

A diffusion exchange model for solute movement in fissured porous rock

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Summary

A model of solute movement in an idealized, fissured, porous medium, involving diffusion exchange between mobile fissure-water and immobile pore-water, is formulated mathematically and solved numerically for a range of values of the input parameters. The insight gained into this mechanism of solute movement is of relevance in predicting the migration of the more soluble pollutants in the major British aquifers, and is of particular significance to the interpretation of the distribution of tritium and nitrate in the unsaturated zone of the Chalk beneath arable land.

Introduction

Background to model development

An understanding of the mechanisms of solute movement in groundwater systems is a fundamental aspect of hydrogeology and is of particular practical significance in the context of pollutant migration. Bedrock (consolidated) aquifers form a most important group in which the hydraulic conductivity (permeability) is predominantly associated with fissure development, but in many of these aquifers the rock matrix itself may possess significant porosity. For the purposes of this paper such formations have been termed fissured porous media. An excellent example is the Chalk in Britain, and the group includes a substantial number of other limestone and sandstone aquifers.

For the Chalk and other comparable porous media, Foster (1975) suggested that a major component of solute movement was controlled by a mechanism involving solute exchange, through lateral molecular diffusion, between mobile fissure water and (relatively) immobile matrix, or pore, water; the mobile fissure water eluting solute from high concentration regions in the matrix and transferring it to regions of lower concentration along its direction of flow. This was of especial significance when interpreting the distribution of thermonuclear tritium and pollutants, such as nitrate, in the unsaturated zone of the Chalk and when predicting the rate of lateral migration of pollutants in the saturated zone of the aquifer (Foster 1976). It has been suggested (Oakes 1977) that such a mechanism would conform to the mathematical theory describing the chromatographic process, with instantaneous

equilibrium between the mobile and stationary water, and, in the case of the Chalk's unsaturated zone, it has gained acceptance by British hydrogeologists (Young *et al.* 1976; Downing *et al.* 1978, 1979; Reeves 1979).

Scope of paper

The primary reason for the construction of the mathematical model, described in this paper, was to give a detailed insight into the behaviour of this diffusion exchange mechanism for solute transport in fissured porous media, and to establish the extent to which the 'chromatographic' equilibrium approximation was valid. The model has been further developed to aid the interpretation of tritium, nitrate and other solute profiles of pore-waters from the Chalk's unsaturated zone (Fig. 1), but not at this stage to simulate their profiles, which are extremely complex in detail.

The model

Description

The migration of solutes in fissured porous media will be primarily controlled by the average geometry of the fissure system, assuming the rock matrix has relatively homogeneous properties. A substantial problem that arises in modelling, however, is to characterize this system by as few parameters as possible, while endeavouring to retain all the essential features of its behaviour. The geometry selected (Fig. 2) was intended to be the simplest that would retain such features.

Fissures (joints) were taken to be semi-infinite planar openings (of width w) at a uniform spacing, a , dividing the porous rock-mass into blocks. Because of the periodicity of this geometry, only a single, repeating, two-dimensional unit need be considered (Fig. 2). The fissures are assumed to be saturated with water which, having entered the system (at $y=0$) with known solute concentration, $f(t)$, passes down them at a velocity, u , with negligible dispersion in the y direction. The lateral gradient of solute concentration in the fissures is assumed to be negligible and, at each depth, this concentration is assumed to be equal to

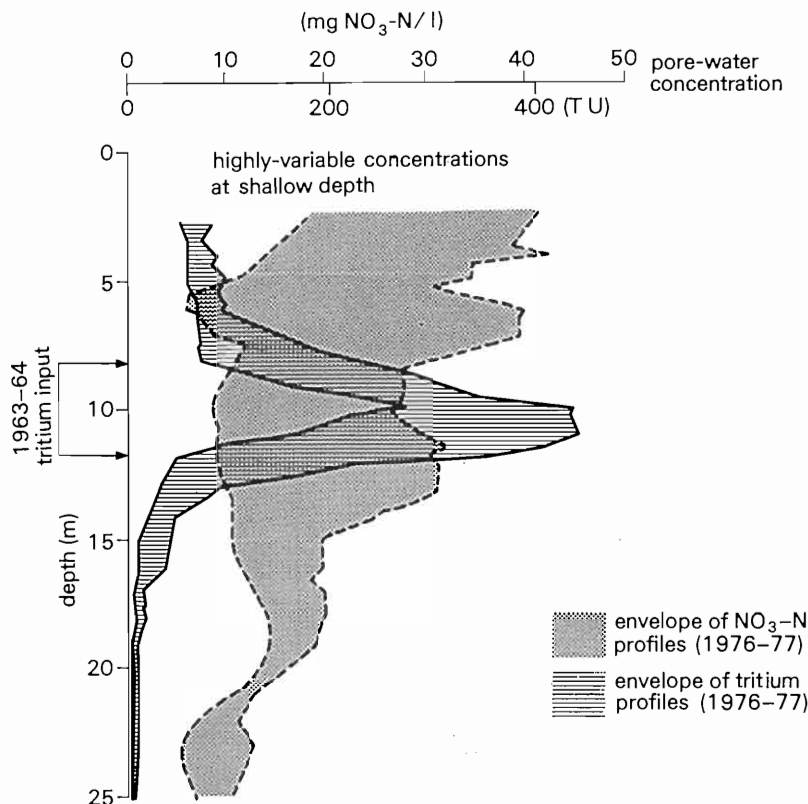


FIG. 1. Summary of nitrate and tritium profiles in the unsaturated zone of the Chalk beneath long-standing arable land in West Norfolk.

that in the matrix pore-water at the surface of the block (i.e. at all points with $x=0$).

The rock matrix was taken to be a homogeneous medium of porosity ϕ , which is fully saturated with immobile pore-water. The solute moves through the saturated porous matrix in the x direction only (perpendicular to the fissures) by aqueous molecular diffusion, according to Fick's law, with a diffusion coefficient D . The initial solute concentration in the pore-water of the matrix is a known function of depth only, $g(y)$.

The simplification of ignoring vertical diffusion in the matrix was considered justified since, in practice, hydrodynamic dispersion in the fissures (not included in this model) would probably over-shadow vertical diffusion.

Mathematical formulation

Let $c(x, y, t)$ be the solute concentration per unit volume of fluid at time, t . Given the above assumptions, this function will be the solution of the following equations:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{in } 0 < x < a/2. \quad (1)$$

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial y} = \frac{2\phi D}{w} \frac{\partial c}{\partial x} \quad \text{at } x=0. \quad (2)$$

$$\frac{\partial c}{\partial x} = 0 \quad \text{at } x = a/2. \quad (3)$$

$$c(0, 0, t) = f(t). \quad (4)$$

$$c(x, y, 0) = g(y). \quad (5)$$

Equations (1) and (2) represent conservation of mass in the matrix and the fissure, respectively. Equation (3) expresses the fact that, due to symmetry, there can be no net movement of solute across the centre of a block. Equations (4) and (5) define the initial conditions.

The 'Chromatographic' approximation

The only condition for which Foster's (1975) diffusion exchange mechanism has been evaluated is that in

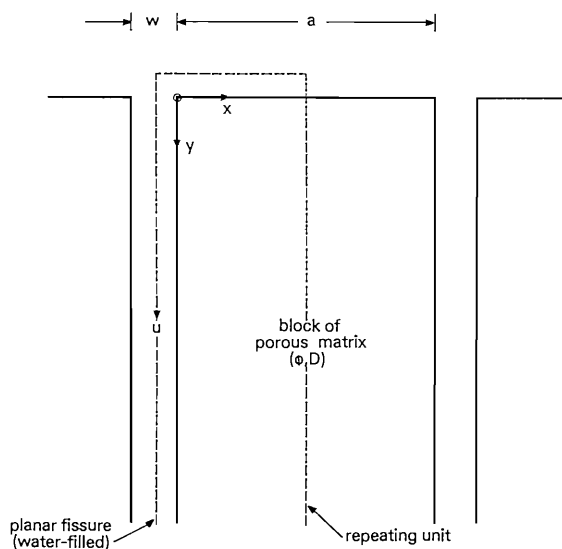


FIG. 2. Definition of model geometry.

which the diffusion coefficient is, in effect, infinite (Oakes 1977). The behaviour of the fissured porous medium is then similar to that of a partition chromatographic column. It is instructive to develop this limiting case of the present model, particularly in the context of interpreting field data from the unsaturated zone.

Consider the evolution from an initial profile, $g(y)$. If D is infinite, solute exchange between the stationary pore-water and mobile fissure-water will be instantaneous and the solute profile will move downwards (in the y direction) without distortion, according to:

$$c(x, y, t) = g(y - V_{\infty}t) \quad \text{for } y \geq V_{\infty}t,$$

where

$$V_{\infty} = u \frac{w}{(\phi a + w)} \quad (6)$$

is the velocity of movement of the undistorted profile. (A rigorous proof of this result can be obtained from Equations (1)–(5)). From the geometry of the model, the amount of infiltration (I) per unit area in time (T) is expressed by:

$$I = \frac{1}{(1 + a/w)} \int_0^T u \, dt$$

or, using Equation (6):

$$I = \frac{(\phi a + w)}{(a + w)} \int_0^T V_{\infty} \, dt.$$

This integral is the distance (X) that the profile moves in time (T) and, since (in all practical cases) a is

orders-of-magnitude greater than w , this latter equation reduces to:

$$X = I/\phi. \quad (7)$$

The question that immediately arises is for what finite values of diffusion coefficient (D) does Equation (7) cease to be a good approximation; the values for tritium (^3H), nitrate (NO_3) and chloride (Cl) being of especial interest in the context of the present paper.

Behaviour of model

Equations (1)–(5) do not appear capable of being solved analytically without further excessive simplifying assumptions. In order to study the behaviour of the model they were, therefore, solved numerically for selected combinations of values for the parameters.

The porosity (ϕ) was fixed at 0.35 throughout; this being a typical value for the Chalk, the formation of most immediate interest. The flow velocity in the fissures (u) was fixed, also somewhat arbitrarily, at 1.0 m/d in many of the numerical solutions, but sensitivity to increases (to 5.0 m/d) in this most significant parameter was examined. It is accepted that much higher values of u may be appropriate, in many areas, at some fissured horizons in the saturated zone.

Diffusion coefficients

The laboratory measurement of aqueous diffusion coefficients in porous media presents numerous practical difficulties and the only attempt, known to the authors,* to make a measurement on saturated Chalk was reported by Oakes (1977), who quoted a value for Cl of $1.3 \times 10^{-9} \text{ m}^2/\text{s}$ (presumably at room temperature). This value appears anomalously high when compared to other published data. Stoessell & Hanor (1975) reported D for Cl in saturated, epoxy-cemented sand ($\phi = 0.3$) to be in the range $3\text{--}5 \times 10^{-10} \text{ m}^2/\text{s}$ (at 35°C) and Barraclough & Nye (1979), in experiments on soil blocks with 30–35% water-saturated porosity, obtained values in the range $3\text{--}7 \times 10^{-10} \text{ m}^2/\text{s}$ (at 25°C); D clearly decreasing as moisture content is reduced below full saturation.

No corresponding results are known for NO_3^* , although this ion has a similar self-diffusion coefficient in water to that of Cl (Parsons 1959; Erdey-Gruz 1974). The ratio of the matrix-diffusion coefficient to the self-diffusion coefficient depends on parameters that will, in general, vary from one solute to another (Nye 1966); however, column experiments (Mercer & Hill 1976, 1977) suggest that NO_3 and Cl behave similarly in powdered Chalk and Chalk soils.

* Since this paper was completed, values of D ranging from 0.4×10^{-10} to $3.0 \times 10^{-10} \text{ m}^2/\text{s}$ have been measured for NO_3 and Cl (at 20°C) in a variety of saturated Chalk samples with different porosities (Mercer, E. R., personal communication).

The self-diffusion coefficient of ^3H has been measured by Mills (1973), who gave values of 1.3×10^{-9} , 1.7×10^{-9} and $2.2 \times 10^{-9} \text{ m}^2/\text{s}$ at 5° , 15° and 25°C , respectively. These results illustrate the sensitivity of D to temperature; interpolation gives a value of about $1.5 \times 10^{-9} \text{ m}^2/\text{s}$ at 10°C , the average temperature of groundwater in Britain.

Considerable uncertainty must remain as to the appropriate values of D for ^3H , NO_3 and Cl in saturated or near-saturated Chalk at 10°C , and variation over the whole range 10^{-9} – $10^{-10} \text{ m}^2/\text{s}$, at least, must be considered possible.

Fissure geometry

It is very difficult, also, to make *in situ* measurements of fissure aperture (width), although some idea of the sizes of the blocks separating joints and fissures can be obtained by direct observation in excavations and by televisual examination of borehole walls. For the Chalk in Britain, variation of a and w in the range

2–10 cm and 0.2–1.0 mm, respectively, were initially considered. It is recognized that, in the unsaturated zone, fissures of the above range of aperture will conduct water only at low negative potentials (suctions) and a fissure system with smaller values of a and w may also play an important role in the flow of water: whereas, in the saturated zone, values of a and w may exceed the maximum values considered (Foster & Milton 1974; Reeves 1979; Foster & Smith-Carington 1980).

Profile characterization

During most of the use of the model the initial solute concentration in the matrix $g(y)$, was taken to be a Gaussian function, since this can be characterized by just two parameters, magnitude of peak (C_0) and standard deviation (S_0): normally the values $C_0=1$ and $S_0=20 \text{ cm}$ were used. The surface input concentration was taken to be zero [i.e. $f(t)=0$] for the results reported below.

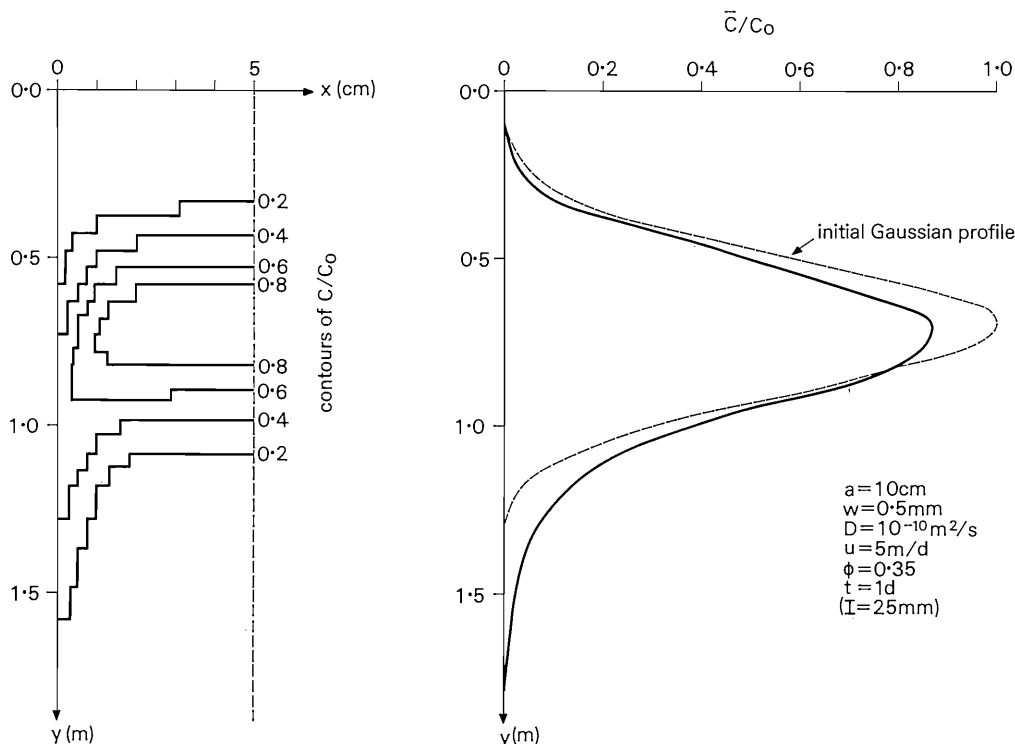


FIG. 3. Concentration contours within the porous matrix block and the corresponding mean concentration profile (Eq. 8).

As the flow of water in the fissure proceeds, the concentration across the matrix slab at any depth becomes a function of x (Fig. 3). Of main interest is the average value:

$$\bar{c}(y, t) = \frac{2}{a} \int_0^{a/2} c(x, y, t) dx. \quad (8)$$

as this gives the best approximation to the results obtained from borehole core-sampling. Since, to greater or lesser extent, all the distributions become non-Gaussian (Fig. 3), the rates of movement of both the peak (V_{max}) and the mean (\bar{V}) of the distribution, $\bar{c}(y, t)$, were determined.

Output from model

For a given geometry ($a = 2$ cm, $w = 1$ mm, $\phi = 0.35$), the sensitivity of profile development to variation of D is illustrated by Fig. 4; these model runs

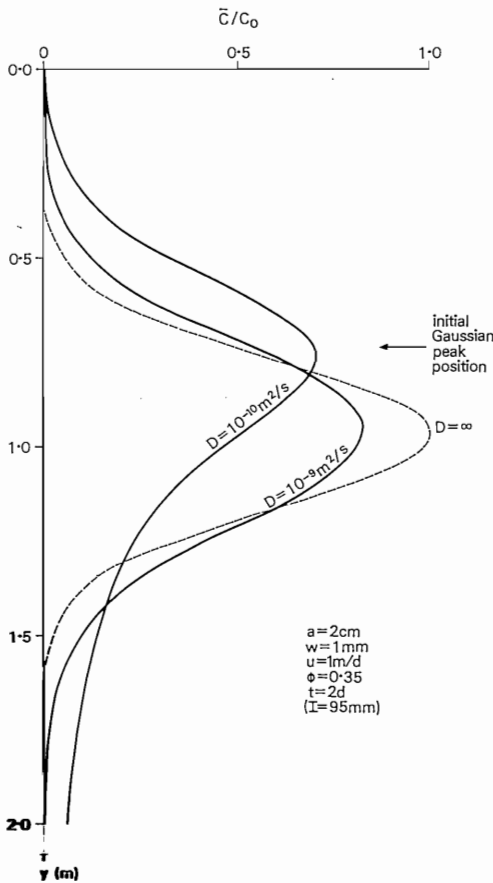


FIG. 4. Variation of profile development with diffusion coefficient.

assumed $u = 1$ m/d over a time interval of 2 days. It is evident that a slow downward movement of solute results, but that while the original Gaussian distribution is essentially preserved for the larger value of D ($10^{-9} \text{ m}^2/\text{s}$), for the smaller value ($10^{-10} \text{ m}^2/\text{s}$) the peak remains almost stationary and a marked 'forward tail' develops. This sensitivity is further evaluated in Fig. 5 for two geometries (which are probably not unrealistic for the Chalk); the rate of movement of the peak and mean of the distribution being compared to the corresponding value for the 'chromatographic approximation case' (V_{max}/V_{∞} and \bar{V}/V_{∞}). It is evident that these ratios depart rapidly from the unity asymptote as values of D decrease below about $10^{-9} \text{ m}^2/\text{s}$ and, at the same time, the peaks of the distributions lag increasingly behind the means.

In the range of D under special consideration (10^{-9} – $10^{-10} \text{ m}^2/\text{s}$), these effects are even more pronounced if u is increased to 5 m/d (Fig. 5); profile development clearly being highly sensitive, also, to variations in the rate of water flow in fissures.

It is further apparent that for given values of u , and D , the extent of the departure from the 'chromatographic approximation' increases with increasing w , but to a lesser extent with increasing a (Fig. 6).

It must, however, be noted that V_{max} is not constant throughout the initial period during which infiltration is simulated (Fig. 7); the V_{max} and \bar{V} values given above are averages taken over the first 24 hours of infiltration. This represents a significant complication when considering the output from this model.

The intermittent nature of infiltration will also have an effect on profile development. This may not, however, lead to a serious restriction on the applicability of the model since solute will tend to equilibrate (horizontally) across the matrix between infiltration events so that, at the beginning of each infiltration period, the profile will be near to the model assumption of uniform horizontal concentration.

Relevance of model results

Unsaturated zone

During its development the model was also run with the initial matrix concentration $g(y) = 0$ and the surface input concentration $f(t) = 1$. For certain combinations of a , w , D and u , this demonstrated that the diffusion exchange mechanism was extremely effective in transferring solute from the fissure water to the matrix, as suggested by Foster (1975). The mechanism also provides a ready explanation of how solutes (and pollutants) present in the unsaturated zone in the matrix of fissured porous media migrate across near horizontal (bedding-plane) discontinuities. Moreover, the model is, at the same time, compatible with the

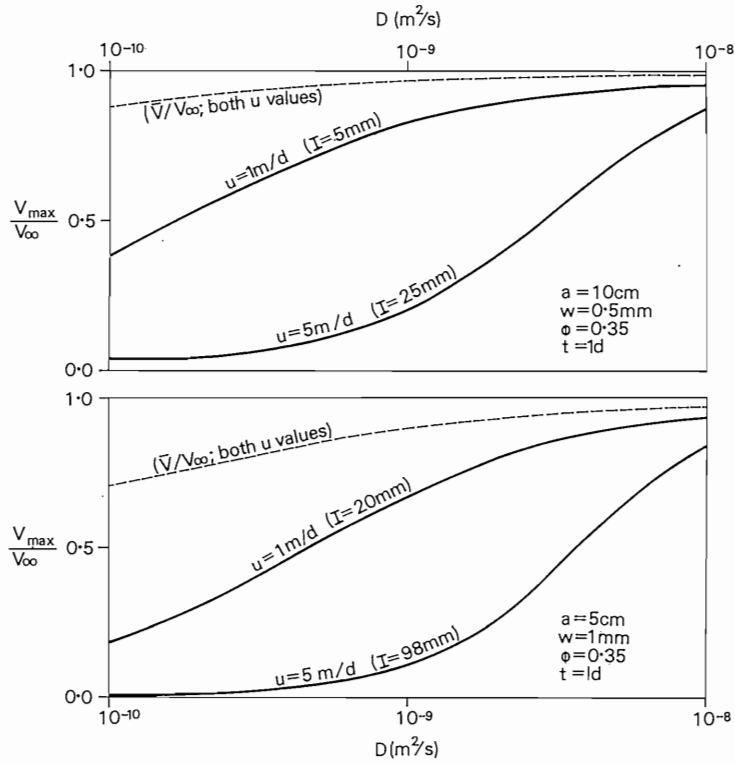


FIG. 5. Variation of profile velocity with diffusion coefficient for two geometries.

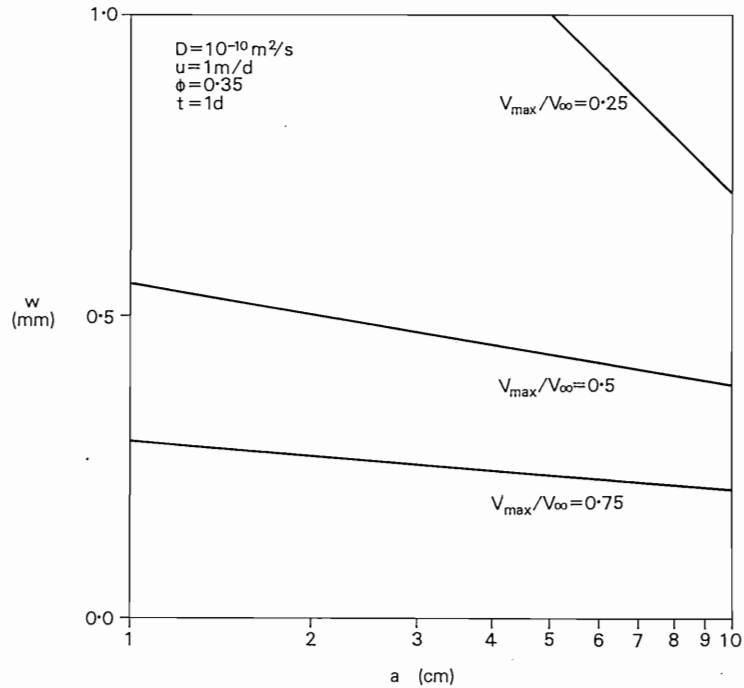


FIG. 6. Approximate variation of V_{max}/V_{∞} with geometry for a given diffusion coefficient.

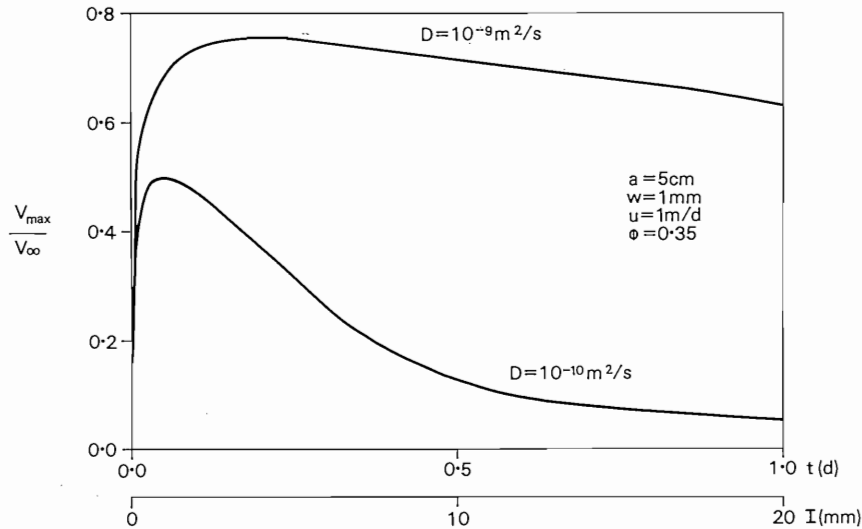


FIG. 7. Temporal variation of peak velocity for a single geometry and two diffusion coefficients.

rapid penetration of pollutants from the land surface to the water-table, which is occasionally observed in fissured porous media. This could occur through high hydraulic loading at times of minimal soil moisture deficit (following high intensity rainfall or some kind of artificial irrigation), when fissures of larger aperture (w) would be expected to conduct groundwater flow at relatively high velocity (u) with only minor attenuation by the matrix.

The natural ^3H profiles from the Chalk's unsaturated zone (Fig. 1) are remarkable for the preservation, with only minor dispersion, of the peak associated with rainfall and infiltration in the springs of 1963 and 1964. The ^3H input concentration of infiltration and the behaviour of ^3H in the soil are both uncertain and it should be noted that a significant by-pass of this slow mode of downward ^3H movement exists (Foster & Smith-Carington 1980). Nevertheless, as far as the slow mode is concerned, the preservation of this peak implies that the uppermost 10 m or so of the Chalk's unsaturated zone (at least) contains a fissure system characterized by such values of w , u and a that $(V_{\max}/V_{\infty}) \rightarrow (\bar{V}/V_{\infty}) \rightarrow 1$, for the operative value of D . Even so, the existence of small 'forward tails' on the peak would be expected from the results of the model. Although difficult to distinguish in the field data from the effect of complexity in surface input concentrations, such 'forward tails' have been identified but were not attributed to this process (Smith *et al.* 1970).

The $\text{NO}_3\text{-N}$ profiles for the Chalk's unsaturated zone from beneath long-standing arable land appear

to possess a characteristic shape (Fig. 1), with concentrations decreasing with depth, despite exhibiting fairly wide variation in detail.

The factors controlling water and solute movement in the uppermost 2–3 m of the unsaturated zone (where highly variable concentrations with depth and time have been observed) are complex and include:

(a) The existence of high negative potentials (suctions) exerted by the matrix of the Chalk, as a result of reduced moisture content, in summer and early autumn.

(b) Some upward movement and direct uptake of water and nutrients from depth by plants, in late spring and summer.

It is known that initial soil drainage in autumn always contains very high solute concentrations (especially of $\text{NO}_3\text{-N}$) and because of the prevailing suctions these will enter the Chalk's matrix at shallow depths. The much larger volume of winter and early spring drainage has, in general, relatively low solute concentrations and would be expected to elute solutes from the (then saturated) shallow matrix of the Chalk by the diffusion exchange mechanism.

The initial conditions selected for the numerical solutions of the present model and the results obtained (Figs 4–7) are most appropriate for the evaluation of this process, but it should be noted that w , u and a will vary with depth in the unsaturated zone. Profile development will be very sensitive to diffusion coefficient and significant differences in the behaviour of ^3H and $\text{NO}_3\text{-N}$ could be concomitant upon their differences in D (Figs 4–5). Moreover, the sensitivity of the

results to D and to u also suggest that it is possible for a quasi-steady state $\text{NO}_3\text{-N}$ peak, with a pronounced 'forward tail' to become established at shallow depth beneath arable land, because of insufficient time for elution to proceed very far during each winter's infiltration sequence. Profiles of the observed characteristic shape could have developed in this way. If this were the case, it would imply substantially lower rates of leaching of nutrients from arable land than might at first seem apparent, and give less cause for concern about the long-term future of groundwater quality of the Chalk; nevertheless, $\text{NO}_3\text{-N}$ concentrations are likely to continue to rise. Final interpretation must await the results of sequential re-drilling in selected arable fields over a period of more than 5 years.

Saturated zone

The saturated zone of fissured porous aquifers may commonly be characterized by higher fissure-flow velocities (in excess of 10 m/d), particularly close to the water-table in unconfined aquifer situations and more generally near to pumping boreholes. In carbonate aquifers, like the Chalk, fissure apertures are often enlarged by solution.

Thus the results from the present model (Figs 5–6) suggest that:

(a) Once having entered the Chalk matrix, by some mechanism, solutes (pollutants) could take a very long time to be completely eluted out.

(b) Conversely, newly-introduced solutes (pollutants) in the fissure water may not be significantly attenuated, in their horizontal movement, by the diffusion exchange mechanism.

Moreover, the results of tracer experiments using water-soluble non-reactive salts to evaluate groundwater dispersion coefficients are likely to produce results varying with the local hydraulic gradient, since this will control fissure-flow velocity and in turn the extent to which the diffusion exchange with the matrix will occur.

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