FRANK M. DUNNIVANT
ELLIOT ANDERS

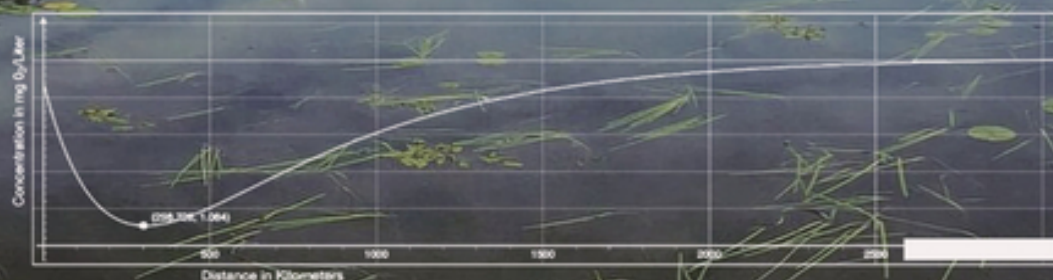# POLLUTANT FATE AND TRANSPORT IN ENVIRONMENTAL MULTIMEDIA

$$[H_2A] = C_T \left(\frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}} \right)$$

$$D = \frac{k_d BOD_{ultimate}}{k_r - k_d} \left(e^{-k_d\left(\frac{x}{v}\right)} - e^{-k_r\left(\frac{x}{v}\right)} \right) + D_o e^{-k_r\left(\frac{x}{v}\right)}$$

$$p\varepsilon = -\log\{e^-\}$$

$$W = Q_w\, C_w + Q_i\, C_i + Q_{trib}\, C_{trib} + P\, A_s\, C_p + V\, C_s$$

NPDES   CWA   CERCLA

$$DO = \frac{\%\ Saturation}{100} * Saturation\ Concentration - \left(\frac{k'BOD_L}{k_2' - k'}(e^{k'(x/v)} - e^{k_2'(x/v)}) + D_0 * e^{k_2'(x/v)} \right)$$

with website

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Pollutant Fate and Transport in Environmental Multimedia

Pollutant Fate and Transport in Environmental Multimedia

Frank M. Dunnivant
Elliot Anders

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To the chemists who have had a positive influence on my career: Loretta McLean, John Coates, Alan Elzerman, Philip Jardine, and Rene Schwarzenbach. And to my family, Marion, Lukas, and Marley. Thanks to all of you,

Frank M. Dunnivant

To my family, Tessa, Jude, and Elsa, thank you for supporting me throughout.

Elliot Anders

Contents

Preface

While there are many of textbooks on environmental chemistry and fate and transport phenomena, and they each have their place in education, this is the first book to truly integrate the subjects chemistry, fate and transport modeling, assessment, laws, and environmental laboratory experiments. The entire text was edited to ensure a consistent modeling theme that is vital to the regulatory applications of environmental fate and transport of contaminant science. These applications are truly multimedia in scope and encompass modern-day regulations in successful EPA approaches in the Clean Air Water and Drinking Water Acts. The related RCRA and CERCLA (Superfund) programs address hazardous and toxic materials and ensure that environmental and human health are equally protected. These laws use mathematical models to assess contaminant exposure that contribute to multiple adverse effects in the biosphere. Most books in this genre are conceptual in nature or require a working knowledge of differential calculus to effectively derive and use new models. This prerequisite effectively eliminates many people from working in fate and transport.

We approach each of these topics initially from a conceptual perspective, and then, we explain the concepts in terms of the math necessary to model the problem. The only prerequisites for understanding the concepts covered in this book are a basic knowledge of algebra and first-year college chemistry. Mathematic enthusiasts will find the extensive, step-by-step, end-of-chapter derivations useful. This last feature is unique to all other textbooks. For the fate and transport modeling chapters (Chapters 4–9), we have included a simple, user-friendly web-based, online simulator, Fate®, which uses basic step and pulse models to predict the fate and transport of pollutants in lake, river, groundwater, and atmospheric systems. Fate® can be an effective teaching and learning tool, as discussed in the "How to Use Fate" section of the introductory materials.

This book is the result of a challenge I made to one of my senior chemistry students. I challenged Elliot Anders, the coauthor of this book, to create a new version of EnviroLand, the precursor to Fate®. If he did so, I told him, I would write a book to accompany it. To my surprise, Elliot finished the software in a few months and to meet my end of the bet, I had to write the 2006 textbook around the software. We feel that this textbook provides a very unique instructional tool for students and environmental professions who lack the rigorous mathematical backgrounds to be able to derive the governing fate and transport equations, but nonetheless require an understanding of the subject. This book can be used to teach a variety of classes, from a new type of environmental chemistry course to new fate and transport courses for support personnel who want to work in the environmental arena. I use the book to teach environmental chemistry to undergraduate students majoring in chemistry, geology, and biology, to mostly prepare them for work in the environmental consulting arena and government. These students usually have sufficient background to work in environmental remediation but lack the basic engineering knowledge to be truly effective in this area. I have had great success in expanding the academic horizons of science students to areas of chemistry, modeling, risk assessment, and environmental legislation. In addition, there is no reason that this book cannot be used in a graduate course in fate and transport, since it provides an especially extensive and complete development of fate and transport models. In this case, the professor can use the book as a conceptual guide while teaching the derivation portion of the course in the classroom.

New additions to this book include free software available at https://sites.google.com/a/whitman.edu/frank-dunnivant-webpage/environmentalsoftware:

- an Web-based Pollutant Fate and Transport Simulator, (Fate®)
- a pC-pH Simulator
- Water and Wastewater Plant Tour Video
- EnviroLab
- More end-of-chapter problems with answers to the more complicated problems

- New environmental lab chapters on the United States, European Union, and China
- Student lab results for suggested experiments
- A supporting discussion-based book entitled *Environmental Success Stories* with Columbia University Press

We hope you enjoy our approach to environmental chemistry and pollutant fate and transport modeling.

Frank M. Dunnivant
September 2018

Acknowledgments

A book of this detail and 20-year effort has involved many people. First, I thank my coauthor, Elliot Anders, for challenging me to make the software better than the original Visual Basic version. Next, I thank Raymond Whittemore for writing, editing, and making many, many excellent suggestions. Note Dr. Whittemore's experience with, and knowledge of regulatory modeling were essential to the revised theme of this edition. Ray participated in water quality modeling training workshops for more than a decade for EPA's Exposure Assessment Laboratory in Athens, GA. Late in his career, he participated in the EPA Council for Regulatory Environmental Modeling (CREM) development in a leadership role in the surface water quality modeling group discussions.

Then, I thank Dr. Nate Boland and his students for testing this book and materials in his Environmental Chemistry and Engineering class at Whitman College. Certainly, a great thank you goes to my former student John Brooksbank for derivations of the many pollutant fate and transport equations that do not appear in any textbook in this detail. Many students can earn an A in differential equations but few can apply the knowledge like John has. The end-of-chapter problems, answers, and laboratory experiment results have been provided by 19 years of students taking my classes. I thank all of you for a job well done.

Acronyms

α	alpha type of radiation	CF	Risk: pollutant concentration in the fish or shellfish (mg/kg)
ADD	average daily doses	CF	Risk: pollutant concentration in the fish (mg/kg d)
AF	Risk: soil to skin adherence factor (mg/cm^2)	CFL	compact fluorescent lamp
AID	maximum acceptable daily intake	CH_4	chemical formula for methane (gas)
Al_2O_3	aluminum oxide	CO	carbon monoxide; Colorado, a state in the United States
A_s	mean lake or system surface area, m^2	CO_2	carbon dioxide
AT	Risk: average time period of exposure (days)	CO_3^{2-}	carbonate
AMD	acid mine drainage	COC	contaminants of concern
β	beta type of radiation	COE	Army Corps of Engineers
BAP	best available practice	C_p	the net pollutant concentration in precipitation, kg/m^3
BFC	bioconcentration factors		
BOD	biochemical oxygen demand	CR	Risk: contact rate (0.050 l/h)
Bq	Becquerel	CREM	EPA Council for Regulatory Modeling
BW	Risk: body weight (kg)	C_s	the average pollutant release from suspended lake sediments, kg/m^3-time
c	the speed of light in a vacuum (2.99×10^8 m/s)		
C	the pollutant concentration in the water (mass/length^3 or volume; mg/l, etc.) or molar charge	CS	Risk: pollutant concentration in the soil (mg/kg)
		CSTR	continuous stirred tank reactor
Ci	curies, a measure of radiation	C_T	the total concentration of all chemical species for this chemical
C_i	the pollutant concentration in the main inlet river or system, kg/m^3		
$C_6H_{12}O_6$	chemical formula for glucose	C_{trib}	the net pollutant concentration of the tributaries, kg/m^3
CA	Risk: pollutant concentration in the air (mg/m^3)	C_w	the pollutant concentration in the wastewater, kg/m^3
CAS	Chemical Abstract Number	CW	Risk: pollutant concentration in the drinking water (mg/L)
CCA	Air Quality Act, The Clean Air Act		
CCRs	coal combustion residuals	CWRA	Clean Water Restoration Act
CDC	Center for Disease Control and Prevention	d	average stream depth
		DBMS	Database Management System
CEAM	EPA Center for Exposure Assessment Modeling	DDT	1,1′-(2,2,2-trichloroethylidene) bis[4-chloro-benzene]
CEC	cation exchange capacity	DEM	Dynamic Estuary Model
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act	DNAPL	dense nonaqueous phase liquid(s)
		DO	dissolved oxygen
		DOD	Department of Defense
CF	Risk: volumetric conversion factor for water (1.00 l/1000. cm^3)	DOE	Department of Energy
		DWEL	drinking water equivalent levels
CF	Risk: pollutant concentration in the food (mg/kg)	e^-	an electron

E	energy; longitudinal eddy diffusion term		k	the first-order removal rate for the pollutant, 1/time
ED	Risk: exposure duration (number of years)		k_d	the first-order BOD decay rate
EDC	endocrine disrupting compound		k_r	the DO re-aeration rate
EDTA	ethylenediaminetetraacetic acid		k_{NOM}	the rate constant in the presence of Natural Organic Matter (NOM)
EF	Risk: exposure frequency (d/yr)		K_a	the acidity equilibrium constant
EFDC	Environmental Fluid Dynamics Code		K_b	the basicity equilibrium constant
E_H	oxidation–reduction potential		K_d	distribution coefficient
EIS	environmental impact statement		K_H	air-water Henry's law constant
EPA	Environmental Protection Agency		K_p	partition coefficient
EPA LUST	Environmental Protection Agency Leaking Underground Storage Tank		K_{sp}	solubility product constant
EPCRA	Emergency Planning and Community Right to Know Act		K_w	the water ionization constant; 1.00×10^{-14} (at 25 °C)
EPTT	extraction procedure toxicity test		λ	the wavelength in meters
ESA	Endangered Species Act		l	liters, a measure of volume
EXAMs	Exposure Analysis Modeling System		LCA	life cycle assessment
F	Faraday constant (96 485 C/mol of electrons)		LCOE	levelized cost of energy
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act		LED	light-emitting diode
			ln	natural logarithm
Fe_2O_3	iron oxide		LNAPL	light nonaqueous phase liquid
$FeCO_3$	iron carbonate		LOAEL	lowest-observed-adverse-effect level
FI	Risk: fraction of soil ingested from the polluted site		LOEL	lowest-observed-effect level
			LUST	leaking underground storage tank
FWPCA	Federal Water Pollution Control Act		J	Joules, a measure of energy
γ	gamma type of radiation		μ	ion strength
g	the acceleration due to gravity (length/time^2)		M	molarity, mol/l
			M_o	the total mass of pollutant in the river
g	grams		meq	milliequalivance
GEOCHEM	a numerical modeling program for determining chemical speciation		NEPA	National Environmental Policy Act
			MIC	methyl isocyanate
GLBTS	Great Lakes Binational Toxics Strategy		MINTECH	a numerical modeling program for determining chemical speciation
η	kinematic viscosity of the fluid (length^2/time)		MINEQL+	a numerical modeling program for determining chemical speciation
h	Planck's constant (6.63×10^{-34} J s)		NIOSH	National Institute for Occupational Safety and Health
H	the water depth (length)		MnO_2	chemical formula for manganese dioxide
H^+ or H_3O^+	hydronium ion, acidic hydrogen		MPRSA	Marine Protection, Research, and Sanctuaries Act
H_2O	chemical formula for water			
HRS	hazardous ranking system		MTBE	methyl *tert*-butyl ether
HCl	hydrochloric acid		NAAQS	national ambient air quality standard
HCO_3^-	hydrogen carbonate, bicarbonate		NEPA	National Environmental Policy Act
H_2CO_3	carbonic acid		N_2	chemical formula for nitrogen gas
HQ	hazard quotient		NOM	natural organic matter
H_2S	hydrogen sulfide gas		NO_x	combinations of nitrogen oxide and nitrogen dioxide
HS^-	chemical formula for hydrogen sulfide ion		NO_3^-	chemical formula for nitrate
INEEL	Idaho National Engineering and Environmental Laboratory		NOAEL	no-observed-adverse-effect level
			NOEL	no-observed-effect level
IR	Risk: inhalation rate (m^3/d)		NPL	National Priorities List
IR	Risk: ingestion rate of water (l/d)		NTA	nitrilotriacetic acid
ISC	industrial source complex		O*	radical gaseous oxygen

OH^-	hydroxide ion	SA	Risk: skin surface area available for contact (cm^3)
OH^*	radical gaseous hydroxide		
O_3	ozone gas	SAP	sampling and analysis plan
OPA	Oil Pollution Act	SARA	Superfund Amendments and Reauthorization Act
OSHA	Occupational Safety and Health Act or Administration		
		SCRAM	support center for regulatory atmospheric modeling
p	as in pC or p(anything); represents the negative log of the quantity; example: pCO_2 represent the negative log of the carbon dioxide molar concentration in pC–pH diagrams		
		SDWA	Safe Drinking Water Act
		SIP	state implementation program(s)
		SPARC	chemical parameter estimator software from EPA
pH	negative log of the hydrogen ion concentration	SOD	sediment oxygen demand
		SO_x	a combination of sulfur dioxide and sulfur trioxide gases
pH_{ZPC}	the pH where there is no surface charge		
		SO_4^{2-}	chemical formula for sulfate
P	annual precipitation, m/time; phosphorus	SWDA	Solid Waste Disposal Act
		T	temperature
Pb	lead	t_o	detention time of water or chemical in a system
PBDE	polybrominated diphenyl ethers		
PCBs	polychlorinated biphenyls	TAN	Test Area North
PFOA	perfluorooctanoate	TAN-05	injection well (Test Area North)
PFOS	perfluoroocotanesulfonate	TCE	trichloroethylene
PPA	Pollution Prevention Act	TCLP	toxicity characteristic leaching procedure
ppb	parts per billion		
ppm	parts per million	TDS	total dissolved solids
PSD	prevention of significant deterioration	TESS	threatened and endangered species system
PZC	point of zero charge in clay titrations		
PZSE	point of zero salt effect	TEA	terminal electron acceptor
Q_e	the outlet or effluent flow of water from the lake or system (m^3/time)	THM	trihalomethane
		TMDL	total maximum daily load
Q_i	the inflow rate of the main river water or system, m^3/time	TRI	toxic release inventory
		TSCA	Toxic Substances Control Act
Q_{trib}	the net inflow rate of water from all other tributaries, m^3/time	TSS	total suspended solids
		US EPA	United States Environmental Protection Agency
Q_w	the inflow rate of water or wastewater, m^3/time		
		USGS	United States Geologic Survey
r	the spherical particle radius (length)	USTs	underground storage tanks
R	ideal gas law constant, with a variety of units; ion radius	v	the frequency of light (1/s)
		V	volume, in $length^3$ or l
r_A	the rate of decrease in pollutant A concentration per unit volume of water (mass/$length^3$-time)	ω	settling velocity of a particle in natural water
		w	average stream width
RCRA	Resource Conservation and Recovery Act	W	the mass input of pollutant to the lake (or system) per unit time, kg/time
r_f	the density of the fluid (mass/length3)	WASP	water quality analysis simulation program
RfD	reference dose		
RI-FS	remedial investigation-feasibility study	WES	Waterways Experiment Station of the Corps of Engineers
r_s	the density of the spherical particle (mass/$length^3$)	Z	charge of an ion
		z/R	ionic potential (charge/radius)
s	the slope or gradient of the stream bed		
S	the suspended solids concentration (mass/$length^3$)		
SA	(cross) sectional area		

Glossary

Adsorption	The process of accumulating an excess of a chemical on a surface. As used in this text, it refers to the concentrating of pollutant on a mineral or NOM-coated mineral surface.
Advection	The transport of pollution in the direction of flow.
Anaerobic	An aquatic or atmospheric system that does not contain oxygen. This term is the same as anoxic.
Anoxic	Devoid of oxygen.
Abiotic reaction	A chemical reaction that takes place without the aid or in the complete absence of microorganisms.
Basel convention	An international treaty regulating the reporting, disposal, and transport of hazardous waste. The United States is currently not a member of this treaty.
Biota	Any living organism in an ecosystem.
Biotic reaction	A chemical reaction that occurs due to a microbial process (enzymes in the microbe cell).
BOD	Biochemical oxygen demand, the amount of dissolved oxygen required by microorganisms to oxidize organic matter present in the water.
Cation exchange capacity (CEC)	The concentration of sorbed cations that can be readily exchanged for other cations.
Confined aquifer	An underground body of flowing water that is located below the layer of strata that is impermeable to water.
Conservative tracer	A chemical tracer that does not degrade and is not sorbed by anything in the water. The chemical moves freely with the water.
Contaminant	A chemical that is out of its proper place. In this text, we will use the term contaminant and pollutant interchangeable.
Dispersion	A mixing process resulting from advection which always dilutes the concentration of pollutant.
DNAPL	Dense nonaqueous phase liquid. An example is carbon tetrachloride.
DO	Dissolved oxygen; the concentration of dissolved oxygen in water, usually from 0 to 14 mg/l.
DOM	Dissolved organic matter. These are components of NOM that are soluble is water.
E	The longitudinal dispersion (eddy) coefficient for streams.
Environmental impact statement	A study required by the National Environmental Policy Act to attempt to determine if any adverse effects will occur from governmental actions such as the building of a building, plant, or even a remediation effort.
Empirical	A relationship based on experiment data.
Epilimnion	The upper region of a stratified lake.
Eutrophication	An overproductive aquatic system. Excess alga growth occurs during the day due to the presence of excess nutrients, but during nighttime hours, the oxygen is depleted below levels that can support aerobic life.

Explanative modeling	A model that attempts to explain how something happened. For example modelers can use mathematical relationships to explain how a pollutant moved to where it is, where it originally came from, or how much pollutant was originally released.	Partitioning	Partitioning is very similar to adsorption but does not involve a site-specific reaction. It is more of a solvation or dissolving of a pollutant into NOM.
Head	The height of a water column.	pC	A way of representing concentration units on the log scale. "p" stands for the negative log of anything. "C" stands for the concentration (in any units) of any chemical species.
Hypolimnion	The lower or bottom region of a stratified lake.		
LNAPL	Light nonaqueous phase liquid. An example is gasoline.	pH	The negative low of the hydrogen ion concentration.
Longitudinal dispersion	The mixing of pollution in water or air in the direction of flow.	Point pollutant source	A source of pollution that can be pinpointed to a specific location. For example the output pipe from an industrial process or sewage treatment plant would be a point source.
Modeling	An attempt to explain a process in a simpler form. Models can take on several forms including physical models that are usually small-scale versions of the real thing. We will limit our discussions in the text to mathematical models, which are very simple mathematical relations of more complicated processes. The more the terms we include in our models, the more the processes we account for in our model and theoretically, the more accurate our model will predict the real system.	Predictive modeling	A model that attempts to predict what will happen at a future time. For example, in this text, we are concerned with predicting the concentration of pollutant at some point (location or time) in the future.
		Pulse or instantaneous release of pollutant	A release of pollutant that occurs over a very short time scale and contains a finite volume or mass of pollutant. This type of release is in contrast to a step or continuous pollutant release.
NAPL	Nonaqueous phase liquid. An example would be oil or gasoline.	Refractory pollutant	A pollutant that does not readily degrade (degrades slowly or not at all).
Nitrobenzene	A benzene molecule with an attached nitro (NO_2) group. Nitrobenzenes can also have other functional groups such as methyl (CH_3), chloro (Cl), and many other chemical groups attached to the benzene ring.	Remediate	To cleanup a waste site to acceptable pollutant concentrations.
		Residence time	The average time a chemical spends in an environmental compartment. This can be obtained by dividing the volume of the compartment or mass of a chemical in a compartment by the outflow from the system (volume / volume per time = average residence time).
NOM	Natural organic matter. NOM results from the accumulation of degradation products from plants and animals in soil and water.		
Nonpoint pollutant source	A source of pollutant that cannot be identified as a specific location. Examples would be runoff from a large area of land such as a parking lot or agricultural setting and atmospheric inputs.	Sensitivity analysis	An iterative process of testing a model where one parameter at a time (volume, rate constant, etc.) is systematically increased or decreased while the result (pollutant concentration) is recorded.

Sorption | A generic term referring to the combination of adsorption and partitioning.

Stratification | A process that results in two distinct layers of water in a lake system. Stratification results due to heating of the surface water and cooling of lower waters by the Earth that sets up a density difference in the two bodies of water. The cool water settles to the bottom of the lake, while the warmer water is present at the surface.

Surface aquifer | The ground water closest to the land surface.

Step or continuous pollutant release | A release of a pollutant that occurs over a long-time scale. Examples include the constant release of sulfide from a pulp mill and the release of nitrate from a sewage treatment plant.

Vadose zone | The portion of the ground that is unsaturated with respect to water.

Variable | A symbol representing a mathematical term or the term of interest in a mathematical expression. For example, velocity is an important term in fate and transport, and it is represented by the variable, v.

Watershed | The drainage area of land surrounding and feeding water into a lake or river basin.

About the Companion Website

This book has a companion website hosted by Wiley:

www.wiley.com/go/Dunnivant/pollutant_fate&Transp_EnvironMultimedia

To the Instructor

The material in this textbook has been used for 19 years to teach an undergraduate course in environmental chemistry to chemistry, biology, and geology students who have not completed linear algebra or differential equations. Students from these disciplines tend to have excellent skills and knowledge in environmental studies but lack an understanding of how to apply this knowledge to environmental applications such as fate and transport modeling and risk assessment. Students feel a strong sense of empowerment as they come to understand how to approach an environmental pollution event and gain an appreciation of the many scientific and political factors controlling the remediation of contaminated sites. Software packages are integrated into the textbook, and we have suggested important technical papers for class discussion for many of the chapters. In addition, we have designed laboratory exercises specific to the topics covered in the lecture material. This textbook would be ideal for an introductory course in environmental chemistry, pollution science, environmental science, environmental engineering, or pollutant fate and transport. One particular useful discussion book is my popular science book, entitled *Environmental Success Stories: Solving Major Ecological Problems & Confronting Climate Change.*

A set of laboratory exercises have been designed for this textbook. As with all laboratory experiments, it will be instrumental that the instructor test the procedures prior to using them. This will ensure the success of your laboratory class. A complete set of instructions for solution preparations, suggested level of difficulty, suggested lab time requirements, apparatus construction guidelines, hints for success, and *detailed example student results* are included in this book.

To the Student

This is a new type of textbook, in the sense that it combines many disciplines to craft a practical discussion of environmental pollution and its remediation. We first start with an overview of the chemistry of fate and transport processes. Next, we introduce you to how professionals model a pollution event in the real world and then present you with a conceptual understanding of the models that these professionals use. At the end of each fate and transport chapter, we incorporate our conceptual ideas into two simple and common models that can be used to predict the pollutant concentration in most environmental systems. Next, we use the results from fate and transport modeling as a basis for our risk assessment calculations to determine whether a hazardous situation is present. The final chapters include environmental legal aspects and case studies of common pollutants that have been spread around the world.

To the Environmental Professional

While most environmental engineers will find this book to be a basic review, many of other environmental professionals who do not understand the derivation of complex environmental models will find this book to be a valuable asset for developing a conceptual and mathematical understanding of the problem. Our goal is to bridge the knowledge gap between the engineers and mathematicians and the many important workers associated with a Superfund site. The only prerequisites for understanding the subjects covered in this book are a working knowledge of algebra and college-level general chemistry. We provide the background and explain everything else. If you are an engineer or modeler working in the environmental arena, you will find this book to be a must for your colleagues.

How to Use the Book with Fate® and Associated Software

This book comes with several online software packages, Fate®, the pC-pH Simulator®, EnviroLab®, and The Water and Wastewater Tutorial®available at https://sites.google.com/a/whitman.edu/frank-dunnivant-webpage/environmentalsoftware. Fate is certainly the most important tool, since it can be used in a variety of ways (https://educationalsolutions.github.io/fate/). First, Fate can be used as an in-class tool to illustrate how each of the fate and transport models work. It enables the instructor to quickly and easily show how changing model input parameters affect the resulting pollutant concentration. Students and instructors will find Fate to be an invaluable resource in working homework problems. All these problems require lengthy, multistep calculations, and each step can be checked with Fate. This decreases the need for students to rely on a tutor or their instructors, who in turn would have to manually examine through the students' work to find errors. We suggest the following approach. First, work the homework problem manually, consulting Fate only when you do not understand which calculation step to complete next. Check your manually calculated answers at each step in the process against Fate to see if you are correct. If you do not understand why you are doing a calculation, then certainly consult your instructor. The pC-pH Diagram Simulator (https://educationalsolutions.github.io/pCpH//open/) works in a similar manner to Fate but is used only in Chapters 2 and 3 to understand acid–base equilibrium and buffers. The Water and Wastewater Tutorial (https://sites.google.com/a/whitman.edu/frank-dunnivant-webpage/environmentalsoftware) can be viewed on your own time or in class to illustrate how modern water and wastewater treatment facilities work. Components of EnviroLab (https://sites.google.com/a/whitman.edu/frank-dunnivant-webpage/environmentalsoftware) are useful in understanding details of several laboratory experiments. Readers will find the Internet sites of EPA, USGS, and the Army Corps of Engineers useful in acquiring source code, documentation manuals, and training for most of those models used in the regulatory domains. Historically, these agencies have supported these models and developed new ones when the science dictates. More importantly, personnel at the state and national levels may assist in their use by the public.

Instructor/Student Resources

The following computer resources are available for this textbook from https://sites.google.com/a/whitman.edu/frankdunnivant- webpage/environmentalsoftware:

Computational Simulators for Chemistry and Fate and Transport Calculations:

Fate-2016 ®
pC-pH ®
Dispersion Calculator for groundwater experiments

Videos:
    Global Issues
    Water
Laboratory Experiment Simulators:
    Alkalinity
    Hardness
    Dissolved Oxygen – Biochemical Oxygen Demand
    Total Suspended Solids
In addition, all lab experiments presented in Chapter 16 have example student results.

Part I

Introduction

Through the history of literature, the guy who poisons the well has been the worst of all villains

Author unknown

1

Sources and Types of Pollutants, Why We Need Modeling, and the Need to Study Historical Pollution Events

1.1 Introduction

A good starting point for our discussions and this book is to ask, "Is there a common sequence of events leading to the identification, characterization, and remediation of an old hazardous waste site?" There are a variety of answers to this question, but a general order of events often occurs as follows:

- 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 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 planning assessment (also called an environmental impact statement, EIS).
- Second, the source of the pollutant is identified at the hazardous waste site or a theoretical release can be simulated.
- Third, a remedial investigation is conducted to determine the mass/volume of pollutant released and responsible parties.
- Fourth, pollutant fate and transport modeling is completed to determine what pollutant concentrations will result at specific points at the site over time (referred to as receptor sites where humans are the receptors of the pollutants).
- Fifth, the results of the pollutant fate and transport modeling are used in risk assessment calculations to estimate health or environmental/ecological risks. A common use of modeling in the twentieth and twenty-first centuries is in air and water quality environmental management and related to compliance with ambient air or water quality standards (EPA 2017a). Essentially, the model purports the allowable discharge or emission rates to maintain acceptable air or water quality.
- And finally, a decision or plan of remediation is negotiated between the local citizens, local and federal governments, and the party responsible for the hazardous waste site.

Today, new pollutant releases from regulated industries take on a slightly different approach. In the Global North, previously referred to as developed countries, most industries act responsibly, but all human-designed, engineered, and operated systems are prone to failures and accidents. In general, a slightly modified sequence of events occur: a spill or accident occurs, emergency response systems respond, and remediation (when possible) occurs. Responsible parties usually pay the incurred expenses, and appropriate fines if regulations have been broken.

These steps also outline our approach in this book. In this chapter, we will look at several historical hazardous waste release events, as well as recent ones, and describe types and sources of potential pollutant releases. In Chapters 2 and 3, we will look in-depth at the chemistry associated with fate and transport phenomena in environmental media. In Chapters 4–10, we will develop and learn to use pulse and step fate and transport models for rivers, lakes, groundwater, and the atmosphere. In Chapter 11, we will introduce basic chemical toxicology and use pollutant concentrations from the fate and transport modeling to perform basic risk assessment calculations to estimate risk to human health, look briefly at cost–benefit analysis, and the relatively new field of environmental life cycle assessment. In Chapters 12–14, we will look at the development and evolution of environmental laws in the United States and Europe. In Chapter 15, we will look at the history of several "world class" pollutants that are present at undesirable concentrations across the globe. In the last Chapter 16, laboratory experiments that support key chemical and modeling concepts will be presented, with actual student results.

1.2 Need for Modeling of Pollutants in Environmental Media

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 state and federal government agencies. Historically, two of the chemicals that fall into this category and receiving much public attention are PCBs (polychlorinated biphenyls) and DDT (1,1′-(2,2,2-trichloroethylidene)bis[4-chloro-benzene]). These compounds accumulate especially well in the environment due to their refractory behavior (they are not easily chemically or biologically degraded). More importantly, their chemical and physical properties are such that they bioaccumulate in fatty tissue in many organisms. Modelers like to divide nature into more easily mathematically described boxes, such as the atmosphere, rivers, lakes, groundwater, and biota (living organisms). In this book, we simplify this further by only considering one section of a river, a small portion of a groundwater aquifer or a small portion of the atmosphere.

There are two basic goals in pollutant modeling: to explain how a pollutant arrived where it is (a form of thermodynamic equilibrium) and to predict how fast a pollutant will move through an environmental compartment in the future (a form of kinetics). Some engineers call this all-compassing field "chemodynamics" to reflect its transport, phase transfer, and equilibrium components. There are several excellent textbooks based on these principles (Thibodeauz 1996; Hemond and Fechner 2000). Later in this chapter, we will look at several examples of major pollutant release events; the approach taken to these reflects the first goal of modeling (an explanation of how a pollutant arrived where it is). Although this approach is very important to understand how pollutants move in the environment, a more common use of modeling today is to predict if and/or how fast a pollutant will move once it is accidentally released. In the United States, this is included in an EIS. Most Global North countries require a variety of industries to perform some type of environmental impact modeling in the unlikely and unfortunate event of an accidental pollutant release, which again is inevitable with most human-engineered systems. This book will concentrate on predictive modeling, but by understanding the processes involved in the predictive modeling approach, it is relatively easy to appreciate how the explanation type of modeling is completed.

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, outflow through the effluent of the system, evaporation, volatilization, and chemical or biological degradation. Transport of chemicals is part of its fate. The same modeling equations and concepts are used for the explanation type of modeling (where pollution already exists) but a reverse process is used. In explanation modeling, the modeling equation is fit to pollutant concentration data from field measurements in order to obtain estimates of mixing and degradation rates in the specific system. Both modeling approaches will become clearer when we reach the modeling chapters in this text, especially beginning in Chapter 4.

1.3 Pollution versus Contamination; Pollutant versus Contaminant

Is there really a difference between the terms pollutant and contaminant? Some would argue no, while others will argue vehemently yes. In the United States, environmentalists and those working for US Environmental Protection Agency (US EPA) prefer the terms pollution and pollutant. But what makes a chemical a pollutant? Basically this distinction is determined by where the chemical is located and how much of the chemical is present. For example, a bottle of mercury chloride is typically not considered a pollutant when it is sitting on the shelf in a chemical storeroom. But pour that same chemical down the drain, and it immediately becomes a pollutant, even at extremely low concentrations. This is the logic behind usage preferred by other branches of the US government, such as the Department of Energy (DOE). The DOE prefers to use the terms contamination and contaminant. If a chemical is in its proper place it is not considered a problem and is thus not a contaminant. Likewise, if a chemical is present in an environmental media below the concentration deemed to be a problem (which is subject to a variety of views and laws), then the chemical is not a problem and contamination is not necessary present. Thus, the legal definition usually specifies two factors, where the pollutant is and its concentration. For example, the first author of this book (Dunnivant) worked on a project for the Idaho National Engineering and Environmental Laboratory (INEEL), one of many US DOE sites, in which we intentionally placed a rapidly degrading radioactive substance in a water-filled lagoon in order to characterize the movement of water and radionuclides in the subsurface media. As long as the chemicals stayed within the controlled boundaries of the lagoon (the approved experimental area) they were not considered a contaminant. But one day a violent storm blew a small amount of the water and sediment a few feet out of the lagoon. The DOE safety officials

overreacted and suspended all operations at the site for a time period that jeopardized a multimillion dollar field experiment! Although the vast majority (we would speculate over 99.99%) of the chemical was still present in the lagoon, the extremely small amount of chemical "released" (amounting to a few specks of dirt) was officially classified as a contamination event. Similarly, in the 1980s chlorinated dioxins and furans were attributed to wood pulp bleaching to achieve acceptable brightness attributes. In these cases, concentrations in the parts per trillion (10^{-12}) and parts per quadrillion (10^{-15}) were routinely part of the technical conversation, and they were termed "pollution" in most cases by technical and lay personnel (EPA 2017b). Today, wood pulp and paper processing plants have replace chlorine with peroxide to achieve the product with less pollution. So, when you use the terms pollution versus contaminant be aware who you talking to. In this book, we will use the more common terms pollutant and pollution.

1.4 Pollution Classifications

There are perhaps as many ways to categorize types of pollution as there are pollutants. One broad way to by physical phase: solid, liquid, or gaseous. This categorization is useful from a standpoint of treatment and disposal. Many treatment technologies are based on the physical phase of the pollutant, such as bag filtration houses for atmospheric particulates or filtration of particles in liquids. Another general but more chemical means of categorization is the inorganic, organic, and radioactive nature of the waste. Mixed waste, a very difficult, if not impossible waste to treat, usually refers to organic and radioactive waste being present in the same waste product. Inorganic waste can be further broken down into non-toxic and toxic metals, metalloids, and non-metals. Metal waste can be subdivided into heavy metals and transition metals. Toxic wastes can be grouped as carcinogens, teratogens, and mutagens (discussed in Chapters 11 and 12). Compounds that are subjects of heightened public awareness, such as PCBs, are divided out even further. Other wastes are listed as hazardous based solely on their origin from a specific industrial process (for example, metal plating wastes) or when a specific chemical is present in the waste stream (for example, the presence of PCBs). As you see there are many ways to categorize or list a waste and each country will have their own system for classifying pollutants. In the modern era, some compounds are known to accumulate in organism tissue with high lipid content that further increases the human health risk associated with their presence.

Another interesting way to categorize waste is by the risk it poses. For example, say you have a hazardous waste site that needs to be remediated and there are 20 pollutants of interest. But, from a risk standpoint, 5 of the 20 pose a significantly higher hazard based on risk assessment calculations (Chapter 11). In some countries, it is customary to focus the remediation effort on these 5 chemicals and disregard the other 15 "less hazardous pollutants." Such an approach is used by the US EPA to calculate health risk based on source and an overview of the approach is shown in Figure 1.1.

1.5 Sources of Pollution

As with types of waste, there are many ways of categorizing sources of waste (or potential pollutants). We will only mention a few of the more useful approaches and give examples of generated volumes from major industrialized countries. First, we will discuss point and nonpoint sources.

Sources of pollutants are commonly divided into one of two types, point or nonpoint sources. Point sources are well-defined sources, such as the end of a pipe, smoke stack, or drain. Nonpoint sources are less well defined, but contain all sources where you cannot directly pinpoint the emission. The distinction becomes a bit more vague depending on physical scale. For example, if you are studying a large watershed (the land surface that drains into a stream or lake), a cattle holding lot could be considered a point source. Obviously, the farm is the source of the cattle waste. But on a smaller scale, what is the point source? The answer is possibly each cow, or the entire holding lot, since the pollution will be spread over its entirety. But, in general the terms point and nonpoint are used to describe sources.

Table 1.1 lists sources of waste by 10 categories: agricultural, chemical industry, mining industry, energy industry, municipal and hazardous landfills, medical industry, food processing, domestic waste, municipal government, and federal government. General wastes for each source are also listed in the right-hand column. This list is certainly not complete, but contains the major sources of waste generated and provides a starting point for discussion of waste sources.

The terminology of wet and dry deposition applies to ambient air and the mode of transport in the atmosphere. Rain and snow can act to "scrub" some contaminants from the air and deposit them on trees, plants, and the soil where erosion and runoff infiltration further distribute them across the surface and subsurface environments.

Since this book deals mostly with the transport of toxins, we will be especially concerned with hazardous
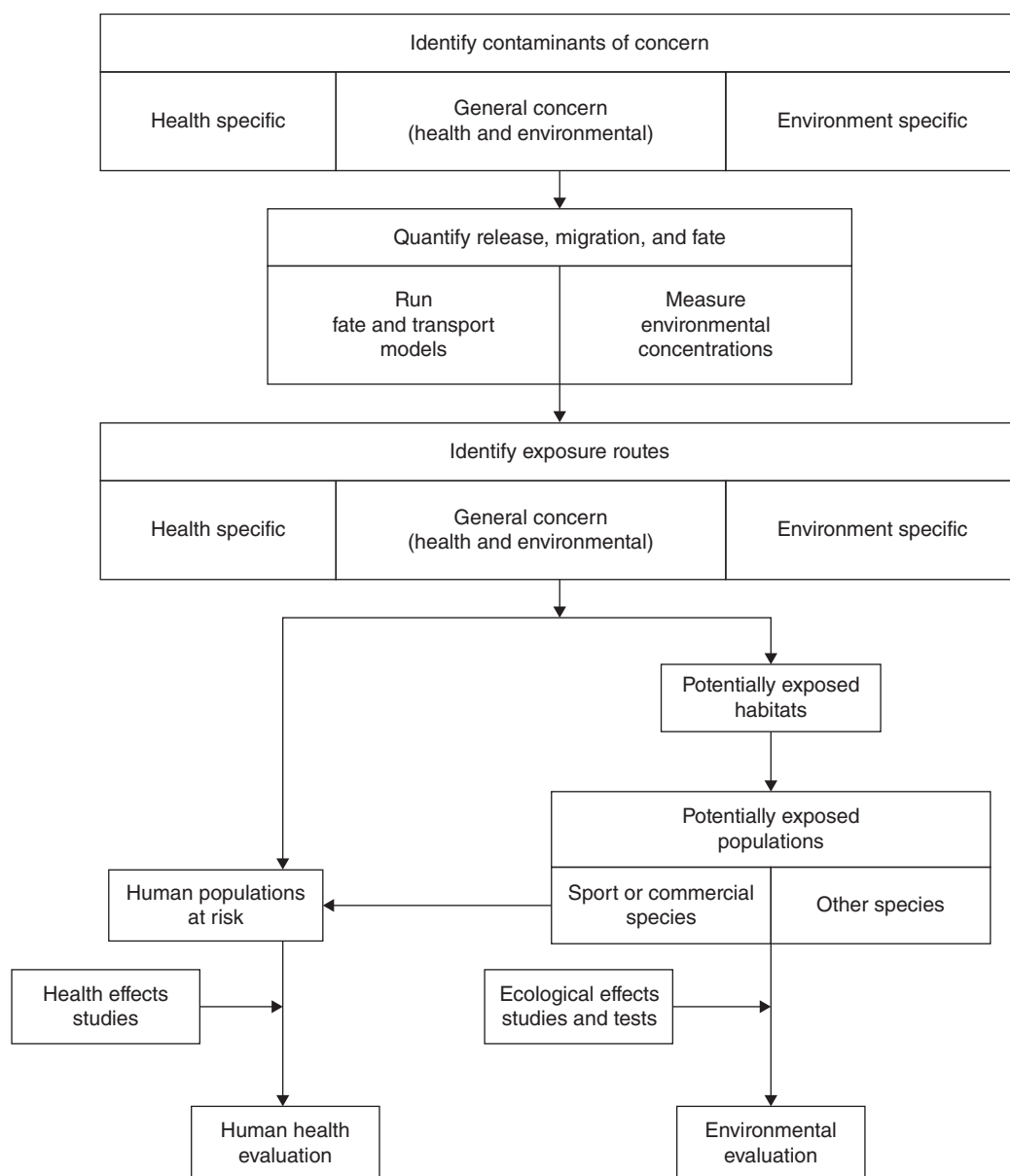
Figure 1.1 An overview of the approach to access human risk used in the United States. Source: DOE.

waste. A summary of the amounts of hazardous waste generated by country members of the Basel Convention (an international treaty regulating the reporting, disposal, and transport of hazardous waste) is given in Table 1.2 for the year 2000. Unfortunately this dataset is no longer available on the Internet, nor is updated total generation data available since data are now reported on an import–export basis. One would only speculate that the magnitudes of these values have increased and, in general, the more developed the country, still the more hazardous waste it generates. This correlation of waste to

economical level is a homework exercise that you should conduct and, by the way, it would make an excellent examination question. You will undoubtedly note the lack of data on two highly industrialized countries: Japan and Germany. Even without these two countries the total amount of hazardous waste annually generated is an obscene 93 992 999 metric tons in year 2000. Another country you will note absence from the list is the United States, since it has not signed the Basel Convention (UN 2000). For comparison purposes, the United States generated 40 821 481 tons in the year 2001 (EPA 2001),