Cycling and transport of nutrients and carbon

Phytoplankton require sunlight and nutrients to grow in the surface ocean. Sustaining phytoplankton growth is difficult in the open ocean because organic particles fall through gravity out of the sunlit, surface ocean into the dark interior, taking essential nutrient elements with them. Without ocean circulation the surface ocean would become a marine desert lacking the nutrients to support photosynthesis. Instead, physical processes continually resupply nutrients to the surface ocean, leading to some interesting consequences: phytoplankton are most abundant at high latitudes and least in the mid latitudes of the open ocean, reflecting the effect of the circulation and mixing of nutrients, rather than the pattern of insolation.

In the dark interior below the sunlit surface layer, inorganic nutrient and carbon distributions are controlled by a combination of physical transport and mixing processes, as well as biologically achieved respiration of organic matter and regeneration of inorganic form, as depicted in Fig. 11.1. Physical transport leads to a layered structure in the inorganic nutrient and carbon distributions over the globe, while respiration increases inorganic concentrations in the waters which have resided at depth for the longest time.

In this chapter, we start in the surface waters and discuss how the growth of phytoplankton is maintained, focussing on the physical transport of nutrients over the North Atlantic. We address the role of boundary currents, physical transfers between the mixed layer and interior, and convection within the surface mixed layer. We discuss how phytoplankton growth is sustained over the mid-latitude subtropical gyres, where wind-induced downwelling inhibits the surface supply of nutrients. We then move below the surface ocean and consider how the global-scale inorganic nutrient and carbon distributions are controlled in the dark interior. The inorganic nutrients are separated into components due to physical transport and biologically mediated transfer. Similarly, dissolved inorganic carbon is separated into components related to physical and biological transfers, as well as the efficiency of air–sea exchange.

11.1 How are basin-scale contrasts in biological productivity maintained?

Phytoplankton growth occurs in the surface ocean whenever there is enough sunlight and sufficient supply of nutrients and trace metals. This connection between biological productivity and surface nutrients is highlighted over the North Atlantic, where enhanced productivity in the high latitudes and the tropics coincides with increased nutrient concentrations at the base of the euphotic zone, while much weaker productivity over the mid latitudes coincides with lower concentrations of nutrients (Fig. 11.2a,b). Elsewhere in the Southern Ocean and parts of the Pacific Ocean, this connection becomes more complicated, since biological
productivity instead becomes limited by the availability of trace metals, so there can be low productivity even if there are high concentrations of the macro-nutrients, nitrate, phosphate and silica.

While this connection between biological productivity and surface concentrations of nutrients and trace metals is to be expected (Fig. 11.2), a more profound question is, how are these patterns sustained? Phytoplankton growth converts inorganic nutrients into organic matter, a fraction of which escapes from the sunlit ocean through gravitational sinking and transport. A return supply of inorganic nutrients is needed to oppose this export and sustain productivity. While sources of nutrients from atmospheric deposition and river run-off are important close to the coast, they are weak over the open ocean. There, surface nutrients are maintained by the physical redistribution of nutrients from the ocean interior.

Nutrients are redistributed through a range of physical transport and mixing processes (as illustrated in Fig. 11.2c), involving the following phenomena: gyre and overturning circulations, convection in the surface mixed layer, exchange between the mixed layer and thermocline, time-dependent eddy and frontal-scale transfers, and diapycnal mixing within the thermocline. We now consider how each of these physical phenomena maintain the production of organic matter in the surface ocean. While we use examples from the North Atlantic, these phenomena are generic and occur throughout the global ocean.

11.1 Boundary current transfer
To understand how productivity is sustained, we start by considering how nutrient-rich waters are redistributed over the upper ocean. As part of the gyre and overturning circulations, the strongest basin flows are the western boundary currents, such as the Gulf Stream, revealed by a surface front in chlorophyll (Fig. 1.17b), separating productive, nutrient-rich water on its northern edge and less productive, nutrient-depleted waters to the south.

More important than this surface signature, the Gulf Stream provides a flux of nutrients directed along its path (Fig. 11.3a) defined by the product of its along-stream velocity and nitrate concentration. This flux reaches a subsurface maximum of more than 10 mmol N m\(^{-2}\) s\(^{-1}\), within a depth range from 250 m to 750 m (Fig. 11.3b). There is no surface signature of this flux as the surface nitrate concentrations are extremely depleted.

The intense nitrate flux provided by the Gulf Stream is referred to as a ‘nutrient stream’ (Pelegrí and Csanady, 1991) and provides a conduit of nutrients which pass mainly into the subpolar gyre, but also partly recirculate in the subtropical gyre (Fig. 11.4a). There are accompanying streams for other tracers, such as dissolved organic nitrogen (DON); DON is preferentially swept around the subtropical gyre (Fig. 11.4b) since DON is more surface intensified than nitrate.

Nutrient streams are important in redistributing essential elements on the basin scale, as depicted in Fig. 11.4c. They connect the
nutrient depleted surface waters of the northern basins with the Southern Ocean. In the Southern Ocean, macro-nutrient concentrations are relatively high in the surface mixed layer, because biological consumption is inhibited by lack of iron and/or light, and is unable to consume all the upwelled nutrients. These water masses, rich in macro nutrients, are subducted into the thermocline and spread northward in each basin, transported via the gyre and overturning circulations; they can be identified by their freshness and are made up of a combination of Sub-Antarctic Mode Water and Antarctic Intermediate Water. In the tropics, the local nutrient concentrations

Figure 11.2 (a) Phosphate concentration (\(\mu\text{mol kg}^{-1}\)) at the base of the euphotic zone, taken to be at a depth of 100 m. (b) Primary production (mol N m\(^{-2}\) y\(^{-1}\)), the rate of production of organic matter by photosynthesis over the North Atlantic, as inferred from remote-sensing-based estimates of surface chlorophyll and temperature for 2005 (Behrenfeld and Falkowski, 1997a), assuming a C : N ratio of 106 : 16. (c) A schematic view of the physical processes acting to maintain biological productivity involving the three-dimensional circulation consisting of boundary currents, separated jets, interior flows, eddy and frontal circulations, as well as spatial variations in convection and diapycnic diffusion.
increase through a local cycle of upwelling, fallout and regeneration. The nutrient-enriched waters then continue into the northern basins via the western boundary current and separated jet. What is the fate of these nutrient-rich waters?

### 11.1.2 Advection of nutrients into the mixed layer

Below the surface in the Gulf Stream, nutrients are transferred along potential density layers which eventually outcrop into the downstream mixed layer, as illustrated in Fig. 11.5a. Close to where the Gulf Stream separates from the coast, the nutrient flux is greatest in the density layers from \( \sigma = 26.7 \) to 27.4 (Fig. 11.3c). These layers outcrop into the mixed layer at the end of winter over both the northern flank of the subtropical gyre and much of the subpolar gyre (Fig. 11.5b). This advective influx of nutrients then maintains high surface concentrations of macro nutrients and vigorous productivity over the subpolar gyre (Fig. 11.5c).

The advection of fluid into the downstream mixed layer is achieved through the reverse of the subduction process: fluid is transferred by a combination of vertical upwelling and horizontal advection into a thickening mixed layer, as depicted in Fig. 11.6a. The associated advective flux of nutrients into the downstream mixed layer at the end of winter is given by

\[
N_H (w_H + u_H \cdot \nabla H) \equiv -N_H S_{ann},
\]

where \( N_H \) is the nutrient concentration, \( u_H \) and \( w_H \) are the horizontal and vertical velocities at the base of the end of winter mixed layer, \( z = -H \), and \( S_{ann} \) is the subduction rate.

This advective transfer of nutrients into the end of winter mixed layer defines two separate biological regimes:
Figure 11.4 Nutrient pathways over the Atlantic. In (a) nitrate (kmol s\(^{-1}\)), and (b) dissolved organic nitrogen (DON) transport (kmol s\(^{-1}\)), displayed as the magnitude of a depth integral of \(vN\), where \(v\) is the horizontal velocity and \(N\) is the nutrient concentration from a numerical isopycnic circulation model at 23\(\circ\), integrated in (a) between \(\sigma_\theta\) surfaces 26.5 and 27.5, and in (b) between the sea surface and \(\sigma_\theta = 26.5\). In (c), a schematic view of the nutrient pathways in the Atlantic; Sub-Antarctic Mode Waters (dark grey shaded) are formed in the southern hemisphere, transferred northward, and eventually subducted into the downstream mixed layer; the transport involves a combination of the horizontal Ekman (dashed line), gyre (black) and intermediate (grey) circulations. Panels (a) and (b) from Williams et al. (2011) and panel (c) from Williams et al. (2006).

- Productive, subpolar gyres where nutrient-rich water is transferred from the thermocline into the winter mixed layer, as marked by positive transfer in Fig. 11.6b.
- Oligotrophic subtropical gyres where nutrient-depleted water is instead subducted from the mixed layer into the thermocline, as marked by negative transfer in Fig. 11.6b.

The sign of this advective transfer broadly reflects the sign of the wind-induced Ekman upwelling (Fig. 11.6c), since Ekman pumping determines the
Figure 11.5 The surface density and nutrient distributions at the end of winter reflect the effect of the underlying circulation: (a) a schematic view of how a nutrient stream (black arrow) associated with the western boundary current transfers nutrients along an isopycnal layer (shading) into the downstream mixed layer (dashed line) at the end of winter, and the nutrients are then vertically redistributed through convection (curved arrows); diagnostics of (b) mixed-layer density, $\sigma$ (kg m$^{-3}$), and (c) nitrate ($\mu$mol kg$^{-1}$) for March from climatology over the North Atlantic (Conkright et al., 2002; Conkright et al., 1994).

sign of the gyre rotation. However, the actual magnitude of the transfer over the subpolar gyre is primarily determined by the horizontal advection into the winter mixed layer.

Hence, nutrients are supplied by advection to the thick, winter mixed layer. How does this transfer then sustain phytoplankton growth in the euphotic zone?

11.1.3 Convective transfer of nutrients
Primary production is confined to the euphotic layer, where the photon flux is sufficient to sustain photosynthesis. The euphotic layer varies in thickness from a few metres in very turbid waters to as much as even 200 m in clear waters.

Whenever the mixed layer is thicker than the euphotic zone, then the nutrient profile is affected by the interplay of biological consumption and convection (Fig. 11.7a). Over each 24-hour period, the mixed layer thickens through surface cooling during the night, entraining nutrient-enriched thermocline waters. The enhanced turbulence homogenises the nutrient profile vertically over the mixed layer. Over the following daytime, sunlight enables photosynthesis which drives the consumption of nutrients within the euphotic layer.

In a similar manner, the seasonal cycle of the mixed layer causes the nutrients advected into the seasonal boundary layer to be vertically
Figure 11.6 (a) A schematic view of a density layer (shaded) outcropping into the mixed layer at the end of winter. Fluid is transferred from the thermocline across the base of the sloping mixed layer (dashed line, $z = -H$) through the advective transfer by horizontal velocity $u$ and vertical velocity, $w$; (b) advective transfer of nitrate into the winter mixed layer, $-S_{ann}NO_3^-$ (mmol N m$^{-2}$ y$^{-1}$), where $S_{ann}$ is the subduction rate, and (c) Ekman upwelling of nitrate, $w_{ek}NO_3^-$ (mmol N m$^{-2}$ y$^{-1}$), defined as positive as upwards. There are two regimes: nitrate transferred into the mixed layer, $-S_{ann}NO_3^- > 0$, or nitrate transferred into the thermocline, $-S_{ann}NO_3^- < 0$; further details in Williams et al. (2006).

Phytoplankton growth is then sustained over much of the open ocean through a two-stage process:

- Nutrients are advected into the seasonal boundary layer through a combination of the horizontal and vertical circulations (as suggested on the gyre scale by Fig. 11.6b).
- Convection redistributes the nutrients vertically within the mixed layer, which then supplies them to the euphotic zone (Fig. 11.7c).

If convection were to occur in isolation from the large-scale advective transfer, then productivity would gradually diminish: the nutrient inventory of the seasonal boundary layer would progressively decline as organic particles sink into deeper waters.

In the simpler case where the mixed layer is shallower than the euphotic zone, such as in the tropics and low latitudes, convection does not provide a source of nutrients. Biological productivity is instead sustained by the direct physical transfer of nutrients into the euphotic zone. This supply is probably achieved here mostly by vertical upwelling and diapycnic diffusion, with a contribution from horizontal transfer across the sloping base of the euphotic zone.
11.2 How is biological productivity sustained in ocean deserts?

Given the view that biological productivity is ultimately sustained by nutrient transfer from the thermocline into the mixed layer, how can we explain the maintenance of photosynthesis in the subtropical gyres where the winds induce widespread downwelling? The subtropical gyres are sometimes viewed as oceanic deserts due to the low rate that nutrients are supplied to the surface. However, primary production does still occur there, albeit at weaker rates than at high latitudes or the tropics. Despite the lower rates of primary production, the extensive area of the subtropical gyres means that they account for up to half of the global export of organic matter.

A range of hypotheses have been set out to explain how the productivity of the subtropical oceans is sustained. At the simplest level, the question is how are nutrients supplied to the euphotic zone from the underlying nutrient-rich waters? This supply is probably achieved primarily via vertical exchanges involving convection, diapycnic mixing and time-varying upwelling (Fig. 11.8). However, for these processes to continue to act...
as a nutrient source, the nutrient concentrations in the waters underlying the euphotic zone need to be maintained, otherwise the vertical supply of nutrients into the euphotic zone gradually weakens over time. The greater penetration of light over the clearer waters of the subtropical gyres leads to production occurring well below the mixed layer, making the nutricline deeper than the thermocline. The supply of nutrients to the upper thermocline of the subtropical gyre involves vertical exchanges with waters in the underlying nutricline and horizontal exchanges with the neighbouring subpolar gyres, the tropics and ultimately the Southern Ocean (Fig. 11.8).

### 11.2.1 Case study of biological export in the North Atlantic subtropical gyre

Quantifying the rate at which organic matter is exported from the euphotic zone is very difficult. The sinking flux of organic particles can be directly measured via sediment traps, although their accuracy near the surface becomes questionable due to the strong horizontal flows. Export production can also be indirectly inferred from the rate at which oxygen accumulates within the euphotic zone (but below the mixed layer) during summer, or the rate at which oxygen is utilised by the respiration of exported material below the euphotic zone.

In the Sargasso Sea, these indirect estimates suggest that export production reaches $0.47 \pm 0.12 \text{ mol N m}^{-2} \text{ y}^{-1}$; three different methods have been applied, all remarkably consistent with each other within error bars; see Table 11.1 for references. To maintain a steady state, this export of organic matter needs to be compensated by sources of nutrients to the euphotic zone. However, the obvious nutrient sources seem to be too weak: for example, for nitrogen, atmospheric deposition only reaches $0.03 \text{ mol N m}^{-2} \text{ y}^{-1}$, and the convective supply of nitrate is about $0.13 \pm 0.05 \text{ mol N m}^{-2} \text{ y}^{-1}$. Hence, there is a shortfall, an additional $0.31 \text{ mol N m}^{-2} \text{ y}^{-1}$ is needed to sustain the estimated export production (Table 11.1).

We now consider physical processes which might enhance the supply of nutrients to the subtropical gyre, discussed first in terms of vertical transfer and then horizontal transfer. We then consider other alternative, biologically mediated sources.

Over the subtropical gyres, large-scale downwelling acts to transfer nutrients from the mixed layer to the thermocline, and inhibit biological production. This large-scale descent is partially opposed by diffusive transfers and time-dependent upwelling.

### 11.2.2 Diffusive transfer

Vertical transport by turbulent mixing processes, such as the breaking of internal waves, leads to a vertical nutrient flux, described by $-\kappa \frac{\partial N}{\partial z}$, where $\kappa$ is the effective diffusivity and $\frac{\partial N}{\partial z}$ is the vertical gradient of nutrient. This diffusive transfer is usually associated with a transfer across density surfaces, referred to as diapycnic transfer.
Table 11.1  Geochemical estimates of export production in the Sargasso Sea and nitrogen sources, based upon McGillicuddy et al. (1998) and more recent updates

<table>
<thead>
<tr>
<th>Export production</th>
<th>Method</th>
<th>Value (mol N m⁻² y⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ utilisation</td>
<td></td>
<td>0.48 ± 0.10</td>
<td>Jenkins and Wallace (1992)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.42 ± 0.09</td>
<td>Jenkins and Goldman (1985)</td>
</tr>
<tr>
<td>O₂ production</td>
<td></td>
<td>0.46 ± 0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.39 ± 0.16</td>
<td>Spitzer and Jenkins (1989)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.51 ± 0.14</td>
<td></td>
</tr>
<tr>
<td>³He flux gauge</td>
<td></td>
<td>0.56 ± 0.16</td>
<td>Jenkins (1988b)</td>
</tr>
</tbody>
</table>

| Nitrogen demand   | mean                    | 0.47 ± 0.12            |                                    |

<table>
<thead>
<tr>
<th>Nitrogen sources</th>
<th>Method</th>
<th>Value (mol N m⁻² y⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric</td>
<td>deposition</td>
<td>0.03</td>
<td>Knap et al. (1986)</td>
</tr>
<tr>
<td>Winter convection</td>
<td>O₂ production</td>
<td>0.17 ± 0.05</td>
<td>Michaels et al. (1994)</td>
</tr>
<tr>
<td></td>
<td>NO₃ removal</td>
<td>0.09 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Diapycnic diffusion</td>
<td>Microstructure</td>
<td>0.05 ± 0.01</td>
<td>Lewis et al. (1986)</td>
</tr>
<tr>
<td></td>
<td>NO₃⁻ and velocity</td>
<td>0.05 to 0.15</td>
<td>Dietze et al. (2004)</td>
</tr>
<tr>
<td>Salt fingering</td>
<td>Model assessment</td>
<td>0.03</td>
<td>Oschlies et al. (2003)</td>
</tr>
<tr>
<td>Ekman flow</td>
<td>Climatology</td>
<td>0.03 ± 0.01</td>
<td>Williams and Follows (1998)</td>
</tr>
<tr>
<td>Eddy upwelling</td>
<td>Model simulation</td>
<td>0.35 ± 0.10</td>
<td>McGillicuddy and Robinson (1997)</td>
</tr>
<tr>
<td></td>
<td>Satellite data and model</td>
<td>0.19 ± 0.10</td>
<td>McGillicuddy et al. (1998)</td>
</tr>
<tr>
<td></td>
<td>Model simulation</td>
<td>&lt;0.05</td>
<td>Oschlies (2002)</td>
</tr>
<tr>
<td>Nitrogen fixation</td>
<td>N*</td>
<td>0.07</td>
<td>Gruber and Sarmiento (1997)</td>
</tr>
<tr>
<td></td>
<td>Excess nitrate</td>
<td>0.02 to 0.08</td>
<td>Hansell et al. (2004)</td>
</tr>
<tr>
<td>Supply of DON</td>
<td>Model and in situ data</td>
<td>0.05 ± 0.02</td>
<td>Roussenov et al. (2006)</td>
</tr>
</tbody>
</table>

| Nitrate supply    | mean using low or high estimates of eddy upwelling | 0.43 to 0.65 |

In regions of strong mechanical forcing, such as in shallow shelf waters, above the shelf break or above rough topography, the effective diffusivity, $\kappa$, can exceed $10^{-4}$ m² s⁻¹. However, over much of the interior of the open ocean, the mechanical forcing is relatively weak and the diffusivity is much smaller; typically, reaching $10^{-5}$ m² s⁻¹ in the upper thermocline. The nutrient flux estimated by $-\kappa \partial N/\partial z$ is then generally too small to sustain the observed biological productivity; for example, diapycnic mixing is estimated to supply only $0.05 \pm 0.01$ mol N m⁻² y⁻¹ in the Sargasso Sea (Table 11.1).

### 11.2.3 Time-dependent upwelling
While the winds induce a large-scale downwelling over the subtropical gyre, there can be more intense vertical velocities (both downward and upward) on finer horizontal scales. One might expect that a transient vertical velocity, reversing in sign, might have a limited effect, since tracer surfaces will be both lifted up and pushed down. However, this turns out not to be the case when there is active photosynthesis. When an isopycnal surface is lifted into the euphotic zone, it can stimulate phytoplankton growth by creating conditions where there is both sufficient sunlight and...
Figure 11.9 A schematic depiction of the ecosystem response to an uplift and depression of the nutricline. When nutrient-rich isopycnal surfaces are raised into the euphotic zone, there is biological production. Conversely, when the nutrient-rich isopycnals are pushed into the dark interior, there is no biological response. In order for the transient upwelling to persist, there needs to be a process maintaining the nutrient concentrations in the thermocline, which might be achieved by respiration of organic fallout and regeneration of inorganic nutrients, diapycnal transfer or a lateral influx of nutrients from the time-mean or time-varying circulations. Adapted from McGillicuddy and Robinson (1997); from Williams and Follows (2003).

There is a caveat to this mechanism: nutrients in the upwelled waters must be continually replenished in order for this transient upwelling to sustain phytoplankton growth over the long term. There are different views as to the importance of time-varying upwelling: several studies argue that eddy-scale upwelling can provide up to 0.35 mol N m$^{-2}$ y$^{-1}$ over the Sargasso Sea, sufficiently large to be the primary term sustaining export production. Other studies argue that, after an initial transient peak, the eddy upwelling provides only 0.05 mol N m$^{-2}$ y$^{-1}$ in the long-term average (Table 11.1). This discrepancy is mainly due to different assumptions in how rapidly nutrients are resupplied in the upper thermocline.

The most important time-varying vertical velocities are probably associated with time-dependent mesoscale eddies, on horizontal scale of several tens of kilometres, analogous to the atmospheric weather systems, and with finer-scale frontal features on a scale of several kilometres.

**Upwelling signals of eddies and fronts**

Most mesoscale eddies are formed by baroclinic instability involving a slantwise exchange of cold water and warm water across a meandering jet (Fig. 11.10a,b). The shallower thermocline and nutricline seen in a cold-core, cyclonic eddy is not due to a simple vertical transfer, since cold fluid sinks and warm fluid rises in slantwise exchange. Instead, cold-core cyclones bring these characteristics with them as they move horizontally across a jet, which has a shallower thermocline and nutricline on its colder side. Likewise, warm-core anticyclones bring a deeper
thermocline and nutricline as they move horizontally into a colder environment. If instead of baroclinic instability, the cyclones are generated by the interaction of the large-scale flow and topographic features, then a vertical uplift of the nutricline should provide enhanced production (Fig. 11.9). There are also eddy–eddy interactions, distortions of the nutricline as eddies come into close proximity, which might intensify features and lead to a local uplift of the nutricline.

In addition to the mesoscale eddy circulation, there are embedded frontal circulations, with horizontal scales of several kilometres to tens of kilometres. They are associated with strong horizontal contrasts in sea-surface temperature (Fig. 11.11a). Frontal-scale circulations are associated with upwelling on the anticyclonic side and downwelling on the cyclonic side of an accelerating jet (Fig. 11.11b). The opposing circulation occurs in the decelerating region. In an analogy of the eddy-scale uplifting of isopycnals and nutricline, frontal-scale upwelling can drive a rectified transfer of nutrients into the euphotic zone, sustaining productivity on a frontal scale (in accord with Fig. 11.9).

There frontal circulations appear to play an important role in idealised numerical model studies (Lévy et al., 2001). Observational support is presently rather tentative due to the intermittent nature and fine horizontal scales. Maxima in surface chlorophyll have, though, been observed on the anticyclonic side of fronts and plumes of short-lived chlorophyll have been observed penetrating into the stratified thermocline on a horizontal scale of several tens of kilometres.

In summary, time-varying upwelling by baroclinic eddies and frontal-scale circulations augment the time-mean, gyre-scale circulation in providing an additional transfer of nutrients into the euphotic zone. However, the magnitude of this contribution is not clearly constrained, and this supply is only effective as long as there is a mechanism by which nutrients are replenished in the upper thermocline.

Accordingly, we now move on to mechanisms that transfer nutrients horizontally (some of which have already been touched upon), considering their effect on both the surface nutrients and the nutrient reservoir within the upper thermocline (Fig. 11.8).
11.2.4 Horizontal transfers of nutrients into the subtropical gyre

The subtropical gyre is defined by the pattern of the overlying winds, inducing an anticyclonic circulation. At the northern and southern edges of the subtropical gyre, the time-averaged geostrophic flow is generally directed along the inter-gyre boundaries rather than across them. Any transfer between the gyres is achieved by departures from the time-averaged geostrophic flow. These cross-gyre flows include the boundary currents and separated jets (Figs. 11.3 to 11.4), surface Ekman transport and transient eddy exchanges.

Surface Ekman transfer

Downwelling over the subtropical gyre is achieved by a convergence of the horizontal Ekman volume flux. These horizontal Ekman fluxes likewise transfer nutrients into the subtropical gyre from the neighbouring nutrient-rich waters in the tropics and subpolar gyre (Fig. 11.12a). The nutrient supply associated with the Ekman flow across the inter-gyre boundaries reaches 10 to 50 mmol N m\(^{-2}\) y\(^{-1}\) (Fig. 11.12b,c), strongest on the flanks of the gyre and weakest towards the centre of the gyre. This Ekman supply is much smaller than that needed to sustain local, annual productivity in the euphotic zone (Table 11.1), but it is comparable to the downward flux of organic matter across the thermocline at a few hundred metres. Hence, this lateral trickle of nutrients into the subtropical gyre is probably important in sustaining the integrated inventory of nutrients within the thermocline.
Figure 11.13 The eddy circulation transfers nitrate and other tracers, as illustrated schematically in (a), as well as revealed in the fine-scale horizontal variations in surface nitrate (μmol kg⁻¹) for model simulations (b) over the North Atlantic, and in (c) a blow-up around 40° N, 40° W. This snapshot is in the month of February in a simulation using a fine-resolution (~1/6°) configuration of the MIT ocean model. Model output provided by O. Jahn.

Surface eddy lateral transfer
Geostrophic eddies on scales of several tens of kilometres transfer properties horizontally, as well as vertically, redistributing heat, nutrients and other tracers over the ocean (Fig. 11.13a). Eddies stir tracers, drawing out filaments, which are eventually dissipated by finer-scale mixing, leading to an eddy flux of tracers, usually directed down the tracer gradient. Eddies provide an influx of nutrients into the subtropical gyre, laterally transferring nutrient-rich surface waters from the subpolar gyre and from regions of coastal upwelling (Fig. 11.13b,c).

The magnitude of this eddy transfer is difficult to quantify from observations given their transient nature and scale, but this view is supported by eddy-resolving model simulations.

11.2.5 Other nutrient sources
In addition to the physical transfer of inorganic compounds, there are other sources of nutrients to the surface oceans. Some organisms can fix dissolved nitrogen gas into organic form, relieving nitrogen limitation and providing a source of nitrogen to the ocean. Dissolved organic forms of nutrients are also transported by the ocean circulation and may be remineralised by heterotrophs to supply inorganic forms, or utilised directly by some phytoplankton. In particular, dissolved organic phosphorus may be a significant source for primary producers in the subtropical oceans.

Nitrogen fixation
The waters of the subtropics can be extremely nutrient depleted, limiting production. Some types of cyanobacteria, referred to as diazotrophs, have exploited the niche where inorganic nitrogen is particularly limited and are able to utilise nitrogen gas to form ammonia and amino acids. There is a price for this flexibility, though: diazotrophs must produce the iron-rich enzyme nitrogenase and expend energy breaking the triple bond of nitrogen gas molecules. Thus they have a higher iron demand, relative to other elements, and slower growth rates relative to other phytoplankton. These trade-offs enable diazotrophs to flourish in nutrient-starved waters where there are sufficiently high iron
sources, such as the tropical and subtropical North Atlantic. A meridional transect reveals enhanced rates of nitrogen fixation, reaching a peak of 70 mmol N m\(^{-2}\) y\(^{-1}\) (converted from the daily to a maximum annual rate) and increased abundances of a key diazotroph, *Trichodesmium*, coincident with enhanced surface concentrations in dissolved iron (Fig. 11.14). The iron supply is significantly enhanced here by atmospheric dust deposition, as indicated by the associated, elevated concentrations of aluminium.

A consequence of production sustained by nitrogen fixation is that the resulting organic matter has a higher than normal proportion of nitrogen relative to phosphorus. The subsequent export and remineralisation of this organic matter increases the concentration of nitrate relative to phosphate in thermocline waters. A signal of elevated nitrate to phosphate concentrations extends over much of the North Atlantic, indicated by excess nitrate, \(\text{DIN}_{\text{ex}} = \text{NO}_3^- - 16\text{PO}_4^{3-}\), with values greater than 2.5 \(\mu\text{mol kg}^{-1}\) in the upper thermocline, as illustrated in Fig. 11.14a.

The contribution of nitrogen fixation to the maintenance of productivity in the subtropical gyres is still uncertain with direct measurements over a year ranging from 0.02 to 0.08 mol N m\(^{-2}\) y\(^{-1}\) (Mahaffey et al., 2005). While nitrogen fixation plays a role in closing the nitrogen budget of the subtropical North Atlantic, it demands a corresponding supply of phosphorus, which has no analogous source.

**Dissolved organic nutrients**

Over much of the ocean, the dissolved inorganic pools of nitrogen and phosphorus are much greater in concentration than the dissolved organic pools of nitrogen (DON) and phosphorus (DOP). However, in the surface waters of the subtropical gyres, where biological consumption draws down the concentrations of inorganic nutrients, surface concentrations of DON and DOP significantly exceed those of nitrate and phosphate, as seen over the North Atlantic in Fig. 11.15a,b.

Dissolved organic matter (DOM) represents a spectrum of molecules with different properties. A fraction of the dissolved organic matter can be...
utilised by bacteria on relatively short timescales of up to a few days or months; typically referred to as labile and semi-labile DOM respectively. Other components are not so easily utilised and are referred to as refractory. A larger fraction of the DON is refractory, perhaps originating from structural proteins, while DOP is generally more labile, originally associated with genetic material or lipids in the cell. DOM, by definition, is the fraction of organic detritus which is transported by the circulation, convection and mixing, and does not sink gravitationally. The transport and remineralisation, or utilisation, of the semi-labile components of DON and DOP are potentially important for the maintenance of productivity in oligotrophic regimes which are bounded by productive regions.

DON and DOP are formed in productive upwelling zones in the tropics or by the coast and transferred by the circulation of the subtropical gyre (Fig. 11.15c); as illustrated in the case of boundary currents and separated jets in Fig. 11.4b. The gradients of DON in the subtropical gyres suggest that its transport and recycling might provide an additional nitrogen source of up to 0.05 mol N m\(^{-2}\) y\(^{-1}\) in the subtropical North Atlantic; a relatively small contribution to annual production in terms of nitrogen. In contrast, the
transport and cycling of DOP is probably more important for the phosphorus budget since DOP is more reactive and there is no equivalent of nitrogen fixation. Numerical model studies suggest that as much as half of the biological export of phosphorus in the region might be sustained by recycling of DOP.

In summary, production over the subtropical gyres is sustained by a range of physically and biologically mediated processes which provide the necessary nitrogen, phosphorus and trace metals. There is still considerable debate as to the relative importance of the different sources for the whole gyre, possibly reflecting uncertainties in the estimates, but also their real spatial variations. For example, eddy transfers are likely to be important near the intense boundary currents where there are strongly sloping density surfaces, nitrogen fixation is locally significant where there is atmospheric dust deposition and the transport of dissolved organic matter might be important near tropical and coastal upwelling sites.

11.3 What sets the nutrient distributions in the ocean interior?

We now consider how macro-nutrients are returned to the dark interior of the ocean by both transport and the export and respiration of organic detritus, setting the basin-scale distributions illustrated in Fig. 11.16.
Some of the nutrients in the euphotic layer are subducted back into deeper waters in inorganic form, without being consumed by living organisms or having been consumed and quickly regenerated. The remaining nutrient transfer is in organic form, either as gravitationally sinking particles or subducted dissolved organic matter. Almost all of the exported organic matter is returned to inorganic form by respiration before arriving at the sea floor. In the following sections, we set out a framework for mapping and interpreting the contributions of subduction and biological export to the ocean’s nutrient and carbon reservoirs.

11.3.1 Preformed and regenerated nutrients

The concentration of an inorganic nutrient, such as phosphate \( \text{PO}_4^{3-} \), below the euphotic layer may be separated into two components (Redfield et al., 1963):

\[
\text{PO}_4^{3-} = \text{PO}_4^{\text{pre}} + \text{PO}_4^{\text{reg}},
\]

(11.2)

the preformed contribution, \( \text{PO}_4^{\text{pre}} \), that which the water parcel had at the time of subduction, and the regenerated contribution, \( \text{PO}_4^{\text{reg}} \), the result of the accumulated regeneration from organic matter in the water parcel since the time of subduction, as depicted in Fig. 11.17. Nutrient utilisation, \( P^* \), is defined as the relative magnitude of the regenerated and total phosphate concentrations in a water parcel below the mixed layer and euphotic zone (Ito and Follows, 2005).

\[
P^* = \frac{\text{PO}_4^{\text{reg}}}{\text{PO}_4^{\text{pre}}},
\]

(11.3)

The limit \( P^* = 0 \) indicates that all of the phosphate in the water parcel was present at the time of subduction, while the limit \( P^* = 1 \) indicates that all of the phosphate in the water parcel is due to the respiration of organic detritus.

11.3.2 Estimating the regenerated contribution using oxygen observations

The regeneration of inorganic nutrients is accompanied by the consumption of dissolved oxygen through respiration. The dissolved oxygen concentration may also be separated into a preformed and a regenerated component (which will have a negative value),

\[
\text{O}_2 = \text{O}_2^{\text{pre}} + \text{O}_2^{\text{reg}}.
\]

(11.4)

In the surface ocean, oxygen is observed to be very close to its saturated concentration due to the relatively short air–sea equilibration timescale, so we assume that

\[
\text{O}_2^{\text{pre}} \approx \text{O}_2^{\text{sat}}(T, S).
\]

(11.5)

Since the mixing ratio of oxygen in the atmosphere is effectively unchanging, the saturation concentration may be described simply in terms of its solubility, varying as a function of temperature, and salinity (Garcia and Gordon, 1992). Potential temperature, \( \theta \), and salinity are conserved below the surface mixed layer so, for an isolated water parcel, their interior values are the same as their surface values at the time of subduction. Assuming fixed elemental ratios, the oxygen consumed in respiration, \( \text{O}_2^{\text{reg}} \), is related to the regenerated phosphate by

\[
\text{O}_2^{\text{reg}} = R_{\text{OP}} \text{PO}_4^{\text{reg}}.
\]

(11.6)

Using Redfield ratios, \( \text{C} : \text{N} : \text{P} : \text{O}_2 = 106 : 16 : 1 : 170 \) (Takahashi et al., 1985), the ratio of oxygen
consumption to phosphate regeneration, $R_{OP}$, is taken to be $-170$. Combining (11.4) to (11.6), allows the regenerated phosphate concentration to be expressed in terms of measured properties ($O_2$, $\theta$ and $S$),

$$PO_4^{\text{reg}} \simeq \frac{(O_2 - O_2^{\text{sat}}(\theta, S))}{R_{OP}} = \frac{-AOU}{R_{OP}},$$  \hspace{1cm} (11.7)

where Apparent Oxygen Utilisation, AOU, is defined as the difference between the saturated and measured oxygen concentrations,

$$AOU \equiv O_2^{\text{sat}}(\theta, S) - O_2.$$

(11.8)

The efficiency of nutrient utilisation, $P^*$ is likewise diagnosed as

$$P^* = \frac{PO_4^{\text{reg}}}{PO_4^3 \simeq -AOU}{R_{OP}PO_4^3}.$$  \hspace{1cm} (11.9)

We now consider diagnostics of $PO_4^{\text{reg}}$ and $P^*$ over the Atlantic and Pacific, while accepting there are some significant uncertainties; deep waters are probably undersaturated in oxygen at the time of subduction (Körtzinger et al., 2004) causing $P^*$ to be over-estimated by as much as 0.2 in some dense water masses (Ito et al., 2004).

11.3.3 Nutrient utilisation in the Atlantic and Pacific basins

The regenerated phosphate, $PO_4^{\text{reg}}$, distributions of the Atlantic and Pacific contrast strongly, as depicted in Fig. 11.18a,b. In the Atlantic basin, the regenerated phosphate, $PO_4^{\text{reg}}$, ranging in value between 0.3 to 0.9 $\mu$mol P kg$^{-1}$, broadly resembles the distribution of water masses. There is elevated $PO_4^{\text{reg}}$ in the intermediate and bottom waters originating from the Southern Ocean, and lower $PO_4^{\text{reg}}$ in the deep waters of the North Atlantic, mimicking the interleaving of fresh and salty waters, respectively. $PO_4^{\text{reg}}$ is particularly elevated over the upper few hundred metres in the

Figure 11.18 Meridional sections of regenerated biological phosphate, $PO_4^{\text{reg}} = -AOU/R_{OP}$, ($\mu$mol kg$^{-1}$) in (a) and (b), diagnosed from apparent oxygen utilisation, AOU (magnitude of AOU in brackets, $\mu$mol kg$^{-1}$) assuming $R_{OP} = -170$; and local nutrient utilisation, $P^* = PO_4^{\text{reg}}/PO_4^3$, in (c) and (d) for the Atlantic and Pacific.
Nutrient utilisation

The regenerated nutrients in the deep ocean are controlled by the efficiency of nutrient utilisation in the euphotic layer: the fraction of upwelled nutrients that is returned to depth in organic form (Francois et al., 1992; Ito and Follows, 2005). This balance is illustrated in a simple model, where $w$ is a vertical exchange velocity (m s$^{-1}$) and $E$ is the biological export ($$\text{mol N m}^{-3} \text{s}^{-1}$).

The nutrient concentration in the deep ocean is the sum of preformed and regenerated contributions, $\{N\} = \{N_{\text{pre}}\} + \{N_{\text{reg}}\}$. The rate of change of surface nutrient concentration, $\{N_{\text{pre}}\}$ (mol N m$^{-3}$) is determined by the balance between the physical nutrient supply, from upwelling of nutrient-rich deep waters minus the subduction of surface waters, and the biological consumption and export, $E$,

$$h A \frac{d\{N_{\text{pre}}\}}{dt} = A w (\{N\} - \{N_{\text{pre}}\}) - h A E, \quad (11.10)$$

where $A$ is the surface area (m$^2$) and $h$ the thickness of the euphotic layer (m). Assuming a steady state, $d/\text{dt} = 0$, (11.10) can be manipulated to provide equilibrium solutions for the regenerated nutrient,

$$\{N_{\text{reg}}\} = \frac{E h}{w}, \quad (11.11)$$

and the extent of nutrient utilisation,

$$P^* = \frac{\{N_{\text{reg}}\}}{\{N\}} = \frac{E h}{w \{N\}. \quad (11.12)}$$

The efficiency of nutrient utilisation is thus set by the competition between the biologically driven downward flux of phosphorus $E h$, versus the physical supply of nutrients to the surface, $w \{N\}$ (both mol m$^{-2}$ s$^{-1}$). The regenerated store of phosphate (and carbon) in the ocean interior is proportional to the nutrient utilisation, $P^*$.

Tropics, enhanced due to high tropical productivity and regeneration from sinking organic particles. The relatively weak signature of PO$_4^{\text{reg}}$ in the deep waters of the North Atlantic, and the dominance of transport-related water mass patterns, reflects the relatively young age and rapid ventilation of these waters. In addition, regenerated phosphate accumulates relatively slowly at depth because most of the exported organic matter is respired higher in the water column.

In contrast, in the Pacific basin, PO$_4^{\text{reg}}$ is much larger, varying from 0.9 to 1.8 $\mu$mol P kg$^{-1}$, in the deep and mid-depth waters, (Fig. 11.18b), and there is a greater vertical contrast than seen in salinity. The deep waters of the Pacific are filled by the northward transport, upwelling and mixing of bottom waters originating in Antarctica. During this slow transit, the waters acquire PO$_4^{\text{reg}}$ from the regeneration of exported organic matter. The ‘oldest’ waters in the ocean, those which have spent the longest time since last at the surface, are at the mid depths in the North Pacific, coincident with the highest values of PO$_4^{\text{reg}}$.

The higher values of PO$_4^{\text{reg}}$ in the deep Pacific compared with the Southern Ocean or Atlantic are consistent with less vigorous physical exchanges of nutrients (see Box 11.1 for a simple model description).

The efficiency of nutrient utilisation, $P^*$, typically reaches 0.3 over the Atlantic basin, only enhanced to 0.5 in the tropical thermocline, but is generally larger over the Pacific basin, ranging from 0.4 to 0.5 (Fig. 11.18c,d). Hence, nutrient utilisation, $P^*$, averaged over the globe is less than
0.5, so the efficiency with which living organisms are consuming and exporting available phosphorus is less than 50% of its full potential. If each mole of exported organic phosphorus brings with it about 106 moles of organic carbon (the Redfield ratio), there is a corresponding store of carbon in the deep ocean, proportional to $\text{PO}_{4}^{\text{reg}}$. Apparently this store of carbon is less than half of its possible upper limit. If the efficiency of nutrient utilisation were to increase, the biological storage of carbon in the deep ocean could be enhanced, as it might have been in other periods of Earth’s history. How large is this biologically mediated reservoir of carbon in the ocean and how does it relate to other reservoirs of carbon in the ocean? These questions are addressed in the next section.

### 11.4 Quantifying the ocean’s carbon reservoirs

The observed distribution of DIC reveals a background concentration of about 2200 μmol kg$^{-1}$ with variations on the order of ±10%. The Atlantic basin has lower concentrations than the Pacific, and DIC decreases towards the surface, as depicted in Fig. 11.19. What are the relative contributions of solubility and biologically mediated processes that set these patterns? To answer this question, we extend the preformed and regenerated framework to the carbon system (Fig. 11.17), broadly following the approach taken by Brewer (1978), Chen and Millero (1979) and Gruber et al. (1996).
11.4.1 Surface ocean
In the surface mixed layer, there is active exchange of dissolved gases with the atmosphere, so that the dissolved inorganic carbon, DIC, may be separated into the sum of two components: $C^\text{sat}$, the concentration the water parcel would have at equilibrium with the partial pressure of carbon dioxide in the overlying atmosphere, and $\Delta C$, the remaining disequilibrium contribution,

$$\text{DIC} = C^\text{sat} + \Delta C. \quad (11.13)$$

The saturated contribution, $C^\text{sat}(p\text{CO}_2, \theta, S, A_T)$, in the surface ocean may be evaluated from the water parcel’s potential temperature, salinity, alkalinity, and partial pressure of $\text{CO}_2$ in the atmosphere (see Section 6.6.4). The magnitude of $\Delta C$ reflects the effect of physical, biological and chemical processes which continually drive the surface waters away from local equilibrium, in competition with the damping effect of air–sea gas exchange. $\Delta C$, the disequilibrium of carbon, is significant due to the slow equilibration timescale, about one year (whereas the disequilibrium of oxygen is usually neglected due to the faster equilibration timescale of a few weeks, see Section 6.6.5).

11.4.2 Subsurface ocean
Below the surface mixed layer, DIC may again be separated into two contributions: the preformed carbon $C^\text{pre}$, the DIC that the water parcel had at the time of subduction, and the regenerated carbon, $C^\text{reg}$, accumulated since subduction due to biologically mediated processes:

$$\text{DIC} = C^\text{pre} + C^\text{reg}. \quad (11.14)$$

Preformed carbon
Preformed carbon, $C^\text{pre}$ may be further separated into saturation and disequilibrium components of the mixed layer at the time of subduction, following (11.13),

$$C^\text{pre} = C^\text{sat} + \Delta C. \quad (11.15)$$

$C^\text{sat}(p\text{CO}_2, \theta, S, A_T^\text{pre})$ may be evaluated for a water parcel in the interior of the ocean: using the local potential temperature $\theta$ and $S$, since they are assumed to be conserved in the interior; and the preformed alkalinity, $A_T^\text{pre}$, estimated from $S$

$$C^\text{sat} = C^\text{sat}_{\text{pre}} + C^\text{sat}_{\text{ant}}. \quad (11.16)$$

$C^\text{sat}_{\text{pre}}$ may be evaluated in the modern ocean using measured $\theta$ and $S$, along with estimated $A_T^\text{pre}$ taking advantage of the tight linear relationship between the two variables in the surface ocean. The reference $p\text{CO}_2^\text{ref}$, related to the mixing ratio $X_{\text{CO}_2}$, needs to be chosen in order to estimate the equilibrium $C^\text{sat}$.

While atmospheric $p\text{CO}_2$ exhibits only small variations with latitude and season, anthropogenic emissions have led to an extremely rapid rise in $X_{\text{CO}_2}$ relative to the preceding millennium, as illustrated in Fig. 11.20. During the pre-industrial period, the atmospheric mixing ratio of $\text{CO}_2$ was very stable, with a time-mean surface value of 278 ppmv evaluated from air-bubbles trapped in Antarctic and Arctic ice sheets (Fig. 11.20). Assuming that during the millennia preceding the industrial revolution, the whole ocean approached equilibrium with the stable $p\text{CO}_2$, then $C^\text{sat}$ may be separated into $C^\text{sat}_{\text{pre}}$, the saturation concentration for the pre-industrial era (where $X_{\text{CO}_2} = 278$ ppmv) and $C^\text{sat}_{\text{ant}}$ representing the anthropogenic contribution due to the increase in $p\text{CO}_2$ since the 1750s.
Box 11.2 | Regenerated alkalinity

The regenerated alkalinity \( A_{\text{reg}}^{\text{T}} \) may be related to contributions from the dissolution of calcium carbonate and the respiration of organic matter to nitrate. Start with the definition of alkalinity as the sum of charge concentration associated with conservative ions,

\[
A_T = [Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + \cdots - [Cl^-] - 2[SO_4^{2-}] - [Br^-] - [F^-] - [NO_3^-] - \cdots
\] (11.17)

Calcium carbonate dissolution and the respiration of organic matter alters \([Ca^{2+}]\) and \([NO_3^-]\), while all other concentrations remain constant, so that the changes in alkalinity may be described as

\[
\delta A_T = 2\delta[Ca^{2+}] - \delta[NO_3^-],
\] (11.18)

so the regenerated alkalinity, \( A_{\text{reg}}^{\text{T}} \), may be diagnosed from \( \delta A_T \). Each mole of calcium released from dissolving calcium carbonate is accompanied by a mole of carbon released into the dissolved inorganic pool, so \( C_{\text{carb}} = \delta[Ca^{2+}] \). Assuming fixed Redfield ratios, for each mole of oxygen consumed in the respiration of organic matter, \( R_{NO} = -16/170 \) moles of nitrate are regenerated, so \( \delta[NO_3^-] = -R_{NO}\text{AOU} \), and then the regenerated alkalinity may be expressed in terms of \( C_{\text{carb}} \) as

\[
A_{\text{reg}}^{\text{T}} = 2C_{\text{carb}} + R_{NO}\text{AOU}.
\] (11.19)

and \( X_{CO_2} \), assuming that temperature, salinity and alkalinity have not significantly changed since the pre-industrial era.

**Regenerated carbon**

The regenerated carbon, \( C_{\text{reg}} \), may be further separated into contributions due to the respiration of organic matter, \( C_{\text{soft}} \) (often termed the *soft-tissue pump*), and the dissolution of calcium carbonate, \( C_{\text{carb}} \) (the *carbonate pump*).

\[
C_{\text{reg}} = C_{\text{soft}} + C_{\text{carb}}.
\] (11.20)

Assuming fixed elemental ratios in biologically mediated transformations between inorganic and organic forms, the *soft-tissue contribution*, \( C_{\text{soft}} \), is simply related to the regenerated phosphate, \( PO_4^{\text{reg}} \), by \( C_{\text{soft}} = R_{CP}PO_4^{\text{reg}} \) and evaluated from AOU,

\[
C_{\text{soft}} = -R_{CO}\text{AOU},
\] (11.21)

where \( R_{CO} = -106/170 \).

The *carbonate contribution*, \( C_{\text{carb}} \), may be estimated from the change in alkalinity, \( A_T \), which is also separated into preformed and regenerated components:

\[
A_T = A_T^{\text{pre}} + A_T^{\text{reg}}.
\] (11.22)

\( A_T^{\text{pre}} \), the alkalinity that the water parcel had when last in the mixed layer, may be estimated from the measured salinity since it has a relatively tight, linear relationship to \( A_T \) in the surface ocean (Section 6.3). Regenerated alkalinity, \( A_T^{\text{reg}} \), is related to \( C_{\text{carb}} \), the source of carbonate ions from the dissolution of \( CaCO_3 \), and AOU due to the regeneration of nitrate from organic matter (see Box 11.2). Combining (11.19) and (11.22), the carbonate pump, \( C_{\text{carb}} \), is then defined by the change in alkalinity due to the production of calcium ions since subduction and any changes associated with the regeneration of nitrate,

\[
C_{\text{carb}} = \frac{1}{2} \left( A_T - A_T^{\text{pre}} - R_{NO}\text{AOU} \right),
\] (11.23)

where \( R_{NO} = -16/170 \). \( C_{\text{carb}} \) can then be evaluated from the measured properties of a water parcel.
and the empirical relationship between surface salinity and alkalinity.

11.4.3 Mapping the carbon reservoirs of the ocean

DIC is thus described as the sum of the saturation, soft-tissue, carbonate and disequilibrium components:

\[ \text{DIC} = C_{\text{sat}}^{\text{pre}} + C_{\text{soft}} + C_{\text{carb}} + C_{\text{ant}} + \Delta C. \]  

(11.24)

Both \( \Delta C \) and \( C_{\text{ant}} \) are very difficult to evaluate from observations. Here we simply combine the two components into a `residual' reservoir, \( C_{\text{res}} = \Delta C + C_{\text{ant}} \). The subsurface DIC concentration, DIC, is then defined as the sum of four contributions,

\[ \text{DIC} = C_{\text{sat}}^{\text{pre}} + C_{\text{soft}} + C_{\text{carb}} + C_{\text{res}}. \]  

(11.25)

Here we evaluate the components \( C_{\text{sat}} \), \( C_{\text{soft}} \) and \( C_{\text{carb}} \) using measurements of DIC, together with concurrent observations of salinity, temperature, alkalinity and oxygen, as described above. Then \( C_{\text{res}} \) is inferred as the residual, subtracting the sum of \( C_{\text{sat}}^{\text{pre}} \), \( C_{\text{soft}} \) and \( C_{\text{carb}} \) from DIC.

Again, there are several sources of uncertainty.

Firstly, the assumption of fixed elemental ratios in all transformations to and from organic matter. Secondly, seawater samples represent a mixture of contributions which have multiple origins and different pathways through the ocean. If the solubility of a gas is not a strictly linear function of temperature and salinity, an error is introduced by inferring saturation from local \( \theta \) and \( S \). Thirdly, it is assumed that water parcels were at equilibrium with respect to oxygen at the time of subduction, but oxygen disequilibrium in subducted dense waters may lead to errors of up to 40 \( \mu \text{mol kg}^{-1} \) in the corresponding \( C_{\text{soft}} \) (Ito et al., 2004). Accepting these caveats, we can gain some insight into the ocean’s carbon reservoirs from this framework.

11.4.4 How are the carbon reservoirs distributed in the ocean?

The components of ocean DIC are diagnosed from observations along sections through the Atlantic and Pacific Oceans and displayed in Figs. 11.21 and 11.22.

**Saturated DIC contribution**

The saturated contribution referenced to the pre-industrial atmosphere, \( C_{\text{pre}}^{\text{sat}} \), accounts for about 90% of DIC over the globe, typically exceeding 2000 \( \mu \text{mol kg}^{-1} \) (Figs. 11.21a and 11.22a). Cooler, denser waters have a higher saturation DIC and there is a strong decrease in \( C_{\text{pre}}^{\text{sat}} \) towards the surface in the thermocline. While surface \( C_{\text{pre}}^{\text{sat}} \) is modulated by both temperature and alkalinity, the increase in \( C_{\text{pre}}^{\text{sat}} \) with depth indicates that temperature is the dominant control. There is very little contrast between the Atlantic and Pacific basins and the deep and bottom waters have nearly uniform values. This enhancement of \( C_{\text{sat}} \) with depth in the ocean is often referred to as the solubility pump.

**Soft-tissue contribution**

The soft-tissue pump, \( C_{\text{soft}} \), is the second largest contribution, ranging between 50 and 100 \( \mu \text{mol kg}^{-1} \) over most of the Atlantic and Southern Oceans, reaching 150 \( \mu \text{mol kg}^{-1} \) in the tropical Atlantic thermocline, and greater than 100 \( \mu \text{mol kg}^{-1} \) over most of the Pacific, reaching 200 \( \mu \text{mol kg}^{-1} \) in the northern basin (Figs. 11.21b and 11.22b). While \( C_{\text{sat}} \) accounts for the largest fraction of DIC globally, \( C_{\text{soft}} \) contributes much of the large-scale structure in the distribution (Fig. 11.19).

\( C_{\text{soft}} \) is proportional to the regenerated phosphate, \( P_{\text{reg}} \) (Fig. 11.18), with the lowest values at mid depths in the Atlantic where there are recently ventilated waters and low regeneration rates below the thermocline. The older waters of the Pacific have the largest accumulation of \( C_{\text{soft}} \) from the carbon regenerated from sinking organic particles. Other than a sharp, near-surface gradient, the waters around Antarctica are relatively homogeneous with respect to \( C_{\text{soft}} \), reflecting the relatively rapid communication by the Antarctic Circumpolar Current around the Southern Ocean.

**Carbonate contribution**

\( C_{\text{carb}} \) measures the direct contribution of the formation and dissolution of sinking calcium carbonate particles to the distribution of DIC. \( C_{\text{carb}} \) is relatively small in the Atlantic, only reaching 20 \( \mu \text{mol kg}^{-1} \) in the Southern Ocean, but increases...
to 60 μmol kg⁻¹ in the deep waters of the Pacific (Figs. 11.21c and 11.22c). Both carbonate and soft-tissue pumps are associated with sinking particles. The organic matter in sinking particles is mostly regenerated at shallower depths, while the dissolution of calcium carbonate occurs at greater depths. Consequently, the carbonate pump affects waters deeper than the soft-tissue pump.

The carbonate pump contribution is of greater magnitude in the Pacific and extends significantly higher within the water column (Figs. 11.21c and 11.22c). The basin-to-basin contrast reflects the reduced [CO₂⁻₃] in the thermocline and deep waters of the Pacific, relative to the Atlantic (Fig. 11.23).

The accumulated DIC from the soft-tissue pump in the older waters of the deep Pacific Ocean decreases the pH and moves the speciation of the carbonate system towards CO₂⁺ and away from CO₂⁻₃ (Fig. 6.12b). The lower carbonate ion concentration in the Pacific then leads to a shallower saturation horizon and an enhanced C_carb. At the same time, less calcium carbonate arrives at the sea floor in the Pacific, witnessed by the smaller percentage of calcium carbonate in North Pacific core-top sediments (Archer, 1996).

**Residual contribution from anthropogenic and disequilibrium components**

The residual contribution, C_res, combines ΔC, the disequilibrium between the surface ocean and atmosphere at the time of subduction, and C_sat, the enhancement of C_sat due to the increase in atmospheric pCO₂ since pre-industrial times. C_res varies from about 75 μmol kg⁻¹ in the upper thermocline of both basins to slightly negative...
Figure 11.22 Meridional diagnostics of Pacific carbon pumps: (a) saturated carbon concentration, $C_{sat}^{pre}$ (µmol kg$^{-1}$), with respect to the pre-industrial atmosphere ($pCO_{2,pre} = 278$ µatm); (b) soft-tissue pump of carbon, $C_{soft}$ (µmol kg$^{-1}$); (c) carbonate pump, $C_{carb}$ (µmol kg$^{-1}$); (d) residual carbon concentration, $C_{res}$ (µmol kg$^{-1}$), which includes contributions from anthropogenic carbon, the disequilibrium component of preformed carbon, and errors introduced through approximations made in the estimation of other terms.

Figure 11.23 Distribution of the carbonate ion, $[CO_3^{2-}]$ (µmol kg$^{-1}$) at 2000 m depth in the global ocean. Evaluated using data from Conkright et al. (2002) and Key et al. (2004).
concentrations over much of the Atlantic basin below the thermocline (Figs. 11.21d and 11.22d). The pattern of the deep $C^{\text{res}}$ is plausible, although its magnitude is comparable to the uncertainties in the analysis.

The residual contribution, $C^{\text{res}}$, has positive values over much of the upper ocean (Figs. 11.21d and 11.22d). This sign is consistent with a dominant contribution from $C^{\text{sat}}_{\text{ant}}$, the influx of anthropogenic carbon over the past century or so, as atmospheric carbon dioxide levels have rapidly increased. The anthropogenic component $C^{\text{sat}}_{\text{ant}}$ has been estimated using the record of atmospheric $pCO_2$ and estimates of ventilation age (the time since subduction) and transport pathways evaluated using other ocean tracers (e.g., Gruber et al., 1996); as illustrated in Figure 11.24.

The anthropogenic signal reveals an influx of carbon over the upper thermocline of both basins (Fig. 11.24), consistent with the thermocline having a ventilation timescale of several decades. There is more anthropogenic carbon being transferred into the deeper waters of the northern North Atlantic, reflecting the more vigorous ventilation there. Most of the deeper waters are still largely unaffected by the anthropogenic CO$_2$.

In the deep waters of the Atlantic, $C^{\text{res}}$ is slightly negative (Fig. 11.21d), probably because these dense waters are cooling at the time of subduction. Cooling increases the solubility of CO$_2$, driving down $pCO_2$ and leading to undersaturation and a negative $\Delta C$. Due to the long air–sea equilibration timescale ($\sim$1 year), air–sea exchange is unable to eradicate this surface disequilibrium, $\Delta C$, and the negative $\Delta C$ signal is subducted into the interior.

In contrast, in the deep waters of the Southern Ocean and Pacific, $C^{\text{res}}$ is slightly positive (Fig. 11.22d). This signal can be attributed to the upwelling of waters rich in regenerated carbon, $C^{\text{soft}}_\text{sat}$, in the Southern Ocean. On reaching the surface layer, the regenerated carbon increases both $pCO_2$ and $\Delta C$. The positive anomaly of $\Delta C$ might be reduced by cooling, biological consumption and gas exchange. However, if the water parcel remains in the mixed layer for only a short time,
relative to air–sea equilibration, the remaining positive anomaly of $\Delta C$ can be subducted into deep waters and propagated over the deep Southern Ocean and Pacific basin (Fig. 11.22d).

### 11.5 Summary

The patterns of biological production and nutrient transport processes are linked over a broad spectrum of space and timescales. On a daily to seasonal timescale, biological productivity in the euphotic zone is mainly sustained by the convective, vertical redistribution of nutrients within the seasonal boundary layer. Time-varying circulations may locally enhance biological production through a rectified transfer of nutrients across the base of the euphotic zone.

On longer timescales, nutrients must be supplied to the seasonal boundary layer to maintain biological productivity and offset the loss due to the export of organic matter to the ocean interior. This supply involves both horizontal and vertical redistributions of nutrients by a range of physical phenomena. A combination of the gyre and overturning circulation transports nutrients over ocean basins, partly achieved via intense western boundary currents and separated jets. Nutrients are transferred along isopycnals in the upper thermocline and are eventually swept downstream into deep mixed layers at the end of winter. This advective influx of nutrients then sustains the convective, vertical transfer of nutrients into the euphotic zone. The imprint of this advective transfer into the mixed layer enhances surface nutrient concentrations in the subpolar gyres and reduces them in the subtropical gyres. There are also transfers of nutrients across gyre boundaries in the upper ocean through boundary currents, surface Ekman flows and time-varying eddies.

The interior nutrient distributions are principally determined by a combination of subduction from the surface mixed layer and regeneration from organic detritus. Subduction is the dominant process in the Atlantic, while the two contributions are comparable in the Pacific. Globally, less than half the nutrients in the deep ocean arrived there through the fallout of organic matter.

The carbon distribution may be understood in terms of contributions from saturation with the atmosphere, regeneration from organic carbon and calcium carbonate, disequilibrium in the surface, and the uptake of anthropogenic $\text{CO}_2$. The vast majority of carbon in the ocean is attributable to near saturation with the atmosphere. The next largest contribution is from the soft-tissue pump, notably a large biologically driven store in the deep Pacific. The carbonate pump provides a smaller contribution, and is modulated by the variations in DIC and pH caused by the other pumps. There is a clear signal of the invasion of anthropogenic carbon in the upper thermocline.

### 11.6 Questions

**Q11.1. Global export production over the oligotrophic, subtropical gyres.**

Export production has been estimated to reach $2 \text{ mol C m}^{-2} \text{ y}^{-1}$ close to Hawaii in the North Pacific subtropical gyre (Emerson et al., 1997). Assuming that this export is representative of other subtropical oceans and that their collective surface area makes up 60% of the global ocean (with the ocean making 71% of the surface area of the Earth), then estimate the following:

(a) the surface area of the subtropical gyres over the globe (assume the Earth’s radius of 6400 km);
(b) the area-integrated export production over the subtropical gyres (note that 1 mole of carbon is equivalent to 12 g of carbon); and
(c) what proportion of the global export estimated as $10 \text{ Pg C y}^{-1}$ is provided by export from the oligotrophic subtropical gyres.

**Q11.2. Nutrient fluxes in boundary currents.**

Consider the nutrient fluxes in a western boundary current and their likely downstream fate.
(a) If a boundary current has an along-stream velocity of 1 m s$^{-1}$ and a nitrate concentration of 10 mmol N m$^{-3}$ over a width of 100 km and a vertical scale of 500 m, then what is the along-stream flux from the area integral of the product of velocity and concentration? Give your answer in units of mol N y$^{-1}$.

(b) If this nutrient flux directed along a boundary current is eventually transferred onto density surfaces outcropping in the downstream, winter mixed layer in the subpolar gyre, then what is the effective nutrient flux per unit horizontal area passing into the winter mixed layer? Assume the surface horizontal area of the winter mixed layer in the subpolar gyre is given by 4000 km by 3000 km. Give your answer in units of mol N m$^{-2}$ y$^{-1}$ and compare your answer to the nutrient transfer estimates in Section 11.1.

Q11.3. Scale analysis of the nitrate budget for the mixed layer.

Consider a simplified nitrate budget over a mixed layer of thickness, $h$, given by

$$ h \frac{\partial N_m}{\partial t} = F_N' + \Lambda(N_{th} - N_m) \frac{\partial h}{\partial t} + K_v \left. \frac{\partial N'}{\partial z} \right|_{z=-h} - U_e \cdot \nabla N_m - h \lambda N_m \tag{11.26} $$

where $N_m$ represents here, $F_N'$ is the air–sea flux into the mixed layer, $\Lambda(N_{th} - N_m) \frac{\partial h}{\partial t}$ is the entrainment flux, $K_v \left. \frac{\partial N'}{\partial z} \right|_{z=-h}$ is the vertical diffusive input at the base of the mixed layer, and $-U_e \cdot \nabla N_m$ is the Ekman advective supply, and $-h \lambda N_m$ represents biological consumption.

Identify (a) the dominant balances for the winter versus the summer, and (b) identify the relative importance of advection over a year. Make the following assumptions:

(i) The air–sea flux from deposition, $F_N'$, typically reaches 0.01 mol N m$^{-2}$ y$^{-1}$;
(ii) The entrainment flux, $\Lambda(N_{th} - N_m) \frac{\partial h}{\partial t}$, only occurs when the mixed layer thickens (represented by $\Lambda = 1$ when $\partial h/\partial t > 0$ and otherwise 0) and $N_{th} - N_m$ represents the difference in nutrient concentration between the thermocline and mixed layer. Estimate this entrainment flux by

$$ -\Lambda h \frac{\partial N}{\partial z} \frac{\partial h}{\partial t} $$

where $h \sim 50$ m in summer and $h \sim 200$ m in winter with the deepening occurring over 6 months, and the vertical nutrient profile is assumed to be $\partial N/\partial z \sim 3 \times 10^{-5}$ mol N m$^{-4}$;
(iii) Assume that the diffusive supply of nutrients has a vertical diffusivity of $K_v = 10^{-5}$ m$^{-2}$ s$^{-1}$;
(iv) The Ekman advective transfer is simply taken from the meridional transfer,

$$ -U_e \cdot \nabla N_m \sim -V_e \frac{\partial N_m}{\partial y}, $$

where the Ekman volume flux per unit length $V_e \sim 1$ m$^2$ s$^{-1}$ (equivalent to an Ekman velocity of 1 cm s$^{-1}$ over a thickness of 100 m) and $\partial N_m/\partial y \sim 10^{-9}$ mol N m$^{-4}$.
(v) The biological consumption of nitrogen is simply represented here by an exponential decay of the mixed-layer nitrate with a decay timescale of $(1/\lambda)$. Assume that the decay timescale is typically the order of 2 weeks in summer, but there is no consumption in winter due to light limitation, and the mixed-layer nutrient concentration is typically, $N_m \sim 0.5 \times 10^{-3}$ mol N m$^{-3}$.

### 11.1.7 Recommended reading

