II. HYDROLOGY

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MATHEMATICAL MODELING OF THE DISTRIBUTION OF NATURAL ^{14}C, ^{234}U, and ^{238}U IN A REGIONAL GROUND-WATER SYSTEM

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Increasing concern with nuclear waste isolation technology is leading to additional studies of naturally occurring isotopes in ground water. Such studies provide information on 1) the use of radionuclides to estimate ground-water travel times and/or residence times. This information can be an extremely useful adjunct to conventional hydrologic data in developing the understanding of regional hydrology needed in the site selection process, and 2) the use of natural radionuclides as analogues to the behavior of radionuclides of concern in nuclear waste.

Many waste isolation decisions will be based on the results of digital models simulating the performance of proposed repositories. It is important not only that such models be demonstrably valid representations of the phenomena they are meant to simulate, but also, that the parameters used in them for specific performance assessments be correct within known limits. A simulation of the measured behavior of naturally occurring radionuclides on a regional scale can serve to validate simulation models themselves or, for models known to be valid, can serve as calibration in a given site situation.

In this paper we will describe the use of a digital ground-water flow and radionuclide transport model to simulate the behavior of ^{14}C and ^{234}U and ^{238}U in the Carrizo Aquifer of south Texas. The hydrology and distribution of ^{14}C in the system have been described by Pearson and White (1967) and the uranium isotope data are from Cowart and Osmond (1974) and Osmond (written commun 1981).

Enough is known about Carrizo hydrology and carbonate geochemistry to permit the calculation of ^{14}C concentrations in the aquifer. Agreement of the calculated values with the measured values validates the model. The validated model is then used to simulate uranium transport and to determine uranium retardation in the system from comparison between calculated and measured ^{234}U/^{238}U ratios.

NUCLIDE TRANSPORT MODEL. A solute moving in a ground-water system can be described by the conservation of mass equation (written here for one-dimensional transport):

$$\frac{\partial}{\partial t}\left[\phi C_f + \rho_s (1-\phi) C_s\right] = -\frac{\partial}{\partial x}(V_D C_f - \phi D \frac{\partial C_f}{\partial x})$$

$$-\lambda\left[\phi C_f + \rho_s (1-\phi) C_s\right] \pm I \qquad (1)$$

On the left of the equal sign is an accumulation term. The first term on the right represents transport of the solute both by convection (the first term in parenthesis) and dispersion (the second term in parenthesis). The second term on the right is a chemical reaction term, and is written here as a simple first order decay, as appropriate for radioisotopes. The third term is a source (+) or sink (-) term. The parameters in the equation are:

C_f, C_s = solute concentration in the moving fluid (f) and on the stationary solid (s), (mass/mass)

ρ_s = solid grain density (mass/volume)

ϕ = porosity (volume/volume)

λ = first order decay constant (time^{-1})

I = source/sink term (mass/time)

V_D = specific discharge (length/time). The magnitude and direction of this term depends on ground-water flow in the system. It equals the discharge (volume/time) per area of flow (length^2) and is often called the Darcy velocity. It should not be confused with the actual velocity of water movement through the pores of the aquifer which is the interstitial velocity, V_i, and equals V_D/ϕ.

D = $\alpha\ \dfrac{V_D}{\phi} + \dfrac{D_m}{\phi\tau}$;

α is the hydrodynamic dispersivity (length) and is an aquifer property the value of which tends to increase with the scale of the modeled system (Pickens and Grisak, 1981). D_m is the conventional molecular diffusion coefficient (length^2/time), and τ

the tortuosity (length/length). Typically,
the dispersivity term is several orders of
magnitude larger than the diffusion term.

Evaluation of the transport equation (1) is greatly
simplified by expressing the solid phase concentration (C_s)
in terms of concentration in the fluid phase (C_f). Most
transport models are intended for use with trace solute
concentrations and include the assumption that the solid and
fluid concentrations are linearly related by: $C_s = k_d C_f$.
The proportionality constant k_d is known as the distribution
coefficient.

With this assumption, the terms in brackets in equation
(1) can be written:

$$\left[\phi C_f + \rho_s (1-\phi) C_s \right] = \left(1 + \frac{(1-\phi)}{\phi} \rho_s k_d\right) \phi \, C_f \qquad (2)$$

The term in parenthesis in (2) equals the retardation
coefficient, R_d, which is the ratio of the interstitial
fluid velocity, V_i, to the rate of movement of the solute
itself, V_c. The total mass of solute present in a given
volume of aquifer equals that present in the fluid phase
(ϕC_f) plus that associated with the solid ($\rho_s (1-\phi) C_s$). The
rate of movement of the dissolved nuclide equals the
interstitial velocity of the fluid itself, while the nuclide
associated with the solid is stationary. The apparent
velocity of the nuclide in the given aquifer volume is then:

$$V_c = \frac{V_i \, \phi \, C_f}{\phi C_f + \rho_s (1-\phi) C_s}, \text{ and, } R_d = \frac{V_i}{V_c} = 1 + \frac{(1-\phi)}{\phi} \rho_s k_d \qquad (3)$$

While some closed-form solutions to Equation (1) are
available, numerical solution techniques have certain
advantages. For adequate simulations in many natural
environments, it is necessary to consider spatial variation
of the hydraulic properties of the aquifer system, and the
consequent variations in the flow field. It is also not
uncommon that chemical variability in a flow system effects
solute transport in a way that can be simulated only by
permitting spatial variation in the distribution
coefficients. Finally, while for simplicity only the one-
dimensional form of a solute transport equation has been
considered here, transport in two or even three dimensions
must normally be treated in order to simulate real field

problems. Multi-dimensional solute transport equations can only be evaluated numerically except for a few very highly idealized physical situations useful only in relatively few real situations.

Digital models for solute transport simulation are complex and require validation before they can be applied with confidence to performance assessment problems. An appropriate validation test is to show that a given model is capable of adequately simulating the behavior of a system similar in such respects as time and distance scale and radioisotope identity to the systems that are to be assessed. The simulation of the ^{14}C distribution in the Carrizo described here was made using the finite-difference model SWENT (<u>S</u>imulator for <u>W</u>ater, <u>E</u>nergy and <u>N</u>uclide <u>T</u>ransport).

FIELD SETTING AND DATA. The Carrizo formation of south Texas is an Eocene coastal plain sandstone which crops out nearly parallel to the coast and dips toward the Gulf of Mexico. In the area of interest in Atascosa and counties to the south, the aquifer is used for water supply at depths to over 1500m. Because of its importance as a water supply, the Carrizo has been intensely studied for over 50 years. A comprehensive report on its hydrology together with a numerical model of its regional flow was made by the Texas Water Development Board (Klempt, Duffin and Elder, 1976). The data required to calculate the ground-water flow term V_D in equation (1) were taken from Klempt's report.

For this report, a vertical cross-section of the Carrizo was modeled, extending from its outcrop in northern Atascosa County down-gradient to the southeast for 100km. The finite difference model comprised 100 blocks of 1km each in the horizontal (x) direction and with vertical (z) dimensions ranging from 45.7 to 243.8m to match the varying aquifer thickness.

To model nuclide transport in the Carrizo requires values of the parameters in the solute transport equation (1) in addition to V_D. The values used and the rationale behind their selection are as follows:

ϕ 35%. Many Carrizo porosity measurements have been made, most between 30 and 40%. The central value was chosen (Pearson and White, 1967).

α   500m.   This   value   was   chosen   to   satisfy
         constraints   imposed   by   the   finite   difference
         procedure used.   While it is, perhaps, 10 or 20
         times   larger   than   values   determined   in   other
         aquifer systems (Anderson, 1979, table 4), these
         determinations were made in systems at least a
         factor of 10 smaller than that described here.
         Because of the scale dependence of dispersivity
         mentioned above, the value chosen is probably
         not inappropriate.

ρ_s 2.6 gm/ml.   The Carrizo is composed mostly of
         quartz sand with only minor amounts of other
         minerals (Pearson and White, 1967).   The density
         chosen is that of quartz.

λ $^{14}C = 1.210 \times 10^{-4} yr^{-1}$;
         $^{238}U = 1.551 \times 10^{-10} yr^{-1}$;
         $^{234}U = 2.841 \times 10^{-6} yr^{-1}$.

c_f mass   nuclide/mass   water.   Values   of   this
         parameter as a function of space were calculated
         using the model and compared with measured ^{14}C
         and $^{234}U/^{238}U$ data for model validation and
         uranium retardation determination, respective-
         ly.   The transformation of measured carbon and
         uranium isotope data to mass fractions and the
         methods   for   selecting   source   rates   (I)   and
         distribution coefficients (k_d) are described
         below.

^{14}C DATA AND SIMULATION RESULTS.   A number of measurements
of the ^{14}C content of Carrizo water in the region modeled
are available.   They include both total dissolved carbonate
contents (C_{tot} = H_2CO_3 + HCO_3^- + CO_3^{-2}) and the ^{14}C content of
the dissolved carbonate as pmc (per cent modern carbon).
From pmc and C_{tot} values, ^{14}C mass fractions can be
calculated using:

$$\frac{gm \, ^{14}C}{gm \, H_2O} = pmc \times C_{tot} \, (\frac{mMol}{kg \, H_2O}) \times 1.64 \times 10^{-19}$$

In calculating this constant, the molecular weight of carbon
is taken as 12gm, the specific activity of modern carbon
(pmc = 100) as 13.56dpm/gmC and the ^{14}C half-life as 5730

years.   100pmc corresponds to 1.37 x 10^{-12}gm ^{14}C/gm C.
Table 1 gives the ^{14}C mass fractions for Carrizo waters
calculated from the pmc and C_{tot} values of Pearson and White
(1967).

The ^{14}C mass fraction in recharge to the Carrizo given
in table 1 is based on 100pmc and a C_{tot} value of 2.21 ±
0.12mMol/kg H_2O. The C_{tot} is that determined by Pearson and
White (1967) using the relationship between the C_{tot} values
of Carrizo samples and their stable ^{13}C isotope contents.
The recharge mass fraction value can be combined with the
recharge rate from the flow calculations (14.2kg H_2O/m^2/yr)
to yield the value of 5.14 x 10^{-13}gm ^{14}C/m^2/yr, the source
term, required for the transport equation (1).

The measured ^{14}C mass fractions are shown in figure 1
along with the simulation modeling results. Those obtained
using $\phi = 0.35$ are in excellent agreement with the field
data, except for samples from two wells in the up-gradient
part of the system. These wells are not directly on the
modeled cross-section and are in areas of less regular
distribution of hydraulic conductivities than elsewhere in
the system (Klempt, Duffin, and Elder, 1976). These points
do not detract from the overall agreement between field and
simulation results which serves to validate the model.

To illustrate the sensitivity of the system to
parameter variability, results of a simulation made using
$\phi = 0.30$ are also shown in figure 1. The lower porosity
leads to slightly higher interstitial water velocities and,
hence, to higher ^{14}C mass fractions. The measured ^{14}C data,
though, are more consistent with the higher porosity value.

URANIUM DATA AND SIMULATION RESULTS. Many measurements of
dissolved uranium concentrations and of ^{234}U activity ratios
have been reported for Carrizo samples and are also given in
table 1.

Uranium solubility is strongly dependent on its
oxidation state. Under oxidizing conditions, as occur near
the Carrizo outcrop, the relatively soluble uranyl (UO_2^+) ion
is stable, and uranium concentrations in the $1 - 10^2$ parts
per billion (ppb) range occur. Under reducing conditions,
as prevail down-gradient, U^{+4} and its complexes are dominant
and uranium concentrations of only $1 - 10 \times 10^{-3}$ ppb occur
(table 1).

^{234}U is a daughter of the much longer-lived ^{238}U. In a sufficiently old, closed system the two isotopes will be in secular equilibrium and their activity ratio (AR) will equal one. As figure 2 and table 1 show, at distances from 0 to ca 20km, where the Carrizo is oxidizing the uranium dissolution is occurring, AR values of 1.0 $\pm$ 0.3 are found. Between ca 20 and 33km, uranium concentrations drop dramatically (table 1), and AR values concentrations as high as 9 occur. Below ca 33km, low dissolved uranium persists, accompanied by a regular decrease in the AR toward the secular equilibrium value of 1. This decrease can be used as a measure of the rate of uranium movement in the Carrizo, which is related, in turn, to the rate of ground-water via the R_d and k_d factors defined above.

The numerical transport model validated using the ^{14}C data was used to simulate ^{234}U and ^{238}U movement in the reducing part of the Carrizo. The simulation began at a distance of 33km where a constant flux of uranium into the solution with an activity ratio of 9 was assumed. The transport of uranium down-gradient from this source was modeled, using several k_d values to account for reaction between dissolved uranium and the aquifer framework which retards the rate of uranium movement relative to that of the water, itself.

The simulation results are compared with the measured uranium AR values in figure 2. The line of $k_d = 0$ shows how the AR would decrease if uranium behaved like ^{14}C in this system and did not react with the aquifer. Uranium transport in the Carrizo is best simulated using a k_d of 6.0. From equation (3), this indicates that the uranium velocity in the Carrizo is only 1/30 of the insterstitial velocity of water.

The agreement between the calculated and measured AR values throughout the system down-gradient of 33km attests to the validity of choosing a simple linear relationship between C_f and C_s. It also supports the use of a constant k_d value throughout a large part of a regional aquifer system, provided that the geochemical behavior of the element of interest is constant throughout the region being simulated.

ACKNOWLEDGMENTS

TABLE 1. ^{14}C Mass fractions, calculated from data of Pearson and
White (1967, table 1) and dissolved uranium concentrations
and activity ratios from Cowart and Osmond (1974) and Osmond
(written commun., 1981). Errors are of counting and chemical
analyses, $\pm$ 2 standard deviations.

Sample no.		^{14}C mass fractions $\times 10^{18}$	Uranium concentration $\times 10^{3}$ ppb	^{234}U/^{238}U activity ratio
Uranium	^{14}C			
Recharge		⟨ 36.2 + 2.0		
414	TX – 91	35.6 + 3.3	202 + 6	0.90 + 0.04
469			629 + 16	1.03 + 0.03
471			2560 + 55	.77 + 0.03
467			29 + 3	1.09 + 0.16
	TX-91	32.7 + 2.5		
2113			7400	0.87
	TX-92	22.8 + 1.8		
2114			18	1.3
472			8 + 1	1.77 + 0.29
	TX-210	29.2 + 1.9		
468			4 + 1	5.48 + 1.63
413	TX-93	16.5 + 1.0	21 + 3.5	1.63 + 0.33
465			3 + 1	9.02 + 1.03
466			4 + 1	6.36 + 1.68
2105			5	6.7
2115			2.7	7.9
	TX-94	6.4 + 0.8		
422	TX-226	4.8 + 0.4	3 + 1	5.14 + 1.87
2107			3	5.2
	TX-96	3.5 + 0.6		
421	TX-216	3.0 + 0.2	1 + 4	3.44 + 1.20
	TX-214	2.1 + 0.3		
411			4 + 2	3.93 + 1.57
	TX-215	2.6		
	TX-92	4.8		
2102			3	4.7
	TX-217	1.1 + 0.2		
2101			1.1	2.5
	TX-219	< 1.8		
417	TX-218	< 1.1	2 + 1	2.71 + 1.00
2104			6	2.80
476			2 + 4	2.08 + 0.51

Fig. 2. Measured and simulated uranium activity ratios with distance down-gradient from outcrop
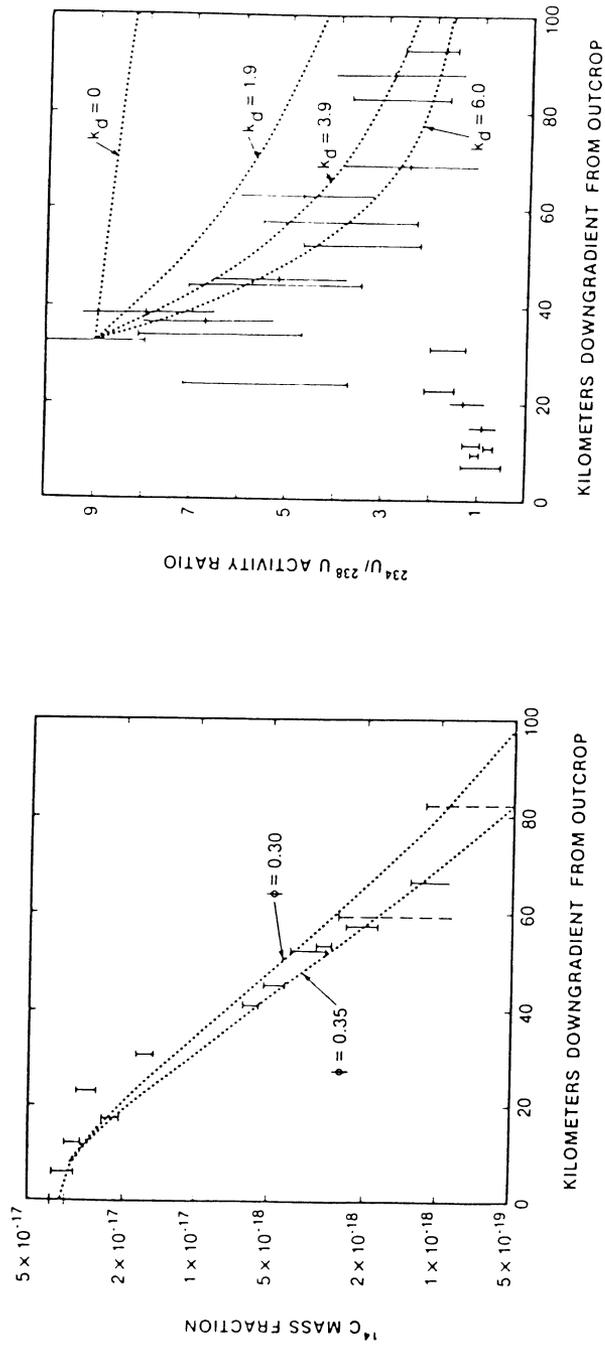
Fig. 1. Measured and simulated ^{14}C contents with distance down-gradient from outcrop

than per unit carbon was required by the transport model used. Oeschger (1974) pointed out that the same approach would also be useful for general ground-water ^{14}C interpretations. These model validation calculations were made as part of the SCEPTER program being carried out by INTERA Environmental Consultants, Inc for the Battelle Projects Management Division, Office of Nuclear Waste Isolation as prime contractor to the U S Department of Energy.

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