A LECTURE NOTE PACKAGE FOR ES718

BY DR. SCHRADH SAENTON

FATE & TRANSPORT

POLLUTANTS IN THE ENVIRONMENT

FATE AND TRANSPORT OF POLLUTANTS IN ENVIRONMENT

FATE AND TRANSPORT OF POLLUTANTS IN ENVIRONMENT

Lecture Notes for ES 718

Dr. Schradh Saenton Department of Geological Sciences Faculty of Science, Chiang Mai University



Faculty of Science Printing House

To my family

CONTENTS

List of Figures	ix
List of Tables	xiii
Preface	XV
List of Symbols	xvii

PART I CONCEPTS OF ENVIRONMENTAL POLLUTION

1	Review; types, properties and characteristics of pollutants					
	1.1	1.1 Units and unit conversion				
		1.1.1	Units for measurement	5		
		1.1.2	Chemical concentration units	8		
	1.2	Basic 1	mathematics and statistics	10		
		1.2.1	Numerical solution to algebraic equation	10		
		1.2.2	Differential equations	12		
		1.2.3	Numerical methods for ODE	16		
		1.2.4	Basic statistics	24		
	1.3	1.3 Pollutants		38		
		1.3.1	Overview of pollutant's fate-and-transport study	38		
		1.3.2	Types of pollutants	39		
		1.3.3	Properties and characteristics of pollutants	43		
	1.4	Mass b	palance	52		
				vii		

VIII CONTENTS

		Problems	56
2	Regu	lated chemicals and quantitative risk assessment	61
	2.1	Toxicology	61
		2.1.1 Toxicity effects to human health	62
		2.1.2 Regulated toxic chemicals	63
	2.2	Risk assessment	65
		2.2.1 Hazard identification	66
		2.2.2 Dose-response and exposure assessment	70
		2.2.3 Risk characterization	75
		Problems	78
3	Adve	ection, diffusion and dispersion processes	81
	3.1	Pollutant source mechanisms	81
	3.2	Transport mechanisms	82
		3.2.1 Advection	86
		3.2.2 Diffusion	88
		3.2.3 Dispersion	96
	3.3	Advection-dispersion-reaction equation	102
		Problems	110

PART II TRANSPORT OF POLLUTANTS IN ENVIRONMENTAL MEDIA

4	Transport of pollutants in soils and groundwater aquifers						
	4.1 Overview of soil and groundwater systems						
	4.2	2 Sources of pollutants in subsurface environment					
	4.3 Conservative transport in saturated zone						
	4.3.1 Advection in saturated zone						
	4.3.2 Dispersion in saturated zone						
	4.3.3 Advective-dispersive transport of conservative tracers						
	4.4 Reactive transport in saturated zone						
		4.4.1	Effect of sorption in transport	132			
		4.4.2	Effect of degradation in transport	137			
	4.5	Transp	ort in unsaturated zone	141			
	4.6	Non-aq	ueous phase liquids, NAPLs	146			
		Probler	ns	150			
References				157			

index

161

LIST OF FIGURES

1.1	Transport and transformation processes for contaminants in the environment: surface water, air and subsurface environments.	4
1.2	Example plots of the dataset which all have $R^2 = 0.70$ evaluated based on two-parameter model of linear regression analysis.	36
1.3	Classification of chemical pollutants and some examples.	39
1.4	Periodic table of the elements (https://sciencenotes.org/).	41
1.5	Example of a typical control volume used in mass balance calculation of a chemical in the lake (modified from [21]).	52
2.1	Steps in risk assessment calculation and management (adapted from [31]).	66
2.2	Dose-response mortality curves for acute toxicity: (a) Chemical A is always more toxic than B; (b) whereas Chemical C is less toxic than D at low doses even though it has a lower LD_{50} (adapted from [29]).	68
2.3	A 2×2 matrix for an epidemiologic rate comparison. Rows divide people by exposure; columns divide them by disease.	68
2.4	Dose response relationship s for human health risk. The slope of the straightline is called <i>potency factor</i> .	70
2.5	Common descriptors for human exposures to environmental agents [38].	76
2.6	Human exposure distributions for (A) a hypothetical systemic (non-cancer) toxicant and (B) a hypothetical carcinogen [38].	77
		ix

X LIST OF FIGURES

3.1	Types of pollutant's source according to their geometry.	83
3.2	Schematic diagram showing transport processes (modified from [37]).	84
3.3	Transport from source to receptor can be simplified by assuming well-mixed in one or more dimensions.	85
3.4	Advective transport process from point at <i>x</i> to at $x + \Delta x$. Chemicals are entrained in a fluid at a mean velocity \bar{u} . A hypothetical concentration gradient is shown below as concentration versus distance. Note that the slope of the line dC/dx is negative when the mass is transported from point <i>x</i> to $x + \Delta x$ into the volume $V = A \times \Delta x$.	87
3.5	Macrodispersion in groundwater caused by mixing and detouring.	96
4.1	Diagram of various types of aquifers.	118
4.2	Groundwater conditions near the ground surface. (a) Saturated and unsaturated zones; (b) profile of moisture content versus depth; (c) pressure head and hydraulic head relationship & water retention under pressure head less than (top) and greater than (bottom) atmospheric pressure; (d) profile of pressure head versus depth; (e) profile of hydraulic head versus depth [16].	119
4.3	Sources of groundwater pollution in subsurface environment [24].	120
4.4	A Plan view of head contour or equipotential line map with flow lines toward a pumping well in homogeneous, unconfined aquifer (top) and a cross-section view of the sloping water table with asymmetrical cone of depression (bottom).	125
4.5	Capture zone of a well pumping from an aquifer with a uniform hydraulic gradient [14].	125
4.6	Chromatographic separation of plumes: chloride (CL, 647 days); carbon tetrachloride (CTET, 633 days); and tetrachloroethylene (PCE, 633 days). Contour interval depicted for CL is 5 mg L ⁻¹ beginning at an outer contour of 10 mg L ⁻¹ . Contour intervals depicted for CTET and PCE are 0.1 μ g L ⁻¹ beginning at an outer contour of 0.1 μ g L ⁻¹ [35]	136
47	Schematic diagram for numn-and-treat system (www.ena.gov.[45])	136
4.8	Fraction of benzene mass that is removed by groundwater extraction. The retardation factor of benzene is assumed to be $R_f = 4.0$. Of benzene mass, 25% is removed after 1 pore volume of groundwater extracted. However, more than 16 pore volumes are needed to remove 99% of the total benzene mass originally present in the contaminated aquifer.	130
4.9	Typical hydraulic conductivity of a certain unsaturated soil as a function of water (moisture) content (θ). Higher conductivity occurs when θ is larger and the pore water is under less suction. Note that the relationship between $K(\theta)$ and θ depends on whether the soil most recently was dried or wetted (modified from [16]).	141

- 4.10 Depiction of important processes that govern VOC transport in vadose one (adapted from [26]).
 4.11 The behavior of NAPL and DNAPL in the subsurface environment.
- NAPL floats on the water table, slowly dissolving into the groundwater flowing by, thus creating a plume in the downgradient direction. DNAPL tends to sink to the bottom of the aquifer, where it may flow contrary to the groundwater flow direction, following instead the slope of an aquiclude such as bedrock. DNAPL may also flow into bedrock fractures, and become exceedingly difficult to either locate or remove [22].
- 145

148

LIST OF TABLES

1.1	Fundamental units in SI and English systems.	6
1.2	Examples of derived units in SI and English systems.	6
1.3	SI prefix used to designate large and small quantities.	7
1.4	Examples of commonly used concentration units in environmental media.	7
1.5	Examples for classification of differential equations.	12
1.6	<i>t</i> -statistics.	25
1.7	<i>F</i> distribution: Critical value of <i>F</i> ($\alpha = 0.05$).	32
1.8	<i>F</i> distribution: Critical value of <i>F</i> ($\alpha = 0.01$).	33
1.9	Chi-square distribution χ^2 .	34
1.10	Some commonly used aggregate measures of pollutants.	43
1.11	Chemical reactions related to fluorite, CaF ₂ , dissolution in pure water.	45
1.12	Solubility, vapor pressure (25 $^{\circ}$ C, 1 atm) and Henry constants of some commonly found pollutants [37, 22, 13].	49
2.1	The ATSDR substance priority list (Agency for Toxic Substances and Disease Registry; www.atsdr.cdc.gov [44]).	62
2.2	Classification of environmental toxicants causing health problems [29].	63
		xiii

XIV LIST OF TABLES

2.3	A conventional rating system for the acute toxicity of chemicals in humans [31].	67
2.4	Toxicity data for some selected potential carcinogens (www.epa.gov/iris [46])	71
2.5	Example recommended exposure factors recommended for risk assessments [40].	73
3.1	Examples of diffusion coefficients of some chemicals in water at 25 °C [20].	89
3.2	Examples of diffusion coefficients of some chemicals in air at 25 $^\circ C$ [20].	89
3.3	Example analytical solutions to transient diffusion (Fick's second law) [8].	94
3.4	Error and complementary error functions.	95
3.5	Typical ranges of dispersion coefficients in rivers, lakes, and sediments [37, 22, 42].	102
4.1	Intrinsic permeability and hydraulic conductivity of some geologic materials [16].	122
4.2	Mathematical expressions for determining the geometry of the capture zone from a single pumping well in a homogeneous and uniform groundwater flow field.	126
4.3	Analytical solution for tracer transport in saturated groundwater in 3-, 2- and 1-D with <i>instantaneous</i> release of mass M .	128
4.4	Analytical solution for tracer transport in saturated groundwater in 3-, 2- and 1-D with <i>continuous</i> release of tracer flux.	129
4.5	Commonly used empirical relationship for soil-water hydraulic conductivity $K(\theta)$.	142
4.6	Comparison of transport parameters in groundwater across saturated and unsaturated zones.	143
4.7	The 25 Most frequently detected groundwater contaminants at hazardous waste sites [32].	147
4.8	Examples of Nonaqueous-Phase Liquids.	147

PREFACE

This lecture note package, *ES718 Fate and Transport of Pollutants in Environment*, is prepared for graduate students in Environmental Science program who are interested in environmental remediation track. It is intended to provide basic understanding of environmental pollution which involves the chemicals' *fate* and *transport* in various environmental media such as air, surface water, soil, and groundwater. The ultimate goal is to provide students necessary background to be able to systematically analyze pollutants' behavior in the environment as well as to predict their concentration and extent of contamination in the environment for better assessment when needed.

Even though I taught this part of the course for several years, I still find difficulties every year to find effective way(s) of teaching students who were especially from a wide variety of educational background. Initially, it was planned to *jump-start* the lecture directly on subsequent chapters which deal with the fate and transport of chemicals in various environmental media. Unfortunately, a majority of students did not have sufficient background in mathematics, statistics, numerical methods, differential equations, basic chemistry, unit conversion, etc. Therefore, this lecture notes ended up having to add more basic materials as appeared in Chapter 1 which is an introductory chapter in order to provide a review of some background materials. I hope this lecture package would be useful and helpful for students who are new to field of *quantitative* environmental pollution.

SCHRADH SAENTON

Chiang Mai, Thailand April 2021

https://cmu.to/ES718

SYMBOLS

- *a*_i Activity of aqueous species i
- *C* Concentration of a chemical, typically a mass per unit volume.
- D, **D** Diffusion coefficient and diffusion coefficient tensor (L²T⁻¹)
- E, \mathbf{E} Dispersion coefficient and dispersion coefficient tensor (L²T⁻¹)
- E_L, E_x Longitudinal dispersion coefficient (L²T⁻¹)
- E_T, E_{T_h}, E_y Transverse, horizontal dispersion coefficient (L²T⁻¹)
- E_V, E_{T_v}, E_z Transverse, vertical dispersion coefficient (L²T⁻¹)
- \dot{E} Emission rate (MT⁻¹)
- F F-statistics
- g Acceleration due to gravity (e.g., 9.81 m s⁻²; 32.17 ft s⁻²)
- ΔG_f° Standard Gibbs free energy of formation (e.g., kJ mol⁻¹)
- $\Delta_r G^\circ$ Standard Gibbs free energy change of a reaction or transformation (e.g., kJ)
- *h* Hydraulic head of groundwater (L)
- ΔH_f° Standard enthalpy of formation (e.g., kJ mol⁻¹)
- $\Delta_r H^\circ$ Standard enthalpy change of a reaction or transformation (e.g., kJ)
- J, \mathbf{J} Mass flux (ML⁻²T⁻¹)
- J_a, \mathbf{J}_a Advective mass flux (ML⁻²T⁻¹)
- J_d , \mathbf{J}_d Diffusive mass flux (ML⁻²T⁻¹)
- J_E , \mathbf{J}_E Dispersive mass flux (ML⁻²T⁻¹)
- *k* Permeability (L^2); first-order degradation rate constant (T^{-1})
- *K* Hydraulic conductivity of a groundwater aquifer (LT^{-1}) ; Equilibrium constant

- XVIII LIST OF SYMBOLS
- **K** Hydraulic conductivity tensor
- K_d Distribution coefficient (L³M⁻¹)
- K_H Henry constant (e.g., atm m³ mol⁻¹; dimensionless)
- *K_p* Partition coefficient (-)
- L Length; Litre (dm^3)
- M Mass
- *p* Pressure head (L)
- *P* Pressure (ML $^{-1}$ T $^{-2}$; kPa or psi)
- q Darcy velocity; seepage velocity; specific discharge (LT^{-1})
- Q Volumetric flow rate or a groundwater pumping rate (L³T⁻¹)
- *R* Gas constant (0.08205 L atm mol⁻¹ K⁻¹ or 8.3143 J mol⁻¹ K⁻¹)
- R_f Retardation factor (-)
- R_h Hydraulic radius (L)
- s Standard deviation; groundwater drawdown (L)
- *s*² Variance
- S Storage coefficient (-); Channel slope (-); Solubility (ML^{-3})
- S_R Sum of square of residuals (or SSE)
- S_s Specific storage (L⁻¹)
- S_s Specific storage of a confined aquifer (L⁻¹)
- S_y Specific yield of an unconfined aquifer (-)
- T Time
- *T* Temperature (°C, °F, K); Transmissivity (L^2T^{-1})
- *v*, *u* Velocity (LT^{-1})
- \bar{v}, \bar{u} Average velocity; average linear pore velocity (in groundwater) (LT⁻¹)
- \bar{v}_s Sorbed contaminant velocity (in groundwater) (LT⁻¹)
- u_* Shear velocity (LT⁻¹)
- V Volume or control volume (L³)
- V_i° Standard molar volume of species i (e.g., m³ mol⁻¹)
- $\Delta_r V^\circ$ Standard molar volume change of a reaction or transformation (e.g., m³)
- \bar{y} Mean of the measurements
- \hat{y} Modeled or predicted values
- α Significance level; dispersivity of an aquifer (L)
- α_L Longitudinal disersivity of an aquifer (L)
- α_{T_h} Transverse dispersivity of an aquifer (L)
- α_{T_v} Vertical dispersivity of an aquifer (L)
- γ_i Activity coefficient of aqueous species
- χ A symbol used in statistics; χ^2 is Chi-square distribution
- κ A von Karman coefficient
- v Stoichiometric coefficient in a balanced chemical reaction
- ϕ Porosity (-)
- ψ Matric potential (atm, kPa)

- μ Expected value of the sample mean (i.e., population mean)
- ρ_b Bulk density of the aquifer (ML⁻³)
- ρ_s Soil's particle density (ML⁻³)
- σ Expected value of the sample standard deviation (i.e., population standard deviation)
- σ^2 Expected value of the sample variance (i.e., population variance)
- θ Water or moisture content in undsaturated zone.
- θ_r Irreducible water content in soil.

PART I

CONCEPTS OF ENVIRONMENTAL POLLUTION

CHAPTER 1

REVIEW; TYPES, PROPERTIES AND CHARACTERISTICS OF POLLUTANTS

Fate-and-transport of pollutants in environment, sometimes called *Environmental Pollution*, refers to the realization of pollutants' existence and the conceptualization of their behavior and movement in various environmental media such as air, soil, surface waters (e.g., rivers, lakes, and estuaries) and groundwater aquifers. A good understanding of pollutants's fate and transport mechanisms as well as the characteristics of environmental systems will allow us to better predict their contamination and migration, to assess any environmental or health risk associated with the pollutants and to design proper and applicable remediation scheme [21, 37].

As environmental scientists, we are always interested in fate and transport of mass in environmental media mainly because of at least three objectives:

- 1. *The understanding of natural systems*. The distribution and fate of contaminants in natural systems is usually dictated or controlled by mass transport. Therefore we may be concerned with processes that span a wide variety of scales: from transport of a compound through a membrane filtration to the distribution of green house gases in the atmosphere.
- The design of engineered systems. Removal and treatment of contaminants require quantification of mass transport rates. Separations and reactive processes are examples of practical cases in which a contaminant must be transport through a mixture.
- 3. *Fate & transport modeling.* The ability to predict the spatial and temporal variation and distribution of a contaminant in both engineered and natural systems is one of the main goals of the study of mass transport in environmental pollution.

Fate and Transport of Pollutants in Environment. By S. Saenton, Chiang Mai University

4 REVIEW; TYPES, PROPERTIES AND CHARACTERISTICS OF POLLUTANTS

Figure 1.1 shows a general concept of fate and transport processes of contaminants in the environment. Understanding the pathways and processes is critical for predicting the extent of contamination, human exposure, health effects and ecosystem impacts. As the pollutants are being transported across the air, water, soil and biological compartments, they undergo physical, chemical and biological transformation within these compartments. Human and other living organisms, namely receptors, are exposed to pollutants through a variety of pathways, with impacts that depend on the magnitude and temporal and spatial distribution of exposure.



Figure 1.1 Transport and transformation processes for contaminants in the environment: surface water, air and subsurface environments.

In order to better understand these complex processes, scientists and engineers from a variety of disciplines have developed a conceptual framework and corresponding mathematical models to describe environmental processes depict in Figure 1.1. The mathematical models can provide a framework for understanding physical, chemical and biological processes that determine the cycling of elements and compounds through the environment. They also provide a basis for relating human activities and environmental impacts and for predicting the changes that might occur in response to alterations in the activities.

There are several basic principles that ES718 students need to understand in order to comprehend environmental pollution and to predict fate-and-transport of pollutants in various environmental media. These basic principles, for examples, include:

- 1. *Mass conservation and mass transport principles*. The principle of mass conservation, together with the constitutive (i.e., empirical) law of mass diffusion and chemical reaction kinetics, can be used to perform mass balance calculation in an environmental compartment or a system.
- 2. *Principles of chemistry*. The principles of chemistry frequently used in environmental pollution include stoichiometry, equilibrium of chemical reactions and interphase partitioning, chemical kinetics, electrochemistry, organic chemistry, etc. These principles are required to understand the behavior of the chemicals in environment.
- 3. *Biological and microbial processes*. In addition to the chemical interaction, the knowledge of introductory microbiology and biological fundamentals would be useful in

predicting the behavior, toxicity and degradation of pollutants in various environmental media.

- 4. *Thermodynamic relations*. This refers to a set of properties and equations that describe a system at equilibrium. For example, an ideal gas law PV = nRT, is an equation of state that relates pressure (*P*) and temperature (*T*) to the volume (*V*) of an ideal gas of *n* number of moles. Another important thermodynamic function is Gibbs free energy change of a chemical reaction (or $\Delta_r G^\circ$) which can be used to calculate the equilibrium constant a reaction $K = \exp(-\Delta_r G^\circ/RT)$.
- 5. *Mathematical and statistical techniques*. The mathematical complexity of the transport equations often requires the solution of ordinary or partial differential equations or a set of linear/non-linear system of algebraic and differential equations. Analytical solutions are usually preferred but numerical methods are commonly required for mathematically complex system. Similar to mathematics, statistics is also an essential tool in all disciplines of science and engineering. It helps interpret experimental and field data and determine whether such data is significantly meaningful.

In this chapter, some important fundamentals as well as mathematical techniques (both analytical and numerical solutions) required for this course will be briefly reviewed. Examples will be given so that students can learn through worked problems. However, before we can proceed through the fundamentals of environmental pollution, it is needed to mention the units of measurements normally used in environmental study. Environmental scientists are frequently required to convert a quantity from one unit of measurement to another such that consistent calculation can be made.

1.1 Units and unit conversion

1.1.1 Units for measurement

A unit of measurement is a definite magnitude of a physical quantity, defined and adopted by convention, that is used as a standard of measurement of the same physical quantity. There are several available measurement units used in scientific communities such as *MKS* (meter-kilogram-second), *CGS* (centimeter-gram-second), *English*, and *SI* systems. Unfortunately, environmental scientists and engineers always use mixed units simply because of convenience! Therefore it is necessary for scientists and engineers to be familiar with several unit systems as well as unit conversion from one system to another.

Table 1.1 shows seven fundamental quantities in both SI (i.e., the modern form of MKS unit system) and English systems. These fundamental quantities consist of length, mass, temperature, time, amount of substance, electrical current, and luminous intensity. Other chemical or physical properties can be derived from these seven fundamental quantities. Table 1.2 shows examples of derived quantities in both unit systems.

An SI prefix is a name or associated symbol that precedes a unit of measure to form a decimal multiple as shown in Table 1.3. SI prefixes are used to reduce the number of zeroes in numerical equivalencies. For example, a quantity of 10^{-6} g can be written as 1.0 μ g. A volume of 10^{-3} m³ (equivalent to 1.0 liter or 1.0 L) can be written as 1.0 dm³. Or, an area of 100×100 m² equals to 1 hm \times 1 hm or 1.0 hectare.

No	Fundamental quantity	SIU	Init	English unit	
INO.	Fundamental quantity	Name	Symbol	Name	Symbol
1	Length (L)	Meter	m	Foot	ft
2	Mass (M)	Kilogram	kg	Slug	slug ^a
3	Temperature (T)	Kelvin ^b	K	Fahrenheit	°F
4	Time (T)	Second	8	Second	s
5	Amount of substance (n)	Mole	mol	Mole	mol
6	Electrical current (A)	Ampere	А	Ampere	А
7	Luminous intensity (I)	Candela	cd	Candela	Cd

Table 1.1Fundamental units in SI and English systems.

^{*a*} Sometimes, a unit of lb_m is used instead of slug. Note: 1 slug = 32.174 lb_m = 14.594 kg ^{*b*} K = 273.15 + °C

υ	ĸ	=	27	3.	15	+	0	U

Dening I Organititat		SI Unit	English Unit		
Derived Quantity	Name/Symbol Equivalent		Name/Symbol	Equivalent	
Velocity (v)	v	${ m m~s^{-1}}$	v	ft s ⁻¹	
Acceleration (a)	а	${\rm m~s^{-2}}$	а	ft s ⁻²	
Volume (V)	V	m ³	V	ft^3	
Density (ρ)	ρ	${\rm kg}~{\rm m}^{-3}$	ρ	slug ft ⁻³	
Force (F)	Newton (N)	$kg m s^{-2}$	pound (lbs)	slug ft s ⁻²	
Pressure (P)	Pascal (Pa)	$kg m^{-1} s^{-2} (N m^{-2})$	psi	$lb in^{-2}$	
Energy (E)	Joule (J)	$kg m^2 s^{-2} (N m)$	Btu	ft lb	
Power (P)	Watts (W)	$\mathrm{J}~\mathrm{s}^{-1}$	Btu s ⁻¹	ft lb s ⁻¹	
Thermal conductivity	k	${\rm W} \; {\rm m}^{-1} \; {\rm K}^{-1}$	Btu h^{-1} ft ⁻¹ °F ⁻¹	-	
Electrical charge (Q)	Coulomb (C)	A s	Same as S	I	
Electrical conductance	Siemens (S)	$A^2 kg^{-1} m^{-2} s^3$	Same as S	I	

 Table 1.2
 Examples of derived units in SI and English systems.

Prefix	Symbol	Multiplier
femto	f	10^{-15}
pico	р	10^{-12}
nano	n	10^{-9}
micro	μ	10^{-6}
milli	m	10^{-3}
centi	с	10^{-2}
deci	d	10^{-1}
deca	da	10^{+1}
hecto	h	10^{+2}
kilo	k	10^{+3}
Mega	М	10^{+6}
Giga	G	10^{+9}
Tera	Т	10^{+12}
Peta	Р	10^{+15}

 Table 1.3
 SI prefix used to designate large and small quantities.

 Table 1.4
 Examples of commonly used concentration units in environmental media.

Media	Concentration type	Example	Explanation	Remark
Water	mass per volume	mg L ⁻¹ ; μ g L ⁻¹	mass of solute (mg or μ g) per 1.0 L of solution	а
	mol per volume	$ m mol~dm^{-3}$	mol of solute per 1.0 L (dm^3) of solution	Molarity (M)
	mol per mass	$mol kg^{-1}$	mol of solute per 1.0 kg of solvent	Molality (m)
Soil	mass per mass	${ m mg}~{ m kg}^{-1}$	mass of solute (mg) per kg of bulk soil mass	b
		wt%	mass of solute (g) per 100 g of bulk soil mass	-
Air	mass per volume	${ m mg}~{ m m}^{-3}$	mass of solute (mg) per 1.0 m^3 of air	-
	volume per volume	ppm _v	volume of solute per 10 ⁶ volume of air	С

^{*a*} For a dilute solution where solution's density is close to 1.0 g cm⁻³: mg L⁻¹ \approx ppm_w and μ g L⁻¹ \approx ppb_w.

 b Sometimes called ppm or $\mathrm{ppm}_\mathrm{w}.$

^c For gaseous species in air only.

1.1.2 Chemical concentration units

Concentration of solutes in solutions (solids, liquids, or gases) are commonly expressed either as mass concentration (e.g., parts per million by mass or ppm, milligrams per liter or mg L⁻¹, milligrams per kilograms or mg kg⁻¹) or as molar concentrations (e.g., molality or mol kg⁻¹, molarity or mol dm⁻³). Table 1.4 shows examples of commonly used concentrations units (in water, soil and air) used among environmental scientists and engineers. Other commonly used units among chemists and geochemists are mole fraction (X) and mass fraction (Y). Mole fraction is used, for example, to predict gas solubility based on Henry's law along with dimensionless Henry's constant. Mass fraction, on the other hand, is used mostly by geochemists in phase equilibria calculation where temperature, pressure, and mass fraction are system's variables. Solute concentration in the air are frequently reported using both units; mg m⁻³ and ppm_v. These units can be converted from one to the another using ideal gas assumption which will be illustrated in the following examples.

EXAMPLE 1.1 Aqueous concentration

A solution made by dissolving 16.0 g of CaCl₂ in 64.0 g of water has a density of 1.18 g cm⁻³ at 25 °C. Express the concentration of Ca²⁺ in the solution in terms of molality, molarity, mg L^{-1} and ppm_w.

► Solution: From periodic table, the formula weight of CaCl₂ is 110.98 g mol⁻¹. Thus, the amount of calcium ion Ca²⁺ in 16.0 g of CaCl₂ is $(16.0 \div 110.98) = 0.1442$ mol or $0.1442 \times 40.08 = 5.7783$ g. Mass of the solution is given as 16.0 + 64.0 = 80.0 g or a volume of solution is $(80 \text{ g}) \div (1.18 \text{ g mL}^{-1}) = 67.7966 \text{ mL}$ or 0.0677966 L (or dm³). Based on these information, the concentration of Ca²⁺ in various units can be calculated as follows.

Molality (m):
$$[Ca^{2+}] = \frac{0.1442 \text{ mol}}{0.064 \text{ kg of water}} = 2.25 \text{ mol kg}^{-1}$$

Molarity (M):
$$[Ca^{2+}] = \frac{0.1442 \text{ mol}}{0.0677966 \text{ dm}^3 \text{ of solution}} = 2.13 \text{ mol dm}^{-3}$$

mg L⁻¹:
$$[Ca^{2+}] = \frac{5.7783 \times 10^3 \text{ mg}}{0.0677966 \text{ L of solution}} = 85,230 \text{ mg L}^{-1}$$

ppm_w:
$$[Ca^{2+}] = \frac{5.7783 \times 10^6 \ \mu g}{80 \ g \text{ of solution}} = 72,230 \text{ ppm}$$

It should be noticed that the concentration in mg L^{-1} and ppm_w units are *not* numerically identical by default for concentrated aqueous solution where solution's density is significantly greater than 1.0 g cm⁻³. The relationship between mg L^{-1} and ppm_w of any solution is given by

$$(\text{mg } L^{-1}) = (\text{ppm}_w) \div (\text{Solution's specific gravity}),$$
 (1.1)

where specific gravity of the solution is dimensionless quantity and it is numerically equal to the density in $g m L^{-1}$ or $g cm^{-3}$ units.

EXAMPLE 1.2 Pressure conversion

Convert the pressure (P) of 1.0 atm or 14.66 psi (lb in⁻²) to Pascal (N m⁻² or Pa).

► Solution: To successfully convert the pressure unit, we need to use unit conversion of length (or area) and force. In this case, a force or weight of 2.2 lb equals to 9.81 N (which is equivalent to a mass of 1.0 kg) and a length of 1.0 in equals to 0.0254 m.

$$P = 14.66 \text{ lb in}^{-2}$$

= $\left[14.66 \frac{\text{lb}}{\text{in}^2}\right] \times \left[\frac{1.0 \text{ in}}{0.0254 \text{ m}}\right]^2 \times \left[\frac{9.81 \text{ N}}{2.2 \text{ lb}}\right]$
= $1.013 \times 10^5 \text{ N m}^{-2} = 101.3 \text{ kPa}$

EXAMPLE 1.3 Gas concentration in air

Assuming that methane (CH₄) is an ideal gas, convert methane concentration of 5.75 ppm_v in air at to mg m⁻³ at 35 °C and 1.0 atm. Given gas constant R = 0.08205 L atm mol⁻¹ K⁻¹.

▶ Solution: Use ieal gas law PV = nRT to calculate a volume of 1.0 mol of CH₄ at 35 °C (308.15 K) and 1.0 atm.

$$V = \frac{nRT}{P} = \frac{1.0 \times 0.08205 \times 308.15}{1.0} = 25.283 \text{ L} = 25.283 \times 10^{-3} \text{ m}^3$$

Using the definition of ppm_v and molecular weight of CH₄ of 16 g mol⁻¹, the conversion of 5.75 ppm_v to mg m⁻³ can be calculated as follows.

5.75 ppm_v of CH₄ =
$$\left(\frac{5.75 \text{ m}^3 \text{ of CH}_4}{10^6 \text{ m}^3 \text{ of air}}\right) \times \left(\frac{1.0 \text{ mol of CH}_4}{25.283 \times 10^{-3} \text{ m}^3 \text{ of CH}_4}\right)$$

 $\times \left(\frac{16 \times 10^3 \text{ mg of CH}_4}{1.0 \text{ mol of CH}_4}\right)$
 = 3.639 mg m⁻³ at 35 °C and 1.0 atm

If the pressure and temperature drops to 20 $^\circ C\,$ and 0.90 atm, methane concentration of 5.75 $ppm_v\,$ will change to

$$5.75 \text{ ppm}_{v} = \frac{5.75 \times 16.0}{26.726} = 3.442 \text{ mg m}^{-3} \text{ at } 20 \text{ }^{\circ}\text{C} \text{ and } 0.9 \text{ atm.}$$

Note that 1.0 mol of ideal gas at 20 °C has a volume of $V = nRT/P = (1 \times 0.08205 \times 293.15)/(0.9) = 26.726$ L. From this example, it can be clear that gas concentration in mg m⁻³ can vary with ambient temperature and pressure.

10 REVIEW; TYPES, PROPERTIES AND CHARACTERISTICS OF POLLUTANTS

1.2 Basic mathematics and statistics

1.2.1 Numerical solution to algebraic equation

Environmental problem usually encounter the need to find a solution of an algebraic equation f(x) = 0. If the function f(x) is explicit and can be easily solved, there would not be any problem finding the value of x_a that gives $f(x_a) = 0$. However, a number of occasions we usually face are that the function f(x) cannot be easily solved for a closed-form. Thus, it is inevitably required to obtain the approximate numerical solution.

Newton-Ralphson method for f(x) = 0:

Consider an algebraic equation f(x) = 0; the solution to above equation can be obtained iteratively using a recursive formula

$$x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)}$$
(1.2)

when f'(x) is the first derivative of f(x). The above formula is called Newton-Raphson method. The solution is said to be converged if $|\frac{x_{i+1}-x_i}{x_i}| \le \varepsilon$ where ε is a tolerance (typically, $\varepsilon = 10^{-4}$).

Newton-Ralphson method for f(x) = 0:

Consider a system of *n* algebraic equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ or

$$f_1(x_1, x_2, \dots, x_n) = 0$$

$$f_2(x_1, x_2, \dots, x_n) = 0$$

$$\vdots$$

$$f_3(x_1, x_2, \dots, x_n) = 0$$

the Newton-Ralphson solution to above system of equation is

$$\mathbf{x}_{i+1} = \mathbf{x}_i - [D\mathbf{f}(\mathbf{x})]^{-1} \mathbf{f}(\mathbf{x}_i)$$
(1.3)

when f'(x) is the first derivative of f(x). The solution is said to be converged if $\max |\frac{x_{i+1}-x_i}{x_i}| \leq \varepsilon$ where ε is a tolerance. The term $[D\mathbf{f}(\mathbf{x})]$ is called Jacobian matrix which consists of derivatives of $\mathbf{f}(\mathbf{x})$ and is defined as

$$D\mathbf{f}(\mathbf{x}) = \left(\frac{\partial f_i}{\partial x_j}\right)_{n \times n} = \begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \cdots & \frac{\partial f_2}{\partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_n}{\partial x_1} & \frac{\partial f_n}{\partial x_2} & \cdots & \frac{\partial f_n}{\partial x_n} \end{bmatrix}$$

EXAMPLE 1.4 Volume of a real gas

An ideal gas law PV = nRT is typically used to find the volume of a gas under a given temperature and pressure with the assumptions that gas molecules do not interact one another and a molecule does not have volume! van der Waals developed a modified version of gas law stating that

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where *a* and *b* are empirical parameters and must be experimentally evaluated. Find a volume of 1.0 mol CO₂ gas at 25 °C and 1 atm using ideal and real gas laws. Given a = 0.396 Pa m⁶mol⁻² and $b = 42.69 \times 10^{-6}$ m³mol⁻¹.

Solution: If ideal gas is assumed, the volume of CO_2 is

$$V = \frac{nRT}{P} = \frac{1.0 \times 8.3143 \times 298.15}{1.01325 \times 10^5} = 24.46 \times 10^{-3} \text{ m}^3.$$

If we assume that CO_2 is a real gas, its molar volume can be calculated as follows. Rearrange the above equation for real gas and we have

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$
$$PV^3 - (Pnb + nRT)V^2 + an^2V - abn^3 = 0$$

Let

$$f(V) = PV^3 - (Pnb + nRT)V^2 + an^2V - abn^3$$

the first derivative of f(V) with respect to V is

$$\frac{df}{dV} = \int f'(V) = 3PV^2 - 2(Pnb + nRT)V + an^2$$

Use Newton-Ralphson formula in (1.2)

$$V_{i+1} = V_i - \frac{f(V_i)}{f'(V_i)}$$

with $\varepsilon = 10^{-6}$ and initial guess $V_0 = 24.46 \times 10^{-3} \text{ m}^3$, molar volume of CO₂ can be calculated and converged after 3 iterations and its volume is $24.35 \times 10^{-3} \text{ m}^3$.

i	V _i	f(V _i)	f'(V _i)	ε
0	2.4465E-02	7.082E-03	6.083E+01	-
1	2.4349E-02	6.698E-05	5.968E+01	0.0047588
2	2.4347E-02	6.195E-09	5.967E+01	4.609E-05
3	2.4347E-02	1.996E-16	5.967E+01	4.264E-09

12 REVIEW; TYPES, PROPERTIES AND CHARACTERISTICS OF POLLUTANTS

1.2.2 Differential equations

The term "*Differential equation*" consists of two words: differential and equation. An equation is represented by an equality of both sides of the mathematical equation while differential means it involves derivatives of some functions. Thus, a differential equation is an equation for a function that relates the values of a function to the values of its derivatives [3]. Several environmental problems can be described using differential equations. The ultimate goal is to seek for the solution (i.e., function) that satisfies the differential equation. In general, the functions usually represent physical quantities, the derivatives represent their rates of change, and the equation defines a relationship between the two. Differential equations play an important role in many disciplines such as science, engineering, finance and economics, etc. The following equations are simple examples of differential equations:

1-D Newton's law of cooling:	$\frac{dT}{dx} = h_s(T - T_a)$
2-D Heat conduction:	$k_x \frac{\partial^2 T}{\partial x^2} + k_y \frac{\partial^2 T}{\partial y^2} = 0$
3-D Groundwater flow:	$S_s \frac{\partial h}{\partial t} = -K_x \frac{\dot{\partial}^2 h}{\partial x^2} - K_y \frac{\partial^2 h}{\partial y^2} - K_z \frac{\partial^2 h}{\partial z^2}$
Chemical in reactor:	$a\frac{dC}{dt} + bC + c = 0$

From these examples, you can see that differential equations relate the derivative(s) of a dependent variable such as T or h to space (x, y, z) and time t. The above examples arise from energy and mass balance equation which are common in science and engineering disciplines. Differential equations can be categorized into two types: ordinary or partial differential equations (ODE or PDE). They can either be linear or nonlinear. And, their order can be first-, second-, or higher-order differential equations. This classification will help select which methods can be effectively used to solve them. Examples of differential equations with different types, orders and linearity are illustrated in Table 1.5.

Table 1.5 Examples for classification of differential equations.

No.	Example	Туре	Order	Linearity
1.	$\frac{dy}{dt} = 2\sin t$	ODE	First	Linear
2.	$\frac{d^2x}{dy^2} + \frac{dx}{dy} + 3x = 0$	ODE	Second	Linear
3.	$\frac{d^2x}{dy^2} + \left(\frac{dx}{dy}\right)^2 + 3x = 2\cos x$	ODE	Second	Nonlinear
4.	$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = 0$	PDE	Second	Linear
5.	$\frac{\partial u}{\partial t} = \alpha \frac{\partial^2 u}{\partial x^2}$ where $u = u(x,t)$	PDE	Second	Linear
6.	$Au_{xx} + 2Bu_{xy} + Cu_{yy} + Du_x + Eu_y = 0$	PDE	Second	Linear
7.	$x^{3}\frac{d^{3}y}{dx^{3}} + x^{2}\frac{d^{2}y}{dx^{2}} + x\frac{dy}{dx} + xy = e^{x}$	ODE	Third	Linear
8.	$\frac{\partial f}{\partial x} + \frac{\partial f}{\partial y} = 6$	PDE	First	Linear

Differential equations in science and engineering are developed for describing some natural and engineered phenomena. Almost all of the differential equations developed in science and engineering disciplines are based on the law of physics and chemistry or, sometimes, observations together with the energy or mass balance principles. For simplicity, we will limit ourselves to the formulation of ODEs in this section The development of a more complex PDEs will be discussed later.

EXAMPLE 1.5 A free fall of an object

An apple of mass *m* dropped from the tree under the force of gravity as shown in the following picture. Develop a differential equation describing the height (i.e., displacement) above ground y(t) as a function of time *t*.



► Solution: Newton's second law of motion, which states that an object's mass times its acceleration equals the total force acting on it, can be applied to the falling object. This leads to the equation,

$$\Sigma F = ma$$
$$-mg = m\frac{d^2y}{dt^2}$$

The above equation is a second-order ordinary differential equation that most of us are already familiar from high school or first-year mechanics class. Two initial conditions must be given to solve for the displacement of an apple which include (1) initial velocity of an apple is zero or v(t = 0) = y'(t = 0) = 0, and (2) initial displacement is y(t = 0) = H. Thus, a more complete form of the governing equation is

$$\frac{d^2y}{dt^2} = -g, \qquad y(0) = H, \quad y'(0) = 0.$$

The solution of the above ODE can be easily found by integrating both sides of the above equation with respect to t twice and applying two initial conditions, and the displacement is

$$y(t) = -\frac{1}{2}gt^2 + H.$$

EXAMPLE 1.6 Cooling of a hot metal ball

A hot, small metal ball of an initial temperature T_0 is placed in a cold air mass of a temperature T_a . Assuming the metal ball loses heat uniformly. Find the expression for metal ball temperature as a function of time.

14 REVIEW; TYPES, PROPERTIES AND CHARACTERISTICS OF POLLUTANTS

► Solution: To solve this problem, we need to apply *Newton's law of cooling* which states that the rate of change of the temperature of an object is proportional to the difference between its own temperature T and the ambient temperature T_a (i.e. the temperature of its surroundings).

$$\frac{dT}{dt} = -h_s(T - T_a) \quad \text{with initial condition} \quad T(t = 0) = T_0$$

where h_s is heat transfer coefficient (s⁻¹), and the solution to the above ODE is

$$T(t) = T_a + (T_0 - T_a)e^{-h_s t}.$$

In environmental problems, there are a large variety of differential equations that can be used to describe the systems ranging from a simple first-order ODE to a very complex non-linear PDE. In this chapter, a solution of a first-order ODE which is also commonly found in simple environmental system will be discussed. Two commonly found types of first-order ODE include *separable variables first-order ODE* and *first-order linear ODE*. Each type employs different solution methods which can be explained in the following sections.

1.2.2.1 Separable variable ODE The separable variables first-order ODE can be written in the form [28]

$$\frac{dy}{dx} = f(x)g(y) \tag{1.4}$$

The above equation shows that all the x-terms along with dx can be put on one side of the equation and all the y-terms along with dy can be put on another side. We can integrate both sides of the equation with respect to each variable to obtain the solution.

EXAMPLE 1.7

Solve the following ODE.

$$\frac{dy}{dx} - y = 0$$

► Solution: The above differential equation can be rewritten as

$$\frac{dy}{dx} = y \quad \Rightarrow \quad \frac{1}{y}dy = dx, \quad y \neq 0$$

Integrating on both sides, we get

$$\int \frac{dy}{y} = \int dx \quad \Rightarrow \quad \ln|y| = x + C_1 \quad \Rightarrow \quad |y| = e^{x + C_1}$$
$$y = C_2 e^x,$$

where $C_2 = \pm e^{C_1} \neq 0$. Note that, the constants C_1 and C_2 can be arbitrarily constants. If additional information on the function such as boundary or initial conditions is given, we can evaluate these constants.
EXAMPLE 1.8

Solve the initial value problem

$$\frac{dy}{dx} - y = 0, \quad y(0) = 5.$$

► Solution: From the previous example, the solution of the given differential equation is in the form $y = C_2 e^x$. In order for the solution to satisfy the given condition y(0) = 5,, we substitute such condition and we will have $5 = C_2 e^0 \Rightarrow C_2 = 5$. So the unique solution to the initial value problem is obtained as $y = 5e^x$.

 \Box

1.2.2.2 *First-order linear ODE* A commonly found problem in science and engineering applications is first-order *linear* ODE. This type of ODE sometimes cannot be solved using separable variables method. In this case, a special technique called *integrating factor method* can be applied. An integrating factor method can be slightly confusing initially, but eventually toward the end it does make sense and is actually very simple. We will start by outlining the method before showing some examples.

Consider the following first-order linear ODE of the form:

$$\frac{dy}{dx} + f(x) \cdot y = g(x), \tag{1.5}$$

where f(x) and g(x) are arbitrary functions of only variable x. Equations of this form are not separable unless f(x) and g(x) are constants. The solution to the above ODE is given as [3, 28]

$$y(x) = \frac{1}{I(x)} \left[\int I(x)g(x)dx + C \right]$$
(1.6)

where *C* is a constant of integration and I(x) is an integrating factor and can be evaluated using the following relationship

$$I(x) = \exp\left(\int f(x)dx\right).$$
(1.7)

EXAMPLE 1.9

Solve a first-order linear ODE: $\frac{dy}{dx} - \frac{1}{x}y = x^2$

► Solution: Comparing the question to the standard form, we can see that $f(x) = -\frac{1}{x}$ and $g(x) = x^2$. So, the integrating factor is

$$I(x) = e^{\int (-\frac{1}{x})dx} = e^{-\ln(x)} = e^{\ln(x^{-1})} = x^{-1}.$$

Substitute the integrating factor I(x) into (1.6), the solution to the above ODE can be obtained as follows.

$$y(x) = \frac{1}{I(x)} \left[\int I(x)g(x)dx + C \right] = \frac{1}{x^{-1}} \left(\int (x^{-1})(x^2)dx + C \right) = \frac{1}{2}x^3 + Cx$$

1.2.3 Numerical methods for ODE

As mentioned earlier, several environmental systems can be described using mathematical model in terms of differential equation or system of differential equations. Some differential equations can be solved analytically by hand whereas the others are too complex to obtain analytical solutions. Thus, they must be approximated using numerical methods which will be described as follows.

1.2.3.1 Simple one-step method for first-order ODE Consider a general form of firstorder ODE with a given initial (or boundary) condition as follows.

$$\frac{du}{dt} = f(t, u), \qquad u(t_0) = u_0$$

The derivative du/dt is approximated using forward difference equation as

 $\frac{du}{dt}\approx\frac{u_{i+}}{dt}$

$$\frac{du}{dt}\approx\frac{u_{i+1}-u_i}{\Delta t}$$

where u_{i+1} and u_i are function u at t_{i+1} and t_i , respectively. And, the value of $\Delta t = t_{i+1} - t_i$. The solution to the above ODE can be approximated by using explicit Euler, implicit Euler and fourth-order Runge-Kutta (RK4) methods as shown below [6].

Explicit Euler:

or

$$\frac{du}{dt} \approx \frac{u_{i+1} - u_i}{\Delta t} = f(t_i, u_i)$$

$$u_{i+1} = u_i + \Delta t \left[f(t_i, u_i) \right]$$
(1.8)

Implicit Euler:

or

$$\frac{du}{dt} \approx \frac{u_{i+1} - u_i}{\Delta t} = f(t_{i+1}, u_{i+1})$$
$$u_{i+1} = u_i + \Delta t \left[f(t_{i+1}, u_{i+1}) \right]$$

(1.9)

4th-order Runge-Kutta (RK4):

$$\frac{du}{dt} \approx \frac{u_{i+1} - u_i}{\Delta t} = \frac{1}{6} \left(\kappa_1 + 2\kappa_2 + 2\kappa_3 + \kappa_4 \right)$$
$$u_{i+1} = u_i + \frac{\Delta t}{6} \left(\kappa_1 + 2\kappa_2 + 2\kappa_3 + \kappa_4 \right)$$
(1.10)

where

or

$$\kappa_1 = f(t_i, u_i)$$

$$\kappa_2 = f(t_i + \frac{1}{2}\Delta t, u_i + \frac{1}{2}\kappa_1\Delta t)$$

$$\kappa_3 = f(t_i + \frac{1}{2}\Delta t, u_i + \frac{1}{2}\kappa_2\Delta t)$$

 κ_4 $f(t_i + \Delta t, u_i + \kappa_3 \Delta t)$

EXAMPLE 1.10

Solve the following ODE for $0 \le t \le 1$.

$$\frac{du}{dt} = 1 - t + 4u, \qquad u(0) = 1$$

Given the analytical solution, for comparison, as $u(t) = -\frac{3}{16} + \frac{1}{4}t + \frac{19}{16}e^{4t}$.

Solution: Use the scheme given in (1.8)-(1.10), we can setup expressions used to approximate the solution to the above ODE.

Explicit Euler:

$$\frac{du}{dt} \approx \frac{u_{i+1} - u_i}{\Delta t} = 1 - t_i + 4u_i \Rightarrow \boxed{u_{i+1} = u_i + \Delta t \left[1 - t_i + 4u_i\right]}$$

Implicit Euler:

$$\frac{du}{dt} \approx \frac{u_{i+1} - u_i}{\Delta t} = 1 - t_{i+1} + 4u_{i+1} \Rightarrow u_{i+1} = \frac{u_i + \Delta t(1 - t_{i+1})}{1 - 4\Delta t}$$

4th Order RK (RK4):

$$\kappa_{1} = 1 - t_{i} + 4u_{i}$$

$$\kappa_{2} = 1 - (t_{i} + \frac{1}{2}\Delta t) + 4(u_{i} + \frac{1}{2}\kappa_{1}\Delta t)$$

$$\kappa_{3} = 1 - (t_{i} + \frac{1}{2}\Delta t) + 4(u_{i} + \frac{1}{2}\kappa_{2}\Delta t)$$

$$\kappa_{4} = 1 - (t_{i} + \Delta t) + 4(u_{i} + \kappa_{3}\Delta t)$$

$$u_{i+1} = u_{i} + \frac{\Delta t}{6}(\kappa_{1} + 2\kappa_{2} + 2\kappa_{3} + \kappa_{4})$$

Use spreadsheet to calculate u_{i+1} with a choice of $\Delta t = 0.1$. It can be clearly seen that the solution from RK4 is more accurate than Euler methods. The RK4 method is the most widely used approximation technique although it requires more computational cost.

Analytical Solution			Explicit	Implicit	RK4									
i	t	и	и	и	и	κ ₁	к ₂	κ3	κ ₄					
0	0	1	1	1	1									
1	0.1	1.609	1.500	1.817	1.609	5.000	5.950	6.140	7.356					
2	0.2	2.505	2.190	3.161	2.505	7.336	8.753	9.036	10.850					
3	0.3	3.830	3.146	5.385	3.829	10.820	12.934	13.357	16.063					
4	0.4	5.794	4.474	9.075	5.793	16.018	19.171	19.802	23.838					
5	0.5	8.712	6.324	15.209	8.709	23.771	28.475	29.416	35.438					
6	0.6	13.053	8.904	25.415	13.048	35.337	42.355	43.758	52.741					
7	0.7	19.516	12.505	42.408	19.507	52.591	63.059	65.153	78.552					
8	0.8	29.145	17.537	70.713	29.131	78.329	93.944	97.067	117.056					
9	0.9	43.498	24.572	117.872	43.474	116.722	140.017	144.676	174.493					
10	1	64.898	34.411	196.453	64.858	173.996	208.745	215.695	260.174					



1.2.3.2 Simple one-step method for "system" of first-order ODEs A system of firstorder ODEs are encountered in several science and engineering disciplines including environmental science. The system of first-order ODEs can either be obtained from a modeling of serial and parallel chemical/biochemical reactions or it can be a result of a reduction of higher-order ODE. Several solution methods have been developed but the most commonly used technique is, still, a fourth-order Runge-Kutta method. Consider a system of firstorder ODE in the form

$$\frac{du_1}{dt} = f_1(u_1, u_2, \dots, u_n, t)
\frac{du_2}{dt} = f_2(u_1, u_2, \dots, u_n, t)
\vdots
\frac{du_n}{dt} = f_n(u_1, u_2, \dots, u_n, t)$$
or
$$\frac{d}{dt} \begin{cases} u_1 \\ u_2 \\ \vdots \\ u_n \end{cases} = \begin{cases} f_1(u_1, u_2, \dots, u_n, t) \\ f_2(u_1, u_2, \dots, u_n, t) \\ \vdots \\ f_n(u_1, u_2, \dots, u_n, t) \end{cases},$$

which can be written, in short, as $\mathbf{U}'(t) = \mathbf{F}(\mathbf{U},t)$ where $\mathbf{U}(t) = [u_1(t), u_2(t), \dots, u_n(t)]^T$ and $\mathbf{F} = [f_1, f_2, \dots f_n]^T$. The solution to the above system of first-order ODE can be approximated using fourth-order Runge-Kutta, similar to (1.10), as follows [6].

4th-order Rung	e-Kutta (RK4) for system of first-order ODE:	
where	$\mathbf{U}_{i+1} = \mathbf{U}_i + \frac{\Delta t}{6} \left(\mathbf{K}_1 + 2\mathbf{K}_2 + 2\mathbf{K}_3 + \mathbf{K}_4 \right)$	(1.11)
	$ \begin{aligned} \mathbf{K}_1 &= \mathbf{F}(t_i, u_i) \\ \mathbf{K}_2 &= \mathbf{F}(t_i + \frac{1}{2}\Delta t, \mathbf{U}_i + \frac{1}{2}\mathbf{K}_1\Delta t) \\ \mathbf{K}_3 &= \mathbf{F}(t_i + \frac{1}{2}\Delta t, \mathbf{U}_i + \frac{1}{2}\mathbf{K}_2\Delta t) \\ \mathbf{K}_4 &= \mathbf{F}(t_i + \Delta t, \mathbf{U}_i + \mathbf{K}_3\Delta t) \end{aligned} $	

18

EXAMPLE 1.11 Fate of NH₃ in a nitrogen biogeochemical cycle

The nitrogen cycle refers to a biogeochemical cycle where nitrogen element is converted into multiple chemical forms as it circulates among atmosphere, terrestrial, and aquatic ecosystems. The conversion of nitrogen can be carried out through both biological and physical processes.

For illustrative purpose of the example, we will consider the fate of reduced nitrogen in the form of ammonia (NH₃) in nitrogen cycle. Ammonia, a product of the decay or degradation of organisms by decomposers, can be converted into nitrite (NO₂⁻) and nitrate (NO₃⁻) via nitrification process. Algae can also use ammonium for its growth. Lastly, ammonia can evaporate into the ambient atmosphere. Assuming that all reactions are first-order kinetics with decay or reaction constants *k* as shown below

Process	Reaction
Nitrification	$NH_3 \xrightarrow{k_1} NO_2^- \xrightarrow{k_2} NO_3^-$
Evaporation	$NH_3 \xrightarrow{k_3} 0$
Assimilation	$NH_3 \xrightarrow{k_4} algae$

Given the initial concentration of ammonia, nitrite and nitrate are 10, 0 and 0 μ g-N m⁻³, respectively and the parameters k_1, k_2, k_3 and k_4 are 0.2, 0.1, 0.05 and 0.15 d⁻¹, respectively. Use RK4 method to approximate temporal change in nitrogen species concentrations.

► Solution: The above parallel and series reaction can be written in terms of differential equations as,

$$\frac{d}{dt}[NH_3] = -(k_1 + k_3 + k_4)[NH_3]$$

$$\frac{d}{dt}[NO_2^{-}] = +k_1[NH_3] - k_2[NO_2^{-}]$$

$$\frac{d}{dt}[NO_3^{-}] = +k_2[NO_2^{-}]$$

where [NH₃], [NO₂⁻] and [NO₃⁻] are concentrations in microgram of nitrogen per cubic meter of air or μ g-N m⁻³. For simplicity, let vector **U** and **F** are species concentration and right-hand-side function, respectively.

$$\mathbf{U} = \begin{cases} u_1 \\ u_2 \\ u_3 \end{cases} = \begin{cases} [\mathrm{NH}_3] \\ [\mathrm{NO}_2^{-1}] \\ [\mathrm{NO}_3^{-1}] \end{cases} \qquad \mathbf{F} = \begin{cases} f_1 \\ f_2 \\ f_3 \end{cases} = \begin{cases} -(k_1 + k_3 + k_4)u_1 \\ +k_1u_1 - k_2u_2 \\ +k_2u_2 \end{cases}$$

Let $\Delta t = 0.5$ d, we can apply (1.11) to solve for the above system of first-order ODE. The spreadsheet calculation as well as the plot of all species concentrations are shown below. We can see that, the ammonia (NH₃) concentrations decreases with time while nitrite (NO₂⁻) increases to maximum concentration and drops subsequently. Lastly, the concentration of nitrate (NO₃⁻) continuously increases with time. This example illustrates an effective use of RK4 scheme in solving environmental problem described by a system of first-order ODEs.



Time (d)	NH ₃	NO ₂	NO ₃	Time (d)	NH ₃	NO ₂	NO ₃
0.0	10	0	0	12.5	0.0674	2.0629	3.5560
0.5	8.1873	1.0254	0.0000	13.0	0.0552	1.9640	3.6617
1.0	6.7032	1.8124	0.0526	13.5	0.0452	1.8690	3.7624
1.5	5.4882	2.4068	0.1455	14.0	0.0370	1.7778	3.8582
2.0	4.4933	2.8462	0.2689	14.5	0.0303	1.6905	3.9494
2.5	3.6789	3.1610	0.4148	15.0	0.0248	1.6069	4.0361
3.0	3.0120	3.3762	0.5769	15.5	0.0203	1.5270	4.1185
3.5	2.4660	3.5120	0.7500	16.0	0.0166	1.4508	4.1968
4.0	2.0190	3.5848	0.9301	16.5	0.0136	1.3781	4.2711
4.5	1.6530	3.6080	1.1139	17.0	0.0111	1.3089	4.3418
5.0	1.3534	3.5925	1.2988	17.5	0.0091	1.2429	4.4089
5.5	1.1081	3.5471	1.4830	18.0	0.0075	1.1801	4.4726
6.0	0.9072	3.4789	1.6649	18.5	0.0061	1.1204	4.5331
6.5	0.7428	3.3935	1.8433	19.0	0.0050	1.0636	4.5906
7.0	0.6081	3.2957	2.0173	19.5	0.0041	1.0096	4.6451
7.5	0.4979	3.1891	2.1862	20.0	0.0034	0.9582	4.6969
8.0	0.4076	3.0766	2.3497	20.5	0.0027	0.9094	4.7460
8.5	0.3338	2.9607	2.5075	21.0	0.0022	0.8631	4.7926
9.0	0.2733	2.8431	2.6593	21.5	0.0018	0.8191	4.8369
9.5	0.2237	2.7254	2.8050	22.0	0.0015	0.7773	4.8789
10.0	0.1832	2.6086	2.9448	22.5	0.0012	0.7376	4.9187
10.5	0.1500	2.4936	3.0785	23.0	0.0010	0.6999	4.9565
11.0	0.1228	2.3811	3.2064	23.5	8000.0	0.6641	4.9924
11.5	0.1005	2.2717	3.3285	24.0	0.0007	0.6301	5.0265
12.0	0.0823	2.1655	3.4449	24.5	0.0006	0.5979	5.0588

20

1.2.3.3 Finite difference method for ODE Another famous numerical method for solving differential equation is called Finite Difference technique. This technique is a simple, yet powerful, tool for approximating the solution of an ODE which depends on space (and also time). In this method, the problem domain is divided (or discretized) into smaller, discrete domain. The difference equation is used to approximate the derivative(s) of an ODE. The formulation will end up with having to solve the system of algebraic equations for the approximated solution.

Before we proceed to the example of finite-difference application, let us introduce the difference equations that can be used to approximate the derivatives [28].

Approximates of 1st	derivatives:								
Forward difference:	$rac{du}{dx}pprox rac{u_{i+1}-u_i}{\Delta x}$	(1.12)							
Backward difference #1:	$\frac{du}{dx} \approx \frac{u_i - u_{i-1}}{\Delta x}$	(1.13)							
Backward difference #2:									
	$\frac{du}{dx} \approx \frac{3u_i - 4u_{i-1} + u_{i-2}}{2\Delta x}$	(1.14)							
Central difference:	$\frac{du}{dx} \approx \frac{u_{i+1} - u_{i-1}}{2\Delta x}$	(1.15)							
Approximate of 2nd derivatives:									
	$\frac{d^2u}{dx^2} \approx \frac{u_{i+1} - 2u_i + u_{i-1}}{(\Delta x)^2}$	(1.16)							

EXAMPLE 1.12 Application of finite-difference method for ODE

Consider the following hypothetical shallow aquifer located between two fully penetrated rivers. The aquifer is being pumped from two wells at a rate of q = -0.01 $m^3 d^{-1}$ per m² (i.e., per area of the aquifer). The cross-section AA' is 1,000 m long and the wells are located at x = 300 and x = 700 m, respectively. The aquifer is recharged with a rate of R = +0.002 m d⁻¹. The hydraulic conductivity of an aquifer is K = 1.25 m d⁻¹ and the depth of both rivers are $h_0 = 15$ and $h_1 = 20$ m, respectively. Calculate the steady-state water table elevation in this aquifer. Given the ordinary differential equation describing groundwater flow in 1-D domain as

$$\frac{d}{dx}\left(Kh\frac{dh}{dx}\right) + R + q = 0,$$

where h = h(x) is a hydraulic head or water table elevation at a distance x. Note that q is negative because the water is being pumped out of an aquifer and the units of R and q are in m d⁻¹.



► Solution: In finite difference formulation, the 1-D aquifer is discretized into 10 blocks (11 nodes) and each block has a length of $\Delta x = 100$ m. Each block has an area $\Delta x \times w$ where w = 1 m is a width of the aquifer. Groundwater pumping occurs only at nodes #4 and #8. The difference equation for 2nd derivative approximation of the governing equation for each node *i* can be written as follows.

$$\begin{split} \left[\frac{d}{dx}\left(Kh\frac{dh}{dx}\right)\right]_{i} &\approx \frac{\left(Kh\frac{dh}{dx}\right)_{i+\frac{1}{2}} - \left(Kh\frac{dh}{dx}\right)_{i-\frac{1}{2}}}{\Delta x} \\ &= \frac{Kh_{i+\frac{1}{2}}\left(\frac{dh}{dx}\right)_{i+\frac{1}{2}} - Kh_{i-\frac{1}{2}}\left(\frac{dh}{dx}\right)_{i-\frac{1}{2}}}{\Delta x} \\ &= \frac{\left[K\left(\frac{h_{i+1}+h_{i}}{2}\right)\left(\frac{h_{i+1}-h_{i}}{\Delta x}\right)\right] - \left[K\left(\frac{h_{i}+h_{i-1}}{2}\right)\left(\frac{h_{i}-h_{i-1}}{\Delta x}\right)\right]}{\Delta x} \\ &= \frac{K}{2(\Delta x)^{2}}\left(h_{i-1}^{2} - 2h_{i}^{2} + h_{i+1}^{2}\right) \end{split}$$

Substitute the above approximation into the governing equation, the difference equation or each node can be derived.

$$\begin{bmatrix} \frac{d}{dx} \left(Kh\frac{dh}{dx} \right) \end{bmatrix}_i = -R_i - q_i$$
$$\frac{K}{2(\Delta x)^2} \left(h_{i-1}^2 - 2h_i^2 + h_{i+1}^2 \right) = -R_i - q_i$$
$$h_{i-1}^2 - 2h_i^2 + h_{i+1}^2 = \frac{2(\Delta x)^2}{K} \left(-R_i - q_i \right)$$

22

For simplicity, let $u = h^2$ and $\varphi = 2(\Delta x)^2/K$, the above expression is reduced to

$$u_{i-1} - 2u_i + u_{i+1} = \varphi(-R_i - q_i).$$

We can write the above difference equation for all nodes i = 2, 3, ..., 10 as follows. It should be clear that it is not necessary to write such equation for nodes #1 and #11 because the heads at both locations are already given where $h_1 = 15$ and $h_{11} = 20$ m (or $u_1 = 15^2$ and $u_{11} = 20^2$), respectively.

i = 2 :
$$u_1 - 2u_2 + u_3 = \varphi(-R_i - q_2)$$

i = 3 : $u_2 - 2u_3 + u_4 = \varphi(-R_i - q_3)$
: : :
i = 10 : $u_9 - 2u_{10} + u_{11} = \varphi(-R_i - q_{10})$

The above algebraic equations can be written in a matrix form where

-2	1	0	0	0	0	0	0	0	u_2		$[-R_2 - u_1]$
1	-2	1	0	0	0	0	0	0	<i>u</i> ₃		$-R_3$
0	1	-2	1	0	0	0	0	0	u_4		$-R_4 - q_4$
0	0	1	-2	1	0	0	0	0	<i>u</i> 5		$-R_5$
0	0	0	1	-2	1	0	0	0	u_6	$= \varphi$	$-R_6$
0	0	0	0	1	-2	1	0	0	<i>u</i> 7		$-R_7$
0	0	0	0	0	1	-2	1	0	u_8		$-R_8 - q_8$
0	0	0	0	0	0	1	-2	1	<i>u</i> 9		$-R_9$
0	0	0	0	0	0	0	1	-2	u_{10}		$-R_{10}-u_{11}$

Note that only non-zero pumping rates $(q_4 \text{ and } q_8)$ are included in the above system of equations. The values of u (or $h = \sqrt{u}$) can be solved using simple matrix inversion or other iterative technique and the steady-state drawdown for this problem is shown below.



1.2.4 Basic statistics

This section will provide review of some basic statistics principles that will be frequently used in this course which include the error of measurements, least-square regression, confidence interval of the modeled parameters, a goodness of fit of the model, etc.

1.2.4.1 Error of the measurement Measurements of chemical constituents in environmental media such as sol, air and water (or groundwater) is not always accurate. They are always associated with either sampling or measurement errors. The accurate value can never be measured. The *error* of observation refers to the difference between measured and actual values. However, the true value of the estimate is not known, we can use the measurement data to estimate the upper and lower limit of the true value.

Error of the measurements:

For any *N* measurement (or sampling) where the data are $x_1, x_2, ..., x_N$, statistical parameters can be calculated as follows [28, 2].

Mean:	$\bar{x} = \frac{x_1 + x_2 + \ldots + x_N}{N} = \frac{\sum x_i}{N}$	
Variance:	$s^{2} = \frac{\sum (x_{i} - \bar{x})^{2}}{N - 1} $ (1.17)	
Standard deviation:	$s = \sqrt{s^2} = \sqrt{\frac{\sum(x_i - \bar{x})^2}{N - 1}} \qquad \qquad$	
Standard error of the mean:	$s_{\bar{x}} = \frac{s}{\sqrt{N}} \qquad $	

The $100(1 - \alpha)$ confidence interval for the true mean (i.e., population mean, μ) can be calculated using *t*-statistics (two-tail) as

$$\mu = \bar{x} \pm (t_{\nu,\alpha/2}) \times (s_{\bar{x}}), \qquad (1.18)$$

where α is a statistical significance level and v = N - 1 is a degree of freedom. Typically, we choose $\alpha = 0.05$ which refers to a 95% confidence interval of μ . The value of two-tailed *t*-statistics can be found from Table 1.6 or by using the command "=T.INV.2T(α ,v)" in Microsoft Excel.

EXAMPLE 1.13 Cadmium concentration in soils

Ten soil samples from cadmium contaminated site show cadmium concentration of 25, 16, 38, 42, 51, 23, 26, 19, 26 and 41 mg kg⁻¹. According to Thailand's Pollution Control Department, the regulated standard of cadmium concentration is 37 mg kg⁻¹, use statistics to make an assessment of this site.

► Solution: Based on the given concentration, the average, variance, standard deviation and standard error of the mean can be calculated as follows.

	$\frac{1}{2} = \frac{1}{2} + \frac{1}$													
One-	tail (α)	0.25	0.2	0.1	0.05	0.025	0.01	0.005	0.001					
Two-	tail (α)	0.5	0.4	0.2	0.1	0.05	0.02	0.01	0.002					
	1	1.0000	1.3764	3.0777	6.3138	12.706	31.821	63.657	318.31					
	2	0.8165	1.0607	1.8856	2.9200	4.3027	6.9646	9.9248	22.327					
	3	0.7649	0.9785	1.6377	2.3534	3.1824	4.5407	5.8409	10.215					
	4	0.7407	0.9410	1.5332	2.1318	2.7764	3.7469	4.6041	7.1732					
	5	0.7267	0.9195	1.4759	2.0150	2.5706	3.3649	4.0321	5.8934					
	6	0.7176	0.9057	1.4398	1.9432	2.4469	3.1427	3.7074	5.2076					
	7	0.7111	0.8960	1.4149	1.8946	2.3646	2.9980	3.4995	4.7853					
	8	0.7064	0.8889	1.3968	1.8595	2.3060	2.8965	3.3554	4.5008					
	9	0.7027	0.8834	1.3830	1.8331	2.2622	2.8214	3.2498	4.2968					
	10	0.6998	0.8791	1.3722	1.8125	2.2281	2.7638	3.1693	4.1437					
	11	0.6974	0.8755	1.3634	1.7959	2.2010	2.7181	3.1058	4.0247					
	12	0.6955	0.8726	1.3562	1.7823	2.1788	2.6810	3.0545	3.9296					
	13	0.6938	0.8702	1.3502	1.7709	2.1604	2.6503	3.0123	3.8520					
	14	0.6924	0.8681	1.3450	1.7613	2.1448	2.6245	2.9768	3.7874					
٦	15	0.6912	0.8662	1.3406	1.7531	2.1314	2.6025	2.9467	3.7328					
lop	16	0.6901	0.8647	1.3368	1.7459	2.1199	2.5835	2.9208	3.6862					
ē	17	0.6892	0.8633	1.3334	1.7396	2.1098	2.5669	2.8982	3.6458					
ц.	18	0.6884	0.8620	1.3304	1.7341	2.1009	2.5524	2.8784	3.6105					
đ	19	0.6876	0.8610	1.3277	1.7291	2.0930	2.5395	2.8609	3.5794					
ree	20	0.6870	0.8600	1.3253	1.7247	2.0860	2.5280	2.8453	3.5518					
eg	21	0.6864	0.8591	1.3232	1.7207	2.0796	2.5176	2.8314	3.5272					
	22	0.6858	0.8583	1.3212	1.7171	2.0739	2.5083	2.8188	3.5050					
	23	0.6853	0.8575	1.3195	1.7139	2.0687	2.4999	2.8073	3.4850					
	24	0.6848	0.8569	1.3178	1.7109	2.0639	2.4922	2.7969	3.4668					
	25	0.6844	0.8562	1.3163	1.7081	2.0595	2.4851	2.7874	3.4502					
	26	0.6840	0.8557	1.3150	1.7056	2.0555	2.4786	2.7787	3.4350					
	27	0.6837	0.8551	1.3137	1.7033	2.0518	2.4727	2.7707	3.4210					
	28	0.6834	0.8546	1.3125	1.7011	2.0484	2.4671	2.7633	3.4082					
	29	0.6830	0.8542	1.3114	1.6991	2.0452	2.4620	2.7564	3.3962					
	30	0.6828	0.8538	1.3104	1.6973	2.0423	2.4573	2.7500	3.3852					
	40	0.6807	0.8507	1.3031	1.6839	2.0211	2.4233	2.7045	3.3069					
	50	0.6794	0.8489	1.2987	1.6759	2.0086	2.4033	2.6778	3.2614					
	60	0.6786	0.8477	1.2958	1.6706	2.0003	2.3901	2.6603	3.2317					
	80	0.6776	0.8461	1.2922	1.6641	1.9901	2.3739	2.6387	3.1953					
	100	0.6770	0.8452	1.2901	1.6602	1.9840	2.3642	2.6259	3.1737					
	1000	0.6747	0.8420	1.2824	1.6464	1.9623	2.3301	2.5808	3.0984					
	×	0.6745	0.8416	1.2816	1.6449	1.9600	2.3264	2.5758	3.0902					

Table 1.6*t*-statistics.

$$\bar{x} = \frac{25 + 16 + 38 + 42 + 51 + 23 + 26 + 19 + 26 + 41}{10} = 30.7 \text{ mg kg}^{-1}$$

$$s^{2} = 132.011$$

$$s = \sqrt{132.011} = 11.490 \text{ mg kg}^{-1}$$

$$s_{\bar{x}} = \frac{11.490}{\sqrt{10}} = 3.633 \text{ mg kg}^{-1}$$

If only the average cadmium concentration ($\bar{x} = 30.7 \text{ mg kg}^{-1}$) is considered, we may conclude that the site is safe because the average concentration is less than the regulate standard.

However, if the 95% confidence interval of a true concentration (μ) is calculated using *t*-statistics of $t_{10-1,0.05/2} = t_{9,0.025} = 2.2622$, the 95% confidence range is

$$\mu = 30.7 \pm (3.633 \times 2.2622) = 30.7 \pm 8.22 = 22.48 \cdot 38.92 \text{ mg kg}^{-1}$$

Based on the above calculation, we can see that the regulated standard of 37 mg kg⁻¹ falls within a 95% confidence range of *true* cadmium concentration. In other words, if we take 100 samples of soils, 95 samples will have concentrations that are in this range. With further statistical analysis (one-tail *t*-test), the possibility of soil sample having cadmium content higher than 37 mg kg⁻¹ is 5.85%.

1.2.4.2 Least square regression Least square regression is widely used in all science and engineering disciplines since it is a basis of finding the best model that can describe measurements. This section will describe a generalized least square regression technique which can be used in find the best model parameters to fit the measured data.

Suppose we have *m* measurements of $y_1, y_2, ..., y_m$ and we believe that the following "linear" model (\hat{y}) of *n* variables $(x_1, x_2, ..., x_n)$ provides best fit to our measured data where

$$\hat{\mathbf{y}} = a_1 x_1 + a_2 x_2 + \ldots + a_n x_n.$$

The ultimate goals is to find the values of model parameters $a_1, a_2, ..., a_n$ that give minimum sum of squared errors or

$$\min\sum(\hat{y}_i-y_i)^2.$$

We begin with writing the equation (based on the model) for all *m* measurements.

$$i = 1: \qquad a_1 x_{1,1} + a_2 x_{2,1} + \dots + a_n x_{n,1} = y_1$$

$$i = 2: \qquad a_1 x_{1,2} + a_2 x_{2,2} + \dots + a_n x_{n,2} = y_2$$

$$\vdots \qquad \vdots$$

$$i = m: \qquad a_1 x_{1,m} + a_2 x_{2,m} + \dots + a_n x_{n,m} = y_m$$

The above expression can be written in a matrix form as

$$\begin{bmatrix} x_{1,1} & x_{2,1} & \cdots & x_{n,1} \\ x_{1,2} & x_{2,2} & \cdots & x_{n,2} \\ \vdots & \vdots & \ddots & \vdots \\ x_{1,m} & x_{2,m} & \cdots & x_{n,m} \end{bmatrix}_{m \times n} \begin{cases} a_1 \\ a_2 \\ \vdots \\ a_n \\ m \times 1 \end{cases} = \begin{cases} y_1 \\ y_2 \\ \vdots \\ y_m \\ m \times 1 \end{cases},$$

or

$$[\mathbf{X}]_{m \times n} \{ \boldsymbol{a} \}_{n \times 1} = \{ \mathbf{y} \}_{m \times 1}$$

The above equation cannot be readily solved for $a_1, a_2, ..., a_n$, because the matrix $[\mathbf{X}]_{m \times n}$ is not a symmetric matrix and, therefore, its inverse cannot be defined. So, we need to do some manipulation here.

Let's multiply both sides of the equation by a transpose of matrix $[\mathbf{X}]_{m \times n}$ or $[\mathbf{X}]_{n \times m}^T$ and we have

$$[\mathbf{X}]_{n \times m}^{T} [\mathbf{X}]_{m \times n} \{ \boldsymbol{a} \}_{n \times 1} = [\mathbf{X}]_{n \times m}^{T} \{ \mathbf{y} \}_{m \times 1}$$

$$([\mathbf{X}]^{T} [\mathbf{X}])_{n \times n} \{ \boldsymbol{a} \}_{n \times 1} = [\mathbf{X}]_{n \times m}^{T} \{ \mathbf{y} \}_{m \times 1}.$$

Now the coefficient matrix $([\mathbf{X}]^T [\mathbf{X}])$ is a square matrix, this means the we can now solve for vector $\{a\}$ by using direct method such as Gauss elimination, iterative method or an inverse.

Linear least square regression:

For *m* measurements of y_1, y_2, \ldots, y_m , a linear model (\hat{y}) of *n* variables (x_1, x_2, \ldots, x_n) or

$$\hat{\mathbf{y}} = a_1 x_1 + a_2 x_2 + \ldots + a_n x_n,$$

can provide the best fit data when the optimized parameters $a_1, a_2, ..., a_n$ gives minimum sum of square error or min $\sum (\hat{y}_i - y_i)^2$. And vector $\{a\}$ can be calculated from using inverse method [28]:

$$\{\boldsymbol{a}\}_{n\times 1} = \left(\left[\mathbf{X} \right]^T \left[\mathbf{X} \right] \right)_{n\times n}^{-1} \left(\left[\mathbf{X} \right]^T \left[\mathbf{X} \right] \right)_{n\times n} \left[\mathbf{X} \right]_{n\times m}^T \{ \mathbf{y} \}_{m\times 1}$$
(1.19)

EXAMPLE 1.14 Rate expression for a chemical reaction

Consider the following irreversible chemical reaction

$$a\mathbf{A} + b\mathbf{B} \xrightarrow{k'} c\mathbf{C} + d\mathbf{D}$$

where the rate of forward reaction r is proposed as

$$r = -\frac{1}{a}\frac{d[\mathbf{A}]}{dt} = -\frac{1}{b}\frac{d[\mathbf{B}]}{dt} = k'[\mathbf{A}]^m[\mathbf{B}]^n$$

and k', [A] and [B] are rate constant, molar concentration of species A and B, respectively.. The parameters m and n are empirical parameters where m + n is called an order of the reaction. Using the following experimental data to find the values of k', m and n in the above rate law that best describes this reaction. Note that, for a balanced chemical reaction, a, b, c and d are $\frac{1}{2}$, 1, 1 and 2, respectively.

▶ Solution: First, we need to calculate the rate of a reaction based on the measured concentrations. In this example, we will use the backward difference formula (1.14) for higher-order of accuracy.

$$\frac{d[\mathbf{A}]}{dt} \approx \frac{3[\mathbf{A}]_i - 4[\mathbf{A}]_{i-1} + [\mathbf{A}]_{i-2}}{2\Delta t} \quad \text{and} \quad \frac{d[\mathbf{B}]}{dt} \approx \frac{3[\mathbf{B}]_i - 4[\mathbf{B}]_{i-1} + [\mathbf{B}]_{i-2}}{2\Delta t}$$

and, the reaction rates r are shown in the table. Notice that rates of reaction calculated from either A or B can be used to find rate law since they are equal.

Time	Species	concentrat	ion (M or n	nol dm ⁻³)	Re	eaction rate, r	(M min ⁻¹)
t (min)	[A]	[B]	[C]	[D]	 $-\frac{1}{a}\frac{d[A]}{dt}$	$-\frac{1}{b}\frac{d[B]}{dt}$	$r = k[\mathbf{A}]^m [\mathbf{B}]^n$
0	1	1	0	0			
1	0.950	0.900	0.100	0.200	From Exper	imental Data	From Least Square
2	0.915	0.831	0.169	0.339	0.0542	0.0542	0.0549
3	0.889	0.778	0.222	0.445	0.0446	0.0446	0.0445
4	0.868	0.735	0.265	0.530	0.0373	0.0373	0.0372
5	0.850	0.700	0.300	0.600	0.0317	0.0317	0.0318
6	0.835	0.670	0.330	0.660	0.0275	0.0275	0.0276
7	0.822	0.644	0.356	0.713	0.0241	0.0241	0.0243
8	0.810	0.621	0.379	0.759	0.0214	0.0214	0.0217
9	0.800	0.600	0.400	0.800	0.0193	0.0193	0.0195
10	0.791	0.582	0.418	0.836	0.0174	0.0174	0.0176
11	0.783	0.565	0.435	0.870	0.0159	0.0159	0.0160
12	0.775	0.550	0.450	0.901	0.0146	0.0146	0.0147
13	0.768	0.536	0.464	0.929	0.0134	0.0134	0.0135
14	0.761	0.523	0.477	0.955	0.0125	0.0125	0.0125
15	0.755	0.511	0.489	0.979	0.0116	0.0116	0.0116

From rate law, $r = k'[A]^m[B]^n$, we can take log transformation in order to linearize the equation and we have

$$\log r = \log k' + m \log [A] + n \log [B].$$

Then, the values of k', m and n can be found from least square equation where

$$\begin{cases} \log k' \\ m \\ n \end{cases} = \left(\left[\mathbf{X} \right]^T \left[\mathbf{X} \right] \right)^{-1} \left(\left[\mathbf{X} \right]^T \left[\mathbf{X} \right] \right) \left[\mathbf{X} \right]^T \left\{ \mathbf{y} \right\}$$

where

$$[\mathbf{X}] = \begin{bmatrix} 1 & \log[A]_1 & \log[B]_1 \\ 1 & \log[A]_2 & \log[B]_2 \\ \vdots & \vdots & \vdots \\ 1 & \log[A]_{14} & \log[B]_{14} \end{bmatrix}_{14 \times 3} \quad \text{and} \quad \mathbf{y} = \begin{cases} \log r_1 \\ \log r_1 \\ \vdots \\ \log r_1 \\ \vdots \\ \log r_{14} \end{cases}_{14 \times 10}$$

The solution from the above system of equation are the optimized model parameters as shown below.

$$\begin{cases} \log k' \\ m \\ n \end{cases} = \begin{cases} -1.0029 \\ 0.1791 \\ 3.1287 \end{cases} \Rightarrow \begin{cases} k \\ m \\ n \end{cases} = \begin{cases} 0.0993 \\ 0.1791 \\ 3.1287 \end{cases} \approx \begin{cases} 0.10 \\ 0.18 \\ 3.13 \end{cases}$$

That is, a chemical reaction $\frac{1}{2}A + B \xrightarrow{k'} C + 2D$ whose rate law is

$$r = k'[\mathbf{A}]^m[\mathbf{B}]^n$$
 M min⁻¹

has a rate constant k' of 0.10 and the reaction orders are 0.18 and 3.13 with respect to A and B, respectively. The overall order of reaction is $0.18 + 3.13 = 3.31 \approx \frac{10}{3}$. The results from regression are, then, used to calculate rates of reaction at each time and they are shown in above table and below picture.



1.2.4.3 Confidence interval for predicted modeled parameters In previous section, the method of linear least square for determining model parameters that produce a good fit between measured and modeled data was developed. However, environmental modelers may not be interested in only the optimized parameter values, the confidence limits of such parameters are often critical. In this section, the confidence intervals for parameters of two commonly used linear models will be discussed.

One-parameter model: A one-parameter (p = 1) linear model is in the form [2] $b = \frac{\sum x_i y_i}{x_i^2}$; $\hat{\mathbf{y}} = b\mathbf{x}$ (1.20)

The $100(1-\alpha)$ confidence interval for *true* model parameter β is

$$\beta = b \pm (t_{\mathbf{v}, \alpha/2}) \times SE(b)$$

where v = n - p; *n* and *p* are the number of data and model parameter, respectively.

$$SE(b) = \sqrt{\frac{s^2}{\sum x_i^2}}$$
 and $s^2 = \frac{\sum (y_i - \hat{y}_i)^2}{n - p}$

Two-parameter model:

A two-parameter (p = 2) linear model is in the form [2]

$$\hat{y} = b_0 + b_1 x$$
; $b_1 = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x_i - \bar{x})^2}$; $b_0 = \bar{y} - b_1 \bar{x}$ (1.21)

The $100(1-\alpha)$ confidence intervals for *true* parameter β_0, β_1 are

$$\beta_0 = b_0 \pm \left(t_{\mathbf{v}, \alpha/2} \right) \times SE(b_0) \quad ; \quad \beta_1 = b_1 \pm \left(t_{\mathbf{v}, \alpha/2} \right) \times SE(b_1)$$

where v = n - p; *n* and *p* are the number of data and model parameter, respectively.

$$SE(b_1) = \sqrt{\left[\frac{1}{\sum(x_i - \bar{x})^2}\right]s^2}; \quad SE(b_0) = \sqrt{\left[\frac{1}{n} + \frac{\bar{x}^2}{\sum(x_i - \bar{x})^2}\right]s^2}; \quad s^2 = \frac{\sum(y_i - \hat{y}_i)^2}{n - p}$$

EXAMPLE 1.15 Contaminant plume concentration

Groundwater monitoring well is located downstream of a TCE (trichloroethene) contaminated site. Groundwater samples were taken three times and the pollutant concentration were reported as shown in the following table. Make an assessment of this monitoring data using significant level of $\alpha = 0.05$.

Date	Day(s)	[TCE] (mg L ⁻¹)	TRUNT
20/1/1998	0	200	
21/7/1998	181	210	-(
25/1/1999	365	230	
			flow





Based on given TCE concentrations in a monitoring well located downstream of a source zone, it is clear that the concentration increases with time (see plot). Regression analysis, using a two-model parameter $\hat{y} = b_0 + b_1 x$, was also developed and the value of slope b_1 is greater than zero (see table and plot). One may readily conclude that [TCE] concentration increases with time and the contaminant plume has not reached steady-state condition.

MW

Date	Day, <i>x</i>	[TCE], <i>y</i>	$(x_i - \bar{x})(y_i - \bar{y})$	$(x_i - \bar{x})^2$	$\hat{y} = b_0 + b_1 x$	$(y_i - \hat{y})^2$		
1/20/1998	0	200	2426.667	33124	198.361	2.6860		
7/21/1998	181	210	3.333	1	213.251	10.5694		
1/25/1999	365	230	3050	33489	228.388	2.5991		
Average	182	213.333	-	-	-	-		
Sum	-	-	5480	66614	-	15.854		
	Slope (1	$(b_1) = 0.0823$		$s^2 = 15.8$	354			
	Intercep	ot $(b_0) = 198$	3.361	$SE(b_1) =$	0.01543			

Further statistical analysis was conduct to evaluate the 95% confidence interval for b_1 (i.e., slope of the straight line). The calculation used $t_{\nu,\alpha/2} = 12.706$ (based on $\nu = n - p = 3 - 2 = 1$ and $\alpha = 0.05$) and the 95% confidence range is

$$\beta_1 = b_1 \pm (t_{\nu,\alpha/2}) \times SE(b_1) = 0.0823 \pm (12.706)(0.01543) = 0.0823 \pm 0.1960 = [-0.1137, 0.2783].$$

Clearly, the interval includes $\beta_1 = 0$ implying that we may not have sufficient data to conclude that the concentration increases with time. More data is needed to make further statistically meaningful assessment.

For any other non-linear model (or linear model), the confidence limits can also be evaluated but the calculation is not as simple as linear models described above. The evaluation of confidence limit is described below and *F*-statistics is needed for such calculation (see Tables 1.7 and 1.8). Alternatively, the value of *F* distribution can also be evaluated using a command "=F.INV.RT (α , v_1 , v_2)" in Microsoft Excel.

Confidence limits of parameters for any model:For any other non-linear model (or linear model) that has *n* parameters, the sum of square that bounds the $100(1 - \alpha)$ % joint confidence region (or S_c) is [2] $S_c = S_R \left[1 + \left(\frac{p}{n-p} \right) F_{p,n-p,\alpha} \right]$ (1.22) S_R sum of squared errors/residuals (SSE) where $S_R = \sum (y_i - \hat{y}_i)^2$ nnumber of data pointspnumber of estimated parameters \hat{y}_i modelled y_i $F_{p,n-p,\alpha}$ the upper α percent value of F distribution with p (or v_1) and n - p (or v_2)

	200	253.7	19.49	8.54	5.65	4.39	3.69	3.25	2.95	2.73	2.56	2.43	2.32	2.23	2.16	2.10	1.88	1.75	1.48	1.34	1.26
	100	253.0	19.49	8.55	5.66	4.41	3.71	3.27	2.97	2.76	2.59	2.46	2.35	2.26	2.19	2.12	1.91	1.78	1.52	1.39	1.32
	50	251.8	19.48	8.58	5.70	4.44	3.75	3.32	3.02	2.80	2.64	2.51	2.40	2.31	2.24	2.18	1.97	1.84	1.60	1.48	1.41
	25	249.3	19.46	8.63	5.77	4.52	3.83	3.40	3.11	2.89	2.73	2.60	2.50	2.41	2.34	2.28	2.07	1.96	1.73	1.62	1.56
	20	248.0	19.45	8.66	5.80	4.56	3.87	3.44	3.15	2.94	2.77	2.65	2.54	2.46	2.39	2.33	2.12	2.01	1.78	1.68	1.62
	15	245.9	19.43	8.70	5.86	4.62	3.94	3.51	3.22	3.01	2.85	2.72	2.62	2.53	2.46	2.40	2.20	2.09	1.87	1.77	1.72
÷	14	245.4	19.42	8.71	5.87	4.64	3.96	3.53	3.24	3.03	2.86	2.74	2.64	2.55	2.48	2.42	2.22	2.11	1.89	1.79	1.74
= 0.05	13	244.7	19.42	8.73	5.89	4.66	3.98	3.55	3.26	3.05	2.89	2.76	2.66	2.58	2.51	2.45	2.25	2.14	1.92	1.82	1.77
f $F(\alpha$	12	243.9	19.41	8.74	5.91	4.68	4.00	3.57	3.28	3.07	2.91	2.79	2.69	2.60	2.53	2.48	2.28	2.16	1.95	1.85	1.80
value o	11	243.0	19.40	8.76	5.94	4.70	4.03	3.60	3.31	3.10	2.94	2.82	2.72	2.63	2.57	2.51	2.31	2.20	1.99	1.89	1.84
ritical	10	241.9	19.40	8.79	5.96	4.74	4.06	3.64	3.35	3.14	2.98	2.85	2.75	2.67	2.60	2.54	2.35	2.24	2.03	1.93	1.88
tion: C	6	240.5	19.38	8.81	6.00	4.77	4.10	3.68	3.39	3.18	3.02	2.90	2.80	2.71	2.65	2.59	2.39	2.28	2.07	1.97	1.93
distribu	8	238.9	19.37	8.85	6.04	4.82	4.15	3.73	3.44	3.23	3.07	2.95	2.85	2.77	2.70	2.64	2.45	2.34	2.13	2.03	1.98
7 F.	7	236.8	19.35	8.89	6.09	4.88	4.21	3.79	3.50	3.29	3.14	3.01	2.91	2.83	2.76	2.71	2.51	2.40	2.20	2.10	2.06
able 1.	9	234.0	19.33	8.94	6.16	4.95	4.28	3.87	3.58	3.37	3.22	3.09	3.00	2.92	2.85	2.79	2.60	2.49	2.29	2.19	2.14
Ε	5	230.2	19.30	9.01	6.26	5.05	4.39	3.97	3.69	3.48	3.33	3.20	3.11	3.03	2.96	2.90	2.71	2.60	2.40	2.31	2.26
	4	224.6	19.25	9.12	6.39	5.19	4.53	4.12	3.84	3.63	3.48	3.36	3.26	3.18	3.11	3.06	2.87	2.76	2.56	2.46	2.42
	3	215.7	19.16	9.28	6.59	5.41	4.76	4.35	4.07	3.86	3.71	3.59	3.49	3.41	3.34	3.29	3.10	2.99	2.79	2.70	2.65
	2	199.5	19.00	9.55	6.94	5.79	5.14	4.74	4.46	4.26	4.10	3.98	3.89	3.81	3.74	3.68	3.49	3.39	3.18	3.09	3.04
	-	161.4	18.51	10.13	7.71	6.61	5.99	5.59	5.32	5.12	4.96	4.84	4.75	4.67	4.60	4.54	4.35	4.24	4.03	3.94	3.89
	↓v2 v1→	£	2	с	4	5	9	7	8	6	10	11	12	13	14	15	20	25	50	100	200

200	6350	99.49	26.18	13.52	9.08	6.93	5.70	4.91	4.36	3.96	3.66	3.41	3.22	3.06	2.92	2.48	2.23	1.76	1.60	1.39
100	6334	99.49	26.24	13.58	9.13	6.99	5.75	4.96	4.41	4.01	3.71	3.47	3.27	3.11	2.98	2.54	2.29	1.82	1.67	1.48
50	6303	99.48	26.35	13.69	9.24	7.09	5.86	5.07	4.52	4.12	3.81	3.57	3.38	3.22	3.08	2.64	2.40	1.95	1.81	1.63
25	6240	99.46	26.58	13.91	9.45	7.30	6.06	5.26	4.71	4.31	4.01	3.76	3.57	3.41	3.28	2.84	2.60	2.17	2.03	1.87
20	6209	99.45	26.69	14.02	9.55	7.40	6.16	5.36	4.81	4.41	4.10	3.86	3.66	3.51	3.37	2.94	2.70	2.27	2.13	1.97
15	6157	99.43	26.87	14.20	9.72	7.56	6.31	5.52	4.96	4.56	4.25	4.01	3.82	3.66	3.52	3.09	2.85	2.42	2.29	2.13
14	6143	99.43	26.92	14.25	9.77	7.60	6.36	5.56	5.01	4.60	4.29	4.05	3.86	3.70	3.56	3.13	2.89	2.46	2.33	2.17
13	6126	99.42	26.98	14.31	9.82	7.66	6.41	5.61	5.05	4.65	4.34	4.10	3.91	3.75	3.61	3.18	2.94	2.51	2.38	2.22
12	6106	99.42	27.05	14.37	9.89	7.72	6.47	5.67	5.11	4.71	4.40	4.16	3.96	3.80	3.67	3.23	2.99	2.56	2.43	2.27
11	6083	99.41	27.13	14.45	9.96	7.79	6.54	5.73	5.18	4.77	4.46	4.22	4.02	3.86	3.73	3.29	3.06	2.63	2.49	2.34
10	6056	99.40	27.23	14.55	10.05	7.87	6.62	5.81	5.26	4.85	4.54	4.30	4.10	3.94	3.80	3.37	3.13	2.70	2.57	2.41
6	6022	99.39	27.35	14.66	10.16	7.98	6.72	5.91	5.35	4.94	4.63	4.39	4.19	4.03	3.89	3.46	3.22	2.78	2.65	2.50
8	5981	99.37	27.49	14.80	10.29	8.10	6.84	6.03	5.47	5.06	4.74	4.50	4.30	4.14	4.00	3.56	3.32	2.89	2.76	2.60
7	5928	99.36	27.67	14.98	10.46	8.26	6.99	6.18	5.61	5.20	4.89	4.64	4.44	4.28	4.14	3.70	3.46	3.02	2.89	2.73
9	5859	99.33	27.91	15.21	10.67	8.47	7.19	6.37	5.80	5.39	5.07	4.82	4.62	4.46	4.32	3.87	3.63	3.19	3.05	2.89
5	5764	99.30	28.24	15.52	10.97	8.75	7.46	6.63	6.06	5.64	5.32	5.06	4.86	4.69	4.56	4.10	3.85	3.41	3.27	3.11
4	5625	99.25	28.71	15.98	11.39	9.15	7.85	7.01	6.42	5.99	5.67	5.41	5.21	5.04	4.89	4.43	4.18	3.72	3.58	3.41
3	5403	99.17	29.46	16.69	12.06	9.78	8.45	7.59	6.99	6.55	6.22	5.95	5.74	5.56	5.42	4.94	4.68	4.20	4.05	3.88
2	5000	00.66	30.82	18.00	13.27	10.92	9.55	8.65	8.02	7.56	7.21	6.93	6.70	6.51	6.36	5.85	5.57	5.06	4.90	4.71
٢	4052	98.50	34.12	21.20	16.26	13.75	12.25	11.26	10.56	10.04	9.65	9.33	9.07	8.86	89.68	8.10	7.77	7.17	6.99	6.76
↓v2 v1→	£	2	с	4	5	9	7	8	6	10	11	12	13	14	15	20	25	50	75	200

Table 1.8 F distribution: Critical value of F ($\alpha = 0.01$).

1.2.4.4 Goodness of fit of the model In a regression analysis, the optimized parameters will produce the best fit to the measured or experimental dataset. There are several ways that can be used to assess a goodness-of-fit of a model such as χ^2 test, paired *t*-test and the use of coefficient of determination (R^2) [28, 2].

A Chi-square test, χ^2 :

A Chi-square test is a method that can be used to test the difference between expected (models) vs. observed (measurements) values at some significance level. The null hypothesis (H_0) assumes "no difference" between measurement and model. Chi-square value can be calculated from

$$\chi_{\text{calc}}^2 = \sum_{i=1}^n \frac{(\hat{y}_i - y_i)^2}{\hat{y}_i}$$
(1.23)

where y_i and \hat{y}_i are measurment and model, respectively. The null hypothesis will be accepted at α significance level if

$$P\left(\chi_{\text{calc}}^2 \leqslant \chi_{\text{crit}}^2\right) = 1 - \alpha,$$

where χ^2_{crit} also depends on the degree of freedom (v = n - 1) and can be found from Table 1.9 or using a command "=CHISQ.INV.RT(α , v)" in Microsoft Excel.

					•					
ν	χ ² .995	χ ² .990	χ ² .975	χ ² .950	χ ² .900	χ ² .100	χ ² .050	χ ² .025	χ ² .010	χ ² .005
1	0.000	0.000	0.001	0.004	0.016	2.706	3.841	5.024	6.635	7.879
2	0.010	0.020	0.051	0.103	0.211	4.605	5.991	7.378	9.210	10.597
3	0.072	0.115	0.216	0.352	0.584	6.251	7.815	9.348	11.345	12.838
4	0.207	0.297	0.484	0.711	1.064	7.779	9.488	11.143	13.277	14.860
5	0.412	0.554	0.831	1.145	1.610	9.236	11.070	12.833	15.086	16.750
6	0.676	0.872	1.237	1.635	2.204	10.645	12.592	14.449	16.812	18.548
7	0.989	1.239	1.690	2.167	2.833	12.017	14.067	16.013	18.475	20.278
8	1.344	1.646	2.180	2.733	3.490	13.362	15.507	17.535	20.090	21.955
9	1.735	2.088	2.700	3.325	4.168	14.684	16.919	19.023	21.666	23.589
10	2.156	2.558	3.247	3.940	4.865	15.987	18.307	20.483	23.209	25.188
11	2.603	3.053	3.816	4.575	5.578	17.275	19.675	21.920	24.725	26.757
12	3.074	3.571	4.404	5.226	6.304	18.549	21.026	23.337	26.217	28.300
13	3.565	4.107	5.009	5.892	7.042	19.812	22.362	24.736	27.688	29.819
14	4.075	4.660	5.629	6.571	7.790	21.064	23.685	26.119	29.141	31.319
15	4.601	5.229	6.262	7.261	8.547	22.307	24.996	27.488	30.578	32.801
20	7.434	8.260	9.591	10.851	12.443	28.412	31.410	34.170	37.566	39.997
25	10.520	11.524	13.120	14.611	16.473	34.382	37.652	40.646	44.314	46.928
50	27.991	29.707	32.357	34.764	37.689	63.167	67.505	71.420	76.154	79.490
75	47.206	49.475	52.942	56.054	59.795	91.061	96.217	100.84	106.39	110.29
100	67.328	70.065	74.222	77.929	82.358	118.50	124.34	129.56	135.81	140.17

Table 1.9 Chi-square distribution χ^2 .

Paired t -test:

The paired *t*-test can be use to test the difference between modeled and measured values which is called $d_i = y_i - \hat{y}_i$. The mean and standard deviation of the differences are calculated from the following formula.

$$\bar{d} = \frac{|\Sigma d_i|}{n} \quad \text{and} \quad s_d = \sqrt{\frac{\Sigma d_i^2 - n\bar{d}^2}{n-1}} \tag{1.24}$$

Null hypothesis (H_0) assumes that the model is not different from the measurement (i.e., \bar{d} is not significantly different from zero). We will accept null hypothesis if

$$P(t_{\text{calc}} \leq t_{\text{crit}}) = \alpha \text{ and } t_{\text{calc}} = \frac{\bar{d}\sqrt{n}}{s_d}$$

where t_{crit} is $t_{\nu,\alpha/2}$ (two-tail) with $\nu = n - 1$.

Coefficient of determination, R²:

The coefficient of determination R^2 is a proportion of the total variability in the dependent variable (y) that is accounted for by the regression equation (i.e., model). A value of $R^2 = 1$ indicates that the fitted equation accounts for all variability of the values of the dependent variables in the sample data. So, we normally tend o assume that a high value of $R^2 \rightarrow 1.0$ assures statistically significant regression equation. The value of R^2 can be calculated from

$$R^{2} = \frac{\sum (\hat{y}_{i} - \bar{y})^{2}}{\sum (y_{i} - \bar{y})^{2}},$$
(1.25)

where y_i , \bar{y} and \hat{y}_i are measurements, average of the measurements and model simulated values, respectively.

The interpretation of R^2 should be handled with care because large value of R^2 only indicates statistically significant regression model but it *does not assure* a useful nor correct model. Figure 1.2 illustrates the four dataset which all have the same R^2 when a linear least square is used.





Figure 1.2 Example plots of the dataset which all have $R^2 = 0.70$ evaluated based on two-parameter model of linear regression analysis.

EXAMPLE 1.16 A test for model's goodness-of-fit

A wastewater discharge with biochemical oxygen demand (BOD) a causes a depletion of dissolved oxygen (DO) in a river. Supposed a model calibration give results of modeled DO (or \hat{y}_i) and measured DO (or y_i) as shown in the following table and plot. Determine if the model calibration is acceptable at significance level of 0.10.



▶ Solution: In order to assess a goodness-of-fit between model and observations using Chi-square test, paired *t*-test and coefficient of determination, some statistical parameters must be calculated as shown in the following table.

Distance	\hat{y}_i	${\mathcal Y}_i$	χ_i^2	d_{i}	d_i^2	$(\hat{y}_i - \overline{y})^2$	$(y_i - \overline{y})^2$
0	8.0	8.0	0	0	0	4.3681	4.3681
5	6.3	6.6	0.01429	0.3	0.09	0.1521	0.4761
10	5.4	5.5	0.00185	0.1	0.01	0.2601	0.1681
20	4.58	4.4	0.00707	-0.18	0.0324	1.7689	2.2801
30	4.64	4.6	0.00034	-0.04	0.0016	1.6129	1.7161
40	5.1	4.5	0.07059	-0.6	0.36	0.6561	1.9881
50	5.5	5.2	0.01636	-0.3	0.09	0.1681	0.5041
60	6.0	6.0	0	0	0	0.0081	0.0081
80	6.7	7.0	0.01343	0.3	0.09	0.6241	1.1881
100	7.2	7.3	0.00139	0.1	0.01	1.6641	1.9321
		Sum =	0.12533	-0.32	0.684	11.2826	14.629

- (a) Chi-square test: Given v = 10 1 = 9 and $\alpha = 0.10$, the value of Chi-distribution can be obtained from the Table 1.9 where $\chi^2_{0.90} = 4.168$. But the calculated χ^2 is 0.1253. Since $\chi^2_{calc} < \chi^2_{crit}$, we accept null hypothesis which means, there is no statistical difference between modeled and measured DO at significance level of 0.10.
- (b) Paired *t*-test: The calculated *t*-statistics from data can be evaluated as follows.

$$\bar{d} = \frac{|-0.32|}{10} = 0.032$$
 $s_d = \sqrt{\frac{0.684 - (10)(0.032)}{10 - 1}} = 0.2736$

and

$$t_{\rm calc} = \frac{0.032 \times \sqrt{10}}{0.2736} = 0.370$$

At $\alpha = 0.10$ and v = 10 - 1 = 9, the value of *t*-statistics (two-tail) $t_{crit} = 1.8331$. Since $t_{calc} < t_{crit}$, we may conclude that *d* is not significantly different from zero or the model and observation are indistinguishable. In other words, there is less than 10% probability that the modeled and observed values could have been selected randomly from different population.

(c) Coefficient of determination: The value of coefficient of determination R^2 can be calculated as

$$R^2 = \frac{11.2826}{14.629} = 0.77.$$

The value of $R^2 > 0.75$ implies a statistically significant regression DO model.

1.3 Pollutants

1.3.1 Overview of pollutant's fate-and-transport study

In the study of fate-and-transport of pollutants in environment, there is a typical sequence of steps that need to be followed in order to successfully identify, characterize and remediate. *First*, a pollutant is observed to be present or the potential of a pollutant release from a proposed industrial site is identified. This can result from a routine monitoring of a pollutant's concentration at the site, through the known manufacturing of the pollutant at the site, through research identifying the cause of an illness or cancer cluster in the community of a site, or during an environmental impact assessment . *Second*, the source of pollutant is identified at hazardous waste site or a theoretical release can be simulated using comprehensive analytical of numerical models. *Third*, a remedial investigation is conducted to determine the mass or volume of pollutant released. *Fourth*, pollutant fate-and-transport modeling is completed to determine what pollutant concentrations will result at specific points at the site over time. *Fifth*, the results of fate-and-transport modeling are used in risk assessment calculations to estimate health, environmental or ecological risks. And, finally, a decision or plan of remediation is negotiated between the local resident, local and central governments, and the party responsible for the hazardous waste sites.

Many pollutants have been found to be ubiquitous in nature; that is every environmental compartment that has been tested has shown some level of contamination. Note that, presently ambient monitoring of water bodies and the atmosphere are both part of the missions of both local and central governments. Historically, two of the major chemicals that fall into this category and has received much attention are PCBs (polychlorinated biphenyls) and DDT. These compounds accumulate especially well in the environment due to their refractory behavior because they are not easily chemically or biologically degraded [30]. More importantly, their chemical and physical properties are such that they bioaccumulate in fatty tissue in many organisms [22]. Modelers always like to divide natural system into more easily mathematically described boxes (or control volume) such as in atmosphere, rivers, lakes, groundwater or biota.

There are two basic goals of pollutant's fate-and-transport modeling: (1) to explain how a pollutant arrived where it is and (2) to predict how fast a pollutant will move through an environmental compartment in the future. In order to predict where a pollutant will go, we use a set of fate equations that describe the chemical and physical processes occurring in the environmental compartment under evaluation such as mixing, effluent outflow, evaporation, volatilization, chemical and biological transformation or degradation. Transport of chemicals is part of their fate. The same mathematical equations, or models, can be used both forward (prediction) or backward (inversion) simulations. The latter case is commonly used to fit field or observed data in order to obtain estimates of mixing and degradation rates in site specific systems.

Pollutants vs. contaminants The terms contamination and pollution (or pollutants vs. contaminants) have been used interchangeably as they both deal with unwanted chemical compounds or any other means. The substances that cause pollution are termed as "pollutants" while those that lead to contamination are called "contaminants." For instance, a waste material in a river may be called as a contaminant or a pollutant.

Another similarity is the remediation process. The clean-up steps for pollution are identical with that of contamination. Moreover, they are linked in a way that the introduction of harmful contaminants leads to pollution. However, pollution is regarded with more negativity due to its more perilous impacts as compared to contamination. Indeed, these occurrences are interconnected and comparable; yet, they still have notable differences.

1.3.2 Types of pollutants

Pollutants vary widely in their physical state, chemical characteristics, and their effects on human health and ecosystems. Before attempting to solve environmental pollution problems as a result of a chemical release, it is useful to fully understand properties of the chemical itself. Pollutants may be broadly divided into two categories: *organic* and *inorganic* which can be further classified as shown in Figure 1.3.



Figure 1.3 Classification of chemical pollutants and some examples.

1.3.2.1 *Inorganic pollutants* Pollutants which are inorganic elements or compounds may broadly be classified as metals, non-metals, transition group elements and radionuclides. Much can be learned about the nature of inorganic atoms by studying the periodic table of the elements (Figure 1.4).

Metals Representative elements are those found in groups IA-VIIA of the periodic table with the group number representing the number of valence electrons. Representative elements form molecules by lending, borrowing or sharing electrons in order to achieve stable electronic configuration of two or eight electrons in valence shell. Among the representative elements, groups IA-IIIA elements are strongly electtropositive *metals* that readily donate to form cations (e.g, Na⁺, Ca²⁺, Al(OH)₂⁺) within molecules or compounds.

Nonmetals Representative *non-metals* are grouped toward the right side of the periodic table. During molecule formation, they borrow or share electrons from other atoms to form anions (e.g., F^- , Cl^- , NO_3^- , SO_4^{2-} , AsO_4^{3-} , SeO_3^{3-}) with stable electronic configuration. The electropositive metals usually form stable compounds with electronegative nonmetals such as NaCl, CaF₂, MgSO₄, etc.

Transition metals Elements in group B (called, *transition* metals) have partially filled electronic shells in *d*-orbital. Because both the outermost and the penultimate electronic shells are incomplete, the transition group metals can form may different types of compounds with other elements resulting in colored salts and complexes. They can engage in ionic, covalent, or coordination bonds. As a result, the transition elements grouped in the middle of the periodic table (IB-VIIIB) can exhibit multiple valencies, or more appropriately, multiple stable oxidation states. For example, cationic forms of chromium in aqueous solution include Cr^{2+} and Cr^{3+} . But, it can also from coordination oxyanions such as chromite CrO_2^{-} , chromate CrO_4^{2-} , dichromate $Cr_2O_7^{2-}$. Speciation is therefore very important when dealing with inorganic compounds, particularly since the toxicity and the mobility of different chemical species can vary widely. For example, chromate ion with Cr(VI) (or, +6 oxidation state) is more toxic and much more mobile in groundwater than the chromite ion with Cr(III) (or, +3 oxidation state).

Radionuclides A number of metals that pose serious environmental hazards are highatomic-weight metals and radionuclides that are located in the lower portion of the periodic table. *Radionuclides* are heavy elements with unstable nucleus. Their nuclei can undergo radioactive decay to attain a more stable nucleus resulting the formation of a different daughter atoms and other products. The process of radioactive decay releases radiation or high energy particles which are, for examples, $\alpha \begin{pmatrix} 4\\2 \text{He} \end{pmatrix}$, $\beta \begin{pmatrix} 0\\-1 \text{e} & 0 \end{pmatrix}$, $\gamma rays$. The effect of the radiation on living cells is to cause cell death at high doses and also to cause cell mutations that become apparent at low doses. Severe health effects have been observed when humans have been exposed to radiation as a result of nuclear weapons explosions or nuclear power plant meltdown. Radionuclides such as uranium and plutonium are highatomic-weight metals grouped in the actinide series at the bottom of the periodic table. Most elements in the lanthanide series are produced from nuclear reactions. Radon, which is a daughter product of uranium decay, is itself a radioactive gas and an important indoor air pollutant. Radium and strontium are heavy alkali earth metals (IIA) used widely in nuclear medicine.

Heavy metals that are non-radiogenic such as mercury (Hg), zinc (Zn), cadmium (Cd and lead (Pb) can also pose serious health hazard. These metals are sparingly soluble in water and are also referred to as trace metals. However, even at low levels, they have been associated with serious health effects such as Minamata disease (Hg) and Itai-Itai (Cd) [30]. Heavy metals may also bioaccumulate and become biomagnified through the food chain.

In summary, inorganic pollutants can occur in purely elemental form such as elemental lead or zinc released to air from metal smelting operations. More frequently, metals and non-metals from cations and anions and a variety of other complex species depending on their oxidation states. Various inorganic species of inorganic pollutants often carry charge and hence are strongly impacted by pH and redox conditions in the environment. Chemical toxicity, in turn, is strongly affected by speciation which is a complex phenomena and will be discussed later.

8 H K	Ð	lum 003	Ð	eon 180	-	gon 948		pton 79.8		Ð	.294	L	don .018	Г		uwor							ilm enstine enotes.org
~ > ~	⊥ ₅	He He	₽Z	20 ^x	18	a ≱ ®	36	T 5.4	54	××	131	°° u	Ra 222	118		yun c		LLU utetium		wrencium	ſ		2015 Todd He science
	17		۳	Fluorine 18.998	⊡ Ω	Chlorine 35.453	35	Bromine 79 904	53	lodine	126.904	85 At	Astatine 209.987	117		unknowr	71		9				0
	16	VIA 6A	0	xygen 5.999	S	ulfur 2.066		CO Renium 8977			27.6	C	lonium 8.982]		morium <	298]	70	Ytterb 173.0	102	n Nobel			
		-	~	n 0	16	4 3.	34	Se o	52		0	2	- 20 20 20	116		L L	。 	Thulium 168 934	01	MD endeleviur 258.1		Ø	
	15	5A 5A	Z	Nitroge 14.00	₽ D	Phospho 30.97	33	Arseni 74.92	51	Sutine	121.76	° B	Bismut 208.98	115	Ununpen	unknov	9	nium 25,0				Actinid	
	14	44 4	C	Carbon 12.011	Si	Silicon 28.086				ມື	18.711	ЪР Д	Lead 207.2	⁺i		[289]	68	1 36	ē	n Fer CRC		anide	
		۰.	9	s=	14	1um 82	32	ເ ເ ເ ເ ເ ເ ເ ເ ເ ເ ເ ເ ເ ເ ເ ເ เ เ เ เ	50	~ [318 1	82	mm 383	=	ţ	uwo	67	Holmium 164 930	L	Einsteiniu 17541		Lantha	
	₩	3≣	لل ع	10.8	13 P	Alumi 26.9	33	5	49	T ibi	114.1	ط	Thall 204.	113	5	unkn			2			loble Gas	
	ents				12	5B II	ا ہ		œ		112.411	° E	Mercury 200.592	<u>6</u>	Coemicium	[277]	99	о е ж С а ж	98	E E E		2	
	em				-	88	e)	Der 546	4	D ¹	.868		old 5.967	-		72]	65	Terbiu 158 0:	97 0	Berkelli 247.0		Halogen	
ĺ	е е						29) 82	47	ء ک	101	م	96	Ξı	um Roent	2						atal	
	۲ ۲		poq	ne	Mass 10	$\left(\right)$	28	Nickel S8 693	46		106.42	ه	Platinun 195.08	110	DS Darmstadt	[269]	64	Bet C	96			Nonme	
		Atomic	Sym	Nar	Atomic 9	 ,≣∞				Selin Marine Mar	02.906	<u>_</u>	idium 92.217		Mt	[268]	63 63		95	Ameri 243		imetal	
	La						27	а 1 5	45		1		== Eg	10	ω Ψ		5	Samariun 150.36		Plutonium 244 064		Sem	
:	odic				00	`	26 26		44	R uthen	101.0	ő	Osmit 190.2	108	Hast	[269	9	ethium 1 013	5			Basic Metal	
	Perio				7	AIIB 78	10	MD anganese 54.938		HC Schnetium	98.907	Ba	Rhenium 186.207	5	Bohrium	[264]	⁶		93	Nep 23		5	
	-				~	<u> </u>	3	mium M	4	denum 1	95	~ >	sten .84	÷	D	[9]	60	Neodymi 144 24	92	Uraniur 238.02		Transiti Metal	
					<u> </u>	≥ ø	24		42	Molybo	95.	74 <	Tung 183	106	Seabo Seabo	52	Ċ			at 036		t lie	
					o.	5B 5	23	Vanadium 50.942	41		92.906	д Та	Tantalum 180.948	105	Dubnium	[262]	59	If Pras	91	E #8		Alka Ea	
					4	4B 4B	i	anium 7 867		ZL	1.224	Ť	fnium 78.49			261]	28		06 06	Thorit 23.2.0		Mkali Aetal	
							22	a Tit	40	N 22	91	12	Har	104	Ruthe					Actinium 227 028		₹2	
						3B III 3B	51	Scandiu 44.956	39	Yttrium	88.90	57-71		89-103			5.	es es	8	se			
	2	ZA IIA	Be	eryllium 9.012	Ма	gnesium 24.305				Sr	87.62	Ba	Barlum 37.328			26.025	antha	Serie	Actin	Seri			
		gen 8	4	е-	12	Ma No	20	mil	38	St.	80	20) E 8	88	<u> </u>	20 2							
- ₹ ₹	Ē	Hydrog 1.00	ل	Lithiu 6.94	, Ž	Sodiu 22.95	19	Potassi 39 09	37	Rubidin	85.46	ů,	Cesiu 132.9	87	Franci	223.0							

Figure 1.4 Periodic table of the elements (https://sciencenotes.org/).

1.3.2.2 Organic pollutants Organic chemicals are named so because most of them were initially discovered or derived from naturally organic matter. All organic compounds contain carbon atom(s) that may form bonds with carbon or other atoms such as hydrogen, oxygen, nitrogen, sulfur or halogen atoms. Industries have produced a variety of synthetic organic chemicals that can be used as, for examples, solvents, detergents, pharmaceutics, petrochemicals, pesticides, herbicides and plastics.

Organic chemicals can be broadly divided into two main categories: *aliphatics* and *aromatics*. Aliphatic compounds consist of a single-bond (alkanes), double-bond (alkenes) or triple-bond (alkynes) carbons in either an open straight/branched chain or a cyclic configuration (see examples in Figure 1.3). Examples of aliphatic hydrocarbons are methane, ethene, trichloroethene and cyclohexane. The aromatic compounds typically consisted of resonance bonds between carbon atoms (i.e., benzene ring) such as BTEX compounds (benzene, toluene, ethylbenzene and xylenes), biphenyls (e.g., polychlorinated biphenyls, PCBs), or polycyclic aromatic hydrocarbons (PAHs) such as naphthalene. Both aliphatics and aromatics can exhibit some special functional groups such as alcohol, ether, aldehyde, ketone carboxylic acid, ester and amine. Another (sub)group of organic chemicals are called *heterocyclic* compounds. One or more carbon atoms in the molecules are replaced by oxygen, nitrogen or sulfur. These compounds are, for examples, furan, pyrrole and dioxane.

Aggregate measures of pollutants In some cases it is convenient to report environmental samples in terms of aggregate concentration of various groups of chemicals. The categorization of these compounds are based primarily on their similarities in chemical structures and properties. For examples, a detection of total petroleum hydrocarbon (TPH) includes all organic pollutants that are part of petroleum product. Volatile organic compounds (VOCs) are a group of hydrocarbons with generally fewer than about 12 carbon atoms that readily volatilize in to air [22]. Semi-volatiles (SVOCs) refer to a less volatile compounds including pesticides such as DDT, dieldrin and endrin. Some organic compounds in wastewater are grouped and called biochemical oxygen demand (BOD) which is a measure of how much oxygen is needed (by microbes) to degrade the dissolved organic compounds in wastewater. Total dissolved solids (TDS) is an aggregate measure for inorganic species in water. Particulate matter (PM) suspended in atmosphere are generally reported as mass per volume unit and often cut off using (aerodynamic) size. For examples PM_{2.5} and PM₁₀ refers to particulate matter of the size smaller than 2.5 and 10 μ m, respectively. Table 1.10 lists some aggregate measures in environmental sampling.

Chemical pollutants may also be grouped based on their physical properties such as water immisciblity and density. A primary example is non-aqueous phase liquid (NAPL) which is a multicomponent mixtures of several organic compounds. Gasoline, diesel fuels and coal tar are examples of NAPLs. Gasoline and diesel fuels are lighter than water and are therefore referred to as LNAPLs while coal tar, chlorinated solvents are typically denser than water and are called DNAPLs. Contaminant of concern in coal tar and gasoline are typically BTEX compounds and polyaromatic compounds such as naphthalene and benzo(*a*)pyrene. Although NAPL aggregate is essentially immiscible in water and exists as a separate phase because of the low aqueous solubility of its organic constituents, individual compound may dissolve in water or volatilize to air at concentration high enough to cause environmental and health impacts. Due to the slow dissolution of NAPL components in groundwater, entrapped NAPL lenses can act as a long-term source of soul and groundwater pollution [10, 13].

Aggregate	Definition	Grouping based on					
TPH	Total petroleum hydrocarbons	Parts of petroleum products					
VOC	Volatile organic compounds]					
SVOC	Semi-volatile organic compounds	} Volatility					
BOD	Biochemical oxygen demand)					
COD	Chemical oxygen demand	Biodegradable organic compounds					
ThOD	Theoretical oxygen demand						
TDS	Total dissolved solids	Dissolved species (cations and anions)					
PM	Particulate matter	Particle size (settling velocity)					
NAPL	Non-aqueous phase liquid	Water immiscibility					
DNAPL	Dense, non-aqueous phase liquid	Water immiscibility, density (denser than water)					
LNAPL	Light, non-aqueous phase liquid	Water immiscibility, density (lighter than water)					
BTEX	Benzene, toluene, ethylbenzene, xylenes	One ring of aromatic hydrocarbon (parts of gasoline)					

Table 1.10Some commonly used aggregate measures of pollutants.

1.3.3 Properties and characteristics of pollutants

The tendency of a pollutant to enter air or water is governed by its chemical properties. Two fundamental properties are referred to *aqueous solubility* and *vapor pressure* which are referred to the ability of a chemical to saturate water or air when present in excess quantity in its pure and natural state.

1.3.3.1 Aqueous solubility Aqueous solubility refers to the maximum concentration of a chemical in the aqueous phase, when the solution is in equilibrium with the pure compounds in its usual phase (gas, liquid or solid) at a specified temperature and and pressure [37, 22]. Although aqueous solubility is temperature dependent, it does not vary significantly over a typical range of temperature encountered in the environment.

Aqueous solubility of an inorganic solid The solubility of a sparingly soluble inorganic salt can be described using the equilibrium principle. For example, a solubility reaction of a mineral fluorite $CaF_2(s)$ can be written as

$$CaF_2(s) \stackrel{H_2O}{\longleftrightarrow} Ca^{2+}(aq) + 2F^{-}(aq)$$

The equilibrium constant describing the above dissolution reaction can be written using law of mass action.

$$K = K_{\rm sp} = \frac{(a_{\rm Ca^{2+}})(a_{\rm F^-})^2}{(a_{\rm CaF_2})}$$

where $K_{\rm sp}$ is called solubility product; $a_{\rm Ca^{2+}} = \gamma_{\rm Ca^{2+}}[{\rm Ca^{2+}}]$, and $a_{\rm F^-} = \gamma_{\rm F^-}[{\rm F^-}]$ are activities of aqueous species Ca²⁺ and F⁻, respectively; the activity of a mineral fluorite $a_{\rm CaF_2} = 1$ because, by definition, it is a pure solid. For simplicity (i.e., hand calculation), it is generally assumed that the activity coefficient $\gamma \approx 1$. Thus, the above equilibrium expression is reduced to $K_{\rm sp} \approx [{\rm Ca}^{2+}][{\rm F^-}]^2$. In order to solve for the solubility, several other reactions (i.e., equations) are needed such as water dissociation, hydrolysis and complexation of Ca²⁺ and F⁻ along with charge and mass balance equations. Numerical methods are typically required to obtain the solution.

Equilibrium constant:

The equilibrium constant (i.e., solubility product) is calculated from thermodynamics standard Gibbs free energy of the reaction $(\Delta_r G^\circ)$ where

$$K_{\rm sp} = K = \exp(-\Delta_r G^{\circ}/RT)$$
 (1.26)

where *R* is Gas constant, T = 298.15 K and $\Delta_r G^{\circ}$ is calculated from

$$\Delta_r \mathbf{G}^\circ = \sum_{\text{products}} \mathbf{v}_i(\Delta \mathbf{G}_{f_i}^\circ) - \sum_{\text{reactants}} \mathbf{v}_i(\Delta \mathbf{G}_{f_i}^\circ), \qquad (1.27)$$

and ΔG_f° is standard Gibbs free energy of formation which can be obtained from thermodynamics table and v_i is stoichiometric coefficients of a balanced chemical reaction. It should be noted that the above expression for *K* in equation (1.26) is valid at standard state of 25 °C and 1 atm. If system's temperature and pressure deviate from standard state, the corrected equilibrium constant can be calculated using van't Hoff equation:

$$\log \frac{K_{T_2}}{K_{T_1}} = -\frac{2.303(\Delta_r \mathrm{H}^\circ)}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(1.28)

and Clapeyron equation:

$$\log \frac{K_{T_2}}{K_{T_1}} = -\frac{2.303(\Delta_r \mathbf{V}^\circ)}{RT} \left(P_2 - P_1\right)$$
(1.29)

where $\Delta_r H^\circ$ is standard enthalpy change of a chemical reaction and $\Delta_r V^\circ$ is partial molar volume change of a reaction. Typically, $\Delta_r V^\circ \approx 0$ for a reaction involves only solids and aqueous species.

$$\Delta_r \mathbf{H}^\circ = \sum_{\text{products}} \mathbf{v}_i(\Delta \mathbf{H}_{f_i}^\circ) - \sum_{\text{reactants}} \mathbf{v}_i(\Delta \mathbf{H}_{f_i}^\circ), \qquad (1.30)$$

$$\Delta_r \mathbf{V}^\circ = \sum_{\text{products}} \mathbf{v}_i(\mathbf{V}_i^\circ) - \sum_{\text{reactants}} \mathbf{v}_i(\mathbf{V}_i^\circ), \qquad (1.31)$$

where V_i° and ΔH_f° are standard molar volume and standard enthalpy of formation of a species *i*, respectively. Extensive standard thermodynamic data is tabulated in several books such as [20].

EXAMPLE 1.17 Dissolution of a mineral fluorite, CaF₂(s)

Find the aqueous solubility of a mineral fluorite in pure water at 25 °C, 1 atm.

► Solution: For simplicity, we assume that the solution is so dilute that the activity effect is negligible and, thus $\gamma \approx 1$ or $a_i \approx [i]$. We can write all chemical reactions involved in the dissolution of fluorite which are dissolution, hydrolysis, complexation, water dissociation, mass and charge balance equations as shown in Table 1.11. The associated equilibrium constants are calculated using (1.26) based standard thermodynamics data from [20].

No.	Reaction	Expression of K	$\Delta_r G^\circ$ (kJ)	log K
1	Dissolution	$K_{sp} = \left[Ca^{2^+}\right] \left[F^-\right]^2$	+59.9	-10.5
	$CaF_{2(s)} \rightleftharpoons Ca^{-1} + 2F$	$\log K_{sp} - \log [Ca^{2+}] - 2\log [F^{-}] = 0$		
2	Water dissociation	$K_{w} = [H^{+}][OH^{-}]$	+79.89	-13.997
	$H_2O_{(\ell)} \rightleftharpoons H^2 + OH$	$\log K_w - \log [H^+] - \log [OH^-] = 0$		
3	Hydrolysis of Ca^{2+} $Ca^{2+} + H_2O \rightleftharpoons CaOH^+ + H^+$	$K_{1} = \frac{\left[CaOH^{+}\right]\left[H^{+}\right]}{\left[Ca^{2^{+}}\right]}$	+72.47	-12.697
		$\log K_1 - \log [CaOH^+] - \log [H^+] + \log [Ca^{2+}] = 0$		
4	Complexation of Ca^{2+} $Ca^{2+} + F^- \rightleftharpoons CaF^+$	$K_2 = \frac{\left[CaF^+\right]}{\left[Ca^{2+}\right]\left[F^-\right]}$	-6.51	1.14
		$\log K_2 - \log [CaF^+] + \log [Ca^{2+}] + \log [F^-] = 0$		
5	Formation of HF $H^+ + F^- \rightleftharpoons HF$	$\mathbf{K}_{3} = \frac{[\mathbf{HF}]}{[\mathbf{H}^{+}][\mathbf{F}^{-}]}$	-18.15	3.18
		$\log\!K_{3} - \log\!\left[HF\right] + \log\!\left[H^{\scriptscriptstyle +}\right] + \log\!\left[F^{\scriptscriptstyle -}\right] = 0$		
6	Formation of HF_2^- $HF + F^- \rightleftharpoons HF_2^-$	$K_{4} = \frac{\left[HF_{2}^{-}\right]}{\left[HF\right]\left[F^{-}\right]}$	-21.58	3.78
		$\log K_4 - \log \left[HF_2^- \right] + \log \left[HF \right] + \log \left[F^- \right] = 0$		
7	Charge Balance $2[Ca^{2+}]+[CaF^+]+[CaOH^+]$	$+ [H^+] = [F^-] + [HF_2^-] + [OH^-]$	1	
8	Mass balance (Total Ca = 1	∕₂ Total F)		
	$\left[\operatorname{Ca}^{2+}\right] + \left[\operatorname{CaF}^{+}\right] + \left[\operatorname{CaOH}^{+}\right] =$	$\frac{1}{2}\left(\left[F^{-}\right]+\left[HF\right]+2\left[HF_{2}^{-}\right]+\left[CaF^{+}\right]\right)$		
8 ur	hknowns \rightarrow [Ca ²⁺] [F ⁻]	$\begin{bmatrix} H^{\scriptscriptstyle +} \end{bmatrix} \begin{bmatrix} OH^{\scriptscriptstyle -} \end{bmatrix} \begin{bmatrix} CaOH^{\scriptscriptstyle +} \end{bmatrix} \begin{bmatrix} CaF^{\scriptscriptstyle +} \end{bmatrix} \begin{bmatrix} HF \end{bmatrix} \begin{bmatrix} HF_2^{\scriptscriptstyle -} \end{bmatrix}$		
	\downarrow \downarrow	$\downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow$		
	<i>x</i> ₁ <i>x</i> ₂	$x_3 x_4 x_5 x_6 x_7 x_8$		

 Table 1.11
 Chemical reactions related to fluorite, CaF2, dissolution in pure water.

There are 8 unknowns with available 8 independent algebraic equations as shown in the Table 1.11. All species concentration can be numerically evaluated using Newton-Ralphson technique as described in (1.3). Note that the species concentration are replaced by variables x_1, x_2, \ldots, x_8 for simplicity. And the system of non-linear algebraic equations that we attempt to solve is

$$\begin{array}{rcl} -10.5 - \log x_1 - 2\log x_2 &=& 0\\ -13.997 - \log x_3 - \log x_4 &=& 0\\ -12.697 - \log x_5 - \log x_3 + \log x_1 &=& 0\\ 1.14 - \log x_6 + \log x_1 + \log x_2 &=& 0\\ 3.18 - \log x_7 + \log x_3 + \log x_2 &=& 0\\ 3.78 - \log x_8 + \log x_7 + \log x_2 &=& 0\\ 2x_1 + x_6 + x_5 + x_3 - x_2 - x_8 - x_4 &=& 0\\ x_1 + x_6 + x_5 - \frac{1}{2}(x_2 + x_7 + 2x_8 + x_6) &=& 0 \end{array} \right\} \Rightarrow \mathbf{f}(\mathbf{x}) = \mathbf{0}.$$

The solution based on Newton-Ralphson scheme is given as

$$\mathbf{x}_{i+1} = \mathbf{x}_i - [D\mathbf{f}(\mathbf{x})]^{-1} \mathbf{f}(\mathbf{x}_i)$$

where the Jacobian matrix is defined as

$$D\mathbf{f}(\mathbf{x}) = \begin{bmatrix} -ax_1^{-1} & -2ax_2^{-1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -ax_3^{-1} & -ax_4^{-1} & 0 & 0 & 0 & 0 \\ ax_1^{-1} & 0 & -ax_3^{-1} & 0 & -ax_5^{-1} & 0 & 0 & 0 \\ ax_1^{-1} & ax_2^{-1} & 0 & 0 & 0 & -ax_6^{-1} & 0 & 0 \\ 0 & ax_2^{-1} & ax_3^{-1} & 0 & 0 & 0 & -ax_7^{-1} & 0 \\ 0 & ax_2^{-1} & 0 & 0 & 0 & 0 & ax_7^{-1} & -ax_8^{-1} \\ 2 & -1 & 1 & -1 & 1 & 1 & 0 & -1 \\ 1 & -\frac{1}{2} & 0 & 0 & 1 & \frac{1}{2} & -\frac{1}{2} & -1 \end{bmatrix}$$

Note: $a = (\ln 10)^{-1}$. By choosing $\varepsilon = 10^{-4}$, the species concentration in mol dm⁻³ are shown in the following table. Thus, the solubility of a mineral fluorite in pure water (neglecting activity effect) is the summation of all calcium ion species which is

SI	pecies	Concentration (mol dm^{-3})
$\overline{x_1}$	Ca ²⁺	1.9886E-04
<i>x</i> ₂	F^{-}	3.9877E-04
<i>x</i> ₃	$\rm H^+$	7.9389E-08
<i>x</i> ₄	OH^-	1.2684E-07
<i>x</i> ₅	CaOH+	5.0326E-10
<i>x</i> ₆	CaF ⁺	1.0947E-06
<i>x</i> 7	HF	4.7916E-08
<i>x</i> ₈	HF^{2-}	7.6069E-11

 $Solubility = [Ca^{2+}] + [CaOH^+] + [CaF^+] = 1.9886 \times 10^{-4} \text{ mol } dm^{-3}.$

Given a formula weight of fluorite (CaF₂) of 78.07 g mol⁻¹, the solubility of fluorite in pure water is $(1.9886 \times 10^{-4} \text{ mol } \text{dm}^{-3}) \times (78.07 \text{ g mol}^{-1}) = 15.5 \text{ mg } \text{L}^{-1}$.

Aqueous species' activity coefficients:

In a natural aquatic system, there are a number of dissolved ionic species whose electrostatic interaction could reduce effective concentration or activity of individual ions. The equilibrium calculation of speciation or any chemical reaction must consider the activity effect. There are a number of empirical relationships that have been proposed to evaluate the activity coefficient of species *i*, γ_i in aqueous solution. However, for natural water, Davies equation [13] is the most commonly used which is given as

$$-\log \gamma_{i} = -0.51 z_{i}^{2} \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 \right) \quad \text{for} \quad I \leq 0.5,$$
 (1.32)

where *I* is an ionic strength of the aqueous solution and can be calculated from the relationship

$$I = \frac{1}{2} \sum C_i z_i^2 \tag{1.33}$$

with C_i and z_i are concentration in mol dm⁻³ or mol kg⁻¹ and charge of the ion, respectively. The calculation of aqueous speciation becomes more complex and non-linear when the activity effect is accounted for and hand calculation is almost impossible because it requires iterative calculation until all required equations are satisfied. Several aqueous speciation programs have been proposed and used for this purpose such as MINTEQ [12] or PHREEQC [34].

EXAMPLE 1.18 Solubility of fluorite in pure water with activity effect

Calculate the solubility of a mineral fluorite, CaF_2 , in (a) pure water and (b) a solution containing 0.001 M CaCl₂. Consider activity effect at 25 °C, 1 atm.

► Solution: As mentioned earlier, the calculation of aqueous speciation when considering activity effect is more complicated and requires iterative calculation. We will use a computer program, MINTEQ, to do this job. What MINTEQ does is similar to previous example but adding more equations for ionic strength and activity coefficients. The results from computer program for species concentration are tabulated in the table.

The solubility in pure water can be tracked from either Ca or F^- whereas the solubility in 0.001 M CaCl₂ solution is easier to track from F^- because the solution already contains Ca²⁺. Using similar method presented in previous example, the solubility of fluorite in

(a) pure water

Solubility = $(2.1115 \times 10^{-4} \text{ mol dm}^{-3}) \times (78.07 \text{ g mol}^{-1}) = 16.5 \text{ mg L}^{-1}$ (b) 0.001 M CaCl₂

Solubility = $(1.0247 \times 10^{-4} \text{ mol } \text{dm}^{-3}) \times (78.07 \text{ g mol}^{-1}) = 8.0 \text{ mg } \text{L}^{-1}$

It should be noted that the pH of the final (or equilibrated) solution after fluorite dissolution is completed is $pH = -\log a_{H^+} = 7.10$ and 7.33 for pure water and 0.001 M CaCl₂ solution, respectively.

Spacias]	Pure Water		0.1 M CaCl ₂					
species	<i>C</i> _{<i>i</i>} , M	a_i	Υi	<i>C</i> _{<i>i</i>} , M	a_i	Υi			
Ca ²⁺	2.1061E-04	1.8781E-04	0.8917	1.0970E-03	8.5360E-04	0.7781			
CaF ⁺	1.0947E-06	1.0638E-06	0.9718	2.4147E-06	2.2679E-06	0.9392			
CaOH+	4.8914E-10	4.7532E-10	0.9717	3.9000E-09	3.6629E-09	0.9392			
F^-	4.2226E-04	4.1034E-04	0.9718	2.0493E-04	1.9247E-04	0.9392			
H^+	8.1690E-08	7.9383E-08	0.9718	4.9848E-08	4.6817E-08	0.9392			
HF	4.9295E-08	4.9302E-08	1.0000	1.3629E-08	1.3639E-08	1.0000			
HF^{2-}	8.2880E-11	8.0540E-11	0.9718	1.1127E-11	1.0451E-11	0.9392			
OH^-	1.3053E-07	1.2685E-07	0.9718	2.2898E-07	2.1507E-07	0.9393			
CaCl ⁺	-	-	-	4.2787E-06	4.0186E-06	0.9392			
Cl-	-	-	-	1.9956E-03	1.8742E-03	0.9392			

Aqueous solubility of an organic compound Aqueous solubility of organic compounds depends largely on the size of the molecule (i.e., number of carbon atoms) and its molecule's polarity. Although aqueous solubility of organic compound is temperature dependent, it does not vary greatly for a given chemical over the typical range of ambient environmental temperature. As for example of solubility, pure liquid trichloroethene (CHCl=CCl₂,TCE) dissolves into water until an aqueous concentration is approximately 1000 mg L⁻¹ is reached. See Table 4.10 for the solubility of some commonly found organic pollutants.

1.3.3.2 Vapor pressure Vapor pressure is another important chemical-specific property which is defined as the *partial pressure* of a chemical in a gas phase that is in equilibrium with the pure liquid or solid chemical. For example, at 20 °C a bottle contains both air and pure liquid TCE, the partial pressure of TCE vapor in the air-filled neck of bottle (i.e., headspace) will be approximately 0.08 atm (61 mm Hg) which corresponds to a 0.0033 mol dm⁻³. The ideal gas law is used to convert vapor pressure into the corresponding moles of vapor per unit volume as

$$C = \frac{n}{V} = \frac{P}{RT}$$

where *P* is partial pressure and *C* is gaseous phase concentration. Vapor pressure is strongly temperature-dependent. Therefore it is always best to record the ambient temperature during field investigation. If soilgas sample exhibits pollutant partial pressure or concentration close to P_v of the chemical at a given temperature, we may speculate the presence of free phase organic compounds in soils. The vapor pressure as a function of temperature can be calculated from *Antoine equation* as follow:

$$\ln P_{\nu} = -\frac{a_1}{a_2 + T} + a_3, \tag{1.34}$$

Chemical	MW ^a	$ ho^b$	S^{c}	$P_v^{\ d}$	K_H^e	$K'_H{}^f$
Acetic acid	60.05	1.05	×	-	-	-
Aroclor 1254	325.06	1.5	0.012	1×10^{-7}	0.0027	0.12
Aroclor 1260	371.22	1.57	0.0027	5.3×10^{-8}	0.0071	0.3
Atrazine	215.68	-	33	4×10^{-10}	3×10^{-9}	1×10^{-7}
Benzene	78.11	0.88	1780	0.125	0.0055	0.24
Benz[a]anthracene	228.29	-	0.00025	6.3×10^{-9}	5.75×10^{-6}	2.4×10^{-4}
Benzo[a]pyrene	252.32	-	4.9×10^{-5}	2.3×10^{-10}	1.2×10^{-6}	4.9×10^{-5}
Carbon tetrachloride	153.82	1.59	800	0.12	0.023	0.97
Chlorobenzene	112.56	1.11	472	0.016	0.0037	0.165
Chloroform	119.38	1.48	8000	0.32	0.0048	0.2
<i>m</i> -Cresol	108.14	-	2780	-	-	-
Cyclohexane	84.16	0.78	60	0.13	0.18	7.3
1,1-Dichloroethane	98.96	1.18	4960	0.3	0.006	0.24
1,2-Dichloroethane	98.96	1.24	8426	0.091	0.001	0.0041
cis-1,2,-Dichloroethene	96.94	1.28	3500	0.26	0.0034	0.25
trans-1,2-Dichloroethene	96.94	1.26	6300	0.45	0.0067	0.23
Ethane	30.07	-	0.0024	39.8	0.49	20
Ethanol	46.07	0.79	∞	0.078	6.3×10^{-6}	-
Ethylbenzene	106.17	0.87	152	0.0125	0.0087	0.37
Lindane	290.9	-	7.3	1.2×10^{-8}	4.8×10^{-7}	2.2×10^{-5}
Methane	16.04	-	-	-	0.66	27
Methylene chloride	84.93	1.33	0.00013	0.46	0.003	0.13
Nephthalene	128.17	1.03	33	0.0003	0.00115	0.049
Nitrogen	28.01	-	-	-	-	-
<i>n</i> -Octane	114.23	0.7	0.72	0.019	2.95	121
Oxygen	32	-	-	-	-	-
Pentachlorophenol	266.34	1.98	14	1.8×10^{-7}	3.4×10^{-6}	0.00015
<i>n</i> -Pentane	72.15	0.63	40.6	0.69	1.23	50.3
Tetrachloroethene (PCE)	165.83	1.62	400	0.02	0.0083	0.34
Phenanthrene	178.23	0.98	6.2	8.9×10^{-7}	3.5×10^{-5}	0.0015
Styrene	104.15	0.91	-	-	-	-
Toluene	92.14	0.87	515	0.037	0.0066	0.28
1,1,1-Trichloroethane (TCA)	133.4	1.34	950	0.13	0.018	0.77
Trichloroethene (TCE)	131.39	1.46	1000	0.08	0.01	0.42
o-Xylene	106.17	0.88	175	0.0087	0.0051	0.22
Vinyl chloride	62.5	0.91	2790	3.4	2.4	99

Table 1.12Solubility, vapor pressure (25 °C, 1 atm) and Henry constants of some commonly found
pollutants [37, 22, 13].

^{*a*}Molecular weight (g mol⁻¹); ^{*b*}Liquid density (g cm⁻³); ^{*c*}Aqueous solubility (mg L⁻¹); ^{*d*}Vapor pressure (atm);

 e Henry's constant (atm m³ mol⁻¹); f Dimensionless Henry's constant (-)

where P_{ν} is the vapor pressure of a chemical at temperature T in Kelvin. The empirical parameters a_1, a_2 and a_3 can be obtained from least-square regression using vapor pressure data from, for example, the CRC Handbook of Chemistry and Physics [20]. Table 4.10 list the values of vapor pressure (P_{ν}) of some commonly found organic pollutants.

EXAMPLE 1.19 Benzene in headspace

A 10-L waste container is half-filled with air and half with benzene-based solvent which is conservatively assumed to be pure liquid of benzene. What is the maximum possible concentration of benzene in air in the container? Express concentration both as mole fraction and in units of mass per volume. What is the maximum possible mass of benzene present in the air of the container? Assume standard temperature and pressure (25 °C, 1 atm).

Solution: Since the solvent is mainly benzene, the maximum possible benzene concentration corresponds to equilibrium conditions with saturation of the air phase at the vapor pressure of benzene since a great excess of pure compound is available.

Equilibrium partial pressure of benzene ($P_{benzene}$) in air equals to vapor pressure of pure benzene P_v (see Table 4.10)

$$P_{\text{benzene}} = P_v = 0.125 \text{ atm}.$$

Mole fraction of benzene in air X_{benzene} can be calculated from its partial pressure as follows.

$$X_{\text{benzene,air}} = \frac{P_{\text{benzene}}}{P_{\text{total}}} = \frac{0.125}{1.0} = 0.125$$

Benzene concentration in air Cbenzene,air can be calculated using ideal gas law.

$$C_{\text{benzene,air}} = \frac{n}{V} = \frac{P_{\text{benzene}}}{RT}$$

= $\frac{0.125 \text{ atm}}{(0.08205 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})}$
= $5.11 \times 10^{-3} \text{ mol dm}^{-3}$

Using the molecular weight of benzene, 78.11 g mol⁻¹, the mass per volume concentration equals to $C_{\text{benzene,air}} = 0.4 \text{ g dm}^{-3}$. Mass of benzene in headspace is

$$M_{\text{benzene,air}} = (0.4 \text{ g dm}^{-3}) \times (5.0 \text{ dm}^3) = 2.0 \text{ g}$$

Thus, 2.0 g of benzene in air is negligible compared to $\frac{5.0 \text{ dm}^3 \text{ of pure benzene}}{0.88 \text{ g cm}^{-3}} = 5680$ g of benzene as a pure phase.

1.3.3.3 Aqueous solubility of gaseous species: The Henry's constant The solubility of gaseous species or volatile (organic) compounds can be described using Henry's constant, K_H , which is defined as a ratio of a partial pressure of a pollutant in air to its aqueous concentration at equilibrium.

$$K_H = \frac{P_i}{C_i} \qquad , \tag{1.35}$$

50
where P_i is partial pressure of the pollutant in air (e.g., in atm) and C_i is the aqueous concentration of a pollutant (e.g., in mol m⁻³). Henry's constant is sometimes reported in a dimensionless form (K'_H) where

$$K'_{H} = \frac{\text{moles or mass of pollutant per volume of air}}{\text{moles or mass of pollutant per volume of water}}$$
(1.36)

and the relationship between typical Henry's constant K_H and dimensionless Henry's constant K'_H is

$$K'_{H} = \frac{K_{H}}{RT} = K^{*}_{aw}$$
(1.37)

where *R* is gas constant, *T* is temperature. The dimensionless Henry's constant is sometimes called K_{aw}^* which is air-water partition coefficient.

Table 4.10 lists the values of Henry's constant for some commonly found pollutants. Larger value of Henry's constant refers to higher tendency of the pollutant to volatilize into atmosphere. If Henry's constant is not tabulated, it can be estimated by dividing the vapor pressure of a chemical at a particular temperature (and pressure) by its aqueous solubility under the same condition.

EXAMPLE 1.20 Oxygen content in soilgas

Consider an unsaturated soil where solid, water and air coexist. Suppose the concentration of dissolved oxygen in soil water at equilibrium with soil air is 100

*mu*M. Given a Henry's constant of 26 (dimensionless) at 20 °C, what is the corresponding oxygen partial pressure and concentration in soilgas? What is the Henry's constant in units of atm $m^3 mol^{-1}$?

► Solution: Oxygen concentration in air is

$$K'_{H} = \frac{[O_{2}]_{air}}{[O_{2}]_{water}} \Rightarrow [O_{2}]_{air} = K'_{H}[O_{2}]_{water} = (100 \ \mu M) \times 26 = 2600 \ \mu M$$

This concentration (n/V) is equivalent to a partial pressure of

$$P_{O_2} = \frac{n}{V} RT$$

= (2600 × 10⁻⁶ mol dm⁻³) × (0.08205 L atm mol⁻¹ K⁻¹)(293.15K)
= 0.0625 atm.

Normal (dimensional) Henry's constant can be calculated using (1.37) where

$$K_H = K'_H \times RT$$

= 26 × (0.08205 L atm mol⁻¹ K⁻¹)(293.15K) × $\left(\frac{1 \text{ m}^3}{1000 \text{ L}}\right)$
= 0.63 atm m³ mol⁻¹.

52 REVIEW; TYPES, PROPERTIES AND CHARACTERISTICS OF POLLUTANTS

1.4 Mass balance

The fate of chemicals in environmental media such as water body, groundwater aquifer, air and soil is determined by two main factors: (1) their reactivity and (2) the rate of their physical transport through environment. In order to formulate mathematical model for pollutant's fate and transport, we need to accurately predict the chemical, physical and biological reactions as well as their transport using *mass balance* modeling approach.

Mass balance

The mass balance of a pollutant in over a *control volume*, *CV* can be calculated using the following expression

$$\dot{m}_{in} - \dot{m}_{out} \pm \dot{m}_{rxn} = \dot{m}_{acc} \tag{1.38}$$

where the symbol *m* refers to the rate of change in pollutant's mass (flowing in or out, being generated, degraded, and/or accumulated) per time; this term has a dimension of mass per time or M/T. The subscripts *in*, *out*, *rxn*, and *acc* denote inflow, outflow, chemical reactions (either generation or degradation), and accumulation rates, respectively.

A control volume is a region of a well-defined boundary where the concentration or mass of pollutant is of interest. It can be a lake, portions of river, a groundwater aquifer or atmosphere below boundary (inversion) layer. Figure 1.5 is an example of a control volume used to perform mass balance. If the system is said to be under "steady-state" condition, there is no change in the storage or accumulation of mass in the system. That is, the accumulation term \dot{m}_{acc} or VdC/dt is essentially zero where C and V are concentration and volume of a system, respectively..



Figure 1.5 Example of a typical control volume used in mass balance calculation of a chemical in the lake (modified from [21]).

Mass input can occur due to emissions (\dot{E}) within the system (e.g., MT⁻¹) emitted by a smoke stack; mass flowing into the system, e.g., a stream flowing into a lake with a flow rate of $(L^{3}T^{-1})$ carrying a substance with a concentration of C_{in} (ML⁻³). Mass output can

occur due to output by flow: e.g., air or water flowing out of a system at a rate of Q_{out} (L³T⁻¹) with a concentration of $C = C_{out}$ (ML⁻³) equal to the concentration in the system. Usually, we assume the input flow rate is equal to the output flow rate; mass loss due to degradation of decay of the pollutant. Degradation refers to mass loss (equivalent to mass output) due to transformation of the pollutant into some other substance. If a pollutant does not undergo transformations (i.e., does not degrade) we say the pollutant is conservative. If it does degrade, the pollutant is non-conservative.

EXAMPLE 1.21 Mass balance at a infinitesimally small mixing point

Two streams of different flow rates carrying a conservative pollutant of different concentration merge into a bigger stream. Use mass balance equation to predict pollutant concentration in the bigger stream (assume complete mix).



► Solution: At steady-state condition, there is neither mass accumulation nor generation in the control volume. Therefore, the rate of mass input equals to rate of mass output (MT^{-1}) .

$$\dot{m}_{in} - \dot{m}_{out} \pm \underbrace{\dot{m}_{rxn}}_{=0} = \underbrace{\dot{m}_{acc}}_{=0}$$

$$(C_1Q_1 + C_2Q_2) - (Q_1 + Q_2)C_3 = 0$$

$$C_3 = \frac{C_1Q_1 + C_2Q_2}{Q_1 + Q_2} = \frac{1 \times 99 + 901 \times 1}{99 + 1} = 10 \text{ mg m}^{-3}$$

For a non-conservative (e.g., reactive or degradative) pollutant which can undergo a decay due to biological transformation. Degradation or decay rate is frequently modeled as a first-order reaction; i.e., loss of compounds is proportional to the amount of substance present or:

$$\frac{dC}{dt} = -kC \qquad [=] \mathrm{ML}^{-3} \mathrm{T}^{-1}$$

where $k [T^{-1}]$ is a first-order reaction rate constant. In order to convert the reaction rate from $ML^{-3}T^{-1}$ to the unit of MT^{-1} (to conform to mass balance equation), the above rate must be multiplied by volume V. Therefore, degradation rate (MT^{-1}) is

Degradation rate =
$$V \frac{dC}{dt} = -kCV$$
 [=] MT⁻¹

REVIEW; TYPES, PROPERTIES AND CHARACTERISTICS OF POLLUTANTS

EXAMPLE 1.22 Steady-state mass balance of a toxic chemical in lake

Calculate steady-state concentration of a toxic chemical in a lake under the following conditions. Assume steady-state ($\dot{m}_{acc} = V dC/dt = 0$) and constant lake volume with a degradation rate of 50 kg d $^{-1}$. Given, input concentration of 100 μg L $^{-1}$, inflow and outflow rate of 100 m³ s⁻¹.

► Solution: Assume a complete mix lake, the outflow concentration always equal to the concentration in the lake at any time or $C = C_{out}$. From mass balance equation,

$$\begin{array}{lll} \dot{m}_{acc} &=& \dot{m}_{in} - \dot{m}_{out} \pm \dot{m}_{rxn} \\ 0 &=& Q_{in} C_{in} - Q_{out} C_{out} - \text{Degradation rate} \\ 0 &=& \left(100 \text{ m}^3 \text{ s}^{-1}\right) \left(100 \ \mu \text{g L}^{-1}\right) - \left(100 \text{ m}^3 \text{ s}^{-1}\right) C_{out} - (50 \text{ kg d}^{-1}), \end{array}$$

and, with necessary unit conversion, the outflow concentration of the pollutant can be calculated as

$$C_{\rm out} = 42.1 \ \mu {\rm g} \ {\rm L}^{-1}.$$

EXAMPLE 1.23 Steady-state concentration of conservative pollutant

A living room with volume of 50 m^3 has two people smoking in it, each smoking 3 cigarettes per hour. An individual cigarette emits 1.40 mg of formaldehyde. Formaldehyde degrades with a reaction rate coefficient of 0.4 h^{-1} . The air flows in and out of the room at the rate of 50 m³ h⁻¹. Estimate the steady-state concentration assuming complete mixing in the room. How does the value compare with the threshold for eye irritation of about 0.05 ppm_w(at temperature 25 °C)?

► Solution: At steady-state condition, there is neither mass accumulation nor generation in the control volume. Therefore, the rate of mass input equals to rate of mass output.

Input :	$\dot{E} = (2 \text{ smokers})(3 \text{ cigs/smoker/h})(1.4 \text{ mg/cig})$	$= 8.4 \text{ mg h}^{-1}$
Output :	$QC = (50 \text{ m}^3 \text{ h}^{-1})(C \text{ mg m}^{-3})$	$= 50C \text{ mg h}^{-1}$
Degradation :	$kCV = (0.4 \text{ h}^{-1})(50 \text{ m}^3)(C \text{ mg m}^{-3})$	$= 20C \text{ mg h}^{-1}$

Perform a mass balance calculation where

$$\dot{m}_{in} - \dot{m}_{out} \pm \dot{m}_{rxn} = 0$$

$$0 - QC + \dot{E} - kCV = 0$$

$$C = \frac{E}{Q + kV} = C_{ss}$$

$$= \frac{8.4}{50 + 20} = 0.12 \text{ mg m}^{-3}$$

54

Thus, the steady-state concentration of formaldehyde in the room (which is equal to formaldehyde concentration leaving the room as well) C_{ss} is 0.12 mg m⁻³.

To convert volumetric concentration (mg m⁻³) to mg kg⁻¹, we need a density of air at 25 °C which is 1.184 kg m⁻³. Thus, $C_{ss} = 0.12/1.184 = 0.10$ mg kg⁻¹ or ppm_w which is greater than a threshold of 0.05 ppm_w for eye irritation.

EXAMPLE 1.24 Transient concentration of non-conservative pollution

From previous example, what is the formaldehyde concentrations in the room after one and two hours? Assume initial concentration of formaldehyde in the room C(t = 0) = 0.

► Solution: In this problem, we would like to know formaldehyde concentration in a room at 1 and 2 h, respectively. In other words, we want to know how formaldehyde concentration varies with time (i.e. transient or unsteady response). In this analysis, we need to start off with mass balance equation.

The above equation is actually a first-order linear ODE which can be solved by using integrating factor as described in (1.6) and the solution is

$$C(t) = \left(\frac{\dot{E}}{Q+kV}\right) - \left[\left(\frac{\dot{E}}{Q+kV}\right) - C_0\right] \exp\left[-\left(\frac{\dot{E}}{Q+kV}\right)t\right]$$
$$C(t) = C_{ss} - (C_{ss} - C_0) \exp\left[-\left(\frac{\dot{E}}{Q+kV}\right)t\right]$$

or

Putting all known parameters into the above equations, the solution to transient formaldehyde concentration is

$$C(t) = 0.12 \left(1 - e^{-1.4t} \right).$$

At 1 and 2 h, the concentrations of formal dehyde are 0.09 and 0.11 mg m⁻³, respectively.

Concluding remarks In this chapter, we have reviewed some basic mathematical and statistical techniques that are essential for this course. Most importantly, students are expected to revisit the mass balance fundamentals again and again when we formulate the transport of pollutants in environmental media in lakes, rivers, soils, aquifers and atmosphere. Please make sure that you understand the concepts behind all the worked examples illustrated in this chapter. The problems at the end of the chapter are intended for student's practice. Some problems may require more critical thinking and time-consuming. Once you are familiar with the fundamentals presented in this chapter, you may then find the rest of the book easier to comprehend.

PROBLEMS

1.1 The gas constant *R* has the value of 0.08205 L atm mol⁻¹ K⁻¹, show that it can be converted to other units such as 8.314 J mol⁻¹ K⁻¹ and 1.987 cal mol⁻¹ K⁻¹.

1.2 What is the molarity of 1.0 m (molal) NaCl solution (at 25 °C and 1 atm)? Given the density of the NaCl solution is 1.0405 kg L^{-1} .

1.3 When dissolved in water, NaCl dissociates into Na⁺ and Cl⁻ ions or NaCl \longrightarrow Na⁺ + Cl⁻. What is the molality of Na⁺ in a solution of 1.35 g NaCl dissolved in 2.4 kg of water? What is the concentration of Na⁺ in ppm_w?

- **1.4** If the proposed air quality standard for ozone (O_3) is 0.08 ppm_v.
 - a) Express that standard in μ g m⁻³ at 1.0 atm and 25 °C.
 - b) At the elevation of Chiang Mai where the atmospheric pressure is 0.90 atm, express the proposed ozone standard at that pressure and $30 \,^{\circ}$ C.

1.5 An air sample collected at 1.0 atm has a density of approximately 1.3 g L⁻¹ and contains SO₂ at concentration of 25 μ g m⁻³. What is this concentration in terms of ppm_w, ppm_v and ppm-by-mol?

1.6 Given the vol.% of dry air at sea level as follows.

Gas	vol.%
O ₂	20.95
N_2	78.09
Ar	0.93
CO_2	0.03

Assume that air is an ideal gas and the condition at the sea level is 1.0 atm and 30 $^{\circ}$ C.

- a) Compute the density of dry air in kg m^{-3} under this condition.
- b) Determine the concentration of argon in air in mg $m^{-3}\,$ and $ppm_w.$

1.7 Solve the following differential equations to obtain closed-form or analytical solution. If the initial condition is given, please determine the constant of integration accordingly.

a)
$$\frac{du}{dt} = 2u - 1$$

b) $f'(x) = \sin^2(x)$
c) $\frac{du}{dt} = 2u - t$, $u(0) = 1$
d) $\frac{d^2u}{dt^2} = 0$, $u(0) = u_0$ and $u(L) = u_L$
e) $\frac{d^2u}{dt^2} = -a$, $u(0) = u_0$ and $u(L) = u_L$

1.8 Given the following differential equation,

$$\frac{du}{dt} = 1 - t^2 + \sin(u), \qquad u(0) = 1.0.$$

Use implicit & explicit Euler and RK4 methods with $\Delta t = 0.025$ to approximate the solution of u(t) for $0 \le t \le 1$.

1.9 A steady-state heat balance for a 10-m metal rod is represented as

$$\frac{d^2T}{dx^2} - 0.15T = 0$$

Find a solution of rod's temperature T = T(x) using (a) analytical solution, and (b) a finitedifference approach with $\Delta x = 1$ m.

1.10 Nano-sized Zero Valent Iron (NZVI) is now widely used as a treating reagent for remediation of wastewater or contaminated groundwater. The efficiency of NZVI depends on the curing time of material coating in the manufacturing process. The speculated relationship between "curing time (x)" and "efficient (y)" takes a simple form

$$\hat{y} = b_0 + b_1 x$$

Based on the results of the experiment shown below, answer the following questions.

Curing time (<i>x</i>), min	Efficiency (y)
120	8.9
150	9.7
150	9.1
165	9.8
180	10.0
180	10.4
180	9.7

- a) Complete a *linear* least square analysis of the data to estimate the parameters for the two-parameter model (i.e., b_0 and b_1).
- b) Assess a goodness-of-fit at $\alpha = 0.05$ significance level using Chi-square test, paired *t*-test and coefficient of determination (R^2).
- c) Calculate the 95% confidence interval for the average durability as a function of curing time.
- d) Calculate the contour plot of the sum of squared error of the joint confidence region and designate the area of 95% joint confidence region. Draw a rectangular box designating the region of 95% confidence interval for two parameters b_0 and b_1 .

1.11 The following experimental data of benzene sorption by lake sediments. Assume that the sorption of benzene in sediment follows Langmuir isotherm where

C,	$K_{S} = \frac{K_L \cdot C_{s,\max}}{1 + K_L \cdot c}$	$\frac{C_w}{C_w}$
Exp. No.	C_w , mg L ⁻¹	$C_s \mathrm{mg}\mathrm{kg}^{-1}$
1	0.01	14.8
2	10.6	723.8
3	18.9	991.4
4	37.3	1227.4
5	55.0	1573.6
6	68.6	1778.1
7	82.5	1935.5

- 58 REVIEW; TYPES, PROPERTIES AND CHARACTERISTICS OF POLLUTANTS
 - a) Complete a *non-linear* least-square analysis of the data to estimate the parameter values (K_L and $C_{s,max}$).
 - b) Assess a goodness-of-fit at $\alpha = 0.05$ significance level using Chi-square test, paired *t*-test and coefficient of determination (R^2).
 - c) Calculate the contour plot of the sum of squared error of the joint confidence region and designate the area of 95% joint confidence region; use K_L and $C_{s,\max}$ as an *x* and *y*-axis, respectively.
 - d) Estimate the 95% confidence interval of K_L and $C_{s,max}$.

1.12 Calculate the ionic strength for the following solution.

- a) A mixture of 0.05 M CaCl₂ and 0.025 M NaCl, and 0.045 M KNO₃
- b) A mixture of 0.097 M CaCl₂, 0.015 M KCl, and 0.405 M NaNo₃

1.13 From previous problem, calculate the activity coefficient of each cation and anion in the solution.

1.14 Use thermodynamics data in [20] to calculate the solubility product of a mineral calcite, $CaCO_3$, at 25 °C. If temperature increases to 35 °C, will $CaCO_3$ be more or less soluble?

1.15 Use computer program MINTEQ [12] or PHREEQC [34] to answer the following questions

- a) Find the pH of a solution containing 0.1 M CH₃COONa and 0.2 M Na₂HPO₄ at 25 $^{\circ}$ C.
- b) Find the solubility of CaCO₃ in pure water and sea water. Use seawater composition data from https://en.wikipedia.org/wiki/Seawater.

1.16 If 10 mg of naphthalene is added to 1 L of water in a 20-L sealed bottle. Assume the aqueous solubility of naphthalene of 2.6×10^{-4} mol dm⁻³, and the vapor pressure of 3×10^{-4} atm at 20 °C.

- a) What is the dimensionless Henry's constant?
- b) What percentage of the total naphthalene ends up in the air-filled volume of the bottle at equilibrium?

1.17 Use Henry's constant and thermodynamics data for H_2CO_3 , HCO_3^- and CO_3^{2-} from [20] to calculate the pH of rain water that is in equilibrium with $CO_2(g)$ in atmosphere. Assume that rainwater is pure water and carbon dioxide content in atmosphere is approximately $10^{-3.5}$ atm. Ignore activity effect in your calculation.

1.18 Repeat previous problem using either MINTEQ or PHREEQC and compare the results. Discuss the difference.

1.19 Use the temperature-dependent vapor pressure of a chemical of your choice from [20] to find the best-fit parameters of Antoine equation:

$$\ln P_{\nu} = \frac{a_1}{a_2 + T} + a_3$$

1.20 A reactor is to be designed in which the oxidation of cyanide (CN^{-}) to cyanate (CNO^{-}) is to occur by the following reaction:

$$\frac{1}{2}O_2 + CN^- = CNO^-$$

The reactor is continuously stirred (i.e., complete mixing). The feed stream flow rate is 380 m³ d⁻¹ and contains 15,000 mg L⁻¹ of CN⁻. The desired reactor effluent concentration is 10 mg L⁻¹ of CN⁻. Assume that oxygen is in excess and the reaction rate is first order with respect to [CN⁻] with a rate constant k = 1 s⁻¹. Determine the volume of a reactor required to achieve the desired treatment objective.

1.21 A water storage tank in a distribution system is filled at a rate of 12.5 m³ d⁻¹. The chlorine (Cl₂) concentration of the water entering the tank from a treatment plant is 6 mg L⁻¹. Chlorine reactions with organic and inorganic constituents are assume to be first-order with the decay constant k = 0.004 h⁻¹. Find the chlorine concentration at

- a) the end of filling the storage tank if the volume at the beginning of the fill period is $2,000 \text{ m}^3$,
- b) the end of the next storage period of 10 h (assuming no withdrawal), and
- c) as a function of time during withdrawal from the storage tank if the rate of withdrawal is 20 m³ d⁻¹.

1.22 A small wastewater treatment plant having a cylindrical reactor with a radius and height of 10 and 5 m, respectively, is used to continuously treated and removed a contaminant "A" from a dirty inflow wastewater. If a degradation rate of a contaminant can be described by

	Time (d)	$C (kg m^{-3})$
$P_{1} = 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1$	1	2.66
Degradation rate = $-kC^2$ kg m ⁻⁹ d ⁻¹	2	3.19
where k is an unknown decay constant (m ³ kg ⁻¹ d ⁻¹).	4	5.19
a) Show that the mass balance of contaminant	6	6.23
"A" in the reactor can be written as	7	7.06
dC Q Q Q Q Q Q Q Q Q	9	9.35
$\frac{dt}{dt} = \frac{1}{V}C_{\rm in} - \frac{1}{V}C - kC^2.$	11	8.02
b) Assume that the reactor is initially clean use	13	8.40
RK4 method (with $\Delta t = 1$ d) to find the best	17	8.12
estimate of degradation constant k. Given	21	8.02
$Q = 150 \text{ m}^3 \text{ d}^{-1}$, $C_{\text{in}} = 25 \text{ kg m}^{-3}$ and the	23	7.45
recorded outflow concentration is shown in	25	8.36
the table.	28	8.28
	30	8.43

CHAPTER 2

REGULATED CHEMICALS AND QUANTITATIVE RISK ASSESSMENT

This chapter begins with a brief introduction to regulated chemical toxicology and followed by quantitative risk assessment from exposure to such chemicals. We will then relate risk assessment to fate and transport modeling.

2.1 Toxicology

Toxicology is the study of chemical or physical effects when introduced to an organism or ecosystem. We will limit our discussions to *environmental toxicology*, where a chemical (pollutant) enters an organism, usually at relatively low concentrations, and look at the various modes of entry to the body, reactions in the body, and excretion of the chemical from the body. The more classic modes of entry to an organism are *dermal adsorption* through the skin, *inhalation* into a more advanced organism through the lungs, *oral ingestion* into the gastrointestinal tract, and *injection* through the skin. This discussion only focuses on the first three since injection is mostly a medicinal mode of entry [27].

The *dose* of a chemical (pollutant) and *duration of exposure* are important concepts in determining risk. The dose or concentration of a chemical is an obvious variable in determining exposure and can vary from low parts per trillion concentrations to the presence of a pure chemical. The duration of exposure of a chemical is commonly divided into (i) acute exposure (usually just one exposure for a short time), (ii) sub-chronic exposure (multiple exposures of a day to month duration), and chronic exposure (long-term exposures or even a life-long exposure). These three categories are used in risk assessment calculation.

Fate and Transport of Pollutants in Environment. By S. Saenton, Chiang Mai University

Various modes of toxic effects are possible given the wide range of chemicals nature provides us with and given the large chemical inventory humans have synthesized and released into the natural, urban, and industrial environments. Organisms have developed a wide range of detoxification approaches. These include simple and rapid excretion by the kidneys, a series of complex biotransformations such as hydrolysis, reduction, oxidation, and conjugations (the addition of functional groups, i.e. methylation, sulfonation, and phosphorylation) performed mostly in the liver, and deposition and storage in more permanent parts of the body [29].

Environmental toxicology is the scientific study of the health effects associated with exposure to toxic chemicals occurring in the natural, work, and living environments. The term also describes the management of environmental toxins and toxicity, and the development of protections for humans and the environment. Table 2.1 lists top 20 substances, in order of priority, which are determined to pose the most significant potential threat to human health. This priority list is not a list of "most toxic" substances but rather a prioritization of substances based on a combina-

Table 2.1The ATSDR substance prioritylist (Agency for Toxic Substances and DiseaseRegistry; www.atsdr.cdc.gov [44]).

Rank	Chemical/Pollutant
1	Arsenic
2	Lead
3	Mercury
4	Vinyl chloride
5	Polychlorinated biphenyls
6	Benzene
7	Cadmium
8	Benzo(a)pyrene
9	Polycyclic aromatic hydrocarbons
10	Benzo(b)fluoranthene
11	Chloroform
12	Aroclor 1260
13	DDT
14	Aroclor 1254
15	Dibenzo(<i>a</i> , <i>h</i>)anthracene
16	Trichloroethylene
17	Chromium (VI)
18	Dieldrin
19	Phosphorus (white)
20	Hexachlorobutadiene

tion of their frequency, toxicity, and potential for human exposure at various sites.

2.1.1 Toxicity effects to human health

An *acute* effect of a contaminant occurs rapidly after exposure to a large amount of that substance. A *chronic* effect of a contaminant results from exposure to small amounts of a substance over a long period of time. In such a case, the effect may not be immediately obvious. Chronic effect are difficult to measure, as the effects may not be seen for years. Long-term exposure to cigarette smoking, low level radiation exposure, and moderate al-cohol use are all thought to produce chronic effects.

Scientists have known that any substance is toxic in sufficient quantities. For example, small amounts of selenium are required by living organisms for proper functioning, but large amounts may cause cancer. The effect of a certain chemical on an individual depends on the dose of the chemical. This relationship is often illustrated by a dose-response curve which shows the relationship between dose and the response of the individual. Lethal doses in humans have been determined for many substances from information gathered from records of homicides, accidental poisonings, and testing on animals [29].

A dose that is lethal to 50% of a population of test animals is called the lethal dose-50% or LD_{50} . Determination of the LD_{50} is required for new synthetic chemicals in order to give a measure of their toxicity. A dose that causes 50% of a population to exhibit any significant response (e.g., hair loss, stunted development) is referred to as the effective dose-50% or ED₅₀. Some toxins have a threshold amount below which there is no apparent effect on the exposed population.

2.1.2 Regulated toxic chemicals

The contamination of the air, water, or soil with potentially harmful substances can affect any person or community. Contaminants (classified in Table 2.2) are often chemicals found in the environment in amounts higher than what would be there naturally. We can be exposed to these contaminants from a variety of residential, commercial, and industrial sources. Sometimes harmful environmental contaminants occur biologically, such as mold or a toxic algae bloom.

Table 2.2	Classification of environmenta	al toxicants causing	ng health	problems	[29]	1.

Contaminant	Definition
Carcinogen	An agent which may produce cancer (uncontrolled cell growth), either by itself or in conjunction with another substance. Examples include formalde- hyde, asbestos, radon, vinyl chloride, and tobacco.
Teratogen	A substance which can cause physical defects in a developing embryo. Examples include alcohol and cigarette smoke.
Mutagen	A material that induces genetic changes (mutations) in the DNA. Examples include radioactive substances, x-rays and ultraviolet radiation.
Neurotoxicant	A substance that can cause an adverse effect on the chemistry, structure or function of the nervous system. Examples include lead and mercury.
Endocrine dis- ruptor	A chemical that may interfere with the body's endocrine (hormonal) system and produce adverse developmental, reproductive, neurological, and immune effects in both humans and wildlife. A wide range of substances, both natural and man-made, are thought to cause endocrine disruption, including pharmaceuticals, dioxin and dioxin-like compounds, arsenic, polychlorinated biphenyls (PCBs), DDT and other pesticides, and plasticizers such as bisphenol A (BPA).

Explanation listed below are description of some commonly found contaminants that are highly toxic to human health (www.epa.gov [45]).

Arsenic is a naturally occurring element that is normally present throughout our environment in water, soil, dust, air, and food. Levels of arsenic can regionally vary due to farming and industrial activity as well as natural geological processes. The arsenic from farming and smelting tends to bind strongly to soil and is expected to remain near the surface of the land for hundreds of years as a long-term source of exposure. Wood that has been treated with chromated copper arsenate (CCA) is commonly found in decks and railing in existing homes and outdoor structures such as playground equipment. Some underground aquifers are located in rock or soil that has naturally high arsenic content. Arsenic may also be found in groundwater, drinking water, foods, including rice and some fish, where it is present due to uptake from soil and water. It can also enter the body by breathing dust containing arsenic. Researchers found that arsenic, even at low levels, can interfere with

the body's endocrine system. Arsenic is also a known human carcinogen associated with skin, lung, bladder, kidney, and liver cancer (www.epa.gov [45]).

Mercury is a naturally occurring metal, a useful chemical in some products, and a potential health risk. Mercury exists in several forms; the types people are usually exposed to are methylmercury and elemental mercury. Elemental mercury at room temperature is a shiny, silver-white liquid which can produce a harmful odorless vapor. Methylmercury, an organic compound, can build up in the bodies of long-living, predatory fish. Although fish and shellfish have many nutritional benefits, consuming large quantities of fish increases a person's exposure to mercury. Pregnant women who eat fish high in mercury on a regular basis run the risk of permanently damaging their developing fetuses. Children born to these mothers may exhibit motor difficulties, sensory problems and cognitive deficits [29].

Bisphenol A (BPA) is a chemical synthesized in large quantities for use in the production of polycarbonate plastics and epoxy resins. Polycarbonate plastics have many applications including use in some food and drink packaging, e.g., water and infant bottles, compact discs, impact-resistant safety equipment, and medical devices. Epoxy resins are used as lacquers to coat metal products such as food cans, bottle tops, and water supply pipes. Some dental sealants and composites may also contribute to BPA exposure. The primary source of exposure to BPA for most people is through the diet. Bisphenol A can leach into food from the protective internal epoxy resin coatings of canned foods and from consumer products such as polycarbonate tableware, food storage containers, water bottles, and baby bottles [27].

Phthalates are a group of synthetic chemicals used to soften and increase the flexibility of plastic and vinyl. Polyvinyl chloride is made softer and more flexible by the addition of phthalates. Phthalates are used in cosmetics and personal care products, including perfume, hair spray, soap, shampoo, nail polish, and skin moisturizers. They are used in consumer products such as flexible plastic and vinyl toys, shower curtains, wallpaper, vinyl miniblinds, food packaging, and plastic that contains phthalates or breathing dust in rooms with vinyl miniblinds, wallpaper, or recently installed flooring that contain phthalates. We can be exposed to phthalates by drinking water that contains phthalates. Phthalates are suspected to be endocrine disruptors [27].

Lead is a metal that occurs naturally in the rocks and soils. It is also produced from burning fossil fuels such as coal, oil, and gasoline; mining; and manufacturing. Lead has no distinctive taste or smell. Lead is used to produce batteries, pipes, roofing, scientific electronic equipment, military tracking systems, medical devices, and products to shield X-rays and nuclear radiation. It is used in ceramic glazes and crystal glassware. Lead and lead compounds are listed as "reasonably anticipated to be a human carcinogen". It can affect almost every organ and system in your body. It can be equally harmful if breathed or swallowed. The part of the body most sensitive to lead exposure is the central nervous system, especially in children, who are more vulnerable to lead poisoning than adults [29].

Formaldehyde is a colorless, flammable gas or liquid that has a pungent, suffocating odor. It is a volatile organic compound, which is an organic compound that easily becomes a vapor or gas. It is also naturally produced in small, harmless amounts in the human body. The primary way we can be exposed to formaldehyde is by breathing air containing it. Releases of formaldehyde into the air occur from industries using or manufacturing

formaldehyde, wood products (such as particle-board, plywood, and furniture), automobile exhaust, cigarette smoke, paints and varnishes, and carpets and permanent press fabrics. Nail polish, and commercially applied floor finish emit formaldehyde. In general, indoor environments consistently have higher concentrations than outdoor environments, because many building materials, consumer products, and fabrics emit formaldehyde. Levels of formaldehyde measured in indoor air range from 0.02 to 4 ppm_v. Formaldehyde levels in outdoor air range from 0.001 to 0.02 ppm_v in urban areas (www.epa.gov [45]).

Radon is a radioactive gas that is naturally-occurring, colorless, and odorless. It comes from the natural decay of uranium or thorium found in nearly all soils. It typically moves up through the ground and into the home through cracks in floors, walls and foundations. It can also be released from building materials or from well water. Radon breaks down quickly, giving off radioactive particles. Long-term exposure to these particles can lead to lung cancer. Radon is the leading cause of lung cancer among nonsmokers and the second leading cause behind smoking [27].

2.2 Risk assessment

The origin of risk assessment arise from the attempt to mathematically quantify how bad a situation is, and which was and is viewed by some environmentalists. We started by reviewing the chemistry of pollution and next presented basic fate and transport modeling procedures for predicting pollutant concentration as a function of chemical and physical conditions in the system. In this chapter, we will calculate the concentration of pollutant reaching a human (the receptors). Based on this information, combined with the results of chemical exposure experiments involving animals, we will attempt to estimate the risk to humans. As you will see, the approaches are simple, and when you consider all of the possible sources of error or uncertainty, from the beginning of the process (pollutant source and mass characterization) through fate and transport modeling (with uncertainties in chemical degradation and physical dispersion), and now to risk assessment which is extrapolated from animal study data to human risk, we should recognize that our risk estimates may be orders of magnitude in error. Thus, risk assessment should be viewed as only one tool in our approach to environmental management.

The National Academy of Sciences [31] suggests that risk assessment be divided into the following four steps: hazard identification, dose-response assessment, exposure assessment, and risk characterization. After a risk assessment has been completed, the important stage of risk management follows, as shown in Figure 2.1. These four steps of risk assessment are described here:

Hazard identification is the process of determining whether or not a particular chemical is causally linked to particular health effects, such as cancer or birth defects. Because human data are so often difficult to obtain, this step usually focuses on whether a chemical is toxic in animals or other test organisms.

Dose-response assessment is the process of characterizing the relationship between the dose of an agent administered or received and the incidence of an adverse health effect. Many different dose-response relationships are possible for any given agent depending on such conditions as whether the response is carcinogenic (cancer causing) or noncarcinogenic and whether the experiment is a one-time acute test or a long-term chronic test.

66 REGULATED CHEMICALS AND QUANTITATIVE RISK ASSESSMENT



Figure 2.1 Steps in risk assessment calculation and management (adapted from [31]).

Because most tests are performed with high doses, the dose-response assessment must include a consideration for the proper method of extrapolating data to low exposure rates that humans are likely to experience. Part of the assessment must also include a method of extrapolating animal data to humans.

Exposure assessment involves determining the size and nature of the population that has been exposed to the toxicant under consideration and the length of time and toxicant concentration to which they have been exposed. Consideration must be given to such factors as the age and health of the exposed population, smoking history, the likelihood that members of the population might be pregnant, and whether or not synergistic effects might occur due to exposure to multiple toxicants.

Risk characterization is the integration of the foregoing three steps, which results in an estimate of the magnitude of the public-health problem.

2.2.1 Hazard identification

The very first step in a risk evaluation is to assess whether or not the chemicals that a person has been exposed to are likely to have any adverse health effects. This is the work of toxicologists who study both the nature of the adverse effects caused by toxic agents as well as the probability of their occurrence. There are two major types of toxicity that could pose a treat after exposure: acute and chronic toxicity.

Acute toxicity or short-term toxicity refers to effects that are caused within a short period of time after a single exposure to the chemical. One way to describe the toxicity of chemicals is by the amount that is required to kill the organism. Table 2.3 shows a conventional toxicity rating scheme that expresses the dose in terms of milligrams of chemical ingested per kilogram of body weight. That is, ingestion of a given amount of toxin will be more dangerous for a small person, such as a child, than a larger adult. Normalizing the dose using body weight is the first step in trying to relate a lethal dose to a laboratory animal to what might be expected in a human. For example, it takes on the order of 20,000

Toxicity rating	Probable lethal dose to human $(mg kg^{-1} \text{ of body weight})$
Practically nontoxic	>15,000
Slightly toxic	5,000-15,000
Moderately toxic	500-5,000
Very toxic	50-500
Extremely toxic	5-50
Super toxic	<5

 Table 2.3
 A conventional rating system for the acute toxicity of chemicals in humans [31].

mg of ordinary sucrose per kilogram to kill a rat. Using the rating system in Table 2.3, sucrose would be considered practically nontoxic. If we scale up that dose to a 70-kg human (without any other adjustments), it might take something like 1.4 kg of sucrose ingested all at one time to be lethal. At the other extreme, the bacteria Clostridium botulinum, responsible for botulism (food poisoning), is lethal with a single dose of only 0.00001 mg kg⁻¹, so it is supertoxic [36].

Not every person in the entire polulation will react the same way to a toxin. Thus, one way to illustrate the variation is with a dose-response curve that shows the percentage of a population that is affected as a function of the dose received. In the dose-response curves of Figure 2.2, a logarithmic scale for dose is shown, which tends to yield the familiar S-shaped curve. Also notice that the dose is expressed as milligrams of chemical ingested per kilogram of body weight. Normalizing with body weight allows the dose to be extrapolated to individuals of different sizes, such as a child versus an adult. Also, it provides a first cut at extrapolating the likely effects on a human when the dose-response curve has been generated using animal tests [29, 27].

The curves of Figure 2.2 show the response to chemical exposure as a mortality rate. The dose that will kill 50 percent of a population is designated LD_{50} , where LD stands for lethal dose. In Figure 2.2A, the dose-response curves for two chemicals are shown. Chemical A has a lower LD_{50} than Chemical B, and it is always more toxic. Figure 2.2B warns us to be aware that just because one chemical has a lower LD_{50} than another does not necessarily mean it is always more toxic. Chemical C has a lower LD_{50} , which would normally suggest it is more toxic than D, but notice it is not as toxic as D at low doses. So the dose-response curve does provide more information than a simple table of LD_{50} doses.

Chronic toxicity In contrast to the short-term responses associated with acute toxicity, most risk assessments are focused on responses that may take years to develop. Measuring the ability of specific chemicals to cause cancer, reproductive failure, and birth defects is much more difficult than the acute toxicity testing just described. Thus, chronic toxicity is any adverse effects caused by a toxic agent after a long period of exposure. Two main types of chronic effects that are of concern: mutagenesis and carcinogenesis. *Mutagenesis* refers to an alteration of DNA in either somatic or germinal cells not associated with the normal process of recombination whereas *mutation* is a permanent, transmissible change in DNA that changes the function or behavior of the cell [27]. The *carcinogenesis* is a cancer development process by a substance called *carcinogen* [29].



Figure 2.2 Dose-response mortality curves for acute toxicity: (a) Chemical A is always more toxic than B; (b) whereas Chemical C is less toxic than D at low doses even though it has a lower LD_{50} (adapted from [29]).

The most important source of human risk information to the exposure of a chemical comes from epidemiologic studies. Epidemiology is the study of the incidence rate of diseases in real populations [29]. By attempting to find correlations between disease rates and various environmental factors, an epidemiologist attempts to show in a quantitative way the relationship between exposure and risk. Preliminary data analysis usually involves setting up a simple 2×2 matrix such as the one shown in Figure 2.3. The rows divide the populations according to those who have and have not been exposed to the risk factor. The columns are based on

	With disease	Without disease
Exposed	N _a	N_b
Not exposed	N_c	N_d

Figure 2.3 A 2×2 matrix for an epidemiologic rate comparison. Rows divide people by exposure; columns divide them by disease.

the numbers of individuals who have and have hotacquired the disease being studied.

Various measures can be applied to the data given in Figure 2.3 to see whether they suggest an association between exposure and disease.

The relative risk is defined as

Relative risk =
$$\frac{N_a/(N_a + N_b)}{N_c/(N_c + N_d)}$$
(2.1)

Notice that the numerator is the fraction of those exposed who have the disease, and the denominator is the fraction of those not exposed who have the disease. If those two ratios are the same, the odds of having the disease would not depend on whether an individual

had been exposed to the risk factor, and the relative risk would be 1.0. Above 1.0, the higher the relative risk, and the more the data suggests an association between exposure and risk.

The attributable risk is defined as

Attributable risk =
$$\frac{N_a}{N_a + N_b} - \frac{N_c}{N_c + N_d}$$
 (2.2)

The attributable risk is the difference between the odds of having the disease with exposure and the odds of having the disease without exposure. An attributable risk of 0.0 suggests no relationship between exposure and risk.

The odds ratio is defined as the cross product of the entries in the matrix:

Odds ratio =
$$\frac{(N_a/N_b)}{(N_c/N_d)}$$
 (2.3)

The odds ratio is similar to the relative risk. Numbers above 1.0 suggest a relationship between exposure and risk.

EXAMPLE 2.1

An evaluation of personnel records for employees of a plant that manufactures vinyl chloride finds that out of 200 workers, 15 developed liver cancer. A control group consisting of individuals with smoking histories similar to the exposed workers, and who were unlikely to have encountered vinyl chloride, had 24 with liver cancers and 450 who did not develop liver cancer. Find the relative risk, attributable risk, and odds ratio for these data.

► Solution:

Exposec

Not xposed With diseaseWithout diseasePutting together the data in a 2×2 matrix
as shown in he figure and relative risk can be
calculated as:151852445024450Attributable risk = $\frac{15/(15+185)}{24/(24+450)} = 1.48$ Attributable risk = $\frac{15}{200} - \frac{24}{474} = 0.024$

Odds ratio =
$$\frac{200 \quad 474}{(24/450)} = 1.52$$

The relative risk and the odds ratio both are above 1.0, so they suggest a relationship between exposure and risk. For those who were exposed, the risk of cancer has increased by 0.024 (the attributable risk) over that of their cohorts who were not exposed. All three measures indicate that further study of the relationship between vinyl chloride and liver cancer would be warranted. 70 **BEGULATED CHEMICALS AND QUANTITATIVE BISK ASSESSMENT**

2.2.2 Dose-response and exposure assessment

Dose-response assessment relationships are used to compare the risk or influence of adverse health impacts for a given dose of chemical. Dose-response relationship can be derived from human health studies conducted during or following a known historic exposure. Such exposure may have occurred as a result of can accident or in an occupational setting. The dose-response curve is a result of chronic toxicity test. To obtain a mathematical relationship between the amount of toxicant that a human is exposed to and the risk that there will be an unhealthy response to that dose.

For chronic toxicity studies, a low dose is administered over a significant portion of the animal's lifetime. The resulting dose-response curve has the incremental risk of cancer (above the background rate)



Figure 2.4 Dose response relationship s for human health risk. The slope of the straightline is called potency factor.

on the y-axis, and the lifetime average daily dose or chronic daily intake (CDI) of toxicant along the x-axis. At low doses, where the dose-response curve is assumed to be linear, the slope of the dose-response curve is called the *potency factor* (PF), or *slope factor*.

Potency factor,
$$PF = \frac{\text{Incremental lifetime cancer risk}}{\text{Chronic daily intake (mg kg^{-1} d^{-1})}}$$
 (2.4)

The denominator in the above equation is the dose averaged over an entire lifetime; it has units of average milligrams of toxicant absorbed per kilogram of body weight per day or mg kg⁻¹ d⁻¹. Since risk has no units, the units for potency factor are therefore (mg kg⁻¹ d⁻¹)⁻¹. If we have a dose-response curve, we can find the potency factor from the slope. In fact, one interpretation of the potency factor is that it is the risk produced by a chronic daily intake of 1.0 mg kg⁻¹ d⁻¹, as shown in Figure 2.4.

Despite the uncertainties in human and animal health studies, consensus values of cancer slope factor are available. Typically the potency factors can be found in an EPA database on toxic substances called the Integrated Risk Information System (IRIS). A short list of some of these chemicals, PFs (for both oral and inhalation exposure routes), and cancer categories is given in Table 2.4. The other factor we need to develop more fully in order to use the basic risk equation is the concept of chronic daily intake. The CDI is, by definition.

Chronic daily intake (CDI) (mg kg⁻¹ d⁻¹) =
$$\frac{\text{Average daily dose (mg d-1)}}{\text{Body weight (kg)}}$$
 (2.5)

The numerator in the above equation is the total lifetime dose averaged over an assumed 70-year lifetime.

Note that the linear model for dose-response relationship assumes no threshold toxicity function. A more complicated model for dose-response can be found, for examples, in [36, 27, 29]. The next example shows how to combine CDI and PF to find a risk.

Cultotener	Potency	factor, PF (mg kg-	$^{-1} d^{-1})^{-1}$
Substance	Oral route	Inhalation route	Dermal route
Arsenic	1.75	50	-
Benzene	0.029	0.029	0.03
Benzol(a)pyrene	11.5	6.11	23.5
Cadmium	-	6.1	-
Carbon tetrachloride	0.13	-	-
Chloroform	0.0061	0.081	0.0305
Chromium(VI)	-	41	-
DDT	0.34	-	0.486
1,1-Dichloroethene	0.58	1.16	0.60
Dieldrin	30	-	-
Heptachlor	3.4	-	-
Hexachloroethane	0.014	-	-
Methylene chloride	0.0075	0.014	0.0079
Nickel and compounds	-	1.19	-
Polychlorinated biphenyls (PCBs)	7.7	-	-
2,3,7,8-TCDD (dioxin)	1.56×10^{5}	1.50×10^{5}	3.00×10^{5}
Tetrachloroethene (PCE)	0.051	0.001-0.0033	-
Trichloroethene (TCE)	0.011	0.013	0.0733
Vinyl chloride	2.3	0.295	1.90

 Table 2.4
 Toxicity data for some selected potential carcinogens (www.epa.gov/iris [46])

EXAMPLE 2.2

When drinking water is disinfected with chlorine, an undesired byproduct, chloroform (CHCl₃), may be formed. Suppose a 70-kg person drinks 2 L of water every day for 70 years with a chloroform concentration of 0.10 mg L^{-1} (the drinking water standard).

- a) Find the upper-bound cancer risk for this individual.
- b) If a city with 500,000 people in it also drinks the same amount of this water, how many extra cancers per year would be expected? Assume the standard 70-year lifetime.
- c) Compare the extra cancers per year caused by chloroform in the drinking water with the expected number of cancer deaths from all causes. Given cancer death rate is 189 per 100,000 per year.

► Solution:

 a) In Table 2.4, the potency factor for chloroform (oral route) is 0.0061 (mg kg⁻¹ d⁻¹)⁻¹. Using (2.5), the chronic daily intake is

CDI (mg kg⁻¹ d⁻¹) =
$$\frac{(0.10 \text{ mg L}^{-1}) \times (2 \text{ L} \text{ d}^{-1})}{(70 \text{ kg})} = 0.00286 \text{ mg kg}^{-1} \text{ d}^{-1}$$

72 REGULATED CHEMICALS AND QUANTITATIVE RISK ASSESSMENT

From (2.4), the incremental lifetime cancer risk is

 $Risk = CDI \times PF = 0.00286 \times 0.0061 = 17.4 \times 10^{-6}$

So, over a 70-year period, the upper-bound estimate of the probability that a person will get cancer from this drinking water is about 17 in 1 million.

b) If there are 17.4 cancers per million people over a 70-year period, then in any given year in a population of 500,000, the number of cancers caused by chloroform would be

$$N = (500,000 \text{ people}) \times \frac{17.4 \text{ cancer}}{10^6 \text{ people}} \times \frac{1}{70 \text{ y}} = 0.12 \text{ cancers per year}$$

c) The total number of cancer deaths that would be expected in a city of 500,000 would be

$$N = (500,000 \text{ people}) \times \frac{189 \text{ cancer}}{10^5 \text{ people}} = 945 \text{ cancer deaths per year}$$

It would seem that an additional 0.12 new cancers per year would not be detectable.

EXAMPLE 2.3

Find the concentration of chloroform in drinking water that would result in a risk for a 70-kg person who drinks $2 L d^{-1}$ throughout his or her entire lifetime.

► Solution:

Use the potency factor (PF) from Table 2.4 gives

$$CDI = \frac{\text{Risk}}{\text{Potency factor}} = \frac{10^{-6}}{0.0061 (\text{mg kg}^{-1} \text{ d}^{-1})^{-1}} = 1.64 \times 10^{-4} \text{ mg kg}^{-1} \text{ d}^{-1}.$$

Since CDI is just the average daily intake divided by body mass, we can write

$$CDI = \frac{(C \text{ mg } L^{-1}) \times (2.0 \text{ L } d^{-1})}{(70 \text{ kg})} = 1.64 \times 10^{-4} \Rightarrow C \approx 0.0057 \text{ mg } L^{-1}$$

where C (mg L⁻¹) is the allowable concentration of chloroform. Thus, a drinking water with $\sim 6 \,\mu g \, L^{-1}$ for chloroform would result in an upper-bound risk of 10^{-6} .

The U.S. EPA has developed a set of recommended default values for daily intakes, exposures, and body weights to be used in risk calculations when more site-specific information is not available. Table 2.5 shows some of these default factors, and the next example illustrates their use.

Table	2.5 Example recommended exposure f	factors recommend	led for risk assessmen	ts [40].	
Landuse	Exposure Pathways	Daily intake	Exposure frequency $(d y^{-1})$	Exposure Duration (y)	W (kg)
Residential	Ingestion of potable water	2 L (adult) 1 L (child)	350	30	70 (adult) 15 (child
	Ingestion of soil and dust	200 mg (child) 100 mg (adult)	350	6 24	15 (child) 70 (adult)
	Inhalation of contaminant	$20 \text{ m}^3 \text{ (adult)}$ $12 \text{ m}^3 \text{ (adult)}$	350	30	70
Industrial & commercial	Ingestion of potable water	1L	250	25	70
	Ingestion of soil and dust	50 mg	250	25	70
	Inhalation of contaminant	20 m ³ (workdays)	250	25	70
Agricultural	Consumption of homegrown produce	42 g (fruit) 80 g (veg.)	350	30	70
Recreational	Consumption of locally caught fish	54 g	350	30	70

74 REGULATED CHEMICALS AND QUANTITATIVE RISK ASSESSMENT

Chronic daily intake (CDI):

In previous examples, it was assumed that everyone drinks contaminated water every day for 70 years. However, when a risk assessment is made for exposures that do not last the entire lifetime, we need to develop the chronic daily intake a little more carefully. In addition, if the intake routes are described in terms of eating or inhalation, the CDI calculation must be adjusted as follows.

Eating: CDI =
$$\frac{(C \operatorname{mg} \operatorname{kg}^{-1}) \times (\operatorname{Intake}, \operatorname{kg} \operatorname{d}^{-1}) \times (\operatorname{Exposure}, \operatorname{d})}{(W \operatorname{kg}) \times (70 \operatorname{y}) \times (365 \operatorname{d} \operatorname{y}^{-1})}$$

Drinking: CDI =
$$\frac{(C \operatorname{mg} \operatorname{L}^{-1}) \times (\operatorname{Intake}, \operatorname{L} \operatorname{d}^{-1}) \times (\operatorname{Exposure}, \operatorname{d})}{(W \operatorname{kg}) \times (70 \operatorname{y}) \times (365 \operatorname{d} \operatorname{y}^{-1})}$$

Inhalation: CDI =
$$\frac{(C \operatorname{mg} \operatorname{m}^{-3}) \times (\operatorname{Intake}, \operatorname{m}^{3} \operatorname{d}^{-1}) \times (\operatorname{Exposure}, \operatorname{d})}{(W \operatorname{kg}) \times (70 \operatorname{y}) \times (365 \operatorname{d} \operatorname{y}^{-1})}$$

(2.6)

EXAMPLE 2.4

Estimate the incremental cancer risk for a 60-kg worker exposed to a particular carcinogen under the following circumstances. Exposure time is 5 days per week, 50 weeks per year, over a 25-year period of time. The worker is assumed to breathe air of 20 m³ per day. The carcinogen has a potency factor of 0.02 (mg kg⁻¹ d⁻¹)⁻¹, and its average concentration is 0.05 mg m⁻³.

► Solution: For an inhalation exposure, the CDI can be calculated as

CDI =
$$\frac{(0.05 \text{ mg m}^{-3})(20 \text{ m}^3 \text{ d}^{-1})(5 \text{ d} \text{ wk}^{-1})(50 \text{ wk y}^{-1})(25 \text{ y})}{(60 \text{ kg})(70 \text{ y})(365 \text{ d} \text{ y}^{-1})}$$

= 0.0041 mg kg⁻¹ d⁻¹

Use a given potency factor of 0.02 (mg kg⁻¹ d⁻¹)⁻¹, an incremental risk can be calculated as

$$Risk = CDI \times PF = 0.0041 \times 0.02 = 81 \times 10^{-6}$$
,

which is much higher than acceptable risk of 10^{-6} .

EXAMPLE 2.5

Suppose an industrial facility that emits benzene into the atmosphere is being proposed for a site near a residential neighborhood. Air quality models predict that 60 percent of the time, prevailing winds will blow the benzene away from the neighborhood, but 40 percent of the time the benzene concentration will be 0.01 mg m^{-3} . Use standard

exposure factors from Table 2.5 to assess the incremental risk to adults in the neighborhood if the facility is allowed to be built. If the acceptable risk is 10^{-6} , should this plant be allowed to be built?

► Solution: From Table 2.5, the chronic daily intake can be determined as

CDI =
$$\frac{(0.01 \text{ mg m}^{-3})(20 \text{ m}^3 \text{ d}^{-1})(350 \text{ d} \text{ y}^{-1})(30 \text{ y})}{(70 \text{ kg})(70 \text{ y})(365 \text{ d} \text{ y}^{-1})} \times 0.40$$

= 0.00047 mg kg⁻¹ d⁻¹

The potency factor from Table 2.4 for benzene is 0.029 (mg kg⁻¹ d⁻¹)⁻¹, so the incremental risk is

$$Risk = CDI \times PF = 0.00047 \times 0.029 = 13 \times 10^{-6}$$

The risk is higher than the acceptable level, so the facility should not be built as it is being proposed.

2.2.3 Risk characterization

The risk characterization provides a summary of the risk assessment, estimating the incidence of the health effect in the target population. In other words, it is an estimation of the probability of occurrence and severity of known or potential adverse health effects in a population based on the preceding steps of hazard identification, hazard characterization, and exposure assessment. It comprises the results of the risk assessment in the form of risk estimates and risk descriptions and provides the best available science-based evidence to support food safety management. If requested by the risk manager, it may also provide information on a range of possible decisions for ensuring consumer safety.

The evaluation of risk characterization is based on a comparison of the results of the dose-response assessment for these agents with the outcome of the exposure assessment for these same agents in the situation of interest. For example, a risk characterization may address the risk from chemicals at a hazardous waste site to those living near the site. While a risk characterization can provide either qualitative or quantitative evaluations of risk, quantitative outcomes are generally most useful.

Although there are obvious advantages to presenting a simple, single number for extra cancers, or some other risk measure, a proper characterization of risk should be much more comprehensive. The final expressions of risk derived in this step will be used by regulatory decision makers in the process of weighing health risks against other societal costs and benefits. The public will also use these expressions to help them decide on the adequacy of proposed measures to manage the risks. Both groups need to appreciate the extraordinary leaps of faith that, by necessity, have had to be used to determine these simple quantitative estimates. It must always be emphasized that these estimates are preliminary, subject to change, and extremely uncertain.

Figure 2.5 shows aggregate of overall exposure distribution for a general population. If overall population is comprised of N subgroups: j = 1, N each with exposure probability density function $f_j(E)$, then the probability density function for the general population f(E) is simply the weighted mixture of the subgroup distributions:

$$f(E) = \int p \times f(E) dE \approx \sum_{j=1}^{N} p_j \times f_j(E)$$
(2.7)



Figure 2.5 Common descriptors for human exposures to environmental agents [38].

where p_i is the fraction of the population in subgroup *j*.

The same weighting procedure applies to the cumulative distribution function:

$$F(E) = \sum_{j=1}^{N} p_j \times F_j(E)$$
(2.8)

and the various statistical mth moments of the exposure distribution:

Expected value
$$[E^m] = \sum_{j=1}^N p_j \times \text{Expected value}[E_j^m]$$
 (2.9)

The resulting exposure distribution is characterized by the common descriptors in Figure 2.5 including measures of central tendency (median and mean) and measures of highend exposure, such as the 90th percentiles near the upper tail of the distribution.

The implications for dose, risk and the incidence are summarized in Figure 2.6. For non-carcinogenic risk where a reference dose is determined, the fraction of population with doses above the reference dose (RfD) is computed. Assuming that the distribution of dose is available, the fraction above the reference dose is

Fraction above
$$\operatorname{RfD} = 1 - F_{D_e}(\operatorname{RfD})$$
 (2.10)

where D_e is exposure (which is equivalent to CDI).

For carcinogenic effect, the exposure and dose distributions are converted to risk estimates and the overall distribution summarized as shown in Figure 2.6. The cancer incidence rate in the population is computed as the average value of the lifetime individual risk times the total number of population *P* divided by the lifetime exposure period (T = 70 y):

Incidence (cancers per year) =
$$\frac{P}{T} \times \int \operatorname{Risk}(x) \times f(x) dx$$
 (2.11)

where $x = D_e$ is an exposure. Assuming the linear, no-threshold dose-response relationship with potency factor, PF, the incidence is determined directly from the average dose $E[D_e]$:

Incidence (cancers per year) = PF ×
$$E[D_e] × \frac{P}{T}$$
. (2.12)

Similar calculations can be conducted for each subgroup to estimate the fraction above the reference dose (RfD) or the incidence of cancer within that subgroup.



Figure 2.6 Human exposure distributions for (A) a hypothetical systemic (non-cancer) toxicant and (B) a hypothetical carcinogen [38].

PROBLEMS

2.1 Consider a carcinogenic VOC with the doseresponse curve shown below. If 70-kg people breath 20 m³ d⁻¹ of air containing 10^{-3} mg m⁻³ of this VOC throughout their entire 70-year lifetime, find the cancer risk (you first need to find the potency).

2.2 Suppose a city's water supply has $0.2 \ \mu g \ L^{-1}$ of polychlorinated biphenyls (PCBs) in it. Using the PCB oral potency factor (Table 2.4) and the EPA recommended exposure factors given in Table 2.5,



- a) What would be the CDI?
- b) What would be the individual lifetime cancer risk for an adult residential consumer?
- c) In a city of 1 million people, use this risk assessment to estimate the number of extra cancers per year caused by the PCBs in the water supply.
- d) Assume the average cancer death rate in the United States is 193 per 100,000 per year. How many cancer deaths would be expected in a city of 1 million? Do you think the incremental cancers caused by PCBs in the drinking water would be detectable?

2.3 Suppose 30 out of 500 rats exposed to a potential carcinogen develop tumors. A control group of 300 rats not exposed to the carcinogen develops only 10 tumors. Based on these data, compute (a) the relative risk, (b) the attributable risk, and (c) the odds ratio. Do these indicators suggest that there might be a relationship between exposure and tumor risk?

2.4 Suppose 5 percent of individuals exposed to a chemical get a tumor, and 2 percent of those not exposed get the same kind of tumor. Find (a) the relative risk, (b) the attributable risk, and (c) the odds ratio.

2.5 Suppose a 70-kg individual drinks 2 L d⁻¹ of water containing 0.1 mg L⁻¹ of 1,1-dichloroethene for 20 years.

- a) Find the hazard quotient for this exposure.
- b) Find the cancer risk.
- c) If the individual drinks this water for 30 years instead of just 20, recompute the hazard quotient and the cancer risk.

2.6 Compute the drinking water equivalent level (DWEL) for methylene chloride based on a 10^{-6} risk for a lifetime consumption of 2 L of water per day for a 70-kg individual.

2.7 Based on a 10^{-6} risk for a 70-kg individual consuming 2 L of water per day, the DWEL for a contaminant is $10 \ \mu g \ L^{-1}$. What potency would produce this value?

2.8 You have just taken a job at a metal plating plant, and some of the metals you work with contain arsenic as an impurity. The heated metals give off arsenic vapors, which create an average concentration of arsenic of 0.00002 mg m^{-3} in the air in the workplace.

a) What is your increased risk of cancer if you continue to work in this job for your entire career?

- b) There are about 220,000 workers in metal casting plants similar to the one in which you work. How many worker deaths above the background cancer rate would be expected due to their occupation?
- c) Of the 220,000 workers in metal casting plants, how many would be expected to die of cancer?

2.9 One way to estimate maximum acceptable concentrations of toxicants in drinking water or air is to pick an acceptable lifetime risk and calculate the concentration that would give that risk assuming agreed-on exposures such as the residential factors given in Table 2.5. Find the acceptable concentrations of the following substances:

- a) Benzene in drinking water (mg L^{-1}), at a lifetime acceptable risk of 10^{-5} .
- b) Trichloroethene in air (mg m⁻³), at a lifetime acceptable risk of 10^{-6} .
- c) Benzene in air (mg m⁻³), at a lifetime acceptable risk of 10^{-5} .
- d) Vinyl chloride in drinking water (mg L^{-1}), at a lifetime acceptable risk of 10^{-4}

2.10 Using exposure factors in Table 2.5, what would be an acceptable concentration of trichloroethylene in the air of an industrial facility if worker risk is to be less than 10^{-4} ? Express the answer in mg m⁻³ and ppm.

2.11 For the following carcinogens, the Thailand's drinking water standards are given. For each, find the lifetime individual cancer risk and the incremental cancers per year in a population of 70 million as computed using a standard risk assessment based on residential exposure factors recommended in Table 2.5.

- a) Trichloroethene (TCE), 0.005 mg L^{-1} .
- b) Benzene, 0.005 mg L^{-1} .
- c) Arsenic, 0.01 mg L^{-1} .
- d) Carbon tetrachloride, 0.005 mg L^{-1} .
- e) Vinyl chloride, 0.002 mg L^{-1} .
- f) Polychlorinated biphenyls (PCBs), 0.0005 mg L^{-1} .

2.12 Suppose a 70-kg man is exposed to of tetrachloroethene in the air at his workplace. If he inhales 24 1 m⁴ d⁻¹, 8 hours per day, 5 days per week, 50 weeks per year, for 30 years, and if tetrachloroethene has an absorption factor of 90 percent and an inhalation potency of 0.002 (mg kg⁻¹ d⁻¹)⁻¹, what would be his lifetime cancer risk? What would the risk be to a 50-kg woman similarly exposed?

2.13 Trichloroethene (TCE) is a common groundwater contaminant. In terms of cancer risk, which would be better: (1) to drink unchlorinated groundwater with 10 ppb (0.010 mg L^{-1}) of TCE; or (2) to switch to a surface water supply that, as a result of chlorination, has a chloroform concentration of 50 ppb?

CHAPTER 3

ADVECTION, DIFFUSION AND DISPERSION PROCESSES

Environmental pollutants can be transported tens of thousands kilometers from their source of release or never migrate more than a few centimeters. The migration distance depends on the physical, chemical and biological characteristics such as partitioning or chemical reactivity as well as biodegradability of the contaminants and to the flow rates of the air, water or groundwater that carry them. This chapter describes the transport processes of pollutant in environmental media from source to receptor locations. Emphasis will be the mathematical treatment of transport in air, surface water and groundwater systems.

3.1 Pollutant source mechanisms

The knowledge of fate-and-transport of pollutant coupled with source mechanisms enable the prediction of spatial and temporal distribution of pollutants. This section introduces each of these components of an environmental model.

The source of contaminant discharge to the environment is typically characterized by a loading or emission rate, given as the mass of pollutant discharged to the environment per unit time. For many problems such as those involving industrial discharges in to the air or surface waters, direct emission rates are determined from monitoring data and given as an input to the fate-and-transport model. Pollutant source can be classified as *point source* and *nonpoint source* [21].

Point Source Pollution Point sources are identifiable source that release pollutants from discrete conveyances, such as a discharge pipe, and are regulated by federal and

Fate and Transport of Pollutants in Environment. By S. Saenton, Chiang Mai University state agencies. The main point source dischargers are factories and sewage treatment plants, which release treated wastewater.

Nonpoint Source Pollution Nonpoint source pollution is a combination of pollutants from a large area rather than from specific identifiable sources such as discharge pipes. Runoff is generally associated with nonpoint source pollution, as water is emptied into streams or rivers after accumulating contaminants from sources like gardens, crop fields or residential areas.

The spatial resolution of pollutant source also depends on the properties of the contaminant and the receiving environment. Emissions may be characterized as occurring from a *point, line, area* or a *volumetric* source as shown in Figure 3.1. Industrial smoke stacks, discharge pipes, and underground storage tanks are often characterize as point sources. Motor vehicle emissions from a highway, runoff to surface water, and dissolution from a broadly distributed spill are examples of distributed sources. If the area of environmental impacts is large relative to the dimensions of the source, distributed sources can be regarded as a single point source.

Source geometry is is often idealized to simplify the spatial modeling of pollutant transport from source to receptor. The arrows represent pollutant emissions. A smoke stack is a representative of a point source with emissions in a unit of mass per time. A highway with cars emitting pollutants might be viewed as a line source with an emission rate per unit length. In a regional-scale model, the consolidated emissions from an entire urban area might be viewed as an area source with emissions rate per unit area. Dissolution of non-aqueous phase liquids (NAPLs) from the spill zones in groundwater aquifer can be regarded as volumetric source with emissions rate per unit volume.

3.2 Transport mechanisms

Once a pollutant is released into an environmental medium, pollutant transport occurs through three mechanisms: *advection*, *diffusion* and *dispersion* which are common to surface water, groundwater, and air. Advection is the transport of contaminants to along with the flowing air or water. **Diffusion** refers to a mixing of contaminants that is driven by the concentration gradient and is usually viewed as occurring in two ways:

- *Molecular diffusion*: The molecular diffusion is a mixing of dissolved chemicals due to the random walk of molecules within the fluid. It is caused by kinetic energy of molecular vibrational, rotational and translational motion. This process corresponds to an increase in entropy where the dissolved substances move from zones of high concentration to low concentration according to Fick's law (which will be discuss later) [7].
- *Turbulent diffusion*: The turbulent (or eddy) diffusion is a mixing due to turbulent motion in the fluid which is a scale-dependent phenomenon. If fluid motions are considered at a sufficiently small scale, this process is recognized as advection [7]. The turbulent is always several orders of magnitude larger than the molecular diffusion.

Dispersion (or, more correctly, a shear dispersion) process is defined as mixing due to velocity gradient in the flowing fluid caused by shear forces. Figure 3.2 shows schematic representation of the transport processes.



Figure 3.1 Types of pollutant's source according to their geometry.

84 ADVECTION, DIFFUSION AND DISPERSION PROCESSES

Transport of chemicals in streams, rivers and air is predominantly controlled by advection whereas the transport in lakes, estuaries, soils and groundwater is often dispersion controlled [37]. Both turbulent diffusion and shear dispersion are often represented in environmental models as analogous to the molecular diffusion, that is, having mass fluxes that are proportional to the concentration gradient



Figure 3.2 Schematic diagram showing transport processes (modified from [37]).

The dimensionality of pollutant transport in environmental systems depends on whether complete mixing can be assumed across various dimensions of the system, as shown in Figure 3.3. The transport through natural systems is often represented using idealized reactor types from chemical engineering. The simplest of these reactors is the completely (or continuously) stirred tank reactor (CSTR) which is assumed to be well mixed across its entire volume (or across *x*-,*y*- and *z*-directions). As a result, the CSTR actually represents

a *zero*-dimensional transport system with only advection in and out but no concentration gradient within the tank.

The simplest model representing spatial variation in pollutant concentrations is the plugflow reactor (PFR), which represents the case of purely advective transport in one dimension with no dispersion. A PFR is often used for modeling chemicals transport in streams, rivers and air under high flow condition. If the dispersion process along the flow path is significant, a PFDR or plug-flow with dispersion reactor can be used. If no complete mixing is assumed in any direction, a normal advection-dispersion reactor (ADR) can be used Examples of environmental system that usually assume both advection and dispersion are groundwater aquifer or atmosphere (see Figure 3.3).



Figure 3.3 Transport from source to receptor can be simplified by assuming well-mixed in one or more dimensions.

Processes which move pollutants and other compounds through the air, surface water, or subsurface environment or through engineered systems (for example, treatment reactors) are of particular interest to environmental engineers and scientists. Pollutant transport acts to move pollutants from the location at which they are generated, resulting in impacts which can be distant from the pollution source. On the other hand some pollutants, such as sewage sludge, can be degraded in the environment if they are sufficiently dilute. For these pollutants, slow transport, slow dilution, can result in excessively high pollutant concentrations, with resulting increased adverse impacts.

In the following sections, we will discuss the processes which distribute pollutants in the environment. The goals of this discussion are twofold: to provide an understanding of the processes which cause pollutant transport, and to present and apply the mathematical formulas used to calculate pollutant fluxes.

3.2.1 Advection

Advective transport is a movement of mass entrained in a current and traveling from one point to another. For a chemical traveling in a flowing media (streams, rivers, ground-water, or air), advective transport flux J_a is a product of average flow rate and the mean concentration or,

$$J_a = \bar{u}C \qquad \text{or} \qquad \mathbf{J}_a = \bar{\mathbf{u}}C \quad ([=] \,\mathrm{ML}^{-2}\mathrm{T}^{-1}) \tag{3.1}$$

where $\bar{u} = Q/A$ is a total volumetric flow rate (L³T⁻¹) divided by the cross-sectional area. Under steady-state flow condition $(dQ/dt = 0 = d\bar{u}/dt)$ and steady-state with respect to chemical concentration (dC/dt = 0), mass discharge rate is constant with respect to time. If either the flow rate or the concentration becomes time-dependent, then mass discharge rate is time-dependent. Consider a stream shown in Figure 3.4, *total* mass inside a control volume at any instance may be written as a volume times concentration $(V \times C)$ where $V = A \times \Delta x$. The change in mass with respect to time due to advection may be written using mass balance equation (with no chemical reaction) as follows.

$$\dot{m}_{acc} = \dot{m}_{in} - \dot{m}_{out}$$

$$\frac{d}{dt}(VC) = QC_x - QC_{x+\Delta x}$$

$$V\frac{dC}{dt} = -Q(C_{x+\Delta x} - C_x)$$

$$A\Delta x\frac{dC}{dt} = -\bar{u}A(C_{x+\Delta x} - C_x)$$

$$\frac{dC}{dt} = -\bar{u}\left(\frac{C_{x+\Delta x} - C_x}{\Delta x}\right)$$

Take a limit of $\Delta x \rightarrow 0$, the above difference equation becomes a partial differential equation for advective transport in one-dimension.

$$\frac{\partial C}{\partial t} = -\bar{u}\frac{\partial C}{\partial x},\tag{3.2}$$

where C = C(x,t). The right-hand-side term of (3.2) is valid under an assumption of *steady* flow condition such that $\bar{u} = Q/A$ is a constant mean velocity of the flowing media (e.g., river, groundwater, air). The negative sign in (3.2) is necessary to reflect an increasing concentration within the control volume if mass inflow is greater than mass outflow. It should be noted that, in Figure 3.4, a negative slope or concentration gradient dC/dx produces a positive change in concentration with respect to time dC/dt. Thus, the negative slope of concentration gradient into a positive mass flux in the control volume.

Equation (3.2) is a mathematical description of advection when flowrate and/or concentration are changing. It is a time-variable equation as opposed to the steady-state equation of mass flux shown in (3.1). Under time variable conditions, it is sometimes necessary to estimate the total mass that has passed a point in a given time between t_1 and t_2 . This can be calculated by integrating mass discharge rate with respect to time:

$$M = \int_{t_1}^{t_2} Q(t) \cdot C(t) dt$$


Figure 3.4 Advective transport process from point at *x* to at $x + \Delta x$. Chemicals are entrained in a fluid at a mean velocity \bar{u} . A hypothetical concentration gradient is shown below as concentration versus distance. Note that the slope of the line dC/dx is negative when the mass is transported from point *x* to $x + \Delta x$ into the volume $V = A \times \Delta x$.

where *M* is the total mass passing a certain point during t_1 to t_2 . If steady flow condition prevails, *Q* is constant with time, the above expression can be reduced to

$$M = Q \int_{t_1}^{t_2} C(t) dt$$

If the change in concentration with respect to time can be described by a mathematical equation, it may be possible to integrate the above equation directly. The process is analogous to estimation of the area under the curve of concentration vs. time plot and multiplying by the flow rate to obtain total mass.

EXAMPLE 3.1 Advective mass flow rate of a chemical in a river

Calculate the total mass flow rate in kg d⁻¹ of a pesticide atrazine passing a point in a river draining a large agricultural basin. The mean concentration of pesticide is 1.0 μ g L⁻¹ and stream flow rate is 50 m³ s⁻¹.

► Solution:

Total mass flow rate =
$$Q \times C = (50 \text{ m}^3 \text{ s}^{-1}) (1.0 \ \mu \text{g L}^{-1})$$

With necessary unit conversion, the total atrazine mass flow rate is 4.3 kg d^{-1} .

EXAMPLE 3.2 Advective mass flux in a river

If alachlor concentration in a river is 20 mg L⁻¹ and the average river velocity is 100 cm s⁻¹, what is the average mass flux J_a in the downstream direction?

► Solution:

$$J_a = \bar{u}C = (100 \text{ cm s}^{-1}) (20 \text{ mg L}^{-1})$$

With necessary unit conversion, the mass flux is $J_a = 2.0 \text{ mg cm}^{-2} \text{ s}^{-1}$.

88 ADVECTION, DIFFUSION AND DISPERSION PROCESSES

EXAMPLE 3.3 Phosphorous loading flux

Calculate the average mass flux J_a of phosphorus downstream of the sewage pipe. Given a cross-sectional area of the river of 30 m², the flow rate of river is 25 m³ s⁻¹, and [PO₄³⁻] is 0.2 mg L⁻¹.

▶ Solution: From the above information, average river velocity is $\bar{u} = Q/A = 0.83$ m s⁻¹. Then, phosphorous mass flux downstream of a sewage pipe is

$$J_a = \bar{u}C = (0.83 \text{ m s}^{-1})(0.20 \text{ mg L}^{-1}) = 0.17 \text{ g m}^2 \text{s}^{-1}.$$

EXAMPLE 3.4 Advective mass flux in groundwater aquifer

Dissolved nitrate (NO₃⁻) of concentration 18 mg L⁻¹ is being advected with flowing groundwater at an average seepage velocity (or groundwater velocity; Darcy velocity; or specific discharge) of 0.331 m d⁻¹. Groundwater from the aquifer discharges into a stream. What is the mass flux of nitrate into the stream if the aquifer is 1.80 m thick and 123 m wide where it discharges into the stream?

► Solution: From equation (3.1), advective mass flux can be calculated as

$$J_a = \bar{u}C = (0.331 \text{ m}^3 \text{ d}^{-1}) (18 \text{ mg } \text{L}^{-1})$$

With necessary unit conversion, the mass flux is $J_a = 1.34$ g m⁻² d⁻¹ and the total nitrate flux into the stream is one dimensional mass flux times cross-sectional area where the aquifer discharges into the stream and,

Total nitrate flux =
$$J_a \times A = (1.34 \text{ g m}^{-2} \text{ d}^{-1}) (123 \times 1.80 \text{ m}^2) = 297 \text{ g d}^{-1}$$

3.2.2 Diffusion

Diffusion results from random motions of two types: the random motion of molecules in a fluid, and the random eddies which arise in turbulent flow. Diffusion from the random molecular motion is termed *molecular diffusion* whereas diffusion which results from turbulent eddies is called *turbulent or eddy diffusion*. The molecular diffusion is generally a dominant process under *no flow* or low flow condition. Under a flowing media, molecular diffusion is negligible and another process, eddy diffusion (or dispersion) becomes more significant. In this section, we will discuss about the molecular diffusion and the dispersion or eddy diffusion will be illustrated later.

Molecular diffusion is a mass movement as a result of translational, vibrational, and rotational movement of molecules [8]. Fick proposed a mass transfer process by diffusion where diffusive mass flux is proportional to the concentration gradient called *Fick's first law* for *steady-state* diffusion:

$$J_d = -D \frac{dC}{dx}$$
 or $\mathbf{J}_d = -\mathbf{D} \nabla C \quad (\mathbf{M} \mathbf{L}^{-2} \mathbf{T}^{-1})$ (3.3)

where J_d or \mathbf{J}_d are diffusive mass flux, dC/dx or ∇C are concentration gradient (ML⁻⁴), and D or \mathbf{D} are molecular diffusion coefficient (L²T⁻¹).

The negative sign on the right-hand-side of the above equation is necessary to convert a negative concentration gradient in to a positive mass flux according to mathematical convention. The molecular diffusion coefficient is a fundamental property of a chemical and a solvent (or medium) and they are tabulated for a number of chemicals in *Handbook of Chemistry and Physics* [20] which were determined either from experiments or thermodynamics calculation. In water, most chemicals have diffusion coefficients in the order of 10^{-5} cm²s⁻¹ indicating a slow movement of mass. Examples of molecular diffusion coefficients in water and air are listed in Tables 3.1 and 3.2. Molecular diffusion occurs in nature as chemical transport through thin, laminar boundary layers, such as air-water, sediment-water or particle-water interfaces, or in sediment pore waters.

Species	$D (\mathrm{cm}^2 \mathrm{s}^{-1})$	Species	$D (\mathrm{cm}^2 \mathrm{s}^{-1})$
H ⁺	$9.31 imes 10^{-5}$	OH-	$5.27 imes10^{-5}$
Na ⁺	1.33×10^{-5}	F^-	1.46×10^{-5}
K ⁺	1.96×10^{-5}	Cl-	$2.03 imes 10^{-5}$
Rb ⁺	2.06×10^{-5}	Br ⁻	2.01×10^{-5}
Cs ⁺	2.07×10^{-5}	HS ⁻	1.73×10^{-5}
Mg ²⁺	0.71×10^{-5}	HCO ₃ ⁻	1.18×10^{-5}
Ca ²⁺	0.79×10^{-5}	SO_4^{2-}	1.07×10^{-5}
Sr ²⁺	0.79×10^{-5}	CO_{3}^{2-}	0.96×10^{-5}
Ba ²⁺	0.85×10^{-5}	Tetrachloroethene	0.75×10^{-5}
Mn ²⁺	0.69×10^{-5}	Trichloroethene	$0.83 imes 10^{-5}$
Fe ²⁺	$0.72 imes 10^{-5}$	Benzene	$0.90 imes 10^{-5}$
Cr ³⁺	0.59×10^{-5}	Toluene	$0.80 imes 10^{-5}$
Fe ³⁺	$0.61 imes 10^{-5}$	Ethylbenzene	$0.72 imes 10^{-5}$

Table 3.1Examples of diffusion coefficients of some chemicals in water at 25 °C [20].

Table 3.2 Examples of diffusion coefficients of some chemicals in air at 25 °C [20].

Species	$D (\mathrm{cm}^2 \mathrm{s}^{-1})$
H ₂ O	0.282
O ₂	0.176
CO ₂	0.151
SF ₆	0.15
CH ₄	0.21
Ethane	0.15
Ethene	0.16
Benzene	0.09
Toluene	0.08
Formaldehyde	8.92

90 ADVECTION. DIFFUSION AND DISPERSION PROCESSES

EXAMPLE 3.5 Diffusion of a pollutant from a water body to lake sediment

Calculate diffusive benzene (C_6H_6) mass flux from a water body in a lake with aqueous concentration of 18 mg L^{-1} into the clean sediment. Assume the diffusion occurs through a static thin film of water of $\delta = 0.2$ m.

► Solution: From a given information, by assuming a linear concentration profile of benzene as shown in the picture, the concentration gradient can be calculated as

$$\frac{dC}{dz} = \frac{18 - 0}{0.2 - 0} = 90 \frac{\text{mg L}^{-1}}{\text{m}} = 90 \times 10^3 \frac{\text{mg}}{\text{m}^4}.$$

Using a diffusion coefficient of benzene given in Table 3.1, the diffusive mass flux of benzene transport from water body to the sediment is

$$J_d = -D\frac{dC}{dz} = -\left(0.9 \times 10^{-5} \ \frac{\mathrm{cm}^2}{\mathrm{s}}\right) \left(90 \times 10^3 \ \frac{\mathrm{mg}}{\mathrm{m}^4}\right) = -8.1 \times 10^{-5} \ \frac{\mathrm{mg}}{\mathrm{m}^2 \mathrm{s}}.$$

The diffusive mass flux is negative indicating that the mass transport is in the negative z direction (i.e., diffusing into the sediment).

EXAMPLE 3.6 Molecular diffusion through a thin film

The molecular diffusion coefficient of caffeine (C₉H₈O) in water is 0.63×10^{-5} cm²s⁻¹. For a 1.0 mg L^{-1} solution, calculate the total mass flux in mg s⁻¹ through an intestinal membrane (0.1 m² area) with a liquid film approximately 60 μ m thick. How long would it take for 1.0 mg of caffeine to move through 0.1 m² of intestine, assuming the above flux rate?

► Solution: Assuming zero caffeine concentration inside intestine, the total mass flux $(J_d \times A)$ is

$$J_d \times A = -DA \frac{dC}{dx} \approx -\left(0.63 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}\right) (0.1 \text{ m}^2) \left[\frac{(0-1.0) \text{ mg L}^{-1}}{60 \,\mu\text{m}}\right]$$

= 1.05 × 10⁻³ mg s⁻¹

Therefore, time required for 1.0 mg of caffeine to move through intestine membrane is

$$t = {1.0 \text{ mg} \over 1.05 \times 10^{-3} \text{ mg s}^{-1}} = 15.9 \text{ min.}$$





EXAMPLE 3.7 Gasoline-contaminated aquifer [22]

Gasoline-contaminated aquifer has been transported under a residential area nearby a gasoline station. Two meters beneath the 100-m² dirt floor of the residential basement, the concentration of hydrocarbon vapor in soil gas is 25 ppm_w. Estimate mass flux of gasoline vapor and the daily rate of vapor inflow transported into the basement by molecular diffusion. Assume the average diffusion coefficient of gasoline vapor in soil is 10^{-2} cm²s⁻¹. Also, assume that the basement is well ventilate, so that the gasoline vapor concentration in the basement is much less than 25 ppm_w. Given air density of 1.2 g L⁻¹ at 1 atm and 20 °C.



► Solution: In the calculation of a mass balance or mass flux, a concentration must be in mass/volume. Given a concentration of gasoline of 25 ppm_w and air density of 1.2 g L^{-1} , a concentration can be converted as

$$C = 25 \text{ ppm}_{w} = \frac{25 \text{ g of gasoline}}{10^{6} \text{ g of air}} \times \frac{1.2 \text{ g of air}}{1000 \text{ cm}^{3} \text{ of air}} = 3 \times 10^{-8} \text{ g cm}^{-3}.$$

The concentration gradient dC/dz can be approximated from

$$\frac{dC}{dz} \approx \frac{(3 \times 10^{-8} - 0) \text{ g cm}^{-3}}{(-200 - 0) \text{ cm}} = -1.5 \times 10^{-10} \text{ g cm}^{-4}.$$

Then, diffusive mass flux of vapor is

$$J_d = -D\frac{dC}{dz} = -(10^{-2} \text{ cm}^2 \text{s}^{-1})(-1.5 \times 10^{-10} \text{ g cm}^{-4})$$

= +1.5 × 10⁻¹² g cm⁻²s⁻¹.

The positive flux means that gasoline vapor is transported upward. And the daily rate of gasoline vapor into the house is

Daily gasoline vapor flow = $(1.5 \times 10^{-12} \text{ g cm}^{-2} \text{s}^{-1})(100 \text{ m}^2) = 0.13 \text{ g d}^{-1}$.

This flux should not be a cause of flammability but it may pose health threat since most gasoline constituents are carcinogenic compounds.

92 ADVECTION, DIFFUSION AND DISPERSION PROCESSES

Fick's second law of diffusion While Fick's first law describes the diffusion of a chemical under steady-state condition, the Fick's second law of diffusion is a treatment of transient or time-dependent diffusion. It is actually a continuation of of the first law. We will derive Fick's second law using 1-D domain as for illustration. Then, a generalized 3-D diffusion equation would follow the same principle.

Consider a control volume of any one-dimensional (non-flowing or slow flowing) environmental media as shown below, a mass balance of a non-reactive chemical due to diffusion over such control volume $V = A \times \Delta x$ is



$$\begin{split} \dot{m}_{acc} &= \dot{m}_{in} - \dot{m}_{out} \\ \frac{d}{dt} (VC) &= J_d(x) \times A - J_d(x + \Delta x) \times A \\ V \frac{dC}{dt} &= A \Delta x \frac{dC}{dt} &= -A \left(J_d(x + \Delta x) - J_d(x) \right) \\ \frac{dC}{dt} &= -\left(\frac{J_d(x + \Delta x) - J_d(x)}{\Delta x} \right) \end{split}$$

Take limit $\Delta x \rightarrow 0$, the difference equation follow the definition of derivative as follows.

$$\lim_{\Delta x \to 0} \frac{J_d(x + \Delta x) - J_d(x)}{\Delta x} = \frac{dJ_d}{dx}$$

Then, the mass balance equation becomes

$$\frac{\partial C}{\partial t} = -\frac{\partial J_d}{\partial x}.$$

Substitute $J_d = -DdC/dx$ from Fick's first law of diffusion into the above expression, the Fick's second law of diffusion in one-dimension for non-reactive (non-decay) chemical can be derived as follows.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2}$$

A more generalized Fick's second law for diffusion in 3-D domain can be seen in the following box. Fick's second law of diffusion is an example of partial differential equation (PDE) whose solutions depend on the initial condition (IC) and boundary conditions (BC). Due to the complexity of the boundaries, the above partial differential equation is generally approximated by using numerical method such as finite-difference technique, the easiest method to understand, which will be discussed later in this chapter. Examples of analytical solutions (closed-form solutions) for the above diffusion PDE are shown in Table 3.3.

Fick's firs law (steady-state diffusion):

Fick's law of diffusion:

$$J_d = -D\frac{dC}{dx}; \qquad \mathbf{J}_d = \mathbf{\bar{u}}C$$

Fick's second law (transient diffusion):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}; \qquad \frac{\partial C}{\partial t} = \nabla \cdot (\mathbf{D} \nabla C)$$
(3.4)

where **D** is the diffusion coefficient tensor in principal directions; J_d is a mass flux in 3-D and ∇C is a concentration gradient vector in 3-D.

D =	$\begin{bmatrix} D_x \\ 0 \end{bmatrix}$	0 D_y	0 0	;	$\mathbf{J}_{d} = \left\{ egin{matrix} J_{d,x} \ J_{d,y} \ \end{pmatrix} ;$	and	$\nabla C = \begin{cases} \frac{\partial C}{\partial x} \\ \frac{\partial C}{\partial y} \end{cases}$
	0	0	D_z		$J_{d,z}$		$\left(\frac{\partial C}{\partial x}\right)$

EXAMPLE 3.8 Pollutant diffusion in groundwater aquifer

A long trench was dug in an initially clean and shallow aquifer. The trench fully penetrated the and received a dump of non-degradable and non-sorptive pollutant which generated a constant aqueous concentration of pollutant of $C_0 = 100 \text{ mg L}^{-1}$. Assuming effective diffusion coefficient of a pollutant in groundwater of $10^{-5} \text{ cm}^2 \text{s}^{-1}$, predict the concentration of contaminant at either side of the trench.



► Solution: Based on a given information, this problem can be simplified to a semiinfinite 1-D problem where the pollutant source has a constant concentration $C_0 = 100$ mg L⁻¹ in the trench. The diffusion occurs both sides of the trench. The solution to 1-D, transient diffusion (Fick's second law) is given in Table 3.3 as:

$$C(x,t) = C_0 \left[1 - \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right) \right].$$

	Table 3.3 Example analy	tical solutions to transient	t diffusion (Fick's second law) [8].
Domain	Source	IC & BC	Solution
1-D Infinite $(-\infty, +\infty)$	Instantaneous input, M (ML ⁻²)	c(x,t=0)=0	$C(x,t) = \frac{M}{\sqrt{4\pi Dt}} \times \exp\left(-\frac{x^2}{4Dt}\right)$
	at $x = 0$	$M = \int C dx$ $c(x \to \pm \infty, t) = 0$	· ·
1-D Semi-infinite $[0, +\infty)$	Constant concentration (ML ⁻³)	C(x,t=0)=0	$C(x,t) = C_0 \left[1 - \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right) \right]$
	at $x = 0$	$C(x=0,t) = C_0$	where $\operatorname{erf}(\xi) = \frac{2}{\sqrt{\pi}} \int_0^{\xi} e^{-t^2} dt$
		$C(x = +\infty, t) = 0$	
1-D Semi-infinite $[0, +\infty)$	Constant mass flux $(ML^{-2}T^{-1})$	C(x,t=0)=0	$C(x,t) = 2J_0 \sqrt{\frac{t}{\pi D}} \times \exp\left(-\frac{x}{\sqrt{4Dt}}\right) - \frac{J_0 x}{D} \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right)$
	at $x = 0$	$egin{aligned} -D & rac{\partial C}{\partial x} \\ \hline C(x ightarrow +\infty, t) = 0 \end{aligned}$	where $\operatorname{erfc}(\xi) = 1 - \operatorname{erf}(\xi)$
2-D Infinite	Instantaneous input, M (ML ⁻¹)	C(x,t=0)=0	$C(x, y, t) = \frac{M}{4\pi t \sqrt{D_v D_v}} \times \exp\left(-\frac{x^2}{4D_v t} - \frac{y^2}{4D_v t}\right)$
	at $(x, y) = (0, 0)$	$M = \iint Cdxdy$ $C(x, y \to \pm \infty, t) = 0$	
3-D Infinite	Instantaneous input, M (M)	C(x,t=0)=0	$C(x, y, z, t) = \frac{M}{8(\pi t)^{3/2} \sqrt{D_t D_t D_t}} \times \exp\left(-\frac{x^2}{4D_x t} - \frac{y^2}{4D_y t} - \frac{z^2}{4D_y t}\right)$
	at $(x, y, z) = (0, 0, 0)$	$M = \iiint Cdxdyxz$ $C(x, y, z \to \pm \infty, t) = 0$	

Using the Error function, $\operatorname{erf}(\xi)$, given in Table 3.4 or a command "=erf(...)" in Microsoft Excel, to calculate for concentration at a distance x and time t. The concentration profile is shown as follows.



This example shows that diffusion, as a transport process, is extremely slow. In fact, mass is typically transported at a much faster rate than molecular diffusion due to the flowing media (advection), eddy diffusion and a shear dispersion which will be discussed in the next section.

	Table 3.4	Error and con	nplementary eri	for function	ns.
ξ	$\operatorname{erf}(\xi)$	$erfc(\xi)$	ξ	$erf(\xi)$	$erfc(\xi)$
0	0	1	1.6	0.9763	0.0237
0.1	0.1125	0.8875	1.7	0.9838	0.0162
0.2	0.2227	0.7773	1.8	0.9891	0.0109
0.3	0.3286	0.6714	1.9	0.9928	0.0072
0.4	0.4284	0.5716	2.0	0.9953	0.0047
0.5	0.5205	0.4795	2.1	0.9970	0.0030
0.6	0.6039	0.3961	2.2	0.9981	0.0019
0.7	0.6778	0.3222	2.3	0.9989	0.0011
0.8	0.7421	0.2579	2.4	0.9993	6.885E-04
0.9	0.7969	0.2031	2.5	0.9996	4.070E-04
1.0	0.8427	0.1573	2.6	0.9998	2.360E-04
1.1	0.8802	0.1198	2.7	0.9999	1.343E-04
1.2	0.9103	0.0897	2.8	0.9999	7.501E-05
1.3	0.9340	0.0660	2.9	1.0000	4.110E-05
1.4	0.9523	0.0477	3.0	1.0000	2.209E-05
1.5	0.9661	0.0339	4.0	1	0
$erf(\xi)$	$=rac{2}{\sqrt{\pi}}\int_{0}^{\xi}e^{-t^2}$	$dt;$ erfc(ξ)	$= 1 - \operatorname{erf}(\xi);$	$erf(-\xi)$	$=-\mathrm{erf}(\xi)$

 Table 3.4
 Error and complementary error functions

3.2.3 Dispersion

Dispersive mass transfer refers to a spreading of mass from highly concentrated areas to less concentrated areas. The dispersive mass flux is analogous to diffusion, and it can also be described using Fick's first law:

$$J_E = -E\frac{dC}{dx} \quad \text{or} \quad \mathbf{J}_E = -\mathbf{E}\nabla C \quad ([=] \,\mathrm{ML}^{-2}\mathrm{T}^{-1}) \tag{3.5}$$

where *E* and **E** are the dispersion coefficient and dispersion coefficient tensor (L^2T^{-1}), respectively, and dC/dx is the concentration gradient.

Dispersion can be differentiated from diffusion in that it is caused by non-ideal flow patterns (i.e. deviations from plug flow) and is a macroscopic phenomenon, whereas diffusion is caused by random molecular motions (i.e. Brownian motion) and is a microscopic phenomenon. Dispersion is often more significant than diffusion in convection-diffusion problems [7].

As stated earlier, the turbulent or eddy diffusion and shear dispersion are important modes for mass transport in both surface water and air (see Figure 3.2). In subsurface environment, groundwater flow normally lacks the eddy effect that characterizes surface water and air movements because typical groundwater velocities are so much lower. Nevertheless, groundwater must take a tortuous flow path (i.e., detour) as it moves from one point to another, travelling over, under and around soil particles as shown in Figure 3.5. These random detours cause mixing thus the net transport of a chemical from regions of higher concentration to regions of lower concentration. Despite the different physical mechanism causing the mixing, the net mass transport is entirely analogous to turbulent diffusion. Dispersion also occurs at a much larger scale than that of soil particle size; for example, groundwater may detour around regions of relatively less permeable soil that are many cubic meters in volume. At this scale, the process is called *macrodispersion*.



Figure 3.5 Macrodispersion in groundwater caused by mixing and detouring.

Longitudinal dispersion coefficient in rivers Typically the value of longitudinal dispersion coefficient (E_L) in river can be found using conservative tracer experiment. However, if the tracer test is not available or not possible to conduct, longitudinal can be approximated using channel geometry and flow rate. The empirical equation for estimating longitudinal dispersion coefficient, proposed by [15], takes the form

$$E_L = \frac{0.011 \cdot \bar{u} \cdot w^2}{u_* \cdot d} \tag{3.6}$$

where \bar{u} is average stream flow rate (LT⁻¹), w is average channel width (L), d is average stream's depth (L), and u_* is *shear velocity* (LT⁻¹) and is defined as follows.

$$u_* = \sqrt{g \cdot d \cdot S},$$

where g is acceleration due to gravity and S is a dimensionless channel slope. It should be noted that for smaller streams, the value of d should be replaced by a hydraulic radius R_h where

$$R_h = \frac{\text{Stream's cross-sectional area}}{\text{Wetted perimeter}}.$$

Typical values of longitudinal dispersion coefficient is in the range of 0.05-0.3 $m^2 s^{-1}$ for small streams and can be greater than 1000 $m^2 s^{-1}$ for large rivers. Box, shown below, illustrates a transport of a chemical in a stream where dispersion (mixing) occurs while being advected downstream.

Tracer test for determining E_L [22]

A conservative tracer of mass per unit area M (ML⁻²) is instantly released into a river (i.e., pulse injection) with average flow rate of \bar{u} at point x = 0 (time t = 0). While the tracer mass is being advected downstream, it undergoes mixing or spreading by dispersion resulting in a tracer plume downstream. At times $t_3 > t_2 > t_1 > 0$, the plume becomes larger as tracer is dispersed more and more (see below).



The spreading of tracer plume at any time *t* can be modeled using a 1-D advectiondispersion equation which gives Gaussian distribution behavior as described by:

$$C(x,t) = \frac{M}{\sqrt{4\pi E_L t}} \exp\left[-\frac{(x-\bar{u}t)^2}{4E_L t}\right]$$

The value of longitudinal dispersion coefficient can be calculated from temporal moment analysis as

$$E_L = \frac{\sigma^2}{2t}$$

where σ is the spatial standard deviation of the tracer concentration distribution and *t* is the time since pulse injection of tracer. The value of σ will increase with time (more mixing) causing the maximum concentration to decrease with time.

$$C_{\max} = \frac{M}{\sqrt{4\pi E_L t}}$$

The above hypothetical expression assumes the contaminant is instantly released into the flowing river and it is distributed uniformly across the river which is not necessarily true. The mixing length, L, required for transverse dispersion to evenly distribute the chemical across the stream can be approximated by

$$L = \frac{w^2 \cdot i}{2E_L}$$

1

where w is the channel width.

EXAMPLE 3.9 Determination of river's *E_L* from a tracer test

If the t_2 concentration profile in the picture shown in the box (above) was measured 6 h after the tracer release. What is the average stream velocity if the maximum concentration occurs at $L_2 = 1000$ m. Estimate the longitudinal dispersion coefficient for this stream if the standard deviation of the longitudinal plume is $\sigma_L = 360$ m when the plume travels to $L_3 = 2000$ m. What would be the actual mixing length if the average channel width w = 100 m?

► Solution: The average velocity of the stream is $\bar{u} = \frac{L_2}{t_2} = \frac{1000 \text{ m}}{6 \text{ h}} = 166.7 \text{ m h}^{-1}$. At $L_3 = 2000 \text{ m}$, stream travel time is $t_3 = \frac{L_3}{\bar{u}} = \frac{2000}{166.7} = 12 \text{ h}$. Thus, the value of longitudinal dispersion coefficient of the stream is

$$E_L = \frac{\sigma_L^2}{2t} = \frac{360^2}{2 \times 12} = 5400 \text{ m}^2 \text{ h}^{-1}$$

The mixing length is

$$L = \frac{w^2 \cdot \bar{u}}{2E_L} = \frac{100^2 \times 166.7}{2 \times 5400} = 154 \text{ m},$$

which is reasonable for this problem since the tracer is well mixed and becomes uniformly distributed at a distance of 154 m downstream of the release point. **Transverse dispersion coefficient in rivers** Transverse dispersion causes a mixing across the river or stream. The distinction between longitudinal and transverse (or lateral) mixing is that transverse mixing occurs only by turbulence whereas the longitudinal mixing is caused in part by turbulence but is usually dominated by dispersion. This means, there is no advection in the transverse direction of the river.

Elder [11] proposed an empirical expression for predicting the lateral or transverse dispersion coefficient as

$$E_T = \boldsymbol{\varphi} \cdot \boldsymbol{d} \cdot \boldsymbol{u}_*, \tag{3.7}$$

where *d* is the depth of the river at the location of interest, u_* refers to shear velocity, and φ is an empirical parameter whose typical range is 0.17-0.22. The commonly used value of φ is 0.3 for natural streams and canal.

Vertical dispersion coefficient in rivers There are not many studies that have been done on the determination of vertical dispersion coefficient of the river. Jobson and Sayre [25] conducted a tracer experiment and proposed an empirical expression for vertical dispersion coefficient at any depth z of a river as

$$E_V(z) = 0.4z \left(1 - \frac{z}{d}\right) u_*,$$
 (3.8)

where d is a depth of the river at a location of interest.

Vertical dispersion in lakes Vertical mixing in lakes is not actually the same mechanism(s) that occur in river mixing. The term *eddy diffusivity* is often used to describe the turbulent dispersion coefficient in lakes. The chemical and thermal stratification in lake typically limits the vertical mixing in lake, and the eddy diffusivity is usually observed to be minimum in the thermocline part of the lake.

Vertical dispersion is a function of depth and geometry of the lake, wind direction, solar insulation, light penetration and many other factors. There is very little study on the development of an empirical equation for predicting eddy diffusivity in lake. Most methods required advanced numerical modeling technique. Nevertheless, several studies found that the vertical dispersion coefficient (E_V) or eddy diffusivity of the lakes are in the range of $E_V = 0.01 - 10 \text{ cm}^2 \text{s}^{-1}$ [37].

Dispersion in groundwater The process of dispersion in groundwater transport is physically different from both turbulent and molecular diffusion, although it is treated mathematically in most models as analogous to molecular diffusion. As water encounter heterogeneities in in the subsurface, channeling, entrapment, and bypassing occur (see Figure 3.5), all of which together contribute to what is termed *mechanical dispersion*. As a consequence of mechanical dispersion, some water parcels move faster and some slower than the average groundwater velocity, and parcels carrying various amounts of a contaminant appear to be mixed together.

Mechanical dispersion cannot be separated from effective molecular diffusion ($D_{\text{molecular}}$) in the pore water and, hence, the two processes are combined to yield *hydrodynamic dispersion coefficient*, E_i (L^2T^{-1}) where *j* denotes the dispersion in the *j* direction.

$$E_j = E_{\text{mechanical}} + D_{\text{molecular}}$$

The mechanical dispersion coefficient depends on the characteristics of the flow and subsurface heterogeneity. Therefore, the value of hydrodynamic dispersion coefficient in

100 ADVECTION, DIFFUSION AND DISPERSION PROCESSES

the longitudinal direction may differ dramatically from the transverse and vertical dispersion coefficients depending on geologic and hydrogeologic conditions. Based on field observations, mechanical dispersion coefficients are often modelled as proportional to average linear pore velocity (\bar{v}) of groundwater. Faster flow rate would cause more dispersion to take place. The hydrodynamic dispersion coefficient in the direction *j* or E_j can be expressed as

$$E_j = \alpha_j \bar{v} + D, \tag{3.9}$$

where α_j is called dispersivity (L) in the *j* direction, *D* is molecular diffusion coefficient in porous media and \bar{v} is the average linear pore velocity of groundwater. In small scale such as in laboratory, the dispersivity is small and constant whereas, in the field, dispersivity is not constant and is a scale-dependent parameter [10, 13] and can be evaluated from the moment analysis of field tracer test data or by fitting the analytical solution to tracer test data from laboratory/field tests.

Single-well tracer test [18]:

A single-well tracer test for determination of longitudinal dispersivity of an aquifer (α_L) involves an injection of a tracer solution and pumping back of groundwater. The pumped groundwater is monitored for tracer concentration as a function of time (or a function of cumulative volume of water pumped out of the aquifer at various times). This method is sometimes called *push-and-pull* tracer test. The relative concentration of the water being withdrawn from the injection well is given as

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left[\frac{\left(\frac{U_p}{U_i}\right) - 1}{\sqrt{\frac{16}{3} \frac{\alpha_L}{R_f} \left(2 - \sqrt{1 - \frac{U_p}{U_i}}\right) \left(1 - \frac{U_p}{U_i}\right)}} \right]$$
(3.10)

where

 U_p = cumulative volume of water withdrawn at times *t*

 U_i = total volume of water injected during the injection phase

 R_{fr} = average frontal position of the injected water at the end of injection period The value of R_{fr} can be calculated from

$$R_{fr} = \sqrt{\frac{Qt_i}{\pi b\phi}} = \sqrt{\frac{U_i}{\pi b\phi}}$$

where *Q* is the tracer injection rate ($L^{3}T^{-1}$), *t_i* is the total time of injection, *b* is the saturated thickness of an aquifer and ϕ is aquifer's porosity.

EXAMPLE 3.10 Single-well (push-and-pull) tracer test

A single-well tracer test was conducted in a shallow aquifer having a saturated thickness b = 8 m. A bromide solution with [Br⁻] of 23.5 mg L⁻¹ was injected into the aquifer for 241 L. During extraction, bromide concentration as a function of total

				- 2	5 🗖		1				-	
U_p	[Br ⁻]	U_p	[Br ⁻]		Ī	•						
(L)	$(mg L^{-1})$	(L)	$(mg L^{-1})$)								
0	24.8	200	14.3	- 2			-	-				
20	23.0	220	13.3					† •				
40	21.9	240	12.1	- 1 0	5				• .			
60	22.0	260	11.9	E Ú					- 1	• •		
80	20.5	280	9.1	巴 ₁	0			_		•.	_	
100	21.3	300	8.6							•	•	
120	19.0	320	6.7		5 -							
140	18.5	340	4.2								•	•
160	17.1	360	3.1		٥L							
180	16.7				0	;	80	160	24	40	320	400
				-				U	_p (L)			

(or cumulative) extracted volume as shown in the table. Assume aquifer porosity of $\phi = 0.3$, estimate longitudinal dispersion coefficient α_L .

► Solution: Based on a given data of $U_i = 241$ L, $\phi = 0.30$ and b = 8 m, the average frontal position of the injected water at the end of injection period or R_{fr} can be calculated as

$$R_{fr} = \sqrt{\frac{U_i}{\pi b \phi}} = \sqrt{\frac{241 \times 10^{-3} \text{ m}^3}{\pi \times (8 \text{ m}) \times 0.30}} = 0.3169 \text{ m}.$$

Using $C_0 = 23.5 \text{ mg L}^{-1}$, the value of C/C_0 can be calculated as shown in table (see below). Then, by guessing the value of α_L , the calculated (or modeled) value of C/C_0 can be tabulated. The difference between field and modeled values is called error. Using Solver[®] built-in function in Microsoft Excel, a sum of squared error can be minimized and, hence the value of α_L is optimized.



It was found that the optimized value of longitudinal dispersivity that gives minimum sum of squared errors is $\alpha_L = 0.17$ m.

Table 3.5Typical ranges of dispersion coefficients in rivers, lakes, and sediments [37, 22, 42].

Condition	Dispersion coefficient (cm ² s ⁻¹)
Molecular diffusion in water	10^{-5}
Vertical dispersion in deep lakes	$10^{-2} - 10^{0}$
Vertical dispersion in shallow lakes	$1 - 10^{3}$
Horizontal dispersion in lakes	$10^2 - 10^6$
Longitudinal dispersion in streams and estuaries	$10^5 - 10^6$
Transverse (lateral) dispersion in streams	$10^2 - 10^3$
Compact sediments	$10^{-7} - 10^{-5}$
Bioturbated sediment	$10^{-5} - 10^{-4}$
Field-scale dispersion in porous media	$10^{-2} - 10^{1}$
Molecular diffusion in air	10^{-1}
Vertical dispersion in atmospheric boundary layer	$10^4 - 10^6$
Horizontal dispersion in the atmosphere	$10^6 - 10^{10}$

3.3 Advection-dispersion-reaction equation

In general, pollutant transport occurs through advection, diffusion and dispersion. When both advective and dispersive transport processes are significant and reactions (either generation or degradation) are present, the applicable mass transport can be derived as follows.

Consider an air, water or groundwater aquifer of an infinitesimally small control volume of $V = \Delta x \Delta y \Delta z$, we can perform a mass balance calculation by considering mass influx and outflux by advection and dispersion over this volume as well as a chemical reaction (either generation of degradation) of rate r (ML⁻³T⁻¹) within this control volume. The mass balance can be written as:

$$\dot{m}_{acc} = \dot{m}_{in} - \dot{m}_{out} \pm \dot{m}_{rxn}$$

$$\frac{d}{dt} (VC) = \underbrace{(J_{a,x} - J_{a,x+\Delta x}) \Delta y \Delta z + (J_{a,y} - J_{a,y+\Delta y}) \Delta x \Delta z + (J_{a,z} - J_{a,z+\Delta z}) \Delta x \Delta y}_{Advection} + \underbrace{(J_{E,x} - J_{E,x+\Delta x}) \Delta y \Delta z + (J_{E,y} - J_{E,y+\Delta y}) \Delta x \Delta z + (J_{E,z} - J_{E,z+\Delta z}) \Delta x \Delta y}_{Dispersion}$$

$$\frac{\pm (rV)}{Reaction}$$

Divide through the above expression by $V = \Delta x \Delta y \Delta z$ and we have

$$\frac{dC}{dt} = -\left(\frac{J_{a,x+\Delta x} - J_{a,x}}{\Delta x}\right) - \left(\frac{J_{a,y+\Delta y} - J_{a,y}}{\Delta y}\right) - \left(\frac{J_{a,z+\Delta z} - J_{a,z}}{\Delta z}\right) \\ - \left(\frac{J_{E,x+\Delta x} - J_{E,x}}{\Delta x}\right) - \left(\frac{J_{E,y+\Delta y} - J_{E,y}}{\Delta y}\right) - \left(\frac{J_{E,z+\Delta z} - J_{E,z}}{\Delta z}\right) \\ \pm r.$$

Take a limit of $\Delta x, \Delta y, \Delta z \to 0$ or $\lim_{\Delta x, \Delta y, \Delta z \to 0}$, the difference expressions in the above equation become derivative similar to $\lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{\Delta x} = \frac{df}{dx}$ as follows.

$$\frac{\partial C}{\partial t} = -\frac{\partial J_{a,x}}{\partial x} - \frac{\partial J_{a,y}}{\partial y} - \frac{\partial J_{a,z}}{\partial z} - \frac{\partial J_{E,x}}{\partial x} - \frac{\partial J_{E,y}}{\partial y} - \frac{\partial J_{E,z}}{\partial z} \pm r$$

Substitute advective and dispersive fluxes into the above expression where

$$J_{a,x} = u_x C \qquad J_{E,x} = -E_x \partial C / \partial x$$

$$J_{a,y} = u_y C \quad \text{and} \quad J_{E,y} = -E_y \partial C / \partial y$$

$$J_{a,z} = u_z C \qquad J_{E,z} = -E_z \partial C / \partial z$$

the advection-dispersion-reaction equation for mass transport can be obtained as:

$$\frac{\partial C}{\partial t} = -\left[\frac{\partial}{\partial x}(u_x C) + \frac{\partial}{\partial y}(u_y C) + \frac{\partial}{\partial z}(u_z C)\right] \\
+ \left[\frac{\partial}{\partial x}\left(E_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(E_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(E_z \frac{\partial C}{\partial z}\right)\right] \\
\pm r$$
(3.11)

Advection-dispersion-reaction (ADR) equation:

A more generalized advection-dispersion-reaction equation for mass transport in air, surface water or groundwater can be written in as vector notation as:

$$\frac{\partial C}{\partial t} = -\mathbf{u}\nabla C + \nabla \cdot (\mathbf{E}\nabla C) \pm r, \qquad (3.12)$$

where **E** is dispersion coefficient tensor and **u** is velocity vector. If the cartesian coordinate conforms with *principal directions*,

$$\mathbf{E} = \begin{bmatrix} E_x & 0 & 0 \\ 0 & E_y & 0 \\ 0 & 0 & E_z \end{bmatrix}, \qquad \mathbf{u} = \begin{cases} u_x \\ u_y \\ u_z \end{cases}.$$

The solutions to (3.11) and (3.12) require specification of the initial and boundary conditions that characterize the nature of chemical contamination in the environment. In practice, the dimensionality of the transport system can often be simplified based on assumptions about the degree of mixing in x, y and z directions resulting in a zero-, one-, twoor three-dimensional transport systems. If **u**, **E** and r are not constant (i.e., they are either a function of space or time) the above equations (3.11) and (3.12) must be solved using numerical approximations. However, if these parameters are fixed, the advectiondispersion-reaction equation may be solved analytically for idealized cases with simple geometries and boundary conditions. 104 ADVECTION, DIFFUSION AND DISPERSION PROCESSES

Example: 1-D, instantaneous input into the river

Consider a 1-D advection-dispersion-reaction problem with a chemical degradation represented as a first-order kinetic r = -kC where k is reaction rate constant (T⁻¹), the governing equation from (3.11) or (3.12) can be reduced to

$$\frac{\partial C}{\partial t} = -u_x \frac{\partial C}{\partial x} + E_x \frac{\partial^2 C}{\partial x^2} - kC$$

with the following initial and boundary conditions

$$C(x,t=0) = 0$$

$$\int_{-\infty}^{+\infty} C(x,t)dx = M$$

$$\frac{\partial C}{\partial t}\Big|_{(x\to\infty,t)} = 0$$

where *M* is the mass per cross-sectional area of the river (ML^{-2}) . The solution to the above PDE is given as

$$C(x,t) = \frac{M}{\sqrt{2\pi E_x t}} \exp\left[-\frac{(x-u_x t)^2}{4E_x t}\right] e^{-kt}$$
(3.13)

The last term e^{-kt} denotes the degradation reaction causing a decrease in a concentration as the contaminant is transported in the media. The maximum concentration occurs at a location x and time t, where $x - u_x t = 0$, can be calculated as

$$C_{\max}(x = u_x t, t) = \frac{M}{\sqrt{2\pi E_x t}} e^{-kt}.$$
 (3.14)

EXAMPLE 3.11 Pulse release of a chemical at an estuary

Consider an estuary with a cross-sectional area of $A = 1000 \text{ m}^2$ and a volumetric flow rate of $Q = 60 \text{ m}^3 \text{ s}^{-1}$. A spill of a biodegradable chemical of approximately 4000 kg accidentally took place. Calculate the concentration profile of this chemical if the degradation rate constant is 0.1 d⁻¹ and the dispersion coefficient is 30 m²s⁻¹.

► Solution: Given the above information, this instantaneous source strength is

$$M = \frac{4000 \text{ kg}}{1000 \text{ m}^2} = 4 \text{ kg m}^{-2},$$

and a flow velocity is

$$u_x = \frac{Q}{A} = \frac{60}{1000} = 0.06 \text{ m s}^{-1}.$$

The degradation constant $k = 0.1 d^{-1} = 1.157 \times 10^{-6} s^{-1}$. Using all information given above, the concentration profiles at times t = 2,4 and 6 d can be calculated using analytical solution in (3.13). Table and figure below illustrate the concentration profile with denoted maximum concentration.



Example: 1-D, continuous input into porous media

Typically, in a fast flowing system such as surface water and atmosphere, steady-state condition is attained relatively quickly. On the other hand, in a slow flow system such as in groundwater, the advection, dispersion and reaction processes are often slow such that the time-variation of pollutant concentration can be observed, thus, the transient response is often of interest.

Consider a long column packed with soil or sand with a contaminant and water flow introduced at one end can be treated as a semi-infinite medium for the purposes of analyzing 1-D advective-dispersive-reactive transport. Assuming instantaneous mixing throughout the cross-section of the column, with 1-D advection and dispersion occurring in the longitudinal direction with the following boundary conditions.

$$\frac{\partial C}{\partial t} = -u_x \frac{\partial C}{\partial x} + E_x \frac{\partial^2 C}{\partial x^2} - kC$$

with the following initial and boundary conditions

$$C(x,t=0) = 0$$

$$C(x=0,t) = C_0$$

$$C(x \to +\infty,t) = 0$$

where C_0 is a concentration at x = 0 that is kept constant. The solution to the above PDE is given as

$$C(x,t) = \frac{C_0}{2} \left[\operatorname{erfc}\left(\frac{x - u_x t}{\sqrt{4E_L t}}\right) + \exp\left(\frac{u_x x}{E_L}\right) \operatorname{erfc}\left(\frac{x + u_x t}{\sqrt{4E_L t}}\right) \right] e^{-kt}, \quad (3.15)$$

where $\operatorname{erfc}(\xi)$ is a complementary error function (see Table 3.4).

EXAMPLE 3.12 1-D conservative transport in groundwater

A non-reactive (or conservative) tracer is continuously injected at a constant concentration of $C_0 = 10 \text{ mg L}^{-1}$ and at a constant injection rate of $Q = 2 \text{ L h}^{-1}$ into a cylindrical column with cross-sectional area of 20 cm² and 60 cm long. The sand is homogeneous with porosity of $\phi = 0.33$. Assuming that the dispersivity is $\alpha_L = 0.02$ cm. Determine the concentration distribution of the column at times t = 12 and 120 min.

► **Solution**: Based on a given information, the average linear pore velocity of groundwater inside the column is

$$\bar{v} = \frac{1}{\phi} \frac{Q}{A} = \frac{2 \text{ L h}^{-1}}{0.33 \times 20 \text{ cm}^2} = 5.0 \text{ cm min}^{-1}.$$

The hydrodynamic longitudinal dispersion coefficient can be calculated from

$$E_L = \alpha_L \bar{v} + D \approx \alpha_L \bar{v} = (0.02)(5.0) = 0.1 \text{ cm}^2 \text{min}^{-1}.$$

Applying equation (3.15) with k = 0 (non-reactive chemical), the concentration profile can be calculated and shown in the table on the right and in the plot below. It can be clearly seen that at t = 5 and 10 min, the solute fronts do not breakthrough the column length. If the injection continues longer, the entire column will have concentration of $C_0 = 10 \text{ mg L}^{-1}$.

x (cm)	C (mg L ⁻¹) at					
x (on)	t = 5 min	t = 10 min				
0	10.00	10.00				
10	10.00	10.00				
20	10.00	10.00				
22	9.99	10.00				
23	9.77	10.00				
24	8.41	10.00				
25	5.00	10.00				
25	5.00	10.00				
27	0.23	10.00				
28	0.01	10.00				
30	0.00	10.00				
45	0.00	10.00				
46	0.00	9.98				
48	0.00	9.21				
49	0.00	7.60				
50	0.00	5.00				
51	0.00	2.40				
52	0.00	0.79				
53	0.00	0.17				
55	0.00	0.00				
60	0.00	0.00				



Example: 3-D, steady-state Gaussian plume for atmospheric dispersion

The most widely used models for atmospheric dispersion over distances of a few tens of kilometers and averaging times of up to an hour are based on the steady-state advection-dispersion equation:

$$u_x \frac{\partial C}{\partial x} = E_y \frac{\partial^2 C}{\partial y^2} + E_z \frac{\partial^2 C}{\partial z^2}$$

which can be solved analytically for a continuous point source in an unbounded atmosphere with the assumptions that u, E_y, E_z are constant. Assume that the advection only occurs in

the *x*-direction which is oriented directly downwind from the source. The dispersion occurs only in the *y*- and *z*-direction. The dispersion in the *x*-direction is small compared to the advection due to fast flowing system.



For an emission at height *h* and constant emission rate of \dot{E} (MT⁻¹), the solution to the above PDE is given as

$$C(x,y,z) = \frac{\dot{E}}{2\pi\sigma_y\sigma_x u_x} \exp\left[-\frac{y^2}{2\sigma_y} - \frac{(z-h)^2}{2\sigma_z}\right],$$
(3.16)

where σ_y and σ_z is the standard deviation for spreading in the y and z directions respectively. They are defined by

$$\sigma_y = \sqrt{\frac{2xE_y}{u}}$$
 and $\sigma_z = \sqrt{\frac{2xE_z}{u}}$

In most applications, an expression shown in (3.16) is usually modified to account for the fact that the atmosphere is bounded. The lower boundary is commonly treated by assuming that contaminants contacting the ground surface are reflected back in to the atmosphere. This is modeled by introducing a "mirror" source at a height of z = -h and the results can be combined using principle of superposition as follows.

$$C(x, y, z) = \frac{\dot{E}}{2\pi\sigma_y\sigma_xu_x} \exp\left(-\frac{y^2}{2\sigma_y}\right) \times \left[\exp\left(-\frac{(z-h)^2}{2\sigma_z}\right) + \exp\left(-\frac{(z+h)^2}{2\sigma_z}\right)\right] \quad (3.17)$$

Sometimes, a strong atmospheric boundary layer above the emission release height is assumed to cap the dispersion of the plume, forming upper boundary. In this case, the steady-state concentration of a pollutant can be a combination of an infinite number of reflections from the elevated inversion height Z as follows.

$$C(x,y,z) = \frac{\dot{E}}{2\pi\sigma_y\sigma_x u_x} \exp\left(-\frac{y^2}{2\sigma_y}\right) \times \sum_{j=0,\pm 1,\pm 2,\dots}^{\pm\infty} \left[\exp\left[-\frac{(z+h+2jZ)^2}{2\sigma_z}\right] + \exp\left[-\frac{(z-h+2jZ)^2}{2\sigma_z}\right]\right] (3.18)$$

The above equation does not converge easily. However, if the value of $\sigma_z/Z < 0.63$, only the $j = 0, \pm 1$ are required to obtain satisfactory results.

EXAMPLE 3.13 Steady-state pollutant dispersion in atmosphere

Consider a chemical plant that releases 60 g s⁻¹ of xylene from an effective stack height of 40 m. The wind speed is 4 m s⁻¹. A a distance 5 km downwind from the industrial plant, the dispersivities are $\sigma_y = 438$ m and $\sigma_z = 264$ m (which corresponds to a slightly unstable conditions). Estimate xylene concentration along the plume centerline at ground level, 5 km downwind from the plant. Also, assume that xylene degradation is negligible.

► Solution: Assuming the perfect reflection at the ground, equation (3.17) can be used. The centerline is a line that y = 0. Therefore, the problem asks us to solve for C(x = 5000, y = 0, z = 0) which is

$$C(x,y,z) = \frac{\dot{E}}{2\pi\sigma_y\sigma_x u_x} \exp\left(-\frac{y^2}{2\sigma_y}\right) \times \left[\exp\left(-\frac{(z-h)^2}{2\sigma_z}\right) + \exp\left(-\frac{(z+h)^2}{2\sigma_z}\right)\right]$$

= $\frac{(60 \text{ g s}^{-1})}{2\pi(438 \text{ m})(264 \text{ m})(4 \text{ m s}^{-1})} \times \exp(0) \times$
= $\left[\exp\left(-\frac{(0-40)^2}{2\times 264}\right) + \exp\left(-\frac{(0+40)^2}{2\times 264}\right)\right]$
= $4.1 \times 10^{-5} \text{ g m}^{-3}$
= $41 \ \mu \text{ g m}^{-3}$.

The concentration of xylene directly 5 km downwind at a ground elevation is 41 μ g m⁻³.

Example: 3-D, pollutant transport in groundwater with decay

Groundwater flow in aquifer is genuinely three-dimensional in nature. The simplified transport equation in 3-D domain with first-order degradation in a unidirectional flow field in *x*-direction (i.e., $\bar{u}_x \neq 0, \bar{u}_y = \bar{u}_z = 0$) is given as

$$R_f \frac{\partial C}{\partial t} = -\bar{u}_x \frac{\partial C}{\partial x} + E_x \frac{\partial^2 C}{\partial x^2} + E_y \frac{\partial^2 C}{\partial y^2} + E_z \frac{\partial^2 C}{\partial z^2} - kR_f C$$

where R_f is the retardation factor which accounts for an equilibrium and reversible sorption of pollutant on soil's particles.

$$R_f = 1 + \frac{K_d \rho_b}{\phi} = 1 + \frac{K_d \rho_s (1 - \phi)}{\phi}$$
 (3.19)

where K_d , ρ_b and ρ_s are distribution coefficient (L^3M^{-1}) , bulk density of the aquifer and soil's particle density, respectively. The parameter *k* denotes a first-order degradation rate constant (T^{-1}) . The solution to the above PDE for constant concentration C_0 from a planar source of dimension $Y \times Z$ is given as (3.20) [10].



$$C(x, y, z, t) = \frac{C_0}{8} \exp\left[\frac{x\bar{u}_x}{2E_x} \left(1 - \sqrt{\frac{1 + 4kE_x/\bar{u}_x}{(\bar{u}_x/R_f)}}\right)\right] \\ \times \operatorname{erfc}\left[\frac{x - (\bar{u}_x t/R_f)\sqrt{1 + 4kE_xR_f/\bar{u}_x^2}}{2\sqrt{E_x t/R_f}}\right] \\ \times \left[\operatorname{erf}\left(\frac{y + Y/2}{2\sqrt{E_y x/\bar{u}_x}}\right) - \operatorname{erf}\left(\frac{y - Y/2}{2\sqrt{E_y x/\bar{u}_x}}\right)\right] \\ \times \left[\operatorname{erf}\left(\frac{z + Z/2}{2\sqrt{E_z x/\bar{u}_x}}\right) - \operatorname{erf}\left(\frac{z - Z/2}{2\sqrt{E_z x/\bar{u}_x}}\right)\right]$$
(3.20)

EXAMPLE 3.14 Underground storage tank leakage

Drums of carbon tetrachloride (CCl₄,CT) were buried in a sandy aquifer 15 years ago. Given the average linear pore velocity $\bar{u}_x = 1 \times 10^{-6}$ m s⁻¹. The retardation factors of is 1.5, respectively. The source concentrations of CT is 500 µg L⁻¹. The leakage resulted in a planar source with Y = 25 and Z = 5 m. The estimated dispersivities are $\alpha_x = 1.0, \alpha_y = 0.1$ and $\alpha_z = 0.01$ m, respectively. Calculate concentration of each contaminant along the plane of symmetry of the plume at point y = 0, z = 0 at t = 15 y assuming (a) no biodegradation and (b) CT is biodegradable with first-order degradation constants of 5×10^{-4} d⁻¹.

► Solution: Assume that groundwater flow only in the *x*-direction at a constant rate of $\bar{u}_x = 1 \times 10^{-6}$ m s⁻¹. The dispersion coefficients in all directions are $E_x = \alpha_x \bar{u}_x + D \approx \alpha_x \bar{u}_x = 10^{-6}$; $E_y = \alpha_y \bar{u}_x = 10^{-7}$; $E_z = \alpha_z \bar{u}_x = 10^{-8}$ m²s⁻¹. Along the plane of symmetry of y = 0, z = 0, mass transport equation (3.20) can be used to predict the concentration profile along the *x* direction at t = 20 y. The concentration profile at a plane of symmetry is shown below.



It is obvious that when carbon tetrachloride undergo biodegradation during its transport through a groundwater aquifer, the concentration continuously decreases and its value is much lower than when biodegradation is negligible.

PROBLEMS

- **3.1** Calculate flux of a chemical from the following conditions.
 - a) Organic nitrogen (org-N) in wastewater infiltration basin, if org-N concentration is 10 mg L^{-1} and wastewater seeps in to the soil at a rate of 2 cm hr⁻¹.
 - b) A salt in a horizontal tube 10 cm in length connecting a tank of seawater (salinity = 30 mg L^{-1}) and a tank of fresh water (salinity \approx 0), assuming no advection occurs.
 - c) CO_2 in an automobile exhaust pipe, where gas velocity is 30 cm s⁻¹ and CO_2 concentration is 0.05 g L⁻¹.
- **3.2** What is the flux density of the following situation?
 - a) Chloride in a river whose average velocity is 0.1 m s^{-1} and whose chloride concentration is $0.220 \text{ mol dm}^{-3}$.
 - b) Chloride across the freshwater-saltwater interface in an estuary where the chloride concentrations changes from 20 to 2 ppt (parts per thousand by mass) in a distance of 5 m.
 - c) Octane vapor in a 4-m tall tank that is open at the top and contains a thin layer of liquid octane at the bottom? Neglect any possible turbulence and use molecular weight of 114 g mol^{-1} and a vapor pressure of 0.019 atm for octane.

3.3 A large tank of water containing 500 ppm_w of salt is connected to a large tank of distilled water with a narrow tube 10 cm long. Pressures are adjusted so that there us no bulk fluid flow. What is the approximate flux density of the salt in the tube due to molecular diffusion when the salt gradient in the tube has become steady?

3.4 The following sketch represents the concentration of a colored dye at two different times t_1 and t_2 in a water filled tube. The concentration gradient at each point is equal to the slope of the curve. Given the diffusion coefficient $D = 10^{-5} \text{ cm}^2 \text{s}^{-1}$, Answer the following questions.



- a) Estimate the diffusive flux of dye at points 1.5 and 2.0 cm along the tube at times t_1 and t_2 .
- b) How is the answer to (a) for time t_1 consistent with the development to the t_2 profile.

3.5 A permeation tube is a device for preparing gas standards having a known concentration of some trace constituents of interest. For example, one could be made for carbon tetrachloride (CCl_4), by sealing some liquid in a plastic tube of small but finite permeability for the chemical. When the tube is placed in a flowing gas steam, CCl_4 vapor slowly diffuses through the plastic into the gas stream.

- a) What rate of CCl₄ release do you expect to occur if the tube has a wall area of 8 cm² and a thickness of 1 mm? Given the density of CCl₄ is 1.6 g cm⁻³ and the diffusion coefficient is 10^{-10} cm²s⁻¹.
- b) Assume that the permeability of the tube is well known and the inside of the tube is fully in contact with the liquid. What other conditions must be met to ensure that the concentration of CCl₄ thus created in the gas stream is constant?

3.6 A tanker truck overturned and spilled approximately 10,000 gal of gasoline which resulted in a large pool. Assume that the gasoline consists primarily of 2,2,4-trimethylpentane which has molecular weight of 114 g mol⁻¹, aqueous solubility of 2.44 mg L⁻¹, and Henry's constant of 3.1×10^3 atm dm³mol⁻¹. Calculate the loss rate in g cm⁻²s⁻¹ if the average wind speed was 12 mile per hour.

3.7 A leaking tank drops 1,1,1-trichloroethane (TCA), which is nonaqueous phase liquid (NAPL), into a small stream at a rate of 10 mg min⁻¹. Stream discharge is 10 L min⁻¹, and depth of stream is 25 cm.

- a) What is the maximum concentration of 1,1,1-TCA in water downstream of the tank?
- b) Does any of NAPL accumulate on the stream bottom? Discuss your answer.
- c) What is the maximum flux of 1,1,1-TCA from water to oil? Assume a reaeration coefficient of 0.4 h^{-1} .

3.8 Phosphate is usually trapped in lake sediments by sorption to an oxidized microzone that contains Fe(III) oxides when overlying water contains oxygen.

- a) If a chemical begins to diffuse out of the sediment after the onset of anoxia. How far up into the lake will appreciable concentrations develop if the lake remains stratified for 4 months and if mass transport is by turbulent diffusion with $D = 10^{-3} \text{ cm}^2 \text{s}^{-1}$? Transport distance can be approximated by $\sqrt{D \cdot t}$ where *D* is the Fickian transport coefficient and *t* is time.
- b) What is the lowest value of D could have, and under what conditions?

3.9 A spill suddenly releases 100 kg of the pesticide Malathion into a stream whose discharge is $10^4 \text{ m}^3 \text{ d}^{-1}$, and mean depth and wide are 30 cm and 2 m, respectively. Assume $D = 10 \text{ m}^2 \text{min}^1$.

- a) If Malathion photodegrades with half-life of $t_{1/2} = 12$ hr, determine the peak concentration that would be experience at a municipal water intakes at 1 and 15 km downstream.
- b) What process is more important in reducing Malathion concentration between the above two locations? Note: In order to decide which is more important, you may look at the ratio of concentrations that would occur at 15 and 1 km in the absence of dispersion or in the absence of photodegradation, and compare.

3.10 A stream has a channel area of 0.3 m² and a discharge of 0.07 m²s⁻¹. If 2 g of rhodamine dye (6.7 g m⁻² are suddenly introduced at point A in the channel at time t = 0.

- a) When does the maximum concentration of dye appear at point B located 25 m downstream?
- b) At the instant that maximum dye concentration appears at point B, the spatial variance of the dye is 0.9 m^2 . What is the 1-d dispersion coefficient associated with the stream at these flow conditions?
- c) What is the dye concentration at point B at this instant?

d) What is the advective flux of the dye at point B at this instant? What is the Fickian flux of dye at B at this instant?

3.11 A very short pulse injection of tracer is made into a column. When the center of mass has travelled 2 m, the standard deviation is 0.1 m. The molecular diffusion coefficient is 10^{-5} cm²s⁻¹.

- a) What is the longitudinal dispersion coefficient *E* if the average velocity of pore water is 1 mm s^{-1} .
- b) What is the dispersivity α ?
- c) How does E vary with velocity? How does α vary with velocity?
- d) If the tracer were replaced by a different tracer having much lower molecular diffusivity of 10^{-8} cm²s⁻¹, would the tracerdistribute be different at this point in the column?

3.12 (*Instantaneous source*) A storage tank breaks during an earthquake event, spilling gasoline treated with MTBE into the surrounding soil and contaminating the groundwater. Create a plot of concentration of MTBE downgradient (from 0-22 m) 10 years after spill, using the following parameters.

Cross-sectional area	50 m^2
Groundwater velocity	5 m y^{-1}
Initial MTBE concentration	35 mg m^{-3}
Volume of spill	100 m ³
Half-life of MTBE	1 y
Dispersion coefficient	$10 \text{ m}^2 \text{ y}^{-1}$
Bulk density	$1.6 {\rm ~g} {\rm ~cm}^{-3}$
K_d	$1.072 \text{ cm}^3 \text{g}^{-1}$
Porosity	0.23

3.13 (*Continuous source*) Arsenic contaminates groundwater naturally from a long-time geologic processes. The sandy aquifer has a bulk density of 1.08 g cm⁻³ and a solid density of 2.63 g cm⁻³. The distribution coefficient (K_d) in this scenario is 0.027 cm³g⁻¹. Consider that the initial concentration of arsenic at the source is 21 μ g L⁻¹, the longitudinal dispersion is 10 m² d⁻¹, and the average linear pore velocity is 100 m y⁻¹. Using this information, determine what the equilibrium arsenic concentration (in μ g L⁻¹) will be at a distance of 100 m.

3.14 A factory town covers an area of 10×10 km², and contains SO₂ sources which lead to total emission of 1000 kg h⁻¹. Given a mixing height of 0.3 km and a wind speed of 0.8 m s⁻¹, what is the approximate steady-state SO₂ concentration you would expect in the air?

3.15 A smelter releases 10 kg d^{-1} of zing fumes via a stack whose effective height is 120 m. When the wind velocity is 10 mile per hour (mph)from the southwest, measurably elevated atmospheric zinc levels occur in residential areas east and north of the smelter.

a) Estimate maximum steady-state zinc concentrations in the air at ground level as a function of distance from the stack (these maximum concentrations will occur along the plume centerline).

- b) Estimate steady-state concentrations of zinc at ground level 10 km from the smelter, at distances of 100 m, 300 m and 1 km from the plume centerline (Use stability category B).
- **3.16** A smelter emits SO₂ at a rate of 1 g min⁻¹. via a smack whose effective height is 80 m.
 - a) Estimate maximum SO₂ concentration that would be expected at ground level, at a point located 2.0 km directly downwind when wind speed is 2.5 m s^{-1} , and insolation is slight.
 - b) By approximately what factor is SO_2 concentration expected to change if the wind direction shifts by 5°.

PART II

TRANSPORT OF POLLUTANTS IN ENVIRONMENTAL MEDIA

CHAPTER 4

TRANSPORT OF POLLUTANTS IN SOILS AND GROUNDWATER AQUIFERS

4.1 Overview of soil and groundwater systems

The subsurface soil-water system consists of the unsaturated zone and the saturated zone. The unsaturated zone occurs in the upper, near surface layers of soil that are not fully saturated with water, while the saturated zone typically represents deeper where all the void spaces between the soil particles are filled up with water. Saturation occurs as water from precipitation events percolates through the upper layer of soil and seeps down, recharging the deeper layers, which then form the saturated zone. The *water table* is not a thin, crisp line, but rather a smear or fuzzy zone called capillary fringe. The nature of the geologic formations that occur below the water table governs the ability of these formation to store and transmit water. Figure 4.1 shows various types of aquifers which are referred to a water-bearing geologic unit in a saturated zone, while aquitards and aquicludes refer to formations that are largely impervious to water and excluded its passage through the subsurface. Aquifers are tapped for water supply purposes by means of the shallow dug wells or deeper groundwater wells. Aquifers may be bounded above and below by aquitards - such aquifers are termed confined aquifers . Confined aquifer is generally pressurized resulting in a water level higher than the top of formation (called *potentiometric surface*). An aquifer that is bounded by an aquitard below, but is open to atmosphere via the water table and unsaturated zone, is termed an *unconfined* or phreatic aquifer. Another type of aquifer that does not store sufficiently large quantity of water is called *perched* aquifer and its water level is located at a line called perched water table.

Fate and Transport of Pollutants in Environment. By S. Saenton, Chiang Mai University

118 TRANSPORT OF POLI LITANTS IN SOILS AND GROUNDWATER AQUIFERS



Diagram of various types of aquifers. Figure 4.1

The unsaturated zone is also referred to as the vadose zone. The unsaturated zone is packed with soil particles. The interparticle void spaces contain air as well as water so that the soil porosity is the sum of air content and the moisture content in the system. As one proceeds deeper into the vadose zone, the moisture content increases until it equals to porosity, that is, all the void spaces are filled with water and the air content becomes zero. At this depth, the water table has been reached. The fluid pressure at the water table is equal to atmospheric pressure, increasing with depth because of the increasing weight of the water column. The fluid pressure above the water table, i.e., in the vadose zone, is less than atmospheric pressure due to the suction created by the capillary action of the intraparticle void spaces. The suction pressure is also termed matric potential (ψ) and is represented as a negative pressure. The matric potential increases as the soil moisture content decreases. The drier the soil is, the more water will be sucked out of the tube, demonstrating greater suction, and hence a larger matric potential. At the capillary fringe, the soil pores are saturated do to capillary action although the fluid pressure is less than atmospheric. Figure 4.2 illustrates the vertical variation in soil moisture content at fluid pressure in the unsaturated and saturated zones.

The objective of this chapter is to describe the movement of water and the associated transport of chemical pollutants in both saturated and unsaturated zones of the subsurface. Contamination of saturated zone has been utmost concern because the waters in these layers are typically tapped for consumption. The transport in saturated zone will be discussed first and followed by the transport in unsaturated zone.



Figure 4.2 Groundwater conditions near the ground surface. (a) Saturated and unsaturated zones; (b) profile of moisture content versus depth; (c) pressure head and hydraulic head relationship & water retention under pressure head less than (top) and greater than (bottom) atmospheric pressure; (d) profile of pressure head versus depth; (e) profile of hydraulic head versus depth [16].

120 TRANSPORT OF POLLUTANTS IN SOILS AND GROUNDWATER AQUIFERS

4.2 Sources of pollutants in subsurface environment

Groundwater can become contaminated in numerous ways, as shown in Figure 4.3. Disposal of chemicals by burying them in drums which subsequently corrode and leak, or by ponding the chemicals in lagoons (shallow depressions on the soil surface), leads directly to groundwater contamination as liquid or dissolved chemicals percolate through the unsaturated zone to the water table during recharge. If immiscible liquid chemicals such as petroleum-based solvents and fuels are released into the soil, a phase of NAPL (nonaqueous phase liquid) can also be established. If released in sufficient amounts, NAPLs can percolate to the water table. NAPLs that are less dense than water (LNAPLs), such as gasoline, will float on the surface of the water table, just as they do on the surfaces of rivers, lakes, and other surface waters. Leaking underground storage tanks (LUSTs) at gasoline stations often have LNAPL floating on the water table beneath them. Liquid organic chemicals that are denser than water, such as the solvent trichloroethene (TCE), can move downward through the saturated zone, partially displacing water, and settle at the bottom of an aquifer. Such a pool of DNAPL can reside at the bottom of an aquifer for decades or longer, continuing to dissolve slowly into the overlying water, thereby presenting a waste stream of extremely long duration. DNAPLs tend to flow independently of water and usually are not responsive to removal by pumping.



Figure 4.3 Sources of groundwater pollution in subsurface environment [24].

Subsurface chemical pollutants also come from septic tanks, which are widely used for the underground disposal of nonindustrial wastewater in most of Thailand's household. The pollutants of concern from septic tanks include pathogens as well as nutrients such as ammonium and phosphorus. Sometimes, other toxic materials may be released via septic systems; for example, solvents such as methylene chloride (dichloromethane, Cl₂CH₂) were formerly added to septic systems as degreasing agents. The effluent from septic systems is initially discharged into the unsaturated zone. Depending on moisture conditions, it may spread laterally for a considerable distance before reaching the water table via recharge. Upon reaching the water table, septic tank effluent tends to form a plume of water having high concentrations of chemicals such as ammonium, phosphorus, chloride, dissolved organic carbon (DOC), and detergent residues.

Other point sources of groundwater pollution include both deep injection wells and shallower dry wells used to inject chemical wastes (including radioactive waste) directly into the subsurface environment. While it is customary to make waste injections into deep aquifers that are salty or otherwise unusable for potable water, it is not unusual for injection wells to leak, or to force the flow of water from one layer of aquifer into another, resulting in contamination of an otherwise usable source of groundwater. Agriculture is an important nonpoint source of groundwater pollution in rural areas. Widespread application of agricultural chemicals such as fertilizers and pesticides often leads to groundwater degradation due to the downward transport of these chemicals to the water table during recharge. In all cases, an understanding of groundwater movement is necessary to adequately estimate both the rate of flow of contaminated water and the direction in which it is moving in an aquifer.

4.3 Conservative transport in saturated zone

This section describes transport in the saturated zone of a tracer or conservative chemical that neither sorbs nor undergoes degradation so that its mass in groundwater is conserved at all times. Advection, diffusion and dispersion processes that determine tracer transport in the saturated zone are described here.

4.3.1 Advection in saturated zone

The average linear pore velocity (\bar{v}) of water in the saturated is derived from Darcy velocity (v or q) which is defined as the volumetric flow rate Q of water per unit cross-sectional area (A) of an aquifer perpendicular to the flow direction. According to Darcy's law, Darcy velocity is proportional to the gradient of the hydraulic head h in the aquifer with a proportionality constant denoted by the hydraulic conductivity K of the aquifer medium and for the *x*-direction:

$$v_x = q_x = \frac{Q}{A} = -K_x \frac{dh}{dx} \approx -K_x \frac{\Delta h}{\Delta x}$$
(4.1)

The effective or average linear pore velocity \bar{v} is derived from the Darcy velocity q as:

$$\bar{v_x} = \frac{q_x}{\phi} = \frac{Q}{\phi A} = -\frac{K_x}{\phi} \frac{dh}{dx} \approx -\frac{K_x}{\phi} \frac{\Delta h}{\Delta x},$$
(4.2)

where ϕ is aquifer porosity. The hydraulic head *h* in the above equations represents the sum of pressure head (ψ or *p*) and the elevation head (*z*) above the datum or

$$h = z + p$$
 or $h = z + \psi$ (4.3)

122 TRANSPORT OF POLLUTANTS IN SOILS AND GROUNDWATER AQUIFERS

The above expressions can be written in a more general form in 3-D space using vector notation where

$$\mathbf{q} = -\mathbf{K}\nabla h$$
, and $\bar{\mathbf{v}} = -\frac{1}{\phi}\mathbf{K}\nabla h$ (4.4)

and

$$\mathbf{v} = \begin{cases} v_x \\ v_y \\ v_z \end{cases}; \mathbf{q} = \begin{cases} q_x \\ q_y \\ q_z \end{cases}; \quad \mathbf{\bar{v}} = \begin{cases} \bar{v}_x \\ \bar{v}_y \\ \bar{v}_z \end{cases}; \quad \nabla h = \begin{cases} \frac{\partial h}{\partial x} \\ \frac{\partial h}{\partial y} \\ \frac{\partial h}{\partial z} \end{cases}; \quad \mathbf{K} = \begin{bmatrix} K_x & 0 & 0 \\ 0 & K_y & 0 \\ 0 & 0 & K_z \end{bmatrix}.$$

Hydraulic head typically varies spatially (and, temporally) and, thus, the hydraulic gradient causing the groundwater velocity to vary with space and time. The value of *hydraulic conductivity* is a property of the porous medium and the fluid (in this case, a water) which is related to the *intrinsic permeability* (k) of the porous medium:

$$K = \frac{k\rho_w g}{\mu_w},\tag{4.5}$$

where ρ_w and μ_w are density and dynamic viscosity of water, respectively. The value of hydraulic conductivity is usually evaluated using field test such as pumping test or slug test. Typical range of intrinsic permeability and hydraulic conductivity of some geologic materials are shown in Table 4.1.

Consolidation	A quifor motoriala	Intrinsic permeability	Hydraulic conductivity
Consolidation	Aquiter materials	$k (\mathrm{cm}^2)$	$K (\mathrm{cm} \mathrm{s}^{-1})$
Unconsolidated	Gravel	$10^{-6} - 10^{-3}$	$10^{-1} - 10^2$
	Clean sand	$10^{-9} - 10^{-5}$	$10^{-4} - 10^{1}$
	Silty sand	$10^{-10} - 10^{-6}$	$10^{-5} - 10^{-1}$
	Silt, loess	$10^{-12} - 10^{-8}$	$10^{-7} - 10^{-3}$
	Gracial till	$10^{-15} - 10^{-9}$	$10^{-10} - 10^{-4}$
	Clay	$10^{-15} - 10^{-12} \\$	$10^{-10} - 10^{-7}$
	Karst limestone	$10^{-9} - 10^{-5}$	$10^{-4} - 10^{1}$
	Fractured rocks	$10^{-11} - 10^{-7}$	$10^{-6} - 10^{-2}$
	Limestone & dolomite	$10^{-12} - 10^{-9}$	$10^{-7} - 10^{-4}$
Consolidated	Sandstone	$10^{-13} - 10^{-9}$	$10^{-8} - 10^{-4}$
	Shale	$10^{16} - 10^{-12}$	$10^{-11} - 10^{-7}$
	Unfractured rocks	$10^{-17} - 10^{-13}$	$10^{-12} - 10^{-8}$

 Table 4.1
 Intrinsic permeability and hydraulic conductivity of some geologic materials [16].

The hydraulic gradient ∇h is computed from head data gathered from several locations in the aquifer. Head contours (equipotential lines) can be drawn and the gradient can be determined from such map. If the aquifer is isotropic, the flow lines are perpendicular to equipotential lines. The following examples show how to evaluate hydraulic gradient and flow direction.
EXAMPLE 4.1

From the following hypothetical aquifer, if the average mean sea level (amsl.) is used as the datum and hydraulic conductivity of the aquifer is 0.5 m d^{-1} , find hydraulic heads at each well and the corresponding hydraulic gradient and Darcy velocity.



▶ Solution: According to the definition of hydraulic head, h = z + p where z is the height of the screen above the datum and p is the height of the water column above the screen, the hydraulic heads are both wells are

$$h_1 = z_1 + p_1 = z_1 + (100 - 10 - z_1) = 90$$
 m amsl.
 $h_2 = z_2 + p_2 = z_2 + (95 - 15 - z_2) = 80$ m amsl.

The hydraulic gradient between two wells, assuming unidirectional flow, is

$$abla h = rac{dh}{dx} pprox rac{\Delta h}{\Delta x} = rac{h_2 - h_1}{x_2 - x_1} = rac{80 - 90}{2000 - 0} = -0.005,$$

with the +x pointing toward the right direction. Note that $h_L = h_2 - h_1 = -10$ m is called a head loss. Given the hydraulic conductivity (*K*) of 0.5 m d⁻¹, the Darcy velocity can be calculated as

$$v_x = q_x = -K\nabla h = -(0.5)(0.005) = 0.0025 \text{ m d}^{-1},$$

which is a flow toward the right (+x) direction.

If the piezometric head is known at three observation wells A,B, and C that are not aligned in a straight line, then both the direction of the groundwater flow and the hydraulic gradient can be approximated as illustrated in Example 4.2,

EXAMPLE 4.2

According the map below (left), the hydraulic heads are measured at wells A, B and C. If the hydraulic conductivity of the aquifer is 2.0 m d^{-1} and the porosity is 0.3, find the hydraulic gradient, flow direction, Groundwater velocity and average linear pore velocity.



► Solution: In order to find the flow direction, we may follow the following steps:

- (1) select observation well C with the intermediate head (h = 25.17 m).
- (2) By linear interpolation, find the location of the point P having the intermediate head on the line connecting the observation wells A and B with the maximum and minimum heads. And, the distance x or \overline{AP} is

$$\mathbf{x} = \overline{AP} = \frac{25.30 - 25.17}{25.30 - 25.00} \times 230.5 = 99.88 \text{ m}.$$

- (3) Connect point P with the intermediate well, this line (\overline{CP}) is a segment of a piezometric contour line (i.e., equipotential line).
- (4) Draw a line perpendicular to this contour that passes either through the maximum head or through the minimum head observation well. In this case, a \overline{BD} line is in the direction of groundwater movement (i.e., flow line) which as a distance measured as $\overline{BD} = 114.29$ m.
- (5) The ratio of the head difference between the ends of the perpendicular line and the length of this line is the hydraulic gradient or

$$abla h \approx rac{\Delta h}{\Delta L} = rac{25.17 - 25.00}{114.29} = 0.0015.$$

The groundwater velocity (v or q) and average linear pore velocity (\bar{v}) are

$$v = |-K\nabla h| = (2.0)(0.0015) = 0.003 \text{ m d}^{-1}$$

 $\bar{v} = \frac{v}{\phi} = \frac{0.003}{0.3} = 0.01 \text{ m d}^{-1}.$

Capture zone analysis Figure 4.4 shows a set of flow lines representing the capture zone from which water is pulled into a well located in an aquifer having a uniform regional flow. The width of the region from which water is intercepted increases as the pumping rate increases and decreases as the regional specific discharge of the aquifer increases. Capture zone analysis can be used in the design of pump-and-treat system where contaminated groundwater is extracted and treated.



Figure 4.4 A Plan view of head contour or equipotential line map with flow lines toward a pumping well in homogeneous, unconfined aquifer (top) and a cross-section view of the sloping water table with asymmetrical cone of depression (bottom).

Figure 4.5 shows the analysis of capture zone boundary with the pumping located at (x,y) = (0,0). The mathematical expressions for determining the edge of the capture zone, stagnation point x_0 as well as the maximum extent of the capture zone for *confined* and *unconfined* aquifers are slightly different and they are given in Table 4.2.



Figure 4.5 Capture zone of a well pumping from an aquifer with a uniform hydraulic gradient [14].

Expression	Confined aquifer [39]	Unconfined aquifer [19]
Edge of capture zone	$x = \frac{-y}{\tan(2\pi K biy/Q)}$	$x = \frac{-y}{\tan[\pi K(h_1^2 - h_2^2)y/QL]}$
Stagnation point	$x_0 = -\frac{Q}{2\pi Kbi}$	$x_0 = \frac{1 - QL}{\pi K(h_1^2 - h_2^2)}$
Maximum extent	$y_{\max} = \pm \frac{Q}{2Kbi}$	$y_{\max} = \pm \frac{Q\hat{L}}{K(h_1^2 - h_2^2)}$
Parameters	Q = pumping rate	L = distance between monitoring wells
	i = hydraulic gradient	$h_1 =$ hydraulic head at well #1
	b = aquifer thickness	$h_2 =$ hydraulic head at well #2
	K = hydraulic conductivity	Note: $h_1 > h_2$

Table 4.2 Mathematical expressions for determining the geometry of the capture zone from a single pumping well in a homogeneous and uniform groundwater flow field.

EXAMPLE 4.3

A well serving a small brewery is pumped at an average rate of 10 L s⁻¹. Customer complaints about the beer lead to the discovery of hydrocarbons, possibly from gasoline, in the well water. The brewery owners file suit against every gasoline service station within 2.5 km of the well. Station A is 2000 m north and 300 m east; station B is 300 m due east; and station C is 200 m southwest. Assume that confined aquifer, with a thickness of 15 m, has a hydraulic conductivity of 2×10^{-4} m s⁻¹, and has a regional hydraulic gradient of 0.004 from north to south. Which of the lawyers will have a difficult time defending his or her client?

► Solution: Let the pumping well located at the (x,y) = (0,0), the capture zone envelop can be calculated as follows.

$$x_0 = -\frac{Q}{2\pi Kbi} = -\frac{(0.010 \text{ m}^3 \text{ s}^{-1})}{2\pi (2 \times 10^{-4} \text{ m} \text{ s}^{-1})(15 \text{ m})(0.004)} = -132 \text{ m}$$

$$y_{\max} = \pm \frac{Q}{2Kbi} = \pm 417 \text{ m}.$$

And the capture zone line can be evaluated from and expression

$$x = \frac{-y}{\tan(2\pi K biy/Q)}.$$

By plotting three gas station locations (A,B and C) along with the capture zone (see below), it appears that only station A lies within the capture zone of the pumping well implying that the gasoline smell from the drinking water well may come from gas station A.

It should however be noted that this analysis is based only on the *advective* transport. If diffusive, dispersive and reactive (i.e., degradation and sorption) processes are considered, the outcomes may be different.



4.3.2 Dispersion in saturated zone

Dispersion of chemicals in groundwater occurs do to channeling and mixing of water as it moves through the porous medium (i.e, mechanical dispersion), as well as molecular diffusion of the chemicals in groundwater. As we have already seen in Chapter 3, both processes are combined and represented a hydrodynamic dispersion coefficient (E) which can be defined as

$$E_{L} = \alpha_{L} \bar{v} + D_{m}$$

$$E_{T_{h}} = \alpha_{T_{h}} \bar{v} + D_{m}$$

$$E_{T_{v}} = \alpha_{T_{v}} \bar{v} + D_{m}$$

$$(4.6)$$

where the subscript *L* refers to longitudinal direction aligned with the primary or principal flow direction; and subscript T_h and T_v refer to the dispersion in the transverse horizontal and vertical directions, respectively. The first term on the right-hand-side represents mechanical dispersion that results when groundwater flowing at an average velocity \bar{v} , encounters porous media with channeling properties that yield a dispersivity α . The second term on the right-hand-side represents the effective molecular coefficient for the chemical of interest in soil water D_m which incorporates tortuosity effects in soil. Molecular diffusion in groundwater typically occurs very slowly and can often be neglected in comparison with hydrodynamic dispersion.

When Fickian dispersion is assumed to occur, that is, the dispersivities (α) and dispersion coefficient *E* are assumed to be constant, the variance σ^2 in the location of chemical plume relative to their mean position increases with travel time *t* as:

$$\begin{array}{rcl}
\sigma_L^2 &=& 2E_L t \\
\sigma_{T_h}^2 &=& 2E_{T_h} t \\
\sigma_{T_v}^2 &=& 2E_{T_v} t
\end{array}$$
(4.7)

The dispersion coefficients *E* determined from above equation are used directly in ground-water models, instead of the standard deviation parameters (σ) used in the Gaussian models for air pollution modeling.

The dispersivity is a parameter that is strongly influenced by the spatial scale of the problem domain. If not determined experimentally, general assumption of an idealized aquifer with unique and uniform dispersivity gives $\alpha_L = 0.1x$ where x is the size of the problem or the distance to which the pollutant is transported [13]. Other rules of thumb are that the transverse dispersivities are approximated as $\alpha_{T_h} = 0.1\alpha_L$ and $\alpha_{T_v} = 0.01\alpha_L$ [18, 17]. The above guidelines provide rough estimates of dispersivities. Field tracer tests must be conducted to obtain more accurate values.

4.3.3 Advective-dispersive transport of conservative tracers

In an ideal aquifer, with steady-state water flow and uniform dispersivity, the advection and dispersion processes described in the previous sections can be coupled together to yield a contaminant mass-balance equation employing the control volume approach. For a conservative tracer that undergoes no chemical reaction or sorption to soil, the mass transport equation in 3-D can be written as:

$$\frac{\partial C}{\partial t} = -\bar{v}\frac{\partial C}{\partial x} + E_L\frac{\partial^2 C}{\partial x^2} + E_{T_h}\frac{\partial^2 C}{\partial y^2} + E_{T_v}\frac{\partial^2 C}{\partial z^2},\tag{4.8}$$

with an assumption that principal flow direction is in *x*-direction. Equation 4.8 assumes constant advection and dispersion parameters in the aquifer that are invariant with time and space, at the chosen dimensionality and spatial scale of interest. Analytical solutions to the above equation may be determined if initial pollutant concentrations in the aquifer are known; and appropriate and simple boundary conditions are provided for specific pollution problems.

The analytical solution to advection-dispersion of conservative tracer transport in saturated groundwater occurring under two idealized source conditions — an instantaneous release of mass M of a chemical to groundwater and a continuous point input of a chemical at concentration C_0 are summarized in Table 4.3 and Table 4.4, respectively.

Table 4.3	Analytical	solution	for tracer	transport in	saturated	ground	lwater i	n 3-,	2- and	1-D	with
instantaneoi	us release o	f mass M									

Dimension	Analytical solution
3-D [23]	$C(x,y,z,t) = M \qquad \qquad M \qquad \qquad \qquad M \qquad \qquad$
M = mass	$C(x, y, z, t) = \frac{1}{8\phi(\pi t)^{3/2}} \exp\left[-\frac{1}{4E_L t} - \frac{1}{4E_{T_h} t} - \frac{1}{4E_{T_h} t}\right]$
2-D [43]	$C(x, y, t) = M_z$ $exp\left[(x - \overline{v}t)^2 - y^2 \right]$
$M_z = \text{mass/depth}$	$C(x, y, t) = \frac{1}{4\pi\phi t \sqrt{E_L E_T}} \exp\left[-\frac{1}{4E_L t} - \frac{1}{4E_T t}\right]$
1-D [23]	$C(x,t) = M_a \exp\left[(x - \bar{v}t)^2 \right]$
$M_a = \text{mass/area}$	$C(x,t) = \frac{1}{2\phi\sqrt{\pi t E_L}} \exp\left[-\frac{1}{4E_L t}\right]$

EXAMPLE 4.4

Benzene (1000 g) was instantaneous released a year a go into a saturated aquifer which has a saturated thickness of 10 m, a hydraulic gradient of 0.1, a hydraulic conductivity of 0.1 m d⁻¹, and a soil porosity of 0.33. Assume no sorption, volatilization, or reaction/degradation of benzene occurs in this confined aquifer. (1) Determine present-day benzene concentrations in a residential well located 100 m downgradient from

Dimension	Analytical solution
$3-D [23]$ $\dot{M} = \frac{\text{mass}}{\text{time}}$	$C(x, y, z, t) = \frac{\dot{M}}{8\pi\phi r\sqrt{E_{T_h}E_{T_v}}} \exp\left[\frac{(x-r)\bar{v}}{2E_L}\right] \operatorname{erfc}\left[\frac{r-\bar{v}t}{2\sqrt{E_Lt}}\right]$ $r = \sqrt{x^2 + y^2}\frac{E_L}{E_{T_h}} + z^2\frac{E_L}{E_{T_v}}$
$\frac{2\text{-D [43]}}{\dot{M_z} = \frac{\text{mass}}{\text{depth} \times \text{time}}}$	$C(x, y, t) = \frac{\dot{M}_z}{4\phi\sqrt{\pi r\bar{v}E_T}} \exp\left[\frac{(x-r)\bar{v}}{2E_L}\right] \operatorname{erfc}\left[\frac{r-\bar{v}t}{2\sqrt{E_L t}}\right]$ $r = \sqrt{x^2 + y^2} \frac{E_L}{E_T}$
$\overline{\text{1-D [33]}}$ $\overline{\dot{M}_a} = \frac{\text{mass}}{\text{area} \times \text{time}}$	$C(x,t) = \frac{\dot{M}_z}{2\phi\bar{v}}\operatorname{erfc}\left[\frac{x-\bar{v}t}{2\sqrt{E_L t}}\right] = \frac{C_0}{2}\operatorname{erfc}\left[\frac{x-\bar{v}t}{2\sqrt{E_L t}}\right]$

Table 4.4Analytical solution for tracer transport in saturated groundwater in 3-, 2- and 1-D withcontinuous release of tracer flux.

the spill. (2) A consultant tells the homeowners that this is the maximum benzene concentration that the will ever see. Perform your calculations and determine if you agree.

► Solution: Choose the simplest and most appropriate model to describe benzene transport in the aquifer. Since the aquifer is fairly shallow (10 m), we may assume that the water is well-mixed in the *z*-direction and use the two-dimensional instantaneous release equation from Table 4.3.

 M_z , the total benzene mass released to water per unit aquifer thickness is given as

$$M_z = \frac{1000 \text{ g}}{10 \text{ m}} = 100 \text{ g m}^{-1}.$$

The average linear pore velocity \bar{v} is computed as

$$\bar{v} = \left| -\frac{K}{\phi} \nabla h \right| = \frac{(0.1 \text{ m d}^{-1})}{0.33} (0.1)(365 \text{ d y}^{-1}) = 11.1 \text{ m y}^{-1}.$$

With no specific information given about the dispersivity, we may use the rule of thumb to approximate longitudinal dispersion coefficient as:

$$\alpha_L = 0.1x = 0.1(100) = 10$$
 m, and $E_L = \alpha_L \bar{v} = (10)(11.1) = 111$ m²y⁻¹,

and the transverse dispersion coefficient is

$$\alpha_T = 0.1 \alpha_L = 1$$
 m, and $E_T = \alpha_T \bar{v} = (1)(11.1) = 11.1$ m²y⁻¹.

(1) *Present-day benzene concentration*: The concentration of benzene in groundwater at the well located at (x, y) = (100, 0) downstream) at t = 1 y after release is

$$C(x, y, t) = \frac{M_z}{4\pi\phi t\sqrt{E_L E_T}} \exp\left[-\frac{(x-\bar{v}t)^2}{4E_L t} - \frac{y^2}{4E_T t}\right]$$

= $\frac{100}{4\pi(0.33)(1)\sqrt{111 \times 11.1}} \exp\left[-\frac{(100-11.1 \times 1)^2}{4 \times 111 \times 1} - 0\right]$
= $1.28 \times 10^{-8} \text{ g m}^{-3} = 1.28 \times 10^{-5} \,\mu\text{g L}^{-1}.$

(2) *Maximum concentration* occurs at the center of the plume and it takes $(100 \text{ m}) \div (11.1 \text{ m y}^{-1}) = 9.01 \text{ y}$ for the plume's centroid to travel 100 m downgradient. Thus, the maximum concentration at 9.01 y (at x = 100, y = 0 m) is

$$C(x,y,t) = \frac{100}{4\pi(0.33)(9.01)\sqrt{111 \times 11.1}} \exp[-0-0]$$

= 0.076 g m⁻³ = 76 µg L⁻¹.

The maximum concentration of 76 μ g L⁻¹ is expected to arrive at the groundwater well located 100 m downgradient after 1 y of spill which is much higher than the consultant originally claimed.

EXAMPLE 4.5

A 50-mg L⁻¹ bromide (Br⁻) tracer solution was injected continuously starting from time t = 0 in to a porous packed laboratory column of length 22.78 cm and cross-sectional area A = 29.16 cm². The volumetric flow rate of the aqueous solution through the column was measure at 1.10 cm³min⁻¹. The effluent tracer concentrations was measured as shown in the table (and plot). Find the value of longitudinal dispersivity (α_L) of the soil in the column.

Time	[Br ⁻]	Time	[Br ⁻]	Time	[Br ⁻]
(min)	$(mg \ L^{-1})$	(min)	$(mg \ L^{-1})$	(min)	$(mg \ L^{-1})$
0	0.12	120	0.22	255	43.79
15	-	135	0.17	270	46.87
30	0.13	150	0.78	300	49.10
40	0.12	165	2.14	330	50.50
45	0.16	180	9.48	360	50.36
60	-	195	16.03	420	50.73
75	-	210	20.99	480	50.63
90	-	225	31.40	630	50.98
105	0.13	240	35.20		

► Solution: The tabulated time-concentration data can be used to generate a breakthrough curve (BTC) as shown below. We will be using two approaches to find the dispersivity from the above experimental data: (1) using the definition of dispersion coefficient and (2) using an inversion (non-linear) optimization approach.



<u>Method 1</u> Using definition of dispersion coefficient: From the data given above, the breakthrough time is the time at which 50% or 50th-percentile of injected concentration or 25 mg L⁻¹ is observed at the effluent. In this case, the breakthrough time $t_b = 215.8$ min over the column length of L = 22.78 cm. Thus, the average linear pore velocity \bar{v} is

$$\bar{v} = \frac{L}{t_b} = \frac{22.78}{215.8} = 0.106 \text{ cm min}^{-1}.$$

The seepage or Darcy velocity v can be found from the flow rate $Q = 1.10 \text{ cm}^3 \text{min}^{-1}$ with the cross-sectional area of $A = 29.16 \text{ cm}^2$ where

$$v = \frac{Q}{A} = \frac{1.10}{29.16} = 0.0377 \,\mathrm{cm} \,\mathrm{min}^{-1}$$

The porosity ϕ of the packed soil can be found from the relationship between *v* and \bar{v} where

$$\bar{v} = \frac{v}{\phi} \Rightarrow \phi = \frac{v}{\bar{v}} = \frac{0.0377}{0.106} = 0.357$$

Next, we need to find the spreading in both time and space of the bromide plume by employing the knowledge about statistics where the difference between 16th and 84th percentile of the concentration (and time) accounts for two standard deviation. In this case, the 16th and 84th percentiles are (0.16)(50) = 8 and (0.84)(50) = 42 mg L⁻¹, respectively. These concentrations correspond to the time $t_{16} = 177$ and $t_{84} = 248$ min, respectively (approximate from the plot). That is

$$2\sigma_t = t_{84} - t_{16} = 248 - 177 = 71 \text{ min } \Rightarrow \sigma_t = 35.5 \text{ min}$$

The time standard deviation of $\sigma_t 35.5$ min can be converted into distance standard deviation σ_x using average linear pore velocity as

$$\sigma_x = \bar{v} \times \sigma_t = (0.106)(35.5) = 3.763$$
 cm.

Using the definition of longitudinal dispersion coefficient in (4.7), the dispersion coefficient of this column setup at the outlet ($x = L; t = t_b$) is

$$\sigma_x^2 = \sigma_L^2 = 2E_L t \Rightarrow E_L = \frac{\sigma_x^2}{2t_b} = \frac{3.763^2}{2 \times 215.8} = 0.0328 \text{ cm}^2 \text{min}^{-1},$$

and the longitudinal dispersivity α_L is

$$E_L = \alpha_L \bar{\nu} \Rightarrow \alpha_L = \frac{E_L}{\bar{\nu}} = \frac{0.0328}{0.106} = 0.31 \text{ cm}.$$

In short, the dispersivity from column test can be found from the following relationship:

$$\alpha_L = \frac{L(t_{84} - t_{16})^2}{8t_b^2}$$
(4.9)

<u>Method 2</u> Using inversion optimization based on the analytical solution. For a continuous injection at a constant concentration C_0 to the column, the equation for break-through curve is given by [33] as

$$C(x,t) = \frac{C_0}{2} \operatorname{erfc}\left[\frac{x - \bar{v}t}{2\sqrt{\alpha_L \bar{v}t}}\right].$$

Using \bar{v} of 0.106 cm min⁻¹ and a Solver function in Microsoft Excel[©], the sum of squared error between measured and modeled bromide concentrations can be minimized, the optimized value of dispersivity is

$$\alpha_L = 0.33$$
 cm.

The plot between modeled and measured are shown above which proves how powerful the analytical solution is when combined with inverse modeling (i.e., optimization) technique.

4.4 Reactive transport in saturated zone

Reactive transport refers to a mass movement process whereby the pollutant may undergo physicochemical or chemical reactions such as sorption and degradation during its course of transport. These processes will affect plume shape and size as well as pollutant's concentration within the plume compared to the conservative chemical.

4.4.1 Effect of sorption in transport

The analytical solutions presented in Table 4.3 and Table 4.4 describe the transport of a non-sorbing and non-reactive tracer chemical in a homogeneous saturated groundwater system. In the case for reactive pollutant that readily sorbs to the aquifer matrix, the soil acts as an additional compartment in the groundwater system. This affects the control volume mass balance in the following way.

Assuming instantaneous equilibrium between chemical concentration in water represented on a mass/volume basis, $C(\mathbf{x},t)$, and the chemical concentration in the adjacent soil, $C_s(\mathbf{x},t)$, represented on a mass/mass basis, the total mass of a chemical $M_{\text{total}}(\mathbf{x},t)$ present within a bulk volume V_{bulk} of an aquifer is given ass:

$$M_{\text{total}}(\mathbf{x},t) = \phi V_{\text{bulk}}C(\mathbf{x},t) + \rho_b V_{\text{bulk}}C_s(\mathbf{x},t)$$

$$= \phi V_{\text{bulk}}C(\mathbf{x},t) + \rho_b V_{\text{bulk}}K_dC(\mathbf{x},t)$$

$$= V_{\text{bulk}}(\phi + \rho_b K_d)C(\mathbf{x},t)$$

where ρ_b is the bulk density of aquifer materials, and K_d is the distribution coefficient (L^3M^{-1}) representing the equilibrium constant for sorption of a chemical between solid and aqueous phases, and

$$K_d = rac{dC_s}{dC} pprox rac{C_s}{C}.$$

The rate of change of total pollutant mass in the control volume is given by:

$$\frac{dM_{\text{total}}(\mathbf{x},t)}{dt} = V_{\text{bulk}}(\phi + \rho_b K_d) \frac{dC(\mathbf{x},t)}{dt}.$$

By recognizing that the advective and dispersive transport processes for pollutant mass to and from the control volume occur in the liquid volume ϕV_{bulk} , the mass balance equation in *one-dimensional* system is given by:

$$\frac{\partial M_{\text{total}}(x,t)}{\partial t} = V_{\text{bulk}}(\phi + \rho_b K_d) \frac{\partial C(x,t)}{\partial t} = \phi V_{\text{bulk}}\left(-\bar{v}\frac{\partial C(x,t)}{\partial x}\right) + \phi V_{\text{bulk}} E_L \frac{\partial^2 C(x,t)}{\partial x^2}$$

Dividing the above equation by ϕV_{bulk} yields the following equation

$$\left(1+\frac{\rho_b K_d}{\phi}\right)\frac{\partial C(x,t)}{\partial t}=-\bar{v}\frac{\partial C(x,t)}{\partial x}+E_L\frac{\partial^2 C(x,t)}{\partial x^2}$$

The term in parenthesis on the left-hand-side of the above equation represents the *retardation factor*, R_f , which is defined as

$$R_f = 1 + \frac{\rho_b K_d}{\phi} = \frac{\phi V_{\text{bulk}} + K_d \rho_b \phi V_{\text{bulk}} C(x, t)}{\phi V_{\text{bulk}} C(x, t)}$$
$$= \frac{\text{Pollutant mass in soil and water}}{\text{Pollutant mass in water alone}}$$

The one-dimensional advection-dispersion-sorption transport of a pollutant in groundwater becomes

$$R_f \frac{\partial C}{\partial t} = -\bar{v} \frac{\partial C}{\partial x} + E_L \frac{\partial^2 C}{\partial x^2}.$$
(4.10)

If we further divide the above equation by R_f , the above equation becomes

$$\frac{\partial C}{\partial t} = -\bar{v}_s \frac{\partial C}{\partial x} + \alpha_L \bar{v}_s \frac{\partial^2 C}{\partial x^2}, \qquad (4.11)$$

where \bar{v}_s represents the sorbed contaminant velocity, obtained as:

$$\bar{v}_s = \frac{\bar{v}}{R_f} = \frac{\text{Pore velocity}}{\text{Retardation factor}}$$
 (4.12)

The contaminant velocity \bar{v}_s represents the apparent reduction in the advective velocity of the pollutant which is *reduced* by a factor of R_f due to equilibrium sorption to the soil which effectively "retards" the contaminant migration. Both advective transport and dispersive spread of the contaminant appears to be slowed down but, in fact, merely retained in the soil.

It should be noted that the advection-dispersion-retardation equations shown in (4.10) and (4.11) are very similar to (4.8) with \bar{v} being replaced with \bar{v}_s for the sorbed contaminant. Therefore, assuming that an instantaneous linear soil-water equilibrium partition

coefficient is valid, sorbed contaminant transport may be described with the same models that describe non-sorbing tracers (Table 4.3 and Table 4.4), except that the pore velocity \bar{v} is now replaced with the sorbed contaminant velocity \bar{v}_s . Correspondingly, the dispersion coefficients for the sorbed contaminant become

$$E_{L,s} \approx \alpha_L \bar{v}_s; \qquad E_{T_h,s} \approx \alpha_{T_h} \bar{v}_s; \qquad E_{T_v,s} \approx \alpha_{T_v} \bar{v}_s.$$

The tracer mass released term in equations in Table 4.3 and Table 4.4 is equivalent to the pollutant mass released to the aqueous phase alone, that is

$$M = M_{\rm aq} = \frac{M_{\rm total}}{R_f},$$

where M_{total} is the total mass of chemical released to the aquifer (prior to partitioning to the soil). For continuous sources releasing pollutants at an aqueous concentration of C_0 , the constant concentration term is not significant impacted by retardation because an infinite supply of pollutants is assumed to be present such that the soil is assumed to contain pollutant at equilibrium with C_0 .

EXAMPLE 4.6

Repeat Example 4.4 but, now, include the effect of retardation. Assume that $K_d = 0.5$ L kg⁻¹ and the bulk density of soil is 2.0 g cm⁻³.

► Solution: Determined the present-day benzene concentrations in a residential well located 100 m downgradient from the spill. We now calculate travel velocity of the benzene incorporating the effect of sorption where $\bar{v}_s = \bar{v}/R$ where the retardation factor $R_f = 1 + \rho_b K_d/\phi = 1 + (2.0 \text{ kg L}^{-1})(0.5 \text{ L kg}^{-1})/(0.33) \approx 4.0$.

$$\bar{v}_s = \frac{11.1}{4.0} = 2.8 \text{ m y}^{-1}.$$

The benzene mass released into water is influenced by sorption and is determined as:

$$M = M_{aq} = \frac{M_{total}}{R_f} = \frac{1000}{4} = 250 \text{ g};$$
 $M_z = \frac{M}{b} = \frac{250}{10} = 25 \text{ g m}^{-1}.$

Using the same values for dispersivities ($\alpha_L = 10, \alpha_T = 1$ m), the dispersion coefficients for the sorbed contaminant can be computed as

$$E_{L,s} = \alpha_L \bar{v}_s = 28 \text{ m}^2 \text{y}^{-1}; \qquad E_{T,s} = \alpha_T \bar{v}_s = 2.8 \text{ m}^2 \text{y}^{-1}$$

Then the concentration of benzene in groundwater at 100-m downgradient well oneyear after spill is

$$C(x, y, t) = \frac{M_z}{4\pi\phi t \sqrt{E_{L,s}E_{T,s}}} \exp\left[-\frac{(x-\bar{v}_s t)^2}{4E_{L,s}t} - \frac{y^2}{4E_{T,s}t}\right]$$

= $\frac{25}{4\pi(0.33)(1)\sqrt{28\times2.8}} \exp\left[-\frac{(100-2.8\times1)^2}{4\times28\times1} - 0\right]$
= 1.58×10^{-37} g m⁻³ = 1.58×10^{-34} µg L⁻¹ ≈ 0.

The maximum concentration occurs at the centroid of the contaminant plume. Apparently, the plume moves 4 times slower than the non-sorbing condition and the travel time is

$$t = \frac{x}{\bar{v}_s} = \frac{100}{2.8} = 35.7 \text{ y}.$$

The maximum concentration is

$$C_{\text{max}} = \frac{25}{4\pi (0.33)(35.7)\sqrt{28 \times 2.8}} \exp[-0 - 0]$$

= 19.1 × 10⁻³ g m⁻³ = 19.1 µg L⁻¹.

25

The above calculation assumes benzene sorbs instantaneously and reversibly to soil, but no chemical reaction or degradation of benzene occurs in groundwater over 35 years. Thus, of the total 1000 g of benzene released into the subsurface, only 250 g travels in the aqueous phase (M_{aq}), while the rest 750 g are sorbed under instantaneous equilibrium conditions to the soil in contact with the moving groundwater. The benzene concentrations at 100 m downgradient are essentially zero at 1 year after spill, but predicted to peak to 19.1 μ g L⁻¹ at about 35 years, assuming no reaction nor degradation of benzene in groundwater.

The impact of sorption-retardation on contaminant transport is frequently seen in the field scale. This, one can expect tracers and water to travel fastest (at average linear pore velocity \bar{v}) followed by various contaminants (each traveling at a velocity of $\bar{v}_s = \bar{v}/R_f$). For a more hydrophobic contaminant, the soil-water distribution coefficient (K_d) is larger causing a corresponding increase in R_f and a resulting decrease in \bar{v}_s . When a mixture of contaminants is released into groundwater, the lighter and less hydrophobic chemicals (e.g., Cl⁻) travel faster while the more hydrophobic contaminants (CCl₄,C₂Cl₄) move much slower. Example of separation of contaminants due to sorption has been documented at Borden aquifer as shown in Figure 4.6 [35].

Implication of sorption on pump-and-treat remediation As mentioned earlier, sorption of pollutants on soil matrix may slow down the transport process and cause a ineffectiveness of contaminated groundwater's pump-and-treat scheme (see Figure 4.7) because of sorption. The inverse of the retardation factor is a useful parameter that represents the fraction of pollutant released into the aquifer that is present in water and will be flushed under pump-and-treat operations assuming soil-water equilibrium is always maintained. Calculation employing the retardation factor provide a first-cut estimate of the degree of pollutant removal that occurs with water removal by pumping, under optimistic conditions of rapid soil-water partitioning equilibrium.

For example, let M_{total} represent the total mass of benzene initially present in an aquifer, including the benzene mass present in water and that sorbed on soil. After the first pore volume of groundwater is extracted, the mass of benzene remaining the aquifer is

$$M_{\text{remain},1} = M_{\text{total}} \left(1 - R_f^{-1} \right),$$

of which the fraction $1/R_f$ is flushed out with the second pore volume. The benzene mass remaining in the aquifer after the second pore volume is flushed is

$$M_{\text{remain},2} = \left[M_{\text{total}}\left(1-R_f^{-1}\right)\right] \left(1-R_f^{-1}\right) = M_{\text{total}}\left(1-R_f^{-1}\right)^2.$$



Figure 4.6 Chromatographic separation of plumes: chloride (CL, 647 days); carbon tetrachloride (CTET, 633 days); and tetrachloroethylene (PCE, 633 days). Contour interval depicted for CL is 5 mg L⁻¹ beginning at an outer contour of 10 mg L⁻¹. Contour intervals depicted for CTET and PCE are 0.1 μ g L⁻¹ beginning at an outer contour of 0.1 μ g L⁻¹ [35].



Figure 4.7 Schematic diagram for pump-and-treat system (www.epa.gov [45]).

By induction, the mass of pollutant remaining in the aquifer after the n^{th} pore volume has been flushed is

$$M_{\text{remain},n} = M_{\text{total}} \left(1 - R_f^{-1} \right)^n,$$

and the cumulative fraction of initial mass flushed after *j* pore volume is

$$F_n = \frac{M_{\text{total}} - M_{\text{remain},n}}{M_{\text{total}}} = 1 - \left(1 - R_f^{-1}\right)^n.$$
(4.13)

Equation 4.13 can be used to predict the removal of benzene in the aquifer by groundwater extraction (i.e., pump-and-treat). If benzene and aquifer material has retardation factor of $R_f = 4$, Figure 4.8 shows that maximum fraction of pollutant mass removal occurs when the first pore volume of groundwater is flushed, after which the mass removed keeps decreasing because of decreasing total contaminant mass in the aquifer and hence a corresponding decrease in equilibrium concentration in the water. Groundwater pump-and-treat becomes increasingly impractical as a remedy for extracting hydrophobic contaminants with large retardation factors from the subsurface.



Figure 4.8 Fraction of benzene mass that is removed by groundwater extraction. The retardation factor of benzene is assumed to be $R_f = 4.0$. Of benzene mass, 25% is removed after 1 pore volume of groundwater extracted. However, more than 16 pore volumes are needed to remove 99% of the total benzene mass originally present in the contaminated aquifer.

4.4.2 Effect of degradation in transport

The removal of contaminant due to degradation (e.g., hydrolysis, photolysis or pseudofirst-order biodegradation kinetics) can be incorporated into the advection-dispersion-sorption equation as (using 1-D equation as an example)

$$R_f \frac{\partial C}{\partial t} = -\bar{v} \frac{\partial C}{\partial x} + E_L \frac{\partial^2 C}{\partial x^2} - k'C, \qquad (4.14)$$

with

$$k' = k_w + \frac{\rho_b K_d}{\phi} k_d$$

where k_w is the degradation rate constant (T⁻¹) of a pollutant in the aqueous phase and k_s is the degradation rate constant of a contaminant while being sorbed on soil particles. This k' represents the effective contaminant degradation rate constant that are not the same for water and soil. For example, the organic pollutant may be rapidly biodegradable in water but not with sorbed on soil particles. If a chemical degradation rates in both water and soil are identical or $k_w = k_s = k$ then

$$k' = k + \frac{\rho_b K_d}{\phi} k = \left(1 + \frac{\rho_b K_d}{\phi}\right) k = R_f k.$$

The analytical solutions to (4.14) for *instantaneous* release of *reactive* pollutants that undergo degradation with $k_w = k_s = k$ can utilize the expressions shown in Table 4.3 with additional multiplicative term e^{-kt} accounting for the degradation or

$$C_{k>0}(\mathbf{x},t) = C_{k=0}(\mathbf{x},t) \exp(-kt)$$

where $C_{k>0}(\mathbf{x},t)$ and $C_{k=0}(\mathbf{x},t)$ are concentrations for degradation and non-degradation cases, respectively.

EXAMPLE 4.7

Consider a hypothetical 1-D aquifer with a porosity of 0.25, an average linear pore velocity $\bar{v} = 12 \text{ m y}^{-1}$ and a longitudinal dispersivity of 2 m. Predict the spatial concentration of a contaminant at t = 5 y with an instant release of mass/area release rate of $M_a = 100 \text{ mg m}^{-2}$ for the following cases (a) conservative (b) sorption with $R_f = 3$ and (c) sorption with $R_f = 3$ and degradation with $k = 0.0005 \text{ d}^{-1}$.

► Solution: The analytical solution from Table 4.3 is applicable with some modifications for case (b) and (c) as follows. And, the spatial distribution of chemical concentration at t = 5 y is shown in the plot below.

- (a) Conservative
- (b) Sorption

$$C(x,t) = \frac{M_a}{2\phi\sqrt{\pi t E_L}} \exp\left[-\frac{(x-\bar{v}t)^2}{4E_L t}\right]$$

$$C(x,t) = \frac{M_a/R_f}{2\phi\sqrt{\pi t E_L/R_f}} \exp\left[-\frac{(x-\bar{v}t/R_f)^2}{4E_L t/R_f}\right]$$

$$C(x,t) = \frac{M_a/R_f}{2\phi\sqrt{\pi t E_L/R_f}} \exp\left[-\frac{(x-\bar{v}t/R_f)^2}{4E_L t/R_f}\right] \exp(-kt)$$

(c) Sorption+Degradation C(x,t) =



As shown in the plot, the contaminant center of mass travels at the sorbed velocity $\bar{v}_s = \bar{v}/R_f$ which is three times slower than the conservative case. When the degradation is considered (along with sorption), the contaminant moves at the same rate but with lower concentration due to decay.

For continuous injection of pollutant with constant concentration in a 1-D domain, firstorder degradation can be incorporated into a solution proposed by [33] in Table 4.4 yielding the following analytical solution that addresses advection, dispersion, sorption and degradation as follows

$$C(x,t) = \frac{C_0}{2} \exp\left[\frac{(\bar{v}-u)x}{2E_L}\right] \operatorname{erfc}\left(\frac{R_f x - ut}{2\sqrt{R_f E_L t}}\right),\tag{4.15}$$

where *u* is defined as

$$\frac{u}{\bar{v}} = \sqrt{1 + \frac{4\alpha_L k'}{\bar{v}}}$$

If the degradation is not significant compared to advection or

$$\frac{4\alpha_L k'}{\bar{v}} \ll 1 \qquad \text{or} \qquad k' \ll \frac{\bar{v}}{4\alpha_L}$$

which results in the following approximation

$$\sqrt{1+\frac{4\alpha_L k'}{\bar{v}}}\approx \frac{1}{2}\left(1+\frac{4\alpha_L k'}{\bar{v}}\right)\Rightarrow \bar{v}-u\approx -2k'\alpha_L.$$

The concentration in (4.15) can be reduced to

$$C(x,t) = \frac{C_0}{2} \operatorname{erfc}\left(\frac{x - \bar{v}_s t}{2\sqrt{\alpha_L \bar{v}_s t}}\right) \exp\left(-\frac{kx}{\bar{v}_s}\right) \quad \text{for} \quad k' \ll \frac{\bar{v}}{4\alpha_L}.$$

EXAMPLE 4.8

Consider a hypothetical 1-D aquifer with an average linear pore velocity $\bar{v} = 12 \text{ m y}^{-1}$ and a longitudinal dispersivity of 2 m. Predict the spatial concentration of a contaminant at t = 5 y with a continuous release of contaminant with $C_0 = 6 \text{ mg } \text{L}^{-1}$ for the following cases (a) conservative (b) sorption with $R_f = 3$ and (c) sorption with $R_f = 3$ and degradation with $k = 0.0005 \text{ d}^{-1}$.

► Solution: The analytical solution from Table 4.4 is applicable for (a) and equation (4.15) with $u = \overline{v}$ is applicable for (b) and equation (4.15) is valid for (c). And, the spatial distribution of chemical concentration at t = 5 y is shown in the plot below.

(a) Conservative
$$C(x,t) = \frac{C_0}{2} \operatorname{erfc}\left(\frac{x - \bar{v}t}{2\sqrt{E_L t}}\right)$$

(b) Sorption
$$C(x,t) = \frac{C_0}{2} \operatorname{erfc}\left(\frac{R_f x - \bar{v}t}{2\sqrt{R_f E_L t}}\right)$$

(c) Sorption+Degradation
$$C(x,t) = \frac{C_0}{2} \exp\left[\frac{(\bar{v} - u)x}{2E_L}\right] \operatorname{erfc}\left(\frac{R_f x - ut}{2\sqrt{R_f E_L t}}\right)$$



From the above plot of spatial distribution of pollutant's concentration, we can see the effect of sorption as well as the degradation on the transport in groundwater.

EXAMPLE 4.9

Repeat Example 4.6 but, now, include the effect of degradation. Assume that benzene's half-life is 2 d.

► Solution: Assuming benzene undergoes biodegradation at the same rate in soil and water, therefore the degradation constant is

$$k_w = k_s = k = \frac{\ln 2}{t_{\frac{1}{2}}} = 0.346 \text{ d}^{-1} = 126.6 \text{ y}^{-1}.$$

The maximum concentration at t = 35.7 y can be calculated from the conservative benzene concentration $C_{k=0}$ as

$$C_{k>0} = (C_{k=0}) \times \exp(-kt)$$

= (19.1 \mu g L^{-1}) \times \exp(-126.6 \times 35.7)
\approx 0.

After 35.7 y, the benzene concentration with $t_{\frac{1}{2}} = 2$ d is essentially zero or completely biodegraded.

The results from Example 4.4, 4.6 and 4.9 indicate large discrepancies in predicted benzene concentrations downgradient depending upon the processes considered in the model. A suitable model for contaminant transport at a particular site must incorporate all relevant processes operational at that site. Simple analytical equations such as those presented in this Chapter enable screening level comparisons of model predictions with the broad trends observed in the field. Numerical models can then be implemented to incorporate important site-specific features related to media heterogeneities, or temporal changes in hydraulic head, chemical reaction rates, and so forth, as well as links between surface water systems and saturated and unsaturated zones in an aquifer.

4.5 Transport in unsaturated zone

When pollutant chemicals spilled or disposed on the land surface, before reaching the saturated zone, they must first move through the unsaturated zone (vadose zone). While vadose zone contamination is of concern, the fate and transport of chemicals in the vadose zone also are of interest because they affect the transmission of chemicals to the saturated zone. The upper layer of the vadose zone is usually soil, a zone occupied and significantly modified by the biota, including plant roots, microbes, and animals [16]. The physical and chemical nature of a soil is determined by the climate, the type of vegetation occurring in the area, and the nature of the parent geologic material (e.g., bedrock, glacial till, outwash sands, and gravels) from which the soil is developed.

The movement of water in the vadose zone is more difficult to describe than flow in the saturated zone, because water transport occurs only via water-filled pores and the fraction of the pore spaces filled with water (the percent saturation) is highly variable. The water content θ refers to the fraction of the bulk soil volume that contains water; θ can range between zero and ϕ , the soil porosity. The relationship between the hydraulic conductivity K, and the water content θ , is complex and difficult to predict; therefore, it is usually measured experimentally and expressed in the form of a $K - \theta$ curve, as shown in Figure 4.9. The wetting-drying hysteresis is commonly observed for all geologic materials. One major complication in the $K - \theta$ relationship is hysteresis; hydraulic conductivity differs depending on whether the porous media most recently have been dried or wetted to obtain a given moisture content. For dry material, regardless of its texture, hydraulic conductivity is low.



Figure 4.9 Typical hydraulic conductivity of a certain unsaturated soil as a function of water (moisture) content (θ). Higher conductivity occurs when θ is larger and the pore water is under less suction. Note that the relationship between $K(\theta)$ and θ depends on whether the soil most recently was dried or wetted (modified from [16]).

The primary movement of water in the vadose zone occurs vertically from the top surface of soil toward the water table after precipitation and infiltration events. Although the pressure head (p or ψ) at the top layers of soil is negative (when dry) and the pressure head at the water table is zero, the total head of top surface of soil is positive and greater than total head at the water table due to the addition of elevation head (z). As a result, the water flows vertically downward from top surface to the water table. A relationship

equivalent to Darcy's law, called Richards equation can be written to describe the vertical gradient-driven flow of water in the vadose zone. Under stead-state condition assuming uniform moisture in the vadose zone, the Richards equation is written as

$$q_z = -K(\theta)\frac{\partial h}{\partial z} = -K(\theta)\frac{\partial [z+\psi]}{\partial z} = -K(\theta)\left[1 + \frac{\partial \psi}{\partial z}\right].$$
(4.16)

For uniform moisture conditions in the soil, that is when ψ does not vary significantly with depth z or $\partial \psi / \partial z \rightarrow 0$, the above equation can be approximated by

$$q_z \approx -K(\theta), \tag{4.17}$$

where q_z is infiltration rate and $K(\theta)$ is hydraulic conductivity which depends on water content θ . Table 4.5 shows the commonly used empirical relationship for soil-water hydraulic conductivity.

Table 4.5 Commonly used empirical relationship for soil-water hydraulic conductivity $K(\theta)$.

Expression	Parameters
Brooks-Corey imbibition [4]	
$K(\theta) = K \left(\theta - \theta_r \right)^{3+2/\lambda}$	$K(\theta)$ = unsaturated hydraulic conductivity
$K(\theta) = K\left(\frac{1}{\phi - \theta_r}\right)$	K = saturated hydraulic conductivity
Campbell's equation [5]	λ = pore-size distribution index
$\kappa(\theta) = \kappa \left(\theta \right)^{3+2b}$	θ_r = irreducible water content
$\mathbf{R}(0) = \mathbf{R}\left(\phi\right)$	$\phi = \text{porosity}$
van Genuchten equation [41]	$b =$ inverse of sloe of $\psi - \theta$ plot
$\underline{K(\theta) = K\left(\frac{\theta - \theta_r}{\phi - \theta_r}\right)^{0.5} \left(1 - \left[1 - \left(\frac{\theta - \theta_r}{\phi - \theta_r}\right)^{1/c}\right]^c\right)^2}$	<i>c</i> = empirical parameter from curve-fitting

For the purpose of discussion in this chapter, we may proceed with the assumption that steady infiltration is occurring in the vadose zone at a rate of q_z determined from (4.16). The infiltration rate is equivalent is equivalent to the Darcy velocity in the saturated zone and needs to be corrected for the true cross-sectional area available for water flow, to obtain he unsaturated zone pore velocity \bar{v} . Noting that only moisture-filled pores participate in the water flow process, the effective average linear pore water velocity in the unsaturated zone is computed as

$$\bar{v} = \frac{q_z}{\theta}.\tag{4.18}$$

Thus, the moisture content θ determines the advective velocity in the vadose zone. For the saturated zone, the porosity ϕ is used since the porosity is equal to the moisture content in the saturated zone.

Dispersion in the vadose zone is defined as in the saturated zone, however, the longitudinal direction of flow is in the vertical (z) direction. Since vadose zone transport occurs over much smaller distance scales, for example, a few meters below ground surface, vadose zone transport is often modeled as a one-dimensional transport system, with dispersion occurring primarily in the longitudinal direction (z-axis). The magnitude of the dispersivity can be assumed to be simular to grainsize of soil; thus α_L is typically in the order of a few millimeters in the vadose zone [10]. **Contaminant transport in unsaturated zone: an analogy to saturated zone** With advection and dispersion in the unsaturated zone characterized above, the two processes can be coupled using mass balance differential equations with numerical or analytical solutions similar to those outlined for the saturated zone transport. In our cases, the one-dimensional transport equations described earlier in Table 4.3 and Table 4.4 are suitable for use in the vadose zone after re-orienting the *principal* flow direction to vertical axis. In the absence of reaction, the center of mass of pollutant will travel through the vadose zone at an average linear pore velocity \bar{v} determined from (4.18).

The concept of retardation factor in the vadose zone groundwater is also similar tothat in the saturated zone, except that the pollutant can now *partition* iboth to air as well as to soil. Both partitioning processes retard pollutant velocity in pore water. Similar to the definition of the retardation factor for the saturated zone, unsaturated zone's retardation factor is given as

$$R_f = \frac{\text{Total pollutant mass in air, water and soil}}{\text{Pollutant mass in water alone}} = \frac{\theta + \rho_b K_d + \theta_a K_{aw}^*}{\theta}, \quad (4.19)$$

where $\theta_a = \phi - \theta$ is volumetric air content, K_{aw}^* is a dimensionless air-water partition coefficient of the pollutant. The treatment of retardation and reaction is the same as in the case of the saturated zone. Thus, by learning the analogous parameters representing contaminant transport in the saturated and unsaturated zones in Table 4.6, we can develop a consistent framework for solving subsurface pollutant transport problems.

Parameter	Saturated zone	Unsaturated zone
Porosity	φ	$\phi= heta+ heta_a$
Moisture content	θ	$\boldsymbol{ heta} = \boldsymbol{ heta}(z, \boldsymbol{\psi}) \leqslant \boldsymbol{\phi}$
Air content	$\theta_a = 0$	$ heta_a$
Fluid pressure	$P = \rho_w g \psi > P_{atm}$	$P < P_{\text{atm}}$
Pressure head	$\psi > 0$	$\psi < 0$
Hydraulic head	$h = z + \psi$	$h = z + \psi$
Hydraulic conductivity	Κ	$K(\boldsymbol{ heta})$
Darcy velocity	$q = -K\frac{\partial h}{\partial z}$	$q = -K(\theta) \left[1 + \frac{\partial \psi}{\partial z} \right]$
Pore velocity	$ar{v}=q/\phi$	$ar{v}=q/ heta$
Retardation of pollutant	$R_f = 1 + \rho_b K_d / \phi$	$R_f = rac{ heta + ho_b K_d + heta_a K_{aw}}{ heta}$
Retardation by air	-	$R_{f}^{\prime}=rac{1}{ heta_{a}}\left(heta_{a}+rac{ heta}{K_{aw}^{*}}+rac{ heta_{b}K_{d}}{K_{aw}^{*}} ight)$
Contaminant concentration	$C_w = rac{M_{\mathrm{total}}/R_f}{V_w}$	$C_w = \frac{M_{\text{total}}/R_f}{V_w}; C_a = \frac{M_{\text{total}}/R'_f}{V_a}$

 Table 4.6
 Comparison of transport parameters in groundwater across saturated and unsaturated zones.

EXAMPLE 4.10

Compute the retardation factor in water R_f for *dissolved* benzene in the vadose zone. The moisture content of the soil is uniform $\theta = 0.2$ and air content is $\theta_a = 0.4$. Assume $K_d = 0.5 \text{ L kg}^{-1}$ and the bulk density of soil is 2.0 g cm⁻³. What is the average travel

velocity of benzene through this soil if the water infiltration rate $q_z = 1 \text{ m d}^{-1}$, and is assumed steady. Given the Henry's constant for benzene is $K_H = 5.5 \text{ L}$ atm mol⁻¹ (from Table).

► Solution: First, calculate the dimensionless air-water partition coefficient K_{aw} from Henry's constant with T = 25 °C.

$$K_{aw} = \frac{K_H}{RT} = \frac{5.5 \text{ L atm mol}^{-1}}{(0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 0.22$$

The retardation factor can then be calculated using the following relationship.

$$R_f = \frac{\theta + \rho_b K_d + \theta_a K_{aw}}{\theta}$$

= $\frac{0.2 + (2 \text{ kg L}^{-1})(0.5 \text{ L kg}^{-1}) + (0.4)(0.22)}{0.2}$
= 6.4

Therefore, the average travel time for dissolved benzene in unsaturated zone under steady flow is

$$\bar{v}_s = \frac{\bar{v}}{R} = \frac{q_z/\theta}{R} = \frac{(1 \text{ m d}^{-1}) \div (0.2)}{6.4} = 0.39 \text{ m d}^{-1}.$$

From the above Example, the analysis considered only, whether it be in the saturated or the unsaturated zones. For very volatile pollutants, however, volatilization through air in the vadose zone can contribute as well to contaminant transport. Jury et al. [26] presented an analysis of pollutant transport in the vadose zone incorporating movement of pollutants in air via diffusion, coupled with water-phase transport by advection-dispersion-retardation. When the air-phase is in motion such as in soil vapor extraction remedial operations at contaminated sites, advection in air in the vadose zone also needs to be considered. Airflow rates in soil are modeled using Darcy's law driven by air pressure gradients. The media connectivity for air is determined from (4.5) by using density and viscosity of air. The movement of contaminants in air, whether by diffusion or advection, will appear to be retarded by chemical partitioning to water and to soil represented by the retardation factor for air, R'_f . A soil behavior assessment model that considers all these processes, as shown in Figure 4.10, has been developed for Excel spreadsheet implementation and can be used for screening behavior of chemicals in soil [9].

EXAMPLE 4.11

Write a mass balance differential equation for volatile organic compound (VOC) transport in the vadose zone incorporating all processes shown in Figure 4.10.

► Solution:

It is assume that the advection of VOC occurs only due to the vertical movement of groundwater in the unsaturated zone. Dispersion in pore water is assumed to be slow compared to molecular diffusion in pore air. Molecular diffusion in pore aire and pore water is together described employing the effective diffusion coefficient for soil $D_{m,s,\text{eff}}$. The first-order degradation takes place with a rate constant k. Mass balance

TRANSPORT IN UNSATURATED ZONE 145



Figure 4.10 Depiction of important processes that govern VOC transport in vadose one (adapted from [26]).

differential equations are written in terms of the contaminant concentration in the total soil matrix, $C_{s,t}$ including soil particle, pore air and pore water and can be computed from contaminant concentrations in pore water as:

$$C_{s,t} = \frac{\text{Mass of chemical in soil, pore water, and pore air}}{V_{\text{bulk}}}$$
$$= \frac{M_{\text{soil}}K_dC_{s,w} + V_wC_{s,w} + V_aK_{aw}C_{s,w}}{V_{\text{bulk}}}$$
$$= (\rho_bK_d + \theta + \theta_aK_{aw})C_{s,w}$$
$$= R_f \theta C_{s,w}$$

The rate of change in total chemical mass within a bulk volume of soil equals net advective input due to pore water movement plus net diffusive molecular diffusion through bulk soil (including pore air and pore water) minus the removal by reaction in the bulk soil.

$$(\Delta x \Delta y \Delta z) \frac{\partial C_{s,t}(z,t)}{\partial t} = \left[\bar{v} C_{s,w}(z,t) - \bar{v} C_{s,w}(z+\Delta z,t) \right] \times (\theta \Delta y \Delta x) \\ + \left[D_{m,s,\text{eff}} \left(\left. \frac{\partial C_{s,t}}{\partial z} \right|_{z+\Delta z} - \left. \frac{\partial C_{s,t}}{\partial z} \right|_z \right) \right] \times (\Delta y \Delta x) \\ - (\Delta x \Delta y \Delta z) \times k \times C_{s,t}(z,t)$$

Advection occurs in pore water alone and hence the advection term employ the VOC concentration in pore water, $C_{s,w}$ along with the pore velocity \bar{v} and the water-

filled pore cross-sectional area given by $\theta \Delta y \Delta x$. Reaction and diffusion terms are based on total chemical concentration in bulk soil, and hence use the bulk volume $\Delta x \Delta y \Delta z$ and total cross-sectional area $\Delta x \Delta y$, respectively. Substituting the relationship between $C_{s,t}$ and $C_{s,w}$ and dividing the equation by the bulk volume of soil $\Delta x \Delta y \Delta z$, we will have

$$\frac{\partial C_{s,t}(z,t)}{\partial t} = -\frac{\bar{v}}{R_f} \frac{\partial C_{s,t}(z,t)}{\partial z} + D_{m,s,\text{eff}} \frac{\partial^2 C_{s,t}(z,t)}{\partial t^2} - kC_{s,t}(z,t).$$

Depending on the complexity of the boundary conditions and soil heterogeneity, the above expression may not have analytical solution. Rather, a numerical solution may be required to obtain the approximate solution which is beyond the scope of this course.

4.6 Non-aqueous phase liquids, NAPLs

The top-25 most frequently detected contaminants found in groundwater at hazardous waste sites are listed in Table 4.7. Nine of these contaminants are inorganic: lead (Pb), chromium (Cr), zinc (Zn), arsenic (As), cadmium (Cd), manganese (Mn), copper (Cu), barium (Ba), and nickel (Ni). Lead, arsenic, and cadmium are not only high on the list, but they are also among the most toxic chemicals found in groundwater. The rest of the top 25 are organic chemicals.

Many of the organic chemicals listed in Table 4.7 do not dissolve very well in water. They are called nonaqueous-phase liquids (NAPLs), and their presence makes the task of restoring an aquifer to drinking water quality very difficult or even impossible. NAPLs are generally divided into two categories: Those that are more dense than water are called dense NAPLs (DNAPLs), whereas those that are less dense than water are called light NAPLs (LNAPLs). Examples of DNAPLs include chlorinated solvents, such as trichloroethylene and tetrachloroethylene, polychlorinated biphenyls (PCBs), pesticides such as chlordane, and polycyclic aromatic hydrocarbons (PAHs). Many of the LNAPLs are fuelhydrocarbons, including crude oil, gasoline, and benzene. Table 4.8 lists some important NAPLs along with their solubility in water and their specific gravity.

As LNAPLs enter the unsaturated zone, some may dissolve into water in the pores, some may volatilize and become mixed with air in other pore spaces, and some may adsorb onto soil particles. When LNAPLs reach the water table, they do not dissolve well and instead spread out to form a layer of contaminant floating on top of the saturated zone, as suggested in Figure 4.11. DNAPLs also sink, dissolve, adsorb, and volatilize in the unsaturated zone, but when they reach the water table, they keep on sinking until they reach a layer of relatively impermeable material. There they form pools that can overflow and sink to the fractured impermeable layer, as shown in Figure 4.11. Portions of DNAPLs tend to form small globules that become trapped in pore spaces, making them virtually impossible to remove by pumping. As they remain lodged in tiny crevices, and as they accumulate in pools on the bottom of aquifers, they slowly dissolve into passing groundwater. Their solubility is so low, however, that removal by dissolution can take centuries. Attempts to remove DNAPLs by extracting groundwater can be nearly impossible.

Table 4.8 lists aqueous solubilities for a selection of NAPLs, and those can be used to make a first-cut estimate of the length of time required to remove NAPLs by groundwater

Table 4.7	The 25 Most frequently detected groundwater contaminants at hazardous waste sites
[32].	

Rank	Compounds	Common Sources
1	Trichloroethylene	Dry cleaning; metal degreasing
2	Lead	Mining; construction material (pipes); manufacturing
3	Tetrachloroethylene	Dry cleaning; metal degreasing
4	Benzene	Gasoline; manufacturing
5	Toluene	Gasoline; manufacturing
6	Chromium	Metal plating
7	Methylene chloride	Degreasing; solvents; paint removal
8	Zinc	Manufacturing; mining
9	1,1,1-Trichloroethane	Metal and plastic cleaning
10	Arsenic	Mining; manufacturing
11	Chloroform	Solvents
12	1,1-Dichloroethane	Degreasing; solvents
13	1,2-Dichloroethene	Transformation product of 1,1,1-trichloroethane
14	Cadmium	Mining; plating
15	Manganese	Manufacturing; mining; occurs in nature as oxide
16	Copper	Manufacturing; mining
17	1,1-Dichloroethene	Manufacturing
18	Vinyl chloride	Plastic and record manufacturing
19	Barium	Manufacturing; energy production
20	1,2-Dichloroethane	Metal degreasing; paint removal
21	Ethylbenzene	Styrene and asphalt manufacturing; gasoline
22	Nickel	Manufacturing; mining
23	Di(2-ethylhexy)phthalate	Plastics manufacturing
24	Xylenes	Solvents; gasoline
25	Phenol	Wood treating; medicines

 Table 4.8
 Examples of Nonaqueous-Phase Liquids.

Pollutants	Specific gravity	Aqueous solubility (mg L^{-1})
DNAPLs		
Carbon tetrachloride	1.58	757
Trichloroethene	1.47	1,100
Tetrachloroethene	1.63	150
Phenol	1.24	93,000
LNAPLs		
Benzene	0.873	1,750
Toluene	0.862	535
<i>p</i> -Xylene	0.861	198



Figure 4.11 The behavior of NAPL and DNAPL in the subsurface environment. NAPL floats on the water table, slowly dissolving into the groundwater flowing by, thus creating a plume in the downgradient direction. DNAPL tends to sink to the bottom of the aquifer, where it may flow contrary to the groundwater flow direction, following instead the slope of an aquiclude such as bedrock. DNAPL may also flow into bedrock fractures, and become exceedingly difficult to either locate or remove [22].

pumping. The solubilities found in Table 4.8 tend to be much higher than those actually found in contaminated aquifers, which tend to be about 10 percent of the theoretical value [32].

EXAMPLE 4.12 Estimated time to remove a TCE spill [30]

Suppose 1 m³ of aquifer is contaminated with 30 L of trichloroethylene (TCE). The aquifer has a porosity of 0.3, groundwater velocity of q = 0.03 m d⁻¹, and the TCE has a dissolved concentration equal to 10 percent of its aqueous solubility. Find the mass of dissolved TCE and the mass of undissolved DNAPL, and estimate the time for TCE to be removed.

► Solution:

From Table 4.8, aqueous solubility of TCE is given as 1,100 mg L⁻¹, but the actual dissolved TCE is only 10% of the maximum solubility or $C_{\text{TCE}} = 110$ mg L⁻¹. The porosity of aquifer is 0.3, so the volume of fluid in 1 m³ aquifer is 0.3 m³ or 300 L. The amount of dissolved TCE is therefore

Dissolved TCE = $(110 \text{ mg } \text{L}^{-1}) \times (300 \text{ L}) = 33,000 \text{ mg} = 33 \text{ g}.$

Based on a given specific gravity TCE in Table 4.8 of 1.47, TCE thus has a density of 1,470 kg m⁻³. Therefore, total TCE spilled mass is $(0.3 \text{ m}^3) \times (1,470 \text{ kg m}^{-3}) = 44.1 \text{ kg or } 44,100 \text{ g}$. Since TCE mass of 33 g has been dissolved in groundwater, the remaining 44,097 g is still in a NAPL phase. That is, 99.92% of the spilled TCE has not yet dissolved.

Based on a groundwater velocity of 0.03 m d^{-1} , the TCE removal rate from a 1-m² cross-sectional area of flow is

TCE removal rate =
$$(0.03 \text{ m d}^{-1})(1 \text{ m}^2)(110 \text{ mg } \text{L}^{-1}) = 3.3 \text{ g d}^{-1}$$
.

Therefore, it will take 44,100/3.3 = 13,363 d or 37 y to completely flush 30 L TCE out of the aquifer.

While Example 4.12 yields an estimate of 37 years to clean this aquifer completely, in actuality it would probably take even longer. As the globules of TCE dissolve, their surface area decreases, and the rate at which they dissolve drops, so the actual time required would be significantly longer than 37 years.

Concluding remarks In this chapter, you have learned the theories, laws and principles related to groundwater contamination and transport. Applications of the analytical solutions were demonstrated through worked examples. It should be emphasized that the use of analytical solution to predict pollutant transport in groundwater should be handled with care because it requires several simplifications such as uniform flow field (i.e., homogeneous aquifers) and simple boundary conditions as well as geometries of the problems are assumed. Considering the complexity of the natural groundwater system as well as aquifer heterogeneities, most groundwater contamination and its transport problems were solved or approximated using numerical solutions which is beyond the scope of this course. If students are interested in numerical modeling, ones may consult with some excellent resources such as Anderson et al. [1].

PROBLEMS

4.1 The hydraulic conductivity of an aquifer is 0.005 cm s^{-1} , the hydraulic gradient is 0.02, and the porosity is 0.2.

- a) What is the specific discharge, q, in this aquifer?
- b) Calculate the maximum velocity at which dissolved salt could move through this aquifer.
- c) Assume the aquifer is 5 m thick. What is its transmissivity $(T = K \times b)$? What is the discharge per unit of distance perpendicular to the water flow $(b \times q)$?

4.2 In a sand having a median grain size of 1 mm and porosity of 0.25, how high must specific discharge be to make the mechanical dispersion coefficient equal to the effective molecular diffusion coefficient?

4.3 A domestic well is located 30 m upstream from a neighbor's septic system. If domestic use of water is $1 \text{ m}^3 \text{ d}^{-1}$, what is the minimum regional flow $(b \times q)$ that will just suffice to keep septic effluent from entering the well (easiest to do analytically)?

4.4 Water moves through a sand column 2 m long with a specific discharge of 0.0042 cm s⁻¹. Sketch the breakthrough curve of an initially sharp front of a tracer if porosity is 0.3 and median sand grain diameter is 2 mm. (Be sure to indicate the width of the breakthrough curve.)

4.5 A small shop has been dumping used solvents into an abandoned well, shown as follows. Sketch a flow net indicating where the solvents are likely to appear at the lake bed. If dissolved solvent moves with the water, roughly how long will it take to travel from the well to the lake?



4.6 A laboratory column of 10 cm² cross-sectional area is 1 m long. Porosity is 0.25 and influent flow rate is 8 L d⁻¹. The hydraulic conductivity is 0.01 cm s⁻¹. At time t = 0, injection of a nonsorbing contaminant into the influent at a constant concentration is started. Estimate contaminant concentration as a function of the time at the outflow.

4.7 Consider three monitoring wells, each located at the vertex of an equilateral triangle. The distance between any pair of wells is 300 m. The head at each well, referenced to some common datum, is as follows: well 1, 100 m; well 2, 100.3 m; well 3, 100.3 m. Sketch the well field and find the magnitude and direction of the hydraulic gradient.

4.8 The aquifer described in previous problem has a hydraulic gradient of 0.00115, a hydraulic conductivity of 1,000 m d^{-1} , and a porosity of 0.23.

a) What is the Darcy velocity?

- b) What is the average linear pore velocity of the groundwater?
- c) If the front edge of a plume is perfectly straight, how long would it take to travel to well 1 after first arriving (simultaneously) at wells 2 and 3, assuming a retardation factor of 2?

4.9 At what rate must well A be pumped to capture all the pollutant plume from the landfill? Natural gradient is 0.001 from north to south, aquifer hydraulic conductivity is 10^{-4} m s⁻¹, and aquifer thickness is 10 m.



4.10 Three wells are located in an (x, y) plane at the following coordinates: well 1, (0,0); well 2, (100 m, 0); and well 3, (100 m, 100 m). The ground surface is level, and the distance from the surface to the water table for each well is as follows: well 1, 10 m; well 2, 10.2 m; well 3, 10.1 m. Sketch the well field and find the hydraulic gradient.

4.11 Based on observations of the rate of travel between two observation wells of a tracer element having retardation factor equal to 1.0, it is determined that the average linear flow velocity in an aquifer is 1.0 m d^{-1} when the hydraulic gradient is 0.0005. A sample of the aquifer is tested and found to have a porosity of 0.20. Estimate the hydraulic conductivity.

4.12 A stagnation point in a capture-zone type curve is a spot where groundwater would have no movement. For the case of a single extraction well, the stagnation point is located where the capture-zone curve crosses the *x*-axis. Use the fact that for small angles $\tan \theta \approx \theta$ to show that the *x*-axis intercept of the capture-zone curve for a single well is $x = -Q/(2\pi b\bar{v})$.

4.13 Suppose a spill of of trichloroethylene (TCE) distributes itself evenly throughout an aquifer 10.0 m thick, forming a rectangular plume 2,000 m long and 250 m wide (see picture below). The aquifer has porosity 0.40, hydraulic gradient 0.001, and hydraulic conductivity 0.001 m s⁻¹.



- a) Given the solubility of TCE, could this much TCE be totally dissolved in the aquifer? What would be the concentration of TCE (mg L^{-1}) in this idealized groundwater plume?
- b) Using capture-zone type curves, design an extraction field to pump out the plume under the assumption that the wells are all lined up along the leading edge of the

plume, with each well to be pumped at the same rate, not to exceed per well. What is the smallest number of wells that could be used to capture the whole plume? What minimum pumping rate would be required for each well?

c) What would the optimal spacing be between the wells (at that minimum pumping rate)?

4.14 A single well is to be used to remove a symmetrical oblong plume of contaminated groundwater in an aquifer 20.0 m thick with porosity 0.30, hydraulic conductivity 0.0001 m s⁻¹, and hydraulic gradient 0.0015. With the plume and capture-zone curve superimposed as shown in below, the angle from the well to the point where the two just touch is 45°, and the width of the plume is 100.0 m. What pumping rate would create these conditions?



4.15 An underground storage tank leaks tetrachloroethylene (PCE) at a rate of $100 \text{ cm}^3 \text{ d}^{-1}$. This continues for one year before the leak is discovered and stopped. The tank lies at the water table, so all of the PCE released enters the sand aquifer (but is not necessarily immediately dissolved in the groundwater). The aquifer is 4.0 m deep and composed of sand. The actual groundwater velocity is 0.09 m d⁻¹, and the hydraulic gradient is 0.0005. The retardation factor for PCE is 6.

- a) What is the hydraulic conductivity of the aquifer?
- b) How far would you expect the PCE to have traveled down gradient during the oneyear period?
- c) Assume the dissolved PCE distributes uniformly in the aquifer and forms a plume 2.0 m wide, 4.0 m deep, and extending as far as you calculated. What is the average PCE concentration in the plume?
- d) If one well is placed on the centerline of the leading edge of the plume, what will its pumping rate need to be to capture the plume?
- e) What is the minimum duration the extraction well will need to be operated to remove all of the PCE from the aquifer? (Assume the concentration of PCE in the groundwater stays at its initial concentration until all of the PCE has been removed.)

4.16 A very short pulse injection of tracer is made into a column. When the center of mass has traveled 2 m, the standard deviation is 0.1 m. The molecular diffusion coefficient is 10^{-15} cm² s⁻¹.

- a) What is the longitudinal dispersion coefficient D if average velocity of pore water is 0.001 m s⁻¹.
- b) What is the dispersivity α ?
- c) How does *E* vary with velocity? How does α vary with velocity?
- d) If the tracer were replaced by a different tracer having much lower molecular diffusivity (perhaps something like latex microspheres having an effective molecular diffusivity of 10⁻⁸ cm² s⁻¹), would the tracer distribution be different at

this point in the column? (Assume the spheres move freely through the porous medium and are not filtered out or stuck.)

e) If the microspheres were 0.1 mm in diameter, would they be likely to pass through the porous medium freely (i.e., would they fit in the pores)?

4.17 A tanker truck full of trichloroethene has ruptured, dumping 25,000 gallons of the solvent. Quick work by cleanup crews has recovered most of it, but some has reached the water table and dissolved in the groundwater. Aquifer characteristics include a 10-m saturated depth, a transmissivity of $T = 2 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$, a regional gradient of 0.0005, and a porosity of 0.25. It is proposed to remove, treat, and reinject the water to clean up the remaining trichloroethene. Water will be removed at well A, treated, and reinjected at well B, 200 m away downgradient. The spill extent is poorly known, but the consultant has assumed that if the steady-state pumping rate is sufficient to cause any contaminant midway between A and B to enter well A, all contaminant eventually will be captured.

- a) What is the maximum concentration of trichloroethene expected in the aquifer?
- b) Discuss the proposed pumping and reinjection scheme with regard to its feasibility.
- c) One treatment alternative being considered is to use columns of peat from a local wetland as an adsorbent. Columns 5 m long and 1 m² in cross section are proposed. If peat has porosity of 0.5, f_{oc} of 50%, density of 1.2 g cm⁻³, and dispersivity of 1 cm, how much water will each peat column treat until break-through?
- d) Another treatment alternative being considered is air bubbling. In this scheme, air bubbles would pass through a column of contaminated water, reaching equilibrium with the water while they rise through the column. How many volumes of gas per unit volume of water are necessary to reduce the trichloroethene concentration below $1 \ \mu g \ L^{-1}$?

4.18 Explosion and fire have damaged the motor pool at an army base. As a renowned safety expert, you are retained to be part of the investigative team. You learn that 10 years ago, an underground storage tank released over 2000 gallon of gasoline to the subsurface environment. You decide to see if an accumulation of gasoline vapor could have led to the explosion, which evidently occurred in the compressor room (compressor controls might spark), a space 6 ft high with a dirt floor. Depth to the water table as indicated on soil logs averages 10 ft below the floor; the leaking tank was about 50 ft away upgradient. Treat the gasoline as if it were hexane, C_6H_{14} , which is flammable in air at concentrations between 1.2 and 7.4% by volume (or by mole fraction or by pressure). Molecular weight of hexane is 86, and vapor pressure is 152 mm Hg at 20 °C.

- a) What is the maximum possible diffusive flux of hexane into the compressor room?
- b) If the ventilation rate of the room is extremely low (e.g., 0.1 air changes per day), could the flammable limit be reached?

4.19 For purposes of capturing a plume of contaminated groundwater, you are asked to design a well that will create a steady-state hydraulic gradient of 0.009 at a distance of 75 m. (The gradient will be superimposed on the preexisting gradient.) Assume a fully penetrating, fully screened well is to be installed.

a) Propose the necessary pumping rate of the well, if the aquifer transmissivity is $15 \text{ m}^2 \text{ d}^{-1}$ and aquifer thickness is 14 m.

- 154 TRANSPORT OF POLLUTANTS IN SOILS AND GROUNDWATER AQUIFERS
 - b) To not violate the assumption of a linear aquifer, one must avoid excessive drawdown relative to the aquifer thickness. In the present case, what drawdown do you expect if your well has a casing diameter of 25 cm (i.e., calculate drawdown for a radius of 0.125 m)? Assume a radius of influence of 40 m.

4.20 In 1990, gasoline contamination is discovered during a routine site assessment at an urban site shown in the figure that follows. It is not known how long before 1990 this contamination reached the site, assuming that it originated off-site.



- a) Based on the following data, make a justified recommendation as to which gas station or stations are the likely culprits (include all assumptions): Station A was established in 1978; Station B in 1985; and Station C, in 1980. At the site, hydraulic conductivity is 100 ft d⁻¹, porosity is 0.3, gradient (in direction indicated) is 0.00225, and transverse dispersivity is 8 ft. *Hints*: (1) Consider advection and dispersion in a vertically well-mixed aquifer. (ii) Transverse dispersivity is horizontal dispersivity in the direction perpendicular to groundwater flow. (iii) There is no water supply or other pumping well at the site. iv. You may neglect longitudinal dispersion (dispersion in the direction of groundwater flow).
- b) What are the inherent weaknesses in this analysis? What specific warnings or caveats would you convey to the lawyers? In what ways could this analysis be improved given more time and money?

4.21 A sandstone aquifer has hydraulic conductivity and porosity 0.1 m d^{-1} and 0.3, respectively, and head measured at three locations as shown in the figure below (Scale: 1:40,000). The hydraulic head measured (above sea level) at location A is 20 m, at location B is 30 m and at C is 23.3m.



a) Determine the average groundwater flow in this region of the aquifer. Toxic aqueous waste containing a total of 20 grams of toluene is rapidly released into the above aquifer (by illegal dumping). The release site is located 500 meters up-gradient from your house which has a drinking water well that accesses the aquifer.

- b) Estimate when maximum toluene concentrations will be seen in your drinking water. Approximately what will that maximum concentration be if you assume no retardation or reaction for toluene in this aquifer.
- c) Redo the problem, now, include retardation but no reaction. (K_{oc} for toluene = 20 L kg⁻¹, $f_{oc} = 1\%$; porosity = 0.4; bulk density of soil = 2 g cm⁻³).
- d) Redo the problem again, now, include both retardation and reaction. $(t_{\frac{1}{4}} = 4 \text{ h})$.

4.22 From previous problem, for the case of instantaneous chemical releases, we used the travel time to approximate the time at which maximum chemical concentrations would occur at a certain subsurface location. Plot a graph showing the change in chemical concentration with time at the receptor location in Question 9.1, and determine exactly when maximum chemical concentrations will occur at the home, and what that maximum will be. Use same assumptions as above. Use principles of differential calculus to obtain an analytical expression for t_{max} . Verify with the graphical solution.

4.23 Consider a continuous source condition in the same aquifer. Assume the continuous source is a NAPL gasoline spill in which NAPL composed of 1% toluene is spilled into an aquifer.

- a) What would be toluene concentration in water in equilibrium with the NAPL? This is the source concentration, C_0 .
- b) When would you expect to see aqueous toluene concentration equal to one half of C_0 , at a drinking water well located 100 m downstream from the spill zone, if there was no dispersion? Assume one dimensional transport from source to receptor. Use retardation factors from above.
- c) When would you expect to see concentrations one half of C0 at well 1, if there was dispersion occurring? Use longitudinal dispersivity of 3 m.
- d) When would you expect to see concentrations one-tenth of C_0 at well 1, if there was dispersion occurring, with longitudinal dispersivity of 3 m. How would your answer change if dispersivity was later found to be 30 m.
- e) How would chemical reaction affect your answer? Assume a half-life of 4 hours for toluene in this groundwater.

4.24 100-g of benzene is now spilled into a well that penetrates an aquifer in which average ground water velocity is 10 m y⁻¹. The aquifer is 5 m thick. Assume longitudinal dispersivity is 20 m, and transverse dispersivity is 2 m. When will maximum benzene concentrations occur at your house? What will the maximum benzene concentration be? At this time what is the benzene concentration at your neighbors house located 20 meters away? Your house is 200 m downgradient from the spill site. Compute how chemical reaction (k = 1 h⁻¹) will affect your answers.

4.25 Consider an aquifer area $(20 \times 20 \times 3 \text{ m}^3)$ with porosity 0.33, contaminated with benzene. Average groundwater pore velocities in this zone are approximately 40 m y⁻¹. The total mass of benzene in this zone (including that in water and soil) is estimated to be 200 g. Compute the fraction of benzene mass removed from the aquifer when one pore volume of water is extracted (assume instantaneous soil-water equilibrium). Assume a K_d of 2 L kg⁻¹ for benzene and a soil bulk density of 2 g cm⁻³. Estimate how many pore volumes are required to be flushed so that benzene mass remaining in the aquifer is reduced to 20 g (90% removal). How much time does this correspond to?

4.26 Sketch concentration changes with time at a well located 100 m from a source continuously emitting a number of pollutants at a constant concentration C_0 . Groundwater velocity is 5 m y⁻¹. Sketch the behavior of the tracer chemical as well as that of a sorbing contaminant that has a $R_f = 5$. Show both tracer and sorbed chemical on same graph. Note key differences between the two.

4.27 Sketch concentration changes with downgradient distance at 50 y after a fixed mass of a mixture of chemicals was instantaneously injected into an aquifer. Groundwater velocity is 5 m y⁻¹. Sketch the behavior of the tracer chemical as well as that of a sorbing contaminant that has a $R_f = 5$. Show both tracer and sorbed chemical on same graph. Note key differences between the two.

REFERENCES

- 1. M.P. Anderson, W.W. Woessner, and R.J. Hunt. *Applied Groundwater Modeling: Simulation of Flow and Advective Transport, 2nd Edition.* Elsevier, Inc., London, UK., 2015.
- V. Barnett. *Environmental Statistics Methods and Applications*. John Wiley & Sons, Ltd., West Sussex, UK, 2004.
- 3. W.E. Boyce and R.C. DiPrima. *Elementary Differential Equations and Boundary Value Problems, 10th Edition.* John Wiley & Sons, Inc., New Jersey, USA, 2012.
- R.H Brooks and A.T. Corey. Properties of porous media affecting fluid flow. In *Proceedings* of American Society of Civil Engineers, Irrigation and Drainage Division, volume 92 no. IR2, pages 61–87. ASCE, Washington, USA., 1966.
- G.S. Campbell. A simple method for determining unsaturated conductivity from moisture retention data. *Soil Science*, 117:311–314, 1974.
- 6. S.C. Chapra. Applied Numerical Methods with MATLAB for Engineers and Scientists. McGraw-Hill, Inc., New York, USA, 2012.
- M.M. Clark. Transport Modeling for Environmental Engineers and Scientists. John Wiley & Sons, Inc., New York, USA, 1996.
- E.L. Cussler. *Diffusion and Mass Transfer in Fluid Systems*. Cambridge University Press, New York, USA, 1984.
- H.E. Dawson. Screening-level tools for modeling fate and transport of NAPLs and trace organic chemicals in soil and groundwater: SOILMOD, TRANS1D, NAPLMOB. Special program and consulting education, Colorado School of Mines, 1995.
- P.A. Domenico and F.W. Schwartz. *Physical and Chemical Hydrogeology, 2nd Edition*. John Wiley & Sons, Inc., New York, USA, 1998.
- 11. J.W. Elder. The dispersion of marked fluid in turbulent shear flow. J. Fluid Mech., 5(4):544–560, 1959.

Fate and Transport of Pollutants in Environment. By S. Saenton, Chiang Mai University

158 REFERENCES

- A.R. Felmy, D. Girvin, and E.A. Jenne. *MINTEQ: A computer program for calculating aqueous geochemical equilibria*. U.S. Environmental Protection Agency: Environmental Research Laboratory, Athens, GA, USA, 1984.
- 13. C.W. Fetter, T. Boving, and D. Kreamer. *Contaminant Hydrogeology, 3rd Edition*. Waveland Press, Inc., Long Groove, IL, USA, 2018.
- 14. C.W. Fetter, Jr. Applied Hydrogeology, 4th Edition. Pearson Education, Ltd., Essex, UK, 2014.
- 15. H.B. Fischer, E.J. List, R.C.Y. Koh, J. Imberger, and N.H. Brooks. *Mixing in Inland and Coastal Waters*. Academic Press, New York, USA, 1979.
- R.A. Freeze and J.A. Cherry. *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, NJ, USA, 1979.
- L.W. Gelhar and C.L Axness. Three-dimensional stochastic analysis of macrodispersion in aquifers. *Water Resour. Res.*, 19:161–180, 1983.
- L.W. Gelhar and M.A. Colins. General analysis of longitudinal dispersion in non-uniform flow. Water Resour. Res., 10:1337–1354, 1971.
- 19. S. Grubb. Analytical model for estimation of steady-state capture zones of pumping wells in confined and unconfined aquifers. *Ground water*, 31:27–32, 1993.
- W.M. Haynes, D.R. Lide, and T.J. Bruno. CRC Handbook of Chemistry and Physics, 97th Edition. Taylor & Francis Group, LLC, New York, USA, 2017.
- 21. H.F. Hemond and E.J. Fechner. *Chemical Fate and Transport in the Environment, 3rd Edition*. Elsevier, Inc., California, USA, 2015.
- 22. H.F. Hemond and E.J. Fechner-Levy. *Chemical Fate and Transport in the Environment, 2nd Ed.* Academic Press, California, USA, 2000.
- B. Hunt. Dispersive sources in uniform ground-water flow. Am. Soc. Civil Eng. J. Hydraulics Div., 104:75–85, 1978.
- 24. D.M. Tartakovsky J.H. Cushman, editor. *The Handbook of Groundwater Engineering, 3rd Edition.* CRC Press, 2016.
- H.E. Jobson and W.W. Sayre. Vertical transer in open channel flow. J. Hydraul. Div. ASCE, 96(3):703–724, 1970.
- W.A. Jury, D. Russo, G. Streile, and H. El Abdul. Evaluation of voltilization by organic chemicals residing below the soil surface. *Water Resour. Res.*, 26:13–20, 1990.
- 27. C.D. Klaassen and J.B. Watkins III. *Introduction to Environmental Toxicology, 3rd Edition*. Lewis Publishers, New York, USA, 2003.
- E. Kreyszig. Advanced Engineering Mathematics, 9th Edition. John Wiley & Sons, Inc., Singapore, 2006.
- 29. W.G. Landis and M.-H. Yu. *Casarett & Doull's Essentials of Toxicology, 3rd Edition*. The McGraw-Hill Companies, New York, USA, 2015.
- 30. G.M. Masters and W.P. Ela. Introduction to Environmental Engineering and Science, 3rd Edition. Pearson, Essex, UK, 2014.
- 31. National Academy of Sciences. *Risk Assessment in the Federal Government: Managing the Process*. National Academy Press, Washington, DC, USA, 1983.
- 32. National Research Council. Alternatives for ground water cleanup. Technical report, National Academy Press, Washington DC, USA., 1994.
- A. Ogata and R.B. Banks. A solution of the differential equation of longitudinal dispersion in porous media. U.S. Geological Survey Professional Paper, 411-A:27–36, 1961.
- 34. D.L. Parkhurst and C.A.J Appelo. Description of input and examples for PHREEQC version 3: A computer program for speciation, batch-reaction, one-dimensional transport, and inverse
geochemical calculations. U.S. Geological Survey Techniques and Methods, book 6, chap. A43, Denver, CO, USA, 2013.

- P.V. Roberts, M.N. Goltz, and D.M. Mackay. A natural gradient experiment on solute transport in a sand aquifer: 3. retardation estimates and mass balances for organic solutes. *Water Resour. Res.*, 22:2047–2058, 1986.
- 36. J.V. Rodricks. *Calculated Risks: The Toxicity and Human Health Risks of Chemicals in Our Environment*. Cambridge University Press, Cambridge, UK, 1992.
- 37. J.L. Schnoor. *Environmental Modeling: Fate and Transport of Pollutants in Water, Air, and Soil.* John Wiley & Sons, Inc., New York, USA, 1996.
- K. Sexton, M.A. Callahan, and E.F. Bryan. Estimating exposure and dose to characterize health risks: The role of human issue monitoring in exposure assessment. *Environ. Health Perspect.*, 103:13–29, 1995.
- D.K. Todd and L.W. Mays. Groundwater Hydrology, 3rd Edition. John Wiley & Sons, Inc., NJ, USA, 2005.
- U.S. EPA. Human Health Evaluation Manual, Supplemental Guidance: Standard Default Exposure Factors, OSWER Directive 9285.6-03. Cambridge University Press, Washington, DC, USA., 1991.
- 41. M.T. van Genuchten. A closed-form equation of predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.*, 49:213–233, 1980.
- W.J. Weber, Jr. Environmental Systems and Processes: Principles, Modeling and Design. John Wiley & Sons, Inc., New York, USA, 2001.
- 43. J.M. Wilson and P.J. Miller. Two-dimensional plume in uniform ground-water flow. *Am. Soc. Civil Eng. J. Hydraulics Div.*, 104:503–514, 1978.
- 44. www.atsdr.cdc.gov.
- 45. www.epa.gov.
- 46. www.epa.gov/iris.

INDEX

activity, 43 activity coefficient, 43, 47 advection, 82, 86 Antoine equation, 48 aqueous solubility, 43 aquiclude, 117 aquifer, 117 confined, 117 perched, 117 unconfined, 117 aquitard, 117 assessment environmental impact, 38 risk, 38

BTEX, 42

capillary fringe, 117 capture zone, 125 carcinogen, 67 carcinogenesis, 67 chronic daily intake, 70 control volume, 38, 52

Darcy's law, 121 Davies equation, 47 degradation, 137 differential equation, 12 system of 1st order ODE, 18 first-order linear, 15 partial differential equation, 92

Fate and Transport of Pollutants in Environment. By S. Saenton, Chiang Mai University

separable variables, 14 diffusion, 82 molecular diffusion, 82, 88, 127 turbulent diffusion, 82 dispersion, 82, 96, 127 dispersion coefficient hydrodynamic, 99 longitudinal, 96 transverse, 99 vertical, 99 macrodispersion, 96 mechanical dispersion, 99 shear dispersion, 82 dispersivity, 100 dose effective dose, 63 lethal dose, 62, 67 eddy diffusivity, 99 epidemiology, 68 equipotential lines, 122 exposure, 61 acute, 61 chronic, 61 Fick's law, 82 first law, 88 second law, 92 gradient concentration gradient, 82, 84, 86, 88

161

162 INDEX

Henry's constant, 50 hydraulic conductivity, 122 hydraulic head, 121 intrinsic permeability, 122 ionic strength, 47 mass balance, 52 steady-state, 54 transient, 55 matric potential, 118 mechanical dispersion, 127 Microsoft Excel Solver, 101 MINTEQ, 47 mutagenesis, 67 mutation, 67 NAPL, 42, 146 DNAPL, 42, 146 LNAPL, 42, 146 numerical methods, 16 4th order Runge-Kutta, 16 Euler, 16 finite-difference, 21 Newton-Ralphson, 10, 45 partial pressure, 48 partition coefficient air-water, 51 PHREEQC, 47 pollutants, 38 definition, 38 properties, 43 types, 39 inorganic, 39 organic, 39 potency factor, 70 potentiometric surface, 117 principal directions, 103 rate constant, 138 reactor advection-dispersion, 85 continuously stirred tank, 84 plug-flow, 85 plug-flow with dispersion, 85 retardation factor, 133 Richards equation, 142 risk assessment, 65 risk characterization, 75 saturated zone, 117 slope factor, 70 soil vapor extraction, 144 sorption, 132 source of pollutant, 81 nonpoint source, 82

point source, 82

statistics, 24

stratification chemical, 99 thermal, 99 toxicology, 61 environmental toxicology, 61 tracer test push-and-pull, 100 single-well, 100 units, 5 concentration, 8 derived units, 6 fundamental units, 6 unit conversion, 5 unsaturated zone, 117 vadose zone, 118 vapor pressure, 43, 48 velocity Darcy velocity, 88, 121 groundwater velocity, 88 pore velocity, 121 seepage velocity, 88 shear velocity, 97 specific discharge, 88 VOC, 144 water table, 117

confidence interval, 29

goodness-of-fit, 34

Chi-square, 34

paired t-test, 35

least-square regression, 26 measurement errors, 24

coefficient of determination, 35

