

# Oceanography background: dissolved chemicals, circulation and biology in the sea

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## 1.1 | A chemical perspective

This book describes a chemical perspective on the science of oceanography. The goal is to understand the mechanisms that control the distributions of chemical compounds in the sea. The “chemical perspective” uses measured chemical distributions to infer the biological, physical, chemical and geological processes in the sea. This method has enormous information potential because of the variety of chemical compounds and the diversity of their chemical behaviors and distributions. It is complicated by the requirement that one must

understand something about the reactions and time scales that control the chemical distributions. Chemical concentrations in the sea “remember” the mechanisms that shape them over their oceanic lifetime. The time scales of important mechanisms range from seconds or less for very rapid photochemical reactions to more than 100 million years for the mineral-forming reactions that control relatively unreactive elements in seawater. The great range in time scales is associated with an equally large range in space scales, from chemical fluxes associated with individual organisms to global processes like river inflow and hydrothermal circulation.

Studies of chemical oceanography have evolved from those focused on discovering what is in seawater and the physical-chemical interactions among constituents to those that seek to identify the rates and mechanisms responsible for distributions. Although there is still important research that might be labeled “pure marine chemistry,” much of the field has turned to the chemical perspective described here, resulting in a fascinating array of new research frontiers. We mention just a few of the exciting areas that are presently mature. Chemical alterations associated with hydrothermal processes at mid-ocean ridges have ramifications for whole-ocean mass balance of some elements and are regions of redox reactions catalyzed by microbial processes that may have been the origin of life on Earth. The ocean’s role in the global carbon cycle is an important process controlling the fate of anthropogenic CO<sub>2</sub> added to the atmosphere, which has ramifications for global climate, today and in the future. The study of mechanisms by which dissolved metals limit marine biological production has been demonstrated by large-scale iron addition experiments in regions where the surface ocean is rich in phosphorus and nitrate. Investigations of isotope and chemical tracers in calcite shells and the structure of individual organic compounds buried in marine sediments provide analytical constraints for understanding how the ocean influenced atmospheric CO<sub>2</sub> and climate during past glacial ages. These are just a few examples that are relevant to oceanography and the global environment in a field that is continuously developing new research avenues.

Because the science of chemical oceanography is focused on distributions of chemical constituents in the sea, its evolution has been controlled to some extent by analytical developments. It is not our goal to dwell on analytical methods; however, discoveries of new mechanisms and processes often follow the development of better techniques to make accurate measurements. Probably the most recent example has been the evolution of a variety of mass spectrometers capable of precisely determining extremely low concentrations of metals, isotopes on individual organic compounds, and atmospheric gas ratios on small samples. There have been a host of other breakthroughs that are too numerous to mention that have had a great influence on our ability to interpret the ocean’s secrets.

The evolution of analytical methods has been accompanied by increased sophistication and organization in sampling the ocean.

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Table 1.1. | *Areas, volumes and heights of the ocean and atmosphere*

Atmosphere inventory	$1.77 \times 10^{20}$ mol (all gases)
Earth surface area	$5.10 \times 10^{14}$ m <sup>2</sup>
Ocean surface area	$3.62 \times 10^{14}$ m <sup>2</sup> (71% of Earth's area)
Ocean mean depth	3740 m
Ocean volume	$1.35 \times 10^{18}$ m <sup>3</sup>
Ocean mass	$1.38 \times 10^{21}$ kg
River flow rate	$3.5 \times 10^{13}$ m <sup>3</sup> y <sup>-1</sup>

Pilson (1998); the river flow rate is from Broecker and Peng (1982).

This trend has so far involved primarily the effective use of research vessels to mount global sampling programs such as the geochemical sections (GEOSECS) program in the 1970s, and the joint geochemical ocean flux study (JGOFS) and world ocean circulation experiment (WOCE), both in the 1990s. All of these programs were international in scope, employing scientists and research vessels from the world community in a coordinated effort to determine global chemical distributions and processes. International collaboration has been particularly important in the last two of these programs and will continue to grow in order to solve problems that are increasingly complex and expensive to tackle. The promise of remotely determining chemical concentrations by using instruments that operate *in situ* on moorings or unmanned vehicles is real, but at the time of writing this book it is only beginning to have a major impact, primarily because of the limited capability of chemical sensors to maintain long-term stability and accuracy.

We begin the book with a brief discussion of background information about the chemical constituents of seawater, the basics of ocean circulation and marine biological processes. Some important information about the volumes and areas of the ocean and atmosphere are presented in Table 1.1. The goal of this chapter is to create a foundation for the discussion of mechanisms later in the book.

## 1.2 | Constituents of seawater

Chemical concentrations in the ocean and atmosphere have been presented over the years in a variety of units, some of which originated in the field of chemistry and others that gained prominence in the geologic literature (Table 1.2). The modern practice in chemical oceanography is to present concentrations in units of moles or equivalents per kilogram of seawater. Moles and equivalents are more meaningful than mass units because reaction stoichiometry is presented on an atomic or molecular basis. Mass is used in the denominator because it is conservative at all depths of the ocean, whereas volume changes because of the compressibility of water.

Table 1.2. (a) Concentration units encountered in oceanography

Equivalents, eq, is equal to moles  $\times$  absolute value of the charge of the species. Units indicated as "seawater units" are those preferred in oceanography. Molality, molarity, normality and volume ratio all have a long history of use in classical chemistry because of their convenience for laboratory preparations.

Name	Basis	Dimensions	Symbol	Definition						
<i>Concentrations in aqueous solution</i>										
Molal	mass	mol kg <sup>-1</sup>	<i>m</i>	Moles per kilogram of solvent						
Molar	volume	mol l <sup>-1</sup>	<i>M</i>	Moles per liter of solution						
Normal	volume	eq l <sup>-1</sup>	<i>N</i>	Equivalents per liter of solution						
Weight ratio	mass	g kg <sup>-1</sup>		Mass of solute per mass of solution						
Volume ratio	volume	ml l <sup>-1</sup>		Volume of solute per volume of solution						
Seawater units	mass	mol kg <sup>-1</sup>		Moles per kilogram of solution						
Seawater units	mass	eq kg <sup>-1</sup>		Equivalents per kilogram of solution						
<i>Concentrations in the atmosphere</i>										
Mole fraction	moles	mol mol <sup>-1</sup>	<i>X</i>	Moles of gas per moles of dry air (= volume fraction, e.g. ppmv, for ideal gas)						
Fugacity	pressure	bar bar <sup>-1</sup>	<i>f</i>	Gas pressure per atmospheric pressure (= partial pressure, <i>p</i> , for ideal gas)						
<i>(b) Exponential terminology used in oceanography</i>										
Prefix (symbol)	peta- (P)	tera- (T)	giga- (G)	mega- (M)	milli- (m)	micro- ( $\mu$ )	nano- (n)	pico- (p)	femto- (f)	atto- (a)
Unit multiplier	10 <sup>15</sup>	10 <sup>12</sup>	10 <sup>9</sup>	10 <sup>6</sup>	10 <sup>-3</sup>	10 <sup>-6</sup>	10 <sup>-9</sup>	10 <sup>-12</sup>	10 <sup>-15</sup>	10 <sup>-18</sup>

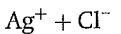
Before launching into a detailed discussion of individual constituents, we would like to introduce the total quantity of dissolved material in seawater, salinity, and the processes that determine it.

### 1.2.1 The salinity of seawater

Salinity is a measure of the total mass in grams of solids dissolved in a kilogram of seawater, a mass ratio. It is composed almost entirely of elements that do not measurably change concentration geographically owing to chemical reactivity. It is thus used as a property against which individual chemical species can be compared to determine their stability in the sea; conservative (unreactive) elements have constant or nearly constant ratios to salinity everywhere in the ocean. Relatively small changes in salinity are important in determining the density of seawater and thermohaline circulation. It can also be useful as a tracer for the mixing of different water masses since salinity values that are determined at the ocean's surface can be traced for great distances within the ocean interior.

For all these reasons it is essential to have a relatively rapid and accurate measurement of seawater salinity. The obvious method

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would be to dry seawater and weigh the leftover residue. This approach does not work very well because high temperatures (c. 500 °C) are required to drive off the tightly bound water in salts such as magnesium chloride and sodium sulfate. At these temperatures some of the salts of the halides, bromides and iodides are volatile and are lost, while magnesium and calcium carbonates react to form oxides, releasing CO<sub>2</sub>. Some of the hydrated calcium and magnesium chlorides decompose, giving off HCl gas. The end result of weighing the dried salts is that you come up "light" because some of the volatile elements are gone. Although there were schemes created to obviate these problems, for many years the preferred method for determining salinity was titration of the chloride ion by using silver nitrate



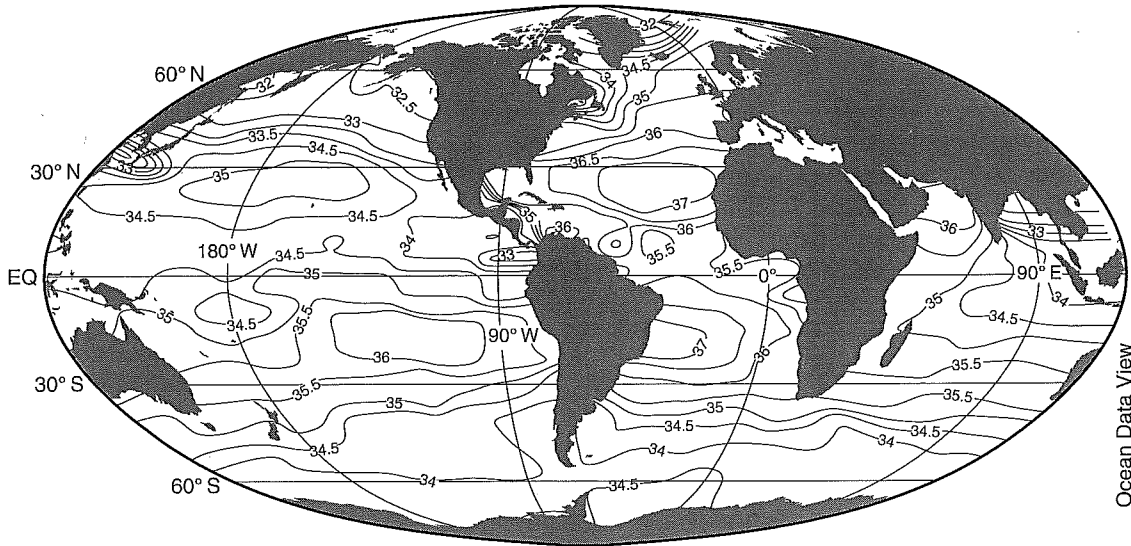
which is quantitative. The chloride concentration, [Cl<sup>-</sup>], could then be related to salinity, *S*, via a constant number,

$$S(\text{ppt}) = 1.80655 \times [\text{Cl}^-](\text{ppt}), \quad (1.2)$$

where ppt indicates parts per thousand (g<sub>solute</sub> kg<sub>seawater</sub><sup>-1</sup>). The exact relationship between chlorinity and salinity, however, has evolved over the years, and it is not as accurate and universal as the present method.

Salinity is presently determined by measuring the conductance of seawater by using a salinometer. The modern definition of salinity uses the *practical salinity scale*, which replaces the chlorinity-salinity relationship with a definition based on a conductivity ratio (Millero, 1996). A seawater sample of salinity *S* = 35 has a conductivity equal to that of a KCl solution containing a mass of 32.435 6 g KCl in 1 kg of solution at 15 °C and 1 atm pressure. No units are necessary on the practical salinity scale; however, in practice, one often sees parts per thousand, ppt, or the abbreviation "psu." New salinometers using this method are capable of extremely high precision so that the salinity ratio can be determined to 1 part in 40 000. At a typical salinity near 35 this procedure enables salinities to be determined to an accuracy of 35.000 ± 0.001. This is much better than most chemical titrations, which, at best, achieve routine accuracy of ± 0.5 parts per thousand.

The distribution of salinity in surface waters of the ocean is presented in Fig. 1.1. Because the concentrations for many major seawater constituents are unaffected by chemical reaction on the time scale of ocean circulation, local salinity distributions are controlled by a balance between two physical processes, evaporation and precipitation. This balance is reflected by low salinities in equatorial regions that result from extensive rain due to rising atmospheric circulation (atmospheric lows) and high salinities in hot dry subtropical gyres that flank the equator to the north and south (20–35 degrees of latitude) where the atmospheric circulation cells descend (atmospheric highs).



**Figure 1.1.** Annual mean surface salinity of the world's ocean. (Plotted by using Ocean Data View (Schlitzer, 2001), and surface salinity in Levitus et al. (1994).)

Salinity and temperature are the primary factors that determine the density of seawater. The densities of most surface seawaters range from 1024 to 1028 kg m<sup>-3</sup>, and it is possible to evaluate density to about ± 0.01 of these units. In order to avoid writing numbers with many significant figures, density is usually presented as the Greek letter sigma,  $\sigma$ , which has the following definition

$$\sigma = (\rho/\rho_0 - 1) \times 1000, \tag{1.3}$$

where  $\rho$  is the density of the sample (kg m<sup>-3</sup>) and  $\rho_0$  is the maximum density of water at 3.98 °C (999.974 kg m<sup>-3</sup>). (Note that the numerical value of this expression is only slightly different from,  $\sigma = \rho - 1000$ , which appears in many texts.) Density is calculated from temperature, salinity and pressure (because of the compressibility of water) by using the international equation of state of seawater (Millero, 1996). The expression above represents the density *in situ* of a seawater sample determined from the measured temperature, salinity and depth. Because all water acquired its temperature and salinity while it was at the ocean surface, it is convenient to know the density corrected to one atmosphere pressure, which is indicated by sigma with a subscript t (sigma-tee),  $\sigma_t$ . By the same reasoning, it is often advantageous when tracing the source of a water parcel to calculate density by using temperature corrected for increases caused by water compression under the influence of pressure. The potential temperature,  $\theta$ , is the temperature the water sample would have if it were raised to the surface with no exchange of heat with the surroundings, i.e., if it changed pressure adiabatically. At the depths of the ocean this is a large effect. A water parcel gains c. 0.5 °C when it sinks from the ocean surface to 4000 m depth (c. 400 atm). Potential temperature is the temperature it had before sinking. Density calculated at one atmosphere and the potential temperature is called sigma-theta,  $\sigma_\theta$ .

Table 1.3. | T  
water masses

Water mass
AABW <sup>a</sup>
NADW <sup>b</sup>
MW <sup>c</sup>
AAIW <sup>d</sup>
<sup>e</sup> T and S char.
<sup>f</sup> Flow rates at

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Table 1.3. Temperature, salinity, and flow rate of major deep-ocean water masses

Water mass	Temperature <sup>e</sup> (°C)	Salinity <sup>e</sup>	Flow estimate <sup>f</sup> (Sverdrups)
AABW <sup>a</sup>	-2.0-0.0	34.6-34.7	5-10
NADW <sup>b</sup>	2.0-3.0	34.9-35.0	15-20
MW <sup>c</sup>	12.0	36.6	—
AAIW <sup>d</sup>	2.0-3.0	34.2	5-10

<sup>a</sup> AABW, Antarctic Bottom Water

<sup>b</sup> NADW, North Atlantic Deep Water

<sup>c</sup> MW, Mediterranean Water

<sup>d</sup> AAIW, Antarctic Intermediate Water

<sup>e</sup> T and S characteristics from Picard and Emery (1982)

<sup>f</sup> Flow rates are in Sverdrups ( $10^6 \text{ m}^3 \text{ s}^{-1}$ ).

Note that the North Atlantic surface water is nearly 2 salinity units saltier than North Pacific surface water. At first this seems counterintuitive because more large rivers drain into the Atlantic. The reason for this difference has to do with the relative rates of evaporation in the high latitudes of the two oceans. North Atlantic surface water is on average warmer ( $10.0^\circ\text{C}$ ) than North Pacific surface water ( $6.7^\circ\text{C}$ ). Warmer water leads to warmer air, which has a higher specific humidity (the mass of water per mass of dry air) and increases evaporation and consequently salinity as well. The temperature difference is due to the warm Gulf Stream waters that flow north along the east coast of North America having a greater impact at high latitudes than their Pacific counterpart, the Kuroshio current. The resulting salinity difference has very important consequences for the nature of global thermohaline circulation. Because salt content (along with temperature) influences the density of seawater, the higher salt content of North Atlantic surface waters gives them greater densities at any given temperature than North Pacific waters. This is the main reason for massive downwelling, all the way to the ocean bottom, in the North Atlantic where the water is cold and salty, but no deep water formation in the North Pacific. There is no North Pacific Deep Water in Table 1.3.

This explanation for the surface salinity differences between the Atlantic and Pacific does not provide the whole story because it overlooks the need to budget atmospheric water transport on a global basis. In fact, the only way to cause a net salinity change in an ocean due to evaporation is via net transport of water vapor to another region on a time scale that is short with respect to the residence time (decades to centuries) of the surface water in question. Simply removing water from an ocean to the atmosphere or to an adjacent landmass is insufficient if that same water rapidly returns to the source ocean. To create a salinity difference between oceans,

water must be removed across a continental divide so that it precipitates either directly on another ocean or into the drainage basin of a river discharging into another ocean.

This budgetary constraint makes global salinity patterns the net result of local evaporation, wind patterns, and continental placement and topography. An ideal “vapor export window” from an ocean would be through a region where initially dry prevailing winds blow continuously over warm ocean surface waters and then across a low continental divide. Inspection of the North Atlantic Ocean shows such a window at about 20°N, where the North East Trade Winds blow westward across the Sahara desert, subtropical Atlantic, and then over the relatively low continental divide of Central America. The surface Atlantic Ocean expresses its highest salinity (*c.* 37.5) at this latitude, and high rainfall over western Panama and Costa Rica indicates substantial vapor export to the subtropical Pacific. In contrast, the expansive subtropical Pacific Ocean has few upwind deserts, and a Trade Wind window that is effectively blocked by Southeast Asia. Thus the percentage of net water loss is much less in the bigger ocean.

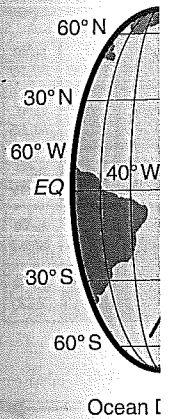
In the large perspective, the North Atlantic Ocean is now saltier than the North Pacific as a result of the present distribution of ocean and atmosphere currents and continents over the surface of the Earth. Other distributions, as occurred in the past owing to different distributions of ice, deserts or continental topography, would produce very different water balances and global current systems.

Temperature differences in the sea are large, ranging between 30°C in equatorial surface waters and -2°C in waters that are in contact with ice. By comparison, salinity is remarkably constant,  $S = 33.0\text{--}37.0$ , necessitating very accurate determinations in order to distinguish differences. The average temperature and salinity of the sea are 3.50°C and 34.72, and 75% of all seawater is within  $\pm 4^\circ\text{C}$  and  $\pm 0.3$  salinity units of these values. Cross sections of the potential temperature and salinity of the Atlantic and Pacific Oceans (Fig. 1.2) demonstrate how water masses can be identified with distinct origins at different densities and hence different depths. The water masses are characterized by the temperature and salinity that is determined at the surface ocean in the area of their formation (Table 1.3). The deepest waters, Antarctic Bottom Water (AABW) and North Atlantic Deep Water (NADW), are formed at the surface in polar regions. AABW is dense because it is formed under the ice in the Weddell and Ross Seas and is thus extremely cold. NADW is not particularly cold, but is highly saline because of the source waters from the Gulf Stream and high evaporation rates in the North Atlantic. Antarctic Intermediate Water (AAIW) is both warmer and less saline than either of the deeper-water masses and thus spreads out in the ocean at a depth of about 1000 m.

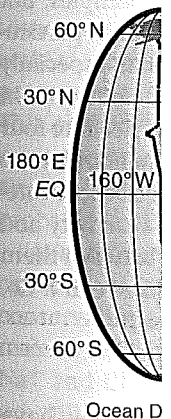
### 1.2.2 Element classification

Chemicals in seawater can be classified into four groups based mainly on the shapes of their dissolved concentration distributions

(A) Atlantic se

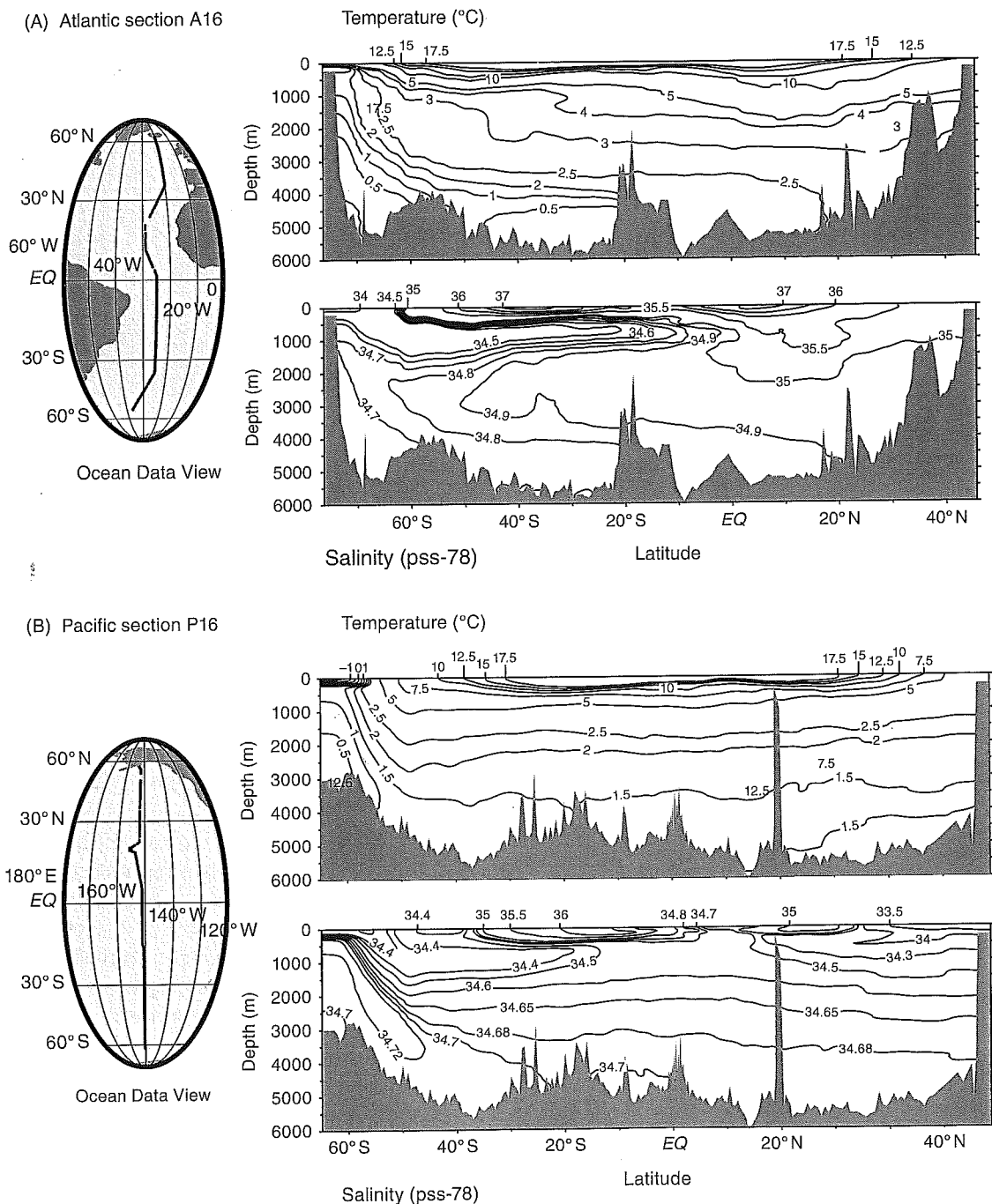


(B) Pacific se

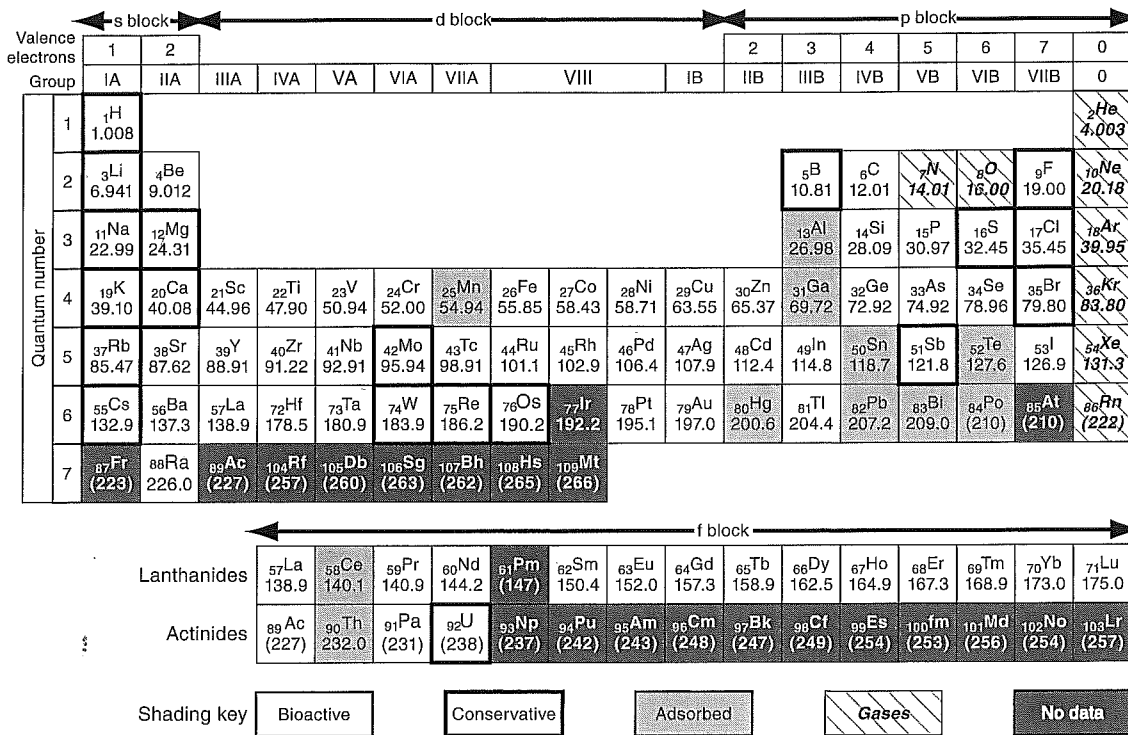


**Figure 1.2.** Lati water masses are WOCE hydrogra





**Figure 1.2.** Latitudinal cross section of the potential temperature and salinity of the Atlantic (A) and Pacific (B) oceans. Different water masses are definable by their characteristic temperature and salinity (Table 1.3). (Plotted by using Ocean Data View and WOCE hydrographic data (Schlitzer, 2001).)



**Figure 1.3.** Periodic table of the elements with the categories of conservative, bioactive, adsorbed, and gaseous elements indicated.

with depth. Most measurements are made on unfiltered samples, but experiments designed to operationally define “dissolved” and “particulate” phases by using 0.45 μm pore-size filters indicate that, especially below the surface 100 m, nearly all the total mass of any element is in the dissolved phase. Chemical species in seawater are classified into four categories in the Periodic Table of Fig. 1.3: *conservative* elements, *bioactive* elements, *adsorbed* or *scavenged* elements, and *gases*. Because these categories are based primarily on the relative importance of reactivity and mixing to elemental ocean distributions, the boundaries between them are sometimes vague. For example many trace metals, like Fe and Co, are both *bioactive* and *adsorbed* and fall into both categories.

**Conservative elements**

To within a few percent, conservative elements in seawater have constant concentration : salinity ratios. That is, their concentrations are not greatly affected by processes other than precipitation and evaporation: the same processes that control salinity in the ocean. This definition is of course operational since the ability to determine the effect of biological and chemical processes on concentration depends on the accuracy and precision of the measurement method. Elements of high concentration tend to be conservative because they are relatively unreactive; however, conservative elements are present in all concentration ranges because some of them are both low in crustal abundance and relatively unreactive. There are of course

Table 1.4.  
Major ions  
than 10 μm  
Cations  
species  
Na<sup>+</sup>  
Mg<sup>2+</sup>  
Ca<sup>2+</sup>  
K<sup>+</sup>  
Sr<sup>2+</sup>  
Li<sup>+</sup>  
Σcations<sup>b</sup>

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Table 1.4. Major ions<sup>a</sup> in surface seawater at salinity  $S = 35$ , and their role in the calculation of alkalinity<sup>b</sup>  
 Major ions are defined here as those charged constituents with concentrations greater than  $10 \mu\text{mol kg}^{-1}$ , excluding the nutrient nitrate, which varies in concentration.

Cations			Anions					
species	mmol $\text{kg}^{-1}$	meq $\text{kg}^{-1}$	Insignificant proton exchange			Significant proton exchange ( $A_T$ ) <sup>a</sup>		
			species	mmol $\text{kg}^{-1}$	meq $\text{kg}^{-1}$	species	mmol $\text{kg}^{-1}$	meq $\text{kg}^{-1}$
$\text{Na}^+$	469.06	469.06	$\text{Cl}^-$	545.86	545.86	$\text{HCO}_3^-$	1.80	1.80
$\text{Mg}^{2+}$	52.82	105.64	$\text{SO}_4^{2-}$	28.24	56.48	$\text{CO}_3^{2-}$	0.25	0.51
$\text{Ca}^{2+}$	10.28	20.56	$\text{Br}^-$	0.84	0.84	$\text{B(OH)}_4^-$	0.11	0.11
$\text{K}^+$	10.21	10.21	$\text{F}^-$	0.07	0.07			
$\text{Sr}^{2+}$	0.09	0.18						
$\text{Li}^+$	0.02	0.02						
$\Sigma\text{cations}^b$		605.67	$\Sigma\text{anions}$		603.25			2.42

Concentrations are from DoE (1994).

<sup>a</sup>The concentration cut-off for the definition of major ions traditionally consists of elements with concentrations greater than  $1 \text{ mg kg}^{-1}$ . The concentration of  $\text{Li}^+$  is below this threshold, but it is added here to achieve the charge balance definition of alkalinity (see Chapter 4).

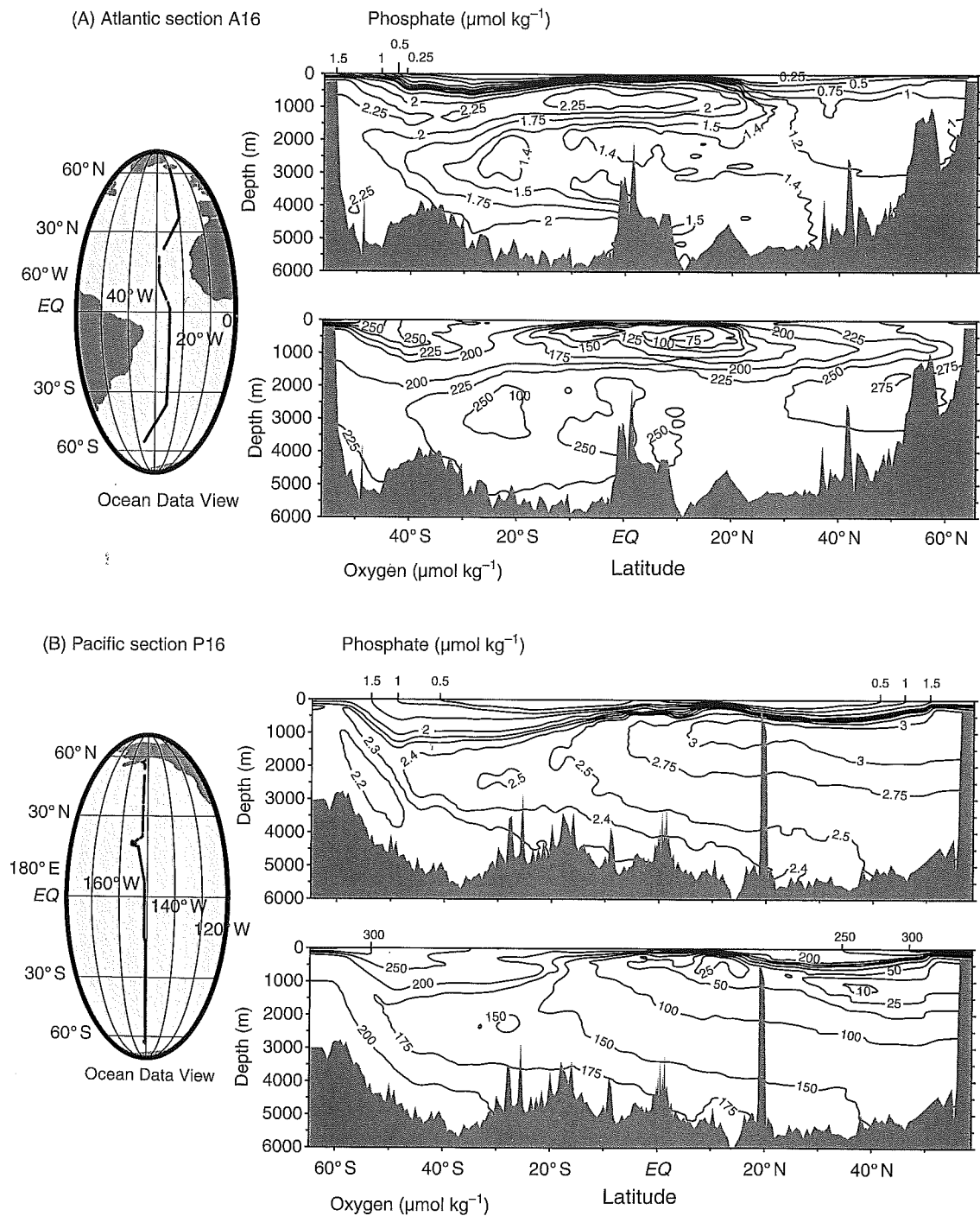
<sup>b</sup>The difference between the total concentrations of cations and anions, ( $\Sigma\text{cations} - \Sigma\text{anions}$ ), in the bottom row, and the sum of the constituents of the last column equals the value of the alkalinity,  $2.42 \text{ meq kg}^{-1}$ . See the discussion in Chapter 4.

some caveats to our classification of conservative ions.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$  are not strictly conservative, as changes on the order of one percent in their concentration : salinity ratios have been identified. This property was discovered by making very accurate titration and mass spectrometric measurements. If equally precise methods were applied to the other elements, changes with respect to salinity would probably be found for some.

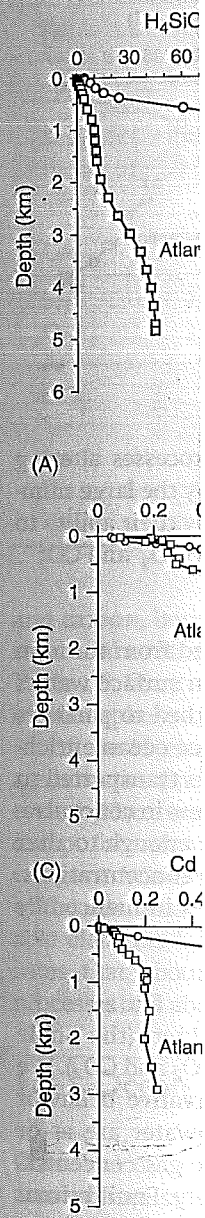
We define the major ions in seawater (Table 1.4) as those with concentrations greater than  $10 \mu\text{mol kg}^{-1}$ . Most of the major ions are conservative (exceptions are  $\text{Sr}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) and these ions make up more than 99.4% of the mass of dissolved solids in seawater.  $\text{Na}^+$  and  $\text{Cl}^-$  account for 86% and  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Mg}^{2+}$  make up 97%. Conservative elements with concentrations less than  $10 \mu\text{mol kg}^{-1}$  are found in rows 5 and 6 of the periodic table where elements with lower crustal abundances occur.

### Bioactive elements

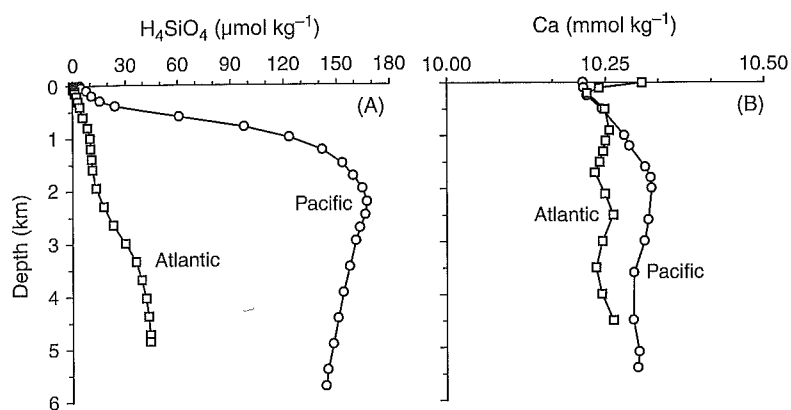
These dissolved constituents of seawater have concentration versus depth profiles characterized by surface water depletion and deep water enrichment caused by plant consumption in the euphotic zone and release at depth when the biological material dies, sinks and degrades. Examples of these elements are nutrients required for phytoplankton growth (P,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$ ), oxygen consumed during



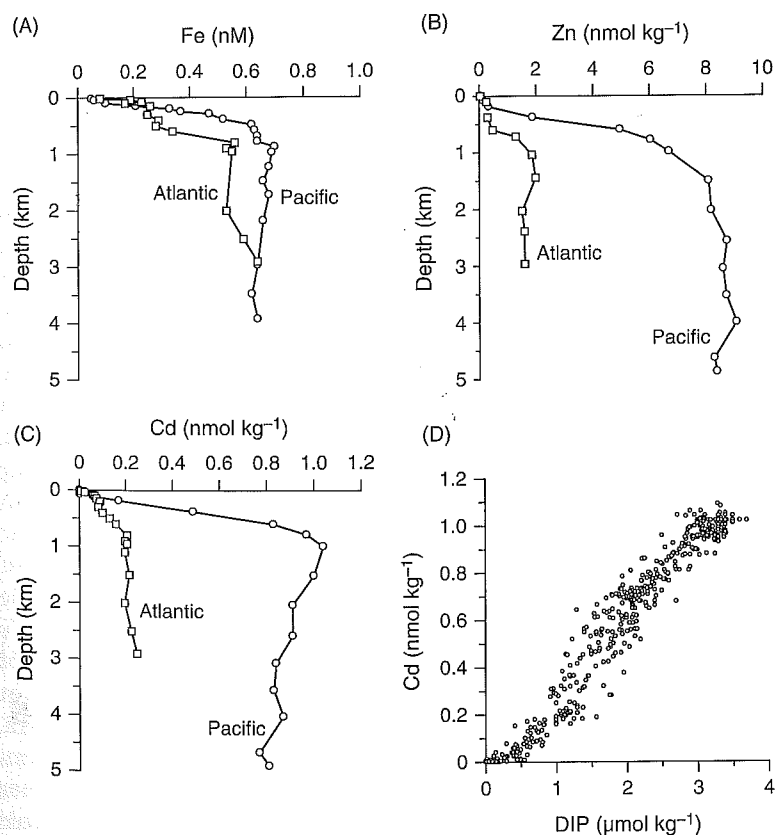
**Figure 1.4.** Latitudinal cross sections for phosphate and the concentration of oxygen in the Atlantic (A) and Pacific (B) Oceans. (Plotted by using Ocean Data View and WOCE hydrographic data (Schlitzer, 2001).)



respiration (Fig. species (Si and C plankton growth tain reasons (e.g. seawater (Table : concentrations that bioactive metals range of nano-c



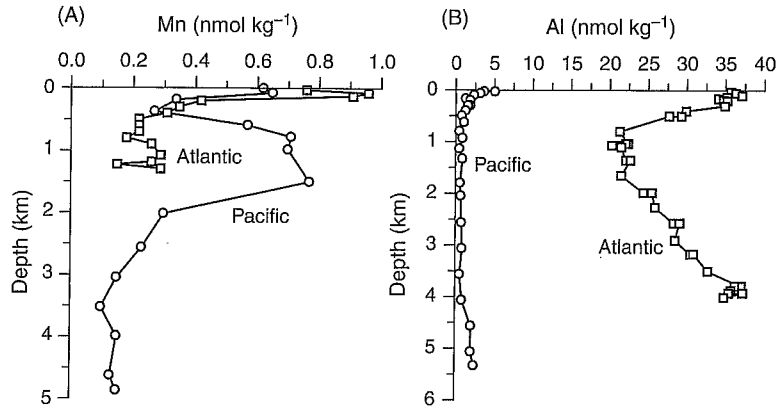
**Figure 1.5.** Vertical profiles of silicic acid (A) and calcium (B). These elements are released to the dissolved phase of seawater upon the dissolution of opal and carbonate tests. (The silicic acid profile was plotted by using Ocean Data View from WOCE data; Ca data are from de Villiers (1994).)



**Figure 1.6.** Vertical profiles of the trace metals (A) Fe, (B) Zn and (C) Cd in the Atlantic and Pacific Oceans; and (D) the global dissolved Cd versus P relationship. The shape of the depth distributions indicates that these metals behave like nutrients in the ocean. (Data from Johnson *et al.* (1997), Bruland (1983) and Boyle (1988).)

respiration (Fig. 1.4), constituents of shells made by some plankton species (Si and Ca) (Fig. 1.5), and trace metals (Fig. 1.6) necessary for plankton growth (e.g. Fe) or incorporated into the plankton for uncertain reasons (e.g. Cd and Zn). Both  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are major ions in seawater (Table 1.4), while the micronutrients P, N, and Si have concentrations that range from nano- to micromoles per kilogram. The bioactive metals are true trace elements, having concentrations in the range of nano- or picomoles per kilogram. The fact that biological

**Figure 1.7.** Profiles of the total concentrations of (A) Mn and (B) Al. These metals show some of the characteristics of metals that are adsorbed from solution in seawater in that their concentrations decrease with depth and from the Atlantic to Pacific Oceans. (Mn data from Bruland (1983), and Al from Pilson (1998).)



uptake and recycling at depth are the dominant processes altering vertical concentration profiles is indicated not only by the large number of elements that are affected (Fig. 1.3), but also by their ability to alter the concentrations of some major ions such as  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ .

**Adsorbed elements**

These elements have depth profiles that are reversed from those in the bioactive category. Concentrations are higher in surface waters and decrease with depth as the elements are adsorbed to particles that fall through the ocean. In some cases the surface ocean enrichment is also a result of metal input by dust particles transported to the sea by wind. Adsorbed elements are exclusively low in concentration, meaning that this mechanism is not pervasive enough to alter the concentrations of elements with higher concentrations. Examples of metals that have concentration profiles influenced by this process are Mn and Al (Fig. 1.7).

**Gases**

Gases dissolved in seawater are either chemically inert (the noble gases in the last column of Fig. 1.3) or bioactive (e.g.  $\text{O}_2$  and  $\text{CO}_2$ ). We give gases a category of their own because conservative behavior in this case means that the concentrations in seawater are at or near equilibrium with their respective atmospheric gas concentrations rather than having a constant ratio with salinity. Equilibrium, or gas saturation, is primarily a function of temperature (cold water can hold more gas at equilibrium), but salinity also plays a role (saltier water can hold less gas at equilibrium). Dissolved gases at the ocean's surface are at or near saturation with respect to their atmospheric partial pressures and, if they are unreactive, maintain this concentration as they are subducted into the ocean's interior. Thus, conservative gases have concentrations that vary with the temperature of the ocean's surface water. Because temperature decreases with depth in the ocean, inert gas concentrations increase with depth. Gases also have the special property of being responsible for the transfer of certain elements, primarily oxygen

**Table 1.5.** The gas which has a constant concentration in the atmosphere. Seawater equilibrates with the atmosphere according to Henry's Law.

Gas	Atmospheric concentration (mole %)
$\text{N}_2$	78.1
$\text{O}_2$	20.9
Ar	0.93
$\text{CO}_2$	0.035
Ne	0.0018
He	0.0005
Kr	0.0001
Xe	0.000008

and carbon, between the atmosphere and the ocean. Table 1.5. More of the atmosphere-ocean exchange. Of the 89 elements, 23 are conservative (including noble gases), 23 are conservative (including noble gases), except for radon, which is in the bioactive category. While the exchange of the dissolved gases is controlled by the atmosphere-ocean exchange, it indicates that about 10% of the processes and about

**1.3 | Ocean circulation**

Chemical dynamics in the atmosphere system and ocean circulation. Chemical composition and processes control one must know. The following brief overview is driven and thermally

**1.3.1 | Wind-driven circulation in the ocean**  
Circulation in the ocean is driven by the atmosphere-ocean interface, mostly density-driven

Table 1.5. *The major gases of the atmosphere excluding water vapor, which has a concentration of a few percent at saturation in the atmosphere*

Seawater equilibrium concentrations were calculated from the Henry's Law coefficients at 20 °C and  $S = 35$ .

Gas	Atmospheric mole fraction (atm)	Seawater equilibrium concentration ( $\mu\text{mol kg}^{-1}$ )
N <sub>2</sub>	$7.808 \times 10^{-1}$	$4.18 \times 10^2$
O <sub>2</sub>	$2.095 \times 10^{-1}$	$2.25 \times 10^2$
Ar	$9.34 \times 10^{-3}$	$1.10 \times 10^1$
CO <sub>2</sub>	$3.65 \times 10^{-4}$	$1.16 \times 10^1$
Ne	$18.2 \times 10^{-6}$	$7.0 \times 10^{-3}$
He	$5.24 \times 10^{-6}$	$2.0 \times 10^{-3}$
Kr	$1.14 \times 10^{-6}$	$2.0 \times 10^{-3}$
Xe	$0.87 \times 10^{-7}$	$3.0 \times 10^{-4}$

and carbon, between the atmosphere and ocean. Atmospheric pressures and concentrations at saturation equilibrium are presented in Table 1.5. More about the utility of gases as tracers and the processes of atmosphere-ocean exchange is presented in Chapters 3 and 10.

Of the 89 elements that have known seawater concentrations, 54 are bioactive (including the three gases that are involved in biological cycles), 23 are conservative (including the rare gases in the last column, except for radon, which is radioactive), and nine are in the adsorbed category. While the conservative elements make up more than 99% of the dissolved solids in seawater, the characterization of all measurable elements by using the vertical-profile classification scheme indicates that about two thirds are noticeably affected by biological processes and about one tenth are primarily controlled by adsorption.

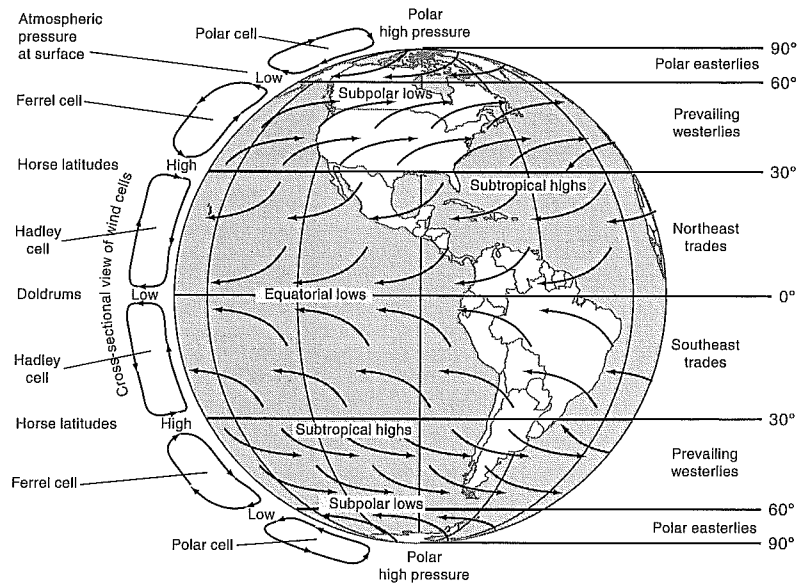
## 1.3 | Ocean circulation

Chemical dynamics and mechanisms of reactions in the ocean-atmosphere system on time scales equal to and less than that of ocean circulation are evaluated by studying the distribution of chemical compounds within the sea. In order to understand the processes controlling the chemical distributions and their rates, one must know something about how the ocean circulates. The following brief descriptive overview describes the main wind-driven and thermohaline current distributions.

### 1.3.1 Wind-driven circulation

Circulation in the near-surface ocean is driven by friction of wind on the atmosphere-ocean interface, whereas in deeper waters it is mostly density-driven. Unequal heating of the Earth's surface creates

**Figure 1.8.** The latitudinal distribution of the wind directions on the Earth's surface. (Redrafted from Pinet (1994).)



winds in the atmosphere that impart frictional energy to ocean surface waters. The mean global atmospheric wind pattern consists of east to westward flowing Trade Winds immediately north and south of the Equator, the Westerlies in mid-latitudes and the Easterlies at high latitudes (Fig. 1.8). Atmospheric pressure lows occur near the Equator and 60° latitude due to rising flow of air. Atmospheric highs are created by downward flow at about 30° in mid-latitudes. The lows are accompanied by higher than average precipitation as rising air is cooled and decreases in its moisture-carrying capacity. Highs are characteristically dry because water-poor cool air sinks, is warmed and increases its capacity to carry water vapor. These atmospheric circulation patterns contribute to the overall surface salinity distribution presented at the outset of the chapter in Fig. 1.1.

Friction on the ocean surface drags the surface water in the direction of the wind. The resulting mean flow in the upper 10-100 m, however, is not in the direction of the wind, but 90° to the right of the wind in the Northern Hemisphere and 90° to the left of the wind in the Southern Hemisphere. This flow is called *Ekman transport*. The deviations from the direction of the wind are due to the *Coriolis force*, which is not a true force but a device used to compensate for the fact that all measurements and forces are made relative to a rotating Earth. To understand the reason for this deviation from the direction of the wind forcing, assume an hypothetical particle is accelerated northward in the ocean surface somewhere near the Equator. The particle has the special properties that keep it at the same depth in the surface waters and lacks friction in the direction it is moving, allowing it to maintain the speed it was given at the beginning of the journey. When the particle leaves the equator it

has both the nor component impa Earth is a sphere, equator (455 km s turn faster than ti northward the Ea perspective of the Ea right. What is real line northward wi the Earth's equat latitudes because cle in motion to t An eastward tend movement to the moving. In the So

Since surface rents. For exam] Southern Hemis] Northern Hemis] mean Ekman tra] wind in the north in this region flow (Fig. 1.9A) in flow (*Ekman suction*). C flow converges fr and creating a lo similar effect is ca For example, the South America cr draws water away port away from t along the coast. V port resulting fro chemical and bio ling (near the Eq rich waters are t high productivity ling (i.e. the sub waters are nearly

Although Ekm of the ocean, the up local circulat of water in areas Ekman divergenc meter or so over the "valleys" it is scale gyre transp Sverdrup transport cal convergence :

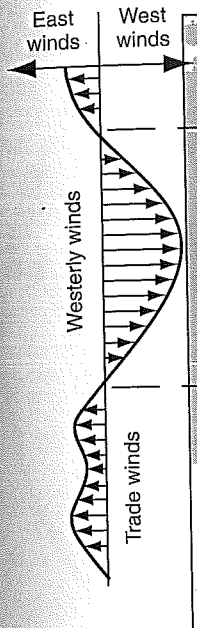
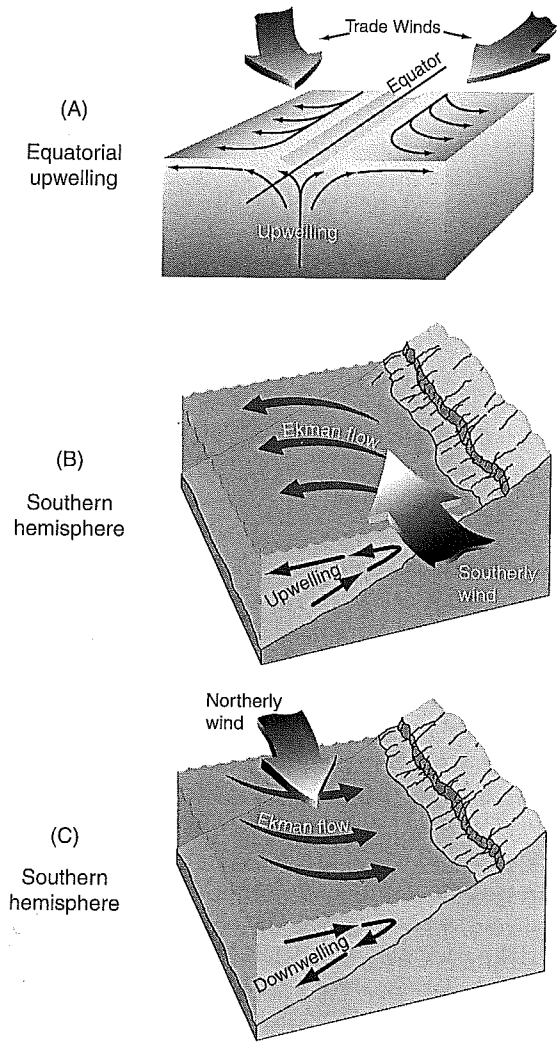


has both the northward component of velocity and an eastward component imparted by the rotation of the Earth. Because the Earth is a sphere, the eastward velocity on its surface is faster at the equator ( $455 \text{ km s}^{-1}$ ) than that at  $30^\circ \text{ N}$  or  $\text{S}$  ( $402 \text{ km s}^{-1}$ ), which is in turn faster than that at  $45^\circ \text{ N}$  or  $\text{S}$  ( $326 \text{ km s}^{-1}$ ). As the particle travels northward the Earth beneath it rotates more slowly. From the perspective of the Earth's surface the particle appears to move to the right. What is really happening is that the particle travels in a straight line northward with respect to a rotating cylinder with a diameter of the Earth's equator, but the surface of the Earth lags behind at higher latitudes because its diameter decreases poleward. Similarly, a particle in motion to the south from the Equator would veer to the east. An eastward tendency for a particle in the Northern Hemisphere is movement to the right of the direction in which the particle is moving. In the Southern Hemisphere it is to the left.

Since surface winds change directions, so do surface ocean currents. For example, the northwest-flowing Trade Winds in the Southern Hemisphere and southwest-flowing Trade Winds in the Northern Hemisphere converge at the equator. Since the resulting mean Ekman transport in surface currents is  $90^\circ$  to the right of the wind in the north and  $90^\circ$  to the left in the south, the surface waters in this region flow away from the Equator. This creates a divergence (Fig. 1.9A) in flow that is "filled in" by upwelling of water from below (*Ekman suction*). Conversely, in the subtropics (c.  $30^\circ$ ) surface water flow converges from the north and south, causing waters to "pile up" and creating a location of general downwelling (*Ekman pumping*). A similar effect is caused by flow of winds along the coasts (Fig. 1.9B, C). For example, the northward flow of winds along the Pacific coast of South America creates a surface water flow to the left (west), which draws water away from the continent (Fig. 1.9B). Surface water transport away from the land is compensated for by upwelling of water along the coast. Vertical movement of water caused by Ekman transport resulting from prevailing winds has important consequences for chemical and biological oceanography because in regions of upwelling (near the Equator and on some continental margins) nutrient-rich waters are brought from below into the sunlight resulting in high productivity and important fisheries. In locations of downwelling (i.e. the subtropical gyres) nutrient concentrations in surface waters are nearly below detection limits.

Although Ekman transport is concentrated in the upper 10–100 m of the ocean, the consequences of upwelling and downwelling set up local circulation patterns that are felt much deeper. Accumulation of water in areas of Ekman convergence and depletion of water in Ekman divergences cause horizontal gradients in water height of a meter or so over basin-scales. As the water flows from the "hills" to the "valleys" it is also influenced by the Coriolis force, creating large-scale gyre transport that is felt to much greater depths. This is called *Sverdrup transport*. An example is the Northern Hemisphere subtropical convergence zone. As water flows downhill from its high level in

**Figure 1.9.** Schematic diagrams illustrating Ekman transport in response to wind forcing at the air-water interface (A) at the Equator and (B, C) near the coastline. (Redrafted from Thurman (1994).)

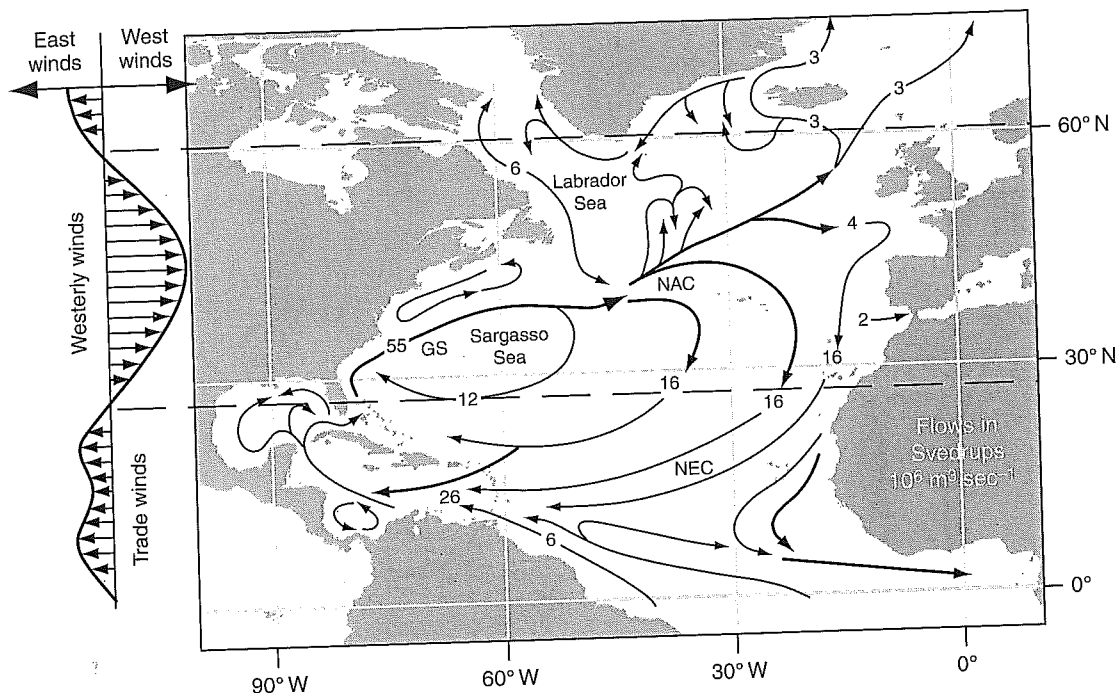


the center of the gyre it is forced to the right by the Coriolis force, creating a large-scale anticyclonic gyre (clockwise flow in the Northern Hemisphere) (Fig. 1.10). In the area of Ekman divergence between 50 and 70 °N in the subarctic oceans, flow of water into the trough is forced to the right, causing a cyclonic gyre (counterclockwise flow in the Northern Hemisphere). In theory the Sverdrup transport extends to the entire depth of the ocean; this maximal theoretical transport is called the *barotropic* component of the Sverdrup transport. In reality, however, ocean stratification at depth weakens the barotropic Sverdrup transport; this weakening is called the *baroclinic* component of the Sverdrup transport.

Warming of the surface ocean by solar heating and turbulence induced by wind stress compete to create a surface mixed layer over most of the ocean that is 10–100 m deep except in some high-latitude areas, where the ocean is mixed more deeply. In the subtropical and

subarctic oceans of the water column to solar heating (density stratification separates the upper from the winter most of the ocean

**1.3.2 Thermo**  
Below 1000–1500 transport is weak *thermohaline* circulation 1500 m consists of Mediterranean water is balanced by up surface. What so layered structure sions throughout ences. The cross masses with the North Atlantic D northward-flowing (AABW) flows be (AAIW) flows on mixed in the Antarctic and i



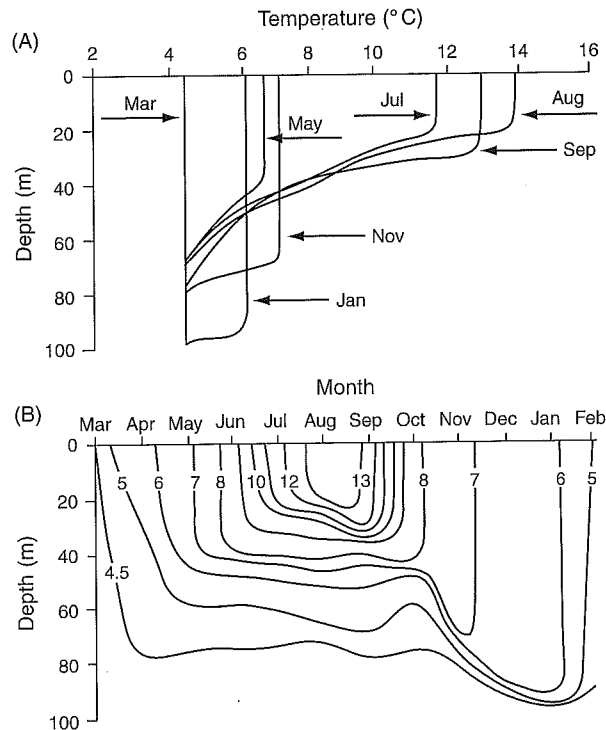
**Figure 1.10.** Schematic diagrams of the Sverdrup transport in the North Atlantic, driven by sea surface topography and the Coriolis force. Arrows indicate flow direction and the thickness indicates magnitude. Numbers are the flow rate in Sverdrups ( $10^6 \text{ m}^3 \text{ s}^{-1}$ ). GS, Gulf Stream; NAC, North Atlantic Current; NEC, North Equatorial Current. (Redrafted from Pinet (1994).)

subarctic oceans there is a “seasonal” thermocline in the upper 100 m of the water column, which shoals and strengthens in summer owing to solar heating (Fig. 1.11). The surface mixed layer gives way to density stratification in the “permanent” *pycnocline* (density gradient) that separates the upper and deep oceans and occupies the depth range from the winter mixed-layer depth (100–200 m) to 1000–1500 m in most of the ocean.

### 1.3.2 Thermohaline circulation

Below 1000–1500 m, temperature gradients are small and Sverdrup transport is weak. In this region large-scale transport is caused by *thermohaline* circulation. The overall water balance of the ocean below 1500 m consists of sinking of water in the polar regions (with salty Mediterranean water (Table 1.2) also mixed in from the side), which is balanced by upwelling and return flow from ocean depths to the surface. What sounds like a vertical balance is in reality a complex layered structure of water masses that can be traced in three dimensions throughout the ocean by salinity, oxygen and nutrient differences. The cross sections of salinity in Fig. 1.2 indicate deep water masses with the T and S properties in Table 1.2. Southward-flowing North Atlantic Deep Water (NADW) is bounded above and below by northward-flowing southern-source waters. Antarctic Bottom Water (AABW) flows beneath the NADW and Antarctic Intermediate Water (AAIW) flows on top. Water masses that reach the Southern Ocean are mixed in the Antarctic Circumpolar Water (ACW) that flows around Antarctica and is more vertically homogeneous than in other parts

**Figure 1.11.** Typical growth and decay of the seasonal thermocline in the subarctic Pacific Ocean ( $50^{\circ}\text{N}$ ,  $145^{\circ}\text{W}$ ). (A) Temperature versus depth for different months. (B) Temperature contours on a depth versus time plot. (Replotted from Knauss, 1978).



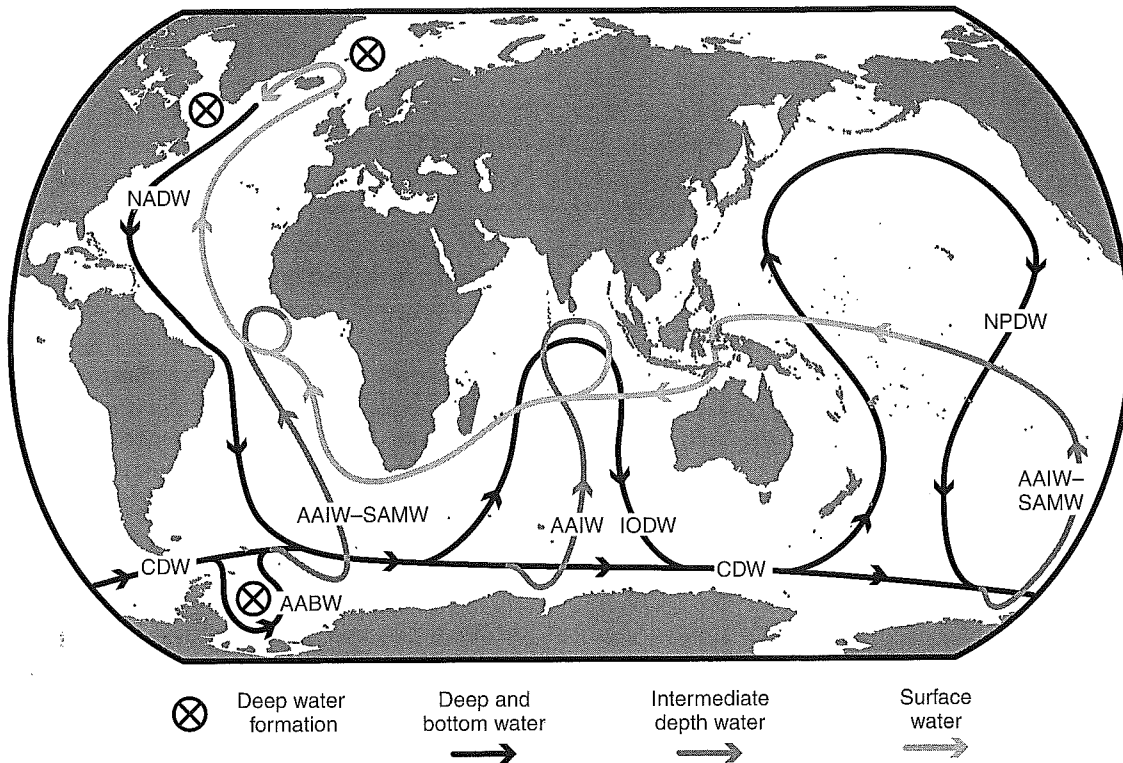
of the ocean. A deep water mass sometimes called Common Water, because it is a mixture of many water masses, enters the Indian and Pacific Oceans (Fig. 1.12). In the Indian Ocean the water flows through the Crozet basin south of Madagascar into the Arabian Sea. Common Water enters the Pacific south of New Zealand and flows northward along the western boundary of the basin at about 4 km into the Northeast Pacific. Carbon-14 dates of the dissolved inorganic carbon of deep waters reveal that the “oldest” water in the deep sea resides in the Northeast Pacific. This means that this water has been isolated from the surface ocean (where the clock is reset or partly reset for  $^{14}\text{C}$ ) longer than any other water in the deep sea.

The original theories of deep-ocean circulation assumed that the return flow from deep water formation was uniform global ocean upwelling through the thermocline. This rising flow created the concave upward temperature and salinity profiles of the deep ocean below 1000 m. More modern concepts and tracer interpretation suggest that bottom water flows north in the Pacific Ocean, upwells, and returns south as the North Pacific Deep Water (NPDW) between 2000 and 3000 m depth. This water eventually makes its way into the thermocline and mixed layers and back to high-latitude regions of deep-water formation in the North Atlantic.

The deep water flow in the ocean is often depicted as a “conveyor belt” in which water that originates at the surface in the North Atlantic Ocean (NADW) flows through the Atlantic, Indian and Pacific Oceans before it upwells and returns (Fig. 1.12). The analogy

**Figure 1.12.** The lines, respectively. Xs. The North Atlantic south to the Antarctic ice shelf around Antarctica Ocean, where it enters Intermediate and Deep in the figure. (Moo

is that deep water of organic matter from near-surface upwelling regulates the rate of the chemical processes removed from origin. This is concentration of Pacific to North recognize that waters have arrived in Fig. 1.12. The circulation is properties of



**Figure 1.12.** The flow directions of the major deep and intermediate waters of the oceans, indicated by the black and dark gray lines, respectively. Shallower return flow is indicated by the light gray line. Locations of deep water formation are indicated by circled Xs. The North Atlantic Deep Water (NADW) occupies 1000–4000 m in the Atlantic and flows from the Norwegian and Greenland Seas south to the Antarctic, where it joins the Circumpolar Deep Water (CDW). Antarctic Bottom Water (AABW) is formed under Antarctic ice shelves, flows north in the Atlantic Ocean and becomes entrained in the CDW, where it joins NADW in the path around Antarctica and into the Indian Ocean, where it becomes Indian Ocean Deep Water (IODW), and ultimately to the Pacific Ocean, where it eventually becomes North Pacific Deep Water (NPDW). The ocean above about 1000 m is ventilated by Intermediate and Mode Waters. The paths of the Antarctic Intermediate (AAIW) and Subantarctic Mode Waters (SAMW) are shown in the figure. (Modified from Gnanadesikan and Halberg (2002).)

is that deep water accumulates metabolic residue from degradation of organic matter and dissolution of opal and calcite that originates from near-surface biological processes just as a conveyor belt accumulates the rain of dust as it proceeds through a factory. Thus, the chemical properties of the NADW become progressively more removed from those of surface waters as it moves at depth from its origin. This is nicely illustrated by the progressive increase in concentration of nutrient phosphate from the North Atlantic to South Pacific to North Pacific in deep waters (Fig. 1.4). It is important to recognize that the conveyor belt analogy ignores the fact that bottom waters have another surface origin in Antarctica (AABW) as depicted in Fig. 1.12. The reason that AABW is not part of the conveyor belt circulation is that these waters do not originate with the chemical properties of low-latitude surface waters as they do in the NADW.

Antarctic Bottom Water, AABW, is formed from water that upwells to the surface in the Antarctic, but it doesn't reside there long enough for biological processes and gas exchange to "reset" nutrient and oxygen concentrations. The circumpolar Southern Ocean acts more as a mixing region for all the water masses that flow there than as a location of renewal of surface water properties to nutrient-poor and oxygen-rich values. We must keep in mind when using the simple conveyor belt analogy that it refers primarily to NADW and does not represent all deep water flow. In reality water masses mix in the deep ocean and upwelling occurs along many regions of the flow path that ultimately leads to the North Pacific.

## 1.4 | Ocean biology

Nearly all chemical reactions in the sea take place via biological metabolism or are catalyzed by biologically produced enzymes. Overwhelmingly, the most important of these processes are photosynthesis and respiration. Photosynthesis uses the sun's energy to create ordered organic compounds that consist of roughly 65% proteins, 20% lipids and 15% carbohydrates. Most of the organic matter produced during marine photosynthesis is in the form of very small (diameter  $<100\ \mu\text{m}$ ) particles, but some is in the form of dissolved organic matter (DOM). Some of the microscopic plants and animals create shells in the form of inorganic minerals that consist primarily of calcite and aragonite ( $\text{CaCO}_3$ ) and opal ( $\text{SiO}_2$ ). Between 10% and 30% of the organic matter and most of the mineral armor produced in the euphotic zone escapes by gravitational settling or water transport and is degraded or dissolved at depth, where it joins the conveyor belt circulation in dissolved inorganic form. A small fraction (0.1%–1.0%) of the particulate organic material produced at the surface escapes all the way to the bottom and accumulates in marine sediments; a greater fraction of the minerals escapes dissolution and is deposited in the sediments.

In order to understand the role of plants and animals in distributing chemical compounds in the sea one must understand something about the biological agents that perform these tasks. In this text we will focus on biota with sizes smaller than a few millimeters in diameter, which includes by far the most important community affecting the distribution of chemical compounds in the sea. As mentioned earlier, the distinction between dissolved and particulate material is usually operationally defined as the material that is separated by passing water through a filter with pore size  $0.45\ \mu\text{m}$ . Particulate material captured this way in the open ocean generally contains a small fraction of the total carbon and other chemical elements found in seawater. Even for carbon, which is the most abundant element in particulate material, the  $>0.45\ \mu\text{m}$  fraction contains  $\leq 1\ \mu\text{mol kg}^{-1}\ \text{C}$  below the euphotic zone relative to the c.  $40\ \mu\text{mol kg}^{-1}\ \text{C}$  found in the dissolved organic form (DOC).

Suspended particles whereas particles can sink as rapid

Plankton are internal structure: ( $<2\ \mu\text{m}$ ), *nanoplankton* ( $>200\ \mu\text{m}$ ) guishes those s) inorganic matter and those that g existing organic (ton). There are a f net heterotrophy based on wheth internal organel that have them a

### 1.4.1 Plankton Bacteria

Bacteria are prokaryotic species that are present in concentrations in seawater, with the importance of photosynthesis in the upper euphotic zone (cyanobacteria. Synechococcus dominate the picoplankton (the term phytoplankton later.) These species contain light absorbing pigments. Chlorophyll was discovered in the 19th century. epifluorescence microscopy of microscopic living organisms. energy from chemical "chemoautotrophic" bacteria. cers of organic matter in basins like the Black Sea. production by the origin of life, but that produced by photosynthesis as *Trichodesmium*.  $\text{N}_2$  gas into  $\text{NH}_3$ . compounds are in vast quantities. gives the nitrogen. are poor in dissolved. Heterotrophic bacteria. dual entities in the and sediments. because they have

Suspended particles with a size  $<20\ \mu\text{m}$  sink very slowly ( $<1\ \text{m d}^{-1}$ ) whereas particles as large as  $100\ \mu\text{m}$  in diameter, usually fecal pellets, can sink as rapidly as  $100\ \text{m d}^{-1}$ .

Plankton are categorized by their size, metabolic function, and internal structure. The size classification consists of *picoplankton* ( $<2\ \mu\text{m}$ ), *nanoplankton* ( $2\text{--}20\ \mu\text{m}$ ), *microplankton* ( $20\text{--}200\ \mu\text{m}$ ), and *mesoplankton* ( $>200\ \mu\text{m}$ ). The classification by metabolic function distinguishes those species that create organic matter from dissolved inorganic matter, the *autotrophs* (phytoplankton and some bacteria), and those that gain energy and nutrition by consuming previously existing organic matter, the *heterotrophs* (some bacteria and zooplankton). There are a few species that can exist by both net autotrophy and net heterotrophy; these are called *mixotrophs*. The final distinction is based on whether single-celled organisms contain a nucleus and internal organelles; those that have none are *prokaryotes* and those that have them are *eukaryotes*.

### 1.4.1 Plankton

#### Bacteria

Bacteria are prokaryotes in the range of  $1\ \mu\text{m}$  in size and consist of species that are both autotrophic and heterotrophic. Bacterial concentrations range from  $10^5$  to  $10^7$  cells per cubic centimeter of seawater, with higher concentrations in the surface ocean. The importance of photoautotrophic bacteria in the role of photosynthesis in the upper ocean has been discovered relatively recently. The cyanobacteria *Synechococcus* and *Prochlorococcus* are now believed to dominate the picophytoplankton in most oceanic regimes. (We use the term phytoplankton because of their autotrophic behavior; see later.) These species are believed to contain most of the green, light-absorbing pigment, chlorophyll, in these regions. Their importance was discovered in the 1970s and 1980s with the development of epifluorescence microscopy as a routine method for studying microscopic living organisms. Species of autotrophic bacteria that generate energy from chemical reactions rather than from sunlight are called "chemoautotrophic" and play an important role as primary producers of organic matter at oxic-anoxic interfaces found in anoxic basins like the Black Sea, and at hydrothermal vents. Organic matter production by this energy pathway may have been important for the origin of life, but in today's ocean it represents only a tiny fraction of that produced by photoautotrophy. Larger prokaryotic bacteria such as *Trichodesmium* form colonies in surface waters and are known to fix  $\text{N}_2$  gas into  $\text{NH}_3$  in regions of the ocean where other nitrogen compounds are in very low concentration. This opportunistic behavior gives the nitrogen fixers an advantage in regions of the oceans that are poor in dissolved nitrogen relative to other nutrients.

Heterotrophic bacteria exist throughout the ocean both as individual entities in seawater (c. 80%) and attached to particle surfaces and sediments. These bacteria consume dissolved organic matter because they have no means other than dissolved transport across

membranes to internalize nutrients. Some may secrete enzymes, which break down large molecules so they can be transported across the cell walls. In the euphotic zone of the ocean heterotrophic bacteria play an important role in organic matter recycling. Below the euphotic zone and in sediments heterotrophic bacteria, in collaboration with larger animals, are responsible for the vast majority of organic matter respiration.

### Phytoplankton

Phytoplankton are unicellular autotrophs which contain the chlorophyll measured in the particulate matter filtered from seawater. The prokaryotic, autotrophic bacteria discussed above are included in this classification, but it is not limited to them. There are many phytoplankton that are eukaryotes. In addition to the autotrophic bacteria there are three other principal types of phytoplankton: diatoms, coccolithophorids, and photoautotrophic flagellates. Diatoms are nano-micro in size, but often form colonies that can be greater than 1 mm long. Their primary distinction is that they produce silica frustules that can be identified under high magnification (Fig. 1.13). Because of the opaline frustules, diatoms control the dissolved silica cycle in the sea, which is characterized by low concentrations in surface waters that increase with depth (Fig. 1.5). These phytoplankton dominate in regions of the ocean where upwelling is important, such as the Southern Ocean and regions of coastal upwelling. A portion of the silica frustules that leave the surface ocean are preserved in sediments. In areas such as the Southern Ocean around Antarctica the sediments consist predominately of diatom frustules because of their dominance in the surface waters. Observations of diatom frustules in sediments and "diatomaceous earth" deposits for the past 100 million years indicate that they have been important phytoplankton since the Cretaceous Period.

Some coccolithophorids are classified as nanoplankton and produce calcite ( $\text{CaCO}_3$ ) plates called coccoliths that protect their protoplasm (Fig. 1.13). Generally coccolithophorids are rarer than diatoms and tend to be most abundant in subtropical gyres and in warm waters. *Emiliana huxleyi* is the most abundant coccolithophorid. Because their calcareous plates reflect light, blooms of coccolithophorids can be seen from space by using satellite images (Brown and Yoder, 1994). A spectacular bloom was observed in September of 1997 in the eastern Bering Sea; this had never been seen before in this region and was probably associated with warmer than usual sea surface temperatures. The calcitic coccoliths make up the bulk of the  $\text{CaCO}_3$ -rich sediments presently preserved in the ocean; nearly pure coccolith deposits such as in the White Cliffs of Dover, England, provide geological evidence that the coccolithophorids have existed for the past 170 million years.

Photoautotrophic flagellates are pico to nanometer-sized plankton, usually with two flagella, whip-like appendages that beat within grooves in the cell wall. They are found in most regions of the ocean,

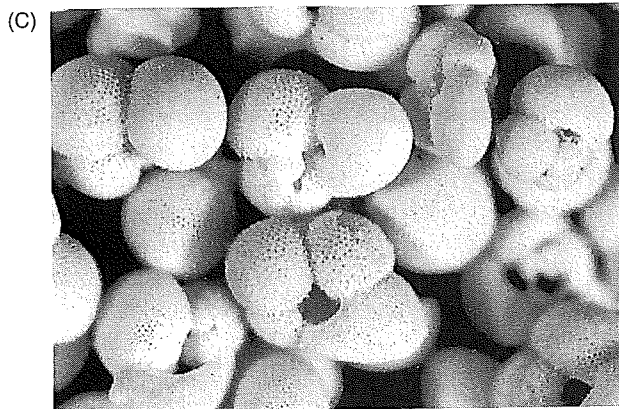
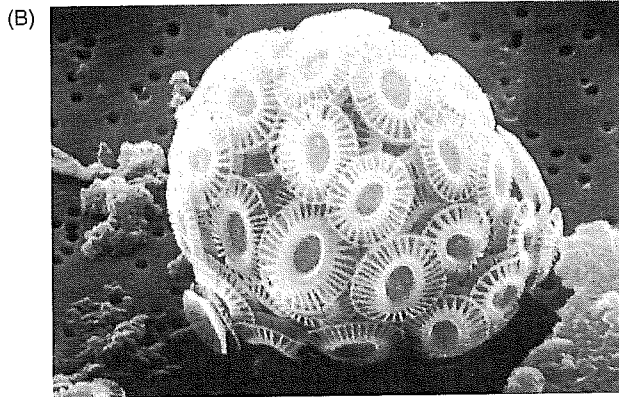
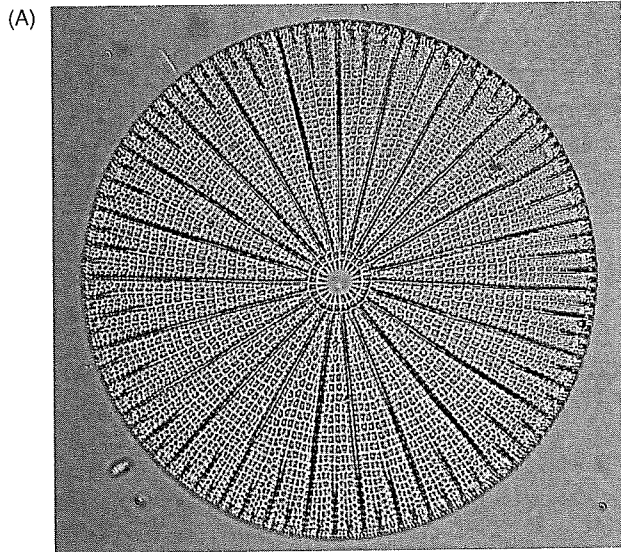
(A)

(B)

(C)

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marine sediments. I  
flagellate with red to  
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**Figure I.13.** Scanning electron micrographs of (A) a diatom frustule (opal), diameter c.20  $\mu\text{m}$ ; (B) a coccolithosphere with armor-like coccoliths on a filter paper ( $\text{CaCO}_3$ ), diameter c.10  $\mu\text{m}$ ; and (C) foraminiferan shells ( $\text{CaCO}_3$ ), from marine sediments, diameter c.100–200  $\mu\text{m}$ . ((C) courtesy of Kathy Newell, University of Washington.)

but they contain no mineral “shell” and are thus poorly preserved in marine sediments. Dinoflagellates are a kind of photoautotrophic flagellate with red to green pigments; they can form large blooms in coastal waters that are sometimes called “red tides.”

### Zooplankton

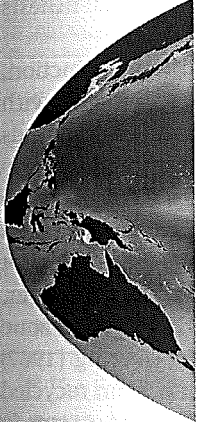
Zooplankton obtain their energy heterotrophically by grazing on both smaller phytoplankton and other zooplankton. They are eukaryotic and exist in sizes from nanometers to centimeters. Food webs that contain pico- and nanometer-sized phytoplankton are generally dominated by nanometer-sized flagellate zooplankton with very fast growth rates. They feed by direct interception, sieving, and filtering. Ciliate zooplankton are a little larger than flagellates and graze on flagellates and small diatoms. Heterotrophic dinoflagellates are larger, nano- to micrometer-sized heterotrophs, and graze on nanophytoplankton and nanozooplankton.

The only zooplankton of any abundance that form mineral shells (or tests) are the Foraminifera, Pteropoda and Radiolaria, which form tests of  $\text{CaCO}_3$  (usually calcite),  $\text{CaCO}_3$  (aragonite) and  $\text{SiO}_2$  (opal), respectively. Of the larger zooplankton (copepods, euphausiids, and crustaceans) copepods play an important role in the flux of chemical species to the ocean interior because they create large (c. 100  $\mu\text{m}$ ) fecal pellets that sink very rapidly (c. 100  $\text{m d}^{-1}$ ) into the deep sea. Sediment trap experiments have shown that fecal pellets often dominate the particle flux in the deep ocean. This can have important consequences for the distribution of metabolic products because their rate of release to the water in dissolved form depends on both the degradation and dissolution rates as well as their sinking velocity. The sinking rate greatly depends on the density difference between the particles and seawater, so fecal pellets that contain the minerals of  $\text{CaCO}_3$  and  $\text{SiO}_2$  will sink much faster than those that only contain organic matter.

#### 1.4.2 Marine metabolism: estimates of abundance and fluxes

The presence and distribution of phytoplankton in the sea is determined primarily by the abundance of chlorophyll. Although this is not a direct measure of the number of cells, because they contain different amounts of chlorophyll under different conditions, it is the most rapid and widely used method of identifying the presence of photosynthetic organisms. Because the color of the ocean can be determined by satellites, it is possible to determine the global content of chlorophyll in the sea over one optical depth, about the first 30 m of surface waters.

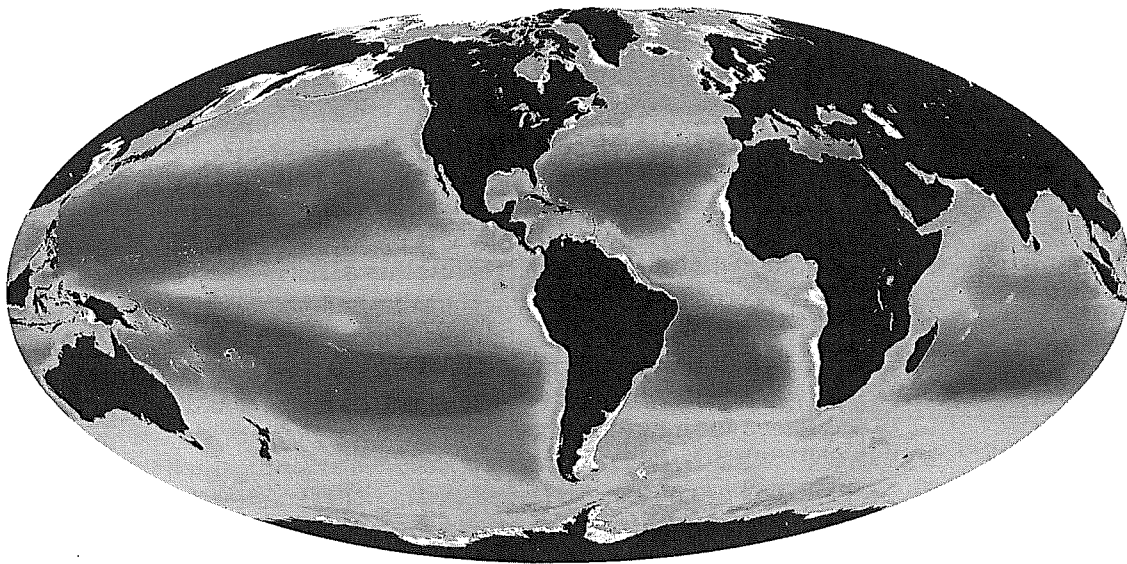
The rate of primary production in the sea is determined by incubating samples with  $^{14}\text{C}$ -labeled DIC and then measuring the amount of the  $^{14}\text{C}$  that is taken up into the particulate material. These experiments are done *in situ* in glass bottles attached at different depths to a floating mooring over a period of 12–24 h or on board ship under controlled temperature and light conditions. It is assumed that the  $^{14}\text{C}$  uptake measures only phytoplankton metabolism because marine zooplankton are not abundant enough or rapid enough grazers to affect the results. A complication arises in interpreting the incubation data because photosynthetic organisms are both autotrophic (during the day) and heterotrophic (during both day and night).



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The biological atmosphere and th to the deep ocean. proportional to ne toplankton produ



Although the net result is autotrophic, they both create organic matter and respire organic matter at different times in their metabolic cycle. The creation of organic compounds from DIC by phytoplankton is called *gross photosynthesis*. The net result of phytoplankton autotrophy and heterotrophy is called *net photosynthesis*.  $^{14}\text{C}$  uptake experiments are believed to measure a flux closer to net than to gross photosynthesis (Marra and Barber, 2004). There are other experimental complications in interpreting the results from these experiments, such as differences between *in situ* and on board incubations, DOM production (which is usually not measured), and possible trace metal contamination from chemical spikes and glassware. None the less, this approach is the most used direct estimate of the flux of carbon through marine autotrophic organisms.

Although one does not expect a direct relationship between the standing stock of marine phytoplankton, as inferred from chlorophyll concentrations, and the rate of DIC transformation to organic carbon, as determined by  $^{14}\text{C}$  incubation experiments, there are regional correlations. These relations have been used with satellite color measurements to estimate global marine primary production (Fig. 1.14). One caveat to keep in mind, however, is that a satellite measures color over only one optical depth. Although biological oceanographers attempt to compensate for this and other factors, there is presently no accurate way to relate surface chlorophyll concentrations with euphotic zone photosynthetic productivity in vast regions of the ocean.

The biological process that most influences the chemistry of the atmosphere and the sea is the flux of organic matter from the surface to the deep ocean. This flux, called the *biological pump*, is not directly proportional to net photosynthesis, as the latter refers only to phytoplankton production. In a steady-state situation or on an annual

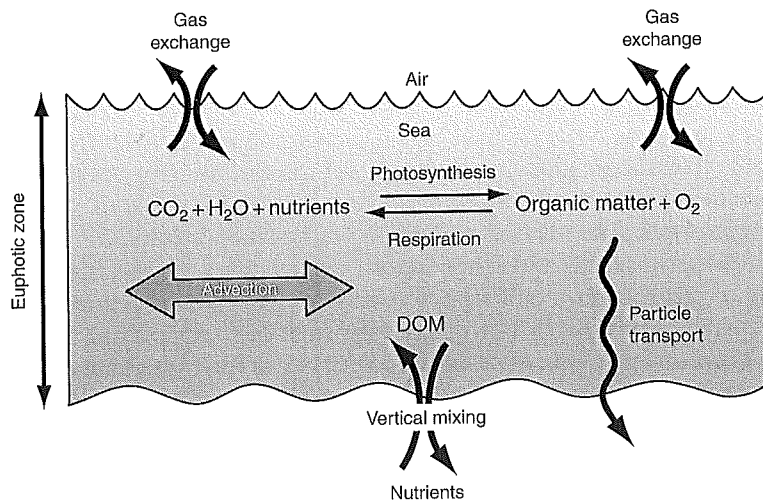
**Figure 1.14.** A global map of surface-ocean chlorophyll derived from satellite ocean color imagery. Images like this are used to determine relative distributions of ocean primary production; however, these are approximate because the relation between surface ocean color and primary productivity is variable and in some cases uncertain. The figure is the average of c. 10 years of SeaWiFS ocean color data, 1997–2007. (The image is from the NASA/MODIS ocean color web site, <http://oceancolor.gsfc.nasa.gov>.) (See Plate I.)

average basis, the mean organic carbon flux out of the euphotic zone should equal the *net community production* of organic carbon. Net community production is the difference between net photosynthesis and heterotrophic respiration occurring in the water.

There is no direct measure of net community carbon production, but methods have been devised, by using incubation techniques with nitrogen isotopes, to determine the uptake of nitrogen compounds ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and urea). During photosynthesis  $\text{NH}_4^+$  and urea are preferred by phytoplankton because they do not need to be reduced before incorporation into organic compounds. Because of this they are taken up immediately when released during respiration and they do not accumulate above very low concentrations in the water.  $\text{NO}_3^-$ , however, accumulates in relatively high concentrations below the euphotic zone and in surface waters at high latitudes. Dugdale and Goering (1967) called the  $^{15}\text{NO}_3^-$  uptake *new production* to distinguish it from recycled production, which is represented by  $^{15}\text{NH}_4^+$  (and urea) uptake. At steady state, over an annual cycle, the rate of  $\text{NO}_3^-$  uptake by photosynthesis should equal the flux of  $\text{NO}_3^-$  into the euphotic zone, which must also equal the particulate and dissolved organic N flux out of the euphotic zone. The fraction of dissolved nitrogen uptake in the euphotic zone that is delivered by  $\text{NO}_3^-$  varies from about 0.1 in regions where there is a well-developed food web to recycle phytoplankton production, to 0.8 in bloom regions where grazers have not become well established.

In an ideal steady-state world the flux of organic carbon from the upper ocean would be equal to net community production, which would be related via a stoichiometric ratio of C:N to new production. This relationship was first suggested by Eppley and Peterson (1979) who termed the ratio of new to total production the *f-ratio*. A schematic picture of the processes that lead to the creation and transport of organic matter from the surface to the deep ocean is presented in Fig. 1.15. Nearly all the reaction rates and reservoir fluxes for N, C and  $\text{O}_2$  in the figure have been measured. Relating the fluxes of the

**Figure 1.15.** A schematic diagram of processes influencing the mass balance of organic matter and oxygen in the euphotic zone of the ocean. Photosynthesis produces organic matter and oxygen; respiration consumes them. Organic matter escapes via settling of particulate organic matter and mixing or advection of dissolved organic matter (DOM) out of the surface ocean. Oxygen leaves by gas exchange between the atmosphere and ocean and mixing or transport to deeper waters.



**Table 1.6.** Stoichiometry of photosynthesis and the ocean. All values are relative.

Source

- Redfield et al., 1963<sup>a</sup>
- Anderson and Sarmienta, 1995<sup>c</sup>
- Anderson, 1995<sup>c</sup>
- Kortzinger et al., 2001<sup>d</sup>
- Hedges et al., 2002<sup>e</sup>

<sup>a</sup>The first and original values for the ocean deep waters are based on constant density sigma-t.   
<sup>b</sup>This value used the sigma-t.   
<sup>c</sup>These values were determined from plankton, with the same sigma-t.   
<sup>d</sup>These values are based on constant density sigma-t.   
<sup>e</sup>These values were determined from a C:P ratio of 106 is a

nutrients N and P to the total organic matter produced about the stoichiometry of photosynthesis and respiration. The ratios of organic compounds are used to determine the Redfield ratios after Alfred Redfield's classic work (Table 1.6) by modern methods. His classic values are based on constant density sigma-t. The rate of organic matter production in the deeper waters are determined by modern methods.

## References

Anderson, L. A. (1995) On the stoichiometry of phytoplankton. *Deep-Sea Research* 42, 101-110.  
 Anderson, L. A. and J. L. Sarmienta (1995) The stoichiometry of phytoplankton determined by nutrient bioassays. *Deep-Sea Research* 42, 111-120.  
 Boyle, E.A. (1988) Cadmium in the ocean. *Paleoceanography* 3, 471-480.  
 Broecker, W.S. and T.F. Andersen (1985) Geological Observatory

Table 1.6. Stoichiometric "Redfield" ratios for consumption of P, N, C and production of O<sub>2</sub> during photosynthesis and the opposite reaction during respiration in the ocean

All values are relative to a phosphorus value of 1.0.

Source	Organic matter			O <sub>2</sub>
	P	N	C	
Redfield <i>et al.</i> , 1963 <sup>a</sup>	1.0	16	106	138
Anderson and Sarmiento, 1994 <sup>b</sup>	1.0	16 ± 1	117 ± 14	170 ± 10
Anderson, 1995 <sup>c</sup>	1.0	16	106	141–161
Kortzinger <i>et al.</i> , 2001 <sup>d</sup>	1.0	17.5 ± 2.0	123 ± 10	165 ± 15
Hedges <i>et al.</i> , 2002 <sup>e</sup>	1.0	17	106	154

<sup>a</sup>The first and original stoichiometry was determined from observations of the NO<sub>3</sub><sup>-</sup>:PO<sub>4</sub><sup>3-</sup> ratios in ocean deep waters and then assuming a stoichiometry for organic matter.

<sup>b</sup>This value used the same approach as <sup>a</sup> and included DIC and O<sub>2</sub> on dineutral surfaces below 400 m.

<sup>c</sup>These values were determined by using C, H and O content of organic compounds that make up plankton, with the assumption that there are 106 moles of C per mole of P.

<sup>d</sup>These values are based on measurements of DIP, DIN, DIC (corrected for anthropogenic CO<sub>2</sub>) and O<sub>2</sub> on constant density surfaces.

<sup>e</sup>These values were determined by chemical and NMR analysis of marine planktonic organic matter. A C:P ratio of 106 is assumed.

nutrients N and P to those of C and O<sub>2</sub> requires some assumptions about the stoichiometry of their production and degradation during photosynthesis and respiration. The ratios at which these elements or compounds are used during marine metabolism are today called *Redfield ratios* after Alfred Redfield, who first suggested that they are constant. His classic values of P:N:C:O<sub>2</sub> have been modified recently (Table 1.6) by modern measurements of the dissolved inorganic ratios on constant density surfaces in the deep ocean and from more accurate knowledge of the elemental makeup of organic matter. The details behind the calculation of Redfield ratios and more about the rates of organic matter transfer between the euphotic zone and deeper waters are discussed in Chapter 6.

## References

- Anderson, L. A. (1995) On the hydrogen and oxygen content of marine phytoplankton. *Deep-Sea Res.* **42**, 1675–80.
- Anderson, L. A. and J. L. Sarmiento (1994) Redfield ratios of remineralization determined by nutrient data analysis. *Global Biogeochem. Cycles* **8**, 65–80.
- Boyle, E.A. (1988) Cadmium: chemical tracer in deepwater paleoceanography. *Paleoceanography* **3**, 471–89.
- Broecker, W.S. and T.-H. Peng (1982) *Tracers in the Sea*. Lamont-Doherty Geological Observatory.

