Carbon and nutrients in the ocean
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Introduction
Of the estimated anthropogenic input of carbon dioxide (CO₂), less than 60% is now present in the atmosphere. The ocean is believed to be taking up much of the remainder, at a rate of about 2 Gt C year⁻¹, where 1 Gt C is 10¹⁵ g of carbon. Ocean waters contain a very large inventory of carbon, about 39 000 Gt C. This is more than 50 times more than the inventory of carbon in the atmosphere, and about 20 times more than the amount of carbon tied up in the terrestrial biota and soils. As long as one is considering processes ranging over hundreds of years, the carbon reservoirs of the sedimentary cycle can be neglected. As a result, the marine carbonate system, being the largest carbon pool in the atmosphere, biosphere, and hydrosphere, is of primary importance for the partition of atmospheric excess carbon dioxide produced by human activities. A relatively small change in the oceanic carbon cycle can have large atmospheric consequences.

Moreover, the ocean has a more complicated carbon cycle than the atmosphere, involving many inorganic and organic forms. Various models of the atmosphere and ocean give different estimates of how much CO₂ is exchanged and where. Many of these models calibrate with the first world-wide data set collected by GEOSECS (Geochemical Ocean Sections Study) between 1972 and 1978. Recognizing that we must improve the observational and conceptual basis of our estimates and predictions, a new world-wide survey has been undertaken under the auspices of the Joint Global Ocean Flux Study (JGOFS) with close collaboration with WOCE (World Ocean Circulation Experiment). JGOFS has been designed to increase our understanding of the ocean carbon cycle, its sensitivity to change, and the regulation of the atmosphere-ocean CO₂ balance. More formally, it has two goals (SCOR, 1990):

1. To determine and understand, on a global scale, the processes controlling the time-varying fluxes of carbon and associated biogenic elements in the ocean, and to evaluate the related exchanges with the atmosphere, seafloor, and continental boundaries;
2. To develop a capability to predict on a global scale the response of oceanic biogeochemical processes to anthropogenic perturbations, in particular those related to climate change.

Clearly, in order to understand the carbon cycle, the "associated biogenic elements" must also be studied. The most important biogenic elements associated are the major nutrients, nitrogen, phosphorus and silicon (SCOR, 1992).

Carbon cycle

One of the most important systems in the oceans is the $\text{CO}_2$-carbonate system, a buffering system that helps to maintain the pH of seawater to within a narrow range. Over 95% of the oceanic carbon is in the form of inorganic, dissolved carbon; the remainder is composed of various forms of organic carbon (living organic matter, particulate and dissolved organic carbon).

$\text{CO}_2$ (gas) hydrates with water rather rapidly (in milliseconds) to form carbonic acid ($\text{H}_2\text{CO}_3$). Once $\text{CO}_2$ is hydrated, it is involved in a series of even more rapid proton transfer steps (submicroseconds) to form bicarbonate ($\text{HCO}_3^-$) and carbonate ($\text{CO}_3^{2-}$) ions:

\[
\begin{align*}
\text{CO}_2 \text{ (gas)} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 & (1) \\
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- & (2) \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} & (3)
\end{align*}
\]

The sum of the three aqueous carbonate species is defined as total $\text{CO}_2$ ($\text{TCO}_2$). A frequently used property is titration alkalinity (TA), the amount of acid needed to neutralize all bicarbonate and carbonate ions, plus a few minor species.

Because of the large buffer factor (or Revelle factor) of seawater, at equilibrium, a 10% change in the partial $\text{CO}_2$ pressure ($\text{pCO}_2$) results in merely 1% change in $\text{TCO}_2$. At the current pH of seawater (about 8), the excess $\text{CO}_2$ added to the oceans reacts with the carbonate ion to form the bicarbonate ion without the use of $\text{H}^+$:

\[
\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCO}_3^- \quad (4)
\]

The concentration of the carbonate ion is limited by the solubility of calcium carbonate as follows:

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3 \quad (5)
\]

In this reaction the solubility of $\text{CaCO}_3$ increases with pressure but decreases with temperature. The surface layer is usually supersaturated with respect to
CaCO₃, but except for isolated regions such as the Bahama Banks, spontaneous precipitation does not occur because organic material and magnesium in seawater retard CaCO₃ formation. Many marine organisms, however, utilize calcium and carbonate ions to form CaCO₃ skeletons and shells. This process occurs mainly in the surface layer. As the organisms die, their shells and skeletons sink to a level where the temperature becomes low enough or the pressure becomes high enough; thus the water becomes undersaturated with respect to CaCO₃, at which point they start to dissolve. Accumulation of undissolved CaCO₃ in the sediments over millions of years makes the sediments a major sink of carbon over the geological time (Chen & Drake, 1986). Since calcium and carbon are always in abundant supply, they are not considered as nutrients. However, in the “silica ocean” such as the Southern Ocean and the western North Pacific where diatoms prosper, siliceous shells are formed and deposited instead (Tsunogai et al., 1986; Noriki & Tsunogai, 1986). Since silicon can be in short supply, it is considered as a nutrient.

Inorganic carbon, nitrogen and phosphorus are also used by marine organisms to grow soft tissue. Soft tissue decomposes quickly in the water column. As a result, the marine organisms act as a “biological pump”, thus removing CO₂ and nutrients from the surface ocean and transferring these elements into the deep ocean and ocean bottom.

The role of the oceans in the global carbon cycle is two-fold: first, it represents a passive reservoir which absorbs excess atmospheric CO₂. Second, changes in the physical state of the ocean (temperature, circulation) and the marine biota may affect the rate of air-sea exchange, and thus future atmospheric CO₂.

The flow of carbon dioxide between atmosphere and ocean is dominated by ocean upwelling and downwelling. High latitude water cools and dissolves more CO₂ before it sinks; water upwelling at the Equator warms and releases CO₂. The rate of carbon entering the oceans at high latitudes and leaving at low by this route is about 40 (± 10) Gt C year⁻¹ (Moore & Bolin, 1986). The gas flux across the sea surface is a product of the partial CO₂ pressure difference (ΔpCO₂) between the air and surface waters and a surface transfer coefficient that increases with wind speed. Thus exchanges of carbon between the atmosphere and the oceans (net air-sea fluxes) can potentially be deduced from measurements of ΔpCO₂. It is clearly shown in Fig. 11.1 that tropical waters are generally supersaturated in pCO₂ as a result of upwelling and warming. Consequently, the tropical oceans are a source of CO₂ to the atmosphere. On the other hand, at around 40° S in the Southern Hemisphere and in the high latitude regions in the Northern Hemisphere, especially in the northern North Atlantic, the pCO₂ is generally undersaturated, depending on the productivity and the nutrients remaining in the water. As a result, these regions become a sink for CO₂.

Many carbonate species and nutrients, especially when normalized to a constant salinity to remove the effects of evaporation and precipitation, are known to
Figure 11.1 The distribution of ΔpCO₂ in the surface ocean: implications for climate and global change on seasonal-to-century timescales. Blue and green show zones where CO₂ is undersaturated; yellow, red and purple show zones where CO₂ is supersaturated. Black areas are data gaps. (Courtesy, T. Takahashi.)

correlate linearly with temperature, although temporal and spatial variations of these trends exist (e.g. nitrate; Chen et al., 1982a; pH, phosphate and silicate: Chen, 1984; calcium: Chen et al., 1982b; alkalinity and total CO₂: Chen & Millero, 1979). The normalized nitrate (NNO₃ = NO₃ × 35/S) values for surface waters are also found to correlate linearly with surface temperature between 2 °C and 17 °C (Fig. 11.2a). There is essentially no nitrate above 17 °C.

The pH, normalized alkalinity (NTA = TA × 35/S), and normalized total CO₂ (NTCO₂ = TCO₂ × 35/S) also correlate linearly with temperature (Fig. 11.2b–d). There may be a slight change in slope at 13 °C for NTA and NTCO₂ near the Subtropical Front near 40° S. The NTA slope also changes slightly at 4 °C near the Antarctic Front.
It is not clear why such linear correlations exist. Chen (1992), based on the INDIVAT 1 data, assumed that the biological activity reduces the \( \text{NNO}_3 \) concentration from 28 \( \mu \text{mol kg}^{-1} \) in the Circumpolar Current near 50° S to almost zero in the subtropical region near 35° S at a rate linearly correlated with the warming of the water from 2 °C to 17 °C. Given the Redfield C/N ratio of 106/16, this consumption of nitrate must produce 185.5 \( \mu \text{mol kg}^{-1} \) of organic carbon. At the same time, the \( \text{NTCO}_2 \) must be reduced by the same amount. In addition, the warming of seawater drives out dissolved \( \text{CO}_2 \) and reduces the \( \text{NTCO}_2 \) by 8 \( \mu \text{mol kg}^{-1} \), assuming that the surface seawater remains at the same degree of saturation with respect to \( \text{CO}_2 \).

Production of organic carbon as soft tissue is associated with the production of inorganic carbon as hard tissue and shells at roughly a four-to-one ratio. Thus, the production of 185.5 \( \mu \text{mol kg}^{-1} \) in organic carbon should result in a further reduction of 46.4 \( \mu \text{mol kg}^{-1} \) in \( \text{NTCO}_2 \) and 63 \( \mu \text{mol kg}^{-1} \) in NTA after taking into consideration the effect of nitrate and phosphate on alkalinity. Consequently, a total reduction in \( \text{CO}_2 \) of 240 \( \mu \text{mol kg}^{-1} \) should be expected and the observed reduction was 215 \( \mu \text{mol kg}^{-1} \). Chen (1992) also observed a NTA reduction of 70 \( \mu \text{mol kg}^{-1} \) vs. the expected 63 \( \mu \text{mol kg}^{-1} \). These correlations, in a way, quantify the relationships between the carbon cycle and the nutrient cycle and indicate that biological activities contribute to most of the reduction in nitrate, alkalinity and total \( \text{CO}_2 \).

For waters north of 35° S (waters warmer than 17 °C), nitrate concentration is so low that other sources of nitrogen, such as ammonia, or nitrogen fixation may be important in biological consumption. Thus, the Redfield Ratio is no longer applicable. Furthermore, the effect of equatorial upwelling becomes important, and simple linear relations cease to exist.

The decrease in \( \text{NNO}_3 \) of 28 \( \mu \text{mol kg}^{-1} \) between 4 °C and 17 °C for INDIGO 1 corresponds to the decrease of 239 \( \mu \text{mol kg}^{-1} \) in \( \text{NTCO}_2 \) and 63 \( \mu \text{mol kg}^{-1} \) in NTA. Chen (1992) observed a similar decrease in \( \text{NTCO}_2 \) and NTA of 200 \( \mu \text{mol kg}^{-1} \), respectively. These results strengthen the suggestion that biological activities contribute to most of the reduction in nitrate, alkalinity and total \( \text{CO}_2 \) before the Antarctic waters reach the tropical zone.

We have mentioned the transfer of \( \text{CO}_2 \) into the deep waters by the "biological pump". Sinking particles, downward mixing of dissolved organic matter, and the vertical zooplankton migration all result in the transfer of biogenic material from the surface to the deep sea. The dissolution of \( \text{CaCO}_3 \) increases alkalinity, calcium, and total \( \text{CO}_2 \). The decomposition of organic matter, be it from calcareous or siliceous organisms, also increases total \( \text{CO}_2 \) and \( \text{pCO}_2 \), but it decreases pH and alkalinity (Brewer et al., 1975). Overall, the dissolution of \( \text{CaCO}_3 \) contributes approximately 15–30% of the total \( \text{CO}_2 \) input into the deep waters (Tsunogai et al., 1973; Chen et al., 1982b; Chen, 1990; Tsunogai & Noriki, 1991). As a result,
Figure 11.2  The correlations of surface (a) $\text{NO}_3$, (b) $\text{pH}$, (c) NTA and (d) $\text{NTCO}_2$ with respect to water temperature in the south Indian Ocean, based on the INDIVAT I (July, 1984), INDIGO I (February–March, 1985) and GEOSECS (December, 1977–April, 1978) data.
deep waters all have higher TA and TCO$_2$ values than the surface (Fig. 11.3a,b). The Pacific deep and bottom waters have higher concentrations than those in the Atlantic because of their older age (hence more CaCO$_3$ and organic carbon dissociation). The northward flowing bottom water in the North Pacific Ocean upwells to form the deep water and flows southward. Consequently, the Pacific deep water, older than the bottom water, has the highest TA and TCO$_2$ concentrations.

### Nutrient cycle

A nutrient element is one which is sometimes in short supply, yet is functionally involved in the processes of living organisms. Traditionally, in oceanography, the term has been applied almost exclusively to nitrogen, phosphorus and silicon, although it is known that minor elements, such as iron, also play an important role (Martin, 1990). The primary processes influencing the nutrient concentrations in the sea are the geophysical and geochemical processes which control the addition to seawater of these elements and those responsible for their dispersion and removal. Rock weathering and the decay of organic material, together with waste discharges, are the major sources of most forms of nutrients to the sea, to which they are usually carried by terrestrial drainage (Spencer, 1975; Mackenzie et al., this volume). For coastal oceans, the human inputs are beginning to be significant compared to weathering (see Hu et al., this volume; Vörösmarty et al., this volume).

The primary biological removal of inorganic nitrogen, phosphorus and silicon from seawater is by phytoplankton. On the shelves, the littoral and benthic algae also remove these elements from seawater, but the total amounts involved are relatively small. The primary and other consumers of the marine food web regenerate these elements to the soluble form. Bacteria, protozoa and autolysis are involved in these regeneration processes.

Assuming C : N : P ratios of 106 : 16 : 1, remineralization can be represented by the equation (Redfield et al., 1963):

$$\text{(CH}_2\text{O)}_{106}\text{(NH}_3\text{)}_{16}\text{H}_3\text{PO}_4 + 138\text{O}_2 \leftrightarrow 106\text{CO}_2 + 122\text{H}_2\text{O} + 16\text{HNO}_3 + \text{H}_3\text{PO}_4$$  \hspace{1cm} (6)

The replenishment of the supply of the nutrients in the surface water depends upon the action of physical processes. The rates of accumulation of inorganic nitrogen, phosphorus and silicon in deep water are controlled by the productivity of the surface layers, by the rates of in situ regeneration, by the vertical mixing and eddy diffusivity, by lateral adjective movements of the deep water, and by diffusion out of the sediments (Spencer, 1975; Gordon et al., 1996).
Figure 11.3 The N–S cross-section of (a) TA, (b) TCO$_2$, (c) NO$_3$, (d) PO$_4$ and (e) SiO$_2$ in the Atlantic and Pacific Oceans (based mainly on the GEOSECS and JGOFS data).
Nitrogen

Nitrogen is found in the sea primarily in the following forms: $\text{NH}_4^+$, $\text{N}_2$, $\text{N}_2\text{O}$, $\text{NO}_2^-$, $\text{NO}_3^-$ and peptides. By far the most abundant species of nitrogen in the sea is nitrogen gas ($\text{N}_2$), but it is essentially unreactive and is not consumed except for nitrogen fixation (Simpson, 1977; Tsunogai et al., 1985; Tsunogai, 1991). $\text{N}_2$ is found throughout most oceanic and coastal waters at near saturation values (Kester, 1975). The next most abundant species, and a biologically active one, is the nitrate ion ($\text{NO}_3^-$). The other bioactive inorganic ions, nitrite ($\text{NO}_2^-$) and ammonium ($\text{NH}_4^+$) are less abundant overall, but are of local significance. There are significant stocks of organic nitrogen in the surface ocean but the biological availability of this nitrogen is not clear. Organic nitrogen is usually considered to be found in the amino form $\text{NH}_2^-$ (Spencer, 1975; Sharp, 1983; Galloway et al., 1995).

Nitrate, as a limiting plant nutrient, is almost exhausted in surface waters in the majority of the world’s oceans; exceptions are at high and low latitudes and in coastal and estuarine waters. Beneath the photic zone, nitrate increases, usually reaching a maximum near the oxygen minimum layer, and then usually decreases slightly below when the Antarctic Bottom Water (AABW) is encountered.

A nitrate cross-section is shown in Fig. 11.3c, starting in the North Atlantic, running south down the western basin to the Antarctic, and then from south to north through the center of the Pacific Ocean based on the GEOSECS and JGOFS data. The North Atlantic Deep Water (NADW) can be seen between about 1.5- and 4-km depths in the Western Atlantic with a profound maximum (isopleths of 16-30 μmol kg$^{-1}$). The Antarctic waters show little variation with depth (32-34 μmol kg$^{-1}$), and are the obvious source of AABW, which is found at the bottom of both basins even beyond the Equator. In the Atlantic, the Antarctic Intermediate Water (AAIW) overlies the NADW as a distinct northward intrusion going as far as 40°N at about 1-km depth. The AAIW is less distinct in the Pacific, but it is obvious that the source of subsurface water is largely Antarctic. Distinct equatorial upwelling can also be seen in both oceans, but it is more dramatic in the Pacific (Sharp, 1983).

The South Pacific also has a deeper, broader nitrate maximum, whereas the North Pacific has a shallower maximum. The concentration of nitrate in the maximum is two-fold greater in the North Pacific (c. 45 μmol kg$^{-1}$) than in the North Atlantic (c. 22 μmol kg$^{-1}$). The Antarctic profile shows much higher surface values than those of lower latitudes and a very shallow nitrate maximum; Antarctic surface values are usually around 25 μmol kg$^{-1}$, and a fairly consistent deep-water value of 32–34 μmol kg$^{-1}$ is characteristic of these waters.

Nitrate values in coastal waters usually decrease going seaward in surface waters and increase along the same axis in deep waters. Upwelling regions have major inputs of new nitrogen from the subsurface open ocean and the surface nitrate
concentrations are higher than regions without upwelling. Upwelling regions often have strong oxygen depletion and periodically show high subsurface ammonium, N₂O and nitrite values (McCarthy & Carpenter, 1983). An example based on the upwelling near the East China Sea continental shelf break is given in a later section.

The primary release of inorganic nitrogen during decomposition is as ammonium which is oxidized microbially into nitrate (nitrification), if not utilized by phytoplankton. Nitrate, however, undergoes denitrification and turns into nitrite, ammonium, N₂O and N₂. Denitrification, and the subsequent loss of N₂, is the main sink for oceanic fixed nitrogen but whether or not this process is at a steady state is currently a matter of concern (Codispoti, 1995; Galloway et al., 1995; Gordon et al., 1996). The reaction is as follows:

\[
(CH₂O)₁₀₆(NH₃)₁₆H₃PO₄ + 94.4HNO₃ \leftrightarrow 106CO₂ + 177.2H₂O + H₃PO₄ + 55.2N₂
\]

**Phosphorus**

Inorganic phosphorus occurs in seawater as orthophosphate. In seawater at pH 8.0 about 1% of the orthophosphate is present as H₂PO₄⁻, 87% as HPO₄²⁻ and 12% as PO₄³⁻ (Spencer, 1975). The maximum concentrations of dissolved inorganic phosphate in the surface waters are in the range of 0.5 to 1.5 μmol kg⁻¹ found in the northern North Pacific Ocean, in the Antarctic Ocean and in areas of upwelling. In general, the lower the temperature, the higher the concentration (Chen, 1984). Lower concentrations occur in the surface water of the tropics where maximum concentrations of 0.1 to 0.2 μmol kg⁻¹ are common. The concentration of phosphate in coastal waters is often higher than in the water further offshore due to land runoff, sewage outflow, and coastal upwelling.

In common with the other nutrients, the concentration of inorganic phosphate increases with depth. The vertical distribution of phosphate in the oceans generally shows a gradual increase from the surface to a maximum value at between 500 and 2000 m. The phosphate maximum layer is most marked in the Atlantic Ocean based on the GEOSECS and JGOFS data (Fig. 11.3d). The layers below this usually have slightly decreasing concentrations with increasing depth. The highest concentrations in deep water occur in the North Pacific (over 3.0 μmol kg⁻¹).

The principal route of removal of inorganic phosphate from the surface ocean is assimilation by the phytoplankton. Subsequently, the inorganic phosphate is released as a result of autolysis, and is rapidly regenerated by microbial action from natural plankton and detritus. Usually, the N/P ratio is 16 during photosynthesis or remineralization (eqn. 6) but when denitrification occurs N₂O or N₂ may escape from the water column leaving phosphate behind (eqn. 7; Gordon et al., 1996).
Silicon

Silicon (Si) is present in seawater in solution and as solid material in suspension. Si plays a key role in the marine ecosystem and is essential for the growth of the extracellular structures of diatoms, silicoflagellates and radiolarians, thus removing Si from the surface ocean and transporting it downward. The higher the Si/N ratio in the surface water, the larger the downward flux of the particulate organic carbon. So, the silicon is also removed more effectively than nitrogen by these organisms. The Si/N ratios in these planktons are higher than the ratio in seawater (Tsunogai, 1979; Tsunogai & Watanabe, 1983).

The particulate silicon consists of the silicious planktons, both living and dead, and of inorganic silicon in various mineralogical forms (Spencer, 1975). The ultimate fate of much of this particulate silicon in suspension is to enter the sediments where most dissolution occurs. The concentration of dissolved silicon in the form of silicic acid, Si(OH)₄, in seawater varies from as low as 0.5 μmol kg⁻¹ for surface water in the tropical region to as high as 50 μmol kg⁻¹ at the surface of the Antarctic region. The concentration of silicic acid in deep ocean waters reaches 125 μmol kg⁻¹ in the Atlantic and higher values of up to 175 μmol kg⁻¹ in the Pacific Ocean (Fig. 11.3e) based on the GEOSECS and JGOFS data. The concentration reaches 240 μmol kg⁻¹ in the deep Bering Sea (Tsunogai et al., 1979). In common with many other elements which are incorporated into living organisms, the concentration of dissolved silicic acid increases with depth. The circulation and exchange of the deep water differs from ocean to ocean, and this clearly affects the accumulation and dispersion of the silicic acid.

Human perturbations

Carbon

The oceanic uptake of CO₂ proceeds by (1) transfer of the CO₂ gas through the air-sea interface, (2) chemical interactions with the oceanic dissolved inorganic carbon, and (3) transport into the thermocline and deep waters by means of water mass transport and mixing processes. Once the CO₂ enters the oceans, the biological pump also works to remove CO₂ from the surface oceans and transports it downward. As a result, the pCO₂ of the surface oceans is reduced, thus favoring the uptake of more CO₂.

Although there are large geographical and seasonal variations of the surface ocean pCO₂, especially in the high latitude regions, averaged annually, the mid- and low-latitude surface waters are close to a constant degree of saturation with respect to the atmosphere. Therefore, processes (2) and (3) mentioned above are the main factors limiting the capacity of the ocean to serve as a reservoir on decadal and centennial time scales. The potential CO₂ uptake, however, occurs
mainly in those parts of the deep ocean that are mixed with surface waters on
decadal time scales or less. Therefore, high latitude regions need to be studied
more extensively, especially in the winter time.

While the annual productivity of plants in the oceans is as great as that on land,
their instantaneous effect on the atmosphere is greatly damped owing to the
slowness of gas exchange between air and sea (Peng & Broecker, 1985). Thus the
marine biota, if in steady state, are believed to play a minor role, if any at all, in the
uptake of excess anthropogenic CO₂. The marine biota, however, play a crucial role
in maintaining the steady-state level of atmospheric CO₂. About three-quarters of
the vertical gradient in dissolved inorganic carbon is generated by the “biological
pump”. In the open ocean, however, this process is believed to be limited by the
availability of nutrients, light, or by phytoplankton population control via grazing,
and not by the abundant carbon (Falkowski & Wilson, 1992). Therefore, a direct
effect of increased dissolved inorganic carbon (less than 2.5% since pre-industrial
times) on carbon fixation and export is thought to be unlikely (Schimel et al.,
1995) although Riebesell et al. (1993) suggested that, under particular conditions,
the rate of photosynthesis might be limited by the availability of CO₂.

The ocean’s inventory of carbon is estimated to be increasing at a rate of about
2 Gt C year⁻¹. In principle, the net uptake of CO₂ by the oceans can be calculated
by global integration of the net flux across the air–sea interface based on the pCO₂
data. However, the gas exchange coefficient is a relatively poorly known quantity
(Wanninkhof, 1992; Watson, 1993). For instance, Takahashi et al. (1995) calculated
the CO₂ flux in the North Atlantic. Results based on the most widely used coeffi­
cients of Tans et al. (1990) and Liss and Merlivat (1986) differ by more than a
factor of two. Furthermore, large geographical and seasonal variations in pCO₂
exist in the atmosphere, and particularly in the surface oceans. These are induced
both by physical processes (storms, upwelling, mixing, sea surface temperature
fluctuations) and by the activity of the biota (Wong & Chan, 1991; Keeling, 1993;
Inoue et al., 1995; Takahashi et al., 1983, 1993, 1995; Boden et al., 1994). Representa­
tive estimates of the seasonally and regionally averaged net air–sea carbon
transfer thus necessitates pCO₂ and wind measurements with high spatial and
temporal resolution. Correction for the skin effect is also necessary (Garcon et al.,

Estimates of the regional net air–sea carbon fluxes have been obtained, albeit
with considerable error margins. However, the global oceanic carbon balance is
more difficult to deduce by this method, as it represents a small residual computed
from summing up the relatively large emissions from super-saturated and uptake
in under-saturated regions. Effects of sporadic storm and interannual changes due
to El Niños on the ocean biology need also to be studied (Wong et al., 1993).

Characterization of the air–sea disequilibrium of the \(^{13}C/^{12}C\) ratio of inorganic
carbon with respect to that of the atmosphere has been used to estimate the net
air–sea flux of CO$_2$ (Tans et al., 1993; Okuda et al., 1995). Tans et al. argue that the signal-to-noise ratio for the air–sea isotopic disequilibrium is potentially much better than that for the air–sea pCO$_2$ disequilibrium. However, the existing $^{13}$C database is very small.

The possibility of using net meridional CO$_2$ fluxes within ocean basins to infer global sources and sinks of CO$_2$ has been explored by Brewer et al. (1989), Tans et al. (1990), Broecker and Peng (1992) and Goyet and Brewer (1993). Goyet and Brewer gave a net southward transport of 0.42 Gt C year$^{-1}$ across 25° N in the Atlantic. More CO$_2$ data coming out of the JGOFS and WOCE expeditions should make this method more widely used.

Beside the approaches mentioned above, inventory-based estimates have been used. For instance, in certain locations, a time series of CO$_2$ measurements is becoming available (Wong et al., 1984). By the end of WOCE, it will be possible to examine carbon inventories over a 20–25-year interval at locations which were previously sampled during the GEOSECS expeditions. Preliminary data indicate that a significant increase of TCO$_2$ can be detected within the upper 1000 to 1200 m in the Brazil Basin over a period of 20 years (Wallace, 1995). The JGOFS also runs a network of time series stations at which regular measurements of key carbon related properties and processes are made.

Other inventory approaches were suggested: those using the $^{13}$C/$^{12}$C isotope anomaly caused by the burning of fossil-fuel (Quay et al., 1992), those based on the distribution of bomb-derived $^{14}$C or $^3$H, or models validated through comparison with the distribution of transient tracers such as bomb-derived $^{14}$C or $^3$H (Bolin, 1983; Broecker et al., 1985; Bolin et al., 1983; Sarmiento et al., 1992; Orr, 1993; Siegenthaler & Sarmiento, 1993; Stocker et al., 1994).

More recently, other transient tracers such as chlorofluorocarbons (CFCs) and CCl$_4$ have also been used to predict excess CO$_2$ penetration (Gammon et al., 1982; Cline et al., 1985; Krysell & Wallace, 1988; Joos et al., 1991a, b; Wallace et al., 1992, 1994; Watanabe et al., 1994; Tokieda et al., 1996). These data have high signal-to-noise ratios and thus the results are precise. In addition, the CFC results agree with those based on CO$_2$ directly (Cline et al., 1985; Wallace, 1995).

The oceanic contribution to the global carbon budget can also be assessed by direct observations of changes in the oceanic carbon content. This approach also suffers from the problem of determining a very small signal against large spatial and temporal background variability. Model estimates of the spatially and temporally variable rate of change induced by the anthropogenic perturbation are of the order of 1 part in 2000 per year on the average. Therefore, on a 10-year time scale, variations in dissolved inorganic carbon would have to be measured with an accuracy of better than 1% in order to determine the carbon balance in a particular oceanic region. While such accuracy can be obtained, a substantial sampling effort is required in some critical regions, together with some other tracers such as
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CFCs (Tsunogai et al., 1993b; Keeling, 1993; Schimel et al., 1995). Repeated observational surveys, especially those in the GEOSECS regions occupied 20 years ago, would reveal regional carbon inventory changes, and thus provide a cross-check for other approaches.

Recently, there are indications that the excess CO₂ signal can be detected by using carbonate data directly (Brewer, 1978; Chen & Millero, 1978, 1979; Chen & Pytkowicz, 1979; Chen, 1982a, b; Anderson et al., 1991; Tsunogai et al., 1993a). The method involves a back-calculation of the CO₂ concentration of a parcel of seawater to its initial concentration at the sea surface by correcting for changes due to the decomposition of organic material (Redfield et al., 1963) and dissolution of carbonate particulates based on the TA, TCO₂ and oxygen data. These back calculated CO₂ concentrations of waters with various ages are then compared with each other and with the contemporary surface CO₂ concentrations to obtain the oceanic CO₂ increase (Chen, 1993b; Tsunogai et al., 1993a). Uncertainties in the Redfield Ratios and in the estimation of the initial TA and TCO₂ values give this approach a low signal to noise ratio of only about 8. Nevertheless, the approach provides model-independent estimates of the spatial variability of the excess CO₂ distribution which can be used to validate model predictions (Wallace, 1995).

Chen (1993b) defined the lower boundary of the excess CO₂ penetration as the depth at which the excess CO₂ concentration is less than 5 µmol kg⁻¹, approximately 12% of the magnitude of the signal. Chen (1993b) reported that the anthropogenic CO₂ has penetrated below the thermocline everywhere in the Atlantic, deeper on the western side.

The deepest penetration of excess CO₂ in the Atlantic occurs in the Northwest region where the excess CO₂ has reached the seafloor. Other than the northwest Atlantic Ocean, the deepest excess CO₂ penetration occurs near 40° S, especially in the region off South America where the Falkland Current joins the Brazil Current Extension.

Winter surface sea ice coverage and intensive upwelling of old Circumpolar Deep Water (CDW) in the Weddell Sea prevent excess CO₂ from moving freely across the air-sea boundary or being advected downward. As a result, little excess CO₂ is found below 200 m in the Weddell Gyre (Poisson & Chen, 1987).

An isogram map of the lower boundary of the excess CO₂ penetration in the Pacific Ocean is shown in Fig. 11.4. The major difference between the Pacific and the Atlantic Ocean is that excess CO₂ does not penetrate much deeper than the permanent thermocline in the Pacific Ocean except in the Sea of Japan (Chen et al., 1995a) because there is no bottom water formation in the North Pacific. In the Sea of Japan, the entire water column contains excess CO₂ due to rapid turnover of the water.

The shallowest penetration outside of the Southern Ocean occurs in the eastern equatorial region where the excess CO₂ only penetrates to 400 m, or shallower. The
Figure 11.4 Isogram of the lower boundary of excess CO$_2$ penetration in the Pacific Ocean (depth contours in km, modified from Chen, 1993a).

The general trend indicates a deeper penetration (800 m) in the western Pacific. Overall, the excess CO$_2$ penetrates to a shallower depth in the equatorial Pacific than in the Atlantic, perhaps reflecting the higher equatorial upwelling rate in the Pacific and less influence of the newly formed water advected from the north. Higher upwelling rates also result in higher supersaturation of CO$_2$ in the surface water in the equatorial Pacific (Fig. 11.1). The $\Delta$pCO$_2$, however, is decreasing with time because of the increasing CO$_2$ concentration in the atmosphere. As a result, less CO$_2$ is expected to be released from the equatorial region in the future.

Similar to what was found in the Weddell Sea, intensive upwelling prevents excess CO$_2$ from reaching more than 200 m deep in the region around 65° S. The excess CO$_2$ penetrates deeper further south, and reaches more than 1000 m off Cape Adare at the northwest corner of the Ross Sea (Chen, 1987).

The deepest excess CO$_2$ penetration in the South Pacific occurs at around 45° S near where the Subantarctic Mode Water is located, but the depth of penetration is
slightly shallower than that found in the South Atlantic Ocean. Intensive vertical mixing in the Drake Passage also seems to result in deeper excess CO$_2$ penetration compared to the situation found elsewhere at the same latitude. The deepest penetration in the North Pacific occurs in the confluence of the Kuroshio and Oyashio currents where the North Pacific Intermediate Water (NPIW) originates (Talley et al., 1995; Tsunogai et al., 1995). This is the region off Japan near the area of circulation of the North Pacific variety of the Subtropical Mode Water (Chen, 1987). Here the $\Delta p$CO$_2$ is near $-60$ μatm (Inoue et al., 1995) and the excess CO$_2$ may have penetrated to a depth of 2000 m (Fig. 11.4).

Talley et al. (1995) reported that the newly formed NPIW has a potential density up to 27.4 $\sigma_0$, corresponding to water as deep as 1200 m. Watanabe et al. (1994) estimated the 27.4 $\sigma_0$ water at 40 years old, based on CFC data at 175° E. Tokieda et al. (1996) estimated the 27.2 $\sigma_0$ water at 33 years old or younger in the northwest Pacific. This relatively young water contains much excess CO$_2$. Indeed, Tsunogai et al. (1993a) reported that the NPIW is an important excess CO$_2$ sink, large enough to account for the missing CO$_2$. Tsunogai et al. (1995) further showed that between the 1970s and 1980s (for a time span of 14 ± 4 years) the bomb $^{14}$C has increased rapidly in the NPIW to as deep as 1000 m. In general, deeper penetration occurs on the western side of the Pacific (Chen, 1987) but, in the South China Sea, intensive upwelling prevents excess CO$_2$ from penetrating more than 500 m deep.

The contours of the excess CO$_2$ penetration in the Indian Ocean are quite similar to those in the Pacific Ocean. No deep penetration can be found in the northern part except in the Red Sea because there is no bottom water formation in the North Indian Ocean. The excess CO$_2$ penetrates the entire Red Sea because of intensive winter vertical mixing in the Gulf of Elat (Krümgalz et al., 1990). The major difference between the Indian and the Pacific Ocean is that excess CO$_2$ penetrates much deeper in the equatorial Indian Ocean, perhaps because of weaker upwelling as compared to the Pacific Ocean (Chen & Chen, 1989; Chen & Wu, 1991).

**Nutrients**

Anthropogenic nutrients are carried to the oceans mainly via rivers (Table 11.1). Some of the nitrogen oxides released to the atmosphere due to fossil fuel burning and the nitrate subsequently formed find their way into the ocean (Laska et al., 1980). Release of combined N in sewage discharges amounts to about 10 g N per person per day (Garside et al., 1976). If we assume, as an upper bound, that the sewage from the entire world population of 5.5 × 10$^9$ persons is discharged to the oceans, the input rate would be about 2 × 10$^{13}$ g N per year. A recent IGBP report (1994) estimated the total anthropogenic inorganic nitrogen and phosphorus inputs to the coastal zone as 2.1 × 10$^{13}$ g N and 1.6 × 10$^{12}$ g P year$^{-1}$. Galloway et
Table 11.1 *Estimations of anthropogenic fluxes of dissolved nutrients in rivers (in $10^{12}$ g year$^{-1}$; modified from GESAMP, 1987*)

<table>
<thead>
<tr>
<th>Authors</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stumm (1973)</td>
<td>–</td>
<td>0.6</td>
</tr>
<tr>
<td>Lerman <em>et al.</em> (1975)</td>
<td>–</td>
<td>1.8</td>
</tr>
<tr>
<td>Soderlund and Svensson (1976)</td>
<td>18</td>
<td>–</td>
</tr>
<tr>
<td>Delwiche and Likens (1977)</td>
<td>35</td>
<td>–</td>
</tr>
<tr>
<td>van Bennekum and Salomons (1981)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(domestic)</td>
<td>11</td>
<td>1.7</td>
</tr>
<tr>
<td>(agricultural*)</td>
<td>8</td>
<td>0.35</td>
</tr>
<tr>
<td>(industrial)</td>
<td>13</td>
<td>1.7</td>
</tr>
<tr>
<td>Total</td>
<td>32</td>
<td>3.75</td>
</tr>
<tr>
<td>Meybeck (1982)</td>
<td>7</td>
<td>1.0</td>
</tr>
<tr>
<td>Wollast (1983)</td>
<td>21</td>
<td>1.7</td>
</tr>
<tr>
<td>Galloway <em>et al.</em> (1995)</td>
<td>41</td>
<td>–</td>
</tr>
</tbody>
</table>

*Particulate N and P fluxes due to land erosion estimated as $28 \times 10^{12}$ g N year$^{-1}$ and $10^{12}$ g P year$^{-1}$ by these authors.

...al. (1995), however, estimated that $5.9 \times 10^{13}$ g N year$^{-1}$ of the nitrogen fixed by human activities are injected into oceans, of which $4.1 \times 10^{13}$ g N year$^{-1}$ are from river flow and the rest are from the atmospheric deposition.

The flux of fixed N to the oceans has not been altered by human activity to an extent that the concentration of combined nitrogen in the oceans has significantly changed (Laws, 1983; Denman *et al.*, 1995; Galloway *et al.*, 1995). On a local scale, however, there is clear evidence of changes in the concentrations of fixed N in coastal systems due to human activities (Laws, 1983; Kempe, 1995). For instance, the NO$_3^-$ concentration near the Yangtze River (Changjiang) estuary increased four-fold between 1963 and 1983, because of the 2.25-fold increase in the use of nitrogen-containing fertilizers in China. The N/P ratio in the estuarine water also doubled in 20 years, but the productivity has not shown much variation (Gu, 1991; Zhang & Gu, 1994). Bolin (1977) and Walsh *et al.* (1981) hypothesized that acceleration of the organic carbon storage in the coastal sediments has occurred partially because the increased primary productivity resulting from large increases in anthropogenic nitrate inputs from rivers. This hypothesis needs to be tested further because the productivity increase over the continental marginal seas is probably still small when compared with the total primary productivity. The excess organic carbon production, due to the nutrient input, is estimated at only 3% of the gross primary productivity. Furthermore, much of the unused shelf primary...
CARBON AND NUTRIENTS IN THE OCEAN

productivity is not available for export, but is rather remineralized on the shelf (Kempe & Pegler, 1991; Biscaye et al., 1994; Hong et al., 1995; Tsunogai et al., 1997).

Joint JGOFS/LOICZ task team on continental margin studies

Biogeochemical processes occur principally in the top 200 meters of the sea, often associated with the continental margins. The continental margins, with waters shallower than 200 m occupy 8% of the ocean surface but less than 0.5% of the ocean volume, also play a major role in oceanic biogeochemical cycling. Around 14% of global ocean production, and up to 50% of global ocean denitrification, occurs in the coastal ocean. The burial sites of 80% of organic carbon derived both from oceanic processes as well as from terrestrial sources, and in excess of 50% of present day global carbonate deposition also occur in the coastal ocean (IGBP, 1994). A potential feedback may result from anthropogenic eutrophication of continental shelf areas due to increased nutrient availability, which may also lead to reduced oxygen concentration as a result of increased microbial respiration. Denitrification and methanogenesis are thus promoted, hence the release of N₂, N₂O and CH₄. The eutrophication accelerates the cycle of organic synthesis and regeneration of nutrients other than silicate but calcareous shells and skeletons are preserved. These processes, however, cannot yet be accurately quantified (Christensen, 1994; Codispoti, 1995; Galloway et al., 1995; Denman et al., 1995).

The flux of carbon from the terrestrial biosphere to the oceans takes place via river transport. Global river discharge of carbon in organic and inorganic forms may be approximately 1–1.4 Gt C year⁻¹ (Schlesinger & Melack, 1981; Degens et al., 1991; Meybeck, 1993; Tsunogai et al., 1997). A substantial fraction of this transport (up to 0.8 Gt C year⁻¹), however, reflects the natural geochemical cycling of carbon and thus does not affect the global budget of the anthropogenic CO₂ perturbation (Sarmiento & Sundquist, 1992). Furthermore, the anthropogenically induced river carbon fluxes reflect, to a large extent, increased soil erosion and not a removal of excess atmospheric CO₂ (Schimel et al., 1995). As mentioned in the preceding section, the discharge of organic matter and nutrients from coastal communities does not have a significant impact on the open world ocean, but can have important effects on the coastal ocean (Weyl, 1981).

The discharge of excess nutrients by rivers might have significantly stimulated carbon fixation (up to 0.5–1 Gt C year⁻¹). At present, however, it is not known how much of this excess organic carbon is simply deoxidized, and how much is permanently sequestered by export to the deep ocean, or in sediments on the shelves and shallow seas. Because of the limited surface area, a burial rate significantly exceeding 0.5 Gt C year⁻¹ is not very likely, as it would require all coastal seas to be undersaturated in pCO₂ by more than 50 μatm on annual average, in order to
supply the carbon from the atmosphere. Such undersaturations have been documented, e.g. in the North Sea and the East China Sea (Kempe & Pegler, 1991; Tsunogai et al., 1997), but it is not certain how these measurements are representative of all coastal oceans. For instance, Holligan and Reiners (1992) estimated a net flux of CO$_2$ (approximately 0.4 Gt C year$^{-1}$) to the atmosphere from the coastal ocean. Based on the above considerations, the role of the coastal ocean cannot be accurately assessed at present (Schimel et al., 1995). In order to address various aspects of the oceanic cycles of carbon and associated elements, and to understand their horizontal and vertical fluxes in the marginal seas, the JGOFS/LOICZ Task Team on Continental Margin Studies was established (Chen et al., 1994).

Case studies on Asian marginal seas

East Asia has some of the largest marginal seas in the world, including the Bering Sea ($2.27 \times 10^6$ km$^2$), the Sea of Okhotsk ($1.53 \times 10^6$ km$^2$), the Sea of Japan ($1.0 \times 10^6$ km$^2$), the East China Sea ($0.77 \times 10^6$ km$^2$ plus the Bohai Gulf at $0.077 \times 10^6$ km$^2$ and the Yellow Sea at $0.38 \times 10^6$ km$^2$), and the South China Sea ($3.5 \times 10^6$ km$^2$). These seas form the linkage between the largest continent and the largest ocean, and receive much land runoff, ventilate the deep oceans, and exchange much material with the open oceans. The role of these marginal seas in the context of carbon and nutrient cycles are briefly discussed below, with more emphasis on the CO$_2$ sink.

The Bering Sea and the Sea of Okhotsk

The Bering Sea and the Sea of Okhotsk are divided into a wide shelf and a deep basin. The shelf water is probably supersaturated with excess CO$_2$ but the deep basin waters are not. Chen (1993c) reported that the excess CO$_2$ seems to penetrate to approximately 1000 m in the Bering Sea, deeper in the eastern and southern regions, with slightly shallower penetration off the Kamchatka Peninsula. Tritium shows similar penetration, but the $^{14}$C concentration does not level off until a slightly deeper depth. There is no published work on the excess CO$_2$ input in the Sea of Okhotsk, but preliminary work suggests that the excess CO$_2$ penetrates to no more than 1000 m in the deep basin (C. T. A. Chen & A. S. Bychkov, unpublished observations, 1996).

The Bering Sea and the Sea of Okhotsk contained, respectively, about 0.21 ($\pm$ 0.05) and 0.18 ($\pm$ 0.08) Gt excess carbon around 1980. These values are small compared with 149 Gt C generated by fossil fuel (Stuiver et al., 1984). The carbonate deposits on the vast Bering Sea and the Sea of Okhotsk shelves, however, could provide a sink for excess CO$_2$ in the near future. The shelf waters are currently about 210 and 150% saturated with respect to calcite and aragonite,
respectively. Because of the shallow depth of the shelves (less than 200 m) relative to the saturation horizons of calcite (400 m) and aragonite (350 m), the upward migration of these saturation horizons due to the excess CO$_2$ input (Feely & Chen, 1982) probably has not changed the dissolution rates of carbonates.

An increase of approximately 200 μatm in pCO$_2$, however, would make the shelf water undersaturated with respect to aragonite and high magnesium calcite, which would then dissolve and neutralize the excess CO$_2$. A doubling of the current CO$_2$ level in the atmosphere by the latter part of the next century would cause the calcites on the shelves to dissolve, providing another large sink for CO$_2$ (Chen, 1993c). Possible removal of anthropogenic CO$_2$ by excess primary productivity, enhanced burial of organic carbon sediments, and offshore transport of regenerated organic matter need also be tied into the carbon cycle studies (Walsh et al., 1990; Tsunogai et al., 1997).

Strong winds coupled with intense vertical mixing and inter-leaving in the winter enhance the oceanic penetration of excess CO$_2$ in the Bering Sea, and in the Sea of Okhotsk. Although winter carbonate data are available in the eastern Bering Sea, no winter carbonate data are available in the western Bering Sea near the Kamchatka Peninsula and in the Sea of Okhotsk, where vertical penetration is enhanced and where subsurface water is believed to be formed (Reid, 1965, 1973; Talley, 1991).

Such winter data are needed in order to obtain complete information on the excess CO$_2$ penetration in the western Bering Sea and in the Sea of Okhotsk. Although these seas have limited capacity to store the excess CO$_2$, they act as conveyor belts which transport excess CO$_2$ to the North Pacific Ocean. Because this subsurface water spreads into the northwest Pacific Ocean, the excess CO$_2$ penetration in the northwest Pacific cannot be studied adequately without knowledge of the source water chemistry (Chen, 1993c).

The Sea of Japan

The Sea of Japan is a deep basin with a narrow shelf except in the far north. It is characterized by the unique homogeneity of subsurface waters. Numerous results of hydrological measurements show an anomalously high concentration of dissolved oxygen, suggesting rapid turnover of the subsurface waters and a potential sink for excess CO$_2$ (Chen et al., 1995a).

The calculated vertical profile of excess CO$_2$ indicates that the entire Sea of Japan has been penetrated by excess CO$_2$, totaling 0.31 (± 0.05) Gt C in 1992 (Chen et al., 1995a). The carbonate data have been used to calculate the ratio of CaCO$_3$ dissolution and the organic carbon decomposition (Chen et al., 1982b). The results vary from 0.05 at 300 m to about 0.17 below 2000 m. These values are lower than the ratios of 0.14 and 0.36 found in the South and North Pacific,
respectively (Chen et al., 1982b; Chen, 1990), or 0.54 in the Bering Sea (Chen, 1993a).

The Sea of Japan is rather deep, with an average depth of over 1500 m, yet the straits connecting it to the outside are all narrow and shallower than 150 m. As a result, the deep waters have no direct exchange with the Pacific, the East China Sea and the Sea of Okhotsk. Since the deep waters of the Sea of Japan are all formed inside the closed basin, they provide a unique opportunity to estimate the Redfield Ratios based on the mass-balance method (Chen et al., 1996). The results are in good agreement with the traditional values represented by eqn. (6).

The East China Sea

The East China Sea (ECS), including the Bohai Gulf and the Yellow Sea, has a wide shelf where the water is probably also saturated with excess CO₂. Between the shelf break and the Ryukyu Island is a deep trench. The hydrography is such that there is upwelling toward the west, bringing older deep water upward (Liu et al., 1992; Chen et al., 1995b). As a result, the excess CO₂ penetrates only to approximately 600 m. The entire ECS contained 0.07 (± 0.02) Gt C excess carbon in 1992.

Since the waters on the ECS shelf are highly supersaturated with respect to calcite and aragonite, sediments on the ECS shelf are not expected to neutralize excess CO₂ in the coming century. The high productivity, however, makes a large portion of the ECS inner and mid-shelf waters undersaturated with respect to CO₂ near the surface (Fig. 11.5, the fugacity is very close to the partial pressure). As a result, the flux of CO₂ into the ECS is large (40 g C m⁻² year⁻¹; Tsunogai et al., 1997). If the rate were applicable to the whole continental shelf in the world it would amount to 1 Gt C year⁻¹. The outer shelf and the Kuroshio region (east of 126° E) is depleted in PO₄ (Fig. 11.6) and the surface water pCO₂ is near saturation.

The South China Sea

The South China Sea (SCS) also has a large shelf in the south and the southwest. The basin is very deep but since there is no deep or intermediate water formation, excess CO₂ cannot go very deep. In addition, there is strong upwelling in the SCS. Thus, even the subsurface water that contained some excess CO₂ would be pushed upward.

Chen and Huang (1995) have calculated the excess CO₂ based on data collected in the northeastern SCS. The deepest penetration is no more than 600 m, shallower than in the west Philippine Sea. The entire SCS probably contained 0.43 (± 0.1) Gt C anthropogenic carbon in 1994.

The saturation horizon of calcite is deeper than 2000 m in the SCS; thus little enhanced dissolution is expected due to the excess CO₂ penetration (Chen &
Figure 11.5  The observed CO₂ fugacity in the surface water and the atmosphere at a cross-section perpendicular to the ECS shelf extending from the mouth of the Yangtze River to Ryukyu Island. (Taken from Tsunogai et al., 1997.)
Figure 11.6  (a) NO₃ and (b) PO₄ concentrations (μmol kg⁻¹) in a cross-section perpendicular to the East China Sea Shelf. (Taken from Chen et al., 1995b.)
Huang, 1995). The saturation horizon of aragonite is 600 m, about the same as the excess CO$_2$ penetration depth but deeper than the saturation horizon found in the Bering Sea (350 m). The upward migration of the saturation horizon (Feely & Chen, 1982) would not affect the calcareous deposits on the SCS shelf to the degree that it affects the Bering Sea deposits.

Since two of the largest rivers in the world, the Yangtze River and the Yellow River (Huanghe), empty into the East China Sea, it has frequently been assumed that the high productivity on the shelf is a result of the riverine nutrient input. However, such an input is not nearly enough to support the high productivity. Further, the Kuroshio is known to be low in nutrient concentration in the surface water (Fig. 11.6). As a result, if only near-surface Kuroshio water moved onto the shelf, the water would not contribute much to the productivity. There must be other sources of nutrients.

**Nutrients from the South China Sea contribute to the high productivity on the East China Sea shelf**

The Taiwan Strait connects the East and South China Seas. The SCS is rather deep but because of its shallow depth, averaging only 50 m with no deep channels, the Strait does not permit exchange of waters between these two seas except for low-nutrient near-surface waters. In summer, the water flows northward through the Strait but, in winter, there is a southward flowing current along the coast of Fujian Province on the western side of the Strait (Guan, 1994).

On the other hand, the Kuroshio feeds the SCS year-round. The nutrient-depleted near-surface Kuroshio water exchanges freely with the SCS all year. However, the nutrient-rich intermediate water, arbitrarily taken as the layer between 350 and 1350 m encompassing the $S_{\text{min}}$ core, seems only to flow out of the SCS and forms the western portion of the Kuroshio (Chen & Huang, 1996). The core of the outflowing SCS $S_{\text{min}}$ layer sits at about 600 m, roughly 200 m shallower than the $S_{\text{min}}$ core of the eastern part of the Kuroshio originating from the west Philippine Sea. As a result, the now northward flowing SCS intermediate water is able to cross the ridge northeast of Taiwan to enter the Okinawa Trough, which is adjacent to the ECS continental shelf.

Ito et al. (1994) and Chen et al. (1995b) have shown that the Kuroshio Intermediate Water (KIW) contributes up to 30% in the upwelling and cross-shelf mixing at the East China Sea shelf break. The upwelled KIW actually originates from the SCS and is high in nutrients (Fig. 11.6), thus contributing a great deal of nutrients to the shelf as compared with the much smaller riverine fluxes (Table 11.2). Furthermore, PO$_4$ flux from the Yangtze River could be identified only in the estuary. The NO$_3$ flux extends further but could still be identified only in the Yangtze River Plume. This suggests that the productivity in much of the East China Sea is influenced by the upwelled subsurface Kuroshio water (Chen, 1996).
Table 11.2  Nutrient inputs to the East China Sea shelf (Chen, 1996)

<table>
<thead>
<tr>
<th></th>
<th>NO₃ (10⁹ mol year⁻¹)</th>
<th>PO₄ (10⁹ mol year⁻¹)</th>
<th>SiO₂ (10⁹ mol year⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riverine</td>
<td>29</td>
<td>0.23</td>
<td>87</td>
</tr>
<tr>
<td>Kuroshio surface water</td>
<td>1.6</td>
<td>0.31</td>
<td>12.6</td>
</tr>
<tr>
<td>Kuroshio tropical water</td>
<td>42</td>
<td>3.1</td>
<td>41.7</td>
</tr>
<tr>
<td>Kuroshio intermediate water</td>
<td>161</td>
<td>10.9</td>
<td>385</td>
</tr>
</tbody>
</table>

Any potential change in the upwelling rate would thus have a much larger effect than the change in the nutrient input from rivers.

Fig. 11.7 shows the NO₃ and PO₄ vs. pH (25°C) for the East China Sea. The light-limited KIW and KTW, although rich in nutrients, do not contribute to primary productivity until reaching the surface. The higher pH values for Kuroshio Surface Water and surface shelf water are a result of primary productivity, which is evidently limited by the availability of PO₄ even when there is still abundant NO₃ near the Yangtze River Plume. Consequently the phosphorus-containing Kosa (yellow sand from the loess in China, containing 0.3% P₂O₅) fallout would enhance the productivity. According to Tsunogai (1991), the Kosa flux amounts to 50 g m⁻² for 3 months in late spring and leads to the new production of 2.40 g C m⁻² year⁻¹ in the Kuroshio region. Similarly, anthropogenic iron input may increase primary productivity in the high nutrient-low chlorophyll regions (Martin, 1990) or in waters where molecular nitrogen-fixing blue-green algae (cyanobacteria) may bloom (Tsunogai, 1979; Tsunogai & Watanabe, 1983), but the global effect is probably small. Denman et al. (1995) concluded that intentional iron fertilization to promote phytoplankton growth, and hence the drawdown of atmospheric CO₂, may not be very effective.

Summary

The schematic diagrams of flow patterns of the marginal seas discussed above are given in Fig. 11.8. The Bering Sea and the Sea of Okhotsk do not have very deep water formation but may contribute to the formation of NPIW (Reid, 1965, 1973; Talley, 1991), thus pumping excess CO₂ to the North Pacific. The Sea of Japan has deep and bottom water formation, but does not export excess CO₂ because of the shallow sills. Sediments in the shelves of these three seas may neutralize excess CO₂ in the latter part of the next century when the shelf waters become undersaturated with respect to calcite and aragonite.

The East China Sea absorbs a large amount of CO₂ because of its high productivity, hence low pCO₂. Yet the East and South China Seas are not important reservoirs for excess CO₂ because of their small size and upwelling. The sediments
Figure 11.7  (a) $\text{NO}_3$ and (b) $\text{PO}_4$ concentrations vs. pH (25°C) for the East China Sea (KIW is the Kuroshio Intermediate Water; KTW is the Kuroshio Tropical Water; KSW is the Kuroshio Surface Water; data taken from Chen et al., 1992). The surface shelf waters with elevated $\text{NO}_3$ concentrations are all near the Yangtze River plume.
Figure 11.8  Schematic diagrams of flow patterns in the Bering Sea, Sea of Okhotsk, Sea of Japan, East China Sea, and South China Sea.
are unlikely to neutralize excess CO$_2$ in the next century, but carbonate is regenerated from organic matter at the bottom. This regenerated carbonate may be exported to, and stored in, the pelagic ocean (Tsunogai et al., 1997).

The excess CO$_2$ budget in the global oceans

As the first attempt on a global scale, we have integrated the amount of excess CO$_2$ contained in each ocean (Chen, 1993b). The vertical integration, however, was from the sea surface to the depth where the excess CO$_2$ concentration equals 5 μmol kg$^{-1}$. We re-evaluated the carbon budget by integrating the excess CO$_2$ to where it is approximately zero, resulting in an increase of about 10%. We also added more data in the marginal seas. The results indicate that the Norwegian and Greenland Seas (between 65–80° N) contained 0.95 (± 0.2) Gt excess carbon in 1982 (Chen et al., 1990). The rest of the North Atlantic Ocean and the South Atlantic Ocean contained 24 (± 4.5) and 13.4 (± 2.5) Gt excess carbon, respectively, around 1973. Overall, the Atlantic Ocean contained 38.4 (± 7) Gt excess carbon around 1973 (Table 11.3). This is slightly higher than the estimate of 33 (± 5) Gt excess carbon in 1983 estimated by Bolin et al. (1989).

The North Pacific Ocean (excluding the marginal seas) and the South Pacific Ocean contained 16 (± 4) and 18.6 (± 4) Gt excess carbon, respectively, around 1980. Overall, the Pacific Ocean contained 35.8 (± 6) Gt excess carbon, less than that found in the Atlantic Ocean despite of the much larger capacity (Table 11.3). This is mainly because the Pacific Ocean lacks deep water formation in the north and because of the higher upwelling rate.

The Red Sea contained 0.07 (± 0.02) Gt excess carbon in 1985 (Chen & Wu, 1991). The entire Indian Ocean contained 18.6 (± 4) Gt excess carbon around 1980. Overall the major oceans contained 76–110 Gt excess carbon around 1980 (Table 11.3). Since data from most marginal seas and the Arctic Ocean are lacking, and the excess CO$_2$ may penetrate deeper in these seas, the global oceans may actually contain 5% more excess CO$_2$ perhaps. The above values compare with 90–120 Gt net release of carbon from terrestrial ecosystems between 1850 and 1980 (Houghton & Skole, 1990) and 150–190 Gt C from total fossil fuel release between 1860 and 1982. The atmosphere contained 118–160 Gt excess carbon in 1980 (Table 11.4). These data indicate that the high estimates for the atmospheric and oceanic sinks (270 Gt C) could account for the low estimates for the fossil fuel and land change sources (240 Gt C). The sum of the high estimates for the sources (310 Gt C), however, is much higher than the combined atmospheric and oceanic sinks (194–270 Gt C). The carbon budget could not yet be balanced with any certainty.
Table 11.3  *Estimated amount of excess carbon in the oceans*

<table>
<thead>
<tr>
<th>Area</th>
<th>Excess carbon (Gt C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenland and Norwegian Seas (65 – 80° N)</td>
<td>0.95 (± 0.2)</td>
</tr>
<tr>
<td>North Atlantic (EQ – 65° N)</td>
<td>24 (± 4.5)</td>
</tr>
<tr>
<td>South Atlantic</td>
<td>13.4 (± 2.5)</td>
</tr>
<tr>
<td>Subtotal</td>
<td>38.4 (± 7)</td>
</tr>
<tr>
<td>Bering Sea</td>
<td>0.21 (± 0.05)</td>
</tr>
<tr>
<td>Sea of Okhotsk</td>
<td>0.18 (± 0.08)</td>
</tr>
<tr>
<td>Sea of Japan</td>
<td>0.31 (± 0.05)</td>
</tr>
<tr>
<td>East China and Yellow Seas</td>
<td>0.07 (± 0.02)</td>
</tr>
<tr>
<td>South China Sea</td>
<td>0.43 (± 0.1)</td>
</tr>
<tr>
<td>North Pacific (excluding the above marginal seas)</td>
<td>16 (± 4)</td>
</tr>
<tr>
<td>South Pacific</td>
<td>18.6 (± 4)</td>
</tr>
<tr>
<td>Subtotal</td>
<td>35.8 (± 6)</td>
</tr>
<tr>
<td>Red Sea</td>
<td>0.073 (± 0.02)</td>
</tr>
<tr>
<td>Indian (excluding the Red Sea)</td>
<td>18.6 (± 4)</td>
</tr>
<tr>
<td><strong>Total (1980)</strong></td>
<td><strong>92.8 (± 17)</strong></td>
</tr>
</tbody>
</table>

Table 11.4  *Estimated values of key sources and sinks in the global carbon cycle*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source (Gt C)</th>
<th>Sink (Gt C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total fossil fuel release 1860 – 1982</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Rotty &amp; Masters, 1985)</td>
<td>150 – 190</td>
<td></td>
</tr>
<tr>
<td>Total land change 1850 – 1980</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Houghton &amp; Skole, 1990)</td>
<td>90 – 120</td>
<td></td>
</tr>
<tr>
<td>Atmospheric excess carbon 1982</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Solomon <em>et al.</em>, 1985)</td>
<td></td>
<td>118 – 160</td>
</tr>
<tr>
<td>Oceanic excess carbon (c. 1980)</td>
<td></td>
<td>76 – 110</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>240 – 310</strong></td>
<td><strong>194 – 270</strong></td>
</tr>
</tbody>
</table>
Acknowledgments

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References


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Dahlem Conferences, Berlin.


Houghton, R. & Skole, D. L. (1990). The long-term flux of carbon between terrestrial ecosystems and the atmosphere as a result of changes in land use. 4 pp., Carbon Dioxide Information Analysis Center, ORNL.


Tsunogai, S. (1979). Dissolved silica as the primary factor determining the composition of phytoplankton classes in the ocean. Bulletin Faculty Fisheries Hokkaido University, 30, 314–22.


