Pollutant Transport Through Barriers

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Methods of predicting contaminant transport through saturated and
unsaturated clayey barriers are reviewed. Particular consideration is
given to the relative importance of advection and dispersion as tran-
sport mechanisms, the soil properties controlling transport, transport
through saturated and unsaturated soils, contaminant transport through
barriers and into adjacent aquifers, and finally, to methods of obtain-
ing solutions to the transport equations. Based on this review, a
number of specific observations and recommendations are made.

Introduction

Any attempt at quantitative predictions of contaminant transport
through soil must necessarily involve

(i)   identifying the primary transport mechanism and contaminant
      sinks;
(ii) formulation of a theoretical (mathematical) model which describes
      these mechanisms;
(iii) determination of relevant parameters; and
(iv) solving the governing equations for the specific problem under
      consideration (i.e., for the appropriate soil and leachate para-
      meters, geometry, boundary and initial conditions).

The primary transport mechanisms are advection and/or dispersion
(which includes mechanical mixing and diffusion). Contaminant sinks
may occur due to mechanisms such as sorption of contaminant (eg. cation
exchange of ions such as Na^+, Ca^{++}, K^+ onto the clay minerals or
sorption onto organic matter in the soil), precipitation (eg. precipi-
tation of heavy metals such as Fe, Pb in carbonate rich soils to form
$FeCO_3$, $PbCO_3$) and biological action (eg. oxidation of organic contami-
nants to form carbon dioxide, biomass and water or the conversion of
nitrate NO_3^- to nitrogen N_2).

Various theoretical models have been proposed for describing the
movement of contaminants through soil. Thoughtful reviews of these
models have been published by Anderson (1979) and Gillham and Cherry
(1982). The majority of these models are deterministic in nature and
may be categorized as either advective (i.e., neglecting dispersion) or
advective-dispersive models. There are certain classes of problems
where a simple advective model may be useful, however for most

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contaminant migration problems dispersion (whether as diffusion through
fine grained soils or as predominantly mechanical mixing in coarse
grained soils) is a significant mechanism which should be considered.
Thus in this paper, attention will be restricted to the advective-
dispersive model.

Stochastic models have also been developed (eg. Tang & Pinder, 1977;
Dievlin et al., 1981 and others). A primary objective of these models
is to allow for heterogeneity, particularly with regard to hydraulic
conductivity in problems of relatively large areal extent. These
approaches show promise, although at this time, they do not appear to
be suitable for use in practical design applications because of the
difficulties in defining the statistical properties of the relevant
parameters together with the large computational cost associated with
stochastic approaches.

In the following sections we will be concerned with the prediction
of contaminant transport using an advective-dispersive model. For
unsaturated soil, the governing partial differential equation 1D condi-
tions can be written in the form

$$\frac{\partial}{\partial t}(\theta c) = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial}{\partial z}(v_a c) - g \qquad (1)$$

where t = time (a)
$\quad \theta$ = volumetric water content (dimensionless)
$\quad c$ = contaminant concentration (in solution) (g/L)
$\quad z$ = position co-ordinate (m)
$\quad D$ = dispersion coefficient (m^2/a)
$\quad v_a$ = specific discharge (Darcy flux) (m/a)
$\quad g$ = a term which takes account of retardation (eg. due to
$\qquad$ sorption: to be discussed later) (g/L / a)

For a saturated soil, Equation 1 reduces to

$$n \frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(n D \frac{\partial c}{\partial z}\right) - \frac{\partial}{\partial z}(n v c) - g \qquad (2)$$

where n = soil porosity (dimensionless)
$\quad v$ = seepage velocity (average linear pore-water velocity) (m/a)
$\quad$ and all other terms are as defined above. Note that the advec-
$\quad$ tive (Darcy) velocity $v_a = nv$.

In the following sections, consideration will be given to the rela-
tive importance of advection and dispersion as transport mechanisms,
the soil properties controlling transport, transport through unsatu-
rated and saturated soils and finally, to methods of obtaining solu-
tions to the transport equation.

Transport Mechanisms and Their Relative Importance

As previously noted, the primary transport mechanisms are advection
and/or dispersion. The advective transport depends on the groundwater
(seepage) velocity (see Eq. 2). Dispersive transport depends on the
dispersion coefficient D which is given by

$$D = D_e + D_m \qquad\qquad (3)$$

where D_e = effective diffusion coefficient of contaminant through
             the soil (m^2/a);
        D_m = coefficient of hydrodynamic (mechanical) dispersion
             (m^2/a)

It is generally assumed that the mechanical dispersion is proportional to the groundwater velocity v viz.

$$D_m = \alpha v \quad (m^2/a) \qquad\qquad (4)$$

where α is the dispersivity (in m).

A considerable number of laboratory tests have been performed to verify the applicability of the advection-dispersion model (Eqs. 2, 3 and 4). The available data would suggest that for the majority of cases (some of the exceptions will be discussed later) the model was quite adequate for practical purposes (eg. see Fried, 1975). The laboratory tests indicate that at "low" velocities the dispersion coefficient is equal to the effective diffusion coefficient while at "high" velocities, the dispersion coefficient increases as a linear function of velocity.

Perkins and Johnston (1963) have published an empirical relationship which provides some insight as to what constitutes "low" and "high" velocities. Based on the results of a number of tests on homogeneous samples, the (longitudinal) dispersion coefficient D was given by

$$D = D_e + 1.75 \ d \ v \ (m^2/a) \qquad\qquad (5)$$

where   d = mean grain diameter of the soil   (m).

The effective diffusion coefficient D_e often lies in the range from 0.005 to 0.05 m^2/a. Adopting these two values, Fig. 1 shows the variation in dispersion coefficient D (from Eq. 5) with velocity for two mean grain sizes (d = 2 μm and 200 μm).

Assuming that Eq. 5 is applicable to saturated homogeneous, unfractured, silts, silty clays or clayey soils with hydraulic conductivity (permeability k) less than 10^{-5} cm/s, mechanical dispersion may be neglected for hydraulic gradients less than 1 (i.e., in most such cases). For a saturated homogeneous sand with hydraulic conductivity of 10^{-3} cm/s or less (and d $\leq$ 200 μm), these results also suggest that diffusion will generally dominate over mechanical dispersion for hydraulic gradients less than 0.01. For coarser sands where hydraulic conductivities or gradients are higher, mechanical dispersion may be significant.

It is evident from Fig. 1 that for d < 200 μm, the dispersion coefficient is quite independent of the groundwater velocity for advective (Darcy, discharge) velocities v_a less than 10^{-1} m/a. This then

raises the question as to how important advective transport is for
these velocities (i.e., $v_a < 10^{-1}$ m/a). To provide some answer to
this question, analyses were performed to determine the peak chemical
flux exiting from beneath a 1.2 m thick clay liner (n = 0.4) as a
function of the advective velocity v_a. For purposes of illustration,
the dispersion coefficient was taken to be 0.018 m^2/a (which is the
effective diffusion coefficient for chloride through a clayey till
barrier from Sarnia; determined by Rowe and Caers, 1986). Unless
otherwise noted, the leachate concentration was assumed to be constant
at $c_0 = 1$ g/L (i.e., $c_0 = 1000$ g/m^3) and the liner was assumed to
be totally washed (i.e., such that the base concentration c_b= 0--see
insert to Fig. 3).

Figure 2a shows the steady state variation in concentration with
depth beneath the "landfill" for the case of pure diffusion ($v_a = 0$)
and for an advective velocity of 0.006 m/a. Notice that the
concentrations for $v_a > 0$ are greater than those for $v_a = 0$
throughout the layer. Furthermore, the concentration gradient ($\partial c/\partial z$)
at the bottom of the liner for $v_a > 0$ is also greater than that for
$v_a = 0$. Thus it follows that for a given soil and contaminant (i.e.,
given value of D), the mass of contaminant (per unit area, per unit
time) passing through the barrier and into the underlying aquifer
(i.e., the exiting chemical flux or exit flux), will increase with
increasing advective velocity v_a.

For situations where v_a does not equal 0, it may be tempting to
estimate the peak flux loading, f, on the aquifer by performing two
simple hand calculations viz.

$$f = -nD\ \partial c/\partial z = nDc_0/H \quad (g/m^2/a) \qquad (\text{assuming } v_a=0) \qquad (6a)$$

$$f = nvc_0 = v_a c_0 \qquad\qquad (g/m^2/a) \qquad (\text{assuming } D=0) \qquad (6b)$$

where H is the thickness of the liner (m) and c_0 is the constant
leachate concentration (1 g/L = 1000 g/m^3).

Figure 2b shows the variation in exit flux with time for the case of
pure diffusion (D = 0.018 m^2/a, $v_a = 0$), pure advection (D = 0,
$v_a = 0.006$ m/a) and advective-diffusive transport (D = 0.018 m^2/a,
$v_a = 0.006$ m/a). Coincidentally, in this example the maximum flux of
6 g/m^2/a is identical for both the pure diffusion and pure advection
cases. Conventional calculations performed neglecting diffusion and
assuming plug flow (D = 0, $v_a = 0.006$ m/a), would suggest that no
contaminant would escape into the aquifer until the seepage front
arrived at the base after 75 years. However, diffusion is important
and due to diffusion alone an exit flux exceeding 10% of the maximum
flux would be expected after only 5 years. Indeed, the maximum flux of
6 g/m^2/a would be attained after only 50 years (compared to 75 for plug
flow). Consideration of both advection and diffusion gives a
substantially higher flux at any time with the peak flux being 55%
higher than the peak flux obtained by considering either diffusion or
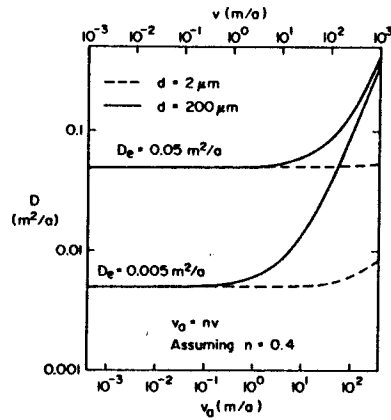advection independently.

Figure 1. Dispersion coefficient D as a function of seepage velocity v and advective velocity v_a (assuming n=0.4) - based on Eq. 5 (Perkins & Johnston, 1963)
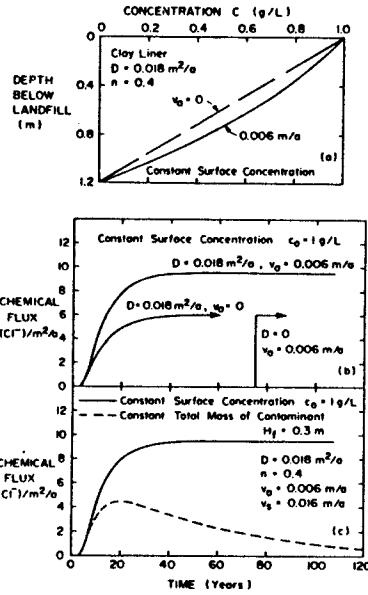
Figure 2. Effect of assumptions concerning the dispersion coefficient and advective velocity on (a) concentration profile through the liner (b) chemical flux passing out of the liner (exit flux) assuming constant contaminant concentration in the landfill (c) chemical flux passing out of the liner - assuming constant total mass of contaminant (H_f=0.3m - see text)

The full line in Fig. 3 shows the increase in the peak exit flux with increasing advective velocity for a constant leachate concentration (c_0 = 1 g/L). An indication of the velocities at which diffusion and advection are dominant can be obtained by comparing these actual flux values with the values calculated from Eq. 6, as shown in Fig. 4. Diffusion is clearly the dominant mechanism for advective velocities less than 2×10^{-4} m/a while advection dominates over diffusion for advective velocities greater than 2×10^{-2} m/a. Both advection and diffusion play a very important role for intermediate velocities.
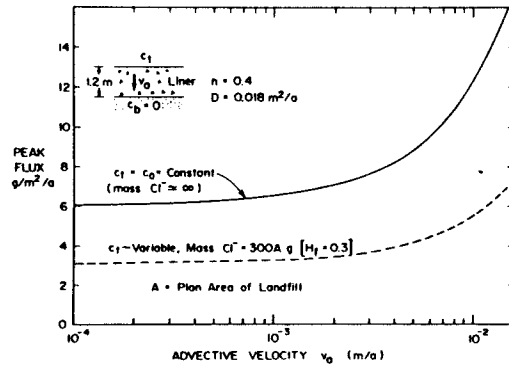
Figure 3. Maximum (peak) chemical flux passing out of the liner as a
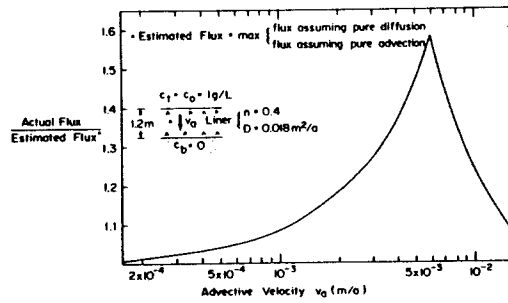function of advective velocity v_a

Figure 4. Error in calculated peak exit flux which arises from not con-
sidering both advective and dispersive-diffusive transport

In many practical situations involving clay barriers, the hydraulic
conductivity will be less than 10^{-7} cm/s and the hydraulic gradient
less than 0.2. These cases will involve advective velocities v_a
0.006 m/a or less.

Figure 5 summarizes the range of velocities in which diffusion and
advection have the dominant effect on the exit flux for the problem
examined. Also shown is the range of velocities over which the
dispersion coefficient is controlled by diffusion or mechanical
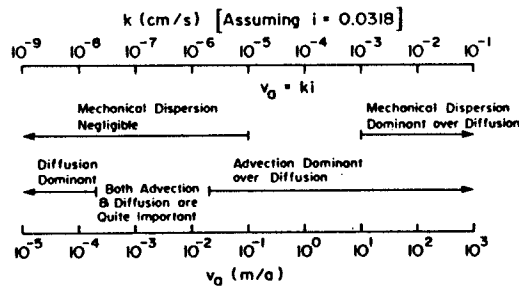dispersion as determined from Eq. 5.

Figure 5. Range of velocities over which Diffusion or Mechanical Dis-
persion controls the Dispersion coefficient D [based on Eq. 5
- see text] and the range of velocities over which Diffusion
or advection dominates the peak exit flux through a 1.2 m
clayey liner (see text for details)

Properties Controlling Transport

From the foregoing discussion, it is evident that the advective
velocity v_a and the dispersion coefficient D are two essential quan-
tities controlling contaminant transport.

The advective velocity v_a depends on the hydraulic gradient and
the hydraulic conductivity of the soil. The determination of hydraulic
conductivity requires studies involving a leachate with characteristics
similar to those anticipated in the actual landfill. This aspect of
soil-leachate compatibility and the determination of hydraulic conduc-
tivity will be dealt with in other papers in this conference and will
not be discussed here.

For problems in which diffusion dominates over mechanical dispersion
(which represents the majority of cases involving clayey barriers, eg.
see Fig. 5), the dispersion coefficient D is often related to the dif-
fusion coefficient of the species in aqueous solution, D_0, by the
expression

$$D = \tau D_0 \qquad (m^2/a) \qquad (7)$$

where the tortuosity of the soil, τ, (dimensionless) is assumed to be a
geometric property of the soil which is independent of the species be-
ing examined. This tortuosity can be determined from diffusion tests
using a non-reactive (conservative) tracer such as Cl^-. The effec-
tive diffusion coefficient (and hence D) for other species is then
estimated using this value of τ and published values of D_0 for the
species of interest. The value of τ generally reported in the litera-
ture for granular soils is about 0.7 (eg. see Perkins and Johnston,
1963; Bear, 1972). However, values of around 0.35 have been deduced
from both the field and laboratory behaviour for a clayey till beneath
a landfill in Sarnia, Ontario (Rowe et al., 1985; Rowe and Caers,
1986).

It should be emphasized that the procedure described above assumes that the effective diffusion coefficient can be directly related to the diffusion coefficient in aqueous solution by a geometrical quantity τ. While this approach appears to work reasonably well for some salt solutions (eg. NaCl, KCl, $CaCl_2$ etc.), it may not be valid for all contaminant species (eg. non polar organics). It is this author's opinion that the effective diffusion coefficient D_e of key contaminant species should be regarded as an empirical parameter which is directly determined for the leachate of interest using an "undisturbed" sample of the proposed barrier/liner material rather than by applying a tortuosity factor to the diffusion coefficient for aqueous solution.

Determination of the dispersion coefficient may require special consideration for unsaturated soils and/or cases where the mechanical dispersion dominates over diffusion. These special cases will be discussed in more detail in the following two sections.

The concentration of contaminant within the pore fluid of a clay barrier can be reduced by processes such as ion exchange, precipitation, bacterial modification etc. These various sink mechanisms will be discussed in more detail by Quigley et al. in another paper at this conference. In principle, it should be possible to incorporate each sink mechanism into the component g of Eqs. 1 and 2. In practice, the most commonly modelled sink mechanism is that of linear sorption viz.

$$g = \rho K \frac{\partial c}{\partial t} \qquad (g/L/a) \qquad\qquad (8)$$

where ρ = dry density of the soil (g/m^3)
        K = "distribution" or "partitioning" coefficient (m^3/g)

Linear sorption arises, for example, when the contaminant species moves from the liquid to solid phase as a result of ion exchange at low solute concentrations. The relevant parameter (referred to as the distribution coefficient K_d) is usually determined from batch tests which involve taking a relatively small powdered mass of the soil, mixing it with a volume of the solution of interest and then allowing enough time for chemical equilibrium to be reached. At low concentration, the ratio of the concentration on the soil (typically in mg/g of soil) to the equilibrium concentration in solution (typically mg/L or mg/m^3) then gives the distribution coefficient K_d.

The difficulty with the approach described above is that one does not know whether the values of K_d determined from this test for small quantities of totally disturbed soil are appropriate to field situations. An alternative approach which allows both the effective diffusion coefficient and the effective "distribution or partitioning" coefficient K to be determined from undisturbed samples of the proposed liner/barrier material has been proposed by Rowe et al. (1985) and is described in detail by Rowe and Caers (1986). A refinement of this technique for volatile organic contaminants is also soon to be published (Barone, personal communication).

The distribution coefficient will depend on the mineralogical composition of the soil as well as the proportion of other non-mineral

constituents and can vary substantially from one soil to another.
Tests should therefore be performed using the actual soil of interest
for the range of contaminant concentration expected in the field.

In tests conducted to determine the distribution coefficient K_d,
processes other than ion exchange may also occur. It is an open
question as to what these processes may be, and as to whether they are
reversible. For this reason, the distribution coefficient in Eq. 8 is
denoted by K rather than K_d (the latter term implying that they truly
are reversible). It may be argued that it is conservative to model
these processes as reversible linear adsorption using the experi-
mentally determined values of K from tests on intact soil, provided
that these processes are in fact manifest as linear sorption over the
concentration range applicable in the field. More research is required
to confirm (or refute) this speculative suggestion.

Combining Eqs. 2 and 8 gives

$$n \frac{\partial c}{\partial t} = nD \frac{\partial^2 c}{\partial z^2} - nv \frac{\partial c}{\partial z} - \rho K \frac{\partial c}{\partial t} \tag{9}$$

This equation can be rewritten (eg Gillham and Cherry, 1982 and many
others) as

$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial z^2} - v^* \frac{\partial c}{\partial z} \tag{10a}$$

where $D^* = D/R$, $v^* = v/R$ and R is referred to as the retardation factor
and is given by

$$R = 1 + \frac{\rho K}{n} \tag{10b}$$

For a soil layer subject to specified concentrations at the boun-
daries, Eqs. 10 can be readily solved in terms of D^* and v^* to give the
variation in concentration with depth throughout the deposit. However,
particular care is required in calculating the chemical flux (i.e.,
mass of contaminant transport) since the flux is controlled by D and v
rather than D^* and v^*. Most computer programs (and analytic solutions)
evaluate Eqs. 10 and the flux using the same values of D and v and
hence the use of parameters D^* and v^* to determine fluxes from these
programs would lead to erroneous results.

In a great many practical situations, the most appropriate model
will involve flux controlled boundary conditions (as discussed in the
following paragraphs). Under these circumstances, the use of
parameters D^* and v^* can lead to very misleading and unconservative
estimates of contaminant concentration as shown by Rowe et al. (1985).

It may be concluded that the parameters D^* and v^* (which incorporate
the retardation factor R) can sometimes be useful, however there is
considerable potential for error arising from the use of these
parameters for all but the most straightforward applications. It is
for this reason that the use of these parameters is not recommended.

In analyses of contaminant transport, it is often assumed that the concentration of contaminant in the waste source (eg. the landfill) remains constant at the maximum expected value. This is a simple and conservative assumption; but it may be too conservative. The assumption of constant source concentration implicitly assumes that additional mass of contaminant is continually being added to the source to replace the contaminant that has been transported into the soil. However, in many situations (eg. a domestic landfill), the mass of contaminant is finite and fixed once the landfill has been completed. Decomposition of the waste will commence following placement. Typically, the concentration of contaminant within the waste will increase with time until a maximum value is reached. An estimate of this value would normally be used in calculations as the "initial" leachate concentration c_0. However, the leachate concentration will then usually decrease with subsequent time as contaminant is transported into the soil.

The mass of contaminant m_0 (g) within the waste, the volume of leachate v_0 (m^3) and the maximum contaminant concentration c_0 (g/m^3) within a leachate can be estimated. These quantities may be related as follows:

$$m_0 = c_0 \, v_0 = c_0 \, A \, H_f \qquad\qquad (11)$$

where A (m^2) is the plan area of the landfill and H_f (m) is the equivalent height of leachate. Normally, the concentration c_0 and the mass of contaminant m_0 can be estimated from previous experience and hence the equivalent height of leachate H_f can be calculated. Clearly, an upper limit on the mass of contaminant is imposed by the total mass of waste within the landfill.

If all the contaminant is in solution at the concentration c_0, then H_f may correspond to the actual volume of leachate within the landfill. However, if some of the contaminant is still in the solid phase when the landfill concentration is c_0, then the calculated height of leachate multiplied by the plan area will exceed the actual volume of leachate in the landfill. This may be regarded as a convenient device for calculation purposes. It is conservative in these cases to adopt a value of H_f which corresponds to a volume of leachate greater than the actual volume. In fact, the common assumption that c_0 is always constant corresponds to the limit as H_f tends to infinity.

To illustrate the implications of considering the finite mass of contaminant, calculations were performed to determine the flux exiting into an aquifer beneath a 1.2 m thick clayey liner assuming that the "initial" contaminant concentration c_0 in the landfill is 1 g/L, and that the mass of contaminant 300 g per square metre plan area. This corresponds to an equivalent height of leachate H_f = 0.3 m. The variation in exit flux with time calculated for this case is shown by the short dashed curve in Fig. 2c and may be directly compared with the corresponding full curve obtained assuming the source leachate concentration remains constant (i.e., $H_f \to \infty$).

When the finite mass of contaminant is considered, the flux (and similarly the concentration at any point) increases to a peak value at some time t_p and then decreases for all subsequent times ($t > t_p$). In this case here, the peak flux calculated assuming $H_f = 0.3$ is less than half the peak flux that was calculated assuming a constant surface (leachate) concentration.

There is a fundamental difference between the assumptions of finite contaminant mass and constant leachate concentration (i.e., $H_f = \infty$, infinite mass). This difference is evident from consideration of the steady state solution. If the mass of contaminant is finite then in an open system both the contaminant concentration and the flux will tend to zero at very large times (i.e., steady state). If the leachate concentration is constant, then the contaminant concentration and flux tend to a maximum steady state value. This latter situation could in some circumstances imply that a landfill design is inadequate when a more realistic analysis of the problem would show that contaminant escaping from the landfill satisfies all environmental requirements.

Figure 3 shows the calculated peak exit flux as a function of advective (Darcy) velocity for the two cases. If the mass of contaminant was 300 g/m^2, the assumption of a constant surface concentration in this case would lead to an overestimate of the peak flux by a factor of two, or more, over the entire range of velocities examined. For thicker liners or problems of larger extent, the effect could be even greater.

It is concluded that the mass of contaminant is an often overlooked parameter which may warrant consideration when predicting contaminant transport.

Transport Through Unsaturated Soils

Contaminant transport through unsaturated soils is often modelled by Eq. 1. This equation bears marked similarity to the governing equation for a saturated soil (Eq. 2) however this similarity may be deceptive. For an unsaturated soil, the volumetric water content, the dispersion coefficient and the specific discharge may vary both spatially and temporally. The movement of contaminant through unsaturated soils is a very complex phenomenon as demonstrated by a number of laboratory and field studies (eg. de Smedt, 1981; Gerhardt, 1984 and others).

The simplest case is that in which there is negligible advective transport through the unsaturated soils. This situation can only arise when the net infiltration is negligible. Under these circumstances, the migration of contaminant in solution will be very slow since the migration will be purely by diffusion and it has been shown (eg. Klute & Letey, 1958; Porter et al., 1960) that the effective diffusion coefficient in unsaturated soils may be substantially lower than in similar saturated soils.

In humid climates, the unsaturated soil will usually be

hydraulically active and advective transport (which may vary with time)
must be considered. As noted above, the diffusion coefficient is
dependent on the volumetric water content and hence will vary both
spatially and temporally in a hydraulically active region. The
advective transport will depend, in part, on the hydraulic conductivity
of the soil. This tends to increase with the volumetric water content
of the soil up to a maximum value for a saturated soil (eg. Gardner,
1958; van Genuchten, 1978). Thus, the hydraulic conductivity of
unsaturated soil will be far more sensitive to point-to-point
variations in grain size distribution than saturated soils and this
alone makes the determination of representative hydraulic
conductivities substantially more difficult. Additional uncertainty
arises from the effects of seasonal variations in infiltration and
assumptions concerning the expected long term weather pattern which may
influence calculated contaminant transport through unsaturated soils.

Various investigators have questioned the direct application of Eq.
1 for unsaturated soils (eg. Gaudet et al., 1977; de Smedt, 1981). The
problem tends to be manifest as an apparent dispersion well in excess
of what would be expected for a saturated soil. In an attempt to ex-
plain this phenomenon, various researchers (eg. Rao et al., 1974;
Gaudet et al., 1977; de Smedt, 1981) have proposed multiple water phase
models which involve advective-dispersive transport through the mobile
water (typically in the smaller saturated pores) together with "side-
ways" transfer of contaminant into (or from) the immobile water (gene-
rally in the larger unsaturated pores). This approach appears to give
reasonable agreement with experiments, although the parameters used are
generally selected by matching the experimental and theoretical beha-
viour. de Smedt (1981) has shown that a reasonable fit to his experi-
mental data could also be obtained using Eq. 1 and an effective disper-
sion coefficient D given by

$$D = \frac{\theta_m}{\theta} D_m + \frac{\theta_{im}^2 v^2}{\theta \theta_m \beta} \qquad (12)$$

where D_m = dispersion coefficient in the mobile water (m²/a)

$\theta_{im}, \theta_m, \theta$ = volumetric water content in the immobile, mobile phases
          and the bulk soil respectively

v = seepage velocity (v_a/θ) (m/a); and

β = coefficient for solute transport between phases (a^{-1}).

An inspection of (12) indicates the difficulties of using this
approach in practice since the parameters β, v, θ_m, θ_{im}, θ may be
expected to vary both temporally and spatially. Furthermore, the para-
meter β must be determined by curve fitting laboratory results for a
particular situation.

It may be concluded that even though some significant progress has
been made concerning the prediction of contaminant transport through
unsaturated soils, this is still a formidable undertaking and the
results obtained for practical situations should be viewed with
considerable caution. In view of the uncertainties, this author
recommends complementing analyses for unsaturated contaminant transport
by a simpler analysis which assumes that the soil is saturated

(adopting appropriate saturated soil parameters). The estimate of contamination for design should then be based on the worst case.

Transport Through Saturated Soils

Diffusion controlled contaminant migration through saturated clayey barriers is the most predictable of all the situations examined in this paper. For example, calculations of contaminant transport through a clayey till beneath a landfill in Sarnia, Ontario have been shown to be quite consistent with the observed field behaviour over a period of 16 years (see Goodall & Quigley, 1977; Crooks & Quigley, 1984; Quigley & Rowe, 1986). It has also been shown that Eq. 2 provides a good model of contaminant transport through soil in laboratory column tests and that parameters deduced from these tests give reasonable predictions of field behaviour (Rowe et al., 1985; Rowe & Caers, 1986).

Desaulniers et al. (1981) examined the upward migration of chloride through 40 m of clayey till from high concentration in the underlying Paleozoic bedrock. This migration, which has been proceeding for approximately 10 000 years, was modelled using Eq. 2 and was found to give quite reasonable results. The same study also examined the down-ward movement of oxygen-18 and deuterium and again it was found that the field migration profile established over a period of about 10 000 years could be reasonably modelled using Eq. 2.

Thus when concerned with predicting long term contaminant migration, the situation where a waste disposal site is located in a deep, unfrac-tured homogeneous clayey deposit where the advective velocity is small can be regarded as ideal. However, many practical situations involve a relatively thin clayey liner (barrier) separating the potential conta-minants from a groundwater aquifer. The advective velocity through the clay liner will usually be sufficiently small that diffusion will govern over mechanical dispersion and may even dominate over the effect of advection (eg. see Fig. 5). On the other hand, in aquifers the advective velocity will usually be sufficiently large that mechanical dispersion and heterogeneity govern the dispersion process. Modelling of this situation should involve consideration of both the liner and aquifer.

The majority of the literature dealing with contaminant transport through soils (eg. see Anderson, 1979) is concerned with movement through aquifers where the velocity v is "relatively large" and where the dispersion coefficient D is assumed to be directly proportional to the velocity v viz.

$$D = D_m = \alpha v \quad (m^2/a) \tag{13}$$

where α (m) is the dispersivity. This approach implicitly assumes that the effects of diffusion are negligible.

The use of the advection-dispersion equation (Eq. 2) for predicting contaminant transport in aquifers has been subject to criticism by various commentators (eg. Gillham & Cherry, 1982a,b). Much of the

criticism relates to the fact that the dispersivity α is not a material constant. Rather, backfigured values of α (obtained by matching numerical calculations to observed plume movement) are highly variable and depend on the scale of the problem being considered. Values may, in fact, vary by several orders of magnitude as one moves from laboratory scale to problems of large areal extent (eg. see Anderson, 1979).

Heterogeneity of aquifers is considered to be the cause of the variability in dispersivity α. It may be envisaged that "fingers" of contaminant will move faster through the more permeable regions than through the less permeable regions. In the absence of diffusion, this approach would be expected to give rise to appreciable, measurable, "fingering" of the contaminant within heterogeneous aquifers. However, as noted by Gillham and Cherry (1982a), field data provides little or no evidence of fingering. To account for the smoothly dispersed zones in heterogeneous materials, Gillham and Cherry hypothesized that

> as contaminants are transported primarily by advection in the more permeable heterogeneities, migration by diffusion occurs into the adjacent heterogeneities of lower permeabilities, thereby reducing the concentrations in the main zones of advection and increasing the concentrations in zones of lesser flow.

When attempting to model movement of contaminant through clayey barriers and into aquifers, it must be recognized that considerable uncertainty will always exist concerning the magnitude of both the dispersion coefficient and the advective velocity v in the aquifer. Thus in practice, sensitivity analyses will be required to indicate the potential consequences of this uncertainty. To provide some insight concerning these effects, Rowe and Booker (1985) examined the case of a landfill separated from a 1 m thick aquifer by a 2 m thick clayey liner. The geometry of the problem and the key parameters considered by Rowe and Booker are shown in the insert to Figs. 6 and 7.

Figure 6 shows the calculated maximum concentrations of contaminant $c_{b(max)}$ ever reached at two points in the aquifer ($x = 100$ m, i.e., at the downgradient edge; and $x = 400$ m, i.e., 300 m downgradient from the landfill) for a range of assumed values of the horizontal dispersion coefficient D_H. (The concentrations are normalized with respect to the initial concentrations of contaminant within the landfill, c_0.) For the case considered, the maximum concentration of contaminant at the edge of the landfill decreases with increasing D_H and it would be conservative to adopt a value of D_H equal to zero (i.e., ignore dispersion). At a point well away from the landfill ($x = 400$ m) the effect of D_H is dependent on the advective velocity in the aquifer.

At low velocities, the maximum concentration of contaminant increases with increasing D_H. The reason for this lies in the fact that at low velocities there can be considerable attenuation of contaminant in the aquifer due to diffusion into the adjacent clay. The longer it takes the contaminant to reach a monitoring point, the greater the potential for attenuation. At low velocities, the assumption of a very high D_H value decreases the time for diffusion into

the clay prior to reaching the monitoring point and hence gives a higher maximum concentration at that point.

At high velocities, the maximum concentration of contaminant decreases with increasing D_H due to the dispersion of the contaminant front. In these cases, the effect of attenuation due to diffusion into the clay is overshadowed by the effect of the increased dispersion.

Figure 7 shows the variation in the maximum base concentration at $x = 100$ m and 400 m together with the time required to reach this maximum, as a function of the assumed advective velocity v_b within the aquifer. Beneath the edge of the landfill ($x = 100$ m), the maximum concentration decreases monotonically with increasing base velocity due to the consequent increased dilution of the contaminant in high volumes of water. However, at points outside the landfill area, there is a critical velocity which gives rise to the greatest "maximum" concentration. As indicated by Rowe and Booker (1985), this situation arises because of the interplay of two different attenuation mechanisms. The first of these, diffusion into the surrounding clayey soil, is dependent on the time required to reach the monitoring point. Generally, the lower the velocity v_b, the more time there is for contaminant to diffuse away and hence the lower the maximum concentration. The second mechanism, dilution, involves decreasing contaminant concentration due to higher volumes of water (i.e., higher v_b).

An important practical consequence of the foregoing is that it is not necessarily conservative to design only for the maximum and minimum expected velocities in the aquifer. In performing sensitivity studies, sufficient analyses should be performed to either determine the critical velocity or, alternatively, to show that the critical velocity does not lie within the practical range of velocities for the case being considered.

In summary, the diffusion controlled movement of contaminant through clayey barriers can be estimated with a reasonable degree of certainty using Eq. 2 and appropriately determined parameters. However, when the liner is in contact with an aquifer, the entire liner-aquifer system should be examined. The values of the dispersion coefficient and advective velocity within the aquifer may be subject to considerable uncertainty and a sensitivity analysis will usually be required to determine the most critical case. It has also been shown that depending on the circumstances it is not always conservative to simply perform analyses for the upper and lower bounds of the expected values of dispersion coefficient and advective velocity within the aquifer. The range of values may need to be examined.

Transport Models

Contaminant transport models consist of two essential parts:
(i) the governing equations (together with the initial and boundary conditions), and
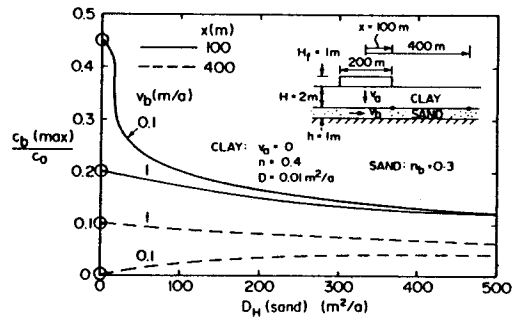
Figure 6. Variation in maximum contaminant concentration within the aquifer with variation in the assumed dispersion coefficient in the aquifer (After Rowe & Booker 1985; reproduced with permission, Canadian Geotechnical Journal).
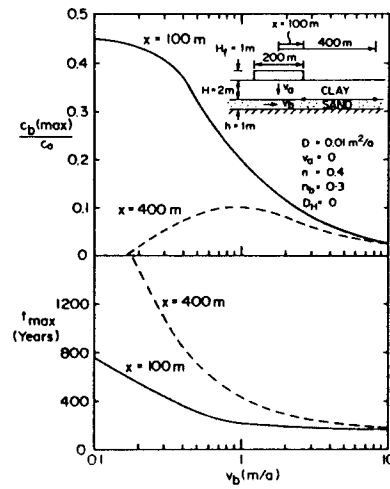

Figure 7. Variation in maximum contaminant concentration within the aquifer with variation in assumed advective velocity v_b (After Rowe and Booker, 1985; reproduced with permission, Canadian Geotechnical Journal).

(ii) the technique for obtaining a solution to the governing equations.

As noted in the introduction, various theoretical models have been proposed (see Anderson, 1979; Gillham & Cherry, 1982). However, at this time, the class of models that appears to be most suited to the prediction of contaminant transport through clay barriers and into aquifers are those models which involve the advection-dispersion equation in its 1D, 2D or 3D form. Restricting attention to this class of models, there remains the question as to how we can use this equation (subject to the appropriate soil properties, boundary and initial conditions) to predict contaminant transport for practical problems. The most frequently used solution techniques may be subdivided into five broad categories, namely analytic, finite layer, boundary element, finite difference and finite element.

Analytic solutions are generally regarded as being the most desirable since they provide a closed form solution for the concentration (and, potentially, flux) at any particular point in space and time. Numerous analytic solutions have been reported in the literature (eg. Lapidus & Amundson, 1952; Ogata & Banks, 1961; Lindstrom et al., 1967; Selim & Mansell, 1976; Rowe & Booker, 1985b; Booker & Rowe, 1986 and others). To make the problem tractable, these solutions have been obtained for highly idealized problems.

The available solutions can be used directly for predicting contaminant migration for a limited range of problems. However, in most cases the actual situation is sufficiently far removed from that assumed in developing the analytic solutions, that these solutions can only be used to provide a general indication of what might happen. A calculation more specific to the actual case would be required for prediction.

Many of the available analytic solutions are sufficiently complex that a computer is required to evaluate the terms in the closed form solutions. This is not always a trivial exercise, particularly at relatively high advective velocities and the user should be aware of potential numerical error associated with computer evaluations of these analytic solutions. Semi-analytic (finite layer) methods may in fact give more accurate results in some cases.

Finite layer techniques typically involve taking a Laplace and, for 2D or 3D conditions, a Fourier transform of the governing equations and then finding an analytic solution in transformed space. In this regard, the approach parallels the development of many analytic solutions. The difference arises from the fact that the finite layer solution involves a less restrictive idealization of the problem and as a consequence of this greater complexity, it is not possible to invert the Laplace (and Fourier) transforms analytically. The transforms can, however, be quite readily inverted numerically and hence the designation as a semi-analytic method.

As an example of a finite layer approach, Rowe and Booker (1985a,b; 1986) have proposed a technique for modelling contaminant transport for 1D, 2D or 3D conditions. This approach involves splitting the soil deposit into separate layers. For example, separate layers may be used

to model surface runoff, the clay cover, the waste, the clay liner and any underlying aquifers or other soil layers. Because of its semi-analytic nature, the concentrations of contaminant (and the fluxes) can be very accurately determined at any specified times and locations of interest without determining the solution at all points and previous times (as is necessary in finite element and finite difference approaches). The analysis requires negligible data preparation, can be performed on a micro-computer and its use generally does not require an extensive knowledge of numerical analysis.

The finite layer technique is ideally suited for situations where the stratigraphy is (approximately) horizontally layered, contaminant sorption is linear and where the designer is concerned with the maximum concentration expected at a number of key locations. The technique is also useful for benchmarking more complex numerical (eg. Finite Element) solutions. The finite layer method is not suitable for problems with complex geometry/stratigraphy (where the deposit cannot be idealized as being layered), or where modelling of non-linearity is essential.

The boundary element technique can be used to solve the advection-dispersion equation (eg. Brebbia & Skerget, 1984) but, to date, has not found significant application in solving contaminant transport problems. This situation is likely to change over the next few years.

Finite difference and finite element methods have found extensive application for the analysis of contaminant transport in soils. There are, in fact, a great many numerical schemes which can be categorized as finite difference or finite element approaches and the differences between these formulations can have a significant impact on the accuracy of the numerical results as well as the complexity of the analysis and the computational costs. The Finite Element Method is regarded by many as the more general approach and its use predominates the recent literature. However, this view is by no means universal and there exists a difference of opinion regarding the advantages of the finite element schemes over alternative numerical approaches such as finite differences.

Even if one restricts attention to the Finite Element Method, there are numerous different algorithms and some controversy. This situation arises from the fact that it is not a trivial exercise to obtain accurate solutions to the advection-dispersion equation using finite elements, particularly when the advective velocity is significant. Without going into the numerical details, some of the problems are demonstrated in Fig. 8 which shows results obtained by Yeh (1984) using two different Finite Element schemes to solve a simple one-dimensional problem where the Peclet number P_e = 50. It can be seen that the finite element solutions do not provide a good definition of the concentration front. Some finite element schemes give unrealistic wiggles near the concentration front including physically impossible concentrations. Other schemes, developed to avoid these wiggles, exhibit nonphysical smearing. The literature contains many examples of a particular scheme being presented as the most appropriate for a particular situation however there is no clear argument for any one

finite element scheme being universally better than some of its rivals
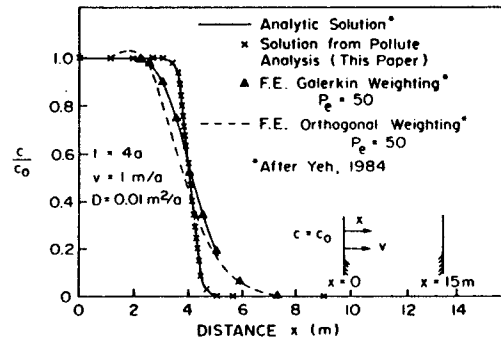(eg. see Allen, 1984).

Figure 8. Comparison of concentration variation with distance as calcu-
lated from: analytical solution, finite layer program
POLLUTE, and two finite element analyses reported by Yeh
(1984)

The finite element method is undoubtedly a very powerful tool which
can be used to model complex geometry as well as non-linearity.
However, as a result of this generality, finite element codes are also
quite complex and their use involves relatively high computational and
data preparation costs. Great care is required in analyzing problems
which are sufficiently complex to warrant a finite element analysis.
These analyses should only be performed by individuals with conside-
rable training and experience in numerical methods. Furthermore, in
any practical applications, it is recommended that prior to analyzing
the practical problem, the problem should be idealized sufficiently to
allow analysis using either analytic solutions or the finite layer
technique. The finite element code and numerical procedure should be
checked by comparing the finite element results for this idealized
problem with the analytic or finite layer solution. Once this check
has been successfully completed then the more complex practical
situation can be examined using the finite element code.

To illustrate the type of comparison that can be conducted between
finite element results and finite layer results, the finite layer
solution (using Program POLLUTE - Rowe et al. 1984) to the problem
examined by Yeh (1984) is shown in Fig. 8. This finite layer solution,
which was obtained in less than a minute on a micro-computer, coincides
with the analytic solution and comparison of this result with the
finite element results illustrates the limitations of the finite
element mesh and procedures used to obtain the finite element results.

Conclusions

Methods of predicting contaminant transport through unsaturated and saturated barriers have been discussed. Based on this review, the following recommendations and conclusions have been made:

1. For typical problems involving barriers, mechanical dispersion does not appear to be a significant factor for problems where the advective (Darcy) velocity is less than 0.1 m/a.

2. When considering contaminant flux from beneath the typical liner examined, advection tends to dominate over diffusion for advective velocities greater than 0.02 m/a. Conversely, diffusion tends to dominate over advection for velocities less than 0.0001 m/a. Both advection and diffusion may play a very important role for intermediate velocities.

3. The effective diffusion coefficient of key contaminant species should be directly determined using an "undisturbed" sample of the proposed barrier/liner material rather than by applying a tortuosity factor to the diffusion coefficient for aqueous solutions.

4. Although the parameter $D^* = D/R$, $v^* = v/R$ (where $R = (1 + \rho K/n)$) may be useful in some instances, there is considerable potential for error arising from the use of these non-physical, composite, parameters and so it is recommended that these parameters should not be used.

5. The mass of contaminant is an often overlooked parameter which may warrant consideration when predicting contaminant transport.

6. Even though some significant progress has been made concerning the prediction of contaminant transport through unsaturated soils, this is still a formidable undertaking and the results of these analyses should be viewed with considerable caution. In view of the uncertainty, these analyses should be supplemented by simpler analyses assuming that the soil is saturated and adopting appropriate saturated soil parameters. The estimate of potential contamination should be based on the worst case.

7. Diffusion controlled contaminant transport through saturated clayey barriers is the most predictable of all situations examined in this paper.

8. When attempting to model movement of contaminant through clayey barriers and into aquifers, it must be recognized that considerable uncertainty will always exist concerning the magnitude of both the dispersion coefficient and advective velocity within the aquifer. Thus in practice, sensitivity analyses will be required to indicate the potential consequences of this uncertainty. It has also been shown that it is not always conservative to simply perform analyses for the upper and lower bounds of the expected values of dispersion coefficient and advective velocity. The range of values may need to be examined.

9. New finite layer techniques provide a relatively simple and accurate means of analyzing contaminant problems where the stratigraphy can be idealized as being horizontally layered.

10. Finite Element (and finite differences) methods represent very powerful numerical tools for calculating contaminant migration profiles for complex problems. However, considerable care and expertise are required to obtain meaningful results and the cost of these analyses can be quite high (both in terms of money and manpower). It is recommended that analytic solutions and techniques such as the finite layer method be used to complement numerical analyses (Finite Element and Finite Diffusion) both as benchmark solutions and as a means of placing limits on the likely range in which solutions from a numerical analysis should lie.

Appendix 1 - References

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