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Diffusion of tritium in arid disposal sites

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Abstract. Tritiated water, released at a point in a uniform, relatively dry soil, diffuses in both the liquid and vapor phases. A model which accords well with published data indicates that the flux density of tritium in the liquid exceeds that in the vapor phase provided the water content is greater than approximately 20% of the total soil porosity. Thus tritium redistribution should be modeled recognizing transfer "in parallel" in both phases. The diffusion equation cast in spherical coordinates, and taking into account radioactive decay, then provides a basis for design of field experiments and predicts the long-term fate of tritiated water released in these experiments. We calculate the evolution of profiles of tritium concentration, within and external to the sphere of released solution, assuming the initial concentration to be uniform. We also predict the speed and the envelope of the tritium maximum as it advances and attenuates in the soil. We briefly discuss effects of variation in the volume fractions of soil water and air on the effective diffusion coefficient of tritium in soil and comment on possible effects of convective transfer by moving water and air.

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1. Introduction

There is concern about the disposal and fate of radioactive materials associated with the energy industry. Specifically, there is uncertainty about the fate of tritium which has been, or may in the future be, buried in arid disposal sites and fear that buried tritium will appear at the soil surface in significant amounts in the vapor phase or will contaminate groundwater.

Smiles et al. [1993] offered a preliminary analysis of a field experiment proposed to better define the risks and opportunities associated with this form of waste management. That experiment envisaged release of a small amount of tritiated water at a point deep in a dry desert soil. The evolution in space and time of concentration profiles was predicted as a basis for field monitoring, and the calculations were extended to offer order-of-magnitude information on the long-term effects of such an injection. This paper summarizes and illustrates some useful aspects of the approach to the problem.

2. Experiment and Consequent Conditions

Smiles et al. [1993] considered the release of 1 L of tritiated water in a dry soil in which the volume fraction of water $\theta_w = 0.06$ over considerable depth and the volume fraction of the soil air $\theta_a = 0.24$. These values are consistent with effects of desiccation and overburden at a depth of 20 m in desert soils where the water table occurs at depths in excess of 200 m. They appear to approximate conditions where the experiment is envisaged.

When tritiated water is injected at a point in this soil, we expect that the invading solution will advance quickly and radially. Gravity will have negligible influence on this process. At the same time the tritiated water will appear to displace the water originally present in this region [*Bond et al.*, 1982; also P. J. Wierenga, private communication, 1993]. The radial distributions of water and tritium immediately after release will then take the form shown in Figure 1 with a spherical saturated front at a radius $r \approx 9.8$ cm within which the tritium "front" lies at a radius $r = 9.25$ cm.

Subsequent redistribution of water within the assumption of continued "pistonlike" displacement of the original water will then result in the tritium front's approaching a limiting radial distance $r = a$ from the point of injection, with a given by the equation

$$a = (3V/4\pi\theta_w)^{1/3} = 15.8 \text{ cm} \qquad (1)$$

if V, the volume of injected water, is 1 L and the final value of θ_w tends to 0.06.

We seek to describe the evolution of the profile of tritiated water as it moves radially from the initial distribution shown in Figure 1. Since the water redistribution will be rapid relative to the diffusive process, we take as the profile at time $t = 0$ that shown with $a = 15.8$ cm.

3. Problem Analysis

The analysis proceeds upon the following assumptions:

1. Tritiated water transfers as if it were water or water vapor and is partitioned between the phases in proportion to the partitioning of water between its liquid and vapor phases. The tritium concentration in the gas phase $C_g = HC_w$, where H ($= 17 \times 10^{-6}$ at 293 K and 760 mm Hg pressure) is the Henry law constant, and C_w is the concentration in the water.

2. Equilibration of water between the liquid and gas phases, in relation to timescales of concern, is virtually instan-

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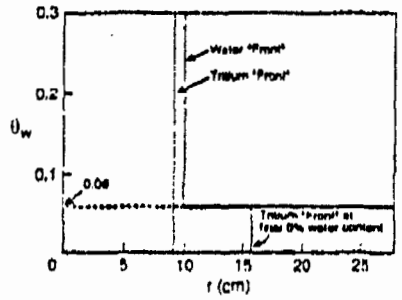

Figure 1. The radial distribution of water and tritium observed immediately following release of 1 L of tritiated water into a soil with an initial volume fraction of water, θ_w, of 0.06, and a total porosity of 0.30. The tritium "front" (at $r = \sim 9.25$ cm) lies behind the water "front" because the system behaves as if the invading solution displaces, in its entirety, the water originally present. The vertical dashed line at radius, $r = 15.8$ cm represents the furthest excursion of tritium when water redistribution is complete. We assume there is no hysteresis and that convection with the liquid water phase is the only means of transfer.

taneous. This assumption was invoked in relation to CO_2 by *Penman* [1940], stated without comment in relation to tritium by *Weeks et al.* [1982], and used by *Phillips et al.* [1988] and by *McCarthy and Johnson* [1993] for volatile organics.

3. The soil water is at static equilibrium (i.e., there is no net flux of the water as liquid or vapor). This is reasonable for the conditions we describe, but we return to it later.

4. Tritium undergoes radioactive decay with a half-life of 12.4 years.

4. Flow Equation

4.1. Material Balance

The material balance equation for spherical flow of tritium is

$$\frac{\partial(\theta_w C_w + \theta_g C_g)}{\partial t} = -\frac{\partial F}{\partial r} - \frac{2F}{r} - k(\theta_w C_w + \theta_g C_g) \qquad (2)$$

In this equation, r and t are radial distance and time; $(\theta_w C_w + \theta_g C_g)$ is the mass of tritiated water/unit soil volume; F is the diffusive flux of tritium (grams per square centimeter of soil per second); and the third term on the right refers to radioactive decay with decay constant k ($= 5.59 \times 10^{-2}$ yr^{-1}).

When the liquid and gas phases are static, F is the sum of F_w, the diffusive flux of tritium in the water, and F_g, that in the gas phase, namely,

$$F = F_w + F_g \qquad (3)$$

When (2) and (3) are combined, we obtain

$$\frac{\partial(\theta_w C_w + \theta_g C_g)}{\partial t} = -\frac{\partial(F_w + F_g)}{\partial r} - \frac{2(F_w + F_g)}{r} - k(\theta_w C_w + \theta_g C_g) \qquad (4)$$

4.2. Flux Equations

The flux of tritium in both the liquid and vapor phases is based on Fick's law for porous media, namely,

$$F = -\epsilon(\theta)D\frac{\partial C}{\partial r} \qquad (5)$$

In (5), ϵ is a factor which accounts for the volume fraction and tortuosity of the relevant phase in porous medium flow (see, for example, *Jury et al.* [1991] and *Millington* [1959]); D is the diffusivity of tritium in the relevant phase; and $\partial C/\partial r$ is the space gradient of the tritium concentration in the relevant phase.

We now assume that the diffusive flux can be calculated by treating liquid and vapor transfer as parallel, additive processes. We also recall that the mass distribution of tritiated water between the liquid and vapor phases is given by $C_g = HC_w$. The total flux of tritium, expressed in terms of the space gradient of the concentration of tritium in the liquid phase and D^*, the effective diffusivity of tritium in the system, is then

$$F_w + F_g = F = -D^*\frac{\partial C_w}{\partial r} \qquad (6)$$

4.3. Effective Diffusivity, D^*

From (5) and (6) and Henry's law it follows that D^* is given by

$$D^* = \epsilon(\theta_w)D_w + \epsilon(\theta_g)HD_g \qquad (7)$$

in which the vapor diffusivity $D_g = 2.57 \times 10^{-1}$ cm^2/s [*Rose*, 1966]; the liquid diffusivity $D_w = 2.26 \times 10^{-5}$ cm^2/s [*Sposito*, 1981], and $H = 17 \times 10^{-3}$. If we now assume that $\epsilon = \theta^{4/3}$ for both the gas and liquid phase diffusion [*Millington*, 1959] (but see, for example, *Currie* [1960]), then the effective diffusivity D^*, according to (7), is given by

$$D^* = 2.26 \times 10^{-5}\theta_w^{4/3} + 2.57 \times 10^{-1}H\theta_g^{4/3}\ cm^2/s$$

$$= 1.183 \times 10^{-6}\ cm^2/s \qquad (8)$$

when $\theta_w = 0.06$ and $\theta_g = 0.24$.

4.4. The Diffusion Equation

Substitution of (6) in the material balance (4) gives

$$\frac{\partial(\theta_w C_w)}{\partial t} = D^*\left(\frac{\partial^2 C_w}{\partial r^2} + \frac{2}{r}\frac{\partial C_w}{\partial r}\right) - k(\theta_w C_w) \qquad (9)$$

Equation (9) sets

$$\theta_w C_w = \theta_w C_w + \theta_g C_g \qquad (10)$$

Equation (9) thus treats as negligible the amount of tritium in the gas phase (e.g., $\theta_w C_w > 10^3\theta_g C_g$ if $\theta_w > 17 \times 10^{-3}\theta_g$); it accounts for transfer in the gas phase through (6) and (7), however.

If we now divide (9) by θ_w, assuming it to be constant in space and time, and introduce the variable C^* defined by the equation

$$C_w/C^* = \exp(-kt) \qquad (11)$$

then (9) becomes

$$\frac{\partial C^*}{\partial t} = (D^*/\theta_w)\left(\frac{\partial^2 C^*}{\partial r^2} + \frac{2}{r}\frac{\partial C^*}{\partial r}\right) \qquad (12)$$

The variable C^* is essentially the "undecayed" solution concentration of tritium. Its introduction reduces (9) to the more manageable (12). After solving (12), we then invoke (11) to

account for decay, and thence recover the actual solution concentration C_w at the relevant value of time t.

5. Solution of the Flow Equation

We seek a solution to (12) for the conditions

$$0 < r < a \qquad t = 0 \qquad C_w = C^* = C_0$$
$$r > a \qquad t = 0 \qquad C_w = C^* = C_i \tag{13}$$

in which C_0 and C_i are the initial solution concentrations in the released water and the soil. The initial concentration of tritium in the soil, C_i, is taken to be zero.

The solution of (12) and (13) [*Lovering*, 1935; *Carslaw and Jaeger*, 1959] is

$$\frac{2C^*}{C_0} = \operatorname{erf}[(R+1)/T^{1/2}] - \operatorname{erf}[(R-1)/T^{1/2}]$$
$$- T^{1/2}/(R\pi^{1/2})\{\exp[-(R-1)^2/T]$$
$$- \exp[-(R+1)^2/T]\} \tag{14}$$

in which R and T are dimensionless groups defined by

$$R = r/a \qquad T = 4D^*t/a^2\theta_w \tag{15}$$

Figure 2 shows the normalized concentration of tritium, C^*/C_0, calculated using (14) and graphed as a function of R, for T in the range $0 < T < 10$.

6. Discussion

6.1. Solution in Dimensionless Form

The information in Figure 2 is described in detail in the caption. Specifically, we note that the tritium concentration is normalized relative to C_0; the radial distance is normalized relative to $a = 15.8$ cm (compare Figure 1); T may be used to calculate the "real" time at which a specific profile is observed, using (15) and appropriate values of D^*, θ_w, a, and t; and radioactive decay is accounted for implicitly in the normalized concentrations since C^* is related to C_w by (9) and recalling that $k = 5.59 \times 10^{-2}$ yr^{-1}.

Because of the regulatory importance of and ability to measure very low tritium concentrations, a great range of C^*/C_0 is required of the calculations. This range makes the calculation of the error function terms in (14) critically important and makes, for example, the otherwise convenient five-term series cited by *Abramowitz and Stegun* [1965, p. 299] inappropriate. It also introduces problems because of the great times and distances over which (13) should apply. We return to some of these issues below.

Note also that for $R < 1$, the concentration of tritium decreases through time T. For any value of $R > 1$, however, the tritium concentration first increases from C_i relatively rapidly and then slowly decreases with time as diffusion continues.

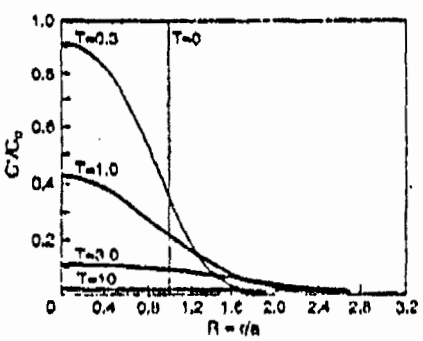

Figure 2. Tritium redistribution in space with time from the concentration profile of the form shown in Figure 1. Concentration C^* (curies per liter) is expressed as a fraction of the initial concentration C_0 (curies per liter). C^* is related to the "decayed" concentration C_w according to (9). Radial distance is normalized as $R = r/a$, where a is the radius of advance of the tritium at time $t = 0$ shown in Figure 1. The profiles are parameterized by $T = 4D^*t/a^2\theta_w$.

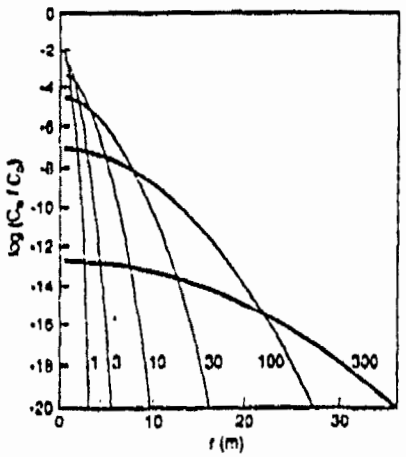

Figure 3. Graph corresponding to Figure 2, showing the physical distribution of tritium when $a = 15.8$ cm, $D^* = 1.18 \times 10^{-6}$ cm^2/s, and $\theta_w = 0.06$ for t in the range $1 < t$ (years) < 300 and r in the range $0 < r$ (meters) < 36. In this graph the concentration $C_w(t)$ is corrected for radioactive decay using (11), but normalized with regard to C_0. The numbers on the curves represent the times when the profiles are realized.

6.2. Solution in Physical Space and Time

Figure 3 shows the data of Figure 2 recalculated as $C_w(t)/C_0$ versus r, for $a = 15.8$ cm, $\theta_w = 0.06$, $\theta_g = 0.24$, and $D^* = 1.18 \times 10^{-6}$ cm^2/s. The profiles are parameterized by t in the range $10 < t$ (years) < 300. In this graph $C_w(t)$ reflects radioactive decay according to (11).

These data predict the soil response to the release of tritiated water and offer a basis for experimental design. Thus 10 years after release of the tritiated water, C_w/C_0 (measured in the liquid phase) 5 m from the point of release of the tritium is approximately 3.4×10^{-18}. This represents a concentration of 3.4×10^{-2} Ci/L if the initial concentration were 10^6 Ci/L. C_g will be 5 orders of magnitude less than this because $H = 17 \times 10^{-6}$. A 1-L gas sample slowly withdrawn from this region will contain $\sim 5.7 \times 10^{-7}$ Ci (2.1×10^4 Bq).

We also see in Figure 3, for $r > a$, how C_w/C_0 increases to a maximum and then decreases as both diffusive redistribution and radioactive decay take effect. Thus at $r = 5$ m, for example, C_w/C_0 is originally zero, is $\sim 3.2 \times 10^{-17}$ after 3 years, increases to $\sim 1.1 \times 10^{-9}$ after 30 years, but by 300 years has decreased again to $\sim 2.3 \times 10^{-13}$. It is $\sim 3.4 \times 10^{-18}$ after 10 and 100 years.

This behavior of the local maximum provides a useful way to consider the diffusive transfer of tritium. Figure 4, for example,

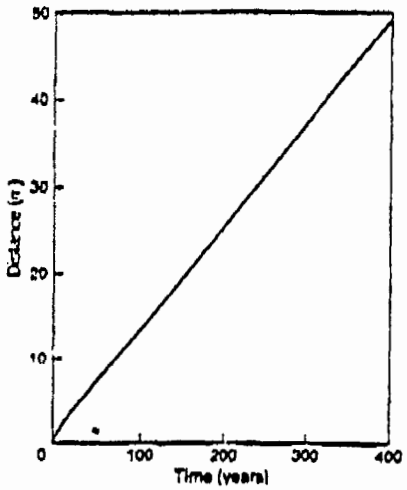

Figure 4. Graph showing the advance, in time, of the maximum tritium concentration, found by determining $\partial(C_w(t)/C_0)/\partial t = 0$, from (16), for r in the range $0 < r$ (meters) < 50. Note the linearity of the relation for $r > \sim 2$ m.

shows the advance of the maximum in $C_w(t)$ (where $\partial(C_w(t)/C_0)/\partial t = 0$) as a function of time. Note the linearity of the graph after the initial 10 years. These data may be obtained exactly by differentiating (13) with respect to t, correcting for radioactive decay using (9), and solving for $\partial(C_w(t)/C_0)/\partial t = 0$. This calculation is tedious, however, and in the present case we used (16), namely,

$$C_w(t)/C_0 = \frac{\pi a^3}{6(\pi D^* t/\theta_w)^{3/2}} \exp\left(-\frac{r^2}{4D^* t/\theta_w} - kt\right) \qquad (16)$$

This equation is the solution of (12) subject to (13) as $a \to 0$. It represents a solution to the purely diffusional problem [*Carslaw and Jaeger*, 1959, p. 257], combined with (11) to account for decay. It offers an excellent approximation for (14) as r increases relative to a, and as t increases. Thus for $D^*/\theta_w = 1.97 \times 10^{-5}$ cm²/s at $r = 50$ cm, the difference between the two solutions is less than 5% after 0.3 years and is less than 1% after 1 year. In relation to (15), we note that J. Knight (personal communication, 1994) has developed and demonstrates an approximate solution of (12) subject to (13) which is more accurate than (16) at short times.

Figure 5 is also calculated using (15). It shows the envelope of maxima of $C_w(t)/C_0$, for all time, for r in the range $0 < r$ (meters) < 28. In it we observe, for example, that at a distance of 6 m from the source $C_w(t)/C_0$ will never exceed 2.67×10^{-7}, while maxima at 10, 20, and 40 m are, respectively, $\sim 2 \times 10^{-9}$, $\sim 6 \times 10^{-14}$ and $\sim 1 \times 10^{-22}$. Figure 4 shows that these maxima are realized at 39, 70, 155, and 320 years, respectively.

Figures 3, 4, and 5 thus provide useful insights into the decay and redistribution process, and (16) provides a useful approximate method for determining the intermediate and long-term distribution of released tritium. Specifically, for our problem, the following considerations are noted:

1. At the water table, no tritium will ever be detectable using present methods. We infer this from the fact that at 60 m from the point of release, $\sim 3.3 \times 10^{-28} \times C_0$ Ci/L will be the greatest value of C_w ever achieved. This represents $\sim 1.2 \times 10^{-14}$ Bq/L and is undetectable by present methods.

2. At the soil surface, and neglecting complications relating to soil structure, water content, temperature, and air pressure variability in the top 2–3 m, we expect the maximum value of C_w/C_0 to be $\sim 6.2 \times 10^{-18}$, and $C_w(\max) = 6.2 \times 10^{-18}$ Ci/L (2.3×10^{-3} Bq/L). This value is approximately 1/50 of the maximum permissible concentration for tritium in water released to an unrestricted area of 3×10^{-6} Ci/L [*Nuclear Regulatory Commission*, 1982]. It will be achieved after ~155 years.

6.3. Qualifying Remarks

We reiterate that these calculations were developed to provide a basis for design of a field experiment which has yet to be approved. The approach is predicated on the assumption that the soil is homogeneous and flow well behaved. This will not always be the case, and a systems approach might be more appropriate for field design for waste storage than a deterministic one. At the same time, a deterministic approach offers a better approach for process studies and for estimation of material properties. It is therefore useful briefly to comment on several issues affecting application of the approach.

6.3.1. Convection of liquid. Convection of tritium will be important if significant liquid flow occurs. Calculations based on data of *Rose et al.* [1965], estimates for similar environments [*Allison et al.*, 1985; *Scanlon*, 1991] based on existing deep soil chloride concentration and water content profiles, and inferred past rainfall rates and chloride concentrations suggest that water fluxes (F_w) of order 10^{-9} cm/s might be observed. *Phillips et al.* [1988] calculate fluxes about an order of magnitude greater. Such fluxes imply a drift toward the water table at a velocity ($= F_w/\theta_w$) of order 10^{-8} to 10^{-7} cm/s. The center of mass of the sphere of tritium might then be expected to arrive at the water table 200 m below between 6000 and 60,000 years. Convection will therefore be unimportant after the initial, and minor, redistribution of the released tritiated water.

6.3.2. Convection of vapor. Limited "pumping" associated with periodic atmospheric pressure and temperature changes may occur 20 m beneath the soil surface. The magnitude of H, as well as rapid equilibration between the phases, ensures that this form of transfer is greatly suppressed, and we assume that

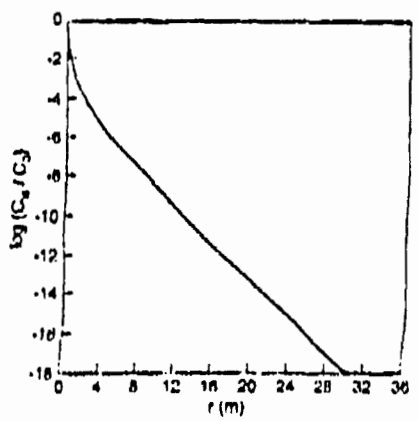

Figure 5. The envelope of maximum values of $C_w(t)/C_0$ for r in the range $0 < r$ (meters) < 30. The local concentration $C_w(t)$ will never exceed maximum values defined by this curve. Thus at $r = 10$ m, $C_w(t)/C_0$ cannot exceed 2.5×10^{-9}, so if $C_0 = 10^6$ Ci/L, then $C_w(t)$ will never exceed 2.5×10^{-3} Ci/L there. According to Figure 4, this concentration will be attained after ~73 years. The corresponding concentrations in the gas phase of the soil will be less than those in the water by the factor 17×10^{-9}.

it can be neglected. In sampling in the proposed experiment we thus assume that air withdrawn at a point in the soil reflects the solution concentration there.

6.3.3. Temperature effects. We similarly assume that temperature variation, in space and time, at this depth can be neglected. The actual temperature cannot be ignored, however. Data of *Scott and Paetzold* [1978], for example, showed an order-of-magnitude increase in their diffusivity at $\theta_w = 0.05$ as the temperature increased from 5°C to 33.5°C. This increase was greater than that anticipated from varying H appropriately in (8). Furthermore, their data showed an increase in diffusivity with increasing water content at 5°C, but a decrease in the diffusivity with increasing water content at 35°C. Simple application of (8) does not predict this, and this suggests a need to more carefully examine transfer of tritiated water in unsaturated soil. *Sposito* [1981] collated data showing the temperature dependence of the self-diffusion coefficient of liquid water.

6.3.4. Coefficients D^* and D^*/θ_w. Both D^* and D^*/θ_w are called diffusion coefficients in soil science literature. Comparison, for example, of discussions of gas flow by *Hillel* [1980] and by *Jury et al.* [1991] demonstrate difficulties and inconsistencies that arise in relation to their definition and interpretation.

D^* is effectively a "transfer coefficient" as defined in (5) and (6). D^*/θ_w, on the other hand, is a "diffusion coefficient" insofar as it is the coefficient in the diffusion equation (12) and it represents "transfer" (D^*) divided by "capacity" (θ_w). D^*/θ_w corresponds exactly to what *Jury et al.* [1991, p. 217] call a "generalized effective liquid-gas diffusion coefficient," but note that *Jury et al.* [1991] define flow in response to $\partial C_g/\partial r$ rather than $\partial C_w/\partial r$, as we have. Specifically, the Jury et al. coefficient in our terminology equals $D^*/(H\theta_g + \theta_w)$, with the denominator arising because they are not able to use our approximating equation (10) in their problem with CO_2.

In this respect we note also that *Phillips et al.* [1988], in considering the fate of weapons-derived tritium, neglected the diffusive flux of tritium in the liquid phase, although they recognized the importance of its storage in that phase. In doing so they followed *Weeks et al.* [1982] who refer to *Penman* [1940]. The former authors dealt with fluorocarbons, while *Penman* [1940] had CO_2 in mind. Both gases are much less soluble in water than is tritium, however, so the diffusive fluxes in the water are relatively less important than that for tritiated water. Equation (6) implies that not till $\theta_w \to 0.06$ does $F_g \approx F_w$ when $\theta_w + \theta_g \approx 0.3$, and generally flux in the gas phase exceeds that in the liquid phase only when $\theta_g \gtrsim 5\theta_w$.

Figure 6 shows values of D^*/θ_w calculated using (8) for a range of water contents and total porosities of 0.3 and 0.4. We also show data measured by *Nakayama and Jackson* [1963], *Scott and Paetzold* [1978], and *Torok et al.* [1991] in this figure. Data calculated using (8) correspond well with the majority of measured values but lie well below the high values of *Torok et al.* [1991] for their sands. Equation (8) does not predict the maximum observed by *Nakayama and Jackson* [1963] at $\theta_w \approx 0.04$, although it does predict a minimum observed (although at much higher water contents) by Scott and Paetzold. It is evident that both porosity and water content must be measured accurately when determining D^*/θ_w.

Despite these agreements, we reiterate that (8) only provides an estimate of D^* for soil systems for which we have no measurement. It is justified solely on its ability to match measured values. *Jury et al.* [1991] identify other empirical forms which might have been used. As $\theta_w \to 0$, all models of this sort fail. This is because at very low water contents, water films

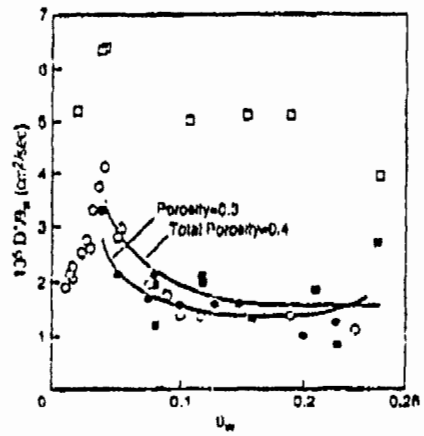

Figure 6. Graph showing variation in D^*/θ_w with θ_w calculated using (8) for total soil porosities of 0.3 and 0.4. The graph also shows data measured by *Nakayama and Jackson* [1963] (open circles), *Scott and Paetzold* [1978] (solid circles), and *Torok et al.* [1991] for sand (open squares) and a sand/clay mixture (solid squares).

become discontinuous, and transfer becomes more complicated than a "simple" parallel flow model can describe [cf. *Philip and de Vries*, 1957; *Phillips et al.*, 1988]. We cannot specify when these perturbations become critical but arbitrarily reject (8) for $\theta_w < 0.04$. In this range we believe that D^* and D^*/θ_w can only be determined experimentally.

6.3.5. Formulation of the diffusion equation in soils. In developing this analysis it emerges that there may be ambiguities in relation to material balance (see, for example, equation (4) of *Scanlon* [1991]) and the significance of concentration gradients, depending on whether the tritium concentration is expressed per unit volume of water or per unit volume of soil. The diffusivity is the same in each case. To avoid these ambiguities, the water content distribution must be specified to define fully the system. In our case the water content is assumed to be uniform, and interpretation is straightforward. In systems where the water content varies spatially and in time, however, the problem is significant. Formulation of the equations in a Lagrangian coordinate system which satisfies material balance for the water may resolve these ambiguities [*Smiles et al.*, 1981; *Wilson and Gelhar*, 1981]. The approach requires that we explicitly define the water content field, by measurement if necessary. It is then relatively unimportant if there are local changes in water content. Furthermore, it is relatively simple to take into account systematic water content change associated, for example, with approach from above to a water table or with local soil texture change.

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Errata #1 (issued July 16, 1996 by Erik Vold) to

LA-UR-96-973,

AN ANALYSIS OF VAPOR PHASE TRANSPORT IN THE UNSATURATED ZONE WITH APPLICATION TO A MESA TOP DISPOSAL FACILITY,
PART I
draft 1, March 14, 1996

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and to

LA-UR-96-1848 DRAFT I - 052296

DETERMINATION OF AN IN-SITU VADOSE ZONE VAPOR PHASE DIFFUSION COEFFICIENT AT A MESA TOP WASTE DISPOSAL FACILITY

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Synopsis of problem:

An important error has been found in the draft document, LA-UR-96-973, by Don Neeper which requires significant correction to LA-UR-96-973 and to the companion paper, LA-UR-96-1848. Additional changes to accomodate Don's review will also be included in the next full revision.

Synopsis of corrections in the two papers

Final vapor flux estimates (magnitudes) in Tables, discussion and in figures are fortuitously correct since two errors canceled each other.

All expressions where vapor flux, Γ_v, is expressed as a function of the effective or in-situ diffusion coefficient, D_v, should be multiplied by the correction factor, M_v/M_a, (molecular weight of water to that of air). This allows the factor in the coefficient to simplify from $(M_v p_a/M_a p_a)$ to (M_v/RT).

The in-situ vapor phase diffusion coefficient derived in LA-UR-96-1848 by comparison of in-field tritium measurements to diffusion modeling should be larger by the factor M_a/M_v. Discussion will be corrected to reflect that this in-situ diffusion is about 60 times greater than expected by classical diffusion in a porous media, rather than the factor of about 40 reported in LA-UR-96-1848, and discussed in both papers.

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Discussion of corrections in the two papers

The problem in LA-UR-96-973 is introduced in Eqn.4, which was written

$$\rho_v = \frac{p_v}{p_a}\rho_a = \frac{p_v}{p_a}\rho_a = \frac{p_v}{p_s}\frac{p_s}{p_a}\rho_a, \qquad \text{OLD(4).}$$

For an ideal gas, $\rho = Mp/RT$. Under the conditions assumed ($T_v = T_a$), Eqn.4 should be:

$$\rho_v = \frac{p_v}{p_a}\rho_a = \frac{M_v p_v}{M_a p_a}\rho_a = \frac{p_v}{p_s}\frac{M_v p_s}{M_a p_a}\rho_a, \qquad \text{NEW(4)}$$

where M_v is the molecular mass for water vapor (18) and M_a is the molecular mass for air (approximately 28.8). Eqn.5 for the vapor flux, Γ_v, and all subsequent equations involving the vapor flux should be corrected by the factor, $M_v/M_a = 18/28.8 = 0.625$.

Thus, for example, the vapor flux in Eqn.9, with the assumption that $exp(h_m/h_c) \sim 1$, should be written,

$$\Gamma_v = -D_v\frac{M_v}{M_a}\frac{p_a}{P_a}\left(\frac{dp_s}{dT}\nabla T - \frac{p_s}{h_c}\frac{dh_m}{d\theta}\nabla\theta\right).$$

Since $T_v = T_a = T$ is assumed, this can be written

$$\Gamma_v = -D_v\frac{M_v}{RT}\left(\frac{dp_s}{dT}\nabla T - \frac{p_s}{h_c}\frac{dh_m}{d\theta}\nabla\theta\right).$$

which shows the correct dependence that the vapor flux depends on vapor molecular weight and temperature and not directly on the density and pressure of air.

This also corrects the ratio, ρ_v/ρ_L, introduced between Eqns.17 and 18, to ~ 0.98×10^{-5} (NOTE: it is this ratio which causes the error in LA-UR-96-1848).

The depths predicted for the vapor phase dominated region will be not be changed by this correction.

The conclusions and discussion are not altered significantly by this correction.

A related error in the derivation of the in-situ diffusion coefficient in LA-UR-96-1848 occurred in a somewhat fortuitous manner, such that this value is too large by the correction factor, M_a/M_v. The implication is that the two errors cancel each other in the vapor flux estimates in LA-UR-96-973, and so the vapor flux values in the Tables and figures and discussion are correct, or at least consistent with the corrected analysis.
However, the value for the effective insitu vapor phase diffusion coefficient, $D_{in\text{-}situ}$, used in both papers is now too small by the correction factor. Discussion in the text which states that the in-situ vapor diffusion is about 40 times larger than expected by classical diffusion processes in porous media should be revised upward by 1/0.625 or the effective in-situ diffusion is about 60 times greater than expected!

Paper LA-UR-96-1848 needs revision to Eqn.15, wherein H is defined, with corrections similar to that described above for Eqn.4 in LA-UR-96-973. Where the text states this is the same H as used by Smiles, et.al. ,this is refering to $H = \rho_v/\rho_w$. Thus, the value of H should be: H = 1.56e-5 x 0.625 = 0.98e-5. This value is used in the divisor of Eqn.37 to obtain the in-situ vapor diffusion coefficient from the effective tritium diffusion observed for the field measurements. Thus, the in-situ vapor diffusion coefficient at this point should be larger by 1/0.625.
Discussion immediately following Eqn.37 and carried into the conclusion section shall be revised to reflect that the in-situ vapor phase diffusion coefficient is found to be about 60 times greater (rather than the factor of 40 given previously) than expected in comparison to classical diffusion in a porous media with the permeabilty values derived from tuff samples.
The in-situ diffusion coefficient is therefore found to be about 1e-3/.625 ~ 1.6 e-3 m^2/s rather than the 1e-3 m^2/s as stated in the reports.