

Table of Contents

1 ENVIRONMENTAL TRANSPORT MODELING	1
1.1 INTRODUCTION.....	1
2 PRELIMINARIES	5
2.1 EQUILIBRIUM BETWEEN ENVIRONMENTAL PHASES	5
2.1.1 Chemical equilibrium in air-water phases.....	5
2.1.2 Chemical equilibrium in water-organic liquid phases.....	6
2.1.3 Chemical equilibrium in the air-water-soil phases . . .	7
2.2 DIFFUSION AND THE DIFFUSION COEFFICIENT	9
2.2.1 Diffusion in free phases.....	9
2.2.2 Effective diffusion coefficient in a porous medium.....	10
2.3 ADVECTION AND THE SURFACE MASS TRANSFER COEFFICIENT	11
2.3.1 Laminar flow boundary layer theory and turbulent flow mass transfer . . .	11
2.3.2 Penetration theory	12
2.4 MASS BALANCE AND TRANSPORT EQUATIONS	12
REFERENCES	15
3 DIFFUSION IN A SEMI-INFINITE SYSTEM	17
3.1 INTRODUCTION.....	17
3.2 ANALYSIS SUMMARY . . .	17
3.2.1 Case 1: Semi-infinite region with uniform initial concentration and zero concentration at the surface	17
3.2.2 Case 2: Semi-infinite region with uniform initial concentration and mass transfer or reaction at the surface	18
3.2.3 Case 3: Semi-infinite region with uniform initial concentration capped by a finite layer with a different uniform initial concentration, and zero concentration at the surface	20
3.2.4 Case 4: Semi-infinite region with uniform initial concentration, zero concentration at the surface, and first-order decay	21
3.2.5 Case 5: Semi-infinite region with uniform initial concentration, mass transfer or reaction at the surface, and first-order decay.....	22
3.2.6 Case 6: Semi-infinite region with uniform initial concentration capped by a finite layer with a different uniform initial concentration, zero concentration at the surface, and first-order decay.....	23
3.3 NUMERICAL EVALUATION	25
3.4 DEVELOPMENT	25
3.4.1 Laplace transformation method.....	25
3.4.2 Principle of superposition.....	29
3.4.3 Variable transformation for first-order decay	30
REFERENCES	32
4 DIFFUSION IN A FINITE LAYER	33
4.1 INTRODUCTION	33
4.2 ANALYSIS SUMMARY	33
4.2.1 Case 1: Finite layer with arbitrary initial concentrations, zero concentration at the surface, and zero flux at the base.....	34
4.2.2 Case 2: Finite layer with uniform initial concentration, zero surface concentration, and zero flux at the base	35
4.2.3 Case 3: Finite layer with arbitrary initial concentrations, mass transfer or reaction at the surface, and zero flux at the base	36
4.2.4 Case 4: Finite layer with uniform initial concentration, mass transfer or reaction at the surface, and zero flux at the base	37
4.2.5 Case 5: Finite layer with arbitrary initial concentrations, zero concentration at the surface, zero flux at the base, and first-order decay	38

Contaminant Transport in Soils and Sediments

4.2.6	Case 6: Finite layer with uniform initial concentration, zero surface concentration, zero flux at the base, and first-order decay.....	39
4.2.7	Case 7: Finite layer with arbitrary initial concentrations, mass transfer or reaction at the surface, zero flux at the base, and first-order decay.....	40
4.2.8	Case 8: Finite layer with uniform initial concentration, mass transfer or reaction at the surface, zero flux at the base, and first-order decay.....	41
4.3	NUMERICAL EVALUATION	42
4.3.1	Evaluation of the initial condition integral.....	42
4.3.2	Cases 1 and 2: zero surface concentration	44
4.3.3	Cases 3 and 4: surface mass transfer	44
4.3.4	Determining transcendental function roots	45
4.4	DEVELOPMENT	46
4.4.1	Separation of variables	46
4.4.2	Solution to the temporal problem.....	46
4.4.3	Solution to the spatial problem	46
4.4.4	Variable transformation for first-order decay	51
REFERENCES	52
5	DIFFUSION IN A TWO-LAYER COMPOSITE SYSTEM	53
5.1	INTRODUCTION	53
5.2	ANALYSIS SUMMARY	53
5.2.1	System dynamics and general solution for a two-layer composite.....	53
5.2.2	System eigenfunctions and eigenvalues	55
5.2.3	Case 1: Two-layer finite system with arbitrary initial concentrations, zero concentration at the surface, and zero flux at the base.....	56
5.2.4	Case 2: Two-layer finite system with arbitrary initial concentrations, mass transfer or reaction at the surface, and zero flux at the base.....	58
5.3	NUMERICAL EVALUATION	60
5.3.1	Concentration calculation.....	61
5.3.2	Surface flux calculation	62
5.3.3	Range of significance for eigenvalues.....	62
5.3.4	Determination of eigenvalues in range	63
5.3.5	Eigenfunction evaluation.....	65
5.3.6	Normalization integral evaluation.....	65
5.3.7	Initialization integral evaluation	65
5.4	DEVELOPMENT	67
5.4.1	Separation of variables.....	67
5.4.2	Solution to the temporal problem	67
5.4.3	Solution to the spatial problem	67
5.4.4	Initial conditions.....	72
5.4.5	Variable transformation for first-order decay	74
REFERENCES	75
6	DIFFUSION IN A THREE-LAYER COMPOSITE SYSTEM	77
6.1	INTRODUCTION	77
6.2	ANALYSIS SUMMARY	77
6.2.1	System dynamics and general solution for a three-layer composite.....	77
6.2.2	System eigenfunctions and eigenvalues.....	79
6.2.3	Case 1: Three-layer finite system with arbitrary initial concentrations, zero concentration at the surface, and zero flux at the base.....	81
6.2.4	Case 2: Three-layer finite system with arbitrary initial concentrations, mass transfer or reaction at the surface, and zero flux at the base	84
6.3	NUMERICAL EVALUATION	87
6.3.1	Concentration calculation.....	87
6.3.2	Surface flux calculation	88
6.3.3	Range of significance for eigenvalues	89

6.3.4	Determination of eigenvalues in range	90
6.3.5	Eigenfunction evaluation	92
6.3.6	Normalization integral evaluation	92
6.3.7	Initialization integral evaluation	92
6.3.8	General numerical evaluation comments	93
6.4	DEVELOPMENT	93
6.4.1	Separation of variables	93
6.4.2	Solution to the temporal problem	94
6.4.3	Solution to the spatial problem	94
6.4.4	Initial conditions	104
6.4.5	Variable transformation for first-order decay	106
REFERENCES	107
7	ADVECTION-DIFFUSION MODELS	109
7.1	INTRODUCTION	109
7.2	ANALYSIS SUMMARY	109
7.2.1	Case 1: Semi-infinite region with uniform initial concentration with a constant concentration boundary condition	109
7.2.2	Case 2: Semi-infinite region with uniform initial concentration with a constant flux boundary condition	110
7.2.3	Case 3: Semi-infinite region with uniform initial concentration with a boundary condition given by a finite-timed pulse at a constant concentration	110
7.2.4	Case 4: Semi-infinite region with uniform initial concentration with a boundary condition given by a finite-timed pulse at a constant flux	111
7.2.5	Case 5: Semi-infinite region with uniform initial concentration capped by a finite region of a different uniform initial condition, with a constant concentration boundary condition	111
7.2.6	Case 6: Semi-infinite region with uniform initial concentration capped by a finite region of a different uniform initial condition, with a constant flux boundary condition	112
7.2.7	Case 7: Semi-infinite region with uniform initial concentration capped by a finite region of a different uniform initial condition, with a boundary condition given by a finite-timed pulse at a constant concentration	113
7.2.8	Case 8: Semi-infinite region with uniform initial concentration capped by a finite region of a different uniform initial condition, with a boundary condition given by a finite-timed pulse at a constant flux	113
7.3	NUMERICAL EVALUATION	114
7.4	DEVELOPMENT	114
REFERENCES	117
8	VOLATILE LIQUID EVAPORATION	119
8.1	INTRODUCTION	119
8.2	ANALYSIS SUMMARY	119
8.2.1	Case 1: Evaporation and vapor diffusion through soil/sediment with uniform initial liquid saturation, with zero vapor concentration at the surface	119
8.2.2	Case 2: Evaporation and vapor diffusion through soil/sediment with uniform initial liquid saturation, with a vapor mass transfer boundary condition at the surface	120
8.2.3	Case 3: Evaporation and vapor diffusion through soil/sediment with uniform initial liquid saturation below a finite clean capped region, with zero vapor concentration at the surface	121
8.2.4	Case 4: Evaporation and vapor diffusion through soil/sediment with uniform initial liquid saturation below a finite clean capped region, with a vapor mass transfer boundary condition at the surface	122
8.3	NUMERICAL EVALUATION	123
8.4	DEVELOPMENT	123
8.4.1	Case I : Evaporation and vapor diffusion through soil/sediment with uniform initial liquid saturation, with zero vapor concentration at the surface	123

Contaminant Transport in Soils and Sediments

8.4.2	Case 2: Evaporation and vapor diffusion through soil/sediment with uniform initial liquid saturation, with a vapor mass transfer boundary condition at the surface..	124
8.4.3	Case 3: Evaporation and vapor diffusion through soil/sediment with uniform initial liquid saturation below a finite clean capped region, with zero vapor concentration at the surface	125
8.4.4	Case 4: Evaporation and vapor diffusion through soil/sediment with uniform initial liquid saturation below a finite clean capped region, with a vapor mass transfer boundary condition at the surface	125
REFERENCES		126
9 DIFFUSION WITH TIME-DEPENDENT PARTITION COEFFICIENTS..		127
9.1 INTRODUCTION ..		127
9.2 MATHEMATICAL ANALYSIS..		127
9.3 ANALYSIS SUMMARY		129
9.3.1	Case 1: Diffusion in a thin layer with time-dependent soil-air partition coefficient, zero surface concentration, a no-flow bottom boundary condition, and constant initial conditions..	129
9.3.2	Case 2: Diffusion time-dependent partition coefficient, zero surface concentration, no flow bottom boundary, and arbitrary initial conditions	133
9.3.3	Case 3: Diffusion in a thin surface boundary layer with time-dependent soil-air partition coefficient, zero surface concentration, a constant concentration source at the lower boundary, and constant initial conditions..	134
9.4 VARIABLE TRANSFORMATIONS ON A VARIETY OF TIME-DEPENDENT AIR-SOIL PARTITION COEFFICIENT FUNCTIONS		140
9.4.1	Constant soil-air partition coefficient..	140
9.4.2	Linear soil-air partition coefficient..	140
9.4.3	Exponential soil-air partition coefficient..	141
9.5 DEVELOPMENT ..		142
9.5.1	Transformation of variables	142
9.5.2	Separation of variables..	142
9.5.3	Time-dependent boundary condition..	145
REFERENCES		148
10 CONSTANT FLUX LIQUID EVAPORATION..		149
10.1 INTRODUCTION		149
10.2 ANALYSIS AND DEVELOPMENT ..		149
REFERENCES		151
APPENDIX		153
A. ERROR FUNCTION		153
B. LAPLACE TRANSFORMATION		155
C. ROOTS OF TRANSCENDENTAL EQUATIONS		158
D. PREDICTING THE DIFFUSION COEFFICIENT IN VAPORS..		160
E. PREDICTING THE DIFFUSION COEFFICIENT IN LIQUIDS..		162
F. SAMPLE CALCULATIONS OF MODELS USING MATHCAD™		165