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Introduction to chemical oceanography

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

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_2 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_2 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.

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

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

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 × 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
Concentrations in aqueous solution				
Molal	mass	mol kg^{-1}	m	Moles per kilogram of solvent
Molar	volume	mol l^{-1}	M	Moles per liter of solution
Normal	volume	eq l^{-1}	N	Equivalents per liter of solution
Weight ratio	mass	g kg^{-1}		Mass of solute per mass of solution
Volume ratio	volume	ml l^{-1}		Volume of solute per volume of solution
Seawater units	mass	mol kg^{-1}		Moles per kilogram of solution
Seawater units	mass	eq kg^{-1}		Equivalents per kilogram of solution
Concentrations in the atmosphere				
Mole fraction	moles	mol mol^{-1}	X	Moles of gas per moles of dry air (= volume fraction, e.g. ppmv, for ideal gas)
Fugacity	pressure	bar bar^{-1}	f	Gas pressure per atmospheric pressure (= partial pressure, p, for ideal gas)

(b) Exponential terminology used in oceanography

Prefix (symbol)	peta- (P)	tera- (T)	giga- (G)	mega- (M)	milli- (m)	micro- (μ)	nano- (n)	pico- (p)	femto- (f)	atto- (a)
Unit multiplier	10^{15}	10^{12}	10^{9}	10^{6}	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}	10^{-18}

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_2. 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

$$\mathrm{Ag^+} + \mathrm{Cl^-} \rightleftarrows \mathrm{AgCl_{(s)}}, \tag{1.1}$$

which is quantitative. The chloride concentration, $[\mathrm{Cl^-}]$, could then be related to salinity, S, via a constant number,

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

where ppt indicates parts per thousand ($\mathrm{g_{solute}\ kg^{-1}_{seawater}}$). 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).

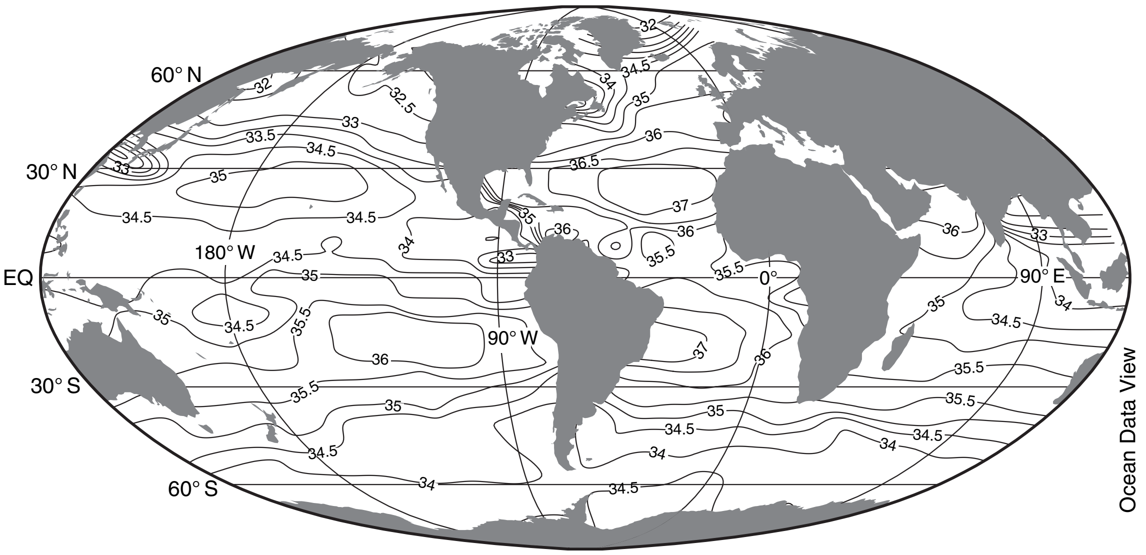

Figure 1.1. Annual mean surface salinity of the world's ocean. (Plotted by using Ocean Data View (Schlitzer, 2001), and surface salinity in Levitus *et al.* (1994).)

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^{-3}, 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, σ, which has the following definition

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

where ρ is the density of the sample (kg m^{-3}) and ρ_0 is the maximum density of water at 3.98 °C (999.974 kg m^{-3}). (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), σ_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, θ, is the temperature the water sample would have if it were raised to the surface with no exchange of temperature 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, σ_θ.

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

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

[a] AABW, Antarctic Bottom Water
[b] NADW, North Atlantic Deep Water
[c] MW, Mediterranean Water
[d] AAIW, Antarctic Intermediate Water
[e] *T* and *S* characteristics from Picard and Emery (1982)
[f] Flow rates are in Sverdrups (10^6 m^3 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 °C) than North Pacific surface water (6.7 °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, $S = 33.0$–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 ± 4 °C and ± 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

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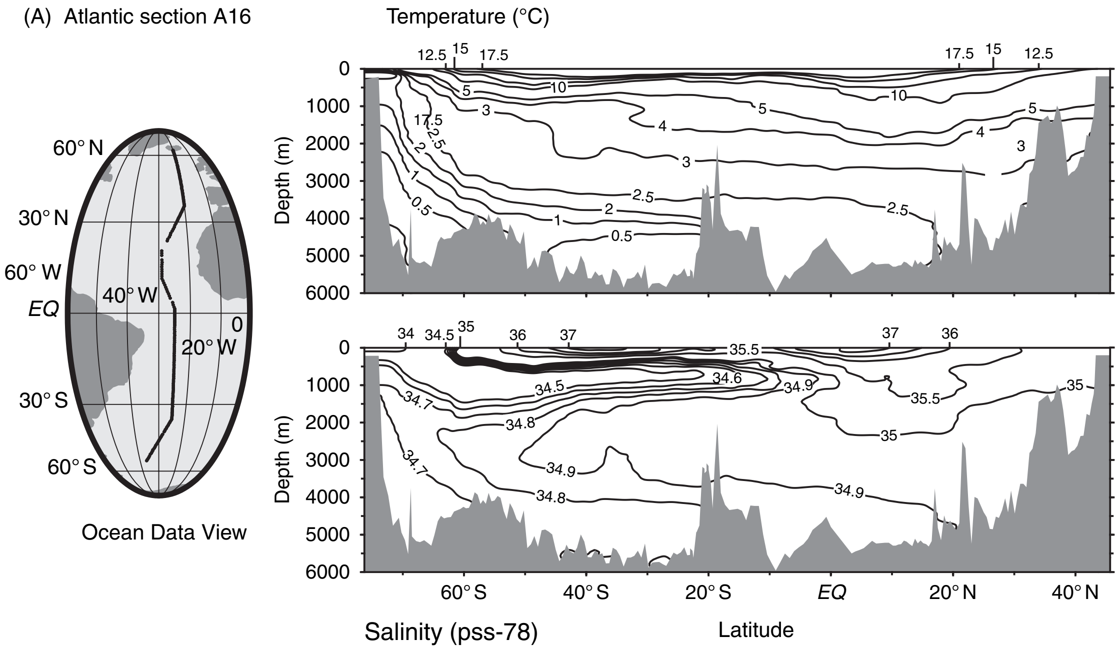
(A) Atlantic section A16



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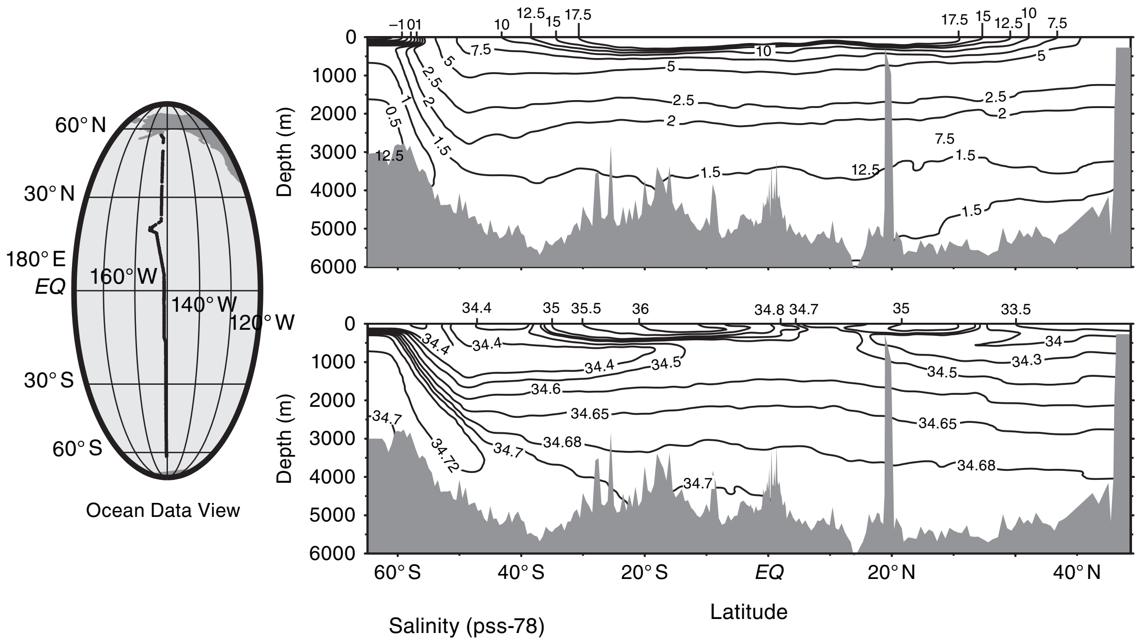

Figure 1.2. Latitudinal cross section of the potential temperature and salinity of the Atlantic (A) and Pacific (B) oceans. Different water masses are definable by their characteristic temperature and salinity (Table 1.3). (Plotted by using Ocean Data View and WOCE hydrographic data (Schlitzer, 2001).)