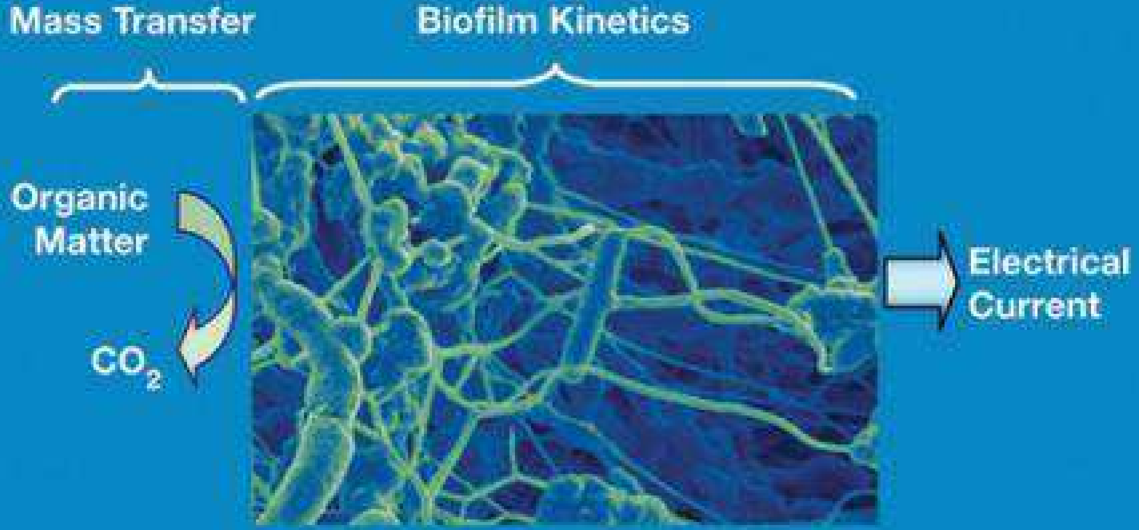
Second Edition

Environmental Transport Processes

Bruce E. Logan


Mass Transfer
Biofilm Kinetics
Organic Matter
CO_2
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To Angela, Alex and Maggie,
for their love and support

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PREFACE

This book was written for Environmental Engineering graduate students as a first course in mass transfer, and for Chemical Engineering students or others who have had a mass transport course but have had no substantial experience in environmental topics. For others interested in the subject of transport phenomena in natural and engineered environmental systems, this book may serve as a reference. Most transport phenomena textbooks are written for chemical engineers designing and operating systems that function under very controlled conditions. When the focus is on chemical production the context of the system is necessarily concentrated chemical solutions often under conditions of high temperature and pressure where the behavior of the solutions is non-ideal. Mathematical models developed for these circumstances are necessarily complex but are restricted to systems that are highly defined.

In this text, the focus is on environmental systems, which typically operate at ambient temperatures and pressures, that can be exceedingly complex in terms of the properties of the chemicals involved. For example, the main components in a natural water sample are humic and fulvic acids, which have no exact chemical structure. Such a poor definition of system components would be unacceptable to a chemical engineer designing a chemical reactor, but the situation is unavoidable in an environmental system. Thus, transport problems derived for environmental systems focus on making transport calculations in highly heterogeneous, and often poorly defined, environments.

The unique focus of this environmental transport text is on the biological and physical interface. Environmental engineers often seem to focus on biological systems and the chemical interface, or the chemical-physical interface. Here, transport and kinetics are both addressed particularly in terms of systems that involve microorganisms, such as aggregates and biofilms. In addition, there is substantial emphasis in the latter chapters on particles, size spectra, and calculations for particles that can be considered both spheres and fractals. While environmental engineers often deal with particle management in an engineered system (such as coagulation and filtration processes), there is little appreciation for how different these processes function due to the fractal nature of the particles. Therefore, there is a focus here on how the fundamental equations can be altered to include the fractal nature of the particles.

In developing this material, I have had to combine information from many different fields. For example, in the early chapters I built upon the approach used by L.J. Thibodeaux in his text *Chemodynamics*. In Chapters 1 and 2 in *Environmental Transport Processes (ETP)*, the description of chemical partitioning will seem familiar to those who have used Thibodeaux's book. Thereafter, material presented in *ETP* is quite different. While Thibodeaux assumed the reader was well versed in transport phenomena, in this book much of the material is devoted to covering transport fundamentals. In Chapter 3 of *ETP,* I therefore present the fundamentals of molecular diffusion and emphasize how diffusivities and molecular size distributions are determined for heterogeneous samples typical of waters and wastewaters. Chapters 4–6 are developed along the lines of more classical chemical engineering calculations and create the "toolbox" of mathematical equations and solutions used in later chapters. Chapters 7–9 combine a great many diverse fields for describing transport in reactors, particularly those with microorganisms. In the last Chapters 10-12 the emphasis is on natural systems both from dispersion of chemicals in solution as well as the slow dissolution from immiscible chemicals such as non-aqueous phase solutions. The last three chapters describe particle dynamics, and were developed using several textbooks and my notes from classes with Dr. James Hunt at the University of California, Berkeley, when I was a graduate student there.

It has been over ten years since the first edition of this book was published, and since then I have pondered how the material might be better edited and presented. In this second edition, I have therefore substantially edited the original text, put in some new information as well as taken out materials that just never seemed to fit or get used. For the first edition, every equation, superscripted or subscripted letter, and Greek letter was completely re-typed by Wiley production staff. In this second edition, I had the opportunity to prepare a camera-ready version that did not need equations to be reformatted. Hopefully this has minimized any errors in the book, but as always I will post any needed corrections to my website.

I have prepared typed solutions to the hundreds of problems at the end of the chapters that I will make available to faculty and instructors that use the book. I am told that these files can be put onto the Wiley website for restricted access. Along with those solutions I will post other computer-based presentations or notes that may be useful to instructors using this book. There is actually still more in the text that can be covered in one semester, so instructors may wish to save some of the later chapters for a separate course, that for example would build only upon particles and fractals.

An enormous number of people have contributed to the first and second edition of this text both directly and indirectly. I am extremely grateful to the excellent and rigorous training given by my transport mentors at UC Berkeley, James Hunt and Hugo Fisher. The material collected here in this book is also due to some wonderful collaborations with my colleagues, especially Alice Alldredge, Robert Arnold, David Kirchman, and Charlie O'Melia. I sincerely appreciate help from the reviewers of the first edition chapters, James Hunt, Bill Ball, James Farrell, Xiaoyan Li, Susan Powers, Lily Sehayek, Kenny Unice, and Terri Camesano. In this second edition, I was fortunate to have wonderful and much appreciated help in reformatting and editing Chapters 2–12 and 15 by Sarah Hayes, Fang Zhang, Yimin Zhang, Valerie Watson, Guangli Liu, Nicholas Rose, Douglas Call, Rachel Wagner, Adam Hutchinson, Geoff Rader, Matthew Yates, Markus Hilpert, Bill Johnson and Lijiao Ren, and Chapters 13 – 14 by Xiaoyan Li.

I am indebted to the hundreds of students that have taken my Environmental Transport class over the years. They have made teaching a joy.

BRUCE E. LOGAN

State College, Pennsylvania
August 2011

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

During the 20th century, the creation of new chemicals and chemical production in the United States both grew exponentially. Unfortunately, the rapid increase in chemical manufacturing during this period was not accompanied by a corresponding increase in responsible disposal practices, resulting in the accidental and intentional release of many chemicals into the environment. The quantity and toxicity of chemicals released frequently exceeded the ability of the biotic environment to degrade these chemicals, and many ecological processes were disrupted, causing vast changes in the normal cycles of terrestrial and aquatic wildlife.

In the United States alone there are over 15,000 registered chemicals, and only a small fraction of these have been researched for their effects on human health and the environment. On a mass production basis, the organic and inorganic chemicals shown in Table 1.1 are the most common. However, production does not directly translate to impact of each chemical on the environment. Many of these chemicals are not regulated by the Safe Drinking Water Act, a law that limits concentrations of toxic chemicals in drinking water (Table 1.2). Although other laws have been enacted to control the release of chemicals into the environment, many sites are already contaminated with these and other chemicals.

Environmental engineers are usually called upon to design systems to treat drinking water and remove toxic chemicals, and to clean up soils contaminated with chemicals. The engineering of these treatment systems requires a good understanding of chemical properties and transport in a system. Predicting the fate and transport of these chemicals in both natural and engineered systems can be difficult, but fortunately, the same engineering disciplines that have been used to manufacture chemicals can be used to understand chemical transport in engineered systems and the natural environment. For example, in order to design chemical reactor and production facilities, chemical engineers have been trained in the fields of equilibrium thermodynamics, chemical reaction kinetics, and mass transfer. These same fields of study can be applied to solve environmental problems. The distribution of chemicals among different phases in the environment is dictated by thermodynamics. The rate of chemical transformation, reaction, and transport, however, may be more critical to calculating the distribution of chemicals in a specific system. Several good textbooks have been developed to focus on chemical equilibrium

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TABLE 1.1 Organic and inorganic chemical production in the USA in 2008.

Organic Chemicals	kg × 10^{-3}	Inorganic Chemicals	kg × 10^{-3}
Acrylonitrile	1,018	Aluminum sulfate	865
Aniline	1,009	Ammonia	9,547
Benzene (units of 10^3 liters)	6,369	Ammonium nitrate	7,279
1,3-Butadiene	1,633	Ammonium sulfate	2,507
Cumene	3,386	Chlorine	9,629
Ethylbenzene	4,104	Hydrochloric acid	3,808
Ethylene	22,554	Nitric acid (100%)	7,503
Ethylene dichloride	8,973	Phosphoric acid (P_2O_5)	9,211
Ethylene oxide	2,903	Sodium chlorate	547
Propylene	14,791	Sodium hydroxide	7,263
Styrene	4,100	Sodium sulfate	322
Urea	5,288	Sulfuric acid	32,443
Vinyl acetate	1,267		

(Data from www.cen-online.org. July 6, 2009)

and reaction rates applicable to environmental processes, but few textbooks have focused on chemical transport phenomena within natural systems.

Although chemical and environmental transport processes share a common mathematical foundation (and perhaps framework), an environmental engineer often has little control over the conditions of the transport calculation or the complexity of the system. The natural variability of ecological processes normally gives rise to situations with too many equations and too few coefficients. Thus, while there may be only one table needed for chemical engineers to describe the properties of a benzene-water system, the environmental engineer may find that the controlling factor is not the solution properties but the adsorptive capacity of a soil in a groundwater aquifer. Therefore, the information contained in this book has been assembled in an effort to teach transport phenomena at a depth and breadth consistent with our understanding of how chemicals are transported in engineered reactors, for water, wastewater, and hazardous waste treatment, and in the natural environment.

1.2 NOTATION FOR CHEMICAL TRANSPORT

In order to develop a mathematical description of chemical distribution in the environment, a consistent notation system is helpful to specify the concentrations, phases, degradation rates, and transport rates of the chemical of interest. Unfortunately, there are too few letters to be used for constants in the many equations needed to describe chemical transport in the systems. For example, k has been used as a mass transport coefficient, rate constant, permeability constant, and Boltzmann's constant, just to name a few. In order to distinguish many of these different factors, we can use upper- and lower-case letters, different fonts, Greek letters, and a string of subscripts. In particular, it may seem like there is always a large number of subscripts attached to a variable. However, a system of subscripts will be set up so that their use can be abbreviated or eliminated depending on the extent to which the use of the variable is unclear as will be shown in the following. This notation scheme, and the general organization of sections 1.2 and 1.3, were inspired by Thibodeaux (1979).

TABLE 1.2 Drinking water contaminants (excludes radionuclides and microbiological contaminants; www.epa.gov/safewater/contaminants/)

Disinfection By-products
Bromate
Chlorite
Haloacetic acids
Total trihalomethanes

Disinfectants
Chloramines
Chlorine
Chlorine dioxide

Organics
Acrylamide
Alachlor
Atrazine
Benzene
Benzo(*a*)pyrene (PAHs)
Carbofuran
Carbon tetrachloride
Chlordane
Chlorobenzene
2,4-D
Dalapon
1,2-Dibromo-3-chloropropane (DBCP)
o-Dichlorobenzene
p-Dichlorobenzene
1,2-Dichloroethane
1,1-Dichloroethylene
cis-1,2-Dichloroethylene
trans-1,2-Dichloroethylene
Dichloromethane
1,2-Dichloropropane
Di(2-ethylhexyl) adipate
Di(2-ethylhexyl) phthalate
Dinoseb
Dioxin (2,3,7,8-TCDD)
Diquat
Endothall
Endrin
Epichlorohydrin
Ethylbenzene
Ethylene dibromide (EDB)
Glyphosphate
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorocyclopentadiene
Lindane
Methoxychlor
Oxamyl (Vydate)
Pentachlorophenol
Pichloram
Polychlorinated biphenyls (PCBs)
Simazine
Styrene
Tetrachloroethylene
Toluene
Toxaphene
2,4,5-TP (Silvex)
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethylene
Vinyl chloride
Xylenes (total)

Inorganics
Antimony
Arsenic
Asbestos
Barium
Beryllium
Cadmium
Chromium
Copper
Cyanide
Fluoride
Lead
Mercury
Nitrate
Nitrite
Selenium
Thallium

Mole and Mass Concentrations

Both mass and molar chemical concentrations are defined here using the letter c. The two different units of concentration are related by the molecular weight, M, or

$$c\,[\text{mole}\,\text{L}^{-3}] = \frac{c\,[\text{mass}\,\text{L}^{-3}]}{M\,[\text{mass moles}^{-1}]} \tag{1-1}$$

where $[\text{L}^{-3}]$ indicates inverse length cubed. Sometimes, in order to distinguish between the two concentration units, for example, when variables with different concentration units are being used in the same equation, ρ will be used for mass concentration, and c for mole concentration. The two are related by

$$c = \frac{\rho}{\text{M}} \tag{1-2}$$

When there is more than one chemical or phase in the system, subscripts will be added. Each chemical will be indicated using a capital letter, such as B, C, D, etc., with the phase indicated with a lower-case letter such as a = air, g = gas, l = liquid, w = water, and s = soil. Thus, we can use a double subscript with an upper- and lower-case letter to indicate concentration for the concentration of chemical C in air, water, or soil as

$$\begin{aligned} c_{Ca} &= \text{concentration of } C \text{ in air} \\ c_{Cw} &= \text{concentration of } C \text{ in water} \\ c_{Cs} &= \text{concentration of } C \text{ in soil} \end{aligned} \tag{1-3}$$

If additional phases are present, we can use other lower-case letters. For example, chemical X in phase o = oil would be c_{Xo}. If we need to specify mass concentration units for additional clarity, the same notation applies when using ρ. Thus, in mass concentration units, we would write, in general, ρ_{ij} for any chemical I in phase j, or ρ_{Co} for chemical C in oil.

The sum of the concentrations of all chemicals in the same phase must be equal to the total phase concentration. For example, the molar and mass concentrations of several chemicals in water would be

$$c_w = c_{Bw} + c_{Cw} + c_{Cw} + \ldots + c_{Ww} \tag{1-4}$$

$$\rho_w = \rho_{Bw} + \rho_{Cw} + \rho_{Cw} + \ldots + \rho_{Ww} \tag{1-5}$$

where c_{Ww} is the concentration of water in the phase we have designated as the water phase. For dilute solutions (see the following), $c_{Ww} \approx c_w$. The total phase concentration is also known as the phase density. For a phase of only pure water, for example, the mass density of the phase is $\rho_w = 1$ kg L^{-3}, or since water has a molecular weight of 18 g mol^{-1}, the molar density of a water phase is $c_w = (1000 \text{ g L}^{-1})/(18 \text{ g mol}^{-1}) = 55.6 \text{ mol L}^{-1}$.

When there is only one phase present, the double subscript notation can be simplified to a single subscript, or the subscripts may be entirely omitted. For example, for the concentration of two different chemicals in water we need only to write c_B or c_C, and for a single chemical in water we can write just c. If the density of water is used in the same calculation, it should be written as ρ_w (even if c is being used in mass concentration units). The elimination of too many subscripts can cause confusion. If c_{Cw} is simplfied to c, and c_w simplified to c, then we would have two different variables using the same symbol! Thus, the phase molar density (or molar density or concentration) should always carry a subscript.

Mole and Mass Fractions

In many instances it is more convenient to express concentrations as mole or mass fractions. It is customary from the chemistry field to designate mole fractions of chemical C in air, water, and soil as

$$\begin{aligned} x_C &= \text{mole fraction of } C \text{ in water} \\ y_C &= \text{mole fraction of } C \text{ in air} \\ z_C &= \text{mole fraction of } C \text{ in soil} \end{aligned} \tag{1-6}$$

The second subscript representing the phase is omitted for mole fractions of chemicals in air, water, and soil since we have adopted different letters for each phase. For a system consisting of only chemical C and water, x_C, can be calculated from the moles of the two chemicals using

$$x_C = \frac{n_C}{n_C + n_W} \tag{1-7}$$

For a multicomponent system of N species, the mole fraction is calculated using

$$x_C = \frac{n_C}{\sum_{i=1}^{N} n_i} \tag{1-8}$$

For phases other than air, water, and soil, a second subscript is needed. The choice of x, y, or z for this new phase depends on whether the chemical is in the gas = y, liquid = x, or solid = z phase. For example, the mole fraction of chemical C in phase o = oil would be written using x for the oil (liquid) phase as x_{Co}.

Mass fractions chemicals can be designated in the same fashion as molar fractions, again with different letters for each phase, according to

$$\begin{aligned} \psi_C &= \text{mass fraction of } C \text{ in air} \\ \varphi_C &= \text{mass fraction of } C \text{ in water} \\ \omega_C &= \text{mass fraction of } C \text{ in soil} \end{aligned} \tag{1-9}$$

Additional species in other phases, for example TCE in oil, would be φ_{To}, where φ is used for an aqueous phase, T = TCE and o = oil.

The advantage of using mass and mole fractions is that the summation of all terms is equal to unity, or

$$\sum_{i=1}^{N} x_i = \sum_{i=1}^{N} y_i = \sum_{i=1}^{N} z_i = \sum_{i=1}^{N} \phi_i = \sum_{i=1}^{N} \psi_i = \sum_{i=1}^{N} \omega_i = 1 \tag{1-10}$$

1.3 SIMPLIFICATIONS FOR ENVIRONMENTAL SYSTEMS

The properties of concentrated gases, liquids, and solids can be difficult to describe when temperatures and pressures vary over a wide range. In chemical engineering processes these phase properties can be tightly controlled to improve process performance and chemical yields and reduce overall costs. In environmental systems, temperature and pressure oftentimes cannot be controlled at all, although they likely vary over a considerably smaller range compared to chemical production reactors. For example, while a chemical process may occur in an engineered reactor at elevated pressures and temperatures of 5 atm and 470 K with little variation in either condition, pressures in natural systems are usually close to 1 atm. Temperatures can average 20°C, but on an absolute temperature scale variations of ± 20°C are <10% when temperature is on an absolute scale (293 K). An important component of chemical transport models for the natural environment is the range of variability in the system. Natural systems can differ only slightly, for example slight variations in water quality or temperature, or they can be substantially different due to large natural changes such as the change in seasons (or sudden storms). Given the difficulties in precisely defining all of the characteristics of a natural system (versus a better-defined chemical reactor), it often makes more sense to use simpler chemical models to describe natural systems. The main challenge in using even these simpler models is defining the parameters needed for these models.

One assumption that can simplify a chemical transport calculation is that all chemicals behave as ideal solutions. When chemical solutions are mixed, it is therefore assumed that they are mutually soluble and that the production or consumption of heat can be ignored. Molecular diameters are also assumed to be similar, as are intermolecular forces of attraction and repulsion in the bulk phase. With these assumptions there are no volume changes when two (or more) solutions are combined. The volume v produced by the mixing of two solutions of v_B and v_C is the sum $v = v_B + v_C$.

The assumption of ideal solutions greatly simplifies calculations between chemical mole fractions and concentrations. For example, consider the case of a binary mixture of chemical C in water. The mole fraction of chemical C in water W is

$$x_C = \frac{n_C}{n_C + n_W} \tag{1-11}$$

Since the solution is ideal, it is also true that $c_C = n_C/v$ and $c_W = n_W/v$. Substituting in these into Equation 1-11 produces

$$x_C = \frac{c_C v}{c_C v + c_W v} = \frac{c_C}{c_C + c_W} \tag{1-12}$$

Thus mole fractions for these solutions can be calculated on the basis of either concentrations or moles.

The assumption of ideal solutions extends to gas phase components. The ideal gas law for all components in the air phase is

$$P v_a = n_a RT \tag{1-13}$$

where v_a is the volume of air, P the total pressure, R the universal gas constant, and T the absolute temperature. For a single chemical C in air, with partial pressure p_{Ca}, the ideal gas law becomes

$$p_{Ca}\, v_a = n_{Ca} RT \tag{1-14}$$

If air is the only phase present in our system, we can simplify our notation and rewrite the same expression as

$$p_C\, v = n_C RT \tag{1-15}$$

The concentration of C in air is

$$c_C = \frac{n_C}{v} = \frac{p_C}{RT} \tag{1-16}$$

TABLE 1.3 Notation and relationships for multiphase and multicomponent systems

Gas	Liquid	Solid
$y_C = c_{Ca} / c_a$	$x_C = c_{Cw} / c_w$	$z_C = c_{Cs} / c_s$
$\rho_{Ca} = c_{Ca} M_C$	$\rho_{Cw} = c_{Cw} M_C$	$\rho_{Cs} = c_{Cs} M_C$
$\psi_C = \rho_{Ca} / \rho_a$	$\varphi_C = \rho_{Cw} / \rho_w$	$\omega_C = \rho_{Cs} / \rho_s$
$1 = y_B + y_C + \ldots + y_N$	$1 = x_B + x_C + \ldots + x_N$	$1 = z_B + z_C + \ldots + z_N$
$\rho = \rho_{Ba} + \rho_{Ca} + \ldots + \rho_{Na}$	$\rho = \rho_{Bw} + \rho_{Cw} + \ldots + \rho_{Nw}$	$\rho = \rho_{Bs} + \rho_{Cs} + \ldots + \rho_{Ns}$
$c_a = c_{Ba} + c_{Ca} + \ldots + c_{Na}$	$c = c_{Bw} + c_{Cw} + \ldots + c_{Nw}$	$c = c_{Bs} + c_{Cs} + \ldots + c_{Ns}$
$\rho_a = c_a M_a$	$\rho_w = c_w M_w$	$\rho_s = c_s M_s$
$1 = \psi_B + \psi_C + \ldots + \psi_N$	$1 = \varphi_B + \varphi_C + \ldots + \varphi_N$	$1 = \omega_B + \omega_C + \ldots + \omega_N$

TABLE 1.4 Additional relationships between mole fractions, mass fractions, and molecular weight

Mole fraction	$x_C = \dfrac{\varphi_C / M_C}{\varphi_B / M_B + \varphi_C / M_C + \ldots + \varphi_N / M_N}$
Mass fraction	$\varphi_C = \dfrac{y_C M_C}{y_B M_B + y_C M_C + \ldots + y_N M_N}$
Molecular weight	$M_w = x_B M_B + x_C M_C + \ldots + x_N M_N$ $\dfrac{1}{M_W} = \dfrac{\varphi_B}{M_B} + \dfrac{\varphi_C}{M_C} + \ldots + \dfrac{\varphi_N}{M_N}$

In most instances it can further be assumed that all mixtures are dilute solutions. Operationally, a dilute solution can be defined as a system where the concentration of a chemical in the phase is less than 5% of the total concentration, or

$$c_{Cj} < 0.05\, c_j \qquad \text{(dilute solution)} \qquad (1\text{-}17)$$

This assumption allows much simpler calculations of mole and mass fractions. For example, for a dilute solution of C in water, $c_{Cw} << c_{Ww}$, so that Equation 1-12 becomes

$$x_C \approx \frac{c_{Cw}}{c_{Ww}} = \frac{c_C}{c_w} \qquad (1\text{-}18)$$

Note that we have simplied the notiation here for the concentration of c and the water phase. Simplified relationships for chemicals in dilute solutions are summarized in Tables 1.3 and 1.4.

Example 1.1

The concentrations of most chemicals in water are much less than the <5% criterion for a dilute solution. Show that a relatively soluble compound such as benzene in water at a concentration of 100 mg L^{-1} would be a dilute solution.

The molar concentration of a mass concentration solution of 100 mg L^{-1} of benzene is

$$c_{Bw} = \frac{\rho_{Bw}}{M_B} = \frac{0.1[\mathrm{g\,L^{-1}}]}{78[\mathrm{g\,mol^{-1}}]} = 0.0013\ \mathrm{mol\,L^{-1}}$$

Since the molar concentration of water is 55.6 mol L^{-1}, the solution is dilute since 0.0013 << 55.6. Furthermore, even at the solubility limit of benzene in water, the solution is dilute. When water is saturated with benzene, $\rho_{Bw,eq} = 1.78$ g L^{-1}, and the molar concentration is

$$c_{Bw} = \frac{\rho_{Bw}}{M_B} = \frac{1.78[\mathrm{g\,L^{-1}}]}{78[\mathrm{g\,mol^{-1}}]} = 0.0228\ \mathrm{mol\,L^{-1}}$$

Based on this 5% criterion for a dilute solution, any aqueous solution that is less than 2.8 mol L^{-1} is a dilute solution. A similar criterion can be developed for the concentration of a chemical in air. The molar concentration of air at 20°C is

$$c_a = \frac{P}{RT} = \frac{1\ \mathrm{atm}}{0.0821[\mathrm{L\,atm\,mol^{-1}K^{-1}}]\,293\ \mathrm{K}} = \frac{\mathrm{mol}}{24.1\ \mathrm{L}} \tag{1-19}$$

The mass concentration of air is obtained from the relationship $\rho_a = c_a M_a$. The molecular weight of air can be approximated as 29 g mol^{-1} by assuming that air is 79% nitrogen and 21% oxygen. This results in $\rho_a = 1.203$ g L^{-1}.

For soils, the assumption of an ideal solution is not strictly valid since soil is not homogeneous and chemical components in soil are not likely to be homogeneously distributed. Although we will discuss the implications of this situation in greater length in the chapter on groundwater transport, in some situations (as a first approximation) we can consider the soil to be well mixed and, for the chemicals in the soil, to be evenly distributed.

The bulk characteristics of air, water and soils are summarized in Table 1.5. The calculated densities are based on 20°C and 1 atm, and for soil assuming pure silica (SiO_2).

TABLE 1.5 Molecular weights and pure phase concentrations of air, water and soil (assuming 20°C and 1 atm)

	Molecular weight	Pure phase concentration	
Phase	M_i [g mol^{-1}]	ρ_i [g L^{-1}]	c_i [mol L^{-1}]
Air	29	1.203	0.0415
Water – fresh	18	998	55.4
– sea	18	1021	56.7
Soil (SiO_2)	60	2650	44.1

Example 1.2

A large volume of chloroform = C is spilled in a closed room. For air at 26°C and 1 atm, calculate: (a) mole fraction, (b) mole concentration, (c) mass concentration, and (d) mass fraction of chloroform in air.

a. At 26°C, the vapor pressure of chloroform is p_C^0 = 200 mmHg. The mole fraction of chloroform in air is:

$$y_C = \frac{p_C^0}{P} = \frac{200\ \text{mmHg}}{760\ \text{mmHg}} = 0.263$$

Note that this is not a dilute solution since 0.263 > 0.05.

b. Before we calculate the mole concentration, we first need to calculate the total molar concentration of air, c_a. One approach is to calculate $c_a = P_a/RT$. Alternatively, we see in Table 1.5 that c_a = 0.0415 mol L^{-1} at 20°C and 1 atm. To correct this concentration to 26°C, we multiply by the ratio of absolute temperatures, or

$$c_{a,T} = c_a \frac{T}{T_T} = (0.0415\ \text{mol L}^{-1})\frac{293\text{K}}{299\text{K}} = 0.0407\ \text{mol L}^{-1}$$

The molar concentration of chloroform in air can be calculated from the mole fraction in part a, or

$$c_{Ca} = y_C\, c_a = (0.263)\ (0.0407\ \text{mol L}^{-1}) = 0.0107\ \text{mol L}^{-1}$$

c. Based on the molecular weight of chloroform of 119.4 g mol^{-1}, the mass concentration of chloroform is

$$\rho_{Ca} = c_{Ca} M_C = (0.0107\ \text{mol L}^{-1})(119.4\,\text{g mol}^{-1}) \times 10^{-3}\,\text{L m}^{-3} = 1280\ \text{g m}^{-3}$$

d. The mass fraction of C in the air-chloroform mixture cannot be calculated by assuming that the solution is dilute. Although $\psi_C = m_C/m_a$ is still valid, it must be recognized that the molecular weight of air is no longer equal to 29 g mol^{-1}, as previously calculated, since the air now contains a large fraction of chloroform. The molecular weight of air, defined as M_a, is calculated from the mole fractions of air = A and chloroform = C as

$$M_a = y_C M_C + y_A M_A = y_C M_C + (1 - y_C)M_A$$

$$M_a = (0.263)(119.4) + (1 - 0.263)(29) = 52.8\ \text{g mol}^{-1}$$

It is left to the reader (problem 1.2) to show that ψ_C can be calculated from the identity

$$\psi_C = \frac{y_C M_C}{M_a} \qquad (1\text{-}20)$$

Using this definition of ψ_C, we have

$$\psi_C = \frac{y_C M_C}{M_a} = \frac{(0.263)\,(119.4\ \text{g mol}^{-1})}{(52.8\,\text{g mol}^{-1})} = 0.595$$

Conventions on Concentrations

Depending on the phase, different concentration units are preferred in the literature. The conventions for different units have emerged partially as a function of convenience, and partly as a function of properties of the system. The potentially most confusing set of units arises for liquid concentrations. For dilute liquid solutions, concentrations are usually reported in parts per million, or ppm. While this choice of units contains good imagery, i.e. a concentration based on "one-in-a-million," it is confusing in terms of analytical concentrations and solution preparations. The definition of ppm is always

$$\text{ppm} = \frac{1 \text{ part } C}{10^6 \text{ parts } B} \tag{1-21}$$

Assuming "parts" refers to "mass" in grams, this can be converted to mass concentration for a chemical C in water, W, as

$$\text{ppm} = \frac{1\,\text{g}\,C}{10^6\,\text{g}\,W} \times \frac{10^3\,\text{mg}\,C}{\text{g}\,C} \times \frac{10^3\,\text{g}\,W}{\text{mg}\,W} \times \frac{1\,\text{kg}\,W}{\text{L}} = \frac{1\,\text{mg}\,C}{\text{L}\,W} \tag{1-22}$$

Example 1.3

If 1 ppm = 1 mg L^{-1}, or 1 mg/10^6 mg, in English units, does 1 ppm = 1 lb/10^6 gal, or 1 lb/10^6 lb?

In order to establish this relationship in English units, let us start with an equivalence that we are sure of, namely that 1 ppm = 1 mg L^{-1}. Converting to lb/gal

$$1\,\text{ppm} = \frac{1\,\text{mg}}{\text{L}} \times \frac{1\,\text{kg}}{10^6\,\text{mg}} \times \frac{3.7854\,\text{L}}{\text{gal}} \times \frac{2.2\,\text{lb}}{1\,\text{kg}} = \frac{8.34\,\text{lb}}{10^6\,\text{gal}}$$

Since 1 ppm = 8.34 lb/10^6 gal, and water has a density of 8.34 lb gal^{-1}, it follows that 1 ppm = 1 lb/10^6 lb. As this example shows, the ppm calculation must always be made in terms of identical units in both the numerator and denominator. The only reason that a one-to-one conversion from ppm to mg L^{-1} works in metric units is that the density of water in metric units is approximately unity (1 kg L^{-1}). If we had a concentrated solution where this density was not correct, then it would follow that 1 ppm would not equal 1 mg L^{-1}.

The preferred unit for concentrations for each phase is: gas, volume volume^{-1} (ppm for air); liquid, mass volume^{-1} (mg L^{-1} for water); and solid, mass mass^{-1} (μg kg^{-1} for soil). The unit ppm for a gas is often written as ppmv to highlight that it is calculated on a volume-basis. Solid-water solutions, such as slurries and sludges, are often given in units of percent. Since a percent is a ratio of 1 to 100, a 5% solids suspension is

$$5\% = \frac{5\,\text{g}}{100\,\text{g}} \times \frac{10^3\text{g}}{1\,\text{L}} \times \frac{10^3\text{mg}}{\text{g}} = 50{,}000\,\frac{\text{mg}}{\text{L}} \tag{1-23}$$

Dilutions Two conventions are used to make dilution calculations. The definitions differ in whether the volume of a solution is considered relative to the total volume or to the volume of the solvent. The actual dilution, **D**, is calculated based on the total volume produced as

$$\mathbf{D} = \frac{\text{volume of total}}{\text{volume of } C} \tag{1-24}$$

but the relative dilution, $\mathbf{D_R}$, is calculated from the ratio of the two volumes, according to