Spherical Diffusion Of Tritium From a Point of Release in a Uniform Unsaturated Soil

A Deterministic Model for Tritium Migration in an Arid Disposal Site

Prepared by
D. E. Smiles, W. R. Gardner, R. K. Schulz

College of Natural Resources
University of California, Berkeley

Spherical Diffusion Of Tritium From a Point of Release in a Uniform Unsaturated Soil

A Deterministic Model for Tritium Migration in an Arid Disposal Site

Prepared by
D. E. Smiles*, W. R. Gardner, R. K. Schulz

Department of Environmental Science, Policy and Management
College of Natural Resources
University of California
Berkeley, CA 94720

*Visiting Professor, University of California, Berkeley
On leave from the Division of Soils, CSIRO, Australia

Disclaimer

This report is not a substitute for NRC regulations, and compliance is not required. The approaches and/or methods described are provided for information only. Publication of this report does no necessarily constitute NRC approval or agreement with the information contained herein.

ABSTRACT

Tritium, when released as tritiated water at a point in a uniform and relatively dry soil, redistributes in both the liquid and vapor phases. The flux density of tritium in the liquid will exceed that in the vapor phase provided the water content is greater than approximately 15% of the total soil porosity. Thus tritium redistribution must be modelled recognizing transfer "in parallel" in both phases.

We use the diffusion equation cast in spherical coordinates to analyze this problem in order to provide a basis for design of field experiments, and to offer observations on the long term behavior of such systems. We take into account radioactive decay.

The solution of the diffusion equation permits calculation of the evolution of profiles of tritium concentration, within and external to the sphere of released solution, assuming the initial concentration within this sphere to be uniform. We also predict the rate of advance of the maximum of tritium as it advances, and attenuates, in the soil. Calculations for the case of 1 million Curies of tritium diluted in 1 liter of water and released at a depth of 20 meters, and 200 meters above the water table, are demonstrated. If the soil has an initial water volume fraction of 0.06 and total porosity of 0.3 they show, for example, that at 5 meters from the point of discharge, the tritium concentration increases to a maximum in 24 years and then slowly declines. That maximum is 1 Curie/liter. The concentration in the gas phase will be 5 orders-of-magnitude less than this. At 60 meters the maximum ever reached in the liquid phase is $\sim 10^{-21}$ Ci/liter; that maximum will be achieved after 408 years. This concentration represents approximately $4*10^{-11}$ disintegrations per second per liter, or 1 tritium atom in 70 liters. For this example, therefore, no tritium reaches the ground water. At the soil surface, however, the maximum will be 1μ Ci/liter and will be achieved after about 130 years. This concentration approximates the maximum permissible concentration for tritium in water released to an unrestricted area.

We briefly discuss the effects of variation in the volume fractions of water and air originally present in the soil on the effective diffusion coefficient of tritium in soil. We consider the effects of a net flux of water in the system, and identify questions to be answered to achieve safe systematic disposal of tritium in the deep unsaturated zone of desert soil.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

This table shows the way variation in θ_w and θ_g affects:

ACKNOWLEDGEMENTS

INTRODUCTION

The United States Department of Energy and the United States Nuclear Regulatory Commission are concerned about the disposal and fate of radioactive materials associated with the energy industry. Specifically, there is uncertainty about the fate of millions of Curies of tritium which have been, or may in future be, buried at the Nevada Test Site and Ward Valley, California and the likelihood that buried tritium will appear at the soil surface in significant concentrations in the vapor phase, or will contaminate the ground water is of concern.

Smiles et al (1993) examined the transfer of tritium from a point of release in relatively dry soil. Regrettably an arithmetic error in the illustrative examples they offered resulted in an estimate of the effective diffusivity an order of magnitude less than we believe to be appropriate. As a result conclusions in that paper concerning the long term fate of tritium in dry soils must be reexamined.

This paper reconsiders the problem. In it we calculate the rate of migration of tritium from the point of release in the soil. We also provide a basis for design of field experiments to better define the risks and opportunities associated with this form of waste management.

We perform calculations to describe consequences of the release of 1 liter of tritiated water in a dry soil in which the volume fraction of water, θ_w is uniform over considerable depth as is the volume fraction of the soil air θ_g. For purposes of illustration we set $\theta_w = 0.06$, and $\theta_g = 0.24$. These values are consistent with effects of desiccation and overburden at a depth of 20 meters in desert soils where the water table occurs at depths in excess of 200 meters. In these circumstances movement of tritium from the point of release will tend to be diffusive and radial and we would not expect significant transfer associated with mass flow of water.

PROBLEM ANALYSIS

Our analysis is based in the following reasonable assumptions:

1. Tritiated water behaves as if it were water with a minor perturbation because the molecular weight of HTO is approximately 10% greater than that of water. We therefore consider the transfer of HTO as if it were water or water vapor, and assume that it is partitioned between the phases in proportion to the partitioning of water between the phases. At standard temperature and pressure the concentration in the gas phase, $C_g = 17*10^{-6}C_w$, where C_w is the concentration in the water phase.

2. In relation to the time scales of concern, equilibration of water between the liquid and gas phases will be effectively instantaneous, and we infer that equilibrium also exists at all times between tritium in the gas and liquid phases. This is because the water and the gas phases in the soil have length scales, L, of order 0.1mm. Equilibration following a change in concentration at the surface of the phase will then have characteristic times $T = L_2/D$ of order 5 seconds for the water, and $5*10^{-4}$ seconds for the gas. In these calculations D is the diffusion coefficient in each phases.

3. The soil water is at static equilibrium. There is thus no net flux of the liquid field as liquid or vapor. This is a reasonable assumption for the desert conditions and depth we describe, but we return to it later.

Within these assumptions we seek to predict the evolution in space and time of concentration profiles of tritium as the initial local high concentration described above redistributes and as the tritium undergoes radioactive decay with a half-life of 12.3 years.

THE FLOW EQUATION

1. Material balance.

The material balance equation for radial flow of tritium is

$$\frac{\partial(\theta_w C_w + \theta_g C_g)}{\partial t} = -\frac{\partial F}{\partial r} - \frac{2F}{r} - k(\theta_w C_w + \theta_g C_g) \tag{1}$$

In this equation:

- r and t are radial distance and time;

- C_w and C_g are concentrations in the gas and water phases;

- θ_w and θ_g are the volume fractions of water and gas;

- F is the diffusive flux of tritium (g/cm^2 of soil/sec); and

- the third term on the right hand side refers to radioactive decay with decay constant, k ($=5.64*10^{-2}$ years^{-1}); and

- $(\theta_w C_w + \theta_g C_g)$ is the mass of tritiated water per unit volume of soil.

When the liquid and gas phases are static, F is given by

$$F = F_w + F_g \tag{2}$$

In eq.(2), F_w is the diffusive flux of tritium [grams/cm^2 of soil/sec] in the water and F_g that in the gas phase.

2

When eqs (1) and (2) are combined we obtain

$$\frac{\partial(\theta_w C_w + \theta_g C_g)}{\partial t} = -\frac{\partial(F_w + F_g)}{\partial r} - \frac{2(F_w + F_g)}{r} - k(\theta_w C_w + \theta_g C_g) \tag{3}$$

2. Flux equations.

The flux of tritium in each phase is based on Fick's Law for porous media viz

$$F = - \epsilon\theta D \frac{\partial c}{\partial r} \tag{4}$$

In eq.(4):

- ϵ is a tortuosity factor appropriate to porous medium flow;

- D is the diffusivity of tritium in the appropriate phase; and

- $\partial C/\partial r$ is the space gradient of the tritium concentration in the relevent phase.

Assuming that tritium diffuses as if it were vapor and liquid water, then the vapor and liquid diffusivities, D_g and D_w, are:

- $D_g = 2.57*10^{-1}$ cm^2/sec (Rose, 1966); and

- $D_w = 2.26*10^{-5}$ cm^2/sec (Sposito, 1981).

The tortuosity in relation to both the gas and liquid phase diffusion is taken to be 0.7 (Currie, 1960, 1961).

We now assume that the diffusive flux can be calculated by treating liquid and vapor transfer as additive processes in parallel; and recall that the mass distribution of tritiated water between the liquid and vapor phases equals the density ratio between the phases [liquid:gas = $1:17*10^{-f}$].

3

The total flux of tritium then becomes (cf Jury et al.1991)

$$F_w + F_g = F = -D^* \cdot \frac{\partial C_w}{\partial r} \tag{5}$$

In this equation the tritium gradient is expressed as the space gradient of the concentration of tritium in the liquid phase. The diffusivity D^* includes diffusion in both phases. D^* is given by

$$D^* = 0.7 \times 2.26 \times 10^{-5} \, \theta_w + 0.7 \times 2.57 \times 10^{-1} \times 17 \times 10^{-6} \, \theta_g \quad cm^2/sec$$
$$= 1.582 \times 10^{-5} \theta_w + 3.028 \times 10^{-6} \, \theta_g \quad cm^2/sec \tag{6}$$

D^* is equal to 1.68×10^{-6} cm^2/sec when $\theta_w = 0.06$ and $\theta g = 0.24$.

Substitution of eq.(6) in the material balance eq.(1) gives

$$\frac{\partial(\theta_w C_w)}{\partial t} = D^*(\frac{\partial^2 C_w}{\partial r^2} + \frac{2}{r} \frac{\partial C_w}{\partial r}) - k(\theta_w C_w) \tag{7}$$

Equation (7) treats as negligible the amount of tritium in the gas phase. That is, it sets

$$\theta_w C_w \approx \theta_w C_w + \theta_g C_g \tag{8}$$

It accounts for diffusion in the gas phase however through eqs (5) and (6).

If we now divide eq.(7) by θ_w, assuming it to be constant in space and time, and then introduce the variable C^* defined by the equation:

$$C_w/C^* = \exp(-kt) \tag{9}$$

4

then eq.(7) becomes

$$\frac{\partial C^*}{\partial t} = (D^*/\theta_w)(\frac{\partial^2 C^*}{\partial r^2} + \frac{2}{r}\frac{\partial C^*}{\partial r}) \tag{10}$$

The variable C^* defined by eq.(9) is essentially the "undecayed" solution concentration of tritium. Its introduction reduces eq.(7) to eq.(10); a form we can solve. After solving eq.(10) we then invoke eq.(9) to account for decay, and thence recover the actual solution concentration C_w at the relevant time, t.[1]

We thus seek to solve eq.(10) for conditions we now describe.

INITIAL AND BOUNDARY CONDITIONS

When tritiated water is injected into this soil we expect that the invading solution will advance quickly and radially as if the soil were a "delta-function" material (Green and Ampt, 1911; Philip, 1969) in which absorption is represented by a steep saturated wet front which advances in response to a constant wetting front potential. Behind the front we assume that the water content will be constant. This model is consistent with the high bulk density and inferred uniformity of this soil. Gravity will have negligible influence on this process.

Release of the tritiated water will thus result initially in a saturated sphere of soil. The radius r of this sphere is given by rearranging the equation

$$V = 4\pi r^3 \theta_g/3 \tag{11}$$

in which:

- V is the volume of solution injected; and

- θ_g is the air filled pore space [we assume complete displacement of air].

When $\theta_g = 0.24$ and, V = 1 liter, then r = 9.96cm.

At the same time the invading tritiated water will appear to displace the water originally present in this region in its entirety [Bond et al.,1982; Wierenga, private communication, 1993]. The radial distributions of water and tritium immediately after release will thus take the form shown in Fig.1.

---

[1] Smiles et al.(1993) failed to divide D^* by θ_w in eq.(10). Their effective diffusion coefficient was therefore too small by 1/0.06.
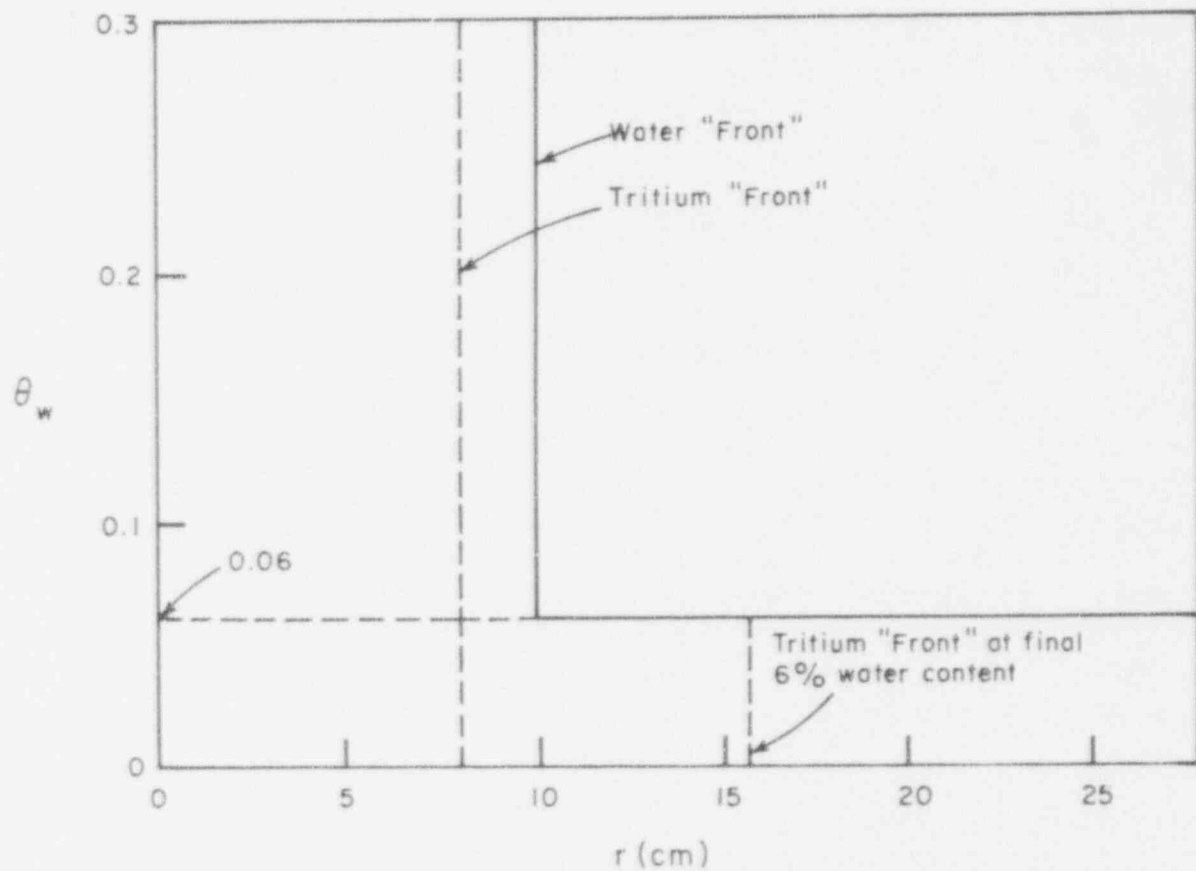
Figure 1 Diagram showing the radial distribution of water and tritium immediately following release of 1 liter of tritiated water into a soil with an initial volume fraction of water, θ_w, of 0.06, and a total porosity of 0.30. The tritium "front" lies behind the water "front" because the system behaves 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 in the water if convection with the liquid water phase were the only means of transfer.

6

Subsequent redistribution of water within the assumption of continued "piston-like" displacement of the original water will then result in the tritium front approaching a limiting radial distance, a, from the point of injection given by the equation

$$a = \sqrt[3]{3V/4\pi\theta_w}$$ (12)

If the final value of θ_w tends to 0.06, then a = 15.8cm.

Redistribution of water will be rapid and will be negligibly affected by gravity.

To describe the evolution in time of profiles of tritium as it moves radially from the initial distribution shown in Fig.2 we therefore solve eq.(10) for the conditions

$$0 < r < a \; ; \; t = 0 \; ; \; C_w = C^* = C_0$$
$$r > a \; ; \; t = 0 \; ; \; C_w = C^* = C_i$$ (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 eqs(10) and (13) (Lovering, 1935; Carslaw and Jaeger, 1959) is

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

in which R and T are dimensionless groups defined by

$$R = r / a \; ; \; T = 4D^*t / a^2\theta_w$$ (15)
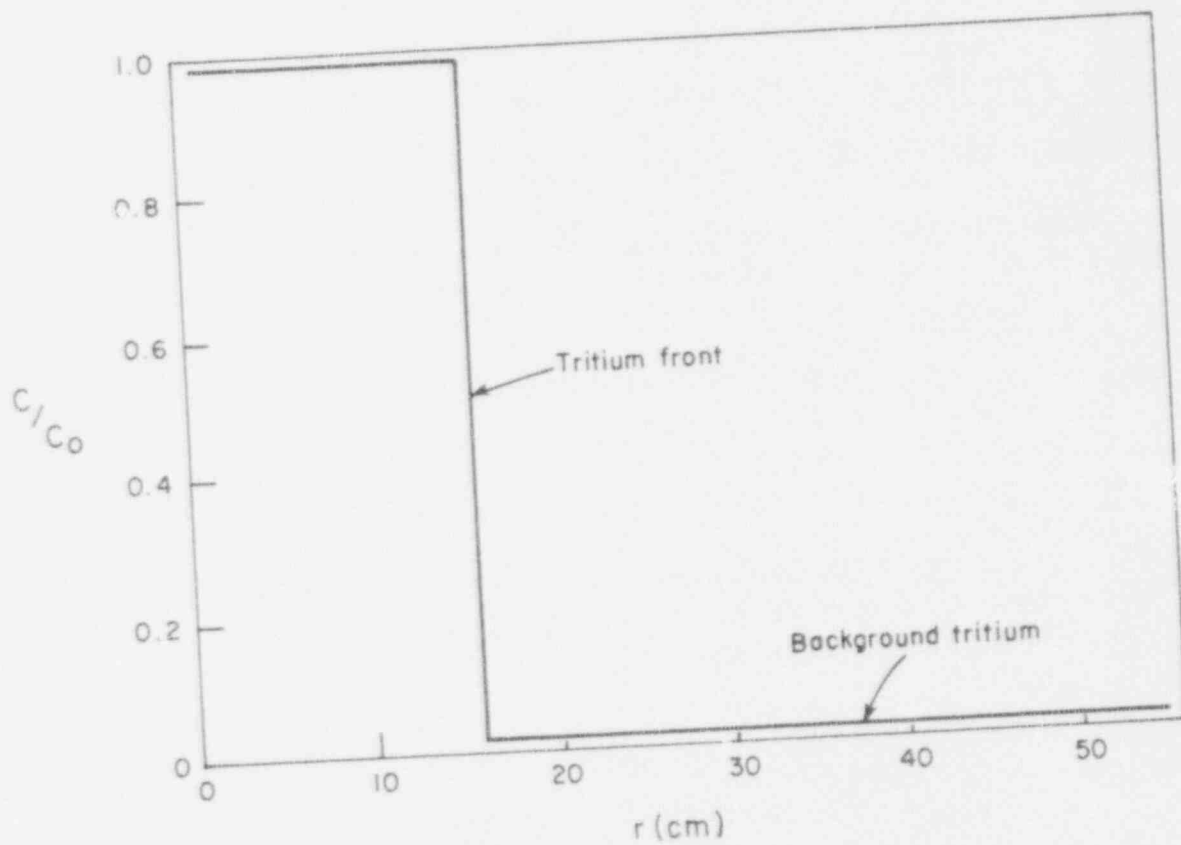
Figure 2   Diagram showing the radial concentration distribution of tritium following redistribution of initial water content and tritium content profiles depicted in Fig.1. The concentration of tritium, C_w, is expressed in Curies/liter of water. It is expressed in this figure as a function of the initial concentration, C_o. The lower horizontal line represents background tritium. The redistribution process will be complete after approximately 15 days. This graph represents the initial and boundary conditions for our calculations on the redistribution of tritium described in the text.

8

Figure 3 shows the normalised concentration of tritium, C^*/C_0, calculated using eq.(14) and graphed as a function of R, for T in the range $0 < T < 10$.

Figure 4 shows $\log(C^*/C_0)$ versus R for T in the range $0 < T < 30$.

DISCUSSION

1. The solution in dimensionless form.

The information provided in Figs 1, 2, 3 and 4 is described in detail in the legends to those figures. The data shown in Figs 3 and 4 are general and flexible. Thus:

a. Tritium concentration is normalized relative to the initial concentration and the data are not restricted to any specific value of C_0.

b. Radial distance is normalized relative to the initial radius of extent, a, of the tritium shown in Fig.2. The solution is thus scale-independent, and the real radius, r, is easily calculated if the initial excursion of tritium, a, is known.

c. The "reduced" time, T, which parameterizes the concentration profiles is used to calculate the "real" time at which a specific profile is observed, using eq.15 and values of D^*, θ_w, a, and t appropriate to the circumstances.

d. Radioactive decay is accounted for implicitly in the normalized concentrations since C^* is related to C_w by eq.(9). It enters the calculation when the actual concentration at a radius, r, at a particular elapsed time, t, is required. It is then invoked using eq.(9) and recalling that $k = 5.64*10^{-2}$ $(years)^{-1}$.

Note the great range of C^*/C_0 required of the calculation. This is because of the importance of, and ability to measure, very low tritium concentrations. This range makes the calculation of the error function terms in eq.(14) critically important and makes, for example, the otherwise convenient five term series cited by Abramowitz and Stegun (1965, p299) inappropriate. 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.

2. The solution in physical space and real time.

Figure 5 shows dimensionless data of the form seen in Figs 3 and 4 recalculated as $C_w(t)/C_0$ versus r, with the profiles parameterized by t in the range $1 < t/(years) < 30$. In this graph C_0 is the original concentration, and $C_w(t)$ reflects radioactive decay according to eq.(9).

9
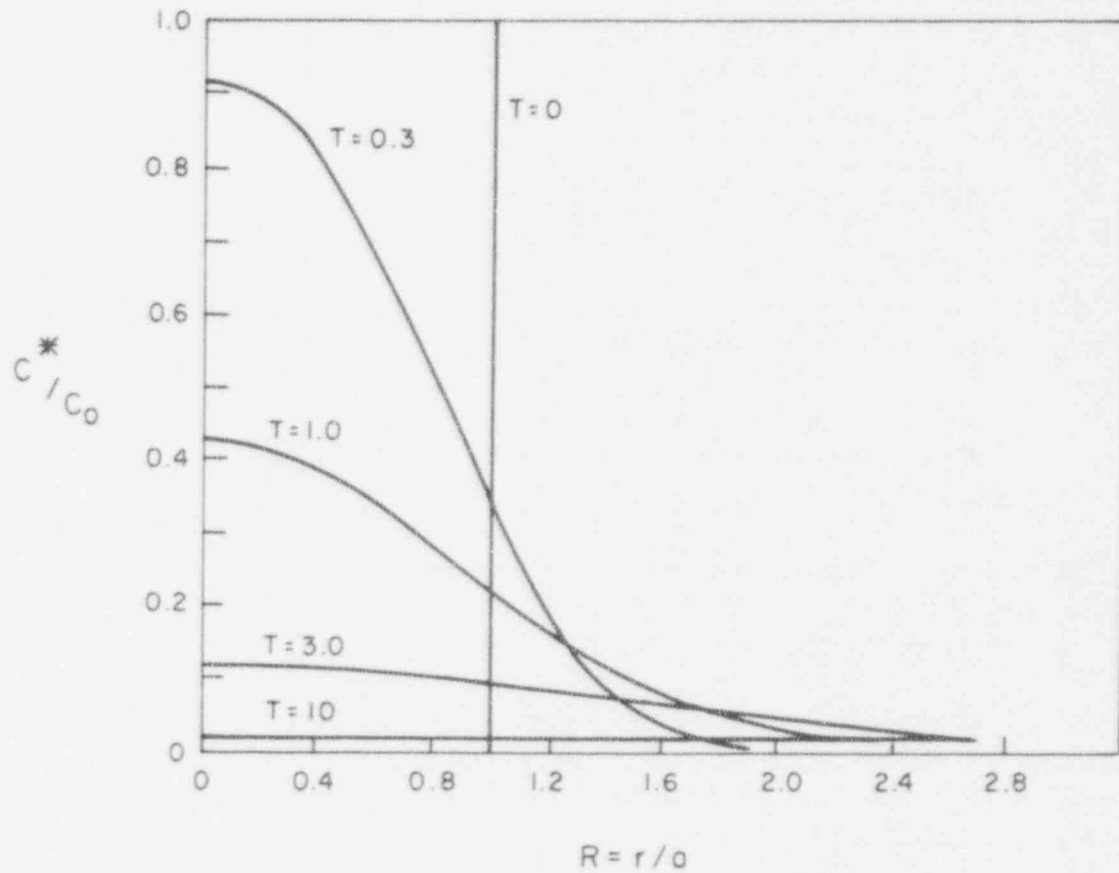
Figure 3   Graph showing the way tritium redistributes in space with time from a concentration profile of the form shown in Fig.2. Concentration, C^* [Ci/l], is expressed in dimensionless form as a fraction of the initial concentration, C_o [Ci/l]. C^* is related to the "decayed" concentration, C_w, according to eq.(9). Radial distance is presented as the dimensionless radius $R = r/a$, where a is the radius of advance of the tritium at time $t = 0$ shown in Fig.2. Each profile is parameterized by the time-like variable $T = 4D^* t/a^2 \theta_w$, the terms of which are explained in the text.

10
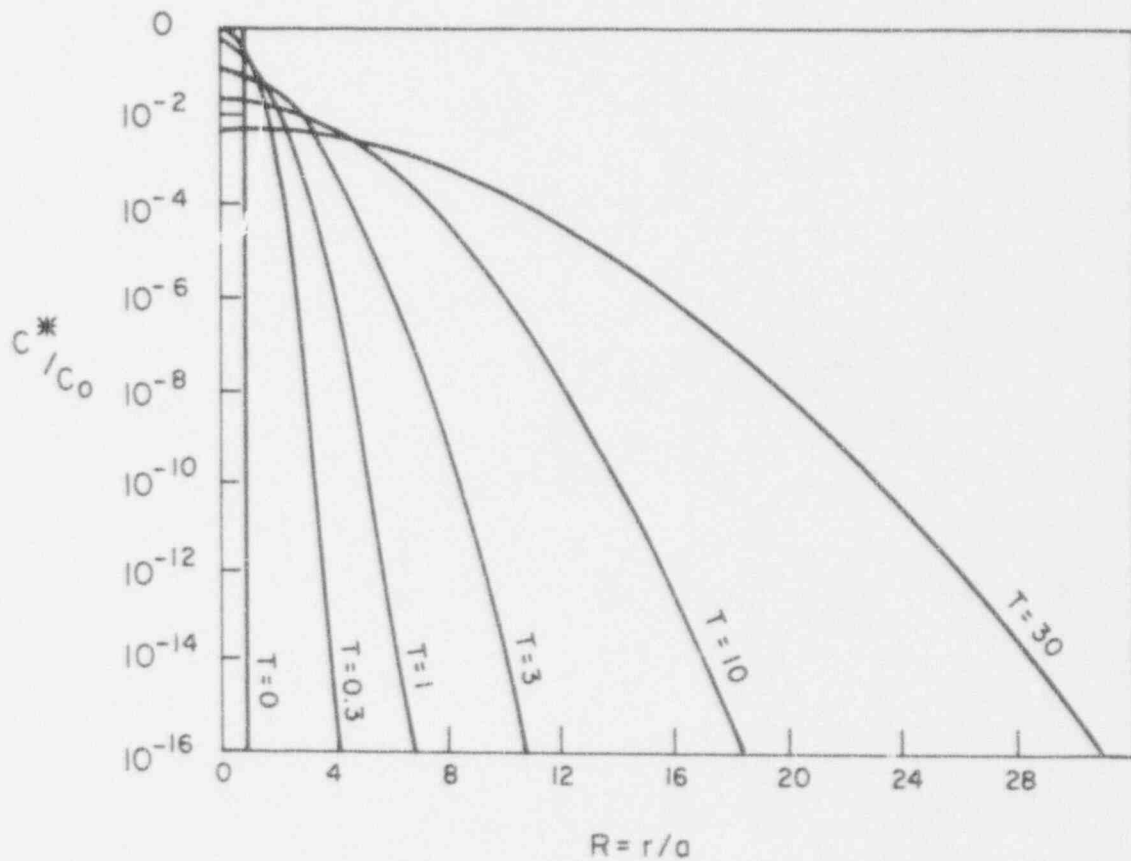
Figure 4   Graph corresponding to Fig.3 showing the way tritium redistributes in space ($R = r/a$) with time ($T = 4D^* t/a^2 \theta_w$) from a concentration profile of the form shown in Fig.2 but with concentration expressed as the logarithm of C^*/C_o.
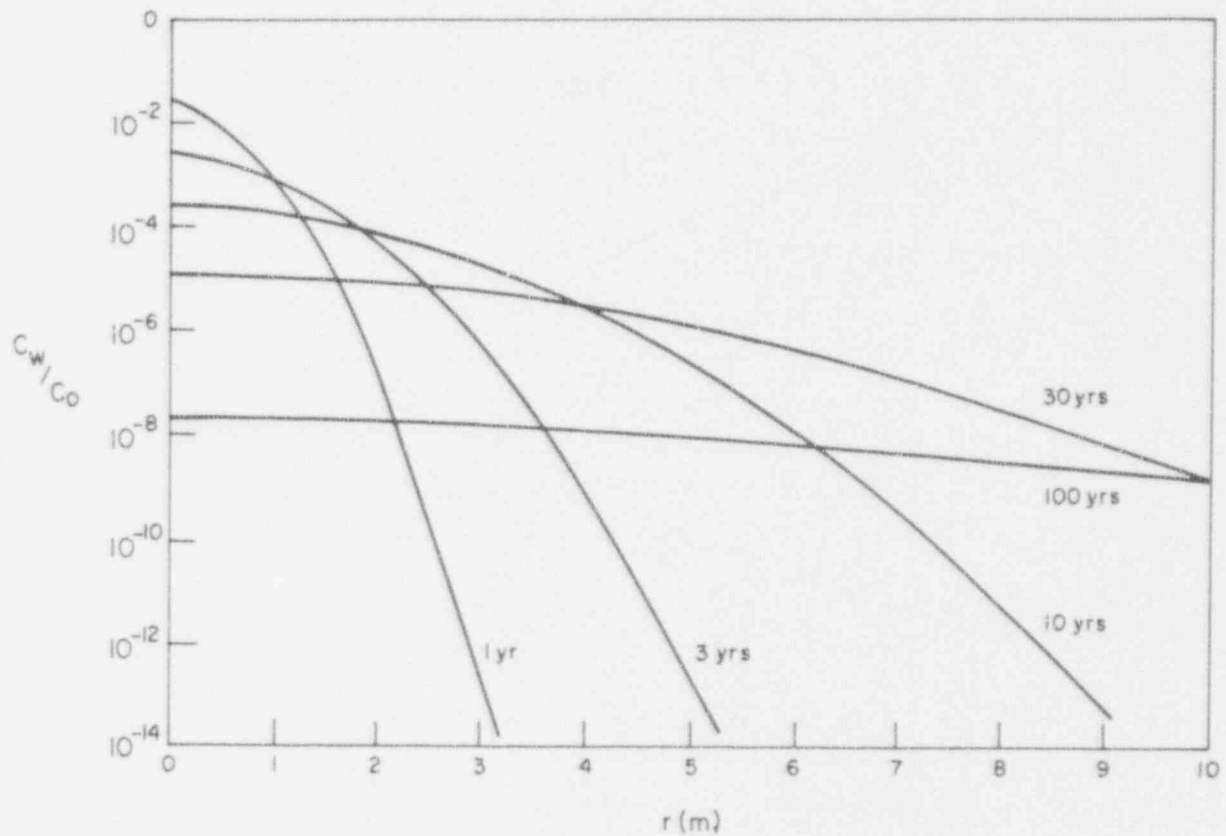
Figure 5   Graph corresponding to Fig.4, showing the physical distribution of tritium in the soil when $a = 15.8$ cm, $D^* = 1.68*10^{-6}$ cm^2/sec, and $\theta_w = 0.06$ for t in the range $1 < t(\text{years}) < 100$, and r in the range $0 < r(\text{meters}) < 10$. In this graph the concentration $C_w(t)$ is corrected for radioactive decay using eq.(9), but normalised in relation to the original concentration C_o.

Figure 6 similarly presents $C_w(t)/C_o$ versus r, for t in the range $3 < t/(years) < 300$. In both Figs 5 and 6 we take a = 15.8 cm, θ_w = 0.06, θ_g = 0.24 and D^* = $1.68*10^{-6}$ cm^2/sec.

The interpretation of these figures is straightforward. Thus in Fig.5 we observe that 3 years after release of the tritiated water, the concentration 100 cm from the point of release of the tritium, $C_w(t=3)$ [measured in the liquid phase], and normalized with regard to the original concentration, C_o, is approximately $1*10^{-3}$. This represents a concentration of 10^3 Ci/liter if the initial concentration were 10^6 Ci/liter. The concentration, C_g, measured in the gas phase will be five orders of magnitude less than this because we must multiply C_w by the partitioning "factor", $17*10^{-6}$ as we explained above. Thus a 1 liter gas sample slowly withdrawn from this region will contain $17*10^{-3}$ Ci [$6.3*10^8$ disintegrations per second].

It will also be observed in Figs 5 and 6 that for r < a (=15.8cm here) the C_w/C_o decreases from t = 0. For a value of r > a (=15.8cm), however, it increases to a maximum and then decreases with diffusive redistribution and as radioactive decay takes effect.

This behavior of the local maximum provides a useful way to consider the process. Thus Fig.7 shows the way C_w/C_o behaves as a function of time for a number of points in $0 < r(meters) < 4$. The relatively rapid increase to, and slow decrease from, the maximum is evident.

Figure 8 shows the advance of the maximum in $C_w(t)$, (where $\partial(C_w(t)/C_o)/\partial t = 0$) as a function of time. Note the linearity of the graph after the initial 10 years.

The data of Fig.8 may be obtained exactly by differentiating eq.(14) with respect to t, correcting for radioactive decay using eq.(9), and solving for $\partial(C_w(t)/C_o)/\partial t = 0$. This calculation is tedious however and in the present case we used eq.(16) viz

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

This equation is the solution of eq.(10) subject to eq.(13) as a → 0. It represents a solution to the purely diffusional problem cited by Carslaw and Jaeger(1959 p.257), combined with eq.(9) to account for decay. It offers an excellent approximation for eq.(14) as r increases relative to a, and as t increases. Thus, for D^*/θ_w = $2.8*10^{-5}$ cm^2/sec 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.

Figure 9 is also calculated using eq.(16). It shows the envelope of maxima of $C_w(t)/C_o$, for all time, for r in the range $0 < r(meters) < 35$. This graph also corresponds closely with the data of Fig.7 confirming the usefulness of eq.(16). We further observe, for example, that at a distance of 6 meters from the source $C_w(t)/C_o$ will never exceed $5.3*10^{-7}$, while maxima at 10, 20 and 40 meters are respectively $\sim9.2*10^{-9}$, $\sim1*10^{-12}$ and $\sim4*10^{-20}$. Fig.8 shows that these maxima are realized at 58, 128, and 268 years respectively.
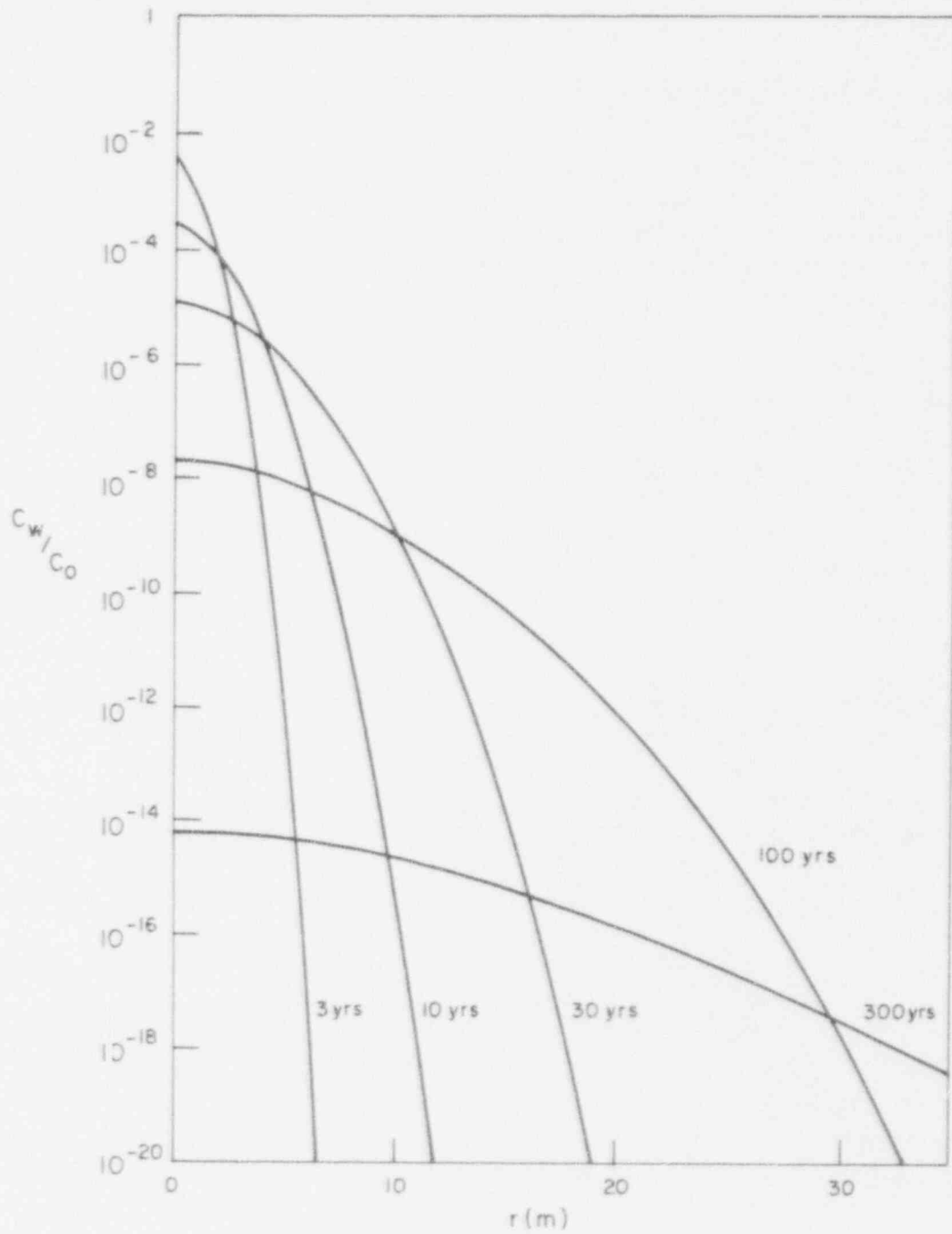
Figure 6   Graph similar to Fig.5 for t in the range 3 < t years < 300, and r in the range 0 < r meters < 50.
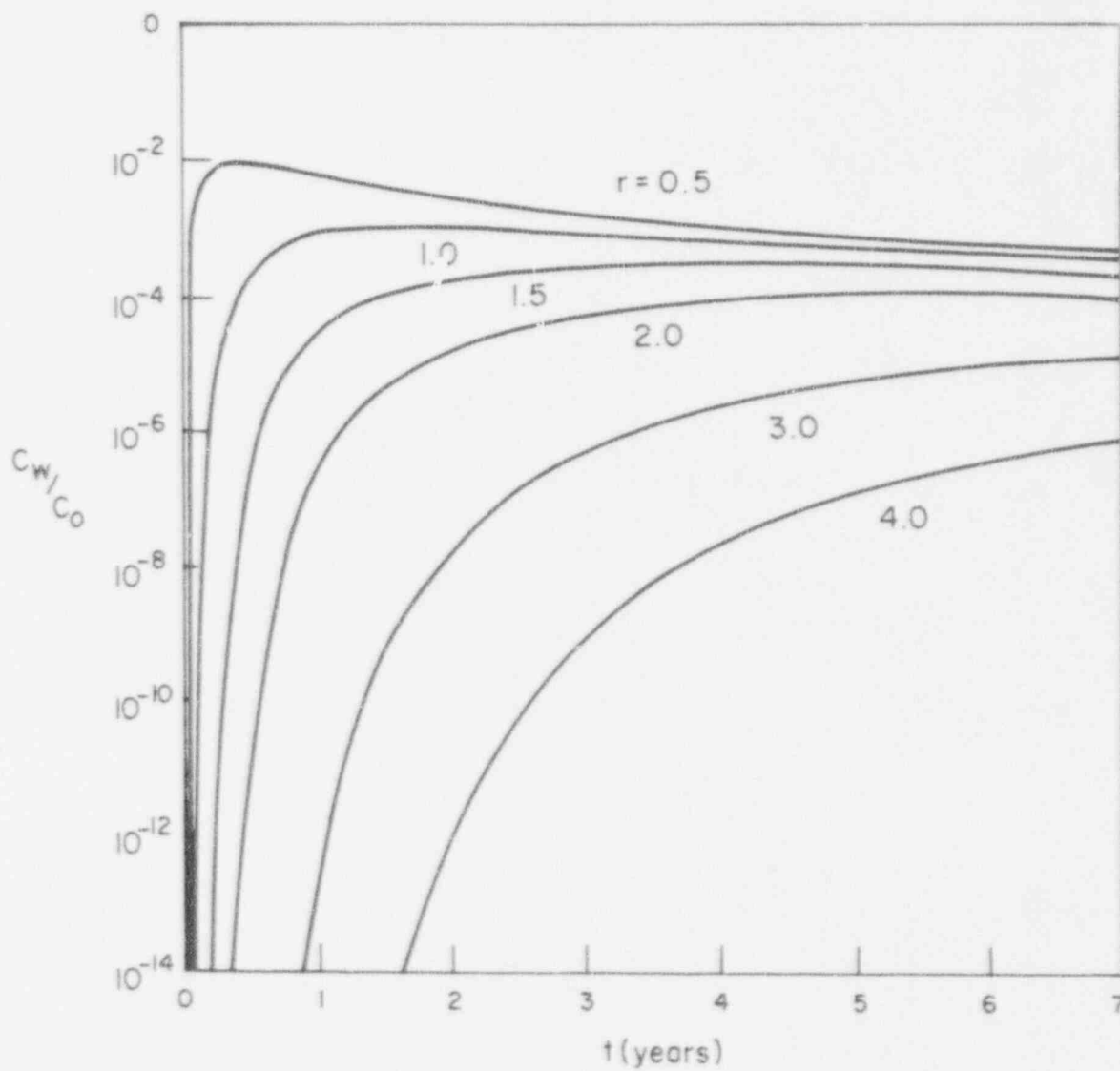
Figure 7   Graphs showing the way $C_w(t)/C_o$ changes with time at r = 0.5, 1, 1.5, 2, 3 and 4 meters from the point of release of the tritium. Note the way that C_w/C_o increases rapidly to a maximum, then declines relatively slowly.

15
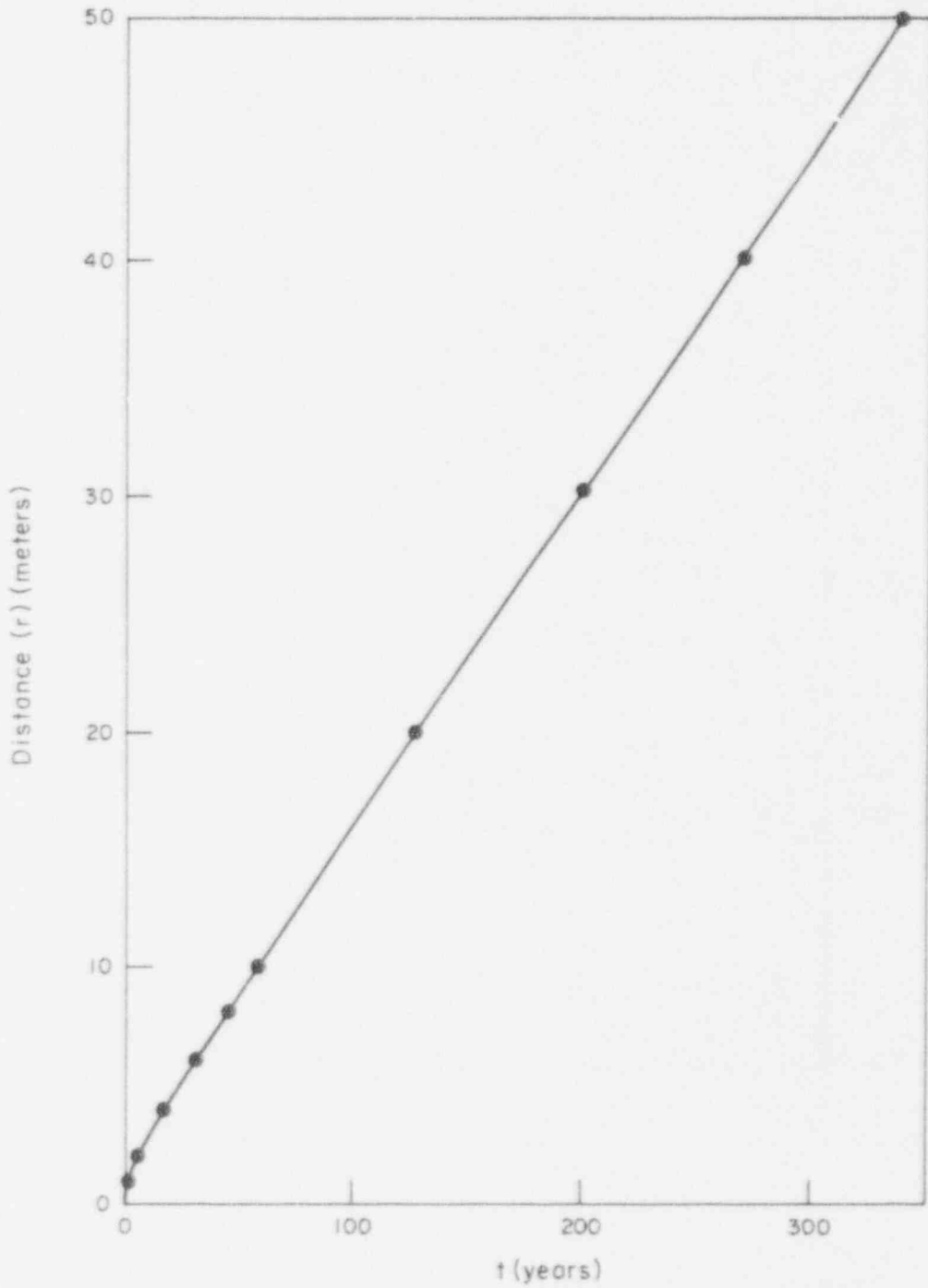
Figure 8   Graph showing the advance, as a function of time, of the maximum tritium concentration, found by differentiating eq.(18) with respect to t for constant r, and setting $\partial(C_w(t)/C_o)/\partial t = 0$, for the case shown in Fig.7, but for the range of r extended to $0 < r(\text{meters}) < 50$, and $t < 350$ years.
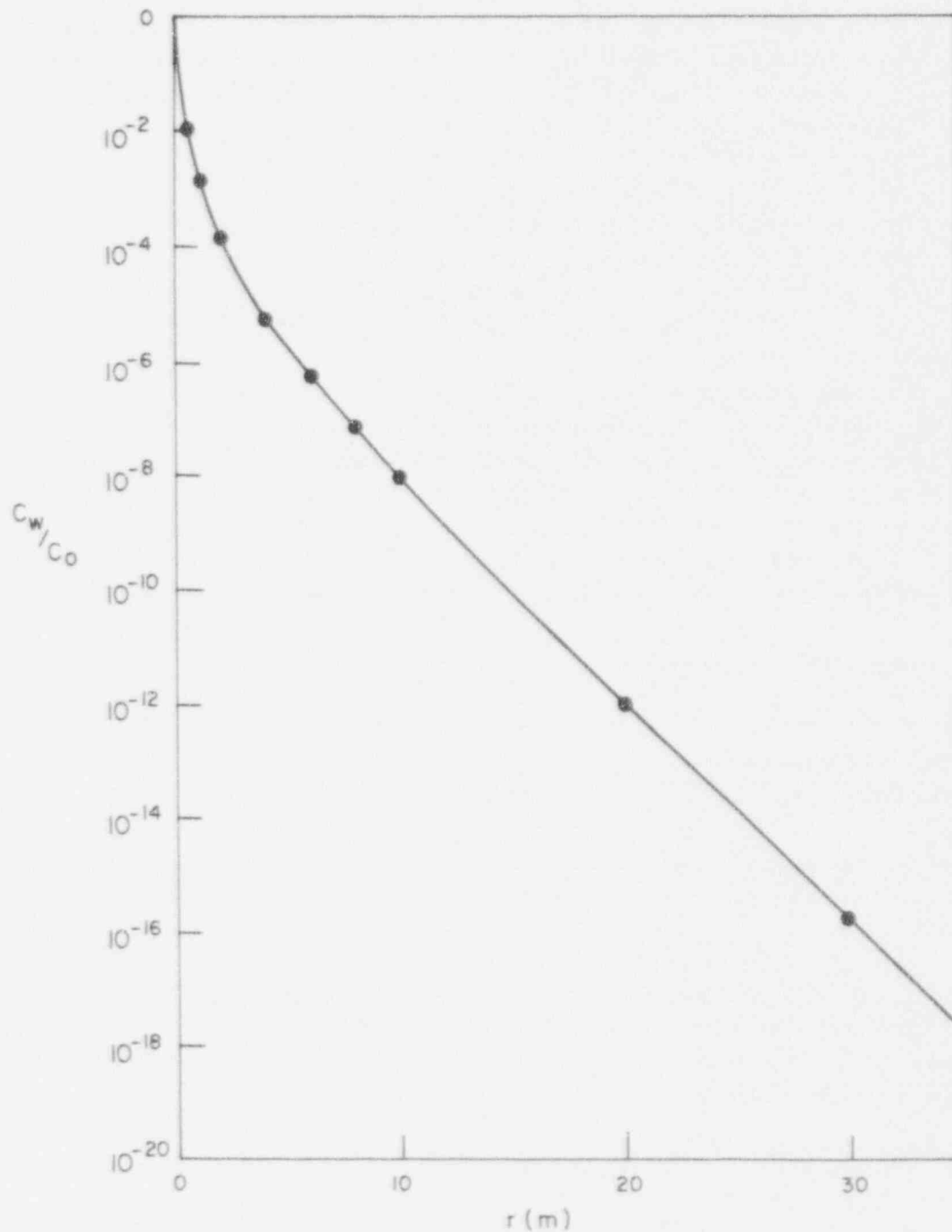
Figure 9   The envelope of maximum values of $C_w(t)/C_o$ for r in the range $0 < r(\text{meters}) < 35$. The local concentration $C_w(t)$ will never exceed maximum values defined by this curve. Thus at r = 10 meters, $C_w(t)/C_o$ will never exceed $9.18*10^{-9}$, so if $C_o = 10^6$ Ci/liter then $C_w(t)$ will never exceed $9.18*10^{-3}$ Ci/liter there. Similarly, the maximum concentration of tritium in the water at 30 meters will be $1.8*10^{-16}$ Ci/liter. It will be attained according to Fig.8 after 198 years. The corresponding concentrations in the gas phase of the soil will be less than that in the water by the factor $17*10^{-6}$.

17

Figures 7, 8 and 9 thus provide useful insights into the decay and redistribution process, and eq.(16) provides a useful approximate method for determining the intermediate and long term distribution of released tritium. Specifically, if one liter of tritiated water had been released at a depth of 20m beneath the soil surface, and 200m above the water table, and if $C_o = 10^6$ Ci/liter, then:

a. At the water table no tritium will ever be detected. We infer this from the fact that the water table is at 200m, and eq.(16) reveals that even at 60 m from the point of release, $\sim 2.5*10^{-27}*C_o$ Ci/liter will be the greatest value of C_w ever achieved. This concentration represents $\sim 9*10^{-11}$ disintegrations/sec/liter and is undetectable by present methods.

b. At the soil surface, however, and neglecting complications relating to soil structure, water content, temperature and air pressure variability in the top 2-3m, we expect the maximum value of C_w/C_o to be $\sim 10^{-12}$. C_w(max) will then be 10^{-6} Ci/liter ($3.7*10^4$ disintegrations/sec/liter). This value approximates the maximum permissable concentration for tritium in water released to an unrestricted area of $3*10^{-6}$ Ci/liter (Nuclear Regulatory Commission, 1992). It will be achieved after 130 years. Note that gas phase concentrations will be approximately 5 orders-of-magnitude less than this.

3. The coefficients D^* and D^*/θ_w.

It is important here to comment on the coefficients D^* and D^*/θ_w. Both of these are called diffusion coefficients in the soil science literature. Comparison of, for example, Hillel (1981) and Jury et al.(1991) illustrate inconsistencies and difficulties that arise in relation to them.

D^* is effectively a "transfer coefficient" as defined in eqs (4) and (5). D^*/θ_w on the other hand is a "diffusion coefficient" in-so-far as it is the coefficient in the diffusion eq.(10) and it represents "transfer" (D^*) divided by "capacity" (θ_w).

Smiles et al.(1993) failed to define clearly these differences and set the coefficient in eq.(10) equal to D^* rather than D^*/θ_w. Thus they used a value of $1.68*10^{-6}$ cm^2/sec (based on eq.6) rather than $2.8*10^{-5}$ cm^2/sec ($=1.68*10^{-6}/0.06$). We demonstrate the extent to which their calculations are erroneous below.

It is also important to comment on the validity of the estimation of D^* based on eq.(6). This equation provides an estimate of D^* for unsaturated soil systems for which we have no measurement. It was invoked firstly to assess the relative importance of tritium transfer in the liquid and gas phases, and then to provide an estimate, through D^*/θ_w, of the way diffusive transfer might be affected by variation in θ_w and the total porosity, $(\theta_w + \theta_g)$. While other empirical equations which introduce functional forms for the tortuosity, might have been used (Jury et al.,1991), their use must also be experimentally justified. As $\theta_w \to 0$ however all models of this sort fail. This is because, at very low water contents, the assumptions which make eq.(6) feasible fail, water films become discontinuous so transfer becomes more complicated than a "simple" parallel flow model can describe (cf Philip and de Vries, 1958). We cannot specify when these perturbations become critical but arbitrarily reject eq.(6) for $\theta_w < 0.04$. In this range we believe that D^* and D^*/θ_w can only be determined experimentally.

4. Effect of variation of D^*/θ_w

The general solution, $C^*(R,T)$, of our problem represented by eq.(14) and illustrated in Figs 3 and 4, is dimensionless, and independent of D^*/θ_w. Calculations of C/C_o in physical space and time require we specify D^*/θ_w (as well as a, r, t, and k) however. It is important to examine the effects of variation in D^*/θ_w in terms of the rate of advance of the maxima shown in Fig.8 and the envelope of maxima shown in Fig.9. We illustrate the effect of variations in total porosity and θ_w on D^*/θ_w using eq.(6).

Table 1 shows the way D^* and D^*/θ_w calculated using eq.(6) vary with θ_w and the total porosity, $(\theta_w + \theta_g)$ for $0.04 < \theta_w < 0.1$ and $0.3 < (\theta_w + \theta_g) < 0.5$. Note in this table that the "transfer coefficient" D^* increases with both increasing water content and increasing porosity. D^*/θ_w on the other hand increases with porosity but decreases as the water content increases. This is because "isotopic dilution" associated with increased "capacity" of the system to store tritium increases with increasing water content.

Figure 10 extends the data of Table 1 and shows values of D^*/θ_w calculated using eq.(6) for a range of water contents and total porosities of 0.3 and 0.45. 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 eq.(6) lie somewhat above the majority of the measured values but agree reasonably well taking into account the high values of Torok et al.(1991) for their sands. Equation (6) does not predict the maximum observed by Nakayama and Jackson (1963) at θ_w ≈ 0.04 nor a minimum observed [although at much higher water contents] by Scott and Paetzold. It is evident that both porosity and water content should be measured accurately when determining D^*/θ_w.

In Figs 11 and 12 we illustrate the effect of variation in D^*/θ_w from $2*10^{-5}$ to $4.5*10^{-5}$ cm^2/sec, on the rate of advance of the maxima, and the envelope of maxima. These figures also show these relations for the much lower diffusivity used by Smiles et al.(1993).

The effect of variation of the diffusivity is great, and clearly calculations using a value of $1.68*10^{-6}$ cm^2/sec are misleading. General conclusions drawn by Smiles et al.(1993) on the basis of their calculations must therefore be disregarded. Even variation within the range of D^*/θ_w from $2*10^{-5}$ to $4.5*10^{-5}$ cm^2/sec produces significant effects. Thus, in Fig.12 we see that at a distance of 20 meters from the origin we might expect the maximum to lie in the range $7*10^{-14} < C/C_o < 2.2*10^{-11}$. Fig.11 shows that these maxima might be observed at t in the range $155 > t(years) > 99$. At 60 meters (beyond the range of the figure) the corresponding ranges in maximum concentration is $4.9*10^{-31} < C/C_o < 4.4*10^{-23}$ at times in the range $495 > t(years) > 321$.

19

TABLE 1

This table shows the way variation in θ_w and θ_g affects:

- the "transfer coefficient" D^* calculated using eq.(6) (Table 1a); and
- the "diffusivity" D^*/θ_w (Table 1b)

Table 1a. $10^6 \times D^*$ (cm^2/sec)

			θ_w		
$(\theta_w + \theta_g)$	0.04	0.06	0.08	0.10	0.12
0.30	1.42	1.68	1.93	2.19	2.44
0.35	1.57	1.83	2.08	2.34	2.59
0.40	1.72	1.98	2.23	2 49	2.74
0.45	1.87	2.13	2.39	2.64	2.90
0.50	2.03	2.28	2.54	2.79	3.05

Table 1b. $10^5 \times D^*/\theta_w$ (cm^2/sec)

			θ_w		
$(\theta_w + \theta_g)$	0.04	0.06	0.08	0.10	0.12
0.30	3.55	2.80	2.41	2.19	2.03
0.35	3.93	3.08	2.60	2.34	2.16
0.40	4.30	3.30	2.79	2.49	2.28
0.45	4.68	3.55	2.99	2.64	2.42
0.50	5.08	3.80	3.18	2.79	2.54

Note in this table that:

- $(\theta_w + \theta_g)$ is the total porosity of the soil;

- D^* is a "transfer coefficient" defined by eq.(6), which takes into account flux in both the liquid and gas phases; and

- D^*/θ_w is a "diffusion coefficient" in-so-far as it represents the transfer coefficient, D^*, divided by a "capacity" term, θ_w.
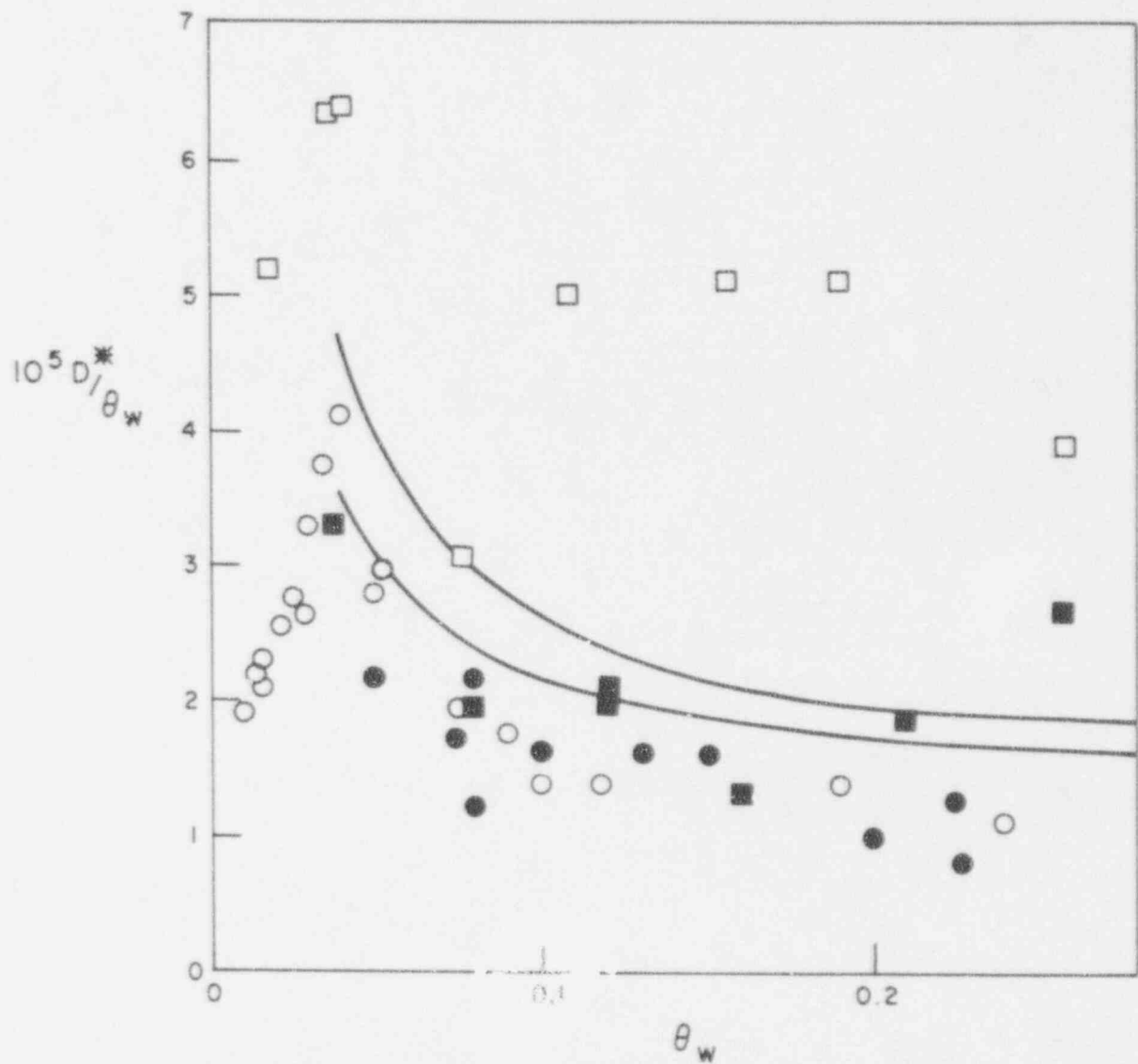
Figure 10   Graph showing variation in D^*/θ_w with θ_w calculated using eq.(6) for soil porosity of 0.3 and 0.45. The graph also shows data measured by Nakayama and Jackson (1963) (O), Scott and Paetzold (1978) (●), and Torok et al.(1991) for sand (□) and a sand/clay mixture (■).
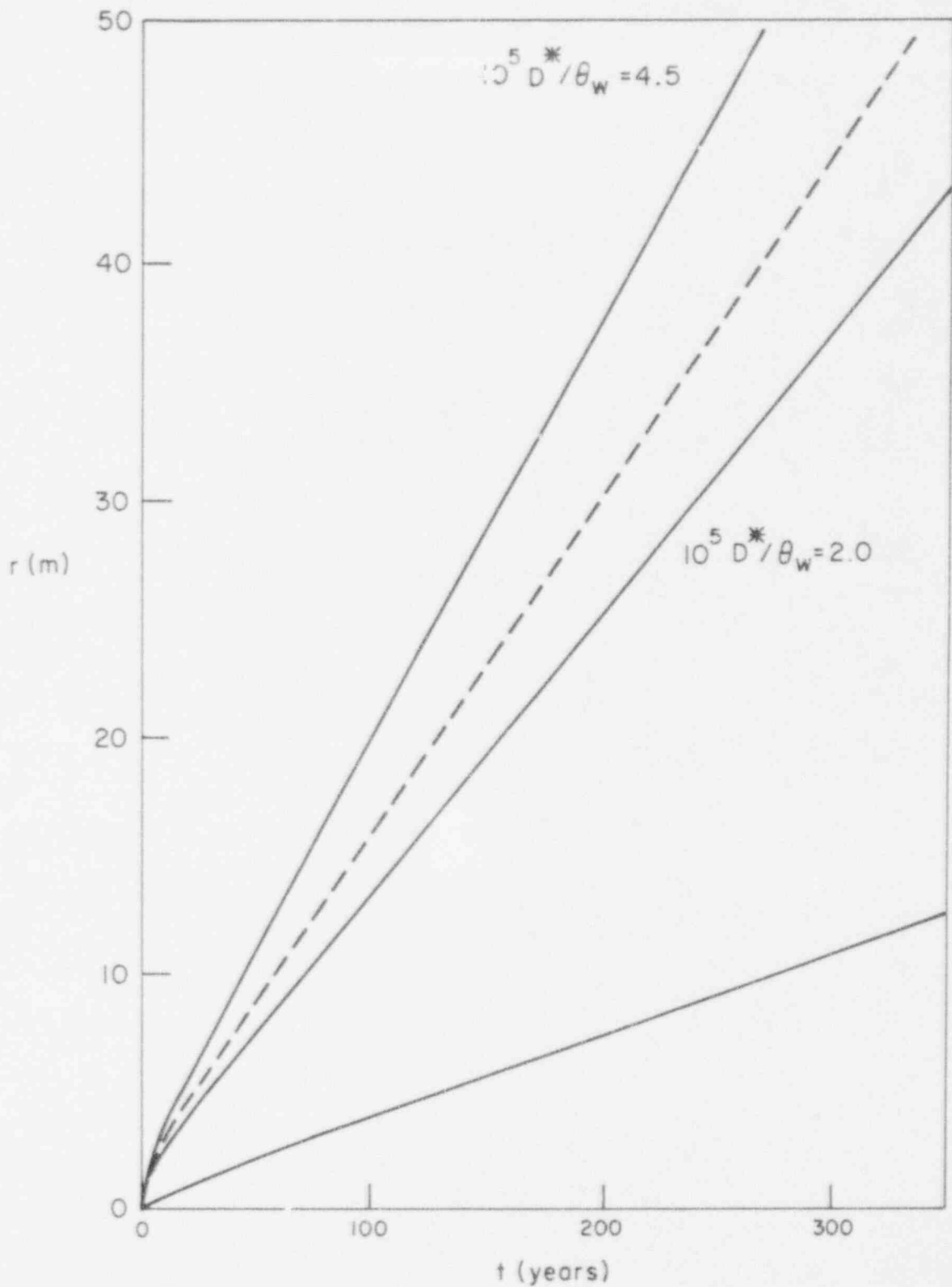
Figure 11   Graph similar to Fig.8 comparing the rate of advance of the maximum tritium concentration, for D^*/θ_w values of $2*10^{-5}$, $2.8*10^{-5}$ and $4.5*10^{-5}$ cm^2/sec. The diffusivity used by Smiles et al (1993) ($1.68*10^{-6}$ cm^2/sec) produces the lowest line and results in a rate of advance approximately one quarter that of the more realistic and greater values of D^*/θ_w.
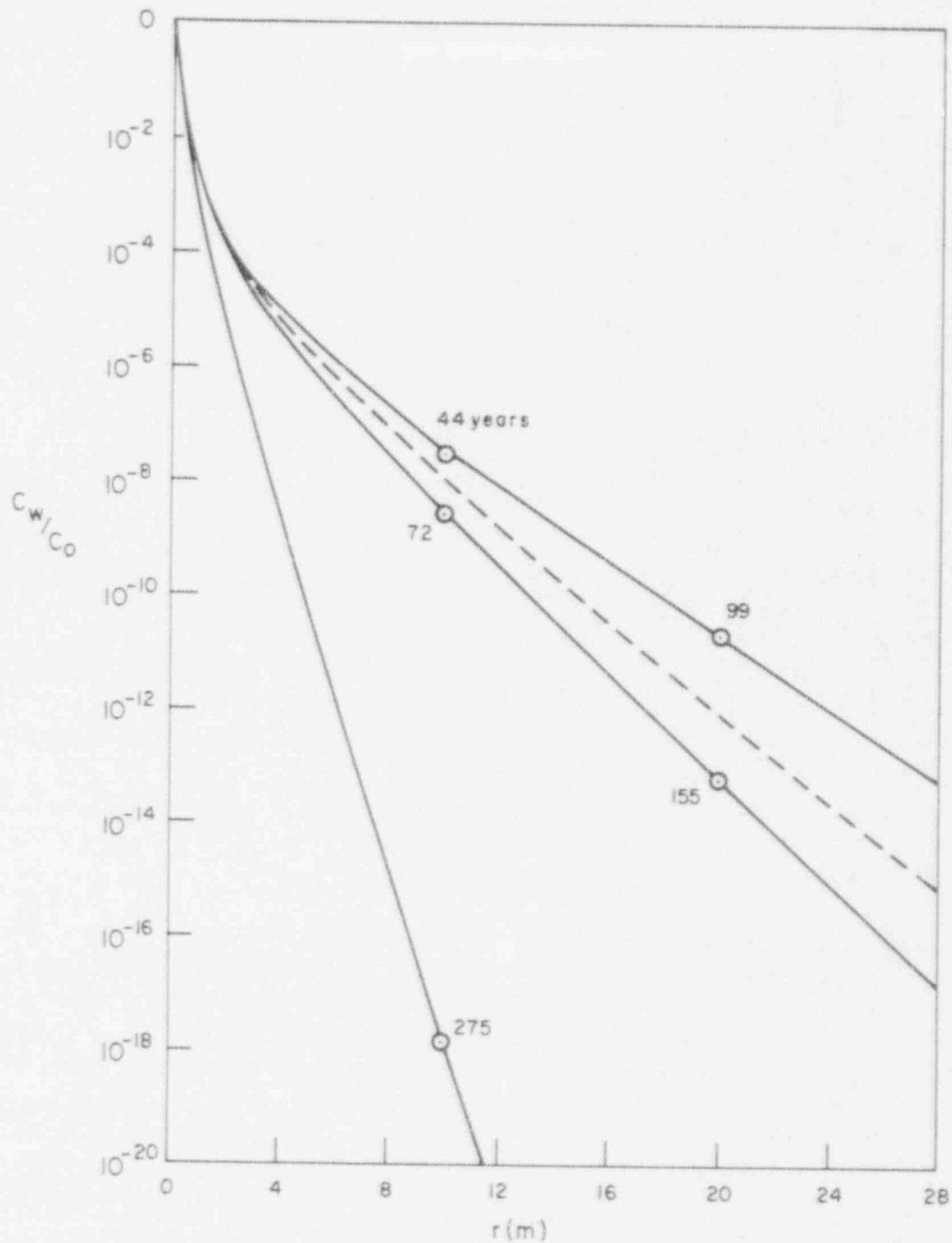
Figure 12   The envelope of maximum values of $\log(C_w(t)/C_o)$ for r in the range $0 < r$ (meters) < 28 for values of D^*/θ_w of $2*10^{-5}$, $2.8*10^{-5}$, $4.5*10^{-5}$, and $1.68*10^{-6}$ cm^2/sec. Numbers on each curve indicate the time (years) at which the maxima are realised. The lower diffusivity reduces the maximum at any point directly and because of the increased time for the maximum to arrive results in greater radioactive decay as well.

23

These data do not affect the conclusions set out above relating to transfer of measureable amounts of tritium to the water table 200 meters below the point of release. The higher maximum value of C_w/C_o at 20 meters associated with $D^*/\theta_w = 4.5*10^{-5}$ cm^2/sec however raises the maximum soil surface concentration to $2.2*10^{-5}$ Ci/liter if $C_o = 10^6$ Ci/liter. This value exceeds the maximum permissable concentration (Nuclear Regulatory Commission, 1992) by a factor of 10. In view of this uncertainty, it is therefore very important to have as good an estimate of D^*/θ_w as possible and we recommend its measurement, at appropriate water contents, under field conditions for soils of concern. In particular, D^*/θ_w should be measured for θ_w in the range $0 < \theta_w < 0.1$ using soil of appropriate bulk density and particle size range. Specifically these experiments should focus on the lower end of the range where empirical equations such as eq.(6) fail.

We offer further comment in relation to:

- net flux of water;

- net flux of the vapor phase;

- temperature effects;

- the influence of the redistribution of injected water;

- formulation of the diffusion equation in soils.

5. Net flux of water.

Convection of tritium would be important if significant liquid flow occurred. Similar soils have hydraulic conductivities, K, at water contents in the range $0.06 < \theta_w < 0.1$ of order 10^{-8} cm/sec (Rose et al., 1965). Assuming unit hydraulic gradient, such conductivities imply a drift towards the water table at a velocity (= K/θ_w) of approximately 10^{-7} cm/sec. The center of influence of the sphere of tritium might then be expected to arrive at the water table 200 m below after approximately 5,000 years. It would not therefore present a problem. Within this framework also the influence of the additional water associated with the injection is trivial. Thus, barring sustained climate change, or sustained application of water to increase K/θ_w by several orders-of-magnitude, we believe that there will be little liquid water movement in the soil as described. Convective transport will therefore be unimportant after the initial, and minor, redistribution of the released tritiated water.

6. Net flux in the vapor phase.

It is difficult to estimate the magnitude, at a depth of 20 m, of "pumping" associated with periodic atmospheric pressure and temperature changes. The great capacity for tritium of the liquid, compared with that of the gas phase, as well as rapid equilibration between the phases, ensures that retardation of this form of transfer is great. We therefore assume that it will produce no net transfer, and can be neglected. In this regard we assume that air slowly withdrawn at a

point in the soil will reflect the solution concentration at that point, and therefore provide an appropriate basis for sampling.

7. 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, and data of Scott and Paetzold (1978) showed an order-of-magnitude increase in their diffusivity at θ_w =0.05 as the temperature increased from 5°C to 33.5°C. That increase had decreased to a two-fold one for θ_w =0.2. Sposito (1981) collates data showing the temperature dependence of the self-diffusion coefficient of liquid water.

8. The influence of the redistribution of the injected water.

We pointed out earlier that the available evidence indicates that as the released water redistributes, it displaces in its entirety the water originally present. No matter how rapidly this process takes place [within reasonable physical conditions], the initial radius of excursion of tritium for our problem will not exceed 15.8 cm. The assumption that the tritium will reach this radius at time zero over-estimates the speed of advance of the profiles shown in Fig.5 and the calculations are therefore conservative.

9. Formulation of the diffusion equation in soils.

In developing this analysis it emerges that ambiguities in relation to material balance, and the significance of concentration gradients, may emerge 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 straight-forward. 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 the material balance equation for the water then offers a rational resolution of these ambiguities. Smiles et al.(1981) and Wilson and Gelhar (1981) set out such a method. 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 then 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.

CONCLUDING REMARKS

When tritiated water is released in a uniform and relatively dry soil it redistributes in both the liquid and vapor phases. The flux density of tritium in each phase is of the same order of magnitude however so tritium redistribution must be modelled as if transfer occurs "in parallel" in the liquid and vapor phases.

The approach we describe uses the diffusion equation cast in spherical coordinates and takes into account radioactive decay. It permits calculation of radial profiles of tritium concentration, within and external to a sphere of released solution. We assume the concentration within this sphere initially to be uniform. The solution also predicts attenuation and rate of advance of the maximum of tritium concentration as it advances in the soil.

The solution is not in principle restricted to spherical sources however because the diffusion equation we solve is linear. We can therefore superimpose solutions for distributed sources. Thus we can solve by the principle of superposition, problems of release from cylindrical sources of any aspect ratio and orientation.

The diffusion equation can also be recast to solve the redistribution problem where there is a steady net flow of the water or of the air within the assumption that equilibrium always exists between the gas and water phases. Neither process would be important in the deep and dry desert soils for which we perform illustrative calculations here.

Finally, it is important to note that while calculated material properties are appropriate for illustrative calculation, they must be supported by field measurement when the theory is used to support engineering application. Thus the diffusivities of tritium in the liquid and gas phases in soil, for example, must be recognised as properties of the soil structure and water content which do not permit prediction. In addition the calculation of D^* embodied in eq.(6), despite the agreement we cite here with measured values, should be supported by experiment, particularly at relatively low water contents.

REFERENCES

Abramowitz M and Stegun IA (1965) Handbook of mathematical functions. Dover, New York.

Bond WJ, Gardiner BN, and Smiles DE (1982) Constant flux absorption of a tritiated calcium chloride solution by a clay soil with anion exclusion. Soil Sci Soc Amer J 46:1133.

Carslaw HS, and Jaeger JC (1959) "Conduction of Heat in Solids" [2nd edition]. Oxford University Press, Oxford.

Currie JA (1960) Gaseous diffusion in porous media. Part 2 - Dry granular materials. Brit J Appl Phys 11:318

Currie JA (1961) Gaseous diffusion in porous media. Part 3 - Wet granular material. Brit J Appl Phys 12:275.

Green WH and Ampt GA (1911) Studies in soil physics. I. The flow of air and water through soils. J Agr Sci 4:1-24.

Hillel D (1980) Fundamentals of Soil Physics. Academic Press, New York.

Jury WA, Gardner WR and Gardner WH (1991) Soil Physics. John Wiley, New York.

Lovering TJ (1935) Theory of heat conduction applied to geological problems. Bull Geol Soc Amer 46:69-93.

Nakayama FS and Jackson RD (1963) Diffusion of tritiated water in soils. Soil Sci Soc Am Proc 27:255-258.

Nuclear Regulatory Commission (1992) "Standards for Protection Against Radiation." 10 CFR 20.1-20.601, Appendix B. *Code of Federal Regulations.* U.S. Government Printing Office, Washington D.C.

Philip JR (1969) Theory of infiltration. in Advances in Hydroscience 5:215.

Philip JR and de Vries DA (1957) Moisture movement in soils under temperature gradients. Trans Amer Geophys Union 38:222-228.

Rose CW (1966) Agricultural Physics. Pergamon, London.

Rose CW, Stern WR and Drummond JE (1965) Determination of hydraulic conductivity as a function of depth and water content, for soil *in situ*. Aust J Soil Res 3:1-10.

Scott HD and Paetzold RF (1978) Effects of soil moisture on the diffusion coefficients and activation energies of tritiated water, chloride and metribuzin. Soil Sci Soc Amer J 42:23-27.

Smiles DE, Gardner WR and Schulz RK (1993) Three dimensional redistribution of tritium from a point of release into a uniform unsaturated soil: A deterministic model for tritium migration in an arid disposal site. NUREG/CR-5980, US Nuclear Regulatory Commission, Washington, DC.

Smiles DE, Perroux KM, Zegelin SJ and Raats PAC (1981) Hydrodynamic dispersion during constant-rate absorption of water by soil. Soil Sci Soc Amer J 45:453-458.

Sposito G (1981) Single particle motions in liquid water.II. The hydrodynamic model. J Chem Phys 74:6943-6949.

Torok J, Blimkie ME, Burton, GR and Tosello NB (1991) Diffusion of tritiated water in unsaturated soil laboratory-scale experiments. AECL Research, Chalk River, Ontario, Canada, KOJ 1JO.

Wilson JL and Gelhar LW (1981) Analysis of longitudinal dispersion in unsaturated flow: 1. The analytical method. Water Resour Res 17:122-130.

2. TITLE AND SUBTITLE

Spherical Diffusion of Tritium From a Point of
Release in a Uniform Unsaturated Soil: A Deterministic Model
for Tritium Migration in an Arid Disposal Site.

3. DATE REPORT PUBLISHED

MONTH	YEAR
October	1993

4. FIN OR GRANT NUMBER
L2491

5. AUTHOR(S)

D. E. Smiles*, W. R. Gardner, and R. K. Schulz

6. TYPE OF REPORT
Technical

7. PERIOD COVERED *(Inclusive Dates)*

8. PERFORMING ORGANIZATION – NAME AND ADDRESS *(If NRC, provide Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address; if contractor, provide name and mailing address.)*

Department of Environmental Science, Policy and Management
College of Natural Resources
University of California
Berkeley, CA 94720

*Visiting Professor, University of California, Berkeley;
on leave from Division of Soils, CSIRO, Australia

9. SPONSORING ORGANIZATION – NAME AND ADDRESS *(If NRC, type "Same as above"; if contractor, provide NRC Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address.)*

Division of Regulatory Applications
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

10. SUPPLEMENTARY NOTES

11. ABSTRACT *(200 words or less)*

This report presents a three-dimensional model for tritium migration in an arid waste disposal site. When tritiated water is released at a point in a uniform and relatively dry soil it redistributes in both the liquid and vapor phases. The flux density of tritium in each phase is of the same order of magnitude however so tritium redistribution is modeled as if transfer occurs "in parallel" in the liquid and vapor phases.

The approach we describe uses the diffusion equation cast in radial (spherical) coordinates and takes into account radioactive decay. It permits calculation of radial profiles of tritium concentration, within and external to a sphere of released solution. We assume the concentration within this sphere initially to be uniform. The solution also predicts attenuation and rate of advance of the maximum of tritium concentration as it advances in the soil. With deep disposal in a desert soil, the model predicts that tritium migration will be short range, with a maximum of a few meters.

12. KEY WORDS/DESCRIPTORS *(List words or phrases that will assist researchers in locating the report.)*

Tritium migration
LLW disposal
Arid LLW sites

Radionuclide migration
Radioactive waste
Titium model

13. AVAILABILITY STATEMENT
Unlimited

14. SECURITY CLASSIFICATION

(This Page)
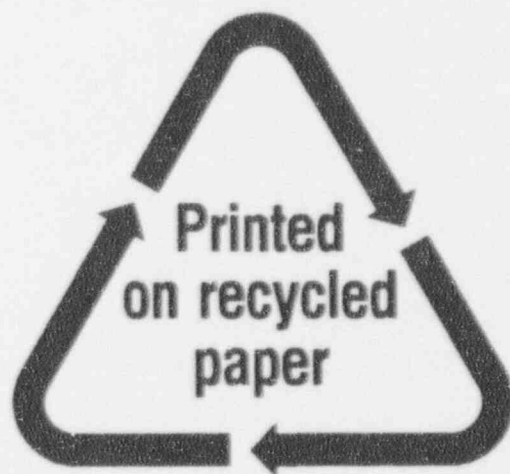Unclassified

(This Report)
Unclassified

15. NUMBER OF PAGES

16. PRICE

**UNITED STATES
NUCLEAR REGULATORY COMMISSION**
WASHINGTON, D.C. 20555-0001

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300