

Tritiated water movement in clay soils of a small catchment under tropical rainforest in North-East Queensland

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1 Introduction

Tritiated water was used to trace soil water movement in kaolinitic clays below the active surface and subsurface stormflow layer, >0.2 m, (Bonell et al. 1981) at two contrasting sites in a tropical rainforest catchment ($17^{\circ}20'S$, $145^{\circ}58'E$) in north-east Queensland. Mean annual rainfall is 4239 mm with a marked concentration (63.5 percent) in the summer months December to March. The deep (c. 6 m) Ultisols-Inceptisols range from light to medium clay (Northcote 1979) with a fine to moderate blocky structure and the largely kaolinitic clay content increases to a maximum of 51 percent at the 0.4-0.5 m depth.

The lower slope (26.5°) tracing site 1 was characterised by hydraulic conductivity, K values (\log mean $K = 0.18 \text{ md}^{-1}$, $n = 10$) (Reynolds et al. 1983) somewhat higher than the upper slope (23.5°) site 2 (\log mean $K = 0.11 \text{ md}^{-1}$, $n = 10$) between 0.20-0.90 m depth. However, within plot K variability was much higher at site 1 with a maximum point estimate of 0.94 md^{-1} cf. 0.28 md^{-1} , site 2. These differences were attributed to the large amount of weathered rock pieces within the soil matrix of site 1. Each experimental plot had lines of soil water extractors (Talsma et al. 1979) inserted 0.10 m apart and located at depths ranging from 0.25-1.50 m. Two transects, 2 m apart, were installed at site 1 to monitor any rapid lateral transfer of tracer. In contrast three lines of extractors were located closer together at site 2 because of the lower hyd-

raulic conductivity, being separated by a gap of 0.30 m between each transect. A line injection ($2.7\mu\text{Ci l}^{-1}$) at 0.2 m depth was carried out on 22 February 1980 slightly above each of the top extractor transects and the pulse's progress monitored until July 1980. Further details of the site physical properties and experimental procedure are reported elsewhere (Bonell et al. 1982, 1983).

2 Results and Conclusions

The tensiometers at both sites indicated near-saturated conditions for most of the experiment. The possible flow lines of soil water at site 2 (Figure 1) show typical conditions following rainfall when positive mat-

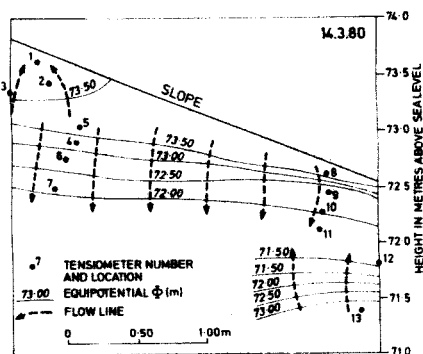


Figure 1. The equipotential and flow lines on 14.3.80 at site 2.

Notes: The hydraulic potential, ϕ is given as: $\phi = \psi_M + Z$ where Z is the elevation above sea level (upward is positive) and ψ_M is the matric potential at a particular point.

ric potentials prevailed. A complicated three dimensional flow pattern is indicated with convergence of soil water through lateral movement into or out of the cross-section. A similar pattern was also observed at site 1 (Bonell et al. 1983) but with downslope flow more favoured. At both sites the translation laterally and vertically of the tritiated pulse appeared to be dominated by interstitial piston flow (Zimmermann et al. 1967) though moving at a faster rate when compared with results from temperate areas and could be attributed to the high frequency of moderate-heavy rainfall in this environment (Figure 2). Tracer downslope movement at site 2, however, was established as being more significant than previously indicated in Figure 1. In addition, the high initial activity in soil water extractors 1-25, 1-35 and 2-35 (Figure 2) and the deeper centre of mass at site 1 on 3.3.80 cf. site 2 were also indicative of short circuiting or preferential macropore flow (Table 1). The latter introduces the effects of the higher hydraulic conductivity

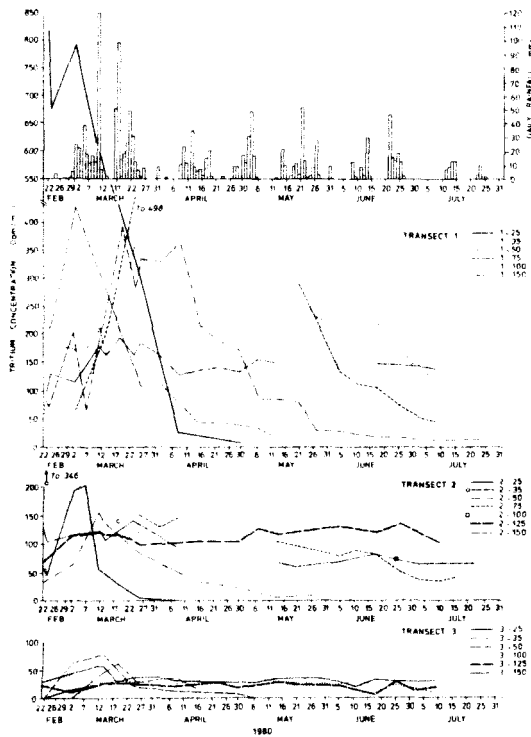


Figure 2. The time series of rainfall and tritium concentrations at site 2. Notes: i) 1-25 is extractor point: top (injection) line 1-0.25 m depth; ii) discontinuities in graphs denote breaks in record due to malfunctioning of soil water extractors. Isolated data are shown as unconnected points, eg 2-35; iii) tritium concentrations expressed in disintegrations per minute per millilitre (dpm/ml).

Table 1. The vertical displacement of tracer along the injection line and recharge on selected dates

| Date | Site | Centre of mass z, (m) | Average volumetric water content, $\bar{\theta}$ | Accumulated inputs from beginning of experiment | | Apparent vertical recharge, R_v | |
|---------|------|-----------------------|--|---|-------------------------------|-----------------------------------|-----------------------------|
| | | | | Rainfall (mm) | Throughfall ¹ (mm) | (mm) | of throughfall ¹ |
| 3.3.80 | 1 | 0.595 | 0.405 | 34.90 | 22.04 | 159.97 | 725.82 ² |
| | 2 | 0.270 | 0.390 | | | 27.30 | 121.88 ² |
| 26.3.80 | 1 | 0.815 | 0.464 | 574.40 | 399.95 | 285.36 | 71.35 |
| | 2 | 0.635 | 0.315 | | | 224.03 | 56.01 |
| 14.5.80 | 1 | 1.060 | 0.457 | 892.80 | 690.89 | 393.02 | 56.89 |
| | 2 | 0.780 | 0.525 | | | 304.50 | 49.92 |
| 26.6.80 | 1 | 1.140 | 0.483 | 1237.50 | 839.50 | 454.02 | 54.08 |
| | 2 | 0.920 | 0.545 | | | 392.40 | 46.74 |

¹ Throughfall calculated from daily rainfall by equation $y = 0.7 + 0.725x$ where $y =$ throughfall (mm), $x =$ rainfall (mm) (Gilmour 1975)

² These high values are the result of short-circuiting

at site 1. There was a faster vertical displacement in this plot and a higher proportion of soil water recharge (Table 1) using Zimmermann et al. (1967) relation:

$$R_v = 1000 (z - 0.20) \bar{\theta}$$

where

- R_v = vertical recharge in mm in a unit area of profile between 0.20 and z
 z = centre of mass of tracer pulse (m)
 θ = average volumetric water content ($\text{cm}^3 \text{cm}^{-3}$) in a unit area of profile on given date, estimated from the soil moisture characteristic curve

Also similar amounts of lateral recharge were required under monsoonal intensities to push soil water downslope and cause a peak response at 0.35 m and 0.50 m depth on the lowest transect (Table 2) despite different selected extractors on lowest transect

| Extractor depth (site no.) | Date of peak response | Accumulated rainfall (mm) | Accumulated throughfall (mm) | θ^{-1} | Lateral recharge $R_c = \frac{\text{Accumulated Throughfall}}{\theta^{-1}}$ (mm) |
|----------------------------|-----------------------|---------------------------|------------------------------|---------------|--|
| 0.35 (1) | 12.3.80 | 279.4 | 193.49 | 0.445 | 86.10 |
| 0.35 (2) | 14.3.80 | 282.0 | 194.45 | 0.480 | 93.34 |
| 0.50 (1) | 9.4.80 | 603.0 | 417.67 | 0.403 | 168.32 |
| 0.50 (2) | 19.3.80 | 433.1 | 301.32 | 0.535 | 161.20 |
| 1.50 (1) | 9.4.80 | 603.0 | 417.67 | 0.450 | 187.95 |
| 1.50 (2) | 12.3.80 | 279.4 | 193.49 | 0.540 | 104.48 |

¹ Average volumetric water content on the given date in a unit area of profile between 0.20 m on top transect and the depth of each extractor on lowest transect

ences in distance between the points of injection viz. 2.0 m site 1, 0.60 m site 2. Greater amounts of recharge were, however, required at 1.50 m for site 1. In contrast no tritium was detected downslope on site 1 in an earlier experiment when lighter rainfalls prevailed (post-monsoon) (Bonell et al. 1983).

Below 1 m the profile remained labelled with tritium at both sites and indicated similar prolonged soil water transit times (eg Figure 2, site 2). A factor delaying the vertical advance of the tritium pulse was upward movement of soil water in various sections of the profile at both sites suggested from the distribution of hydraulic potential.

The experiment shows that both interstitial piston flow and preferential flow can occur simultaneously in these heterogeneous clays under low matric potentials. The effect of spatial variability of hydraulic properties has also been demonstrated. However the long soil water transit times especially below 1.0 m have management implications. Large areas of former tropical rainforest have been cleared for sugar cane farming

and high chemical inputs are required to maintain productivity levels to offset intense leaching of the surface layers by lateral stormflow. These results indicate however the potential for accumulation of agricultural chemicals in the lower layers despite the high rainfalls.

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Factors conditioning the surface waterlogging of leached clay chernozems in Bulgaria

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Leached clay chernozems in Bulgaria have seasonal surface waterlogging due to high clay content (Table 1), humus-accumulation in the A12 horizon and a transition horizon (A13) with a depth of 50-70 below surface which has a low permeability. The latter is due to its extremely compact prismatic structure. The structural aggregates have slanting slickensides. The C horizon is calcareous. The soil reaction of the A horizon is moderately acid (pH 6,2-6,6) and the B horizon is neutral to moderately alkaline. These chernozems have a high potential fertility and are located in flat areas, which make them suitable for mechanized cultivation. However, during agricultural practice, these soils become waterlogged and acquire unfavourable agrotechnical characteristics almost every year during the autumn and winter but particularly during the spring season (2, 3, 4).

The climatic environment in which these soils occur is characterised by an excess of rain over evapotranspiration during the autumn-winter and the spring season. Waterlogging is caused by a low water permeability of the soil and the small slope of its surface, which does not allow run-off. The permeability, measured according to the method of De Boodt, of the A12 horizon and the A13 horizon varied from 0,026 to 0,060 m/day while the permeability of the B horizon varied between 0,010 and 0,015 m/day (Table 1), (2).

The low water permeability is thought to be due to the following factors: (1) There is a high clay content (Table 1), which in the A hori-

zons varies between 48% and 60% and in the B1 horizon between 60% and 62%. Among the secondary clay minerals montmorillonite predominates (2) In part of the soils the percentage of exchangeable Mg is relatively high (20% to 40% of adsorbed cations).

Table 1 - LABORATORY PARAMETERS FOR THE LEACHED CLAY CHERNOZEMS WITH SEASONAL SURFACE WATERLOGGING

| Horizons (cm) | Particle size distribution (%) | | | Permeability m/day | Particle density (g/cm ³) | Bulk density (at pF2,5) (g/cm ³) | Total porosity (pF2,5) (%) | Field water capacity (pF2,5) (%) | Aeration of soil at field water capacity (%) |
|------------------|--------------------------------|----------------|--------|-----------------------|---|---|-------------------------------------|---|---|
| | 0,2- 0,02 | 0,02- 0,002 | <0,002 | | | | | | |
| A11 0-30 | 24,8 | 15,0 | 56,7 | 0,765 | 2,70 | 1,18 | 56 | 28 | 23 |
| A12 30-50 | 24,8 | 14,6 | 57,1 | 0,054 | 2,72 | 1,35 | 50 | 30 | 9 |
| A13 50-72 | 23,8 | 13,8 | 59,6 | 0,026 | 2,73 | 1,40 | 49 | 31 | 5 |
| B1 72-96 | 23,9 | 13,6 | 59,8 | 0,013 | 2,73 | 1,46 | 46 | 31 | 1 |
| B2 96-120 | 25,4 | 14,1 | 57,7 | 0,010 | 2,74 | 1,45 | 47 | 28 | 3 |
| CK 120-150 | 25,4 | 14,1 | 57,7 | 0,110 | 2,74 | 1,45 | 47 | 28 | 6 |

The soils being discussed have, in addition, the following properties (Table 1): (1) The water content at field capacity is high, (2) The A and B horizons are compact. Bulk density: (1,40 g to 1,50 g/cm³ at field water capacity: 1,90 g/cm³ in dry soil) (3). The porosity is high (determined at pF2,5-2,7). In correspondence with the above-mentioned soil properties, the aeration at field water capacity is lower than 10% in the A12 and the B horizons. The above mentioned results, have been checked under laboratory conditions with model experiments. When sand is added to the soil sample (without drying or wetting) the water-permeability in the column increases. After a period of waterlogging, the quantity of exchangeable NH₄⁺, Mn²⁺ and Fe²⁺ slightly increases. The increase is, however, insufficient to cause a significant increase in dispersion. Treatment with gypsum results in a decrease of dispersion and in desorption of exchangeable Mg. After a double suspension in water, the initial degree of dispersion is reestablished. Laboratory treatment with gypsum increased the permeability with 20-50% in a soil sample that had been waterlogged for seven days. Other factors, controlling the low water-permeability are the relief and the agrotechnical activity of man. The relief is flat, with a slope of 0-6‰, which makes surface water run-off impossible or very difficult.

The negative influence of the agrotechnical activity of man has been

evident by tillage with big agricultural machines, which is sometimes performed at high moisture contents. This leads to compaction of the soil, decrease in the humus content of the fallow land and soil structure degradation. Ploughing at a constant depth has caused the formation of slowly permeable plowpans.

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Water and solute movement in a heavy clay soil

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Abstract

Solute movement in soil is conventionally described in terms of diffusive forces that affect the distribution of the salt relative to the water; and convective effects due to soil water flow. We describe a series of experiments that illustrate the application of these ideas to CaCl_2 movement during non-steady, unsaturated water flow in sand and in a structurally stable heavy clay soil. The results are discussed in terms of simple concepts in soil water theory, and surface physical chemistry. The paper concludes by identifying possible areas for further research.

1 Introduction

The distribution of water soluble salt in soil in the natural environment depends on the local soil mineralogy and hydrology. Any perturbation of this system by, for example, irrigation or drainage, change in land management, or addition of fertilizer must be reflected to an extent in a change in this natural distribution. As a consequence, we may observe enhanced soil salinity, or leaching, or the appearance of various water soluble salts in the groundwater, or streams. We may also observe substantial change in soil physical properties because of the effect of change of the soil solution composition. Often these effects are deleterious and their amelioration may be difficult. It is

therefore critical that we develop management strategies that are not potentially deleterious. It is also important that we identify reliable methods for ameliorating areas already affected by high concentrations of water soluble salts. This challenge is complicated by problems related to scale and to field variability in addition to the conceptual difficulties presented by the basic mechanisms of salt and water transport during unsteady, unsaturated soil water flow.

In this paper we describe a program that attempts to define a set of general 'tools' that might help resolve particular problems of salt movement in soils. These tools are, to an extent, expressed in mathematical terms, so it is important that we set out the role of theory, and its mathematical formulation, in the study of properties and behaviour as complicated as those of soil. We then formulate a theory based on processes involved in the interaction of soluble salts with water and soil during unsteady, unsaturated flow and illustrate it with experiments. Finally, we discuss some areas for further research.

2 Role of theory

A rationale for the development of theory is the assumption that well-posed field problems will be tackled most efficiently and fruitfully using strategies based on an understanding of the mechanisms of the processes involved. The formalism of mathematics is then used to set out laws necessary to describe, for example, water, heat and solute movement in soil. The theory derives its authority from critical and well-conceived experiments and its validity must be continually tested and deficiencies in the theory identified in this way must be explored and corrected. The mathematics provides not only a language, but also a logic that often permits us to explore situations more efficiently and perceptively than is possible by experiment alone. Furthermore, solutions to flow equations for many practically important initial and boundary conditions have a valuable illustrative and didactic role. An exposition of the role of mathematics in natural science is presented by Philip (1957).

The theory should be based on a suitably small set of measurable properties of the system. The material properties should be

macroscopic because the generation of space averages from many microscopic measurements in a geometrically complicated body like a soil is a problem of great difficulty. In fact, the scale, variability, and complexity of field soils all conspire to make the application of theory in terms of the solution of equations most unlikely. Indeed, field problems may defy formal solution using scientific methods even though they may be defined in a scientific way. Nevertheless, scientific understanding of basic mechanisms must be central to our problem-solving strategies if only to 'inject some intellectual discipline into the republic of trans-science' (Weinberg, 1972).

3 Theory of solute movement in unsaturated water flow in soil

The dependence of the salt flow on water makes it necessary to write continuity equations for both the water and the soluble salt. In one dimension these equations are

$$\left(\frac{\partial \theta}{\partial t}\right)_x = -\left(\frac{\partial F_w}{\partial x}\right)_t \quad (1)$$

$$\left(\frac{\partial(\theta C)}{\partial t}\right)_x = -\left(\frac{\partial F_s}{\partial x}\right)_t \quad (2)$$

where θ is the volume fraction of water in the soil, C is the solution salt concentration, F_w and F_s are the volume flux of water and the mass flux of salt respectively, and x and t are distance and time.

The mass flux of the salt is given by

$$F_s = F_{s_r} + F_{s_c} = F_{s_r} + CF_w \quad (3)$$

where the subscripts r and c refer respectively to salt movement relative to, and convected with, the water.

Substitution of Equation 3 in Equation 2, differentiation of the composite terms, substitution of Equation 1 and rearrangement then yield

$$\left(\frac{\partial C}{\partial t}\right)_x + \frac{Fw}{\theta} \left(\frac{\partial C}{\partial x}\right)_t = -\frac{1}{\theta} \left(\frac{\partial F_s_r}{\partial x}\right)_t \quad (4)$$

in which the second term on the left-hand side represents flow of salt with the water of average velocity $u = Fw/\theta$. In fact, the left-hand side is the differential of C following the motion of the water (Bird et al., 1960) whence Equation 4 may be written

$$\left(\frac{\partial C}{\partial t}\right)_q = -\left(\frac{\partial F_s_r}{\partial q}\right)_t \quad (5)$$

where $q(x,t)$ is a material coordinate based on the distribution and flow of the water so that

$$\frac{\partial q}{\partial x} = \theta \quad \text{and} \quad \frac{\partial q}{\partial t} = -Fw \quad (6)$$

The q coordinate is discussed by Smiles et al. (1981) and also by Wilson and Gelhar (1981). It is important to note that q satisfies the continuity of water requirement of Equation 1.

Equation 5 is a statement of continuity of salt presented in terms of a material coordinate based on the distribution of the water. Its further development requires definition of F_s_r . This requirement is generally met by the equation

$$F_s_r = -\theta D_s (u) \partial C / \partial x \quad (7)$$

in which D_s is the dispersion coefficient. The nature of D_s is discussed elsewhere (e.g. Fried and Combarous, 1971) but in essence it has both diffusional and hydrodynamic elements represented, for example, by the equation (Rose, 1977)

$$D_s = D_o (\Gamma + aPe^b) \quad (8)$$

In Equation 8, Γ , a and b are empirical constants, D_o is the diffusion coefficient of the solute in bulk solution, and Pe is the Péclet number given by

$$Pe = u\ell/D_0 \quad (9)$$

The Péclet number relates convective and diffusive components of transport using a characteristic length, ℓ (often identified with an average particle size). In general, as Equations 8 and 9 imply, D_s is velocity dependent. When the value of u is small enough, however, D_s may be regarded as velocity-independent.

Substitution of Equation 7 in Equation 5 using Equation 6 leads to the equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial q} \left[\theta^2 D_s(u) \frac{\partial C}{\partial q} \right] \quad (10)$$

Equation 10 provides the theoretical framework against which we develop insights into salt movement in soils.

Since our concern is primarily to investigate salt movement, we have worked with the simplest cases of water flow that reveal substantial evolution, in space and time, of well-defined water content profiles. Constant flux, or constant potential absorption provide two such simple systems. For both cases the material coordinate $q(x,t)$ may be found by integrating the total differential of q using Equation 6. The detail is presented, for example, by Smiles et al. (1981). For experiments subject to conditions defined by

$$\theta = \theta_n, \quad C = C_n, \quad x > 0, \quad t = 0 \quad (11)$$

and either

$$\theta = \theta_o, \quad C = C_o, \quad x = 0, \quad t > 0 \quad (12)$$

or

$$Fw = V_o, \quad C = C_o, \quad x = 0, \quad t > 0 \quad (13)$$

the material coordinate is conveniently defined by the equation

$$q = \int_0^x \theta_{t=t} dx - \int_0^t V_o dt \quad (14)$$

As Smiles et al. (1981) show, the origin of the q coordinate according to this definition coincides with the notional piston-front of the water, i.e. the interface between the initial and the invading water which would exist if the former was completely displaced by the latter.

Thus, for the initial and boundary conditions represented by Equations 11-13, salt movement studies basically centre on examination of the location of a step change in solution concentration (from C_0 to C_n) relative to $q = 0$, and the way the step change is 'smeared' with increasing time.

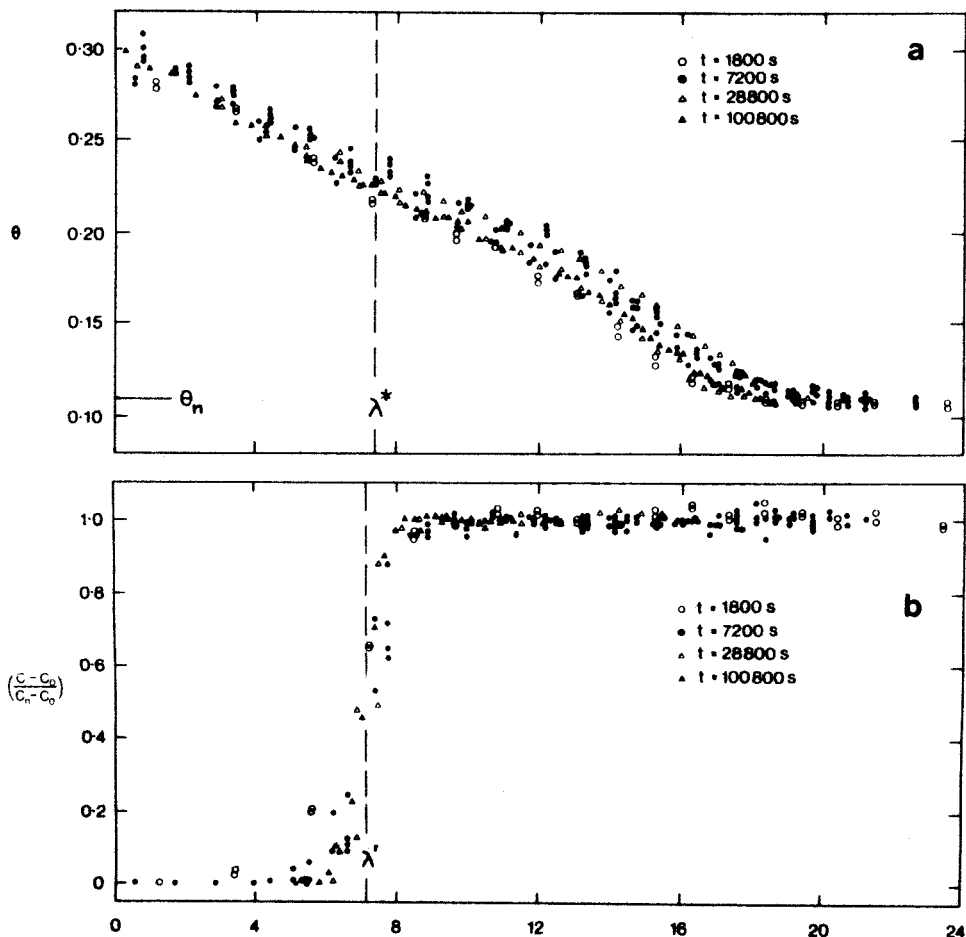


Figure 1. Profiles of (a) water content and (b) normalized solution salt concentration at four times during constant potential horizontal absorption in a mixture of fine sand and kaolinite. The low initial water content θ_n containing 8.5 kg m^{-3} KCl (C_n) was invaded by a solution of 1 kg m^{-3} KCl (C_0) supplied to the soil surface at a zero head. λ^* is the position where $g = 0$ and λ' is the mean position of the salt front (data from Smiles and Philip, 1978)

The simplest experiments that demonstrate the basic aspects of this approach are performed in a chemically unreactive material. When the conditions of Equations 11 and 12 are imposed and it is assumed that the dispersion coefficient is velocity (Péclet number) independent, both the water flow equation and the salt flow equation reduce to ordinary non-linear diffusion equations in terms of the variable $\lambda = xt^{-\frac{1}{2}}$. In this space the piston front is identified by $g = 0$ where $g = qt^{-\frac{1}{2}}$.

Results of a series of such experiments are presented in Figure 1. It is observed that both the water content and the salt concentration profiles preserve similarity in terms of λ . The uniqueness of the salt concentration profiles indicates that D_s was effectively velocity independent in these experiments (Smiles and Philip, 1978). It is also noted that the salt front corresponds closely with the position where $g = 0$, as calculated from the water content profiles using an equation derived from Equation 14. Consequently the piston flow model is valid for this chemically unreactive sand at low velocities.

Further experiments applying constant flux of water (i.e. realizing Equations 11 and 13) confirm these observations (Smiles et al., 1981). When these conditions were applied to a non-swelling heavy clay soil, however, the movement of the salt was substantially altered as is demonstrated in Figure 2.

Theory predicts that for constant flux absorption, water content profiles in terms of $X (= V_0 x)$ should be unique for constant values of $T (= V_0^2 t)$. In addition, if D_s is velocity independent $C(X)$ should be unique. In these coordinates, the piston front is defined by $Q = 0$, where $Q = V_0 q$.

It will be observed that the tritium front corresponds with the plane $Q = 0$ but the chloride profile is different. Two features should be noted:

- a) the amount of both chloride and tritium recovered from the soil agreed with the sum of the amount known to be present initially and the product of C_0 with the volume of water which had entered the soil. In other words, the entry of both substances appears to be unhindered.

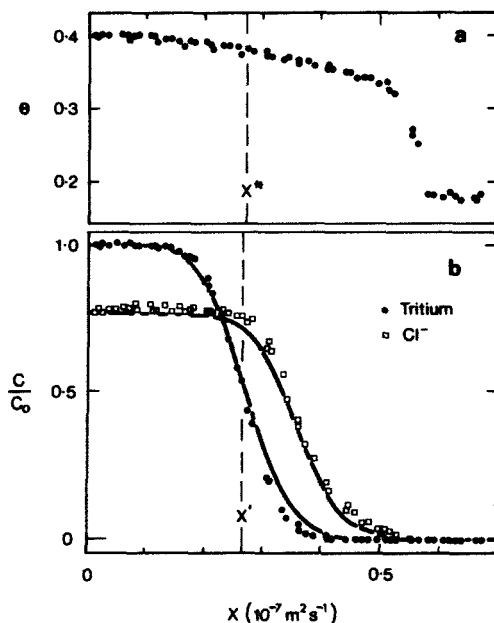


Figure 2. Profiles of (a) water content and (b) normalized concentration for $T = 1.1 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ and values of V_0 between 3.3×10^{-7} and $6.6 \times 10^{-7} \text{ m s}^{-1}$ during constant flux horizontal absorption of a tritiated calcium chloride solution by a clay soil. The low initial water content θ_n , which had a small concentration of tritium and chloride, was displaced by a solution with a specific tritium activity of 0.14 GBq kg^{-1} and a chloride concentration of 200 equiv m^{-3} . X^* is the position where $Q = 0$ and X' is the mean position of the tritium front (data from Bond et al., 1982)

b) the apparent concentration of chloride close to $X = 0$ is about $0.8 C_0$ and the chloride front is proportionately in advance of $Q = 0$. The effect shown in Figure 2 on the chloride profile was discussed for an analogous situation by Smiles and Gardiner (1982) who attributed it to anion exclusion from a volume of soil water equal to the external specific surface of the soil ($1.02 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ based on continuous flow N_2 absorption measurements; K.G. Tiller, personal communication) multiplied by a 'depth' of 0.87 nm . This depth corresponds with calculations of Quirk (1968) for the depth of chloride exclusion at the surface of clay in equilibrium with $100 \text{ equiv m}^{-3} \text{ CaCl}_2$ where there is

no double-layer interaction. The depth is also consistent with the layer of partially hydrated Ca ions adsorbed at the clay surface with a characteristic decay length of about 0.9 nm observed by Israelachvili and Adams, 1978. Such a layer would be inaccessible to chloride ions. Tritium, of course, is not affected by either of the above mechanisms. At this stage, the most important observation is that in a soil with a net negative charge and a substantial specific surface there will, almost inevitably, be water close to the colloid surface that is inaccessible to anions even in quite concentrated divalent salt solutions. The thickness of this layer may be only 2 to 3 water molecules; nevertheless, the actual volume of water involved may be quite great relative to the total water content. Further experiments have shown that the thickness of the layer appears to depend on solution concentration, as Figure 3 illustrates.

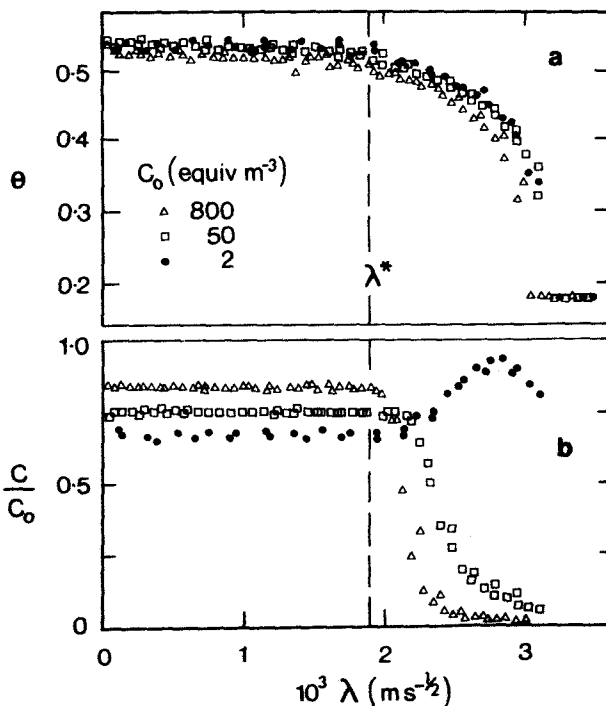


Figure 3. Profiles of (a) water content and (b) normalized chloride concentration during constant potential horizontal absorption of CaCl_2 solutions by a clay soil for three different inflowing solution concentrations C_0 , λ^* is the position where $g = 0$ (data from Bond et al., 1984)

In this figure we observe that as the solution concentration decreases, the amount of inaccessible water increases, as does the displacement of the salt front from $g = 0$. It should be noted with regard to these data, that for the least concentrated invading solution, the equilibrium solution (that 'external' to the double layer) initially present was more concentrated than C_0 . These data are explored in more detail by Bond et al. (1984), who concluded that:

- a) in chemically reactive clay soils, the exclusion of anions from the diffuse double layer at the clay surface significantly affects the shape of the salt concentration profile and, in particular, the position of the salt front;
- b) this double layer effect depends on the concentration of the ambient equilibrium salt solution but, because of double layer interaction associated with soil structure, the effect cannot be predicted *a priori*, although it can be simply measured;
- c) the position of the salt front is determined by both the initial and the inflowing solution concentrations, but control of this position is dominated by the highest concentration solution present.

5 Quantitative prediction of dispersion

For chemically non-reactive soils, dispersion occurs in a region close to $q = 0$ where θ and $D_s(u)$ do not change very much in space, although they may change in time. Equation 10 may then be written

$$\left(\frac{\partial C}{\partial \tau}\right)_q = \left(\frac{\partial^2 C}{\partial q^2}\right)_\tau \quad (15)$$

where the time-like variable τ is given by

$$\tau = \int_0^t (\theta^*)^2 D_s(u^*) dt \quad (16)$$

In Equation 16 the * indicates values of variables at $q = 0$, and the variable τ takes into account the evolution of θ^* and $D_s(u^*)$ up to time t .

Solutions of Equation 15 are available for a variety of initial and boundary conditions (see, for example, Carslaw and Jaeger, 1959). In particular, the conditions defined by Equations 11 and 12 or 13, which imply a step-change in solution concentration at $q = 0$, lead to the solution (Smiles et al., 1981)

$$\frac{C - C_n}{C_o - C_n} = 1/2 \operatorname{erfc} \left(\frac{q}{2\sqrt{\tau}} \right) \quad (17)$$

This equation describes the diffusion of solute about the moving plane $q = 0$ with a diffusivity given by τ/t .

Equation 17 has been tested and found to describe dispersion reasonably well (Smiles et al., 1981; Bond et al., 1982). It is important to note that this solution applies to material space and the water content distribution distorts the salt distribution in real-space.

When we extend the model represented by Equation 10 to chemically reactive soils, the situation is complicated because the inaccessible water content changes across any solution concentration front, and an iterative analysis of the problem appears obligatory. Bond et al. (1982) and Smiles and Bond (1982) pursue the problem in CaCl_2 systems, and discuss the interpretation of salinity profiles observed in the field.

6 Areas for further research

Solute movement is often more complicated than in the examples described here. It is therefore necessary to understand the limitations of the above approach in such situations and to modify it where necessary. Some areas where further experimental and theoretical work is possible are briefly outlined below.

a) Mixed cation systems. Although there have been a number of studies of solute movement incorporating cation exchange (predominantly for steady flow), there remains uncertainty. There is a need, for example, to clarify the nature of the exchange process, particularly the rate of attainment of equilibrium, and to examine the consequences of the effect of exchange on θ_i , through the effect of cation type on the double layer.

- b) Strongly structured soils. As for mixed cation systems, there has been much work done for steady flow, particularly relating to the treatment of 'immobile' or, more correctly, 'slowly accessible' water. Study should be extended to unsteady flow and should consider interactions, of the type described by Blackmore (1976) for example, between structure and chemical/physico-chemical processes.
- c) Structurally unstable soils. The structure and hydraulic properties of many soils depend on cation type and concentration (Collis-George and Smiles, 1963; Quirk and Schofield, 1955). There is scope for quantitative study of the interaction between soil solution, soil structure and water flow during miscible displacement.

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Discussion

G.H. Bolt:

It appears to me that the use of a material coordinate (like your q in Eq. (5)) in solving the partial differential equation describing mixed convection/dispersion transport of solutes was already apparent in the early works on bed-exchange by deVault, Thomas, Glueckauf, and Hiester and Vermeulen of the forties and early fifties (for a review, see Chapter 9 in Bolt, G.H., ed., 1982. *Soil chemistry B. Physico-chemical models*. Elsevier, Amsterdam, 527 pp.). In fact, in those days the name solution throughput parameter was used for minus q ,

negative values of your q referring to regions that had experienced a positive throughput of solution, while the positive values then designate the region that has not yet been 'touched' by the incoming solution.

A question that arises in my mind in relation to this parameter is the merit of attaching the material coordinate to the carrier solution, as compared with its attachment onto the solute described with the differential equation. Although of not too much consequence in the case treated here, it is of importance in case of solute retardation due to adsorption. Even in the present case the decision has to be made if, in the presence of a stagnant liquid phase θ_s , one uses θ or $(\theta - \theta_s)$ to define the material coordinate. Personally, I would favour the latter and would be interested in your comment.

Author:

We do not claim to have introduced the material coordinate as a new concept, merely to have applied it to the more general situation, where θ and u vary with position and time. In this situation the material coordinate is a nonlinear function of distance and time. The exact form of the material coordinate used must certainly take account of the properties of the solute and the presence of any 'stagnant' or inaccessible water. As alluded to in part 5 of our paper, such a material coordinate is described by Bond et al. (1982).

G.H. Bolt:

The penetration of Cl ions exceeding your 'chosen' (see also my earlier comment) zero point of the material coordinate q is interpreted as being associated with anion exclusion. Isn't it necessary, though, to also assume the existence of a relatively immobile layer of solvent in the system? Thus, if all the solvent were fully mobile, the carrier influx would reach up to your point $g = 0$, and the mean Cl penetration could not reach beyond that point. The fact that it does so then must imply that part of the water is (relatively) immobile, so $\theta_m < \theta$. If now this immobile zone (presumably next to the solid surface) is also an anion exclusion zone, one would expect the fairly symmetric diffusion front (as found) located around the point $x = Fw.t/\theta_m$ and not at $x = Fw.t/\theta$. However, immobility and inaccessibility because of a low transfer coefficient would give the same effect. Finally, exclusion of

Cl without immobility of the liquid phase in that zone could not give the pattern as found. Instead, one would enter into some 'salt sieving' - a term I missed in your story - giving rise to increased concentrations.

Summarizing, I venture to state that a) your S-shaped concentration profiles extending beyond $g = 0$ point to the existence of an immobile liquid layer, and only secondarily hint at the possibility of Cl exclusion from that zone (temporary exclusion due to low transfer would already suffice!); b) your low-concentration 'bubble' curve points to the existence of an exclusion zone extending outside the above immobile zone and gives rise to some salt sieving with accompanying local concentration increase. Any comment?

Author:

Figure 2 in the paper shows that when both tritiated water and chloride are present in the inflowing solution, the position of the front of tritiated water is found at the notional 'piston front' of the water, while the chloride front is ahead of this position. From this we conclude that there is no appreciable volume of soil water that is inaccessible to the tritium (i.e. no stagnant zone, as it is usually referred to) and that, regardless of the mobility of the water, there must be a volume of soil water that is inaccessible to the chloride, probably as an result of anion exclusion. Undoubtedly, the water that is inaccessible to the chloride is far less mobile than the inflowing water by virtue of its proximity to the clay surface.

However, we prefer to consider that there is a continuous distribution of water velocities in this soil and no 'immobile zone' as such.

As explained in more detail by Bond et al.(1984), the low concentration 'bubble' in Figure 3 is a consequence of the fact that in that experiment the concentration of the inflowing solution was less than the concentration of the initial solution. There is no need to invoke 'salt sieving' to explain it.

Analysis of solute movement in structured soils¹

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Abstract

The movement of solutes is analyzed using moment techniques. Moments are an empirical procedure for interpreting data without bias towards a specific theory. Data for miscible displacement through packed, saturated soil columns at different flow rates is presented. Application of moment techniques to unsaturated flow conditions as well as theoretically based moments are also discussed.

1 Introduction

The analysis of solute movement consists of several stages including:

- conceptualization of process,
- development of descriptive equations, and
- measurement of solute movement.

At some point the measurements must be reconciled with the descriptive equations. One of the difficulties with analyses of solute movement is the inherent uncertainty of our concepts, and hence, our governing equations. This has combined with a lack of readily available tools to directly characterize data sets. Instead, experiments in solute movements are characterized by model parameters. Unfortunately as the model changes, so do the estimates of model parameters. This detracts

from our confidence in developing a physical interpretation of these parameters.

Moment techniques provide a powerful means of overcoming these problems and allowing analysis of experiments independent of any particular model. Moments can be used to characterize and describe any data set which can be interpreted as a distribution. The output of a classical experiment on miscible displacement readily fits this requirement (Biggar and Nielsen, 1962). Examples abound in the Chemical Engineering and Petroleum Engineering literature of the use of moment techniques for similar problems. However, only one publication in the soils literature exists applying this technique to solute movement (Calvet et al., 1978). Some of the properties of moments will be described in this paper. Moment analysis will then be used to describe solute movement through structured soils.

2 Properties of moments

Distributions representing solute movement may be either a function of space or time. The concentration is interpreted as the density of the distribution. Classical experiments on miscible displacement provide a data set of concentrations varying with time. Studies of solute migration 'in situ' tend to produce data set of concentrations varying with position. Either data set can be analyzed with regard to moments. Although spatial and temporal moments may be related, they are not equivalent. Here the temporal distribution of concentrations will be emphasized.

Ordinary moments (M_n) of concentration (C) with respect to time (t) can be defined as:

$$M_n = \int_0^{\infty} t^n C dt$$

The subscript n is the order of the moment. A second type of moment is called central moment (M_n^*) is frequently more convenient for n greater

than 1:

$$M_n^* = \int_0^{\infty} (t - M_1)^n C dt \quad ; n \geq 2$$

The physical interpretation of the moments follow:

- M_0 or zeroth ordinary moment represents the total amount of solute within a column for spatial moments or total solute eluted for temporal moments.
- M_1 or first ordinary moment describes the mean position of the solute concentration. Note the mean position may not identify the peak or modal position, but is a measure of central tendency. For temporal moments, this is the mean time for elution.
- M_2 or M_2^* are measures of the width in the solute distribution with M_2^* being directly interpreted as a variance.
- M_3 or M_3^* describes the asymmetry in the solute distribution and M_3^* can be used to calculate a skewness. $\text{Skew} = M_3^*/M_2^{*3/2}$.
- M_4 or M_4^* are measures of flatness relative to a normal distribution and extreme values are indicative of multiple peaks. M_4^* can be used to calculate the kurtosis. $\text{Kurtosis} = (M_4^*/M_2^{*2}) - 3$.

Moments possess the following characteristics:

- a) Moments are model independent. They do not invoke any assumptions regarding the mechanisms controlling the movement of solutes.
- b) Moments are orthogonal. The definition insures that each moment is independent of any other moments of different order. This is convenient for analysis of variance and regression.
- c) Moments define a distribution. Not only does the data define a set of moments, but a set of moments unambiguously defines a distribution. Hence, moments summarize the data. It is possible to generate a distribution from the moments using a Gram-Charlier expansion.
- d) Moments are portable. Data sets are cumbersome and rarely accessible in the literature. Moments provide an objective expression of the data which can be presented in a manuscript. This allows an

experiment to be analyzed using models not available to the scientist when the experiment was performed.

- e) Moments can be related to model parameters. This is most readily done for linear models by using Laplace transforms. The n'th derivative of the Laplace transform defines the n'th order ordinary moment.

3 Application of moments to solute movement

Prior to analyzing experimental data on solute movement, a data set based on a specific model was generated to evaluate the behavior of the moments. The classical solution to the dispersion equation (Ogata and Banks, 1961) was used to generate breakthrough curves from which moments were calculated. The equation used was:

$$C = (1/2) \{ \operatorname{erfc}[(1 - T)/\sqrt{T/P}] + \exp(P) \operatorname{erfc}[(1 + T)/\sqrt{T/P}] \}$$

where

C and T are dimensionless concentration and time respectively. Time is expressed as pore volumes or number of displacements of soil solution. $T = Vt/L$

where

V is the convective velocity, L the sampling position and t the time. P is a Peclet number defined as:

$$P = VL/D$$

where

D is the dispersion coefficient. For a Peclet number of 100, the moments were:

$$M_1 = 1.000, M_2^* = .02005, \text{skew} = .425 \text{ and kurtosis} = .25 \quad (1)$$

The value of M_1 describes the rate of movement of the mean solute position. A value of 1.0 indicates the mean passes the position L after displacing exactly one pore volume. M_2^* describes the width in time of the solute history. The width depends directly on the dispersion

coefficient in a simple model such as this. This model allows the theoretical calculation of the moments as:

$$M_1 = 1.0 \quad (2)$$

$$M_2^* = 2/P \quad (3)$$

$$M_3^* = 12/P^2 \text{ and skew} = 4.24/P^{1/2} \quad (4)$$

$$M_4^* = (12/P^2) + 120/P^3 \text{ and kurtosis} = 30/P \quad (5)$$

The skew is always positive which indicates tailing towards longer times or pore volumes. This tailing also increases as the dispersion coefficient increases.

The theoretical moments are a useful means of calculating dispersion coefficients. This is done by equating the theoretical and empirical moments. However, their use is predicated on the validity of the model upon which they are based. The empirical moments do not suffer from this defect and hence can be used to characterize the process of solute transfer. The empirical moments do not require the explicit description of a model or its validation.

Estimation of moments is not completely immune to all problems. The most significant difficulty is the decrease in precision as the order of moment increases. One consequence is that moments higher than fourth are rarely calculated. Even the third and fourth moments may be difficult to estimate. This is reflected in the example by the variation in estimates of the Peclet number. From the second moment, $P = 99.75$, from the third moment $P = 99.53$, while from the fourth moment $P = 121.46$ all in response to the same data set and $P = 100$.

4 Application to structured soils

The techniques of moment analysis will now be applied to studies of solute movement in packed columns of soil aggregates. The work of Biggar and Nielsen (1962) provides a sequence of experiments performed at two different flow rates and three different aggregate sizes. The calculation of the moments based on their data is given in Table 1.

The first moment increases as particle size decreases, while the second central moment decreases as particle size decreases. This trend is maintained regardless of whether the velocity is high or low. However, the higher velocity consistently shows an increased first moment and decreased second central moment when compared to the lower velocity. These interpretations are consistent with the observations of Calvet et al. (1978).

Calvet et al. (1978), however, did not determine the appropriateness of the solution to the classical dispersion equation. Since the Peclet number is unknown, a direct comparison of theoretical (Equation 2-5) and experimental (Equation 1) moments is not possible. However, a check for consistency is possible by comparing different order moments. M_1 from Equation 2 is always equal to 1 and this relation can be used by itself. However, M_2^* and M_3^* from Equations 3 and 4 are related in a fixed manner if the dispersion equation applies to the data.

Eliminating P from Equations 3 and 4 gives the relation $skew = 3\sqrt{M_2^*}$. This holds for the data set represented by the moments of Equation 1 generated earlier. This test for consistency fails for the data of Table 1. The lack of agreement suggests that this solution to the dispersion equation is inappropriate despite its visual goodness-of-fit. Negative values for the skew and kurtosis are also indications of this inappropriateness since Equations 4 and 5 do not allow negative values. This discrepancy may lie with either the governing partial differential equation or the boundary conditions.

A physical interpretation of the transport phenomena described by the moments of Table 1 can be developed using a mixing model suggested by Skopp et al. (1981). At low velocities, mixing between intra- and interaggregate pores is decreased. The soil behaves more like a bimodal pore system with M_2^* and skew increasing with aggregate size as the disparity in pore sizes (between intra- and interaggregate pores) increases.

At the higher velocity, mixing is increased. With the large aggregates the tendency is reduced for solute to spend time in only one of the two dominant pore sizes. M_1 is larger, M_2^* is smaller, although the skew is negative. As aggregate size decreases, mixing becomes more effective and the soil behaves more like a homogeneous material. In other words, at high flow rates and small

aggregate sizes, the moments are closest to that predicted for the classical dispersion equation. However, the negative skew is still indicative that effective homogeneity has not been achieved.

More detailed models can be developed, although most models tend to give complete concentration profile histories. Frequently it is only M_1 , the speed with which the solute moves that is desired. Models such as that of Rose et al. (1982) determine the appearance of the peak. The peak migration, in turn, depends on soil properties as well as water inputs. The simplest use of moments in this connection would be regression of M_1 against water velocity and aggregate size. The data of Table 1 is not sufficiently extensive to consider this form of regression analysis.

5 Application to unsaturated soils

The concept of moment analysis is based on the assumption that a concentration profile or history can be interpreted as a distribution. Unsaturated flow does not preclude the use of moments. Moreover, the uncertainty regarding the best description of the dispersion process lends additional support to the use of moment techniques. Parameter estimation is dependent on model formulation. Consequently, any uncertainty in the accuracy of the model must result in uncertainty in the accuracy of the estimated parameters. The use of moments provides an objective way of characterizing the data which is of increased importance when unsaturated conditions are studied.

6 Summary

Moments have been introduced as a convenient tool to analyze solute distribution data. Moments are defined, and their advantages listed. An example of the application of moments to solute movement through structured soils is given. The observed moments are then interpreted in terms of the physical processes controlling solute movement.

Table 1. Summary statistics for data of Biggar and Nielsen (1962)

| Aggregate size (mm) | M_1 | M_2^* | Skew | Kurtosis |
|-----------------------------------|-------|---------|-------|----------|
| <u>$V = .04$ cm/hr</u> | | | | |
| 1 - 2 | .7406 | .3476 | .843 | -.18 |
| .5 - 1 | .8425 | .3091 | .689 | -.31 |
| .25 - .50 | .9175 | .1710 | .296 | -.46 |
| <u>$V = 2.0$ cm/hr</u> | | | | |
| 1 - 2 | .8121 | .1715 | -.377 | -.070 |
| .5 - 1 | .9692 | .0609 | -.148 | 4.9 |
| .25 - .50 | 1.001 | .0275 | -1.47 | 12.3 |

Notes

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Discussion

G.H. Bolt:

Would you follow me with the statement, 'One of the main advantages of the use of moments for solute-distribution curve description is its sobering action on the model builders'? The higher moments stress the weight of the extreme tail and head sections of the curve, while the model builder too often is so satisfied with reasonable agreement between experiment and model in the central section of the curve that he erroneously concludes that his model has been proved correct: any model is likely to produce some type of S-shape. At the same time, I regret the sensitivity of the higher moments to the boundary conditions (if this is indeed the case), because the latter are precisely the conditions that are so difficult to define in reality.

Author:

If moments induce model builders to think more carefully about critical tests of their hypotheses, then well and good. However, this represents a subjective advantage of the technique rather than an objective advantage in addition to those listed in the paper.

P.A.C. Raats:

You show that for the linear convection/dispersion equation the dispersion coefficient can be inferred from the moments. Have similar parameter identification techniques been worked out for various types of linear models involving mobile and stagnant phases?

Author:

Solutions are given in the chemistry and chemical engineering literature. In many cases reaction terms are also included. The two earliest reports of moment techniques were given separately in papers by Kubin and Kucera.