MATHEMATICAL EQUATIONS OF THE SPREAD OF POLLUTION IN SOILS

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Contents

1. Introduction
2. Convective-Diffusive Equation
3. Effects of Boundary Conditions
4. Chemical Reactions
5. Nonlinear Adsorption
6. Two Species Competition
7. Interaction of Surface Water and Chemical Transport in Soils
8. Column Flow
9. Transient Unsaturated Water and Solute Transport
10. Scale Dependent Solutions
11. Transient Solution Profiles
12. Source Solutions
13. Conclusion
Glossary
Bibliography
Biographical Sketches

Summary

Models describing the spread of pollution through soils are discussed. The spread of pollution is soils is controlled by the flow of water and, in most cases, is described by the convective-dispersive equation. First we consider cases when the water velocity is assumed constant. Effects of boundary conditions, chemical reactions, adsorption and species

competition are described for this case. Then two other cases are discussed; (1) when hydrology controls solute transport and (2) when the convective-dispersive equation is less important. In the former case, erosion due to raindrop impact and the transport of pollutants adsorbed on fine particles is discussed. In the latter case, preferential flows, which can be linked to either structural voids in the soil (e.g. macropores, cracks, etc) or to flow instability are considered. Mathematical expressions describing these cases are presented. In the final section of this chapter we present a discussion of cases when Richards' equation controls water movement. When Richards' equation is used, it is difficult to analyze solute transport due to the strongly nonlinear nature of the equation. However, a few exact analytical solutions have been obtained recently and are presented here.

1. Introduction

The study of chemical transport in soils is important for a number of reasons. Some chemicals are important as they are required for soil and plant health (e.g. micronutrients). Other chemicals may be highly toxic particularly if they are present in high concentrations. A chemical becomes a pollutant if its concentration exceeds some prescribed water quality standard, or if a beneficial water use has been impaired, and if the cause is induced by human activity. The study of the fate of chemicals and chemical pollution in soil is vital for sustaining agricultural productivity and land utility.

The geological media between the land surface and the regional water table below is called the unsaturated zone or vadose zone (Stephens, 1996). The word "vadose" is derived from the Latin word *vadosus* meaning shallow (Looney and Falta, 2000a). In accord with its definition and meaning, the vadose zone includes the crop root layer, the intermediate zone between the root layer and the capillary fringe above the saturated water table. This zone therefore plays an integral role in the global hydrological cycle controlling surface water infiltration, runoff and evaporation and hence the availability of soil water and nutrients to plants. Initial investigations of this zone were focused on water availability to crops and optimal management of the root zone. However, in recent years much more attention has focused on chemical transport in and through this zone as a result of increased use of agrochemicals such as fertilizers and pesticides and increased demands to store and dispose of industrial and municipal wastes such as sewage. This zone is typically the first subsurface environment to encounter surface applied agrochemicals and contaminants and hence all surface and subsurface chemical concentrations and subsequent environmental impacts are inextricably linked to the physical, biological and chemical dynamics including sorption-desorption, volatilization, photolysis and degradation (Looney and Falta, 2000a).

Our current understanding of physical and chemical processes in the vadose zone results largely from more than 70 years of mathematical modeling of variably saturated flow using Richards' equation (Richards, 1931) coupled with the Fickian-based convection-dispersion equation for solute transport. Analytical and numerical solutions of these classical equations are widely used to study and predict water flow and solute transport for specific laboratory and field experiments and to extrapolate these results for other experiments in different soils, crops and climatic conditions. However, many recent studies have demonstrated that the assumptions implicitly adopted in the Richards' and convective-dispersion equations are limiting the scope and application of solutions to these equations for many agricultural and forestry management strategies. The spread of solute and

pollutants in soils is complicated by non-random spatial and temporal variations of physical, chemical and biological components of soils (Hill & Parlange, 1972; Stagnitti, et al. 1995; Parlange, et al.1996; Stagnitti, et al. 1995). One manifestation of spatial and temporal heterogeneity in soils is the phenomenon of preferential flow, a general term used to describe a variety of physical and chemical non-equilibrium flow processes.

This chapter introduces a number of useful equations to study the spread of chemicals and pollution in soils. It begins with the classical descriptions of convection and dispersion and then introduces recent extensions, new solutions and new models incorporating important mechanisms such as preferential flow.

2. Convective-Diffusive Equation

Chemicals carried by water in and on the soil can follow a variety of paths. In the simplest case, a one-dimensional convection takes place which can be accompanied by dispersion, adsorption and chemical reaction. Description of contaminant transport in terms of an average water velocity, v, by the convective-dispersive equation remains the first and fundamental transport equation to be considered. In its simplest form, the concentration of a chemical moved in one-dimension in the x direction, can be described by the following equation,

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} = \frac{\partial}{\partial x}\left[D \frac{\partial c}{\partial x} \right] - f - \frac{\partial c_a}{\partial t} \qquad (1)$$

where v is the average water velocity, D is the dispersion, c_a the concentration of adsorbed chemical and f is the irreversible reaction decay rate. In general, v, D, f, and c_a could be complex functions of c, x, and t. Consequently no "exact" simple analytical solution exists for all cases. When f is a linear function of c, D and v are constant and $c_a = (R-1)c$, where R is the retardation factor (assumed constant), then Eq. (1) is linear with constant coefficients. In this case many exact solutions can be obtained, e.g. using Laplace transforms. van Genuchten and Alvers (1982) have presented numerous exact solutions for Eq. (1) with constant coefficients for a wide variety of boundary and initial conditions.

3. Effects of Boundary Conditions

In a typical laboratory experiment involving a column with a finite length L, boundary conditions at $x = 0$ and $x = L$ must be specified. At $x = 0$, depending on the method of injection, c will be imposed, for instance if water with a constant concentration c_0 is pushed at a constant rate, then the flux of material entering the column is constant, or,

$$c_f \equiv c - (D/v)\frac{\partial c}{\partial x} = c_0 \quad \text{at} \quad x = 0 \qquad (2)$$

where c_f is called the flux concentration (Kreft and Zuber, 1978, 1986; van Genuchten and Parker, 1984) and c is then called the "resident" concentration. Interestingly when Eq. (1)

is linear with constant coefficients then c_f obeys a similar equation with the boundary condition for c_f being simpler than for c at $x = 0$. A standard initial condition might be

$$c = c_f = 0 \quad \text{at} \quad t = 0 \tag{3}$$

The boundary condition at $x = L$ presents some difficulties (Parlange et al. 1992). If discontinuity in c is not permitted at the end of the column and there is no dispersion in the collector, then $c = c_f$ at $x = L$ or

$$\frac{\partial c}{\partial x} = 0 \quad \text{at} \quad x = L \tag{4}$$

and this is true as long as the Péclet number $P_e = vL/D$ is not too small, e.g. at least 4 or more. Péclet numbers of at least 4 are commonly found except when macropores e.g. cracks are present in the column and the "effective" dispersion is dominated by diffusion between cracks and the soil matrix surrounding them. In that case, $P_e > 4$ it can be shown (Parlange and Starr, 1975; 1978; Parlange, et al. 1982) that taking c_f as the solution for a semi-infinite column $c_{f\infty}$ i.e. for $L \rightarrow \infty$, leads to a c, from the definition of c_f in Eq. (2), which satisfies Eq. (1) with an error of order $\exp(-P_e) \ll 1$. For instance taking $f = 0$ and scaling time by R, for a semi-infinite column,

$$2\, c_f / c_0 = \text{erfc}\left[\frac{x - tv}{\sqrt{4Dt}}\right] + \exp\left[\frac{vx}{D}\right]\text{erfc}\left[\frac{x + tv}{\sqrt{4Dt}}\right] \tag{5}$$

then Eq. (2) gives

$$
\begin{aligned}
c = c_{f\infty} &+ c_0 \exp\frac{vx}{D} \left\{ \text{erfc}\frac{L+tv}{\sqrt{4Dt}} - \frac{v}{D}\sqrt{Dt}\left[\frac{1}{\sqrt{\pi}}\exp\frac{-(L+tv)^2}{4Dt} - \frac{L+tv}{\sqrt{4Dt}}\text{erfc}\frac{L+tv}{\sqrt{4Dt}}\right] \right\} \\
&+ \exp\frac{vx}{D}\left\{ -\text{erfc}\frac{x+tv}{\sqrt{4Dt}} + \frac{v}{D}\sqrt{Dt}\left[\frac{1}{\sqrt{\pi}}\exp\frac{-(x+tv)^2}{4Dt} - \frac{x+tv}{\sqrt{4Dt}}\text{erfc}\frac{x+tv}{\sqrt{4Dt}}\right] \right\}
\end{aligned}
\tag{6}
$$

derived from the general solution of Eq. (2)

$$c = c_{f\infty} + \exp\frac{vx}{D}\int_x^L \frac{\partial c_{f\infty}}{\partial x}\exp\frac{-v\overline{x}}{D}\, d\overline{x} \tag{7}$$

given Eq. (6) when Eq. (5) holds. It is convenient to define c_∞ as the solution for c when $L \rightarrow \infty$, then we obtain at once

$$c = c_{\infty} + \exp\frac{v(x-L)}{D}\left[c_{f\infty}(x=L) - c_{\infty}(x=L)\right] \tag{8}$$

Eq. (8) will often be useful in practice when $c_{f\infty}$ and c_{∞} are known. For instance for zero and first order kinetics (i.e. f constant or proportional to c), $c_{f\infty}$ and c_{∞} are established in closed form (Parlange et al. 1982, 1992; Parlange and Starr, 1878; van Genuchten and Alves, 1982) and yield a simple expression for c, with a slight error because c_f is not exactly equal to $c_{f\infty}$. In particular at $x=L$, the breakthrough curve is very simply obtained by

$$c(x=L) = c_f(x=L) \approx c_{f\infty}(x=L) \tag{9}$$

Not surprisingly the maximum error of Eq. (8) is at $x=L$. In Table 1 we consider the case when $P_e = 4$, the minimum acceptable value, and the three cases when $f=0$; $fL/v = 0.2$; and $fL/vc = 1$, which corresponds to no, zero and first order kinetics respectively. The maximum error is at time $v^2t/D = 4$ and the absolute errors are about 0.02 in all three cases.

$vL/D = 4$	no kinetics	zeroth order	first order
c_{f4}	0.6277	0.4788	0.3549
$c(x=L)$ exact	0.6091	0.4549	0.3335

Table 1: Solutions of Eq. (8) for no, zero and first order kinetics

The exact values presented in Table 1 are from van Genuchten and Avles (1982) where they are tabulated using somewhat complex series solutions.

If the Péclet number P_e is very small and dispersion results from molecular diffusion between mobile and immobile water, Eq. (1) should not be used by itself and the region of immobile water should be taken into account explicitly. This concept may have been first introduced by Passioura (1971) for aggregated porous media. The chemical in immobile water is a component of c_a, and explicitly written as $(\theta_{im}/\theta_m)\,\partial c_{im}/\partial t$ in Eq. (1), where θ_{im} and θ_m are the water contents in the immobile and mobile regions and c_{im} is the concentration of the chemical in the immobile region.

An additional equation is now required to find c_{im}. If the exchange process between the two regions is slow compared to transport processes then the rate limited exchange is often modeled by the following equation

$$\theta_{im}\,\partial c_{im}/\partial t = k\,(c_m - c_{im}), \tag{10}$$

where k is a rate coefficient. Parker and Valocchi (1986), van Genuchten and Dalton (1986) and Brusseau et al. (1994) have discussed various mass transfer processes and their models. The other limiting case when the exchange process is rapid would lead to local equilibrium although this limit does not seem to hold in practice. Readers are referred to Wallach and Parlange (1998; 2000) for a thorough discussion of the exchange processes between the two regions.

4. Chemical Reactions

The discussion till now only considered linear equations. If the dispersion term in Eq. (1) can be neglected, at least as a first approximation, then the method of characteristics may be employed to find solutions of the governing equations. Although the method is very general we shall concentrate on a particular case which illustrates the method quite clearly and also makes use of results obtained in the previous section.

First consider the case of no adsorption, D and v constant and f an arbitrary function of c. Barry et al. (1993) solved this case to analyze nitrogen transport and kinetics in soils (also see McLaren (1976), Starr et al. (1974), Starr and Parlange (1975) for applications). When experimental observations are used to estimate f it is particularly convenient to use steady state results. Under steady state, Eq. (1) reduces to,

$$v\frac{dc}{dx} = D\frac{d^2c}{dx^2} - f .$$ (11)

The method of characteristics ignoring dispersion yields a simple solution

$$x = v\int_c^{g_1} \frac{d\overline{c}}{f(\overline{c})} ,$$ (12)

where g_1 is a first approximation to the value of c at $x = 0$. The effect of dispersion can significantly lower the concentration at $x = 0$ below c_0. Indeed it can be shown that ignoring dispersion in the differential results is far less accurate than when ignoring it in the boundary condition at $x = 0$ (Parlange et al. 1982, 1984; Barry et al. 1986). It is also clear that ignoring d^2c/dx^2 in Eq. (11) means that we are not considering any boundary condition such that with a column of length L, Eq. (4) for instance is irrelevant. Indeed it is clear from Eq. (12) that x is infinite at $c = 0$, since $f(0) = 0$. Thus Eq. (12) is relevant for a semi-infinite column. As we previously exhibited in the linear case, c will be close to c_∞ so long as the solution is not in the boundary layer near $x = L$, which has a thickness of order D/v, as shown by Eq. (8). Thus when using experimental data together with Eq. (12), it is crucial to check, *a posteriori* if necessary, that all data of interest are sufficiently far from the end of the column.

At the surface condition, Eq. (4) yields

$$g_1 = c_0 \frac{D}{v^2} f(g_1), \tag{13}$$

Clearly the procedure will be valid as long as the correction due to dispersion is small or

$$v^2 c_0 / D f(c_0) \gg 1. \tag{14}$$

Brams and McLaren (1974) used Eq. (12) in their analysis but did not correct g_1 and used $g_1 = c_0$ which is far less accurate than Eq. (13). It is now easy to iterate using Eq. (12) to estimate $D d^2 c / dx^2$ in Eq. (11) or,

$$x = v \int_c^{g_2} \frac{d\bar{c}}{f(\bar{c})} + \frac{D}{v} \ln \left[\frac{f(g_2)}{f(c)} \right], \tag{15}$$

where g_2 is the new concentration at $x = 0$, or from Eq. (4)

$$g_2 = c_0 - \frac{D f(g_2)}{v^2 + D \left. \dfrac{df}{dc} \right|_{c=g_2}}. \tag{16}$$

Note that Eq. (15) still holds for a semi-infinite column only.

To estimate the accuracy of this procedure consider the more realistic case of Michaelis-Menten kinetics when

$$f(c) = \frac{f_0 c}{K + c}, \tag{17}$$

where f_0 and K are the limiting rate constant and the saturation constant respectively. This function can be introduced easily into Eqs. (12), (13), (15), and (16) and in particular

$$\int_c^g \frac{d\bar{c}}{f(\bar{c})} = \frac{1}{f_0} \left[g - c + K \ln(g/c) \right] \tag{18}$$

for use in Eqs. (12) and (15). Consider a reasonable example of $v c_0 / f_0 = 10$ cm and $K = c_0$ and values of D/v varying from 0.05 to 5 cm. Hence $v^2 c_0 / D f(c_0)$ in Eq. (14) varies between 400, a very large value, and 4, a moderate value. The values of c/c_0 at 0, 5, and 10 cm are obtained numerically (Barry et al. 1993), i.e. they are considered "exact". Then we take the results at 5 and 10 cm and consider them as "observed" and we ask the question what are the errors associated with those values if we use them to predict $v c_0 / f_0$ and k/c_0 when Eqs. (12) and (13) or Eqs. (15) and (16) are chosen. The errors are presented in Table 2 and rounded up to the next whole percent. It is interesting to note that

either Eq. (13) and Eq. (16) produce insignificant errors in the prediction of $c(0)/c_0$ as either g_1/c_0 or g_2/c_0, so in practice using the simpler Eq. (13) rather than Eq. (16) is justified and recommended. In all cases, Eq. (15) is obviously quite reliable, although not shown in Table 2, the error in K/c_0 increases rapidly when $D/v > 5$. Therefore the limit of use for Eq. (15) and (16), or (13), is $v^2 c_0 / Df(c_0) \geq 4$. On the other hand the limit of usability of Eq. (12) is quite poor, even for $v^2 c_0 / Df(c_0)$ as high as 40 the estimate of K/c_0 is not acceptable. This is of course expected, as at least a first order correction due to diffusion should be included. More details can be found in Barry et al. (1993).

D/v	0.05	0.5	2.5	5
$c(0)/c_0$	0.9975	0.9756	0.8902	0.8068
$c(5)/c_0$	0.7644	0.7482	0.6868	0.6287
$c(10)/c$	0.5659	0.5554	0.5164	0.4803
Using Eqs. (12) and (13): Relative Errors in %				
vc_0/f_0	0	-2		
K/c_0	0	7		
Using Eqs. (15) and (16): Relative Errors in %				
vc_0/f_0	0	0	2	1
K/c_0	0	0	-3	-3

Table 2: Exact concentrations at $x = 0, 5,$ and 10 cm.

When $vc_0/f_0 = 10$ cm and $K/c_0 = 1$, for various values of D/v. The errors in parameters' estimation are at the concentrations at 5 and 10 cm

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Biographical Sketches

Frank Stagnitti, a mathematician, soil physicist and environmental scientist, is an expert in the study of agricultural and hydrological systems, particularly in the fields of solute and contaminant transport, bioremediation, ecotoxicology, groundwater flow, coastal processes and wetlands technology. Dr Stagnitti has established an international research profile in the field of environmental systems modeling, is extensively published in this field and has attracted significant research funding within Australia, mainly through the Australian Research Council. Dr Stagnitti has participated in a number of international projects, mainly funded by the EU under the 5th and 6th Framework agreements. Dr Stagnitti is a member of several scientific advisory committees and boards including the Australian Research Council, Center of Excellence in Light Metals and the Victorian Partnership in Advanced Computing. He currently holds the position of Associate Dean Research for the Faculty of Science and Technology at Deakin University and is a full Professor and Chair in Aquatic Science in the School of Life and Environmental Science. Dr Stagnitti is a Fellow of Australian Mathematics Society and a Fellow of Institute of Mathematics and its Applications (UK).

Jean-Yves Parlange, is a Professor of Agricultural and Biological Engineering at Cornell University having previously been a Professor of Applied Mathematics at Griffith University, in Brisbane, Australia. Yves Parlange has been a Fellow of the American Geophysical Union since 1996, received the Hydrology award in 1996, Horton medal in 2002 and elected to the U.S. National Academy of Engineering in 2006. His research interests are many and varied but centre on problems in environmental science and include water movement in porous media, solute transport in soils, surface and subsurface hydrology and erosion and sediment transport.

D. A. Barry, carries out research on porous media, flow and transport processes, particularly the modeling of such processes. He has been involved in many collaborative projects involving combinations of laboratory, field and theoretical work, including infiltration modeling. For example, he has collaborated in the development of a biogeochemical transport models for predicting transport and fate of contaminants in

complex subsurface environments. Other computer-modeling efforts include distributed catchment modeling and modeling of on-shore/off-shore sediment transport on ocean beaches. He is Editor of the journal Advances in Water Resources.

Tammo Steenhuis, is a professor in the Department of Biological and Environmental Engineering at Cornell University. He works with a group of 25 graduate students, postdoctoral researchers and research associates to see if it is possible to do research in hydrology from the nano to watershed scale years. He has collaborated extensively with Yves Parlange during the last 20 years on finding new ways for describing spatial variability in flow fields both above and below the ground.

Ling Li,is a Professor and Chair in Environmental Engineering in School of Engineering at the University of Queensland, Australia. His research and teaching interests are in environmental science and engineering with a particular focus on modeling of environmental systems. His current research work addresses interactions between the ocean and coastal aquifers, and pathways and fluxes of chemicals to coastal waters via submarine groundwater discharge. He is on the editorial board for Advances in Water Resources and is Associate Editor of Hydrogeology Journal.

David Lockington, is the Head of Environmental Engineering in the School of Engineering, as well as the Director of the Centre for Water Studies, at the University of Queensland, Australia. He is also the Director of the Engineering, Technology and Design Research Program in the national Cooperative Research Centre for Sustainable Tourism. His research interests center on modeling fluid flow in unsaturated porous media, variable density groundwater flow and contaminant transport. A particular interest is the use of these models in quantifying coastal catchment processes such as: subsurface estuary dynamics; submarine groundwater discharge; tidal marsh, wetlands and island hydrology; and seawater intrusion. He is a member of the editorial board of Advances in Water Resources and is a Fellow of the Institute of Mathematics and its Applications.

Graham Sander, is a Reader in Hydrology in the Department of Civil and Building Engineering at Loughborough University, England. Prior to his current position he was in the Faculty of Science and the Faculty of Environmental Sciences at Griffith University, Australia. His research and teaching interests are in environmental science and engineering and cover predominantly soil erosion modeling, water and solute transport in porous media and unsaturated two-phase flow. He is on the editorial board for Advances in Water Resources and is Associate Editor of Water Resources Research.