2300	8.0	445	16.6	1937	147
Calcification	2050	2200	7.9	560	20.9	1915	114
Photosynthesis	2050	2300	8.1	339	12.6	1860	178

Although all 4 fertilization ideas have the potential to sequester carbon, the appropriate modeling and *in situ* experiments, which are necessary to assess side effects, costs and benefits, are missing (Lampitt et al. 2008). Any successful attempt to rapidly increase CO₂ input into the ocean will obviously amplify ocean acidification and its consequences. Any purposeful perturbations of the biological pump will without doubt have consequences beyond the sequestration of carbon, and informed decisions to what extent these will be considered acceptable are required.

OUTLOOK

In this review we have highlighted exciting advances in biological oceanography and ocean biogeochemistry, addressing the functioning and efficiency of the biological pump and its potential response to changing pCO₂, temperature, ocean stratification and nutrient availability. However the challenge is to predict how the biological pump will change in the face of the future climate on a global

scale. This question is critical to help inform governmental policy decisions.

The expected simultaneous changes in the carbonate system, temperature, mixing and nutrient regimes of the pelagic environment will manifest themselves differently in distinct regions of the oceans (McGinty et al. 2011). Integrating modifications in the marine carbon cycle expected due to rising temperatures with those due to changes in nutrient availability and ocean acidification and extrapolating these to changes in sequestration flux will be one of the great challenges ahead. While we can predict changes due to individual forces (Table 2), or a combination of forces (Bopp et al. 2001), we are currently unable to predict with certainty if the global biological pump will strengthen or weaken in the next 100 yr.

In this review it became clear that the literature is full of contrasting results, which is largely the consequence of comparing vastly different regions, ecosystems and organisms. Our review points out that the high sensitivity of multiple parameters and their synergistic effects, which ultimately impact export flux and flux attenuation, cannot be captured as global averages: Taking global data sets and finding re-

Table 2. Examples of processes that are expected to change with global change and may impact one or more of the 3 main components of the biological pump. Up arrow: The process is hypothesized to increase new production or flux; down arrow: a decrease in the biological pump is expected. Question mark: The process is known to affect the biological pump, but the direction is not foreseeable. For detailed explanations of different processes see text. POM: particulate organic matter; DOM: dissolved organic matter; TEP: transparent exopolymer particles

New production		Carbon export flux		Carbon sequestration flux
↑ Increased N ₂ -fixation	?	Depends on new production	?	Depends on sinking velocity & packaging of POM
↑ More efficient nutrient utilization ^a	↓	Decrease in diatoms, shift towards smaller phytoplankton	?	Shifts in food web structure: e.g. salps replace euphausiids ^d
↓ Increased stratification ^b	↓	Fewer large blooms due to elevated respiration and grazing	?	Spatial or temporal decoupling between grazers & flux events
↑ Increased nutrient input: iron in HNCL areas	↑	Decreased bioavailability of carbon-rich DOM	↓	Lack of ballasting by coccoliths and diatom frustules
↓ Prolonged periods of recycled production	?	Changes in TEP formation and stickiness ^c	?	Mesopelagic microbial activity
	↓	Glucosidase activity increased at lower pH	↑	Preferential remineralization of nutrients
	?	Formation rate of marine snow		

^ae.g. due to alleviation of light limitation and possibly lower supply from depths
^bThe effect is uncertain, as the supply rate, not only total annual amount, determines efficiency of utilization
^cBoth an increase or a decrease in flux due to changes in TEP dynamic have been postulated
^dShifts in species composition with the opposite effect are just as possible

gional trends thus meets with limited success. A promising way forward is to focus on regional scales, with the ultimate intent to address the global questions by integrating knowledge from all regions.

It may be time for a large, international effort comparable to GOFS/JGOFS (Global Ocean Flux Study/Joint Global Ocean Flux Study). Rather than focus on the euphotic zone its goal would be to understand flux attenuation in the mesopelagic. A taxa-specific understanding of environmental controls of phytoplankton (Boyd et al. 2010), zooplankton and microbial loop activity (driving flux attenuation) combined with a geographically and seasonally explicit understanding of food web structure and environmental changes will be needed to gain a predictive understanding of the biological pump. Such regional predictions may permit global predictions.

Meanwhile a starting point would be to assemble and use region-specific data sets and build a mechanistically realistic model that predicts flux attenuation based on the region-specific food web structure. In some of the most intensively studied regions of the global ocean such a database will supply sufficient data to build predictive models that allow insights into the degree of decoupling between export and sequestration flux and help guide the needed empirical studies.

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