

Fate and Transport of Contaminants in the Environment

© Copyright 2008 by College Publishing. All rights reserved. No part of this publication may be reproduced or transmitted in any form or by any means electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

College Publishing books are printed on acid-free paper.

ISBN: 1-932780-04-1

Library of Congress Control Number: 2008924389

College Publishing

12309 Lynwood Drive

Glen Allen, Virginia 23059

Phone (800) 827-0723 or (804) 364-8410

Fax (804) 364-8408

Email collegepub@mindspring.com

www.collegepublishing.us

Fate and Transport of Contaminants in the Environment

JOHN C. WALTON, P.H.D., P.E.

College Publishing
Glen Allen, Virginia

ALSO BY COLLEGE PUBLISHING

Journal of Green Building (ISSN 1552-6100) www.collegepublishing.us/journal.htm

*Journal of Engineering for Sustainable Development: Energy, Environment,
and Health* (ISSN 1553-4677) www.collegepublishing.us/jesdhome.htm

Writing Style and Standards in Undergraduate Reports (ISBN 0-9679121-7-2)

A C K N O W L E D G M E N T S

This book is dedicated to my wife, June, and our four children: Claire, Arthur, Mariah, and Rory. Many graduate students have contributed to the work, especially Gautam Agrawala, Omar Al Qudah, Drew Hall, Arturo Woocay, Masud Rahman, David Casey, Huanmin Lu, Sazzad Bin-Shafique, Floyd Johnson, Juan Clague, Sergio Solis, Reneé Hilton, Humberto Garcia, and Rob Rice. I would also like to thank the technical reviewers of the text who provided many constructive criticisms.

C O N T E N T S

1		
	Fate and Transport Basic Concepts	1
	Introduction	2
	Examples of Fate and Transport Problems	3
	Energy and Mass	8
	Review Materials	17
	Problem Approach	20
	References	20
	Problems	21
2		
	Transport by Random Motion—	
	Diffusion and Dispersion	23
	Diffusion and Dispersion—Fick's Laws	24
	More Complex Diffusion Equation Solutions	33
	Case History—Rocky Flats Plant Fire, Golden, Colorado	42
	References	46
	Problems	46
3	Interphase Mass Transfer and Partitioning	49
	Interphase Partitioning	50
	Properties Affecting Partitioning and Distribution	52
	Rates of Interphase Mass Transfer	61
	References	64
	Problems	64
4	Mass Balance Models	67

	Introduction	68
	Continuous Stirred Tank Reactors (CSTR)	69
	Modeling Environmental Systems as a Series of Stirred Tank Reactors (Box Models)	71
	Plug Flow Reactors—The Advection/Dispersion Equation	73
	Case History—Crystal Lake, Michigan Average Residence Time	76
	References	79
	Problems	79
5	Water Chemistry	81
	Introduction	82
	pH, Alkalinity, and the Carbonate Buffer System	87
	Oxidation/Reduction Chemistry	93
	Ocean Chemistry	98
	References	101
	Problems	102
6	Groundwater	105
	Groundwater Fundamentals	106
	Groundwater Flow	108
	Analytical Solutions for Groundwater Flow	115
	Transport in Groundwater	119
	Dispersion Versus Distance Examples	125
	References	132
	Problems	133
7	Surface Water	137
	Lakes, Ponds, Reservoirs, Ocean	138
	Streams and Rivers	145
	References	156
	Problems	156
8	Atmosphere	159
	Air Pollution Fundamentals	160
	Air Pollution Meteorology—Stability	163

Air Pollution Meteorology—Complex Terrain	172
Mathematical Modeling of Air Emissions	174
References	183
Problems	183
Index	185

LIST OF FIGURES

Figure 1-1. Temperature inversion as seen from Scenic Point, El Paso, Texas/Cd. Juarez Mexico. The temperature inversion limits mixing in the atmosphere leading to accumulation of airborne pollutants in the valley.	1
Figure 1-2. Example of contaminants leaking from a discharge site for radioactive waste.	3
Figure 1-3. Schematic of a gasoline spill.	5
Figure 1-4. Partitioning of gasoline on soil grains.	5
Figure 1-5. Schematic cross section of a conventional septic system with major chemical reactions shown below.	6
Figure 1-6. Control volume.	9
Figure 1-7. Single room or building as control volume.	11
Figure 1-8. Discharge into a river—control volume example.	11
Figure 1-9. Control volume for a problem of air pollution trapped in a mountain valley during a temperature inversion. The temperature inversion controls how high the smoke rises and forms the top of the control volume.	12
Figure 1-10. Advective velocity in a variety of environments (derived from Lerman, 1979).	13
Figure 1-11. Answer to problem 11.	22
Figure 2-1. Diffusion and dispersion occur at many different scales. Atmospheric dispersion of a volcanic eruptions (NASA).	23
Figure 2-2. Random motion.	25
Figure 2-3. Random motion of 30 particles in the same moving fluid.	25
Figure 2-4. Examples of diffusion and dispersion magnitude. Understanding the range of rates for each environmental process is essential to sorting important processes from unimportant ones in each environmental application.	26
Figure 2-5. Boundary conditions for one-dimensional problem.	27
Figure 2-6. Slowing of diffusion through porous media.	29

Figure 2-7.	
Diffusion coefficients of sodium chloride in water filled sediments of different porosity (Manheim, 1970).	31
Figure 2-8.	
Rate of aqueous diffusion ($D = 10^{-9} \text{ m}^2/\text{s}$). The one -year curve is truncated at the top.	34
Figure 2-9.	
Rate of gaseous diffusion ($D = 10^{-5} \text{ m}^2/\text{s}$). The curve for one hour is dashed and inside the curve for one day. The curves for one hour and one day are truncated at the top.	35
Figure 2-10. Solutions at two different time periods.	35
Figure 2-11. Boundary conditions for step function solution.	36
Figure 2-12. Solution method schematic.	36
Figure 2-13. Solution to equation 38.	37
Figure 2-14. Graph of functions used in analytical solutions.	38
Figure 2-15. Step function analytical solution behavior.	40
Figure 2-16.	
Drums and boxes being placed in trenches at the Radioactive Waste Management Complex, Idaho. Flooding of the trenches occurred during rapid snow melt in 1962 and 1969.	43
Figure 2-17.	
Estimated diffusion time. Dashed lines are when the diffusion coefficient is increased/decreased by a factor of five.	44
Figure 2-18.	
Estimated time for diffusion out of stagnant zones of given 1/2 width with a factor of 5 uncertainty in each direction shown by dashed lines.	45
Figure 3-1.	
A roadside cut near Guadalupe National Park exposes the subsurface environment in an area of fractured limestone rock. Chemicals partition between air, rock, soil, water, and organic liquid phases in complex environments such as this.	49
Figure 3-2. Multiphase distribution of air, oil, water, and soil grains.	51
Figure 3-3. Lily pad leaves are partially supported by the surface tension of water.	53
Figure 3-4.	
Aqueous solubility as a function of molecular weight of simple hydrocarbons.	54
Figure 3-5. Vapor pressure of simple hydrocarbons.	55

Figure 3-6.	Henry's Law Constant of simple hydrocarbons.	57
Figure 3-7.	Octanol/water partition coefficient (K_{ow}) of simple hydrocarbons.	59
Figure 3-8.	Vapor pressure of 1,2 dichloropropane.	63
Figure 3-9.	Estimated evaporation rate of the spill as a function of temperature at two different wind speeds.	63
Figure 3-10.	A few chemicals of interest and brief review of nomenclature (note: figure needs to be completed by student).	65
Figure 4-1.	The wide sediment plume of the Yangtze River as it empties into the East China Sea illustrates the process of mixing and dispersion (NASA Visible Earth Image).	67
Figure 4-2.	Schematics of several idealized reactor types.	69
Figure 4-3.	Solution to example problem Equation 10.	72
Figure 4-4.	Solution to example problem when initial concentration is zero (Equation 11).	72
Figure 4-5.	Solution to example problem when input concentration is zero (Equation 12).	72
Figure 4-6.	River modeled as a series of continuous stirred tank reactors (CSTR).	73
Figure 4-7.	Control volume.	74
Figure 4-8.	Flow from the Platte River at Honor, Michigan.	76
Figure 4-9.	Percentage of pollution remaining assuming a 36-year mean residence time.	77
Figure 5-1.	Spring near Kenosha, Wisconsin. Dissolved iron in the anaerobic groundwater precipitates out of solution when the water contacts atmospheric oxygen.	81
Figure 5-2.	Strontium-90 decay curve with a half life of 29.1 years.	86
Figure 5-3.	Decay curve for tritium with a half life of 12.3 years.	86
Figure 5-4.	Proportion of each of the species in the carbonate buffer system as a function of pH.	87

Figure 5-5. Nomograph relating pH, alkalinity, and total inorganic carbon.	88
Figure 5-6. 1998 Crystal Lake temperature (C) and dissolved oxygen (mg/L).	89
Figure 5-7. Stalactites of calcium carbonate formed by dripping water in a cave, Coffee Cave, NM.	90
Figure 5-8. Exchange of dissolved gases with the atmosphere.	90
Figure 5-9. pH in Crystal Lake during 1998.	91
Figure 5-10. Oxidants used in oxidation/reduction (redox) reactions in the environment when oxygen is depleted (Berner, 1980).	94
Figure 5-11. Trends with depth in Peacock Hill lake.	95
Figure 5-12. Iron bearing spring waters contact the atmosphere causing formation of insoluble iron oxides (rust color).	96
Figure 5-13. A small seep or spring near Kenosha, Wisconsin.	96
Figure 5-14. At a small seep near Kenosha, Wisconsin reduced ferrous iron contacts the atmosphere, oxidizes from ferrous (Fe^{2+}) to insoluble ferric (Fe^{3+}) iron.	97
Figure 5-15. Distribution of (a) temperature, (b) dissolved oxygen, (c) partial pressure of carbon dioxide, and (d) phosphate and nitrate in the North Atlantic Ocean.	99
Figure 5-16. Distribution of (a) iron, (b) lead, (c) copper, and (d) cadmium in the North Atlantic Ocean.	100
Figure 6-1. Groundwater and vadose zone plume originating at an abandoned waste site.	105
Figure 6-2. Schematic of water balance and definition of terms.	106
Figure 6-3. View of the Lake Michigan shoreline from the pier at Frankfort, Michigan.	107
Figure 6-4. Close-up pictures of bluff in Figure 6-3.	107
Figure 6-5. Base flow feeding a stream and perched water.	107

Figure 6-6. Schematic of a groundwater system (modified from USGS web site).	108
Figure 6-7. Drill rig at a gold prospect in Guatemala.	109
Figure 6-8. Control volume.	111
Figure 6-9. Capture zones based upon pumping rate of well relative to flow in aquifer.	118
Figure 6-10. Superposition of well drawdown on existing hydraulic gradient showing water capture by well.	119
Figure 6-11. Pore scale dispersion processes.	120
Figure 6-12. One dimensional transport of a square wave input.	121
Figure 6-13. Alternating lenses of sand and gravel. This is a close up shot of the same bluff shown in Figure 6-3. Notice how homogeneous the slope appears from a distance compared with how complex reality is.	121
Figure 6-14. Relationship between longitudinal dispersivity and scale (Gelhar, 1986). (Note: this is a scan of the original figure.)	126
Figure 6-15. Plume at four different times ($\alpha = 0.2$ m, $\nu = 10$ m/yr).	127
Figure 6-16. Influence of dispersivity on transport at a constant time of 5 years. Notice that the area under the curve (i.e., the total mass in the plume) is the same in each case.	127
Figure 6-17. Influence of R_d . Plume shrinks with large R_d because more of the mass is on the rocks and only the aqueous concentration is shown.	127
Figure 6-18. Retardation with and without decay.	128
Figure 6-19. Two-dimensional impulse release. Plume is normally distributed in the longitudinal and transverse directions.	129
Figure 6-20. Solution of Equation 55.	130
Figure 6-21. Hypothetical disposal site showing elevation of the water table below the site.	131
Figure 6-22. Contours of constant hydraulic head and estimated flow path	

from disposal site.	131
Figure 6-23. Groundwater cross section example, reference for problems.	132
Figure 6-24. Piezometers are inserted at two points along a sand filled tube. The horizontal lines are spaced 10 cm apart, the columns are 1 meter long.	133
Figure 6-25. Groundwater elevations in meters.	134
Figure 7-1. Whitewater Creek, NM, showing interaction between surface and ground water leading to base flow of the stream.	137
Figure 7-2. Water density as a function of temperature.	138
Figure 7-3. Crystal Lake temperature, year 1.	139
Figure 7-4. Crystal Lake, Michigan.	139
Figure 7-5. Crystal Lake temperature, year 2.	140
Figure 7-6. August 18, Crystal Lake temperature, dissolved oxygen, and pH.	142
Figure 7-7. Change in air pressure with elevation.	143
Figure 7-8. Dependence of oxygen solubility in equilibrium with air on temperature at atmospheric pressure.	143
Figure 7-9. Hydrograph of the Gila River, NM, with a drainage basin of 1,864 square miles.	146
Figure 7-10. Binomial probabilities.	148
Figure 7-11. Probability of a DCP spill being transported to sump and contaminating the groundwater below the sump as a function of number of spills.	149
Figure 7-12. Possible specific energy levels for a flow rate of 1 m ³ /s.	151
Figure 7-13. Small hydraulic jump, Redstone Park, New Mexico.	152
Figure 7-14. Hydraulic jump during a flood in El Paso, Texas.	153
Figure 7-15. Schematic of oxygen levels below sewer outfall.	155
Figure 8-1. Industrial smoke stack at Ludington, Michigan. Lower picture modified with Photoshop filters to show smoke plume and change from steam to smoke.	159
Figure 8-2. Hadley cells and their influence on global circulation and precipitation.	160

Figure 8-3.	Lifting condensation level.	163
Figure 8-4.	Orographic cloud over the Cornudas Mountains, NM.	164
Figure 8-5.	Orographic cloud, Cooks Peak, NM.	165
Figure 8-6.	Stable atmosphere.	165
Figure 8-7.	Unstable atmosphere.	166
Figure 8-8.	Break up of temperature inversion.	166
Figure 8-9.	Pollutants are trapped below the mixing height.	167
Figure 8-10.	Diurnal variation of temperature difference between 110 and 11 meters at Brookhaven National Laboratory, Long Island, New York (Slade, 1968).	168
Figure 8-11.	Relationship between atmospheric stability and plume behavior (adopted from Slade, 1968).	169
Figure 8-12.	Gaussian plume, or coning under approximately neutral stability. The first part of the plume contains smoke and steam.	170
Figure 8-13.	Smoke and steam plume rises to its stability height then spreads horizontally. The smoke is initially warmer than the atmosphere. As it rises it cools at the adiabatic lapse rate. The atmospheric lapse rate is less than adiabatic (stable). When the plume cools to the temperature of the surrounding air it no longer rises and spreads horizontally (fanning) in the stable atmosphere.	171
Figure 8-14.	Looping plume under unstable atmospheric conditions.	171
Figure 8-15.	Looping plume at Ludington, Michigan. Looping plumes change shape rapidly.	171
Figure 8-16.	Lee wave formation.	172
Figure 8-17.	Orographic cloud over the Franklin Mountains and lee wave cloud.	172
Figure 8-18.	Idealized valley flow on a clear night.	173
Figure 8-19.	Winds around Oak Ridge National Lab (adapted from Slade, 1968).	173
Figure 8-20.	Examples of laminar (left) and turbulent flow (right).	174
Figure 8-21.	Schematic diagram of Gaussian shaped concentration distribution in a plume. Two standard deviations includes 95% of the mass of	

contaminant in the plume.	176
Figure 8-22. Dilution of a smoke plume by the wind.	177
Figure 8-23. Explanation of ground level plume reflection term in Gaussian Plume equation.	177
Figure 8-24. Sigma y using correlations from Martin, 1976.	178
Figure 8-25. Sigma z using correlations from Martin, 1976.	179
Figure 8-26. Coning plume using (a) an instantaneous (1/25 s) exposure and (b) an exposure time of 5 minutes (Slade, 1968).	179
Figure 8-27. Plume photographs (a) instantaneous (1/50 s) exposure and (b) 5 minute time exposure (Slade, 1968).	180
Figure 8-28. Relationship between elevated hydrogen sulfide concentrations (>50 ppb) and wind speed near a rendering plant.	182
Figure 8-29. Hydrogen sulfide concentrations for the entire year at three monitoring stations plotted as a function of time of day. Notice that the highest concentrations occur during the night and early morning hours.	182

INTRODUCTION

Migration of chemicals in the environment is important to a variety of disciplines. Biologists are concerned with movement of limiting nutrients such as nitrogen and phosphorus that are essential for plant growth. Toxicologists are concerned with estimating human and environmental risk from exposure to toxic chemicals. Climatologists need to understand the sources and sinks for greenhouse gases. Regulatory agencies must evaluate estimated future release of and exposure to hazardous materials and compare them to regulatory and health standards. Geologists, ecologists, and meteorologists are interested in biogeochemical cycles and how they are influenced by anthropogenic activities. Scientists, engineers, and regulators are concerned with cleanup of contaminated sites and minimizing risk to humans and the environment.

This textbook evolved from an interdisciplinary class taught to students with diverse backgrounds who typically had an advanced grasp of some of the material covered and relatively little background in other portions. Engineering students are comfortable with mathematics but often have limited backgrounds in chemistry, biology, and/or geology. Biology and geology students may have difficulty with quantitative treatment requiring differential equations. The goal of this textbook is to introduce an interdisciplinary, non-specialist audience to fundamental concepts of how chemicals migrate in the environment and how this migration is estimated in risk assessments. Mathematical treatment beyond the elementary level is sometimes presented with the intent of pushing students with greater interest or more complete backgrounds toward more complete understanding. This material is not essential to the text and can be skipped (or simply not included in tests) by choice of the instructor.

The text should also be useful for people without specialized knowledge who work with fate and transport in the environment and/or as an introduction to the field. Mathematical treatment up to partial differential equations is present but not required to follow most of the material presented. Increasingly, most calculations of fate and transport are performed by practitioners with specialized computer codes. The focus of this text is on fundamental principles and relatively simplified calculations that explain the concepts and fundamental assumptions underlying most codes predicting contaminant transport, rather than a guide to computer codes.

The text contains a series of chapters providing coverage of background concepts preceding chapters covering the major environments of groundwater, surface water, and the atmosphere. Depending upon the training of the students or reader, some of these chapters could be skipped and/or reordered. The mathematical treatment of contaminant transport in all media is remarkably similar. The essential similarities between the

models used in surface water, groundwater, and air pollution are emphasized in order to provide unifying concepts and bolster understanding of concepts. Generalized transport phenomena concepts are introduced in the first two chapters followed by more specific and detailed application in the media specific chapters.

The text is supplemented with student exercises that can be assigned with homework or worked on in class in cooperative groups. All figures included in the text, figures associated with homework solutions, and supplementary materials are available to the instructor in color to facilitate classroom presentation and explanation of the material. Please visit the author's Web site at www.windowoutdoors.com to access these materials. For instructors a fully worked solutions manual to every problem in the text is available. To receive these solutions please contact the publisher at the address or email provided on the copyright page.