Mass Exchange Between Mobile Freshwater and Immobile Saline Water in the Unsaturated Zone

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A profile of tritium concentrations measured in the unsaturated zone in loessial sediments in a semiarid area is interpreted in terms of mobile and immobile water domains, according to a nonequilibrium transport model. The mobile domain is represented by percolating freshwater from both rain and irrigation, and the immobile one is represented by isolated fossil saline water pockets. The two domains are connected by partially saturated narrow passages within dispersed clay minerals. The transport of the mobile water is described by convective-dispersive flow and by mass exchange between the two water domains. The relevant equations with the given initial and boundary conditions are solved numerically, and the simulated profile is adjusted to fit the measured one. In this study we concentrate on examination of the mass exchange law between the two domains. It was assumed that matrix characteristics vary in time due to the dispersion of clays at the interface between fresh and saline waters. Accordingly, a time-dependent mass exchange was adopted, which made it possible to obtain an adequate reconstruction of the measured tritium profile. By using a least squares optimization procedure it was found that the best fit between the simulated and measured profiles is attained when the fraction of mobile water is 30%, and the rate of mass exchange decreases from 0.60 to 0.01 year^{-1} in 26 years. The proposed model implies is that it is the immobile water domain which contains the memory of the "high tritium period" (thermonuclear tests period) of the 1960s.

1. INTRODUCTION

During the past few decades, several models have been developed for describing the process of transport in the unsaturated zone (as reviewed by Parlange [1980] and Nielsen et al. [1986]). Most of the models focused on conceptual and mathematical aspects and were based on laboratory experiments. However, there appears to be a lack of studies of natural systems which enable confirmation or rejection of these models. In this paper we evaluate the applicability and validity of one of the commonly used flow models in the natural environment using in situ measurements.

A simple model for one-dimensional, steady state, solute transport in porous media is the convective-dispersive flow equation [Lapidus and Amundson, 1952]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{q}{\theta} \frac{\partial C}{\partial x} \qquad (1)$$

where C is the solute concentration ($M\ L^{-3}$); D is the hydrodynamic dispersion coefficient ($L^2\ T^{-1}$); q is the water flux ($L\ T^{-1}$); θ is the water content ($L^3\ L^{-3}$) of the porous medium; t is the time (T); and x is the distance (L) along the flow direction. The dispersion coefficient is usually expressed by the following relation [Bear, 1972]:

$$D = D_0 + \varepsilon V \qquad (2)$$

where D_0 is the molecular diffusion coefficient ($L^2\ T^{-1}$) of the solute in the porous media; V is the macroscopic flow velocity ($L\ T^{-1}$) equal to q/θ; and ε is the longitudinal dispersivity (L). Since several experimental observations cannot be explained

by either this model or by adding the effect of adsorption, the presence of sources and sinks has been hypothesized. A model of this kind was initially introduced in the petroleum and chemical engineering literature [Deans, 1963; Coats and Smith, 1964] and then applied to solute transport [e.g., Van Genuchten and Wierenga, 1976; Gaudet et al., 1977]. According to this model, the water in porous media is partitioned into two domains, namely, mobile (flowing) and immobile (stagnant). The flow velocity distribution is bimodal: convective-dispersive flow occurs only in the mobile domain, whereas the remainder of the pores contain stagnant water. A diffusion-controlled mass exchange between the two water domains occurs concurrently and is assumed to be a first-order mass transfer process. This leads to the equations

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial x^2} - \frac{q}{\phi_m \theta} \frac{\partial C_m}{\partial x} - \alpha(C_m - C_{im}) - \lambda C_m \qquad (3)$$

$$\frac{\partial C_{im}}{\partial t} = \frac{\phi_m}{1 - \phi_m} \alpha(C_m - C_{im}) - \lambda C_{im} \qquad (4)$$

where

$$\phi_m = \frac{\theta_m}{\theta_m + \theta_{im}} = \frac{\theta_m}{\theta} \qquad (5)$$

where the subscripts m and im denote the mobile and immobile water domains, respectively, ϕ_m is the fraction of the immobile water, α is the exchange rate coefficient of solute between the mobile and immobile domains (T^{-1}), and λ is the rate coefficient of radioactive decay (T^{-1}). These equations represent a slight modification of those of Van Genuchten and Wierenga [1976] to include solutes which decay radioactively such as tritium. De Smedt and Wierenga [1984] have shown that dispersion that accounts for the presence of mobile and immobile domains can still be described by the classical transport equation (1) with the dispersion coefficient given by

$$D = \phi_m D_m + \frac{(1 - \phi_m)^2 (q/\theta)^2}{\phi_m \alpha} \qquad (6)$$

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LEGEND

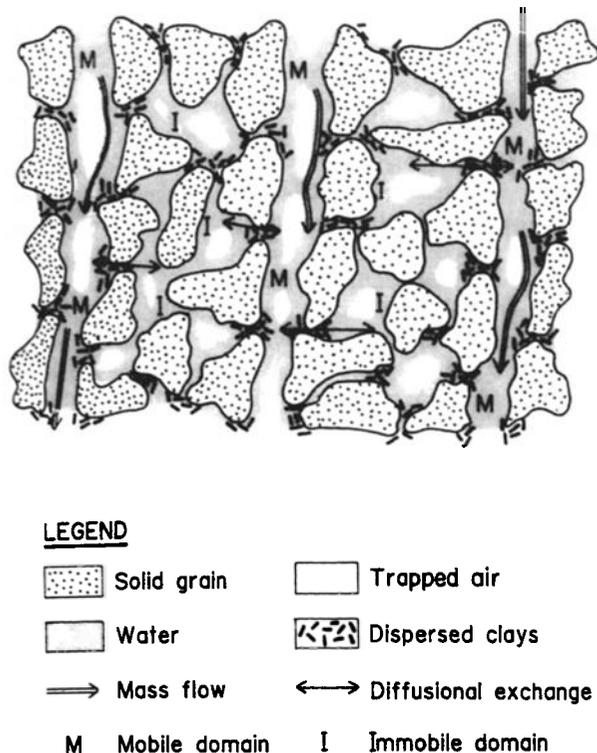|	
:::: Solid grain	☐ Trapped air
☐ Water	Dispersed clays
⟹ Mass flow	⟷ Diffusional exchange
M Mobile domain	I Immobile domain

Fig. 1. Schematic diagram of conceptual model of the unsaturated zone, consisting of mobile and immobile water domains. Gels of dispersed clay minerals separate the two domains. Flow lines in the mobile domain and exchange directions between the two domains are indicated.

which implies that the overall dispersion results from dispersion in the mobile water domain and from exchange between the mobile and immobile domains.

This study represents the first application of the mobile-immobile water domain concept to in situ field data, which are indicative of processes taking place in the natural environment. The objective of this study is to utilize the two-domain model to evaluate the parameters α and ϕ_m on the basis of field observations. The field data used in this study are concentrations of natural tritium produced by thermonuclear tests which entered into rainwater and penetrated the land surface. Details on data collection and analysis are given in the work by Gvirtzman and Magaritz [1986] (hereafter referred to as GM). Based on these results, we suggest a modification of the model represented by (3) and (4) by considering α as time and depth dependent owing to changes of matrix characteristics. The field study is briefly described in section 2, and the existing model ($\alpha = $ const) is applied to the data in section 3. In section 4 we introduce the modification, discuss its relevance to the particular soil characteristics, and apply it to the data. In section 5 we discuss the results obtained by the application of the modified model.

2. REVIEW OF FIELD STUDY

GM reconstructed a 14-year record of water flow along a 10-m profile of unsaturated loess sediments in Omer in the Be'er Sheva basin of Israel. Alternate layers with high and low tritium concentration, corresponding to winter rains and summer irrigations, respectively, were detected down to 8.5 m. According to the tritium peak separation, the average vertical water velocity was calculated to be 0.66 m year^{-1}. The differ-

ence between the measured tritium profile and the input tritium record was explained by the presence of mobile and immobile water domains. It was hypothesized that isolated saline water pockets, which are residuals of the fossil saline solution, constituted the immobile water domain [Magaritz et al., 1988]. The mobile domain was assumed to be composed of recent (since 1957) percolating freshwater of both rain and irrigation waters.

The evolution of this system was explained as follows: until 1957, when cultivation and irrigation started in the area, there was almost no percolation, as all the rain water was evapotranspired. Under these natural conditions, the sediment solution was characterized by relatively high solute concentrations, and with low water content scattered in narrow pores and tightly bound to the matrix. In 1957 water started to percolate downward due to the addition of irrigation water during the summers. The "new" percolating water differed in its chemical composition as the solute concentration of both, rain and irrigation water, was relatively small. In addition, the original saline solution contained no tritium, whereas the new percolating water contained tritium at varying contemporary levels due to atmospheric thermonuclear tests that took place during the 1950s and 1960s. The percolating freshwater entered directly the mobile domain; i.e., it moved through preferential conduits of intergranular width. A "finger-shape" interface was formed between the flowing water and the immobile water. This caused the saline stagnant water to become surrounded by flowing freshwater, thus forming saline pockets. Clay minerals (30% of the solid phase, mainly Montmorillonite) dispersed at the interface between the saline sodic water pockets and the fresh nonsodic water [Goldenberg et al., 1986], causing nearly complete separation between the two water domains. This was accompanied by a slow transfer of solutes from the immobile to the mobile water domains by diffusion and a simultaneous transfer of tritium in the opposite direction. A conceptual model of the unsaturated porous medium, presented in Figure 1, summarizes the conclusions of the previous studies.

GM found that the overall recharge during 26 years of percolation was less than half the pore volume of the 10 m sediment column. Therefore it was postulated that after 26 years of irrigation the sediment solution was still in a transitional state; i.e., the salts of the immobile water pockets have not been leached downward completely.

3. APPLICATION OF THE CONSTANT α MODEL

In seeking to formulate a model of such a complex natural system, all the preferential conduits containing the flowing water were conceptually grouped into one domain and all the isolated pockets into another, resulting in two interacting domains coupled through a mass exchange function. The vertical flow through the sediment column was analyzed as a one-dimensional flow case. At this stage, the model of Van Genuchten and Wierenga [1976] (equations (3) and (4)) was applied. The initial and boundary conditions were determined as follows.

Tritium concentration along the profile until 1957 was assumed negligible, owing to the effect of radioactive decay and negligible vertical water flow prior to cultivation. Under these natural conditions (prior to 1957) all precipitation, 200 mm year^{-1}, was assumed to have been evapotranspired during the dry summers as the potential evaporation rate in this region is
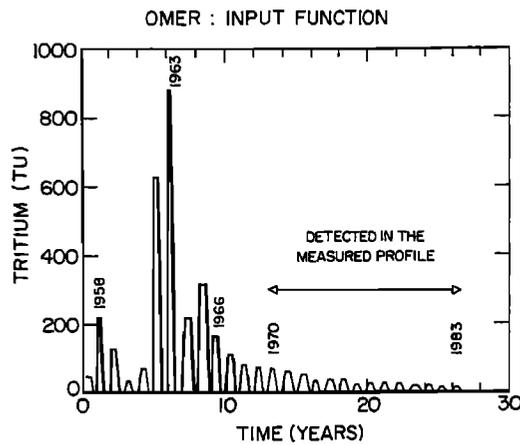
OMER : INPUT FUNCTION

Fig. 2. Tritium concentration in the applied water (rain and irrigation sequentially) during the period 1957 to 1983 at the investigated site. This curve is used as an upper boundary conditions $f(t)$ for solving the system of two partial differential equations (equations (3) and (4)).

1750 mm year^{-1} [GM]. Accordingly, the initial conditions in conjunction with (3) and (4) are

$$C_m(x, 0) = 0 \qquad 0 < x < 15 \text{ m} \qquad (7a)$$

$$C_{im}(x, 0) = 0 \qquad 0 < x < 15 \text{ m} \qquad (7b)$$

The conditions at the upper boundary depend on the tritium concentration in the applied water (rain and irrigation) and are therefore time-dependent. They were determined as follows: the historical record of precipitation and irrigation and their tritium content (as summarized in GM86, Table 2); was transformed into an "input function" $f(t)$, for the period 1957–1983. This input function (see Figure 2) shows that the precipitations during the period 1958–1967 had a relatively high tritium content as a result of the thermonuclear tests [Gat, 1980], whereas the period thereafter had precipitation with a relatively lower tritium content (gradual decrease of tritium concentration). The two periods will be referred to below as the "high tritium period" and the "low tritium period," respectively. The process of the applied water entering directly the mobile domain is described by the upper boundary condition:

$$C_m(0, t) = f(t) \qquad 0 < t < 26 \text{ years} \qquad (8)$$

At the lower boundary, taken at 15 m below the surface, no variation of tritium content with depth was considered, i.e.,

$$\left. \frac{\partial C_m}{\partial x} \right|_{x=15} = 0 \qquad 0 < t < 26 \text{ years} \qquad (9)$$

This is based on the observed profile of tritium content [GM].

In agreement with GM the following values were used: actual vertical velocity of 0.66 m year^{-1}, radioactive decay rate of 0.0558 year^{-1} (as tritium has a half life of 12.43 years), and hydrodynamic dispersion coefficient in the unsaturated porous media of 10^{-3} m^2 year^{-1}.

As for the volumetric moisture content it is obvious that it has increased from its pre-1957 low value, θ_i, to the 0.2 value measured in 1983. This increase was both time and depth dependent and θ could not be considered constant in (3) and (4). We note, however, that this variation of θ in the transition period, following cultivation, has no effect on the final steady profile of θ, which prevailed during most of the reported

period. Owing to (1) the relatively steady influx of water at the surface of the ground during the 26 years of cultivation, (2) below the root zone, from 0.7 m down to 10 m depth, the effect of seasonal drying and wetting is negligible, (3) the homogeneity of the profile lithology, (4) the observed constant moisture content along the profile at the sampling date, and (5) the nearly constant V_m (0.66 ± 0.03 m year^{-1}), we may assume that steady state flow conditions were existing during the whole period throughout the profile. This assumption is justified since our essential purpose was to estimate the transient behavior of the tritium concentration (equations (3) and (4)), and not the transient behavior of the moisture content. Since the immobile water content can be considered as constant in time, the ϕ_m profile should by definition also be constant. This can be illustrated by considering the pre-1957 moisture content as consisting of the real immobile θ_i (equal to $(1 - \phi_m)\theta$) and an additional virtually mobile water domain having the same tritium content. The virtually mobile water was displaced by the newly arriving freshwater. Since the recharge enters the mobile domain only, its flux is determined by

$$q = V_m \theta_m = V_m \theta \phi_m \qquad (10)$$

Given $V_m = 0.66$ m year^{-1} and $\theta = 0.2$, the value of q will be determined upon deriving the value of ϕ_m.

A computer program incorporating NAG Routine D03PGF [Numerical Algorithms Group, 1984] was written to integrate numerically the above system of two partial differential equations, (3) and (4), subject to the initial and boundary conditions (7)–(9). This package is based on Sincovec and Madsen [1975] and Dew and Walsh [1981]. The method of solution is to discretize the space derivatives using finite differencing and to solve the resulting system of ordinary differential equations using Gear's method. (To run the NAG Routine, two redundant boundary conditions for the immobile water domain were added.)

After having the model equations, the initial and boundary conditions and a computer program, we looked for the parameters which would yield a curve that fits the pattern of the field observations. We started by varying the parameters to examine the sensitivity of the final results to the parameter values. For each set of parameters, (3) and (4) were solved numerically, subject to (7)–(9), and the final (1983) tritium profile was plotted. It was found that the final results are sensitive to ϕ_m and α but insensitive to D_m. The numerical values of θ and V_m were determined previously with good accuracy, and the value of λ, the decay rate for tritium, is well-established. No temporal changes in the parameter values were assumed at this stage.

The next step was to apply an optimization program to determine the best θ_m and α which would yield the desirable profile. For each set of parameters, (3) and (4) were solved numerically, subject to (7), (8), and (9), and the resulting tritium curve was compared with the observed data. The calculated (for specific α and ϕ_m) and the measured profiles were compared by summing the squares of differences. However, it was found that the best fit ϕ_m and α produced a profile that had no resemblance to the field observations, which can be characterized by the following two features.

1. The tritium content profile shows a general trend of decrease with depth.

2. The amplitude of the yearly tritium variations diminishes with depth.
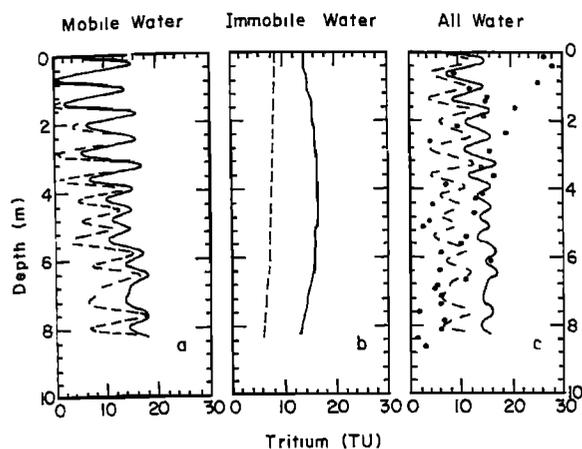
Fig. 3. Calculated tritium profiles (a) of the mobile water domain, (b) the immobile water domain, and (c) a weighted combination of these components, based on the classical model. Profiles were calculated for two values of mass exchange rates: $\alpha = 2 \times 10^{-2}$ year^{-1} (solid curve) and $\alpha = 1 \times 10^{-1}$ year^{-1} (dashed curve). Other parameters used were $\theta = 0.2$, $\phi_m = 0.5$, $D_m = 10^{-3}$ m^2 year^{-1}, and $\lambda = 0.0558$ year^{-1}. Measured data points are also indicated (circles).

Figure 3 shows two calculated profiles. In both cases, the tritium concentration in the upper (lower) part of the profile was smaller (larger) than in the measured profile.

The impossibility to find a set of parameters that would reproduce the pattern of the field observations, could be explained by the following considerations: the tritium profile along the 10-m depth unsaturated zone corresponds to a period during which the tritium content in the applied water was decreasing (1970–1983). Therefore the concentration of tritium in the sediment column should increase with depth. However, the actual profile shows an opposite trend: an excess of tritium in the upper part of the section and a deficiency of tritium in the lower part. GM hypothesized that this is due to the immobile water component. The immobile water domain in the upper part of profile has a memory of the large atmospheric tritium pulse of the high tritium period. During that period, when the mobile water contained very high concentrations of tritium, the diffusive exchange process caused an increase in the tritium content of the immobile water, which was not completely leached out back to the mobile domain during the subsequent low tritium period. The assumed linear exchange process between the mobile and immobile water domains causes the tritium depletion in the immobile water domain during the low tritium period to wipe out the enrichment which took place in the (short) high tritium period. Therefore changing the value of the mass transfer coefficient α only causes a shifting of the immobile curve but has no effect on its general slope.

4. MODIFIED MODEL

Since the above set of equations cannot be parameterized to adequately describe the field data, we were led to assume a model that yields rapid tritium enrichment of the immobile water domain (at the top of the profile) during the 1960s and slow depletion thereafter.

One possible explanation is temporal variations in the flow rate V_m, which might cause storage of irrigation water at the upper part of the profile, i.e., transient flow instead of steady state flow. This explanation, however, is inconsistent with GM who found, based on the distance between individual tritium

peaks, that V_m is very nearly constant (0.66 ± 0.03 m year^{-1}). Given the relatively constant supply of water at the surface during the 26-year-long period of record, and given the uniform lithology of the subsoil, a transient velocity is inconsistent.

Another possibility is to argue about the constraint of the existing model of using a constant value for the mass exchange coefficient α. As was shown earlier, the assumption of a constant exchange coefficient could not yield the actual results. Rao et al. [1980a] observed in laboratory experiments that the mass exchange rate α in (3) and (4) depends mainly on the geometry of the medium. Indeed, the solute concentration gradients between the two water domains and within the stagnant domain are not explicitly accounted for; thus the mass transfer coefficient α compensates for the inadequate description of the geometry. Pruess and Narasimhan [1985] and Wang and Narasimhan [1985] account for this concentration gradient by a detailed geometrical description of the medium as a sequence of nested volume elements (the multiple interacting continua method). In addition, Van Genuchten and Wierenga [1976, 1977] and Gaudet et al. [1977] observed in other laboratory experiments that α varied with velocity of displacement, time, and the water content. In our case the flow velocity and the water content were approximately constant. Therefore it can be assumed that the deviation of the observed tritium concentrations from those predicted by the constant α model should be ascribed to variations in the geometric properties of the medium in the course of time.

To this end we looked for the geochemical and geophysical characteristics of the sediments which could cause modifications in the geometry of the medium and thereby affect the rate of mass transfer between the mobile and immobile water domains. The loessial sediments containing 30% clay minerals and their original saline solution exhibit a dynamic behavior. The finger-shape boundary between the percolating freshwater and the original saline solution creates an assembly of isolated microscale water pockets with different chemical (and isotopical) compositions. In the fossil saline solution, the concentration of Na$^+$ is higher than that of Ca^{2+}; i.e., the solution has high SAR values [Magaritz et al., 1988]. Clay minerals tend to disperse in dilute sodic solutions according to the diffuse double layer theory [Bresler et al., 1982]. Therefore in our study clay minerals (mainly montmorillonite) may be expected to disperse at the interface between the two water types [Goldenberg et al., 1986], and the resulting gels of dispersed clays and swelled clay tactoids cause clogging of some pores and narrowing of passages. A structure of such a system is presented in Figure 1 as a conceptual model of the real structure. The solid phase behaves as a dynamic system as the thickness of the passages between the flowing freshwater, and the stagnant saline waters changes due to changes of fluid chemistry. Therefore a natural modification of the existing model (previous section) was to assume that the mass exchange rate coefficient α depends on the kinetics of dispersion of the clay minerals.

The kinetics of the dispersion process depends on the amount of freshwater which penetrated through the profile. In other words, clogging of the pores due to clay swelling is a function of the cumulative volume of freshwater inflow. As was shown by GM, after 26 years of irrigation the total amount of water which penetrated downward was less than a half pore volume of the 10-m-long column of sediments. As a result, it can be concluded that the diffusive double layer were
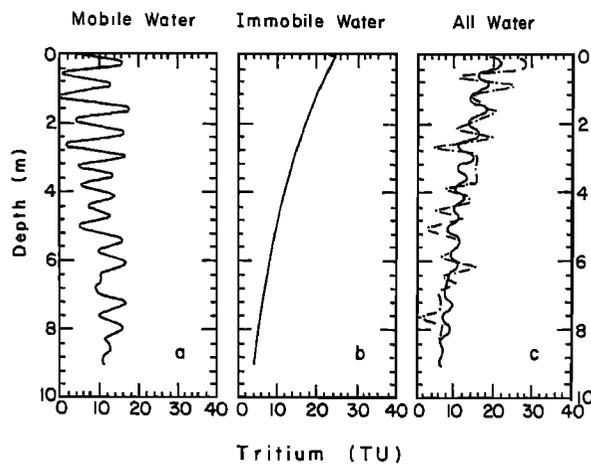
Fig. 4. Calculated tritium profile for 1983. Tritium content in (a) the mobile water, (b) immobile water, and (c) a weighted combination of these components. The best fit parameters, obtained by using optimization procedure, were $\alpha_0 = 0.60$, $\beta = 0.15$, and $\phi_m = 0.30$. The dotted-dashed curve joins the measured data points and agrees with the calculated curve.

enlarged slowly and caused continuous clogging of the pores. While this process is still going on, its rate is decreasing in the course of time. The cumulative net freshwater inflow vary also as a function of depth; i.e., α does not start to decrease at every depth simultaneously. Consequently, we propose that the exchange rate between the water domains α becomes a function of t for each location x, i.e., $\alpha(x, t)$, and follows on exponential decay with time once the freshwater front has reached the particular depth; i.e.,

$$\alpha(x, t) = \alpha_0 e^{-\beta(t - (x/V_m))} \qquad t - (x/V_m) \geq 0 \qquad (11a)$$

$$\alpha(x, t) = \alpha_0 \qquad t - (x/V_m) < 0 \qquad (11b)$$

where α_0 is a constant which displays the initial exchange rate, and β is another constant which expresses the relative rate of decay of the exchange rate, and should be related to the change in the rate of the "clogging" process. A clearer understanding of the relation between β and the geochemical processes will require a more comprehensive study.

The new expression of α (equation (11)) was substituted in (3) and (4) which, along with the appropriate initial and boundary conditions (7)–(9), were run in the computer. Figure 4 shows the profile obtained with the best fit parameters (using a least squares optimization procedure for ϕ_m, α_0, and β). We found that $\alpha = 0.60 \exp(-0.15(t - (x/V_m))$ and $\phi_m = 0.30$. Accordingly, α decreased from 0.60 to 0.01 year^{-1} during the 26 years, and the recharge q (equation (10)) was calculated to be 40 mm year^{-1}. A comparison of Figures 3 and 4 shows that the modified model fits the data much better than the

model with the constant mass exchange rate. The generated profile has the desired characteristics of the measured profile with higher tritium concentrations in its upper part. In the bottom portion of the profile, on the other hand, the model yields low tritium concentrations in the mobile domain (and thus in the immobile domain too) as a result of (1) extensive transfer from the mobile to the immobile domain during the high tritium period at the top of the profile causing depletion of the mobile domain, (2) radioactive decay during percolation, and (3) mixing with the low tritium irrigation water. This model also retains the tritium concentration variations reflecting the alternation of summer irrigation water and winter rains as in the measured profile. The amplitude of these variations decreases with depth as a result of the combined effect of dispersion and mass exchange (equation (6)). In view of the noise involved in field observations and scarcity of space data, this model can not be tested in greater detail.

5. DISCUSSION

The fact that the modified model was able to reproduce the observed tritium profile does not excluded the possibility of proposing alternative models. Thus one may contemplate factors other than dispersion of clay colloids, which could account for the resulted profile. Such a factor could be, for instance, transfer of tritium by osmosis from the fresh mobile water to the saline immobile water in the upper part of the profile. The combined effect of osmosis and of molecular diffusion of salts from the immobile domain to the mobile one, could possibly lead to the diminishing rate of the tritium transfer, and hence to α decreasing in the course of time. A more detailed evaluation of the significance of the various mechanisms causing α to decrease with time is a subject for further investigation.

The coefficient of mass exchange between the mobile and immobile water domains was found to be 0.6 year^{-1} (without the clogging effect). This value is 2–4 orders of magnitude smaller than values obtained in earlier studies (Table 1). There are many reasons for such a discrepancy. De Smedt and Wierenga [1984] found an increase in the transfer coefficient α with increasing pore water velocity. It is also reasonable that α will increase with increasing in the total water content. The values of α reported in earlier studies were determined in laboratories on the basis of miscible displacement experiments in columns, with relatively large velocities. In addition, the artificial conditions of laboratory experiments highly differ from those in our natural system composed of saline and sodic loessial sediments with 30% clays (mainly montmorillonite) and more than 40% silt by means of the contact area between the two water domains. The dispersion of the clay minerals, as a result of the displacement of the original saline water by fresh irrigation and rain water, caused formation of clay gels

TABLE 1. Mass Exchange Rate Coefficient in the Literature

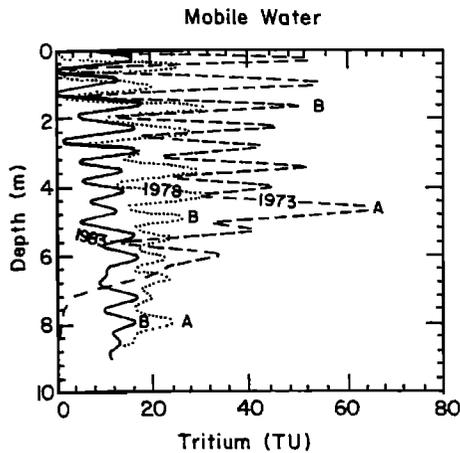| Reference	α Range	θ_v Range	Medium
Van Genuchten and Wierenga [1977]	0.05–0.4 day^{-1}	39–47%	clay loam
Gaudet et al. [1977]	0.03–0.1 hour^{-1}	20–26%	sand
Roa et al. [1980b]	0.05–0.2 hour^{-1}	37–40%	ceramic and glass beads
De Smedt and Wierenga [1984]	1–50 day^{-1}	8–37%	glass beads
Nkedi-Kizza et al. [1984]	0.01–1.0 hour^{-1}	52–58%	oxisol
De Smedt et al. [1986]	3–8 × 10^{-6} s^{-1}	6–34%	sand
This study	0.6 year^{-1}	19%	saline and sodic loess

Fig. 5. Theoretical profiles of tritium content in the mobile water domain for 1973, 1978, and 1983 (the sampling date). In 1973 the profile was enriched with tritium of the "bomb period," and thereafter it was leached downwards and became depleted slowly. The convection, dispersion, exchange, and decay processes are demonstrated by tracing two peaks of winter rains: "A" indicates the rain water of 1966, and "B" indicates that of 1971.

which isolated the immobile water phase, thus slowing down the exchange rate. Also, the flow in our medium takes place under unsaturated conditions with a water recharge of only 40 mm year^{-1}. Therefore the difference between the value of α obtained in our study and those in the laboratory should not be surprising.

According to the modified model, a set of parameters was obtained which was used for reconstruction of the tritium profiles during the past 26 years in the studied area. Cultivation of the area started almost at the same time as the thermonuclear tests in 1957. After 16 years of irrigation (in 1973), the rain and irrigation water percolated downward and accumulated in the upper 10 m of the sediment column. During that time the tritium content of the rains was very high (order of hundreds tritium units) and exchange by diffusion caused significant enrichment of the immobile water domain (Figures 5 and 6). As the water percolated downwards, its yearly peaks gradually smoothed out and depletion of tri-
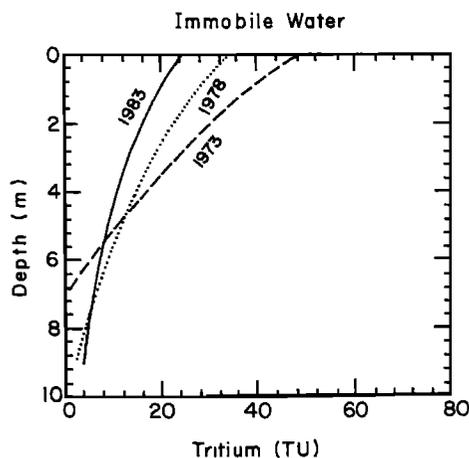
Immobile Water

Fig. 6. Reconstructed profiles of tritium content in the immobile water domain for 1973, 1978, and 1983 (the sampling date). The enrichment and depletion of tritium in the immobile domain is determined by the exchange process with the mobile domain according to the profiles shown in Figure 5.
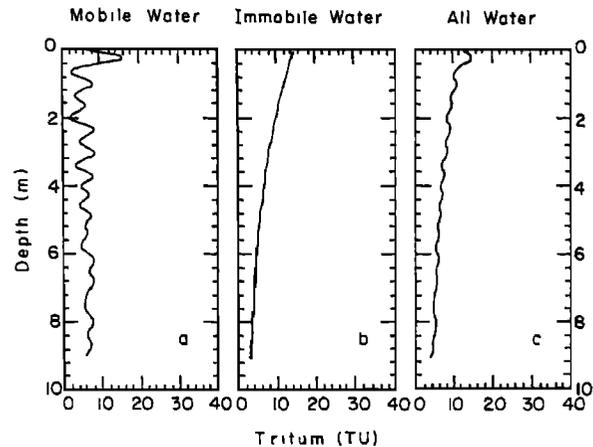

Fig. 7. Predicted tritium profile for 1993. Tritium content in (a) the mobile, (b) immobile water domains, and (c) a weighted combination of these components.

tium occurred as a result of both radioactive decay and exchange with the immobile water domain. In 1973, winter peaks could be resolved down to 6.0 m depth but were unresolved below this depth due to dispersion. Past 1967, the low tritium content of rains produced small yearly peaks of tritium in the mobile domain as shown in Figures 5 and 6.

In depths where the tritium content of the mobile water decreased below that of the immobile water, the direction of the tritium diffusion flux was reversed. Thus tritium depletion of the immobile water domain took place for a period of more than 10 years (up to date). In spite of the tritium depletion, a memory of the 1960s, with enormous amounts of tritium, was still retained. Therefore the tritium content of the immobile domain was higher than that of the mobile domain at the time of sampling.

To predict future trends, the measured tritium profile was used as initial conditions in conjunction with the calculated parameters in (3), (4), and (11). As would be expected, computer simulations indicate that the immobile water domain will continue to be depleted of its tritium content and the memory of the thermonuclear test period will become negligible (Figure 7).

6. SUMMARY AND CONCLUSIONS

The rainfall-irrigation tritium layering tracing method has the advantage of using a long record of a natural sequence of water application, thus having the ability to apply complicated transport models to the field. This study represents the first in situ application of the mobile-immobile water domain concept to the unsaturated zone above a phreatic aquifer. The mobile domain is represented by percolating freshwater from both rain and irrigation, and the immobile one is represented by isolated fossil saline water pockets. The two domains are connected through partially saturated narrow passages between dispersed clay minerals. The relevant equations [*Van Genuchten and Wierenga*, 1976] with a constant mass exchange rate coefficient α failed to reproduce the observed tritium profile. By taking into account the variations of the exchange coefficient with matrix characteristics, we were able to introduce in the previous model a time-dependent rate of mass exchange and to reproduce the measured tritium profile. The assumed changes in the matrix characteristics are attributed to dispersion kinetics of clays at the interface between fresh and saline waters.

It was found that good agreement was obtained when the fraction of the mobile water domain is 30% of the total water content and when the mass exchange rate decreased from 0.60 to 0.01 year^{-1} during 26 years of percolation.

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