

MATHEMATICAL MODELING OF THE DISTRIBUTION OF NATURAL  $^{14}\text{C}$ ,  
 $^{234}\text{U}$ , and  $^{238}\text{U}$  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  $^{14}\text{C}$  and  $^{234}\text{U}$  and  $^{238}\text{U}$  in the Carrizo Aquifer of south Texas. The hydrology and distribution of  $^{14}\text{C}$  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  $^{14}\text{C}$  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  $^{234}\text{U}/^{238}\text{U}$  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):

$$\frac{\partial}{\partial t} [\phi C_f + \rho_s (1-\phi) C_s] = - \frac{\partial}{\partial x} (V_D C_f - \phi D \frac{\partial C_f}{\partial x}) - \lambda [\phi C_f + \rho_s (1-\phi) C_s] \pm I \quad (1)$$

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)

$\rho_s$  = solid grain density (mass/volume)

$\phi$  = porosity (volume/volume)

$\lambda$  = first order decay constant (time<sup>-1</sup>)

$I$  = 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<sup>2</sup>) 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  $V_D/\phi$ .

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

$\alpha$  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<sup>2</sup>/time), and  $\tau$

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:

$$[\phi C_f + \rho_s (1-\phi) C_s] = (1 + \frac{(1-\phi)}{\phi} \rho_s k_d) \phi C_f \quad (2)$$

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 ( $\phi C_f$ ) 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:

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

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  $^{14}\text{C}$  distribution in the Carrizo described here was made using the finite-difference model SWENT (Simulator for Water, Energy and Nuclide Transport).

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:

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

- $\alpha$  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.
- $\rho_s$  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.
- $\lambda$   $^{14}\text{C} = 1.210 \times 10^{-4} \text{yr}^{-1}$ ;  
 $^{238}\text{U} = 1.551 \times 10^{-10} \text{yr}^{-1}$ ;  
 $^{234}\text{U} = 2.841 \times 10^{-6} \text{yr}^{-1}$ .
- $C_f$  mass nuclide/mass water. Values of this parameter as a function of space were calculated using the model and compared with measured  $^{14}\text{C}$  and  $^{234}\text{U}/^{238}\text{U}$  data for model validation and uranium retardation determination, respectively. 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.

$^{14}\text{C}$  DATA AND SIMULATION RESULTS. A number of measurements of the  $^{14}\text{C}$  content of Carrizo water in the region modeled are available. They include both total dissolved carbonate contents ( $C_{\text{tot}} = \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$ ) and the  $^{14}\text{C}$  content of the dissolved carbonate as pmc (per cent modern carbon). From pmc and  $C_{\text{tot}}$  values,  $^{14}\text{C}$  mass fractions can be calculated using:

$$\frac{\text{gm } ^{14}\text{C}}{\text{gm H}_2\text{O}} = \text{pmc} \times C_{\text{tot}} \left( \frac{\text{mMol}}{\text{kg H}_2\text{O}} \right) \times 1.64 \times 10^{-19}$$

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  $^{14}\text{C}$  half-life as 5730

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

The  $^{14}\text{C}$  mass fraction in recharge to the Carrizo given in table 1 is based on 100pmc and a  $C_{\text{tot}}$  value of  $2.21 \pm 0.12 \text{ mMol/kg H}_2\text{O}$ . The  $C_{\text{tot}}$  is that determined by Pearson and White (1967) using the relationship between the  $C_{\text{tot}}$  values of Carrizo samples and their stable  $^{13}\text{C}$  isotope contents. The recharge mass fraction value can be combined with the recharge rate from the flow calculations ( $14.2 \text{ kg H}_2\text{O}/\text{m}^2/\text{yr}$ ) to yield the value of  $5.14 \times 10^{-13} \text{ gm } ^{14}\text{C}/\text{m}^2/\text{yr}$ , the source term, required for the transport equation (1).

The measured  $^{14}\text{C}$  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  $^{14}\text{C}$  mass fractions. The measured  $^{14}\text{C}$  data, though, are more consistent with the higher porosity value.

URANIUM DATA AND SIMULATION RESULTS. Many measurements of dissolved uranium concentrations and of  $^{234}\text{U}$  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 ( $\text{UO}_2^+$ ) ion is stable, and uranium concentrations in the 1 - 10 parts per billion (ppb) range occur. Under reducing conditions, as prevail down-gradient,  $\text{U}^{+4}$  and its complexes are dominant and uranium concentrations of only 1 - 10 x  $10^{-3}$  ppb occur (table 1).

$^{234}\text{U}$  is a daughter of the much longer-lived  $^{238}\text{U}$ . 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 groundwater via the  $R_d$  and  $k_d$  factors defined above.

The numerical transport model validated using the  $^{14}\text{C}$  data was used to simulate  $^{234}\text{U}$  and  $^{238}\text{U}$  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  $^{14}\text{C}$  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 interstitial 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.

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Discussions over the years with Ken Osmond and Jim Cowart helped lead to the present interpretation of uranium isotope data. Expressing  $^{14}\text{C}$  analyses per unit water rather

TABLE 1.  $^{14}\text{C}$  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.		$^{14}\text{C}$ mass	Uranium	$^{234}\text{U}/^{238}\text{U}$
Uranium	$^{14}\text{C}$	fractions $\times 10^{18}$	concentration $\times 10^3$ ppb	activity ratio
Recharge		$36.2 \pm 2.0$		
414	TX - 91	$35.6 \pm 3.3$	$202 \pm 6$	$0.90 \pm 0.04$
469			$629 \pm 16$	$1.03 \pm 0.03$
471			$2560 \pm 55$	$.77 \pm 0.03$
467			$29 \pm 3$	$1.09 \pm 0.16$
	TX-91	$32.7 \pm 2.5$		
2113			7400	0.87
	TX-92	$22.8 \pm 1.8$		
2114			18	1.3
472			$8 \pm 1$	$1.77 \pm 0.29$
	TX-210	$29.2 \pm 1.9$		
468			$4 \pm 1$	$5.48 \pm 1.63$
413	TX-93	$16.5 \pm 1.0$	$21 \pm 3.5$	$1.63 \pm 0.33$
465			$3 \pm 1$	$9.02 \pm 1.03$
466			$4 \pm 1$	$6.36 \pm 1.68$
2105			5	6.7
2115			2.7	7.9
	TX-94	$6.4 \pm 0.8$		
422	TX-226	$4.8 \pm 0.4$	$3 \pm 1$	$5.14 \pm 1.87$
2107			3	5.2
	TX-96	$3.5 \pm 0.6$		
421	TX-216	$3.0 \pm 0.2$	$1 \pm 4$	$3.44 \pm 1.20$
	TX-214	$2.1 \pm 0.3$		
411			$4 \pm 2$	$3.93 \pm 1.57$
	TX-215	2.6		
	TX-92	4.8		
2102			3	4.7
	TX-217	$1.1 \pm 0.2$		
2101			1.1	2.5
	TX-219	< 1.8		
417	TX-218	< 1.1	$2 \pm 1$	$2.71 \pm 1.00$
2104			6	2.80
476			$2 \pm 4$	$2.08 \pm 0.51$

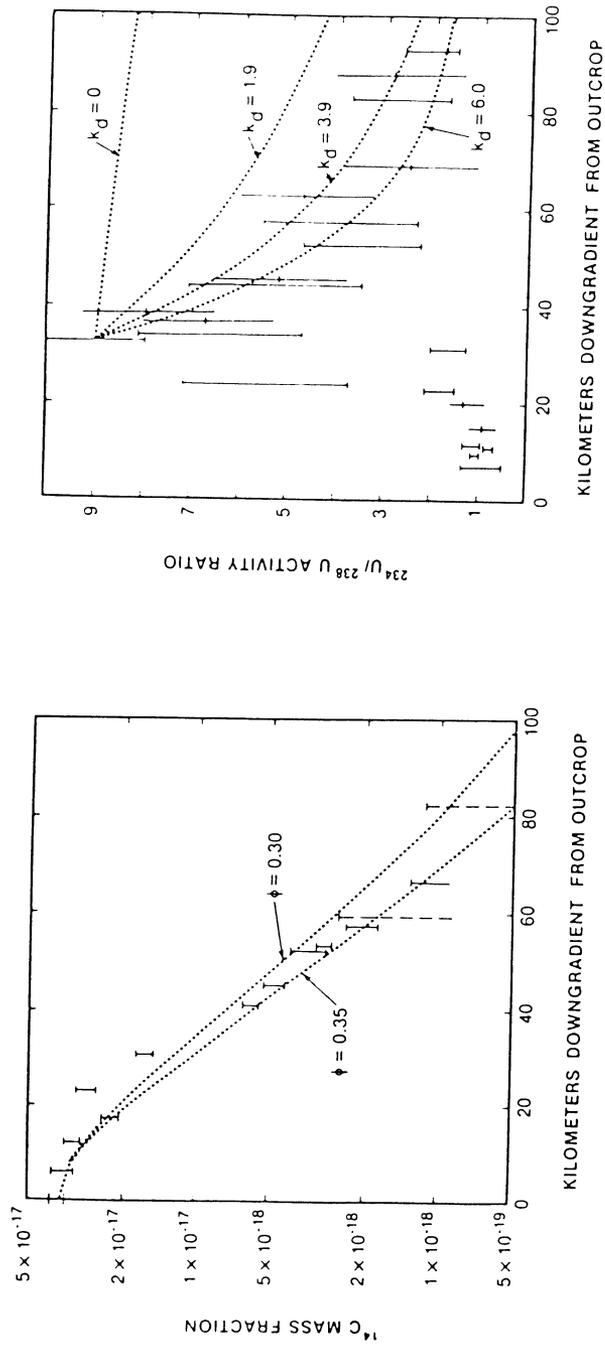


Fig. 1. Measured and simulated  $^{14}\text{C}$  contents with distance down-gradient from outcrop

Fig. 2. Measured and simulated uranium activity ratios 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  $^{14}\text{C}$  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.

## REFERENCES

Anderson, M P, 1979, Using models to simulate the movement of contaminants through groundwater flow systems: CRC Critical Rev Environmental Control, v 9, p 97-156.

Cowart, J B and Osmond, J K, 1974,  $^{234}\text{U}$  and  $^{238}\text{U}$  in the Carrizo Sandstone aquifer of south Texas, in Isotope Techniques in Groundwater Hydrology 1974: IAEA, Vienna, v 2, p 131-149.

Klempt, W B, Duffin, G L, and Elder, G R, 1976, Ground-water resources of the Carrizo Aquifer in the Winter Garden area of Texas: Texas Water Development Bd Rept 210, v 1, 73 p.

Oeschger, Hans, 1974, Discussion in Isotope Techniques in Groundwater Hydrology 1974: IAEA, Vienna, v 2, p 91.

Pearson, F J, Jr and White, D E, 1967, Carbon-14 ages and flow rates of water in Carrizo sand, Atascosa County, Texas: Water Resources Research, v 3, p 151-161.

Pickens, J F and Grisak, F E, 1981, Modeling of scale dependent dispersion in hydrogeologic systems: Water Resources Research, v 17, p 1701-1711.