

Site Characterization Using $^3\text{H}/^3\text{He}$ Ground-Water Ages, Cape Cod, MA

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Abstract

Exploratory drilling to locate new water-supply wells on Cape Cod, Massachusetts encountered fuel-related organic contaminants in a shallow unconfined aquifer. However, the plume could not be traced back to the water table and estimates of ground-water velocities were not consistent with plausible contaminant releases, and thus the source of contamination was not located. In conjunction with an expanded hydrogeologic investigation, tritium and helium isotope analyses were performed to delineate ground-water ages and flow rates. Vertical profiles of ground-water age were used to determine recharge rates that range from 70 to 115 cm/yr. The age of water near the leading edge of the contaminant plume along with estimates of dispersion were used to estimate when the contaminant release occurred (1975 ± 3 years). Recharge estimates, the geometry of the aquifer, and contaminant data were used in a simple mass balance model to determine both the location of the contaminant source and the horizontal ground-water velocity (ranging from 20 ± 12 m/y to 90 ± 20 m/y across the site). Concurrent site investigations revealed fuel floating on the water table within the area (± 250 m) determined by the model. The configuration of the water table and recharge estimates were used to estimate a horizontal hydraulic conductivity of 130 ± 30 m/d. The mean hydraulic conductivity from a subsequent 72 hr, 12 well pumping test was 100 m/d.

Introduction

Quantifying ground-water travel times, even in relatively simple systems, is very difficult and represents one of the major complications in attempting to predict the subsurface transport of contaminants. Recent research (e.g., Schlosser et al., 1988; Solomon et al., 1992; Busenberg and Plummer, 1992) has shown that it is possible to determine the age of shallow ground water directly by using trace amounts of atmospherically derived substances. This paper describes the application of ground-water dating in characterizing contaminant transport at the FS-12 field site on Cape Cod, Massachusetts.

The FS-12 field site is located on and adjacent to the Massachusetts Military Reservation (MMR) on Cape Cod, Massachusetts (Figure 1). Hydrogeologic investigations at this site began in 1991 (HAZWRAP, 1991) after organic compounds were detected in water samples collected during exploratory drilling by the Sandwich Water District. An underground pipeline follows Greenway Road and was used to transport both aviation gasoline (AVGAS) and JP-4 jet fuel. This currently inactive pipeline was reported to have leaked approximately 2000 gallons of JP-4 in 1972. Figure 1 shows the general extent of a benzene plume determined as part of the 1991 investigation. High concentrations of ben-

zene and ethylene dibromide (EDB) were found in several monitoring wells approximately 350 m south of Greenway Road. Although the pipeline was a logical source of the observed contamination, monitoring wells installed in 1991 along Greenway Road and a soil gas survey did not detect contamination. Calculated ground-water velocities, based on hydraulic conductivity estimates from an adjacent site, were not consistent with the timing of reported leaks in the pipeline and the location of the contamination down-gradient (or even plausible given the construction date of the pipeline). Furthermore, the relative proportions of benzene and EDB observed in monitoring wells was not consistent with a JP-4 source. Thus, the source of the observed ground-water contamination was not identified in the 1991 study. An expanded study began in 1992 to characterize more fully the nature and extent of ground-water contamination and to quantify ground-water flow rates and directions. As part of the characterization of the flow system, the ground-water dating project was initiated. Specific objectives of the dating project were to (1) define the distribution of ground-water ages at the FS-12 field site and (2) interpret ages in the context of the ground-water flow system to provide estimates of the location and date of the contaminant release and estimates of ground-water velocities.

Ground-water flow at the FS-12 site occurs in an unconfined aquifer of glacial origin. The site lies mostly within an outwash plain that is flanked by the Buzzards Bay moraine to the west and the Sandwich moraine to the northeast (Oldale, 1982). The outwash plain slopes southward towards the Nantucket sound and consists of approximately 65 m of stratified sands and gravel that are underlain by fine sands and silts of lacustrine origin. Kettle holes are common in the outwash plain and often intersect the water table forming ponds such as Snake Pond on the FS-12 site. The FS-12 site is approximately 7 km from the site of a

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Received May 1994, revised December 1994, accepted January 1995.

FS-12 SITE

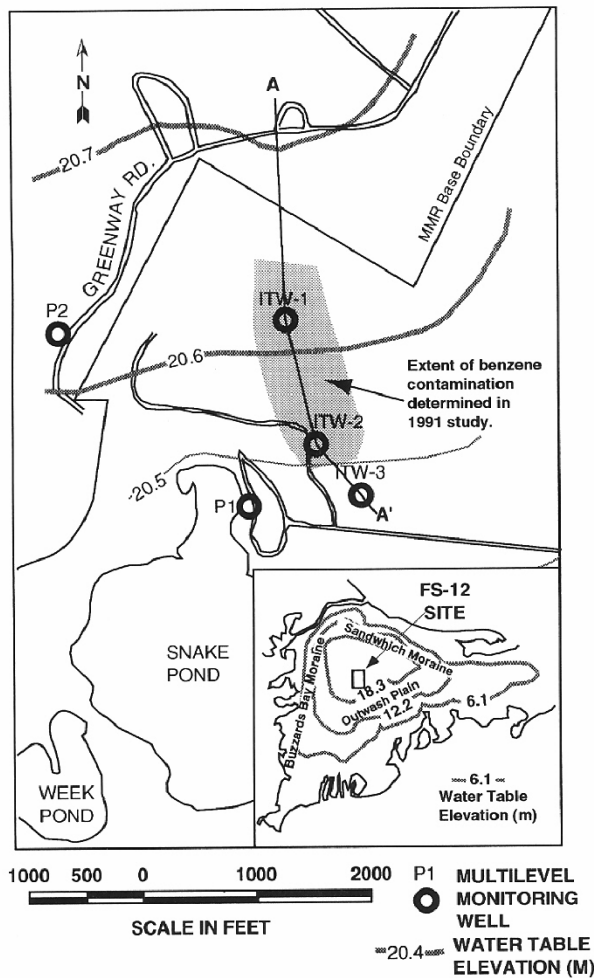


Fig. 1. FS-12 field site with water level contours, the location of multilevel monitoring wells, and the extent of a benzene plume determined in the 1991 study.

well-known natural gradient tracer test (LeBlanc et al., 1991).

The FS-12 site is located near the topographically highest region of Cape Cod. Water level contours form concentric rings, and on a regional scale ground-water flow is radial about the topographic high (Figure 1). At the foci of the water level contours is a ground-water divide where flow is nearly vertical. The unsaturated zone is more than 30 m thick near the ground-water divide and thins to zero within some of the kettle holes.

Ground-water flow at the FS-12 site is primarily from north to south. As shown in Figure 1 the horizontal hydraulic gradient is about 4×10^{-4} . Vertical hydraulic gradients as great as 6×10^{-4} have been measured, but they are highly transient and throughout much of the year are too small to be measured reliably. The ground-water divide is located to the north of Greenway Road (Figure 1); however, this area is part of the impact range of the MMR and the precise location of the divide has not been determined through direct observations.

Overview of $^3\text{H}/^3\text{He}$ Ground-Water Dating

Tritium (^3H), a radioactive isotope of hydrogen (half-life = 12.43 years), arising from aboveground testing of high-yield thermonuclear devices beginning in 1953, has proven to be a useful tracer in ground water and oceanic systems (e.g., Kaufman and Libby, 1954; Brown, 1961; von Buttlar and Wendt, 1958). Before 1953, the ^3H activity in precipitation has been estimated by Kaufman and Libby (1954) to be less than 20 tritium units (TU), and actually may have been less than 5 TU (Robertson and Cherry, 1989). During the mid-1960s, ^3H activities in precipitation rose rapidly to more than 3000 TU in monthly composite samples in the northern hemisphere, resulting in a slug-like input to ground-water systems. Although the absolute ^3H activity in precipitation has varied both spatially and temporally, identifying the position of the mid-1960s peak in shallow aquifers can in principle provide a reference point for determining recharge and ground-water travel times.

Helium-3 (^3He), the stable daughter of ^3H decay, has also proven to be a useful tracer in lacustrine and oceanic systems (Torgersen et al., 1977; Craig and Lupton, 1981) but only recently have combined ^3H and ^3He measurements been interpreted in ground-water systems (e.g., Poreda et al., 1988; Schlosser et al., 1988; Solomon et al., 1992). Ground waters contain dissolved ^3He from a number of sources. These include (1) atmospheric ^3He from equilibrium solubility with the atmosphere, (2) tritiogenic ^3He ($^3\text{He}^*$) from the decay of ^3H , (3) excess ^3He from trapped excess air above equilibrium solubility, (4) nucleogenic ^3He from nuclear fission of ^6Li , and (5) mantle ^3He . Nucleogenic and mantle ^3He are negligible in most shallow aquifers. It is possible to calculate both excess ^3He (if present) and atmospheric ^3He and, thus, by subtraction compute the tritiogenic ^3He . In shallow vadose zones, dissolved ^3He concentrations are controlled by equilibrium solubility with the atmosphere and thus the computed tritiogenic ^3He is zero. Below the water table, total ^3He concentrations will begin to rise because the saturated zone is a closed system with respect to dissolved gases.

The decay of ^3H to ^3He can be represented as

$$^3\text{H}(12.4 \text{ years}) \xrightarrow{\beta^-} ^3\text{He}^*. \quad (1)$$

The $^3\text{H}/^3\text{He}$ age is defined as

$$t_{^3\text{H}/^3\text{He}} = \lambda^{-1} \ln \left(\frac{[^3\text{He}^*]}{[^3\text{H}]} + 1 \right) \quad (2)$$

where $t_{^3\text{H}/^3\text{He}}$ is $^3\text{H}/^3\text{He}$ age; λ is ^3H decay constant; $[^3\text{He}^*]$ is tritiogenic ^3He concentration; and $[^3\text{H}]$ is ^3H activity.

Implicit in the concept of ground-water dating according to equation (2) are the notions that dissolved species are transported at the same rate as ground water and dispersive mixing of dissolved species is not significant; studies in hydrogeologically simple, well-defined flow systems show this to be the case (Solomon et al., 1992; Solomon et al., 1993). Both ^3H and ^3He can generally be considered to be geochemically nonreactive, apart from the radioactive decay of ^3H . For purely advective transport, the $^3\text{H}/^3\text{He}$ age will agree exactly with the ground-water travel time. Further-

more, under such conditions, the $^3\text{H}/^3\text{He}$ age is independent of the ^3H input function because it is the $^3\text{He}^*$ to ^3H ratio that is considered. This is important because relatively few continuous measurements of ^3H in precipitation were made during the 1960s and 1970s, leading to uncertainties in the spatial and temporal distribution of the ^3H input function. Most quantitative studies involving atmospherically derived ^3H have utilized the general shape of the ^3H distribution and the location of the mid-1960s peak, rather than absolute ^3H activities (e.g., Robertson and Cherry, 1989). Solomon and Sudicky (1991) have shown that except near the location of the mid-1960s peak, dispersion has only a minor influence on $^3\text{H}/^3\text{He}$ ages. Tritium and helium isotope techniques have developed extensively as a result of widespread use of these tracers in oceanic and lacustrine systems. Current analytical methods are sufficient for utilizing atmospherically derived ^3H to date ground water ranging from about 0 to 35 years with a typical analytical uncertainty of approximately 10%.

Much of the utility of $^3\text{H}/^3\text{He}$ age dating results from the fact that the ground-water age itself, at any point in the system, is a result of the velocity field encountered along the entire upstream flow path. Thus, a single measurement of age contains "memory" and embodies more information than a point measurement of velocity (or hydraulic conductivity).

Methods

Because unconfined aquifers are highly stratified with respect to ground-water ages, previous studies (e.g. Schlosser et al., 1988; Solomon et al., 1992) have shown that it is important to collect samples from discrete depths. This was accomplished by installing several types of multilevel sampling (MLS) devices. Three MLS systems were installed along the axis of the contaminant plume defined during the 1991 study. Additional MLS systems were installed in uncontaminated areas as shown in Figure 1. Each MLS consists of five to eight separate monitoring tubes (1.3- to 1.6-cm-OD) that sample 10 to 20 cm intervals of the aquifer.

Helium samples from P1 and P2 were collected using the downhole Cu tube method described by Solomon (1992). At the other sites it was not possible to advance the Cu tubes to the required depth (up to 60 m) because of excessive friction between the sampling device and the well. Samples from the deeper sites were collected by filling a 0.25-in.-diam. nylon tube with an attached one-way valve, then filling a CO_2 -purged 0.375-in.-diam. Cu tube at the surface. This method is known as the tubing bailer method. In both cases, the Cu tube was sealed with refrigeration pinch clamps. This method compared favorably with the downhole method at several wells.

Gas concentrations and isotopic analyses were done at the Rare Gas Facility at the University of Rochester. Gases were extracted on a high-vacuum line using the procedure described by Poreda et al. (1988). Helium isotope ratios are expressed as R/R_a , where R is the $^3\text{He}/^4\text{He}$ ratio in the sample and R_a is the $^3\text{He}/^4\text{He}$ ratio in the air standard. Errors in the reported values of R/R_a are about 0.5%. The ^3He "in-growth" technique (Clarke et al., 1976) was used to determine tritium values. Errors in the reported ^3H values

are dependent on the amount of ^3H and are about 3% at 30 TU. Helium and Ne concentrations were determined by peak height comparison with an error of about 2%.

Results

The results of the ^3H , and He isotope ratio determinations and the ^4He , N_2 , and Ne analyses are shown in Table 1. $^3\text{He}/^4\text{He}$ ratios relative to air (R/R_a) range from near 1 at the water table to about 2.5 times R_a at a depth of about 24 m below the water table. Tritium values near the water table range from about 8 to 12 TU. Peak ^3H values are 27 to 36 TU and also occur at a depth of about 24 m.

An important characteristic of the ^4He and Ne data is that many samples are below the equilibrium solubility values [47 and 208 $\mu\text{cc}/\text{kg}$ for He and Ne, respectively at 7°C (Weiss, 1971)], indicating that gas stripping has occurred. In contrast to He and Ne, N_2 values for many samples are above equilibrium solubility [16 cc/kg at 7°C (Weiss, 1970)]; however, the samples from ITW-1 collected in August 1992 are below solubility with respect to N_2 . During the August 1992 sampling, CO_2 was used to operate the air-lift purge pump, whereas N_2 was used for the other sampling events. The most likely cause for the below-solubility values of He and Ne and the above-solubility values of N_2 is a small leak in the packer assembly of the purge pump. Fortunately, the He air-water isotopic fractionation factor is small [1.017 (Benson and Krause, 1980)], and thus the $^3\text{He}/^4\text{He}$ ratio is not significantly affected by gas stripping during sample collection. This is shown by the excellent agreement of the $^3\text{He}/^4\text{He}$ ratio of duplicate samples, even when the total amount of ^4He varies significantly.

Included in Table 1 are isotope data for sites P1 and P2 where samples were collected using the downhole Cu tube method, and purging was done using a suction lift pump. All but one of the samples is supersaturated with respect to atmospheric He and Ne. This supersaturation is either a result of air bubbles from the capillary fringe being swept downward during infiltration and then dissolving as the hydrostatic pressure increases (Heaton and Vogel, 1981), or incomplete purging of the Cu sampling tube (Poreda et al., 1988). Unfortunately, it is not possible to distinguish between incomplete purging and trapped air (Solomon, 1992). An analysis of the data indicates that He and Ne values fall along an air addition line with a recharge temperature of about 7°C . Minor amounts of radiogenic He appear to exist in some deep samples, but this cannot explain the magnitude of the He supersaturation.

Methods used to separate ^3He from other components are found in the Appendix. Ground-water ages and the computed amount of $^3\text{He}^*$ are shown in Table 1. Because the computed age depends mostly on the $^3\text{He}/^4\text{He}$ ratio, the agreement between duplicate samples with highly variable He values is generally less than 10% of the age (Table 1). The vertical distributions of $^3\text{H}/^3\text{He}$ -determined ages at sites P1, P2, ITW-1, ITW-2, and ITW-3 are shown in Figure 2. In general, ages are near zero just below the water table and increase exponentially with depth.

A spike-like input of ^3H to ground-water systems worldwide occurred in the mid-1960s. The vertical distribution of $^3\text{H} + ^3\text{He}^*$ at sites ITW-1, and ITW-3, and the

Table 1. Results of He Isotope Ratios, ⁴He, N₂, Ne, and ³H Analyses, and Computed Tritogenic ³He (³He*) and ³H/³He Ages

ID	Date	Elev. MSL (m)	R ^a /R _a ^b	He (μcc/kg)	N ₂ (cc/kg)	Ne (μcc/kg)	³ H (TU)	³ He* (TU)	Age (years)	³ H + ³ He* (TU)
ITW-1-7	Apr-93	14.9	1.106	48.2	18.2	204.0	12.7	2.5	3.2	15.2
ITW-1-6	Aug-92	10.1	1.107	46.2	13.2	^c NA	9.9	2.4	3.9	12.3
ITW-1-6	Apr-93	10.1	1.100	27.1	21.5	128.0	11.2	2.6	3.7	13.8
ITW-1-5	Apr-93	5.3	1.222	47.6	21.6	224.0	7.8	5.6	9.6	13.4
ITW-1-5	Apr-93	5.3	1.223	47.3	22.2	219.0	7.8	5.5	9.6	13.3
ITW-1-5	Aug-92	5.3	1.240	61.7	17.6	NA	11.9	7.9	9.1	19.8
ITW-1-4	Sep-93	0.5	2.115	29.0	8.1	139.0	23.1	17.7	10.1	40.8
ITW-1-4	Apr-93	0.5	2.530	28.3	28.4	138.0	27.3	39.1	15.9	66.4
ITW-1-4	Apr-93	0.5	2.531	28.6	22.0	142.0	27.3	39.1	15.9	66.4
ITW-1-3	Sep-93	-4.4	2.237	31.5	8.1	135.0	14.8	31.6	20.4	46.6
ITW-1-3	Aug-92	-4.4	2.498	30.5	14.5	NA	36.1	38.2	12.9	74.9
ITW-1-2	Apr-93	-9.2	1.568	29.5	22.0	133.0	10.1	14.7	16.0	24.8
ITW-1-2	Aug-92	-9.2	1.141	24.0	10.2	NA	4.4	3.7	10.8	8.1
ITW-1-1	Apr-93	-14.0	1.020	37.3	23.1	159.0	0.8	0.5	9.3	1.3
ITW-2-5	Sep-93	9.9	1.103	46.2	13.0	198.0	7.4	2.3	4.9	9.7
ITW-2-5	Apr-93	9.9	NA	NA	NA	NA	8.6	NA	NA	NA
ITW-2-4	Sep-93	2.9	1.164	44.7	11.6	183.0	9.2	4.2	6.8	13.4
ITW-2-4	Apr-93	2.9	NA	NA	NA	NA	12.9	NA	NA	NA
ITW-2-3	Apr-93	-4.1	NA	NA	NA	NA	28.3	NA	NA	NA
ITW-2-2	Apr-93	-11.1	NA	NA	NA	NA	6.1	NA	NA	NA
ITW-2-1	Sep-93	-18.1	1.089	28.9	10.0	138.0	0.3	2.3	37.6	2.6
ITW-3-7	Apr-93	8.0	1.071	18.5	16.8	90.0	9.2	1.8	3.3	11.0
ITW-3-6	Apr-93	4.9	1.120	20.0	17.0	98.0	8.5	3.1	5.6	11.6
ITW-3-5	Apr-93	1.8	1.108	21.9	17.4	106.0	7.9	2.8	5.4	10.7
ITW-3-4	Apr-93	-1.3	1.274	14.8	17.3	75.0	9.0	7.1	10.4	16.1
ITW-3-3	Apr-93	-4.4	1.680	19.9	18.4	96.0	14.4	17.6	14.3	32.0
ITW-3-2	Apr-93	-7.5	2.360	18.3	18.8	97.0	24.5	35.2	15.9	59.7
ITW-3-2	Apr-93	-7.5	2.208	25.3	23.4	147.0	24.5	31.3	14.7	55.8
ITW-3-1	Apr-93	-10.6	1.638	17.2	18.7	85.0	5.4	16.5	25.0	21.9
P1-18.5	Sep-93	16.8	1.012	54.0	11.8	NA	8.4	0.0	0.1	8.4
P1-33.5	Nov-92	12.2	1.002	43.8	16.7	NA	7.8	0.1	0.1	7.9
P1-46.5	Sep-93	8.2	1.155	63.9	14.5	305.0	8.6	5.2	8.4	13.8
P1-46.5	Sep-93	8.2	1.189	64.4	14.2	267.0	8.6	6.4	10.0	15.0
P1-48.5	Nov-92	7.5	1.327	48.1	24.6	NA	9.8	8.4	11.1	18.2
P1-61.5	Sep-93	3.5	1.281	64.3	14.6	269.0	10.0	9.7	12.1	19.7
P1-76.5	Sep-93	-1.4	1.617	51.8	13.5	254.0	15.2	17.4	13.7	32.6
P1-76.6	Sep-93	-1.4	1.509	63.5	13.9	250.0	15.2	17.6	13.8	32.8
P2-50.5	Apr-93	14.5	1.013	58.5	15.0	239.0	12.9	0.1	0.1	13.0
P2-65.5	Apr-93	9.9	1.078	51.7	20.0	224.0	9.4	1.9	3.3	11.3
P2-80.5	Apr-93	5.2	1.097	40.3	22.0	188.0	8.4	2.5	4.7	10.9
P2-100.5	Apr-93	-1.1	1.330	56.9	20.6	236.0	9.9	10.1	12.6	20.0
P2-115.5	Apr-93	-5.7	1.883	48.6	22.3	221.0	18.3	23.5	14.8	41.8

^aR = ³He/⁴He ratio of the sample.

^bR_a = ³He/⁴He ratio of the air standard.

^cNA = Not analyzed or unreliable due to contamination (generally a small air leak).

distribution of ³H at ITW-2 is shown in Figure 2. The summing of ³H and ³He* effectively eliminates radioactive decay for ³H and, hence, facilitates detection of peak values. Peak values correspond to precipitation that occurred in the mid-1960s. Peak ³H + ³He* values are about 75 TU and occur at elevations ranging from -3.5 to -7.0 m (msl). The relatively uniform elevation of the ³H bomb (mid-1960s) peak across the site is consistent with other detailed investigations of ³H in unconfined aquifers (e.g., Robertson and Cherry, 1989).

As shown in Figure 2, the ³H/³He age of water from ITW-1 increases with depth to a maximum of 20 years at an elevation of -4.4 m, then decreases to 9 years at an elevation of -14.0 m. Solomon and Sudicky (1991) showed that ³H/³He ages near and especially below the ³H bomb peak

are generally younger than actual travel times due to dispersion. Furthermore, the analytical uncertainty in ages increases dramatically below the bomb peak due to diminished ³H activities. We have no physical evidence for a discontinuity in the flow system that would result in younger water below an elevation of -5 m. Without further investigation we can only postulate that the ages from ITW-1 below the bomb peak are affected by dispersion and analytical/sampling error and are not representative of actual fluid travel times.

Samples were collected during late 1992 and throughout 1993. Peak ³H values in precipitation occurred around 1963, and thus ground water near the bomb peak fell as precipitation about 30 years prior to sample collection. The difference between the total travel time (30 years) and the

$^3\text{H}/^3\text{He}$ age (16 years) is the travel time of water in the unsaturated zone (14 years).

Relationship Between Ground-Water Age and the Contaminant Plume

Figure 3 shows the vertical distribution of benzene and EDB at sites ITW-1, ITW-2, and ITW-3. Peak EDB concentrations occur at elevations of about 0.6 m at ITW-1, -4 m at ITW-2, and at -7 m at ITW-3. Peak benzene concentrations are coincident with peak EDB concentrations at ITW-1 and ITW-2, but benzene was not detected at ITW-3. Figure 3 also shows the vertical distributions of ground-water ages. Site ITW-3 is near the leading edge of the EDB plume (HAZWRAP, 1993), and this water has a $^3\text{H}/^3\text{He}$ age of about 16 years. Thus, water near the toe of the EDB plume was at the water table around 1977. Because of longitudinal dispersion, the leading edge of the contaminant plume moves at a different rate than the average ground-water velocity. Assuming a longitudinal dispersivity of 1 m (Garabedian et al., 1991) the observed contamination at ITW-3 is less than 2 years ahead of the displacement given by the average ground-water velocity. Thus, assuming that EDB behaves as a conservative species (i.e., it is transported at the same rate as ground water), then EDB contamination reached the water table in approximately 1975 (± 3 years).

Complete data on the mobility of EDB at the FS-12 site are not currently available; however, it is likely that retardation is weak in this system because the fraction of organic carbon in the aquifer is very small. If EDB is attenuated relative to ground water, the estimated date that contamination reached the water table would be moved back in time accordingly. It is important to emphasize that the estimate given herein is the arrival of contamination at the water table. The travel time of contaminants in the unsaturated zone has not been evaluated by the isotope data.

Ground-Water Velocities and Recharge Rates

As shown by Solomon and Sudicky (1991), one of the most straightforward uses of vertical $^3\text{H}/^3\text{He}$ age profiles is to estimate vertical ground-water velocities and recharge rates. By definition, recharge to an unconfined aquifer is the fluid flux normal to the water-table surface and is related to the average linear fluid velocity, according to

$$r = V_o \theta \quad (3)$$

where r = recharge rate [L/T]; θ = effective porosity [L^3/L^3]; and V_o = component of the average linear velocity normal to the water table [L/T].

Vogel (1967) developed a simple model based on mass balance for the distribution of travel times in an unconfined aquifer in which recharge is spatially uniform. The relation-

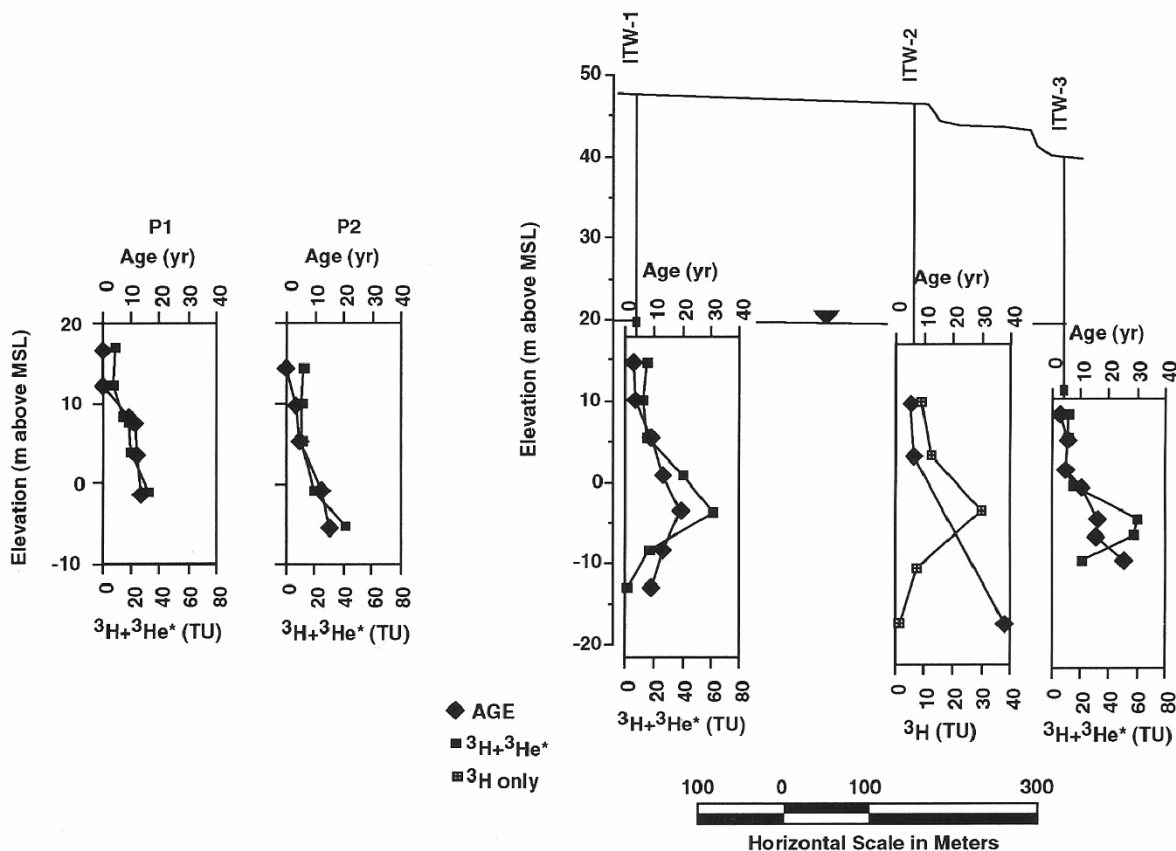


Fig. 2. Profiles of $^3\text{H}/^3\text{He}$ age and $^3\text{H} + ^3\text{He}^*$. The cross section from ITW-1 to ITW-3 is oriented along a ground-water flow line. Note that for ITW-2, only ^3H is plotted because a complete profile of $^3\text{He}^*$ was not obtained. Where duplicate samples were obtained, the plotted values are averages with outliers removed.

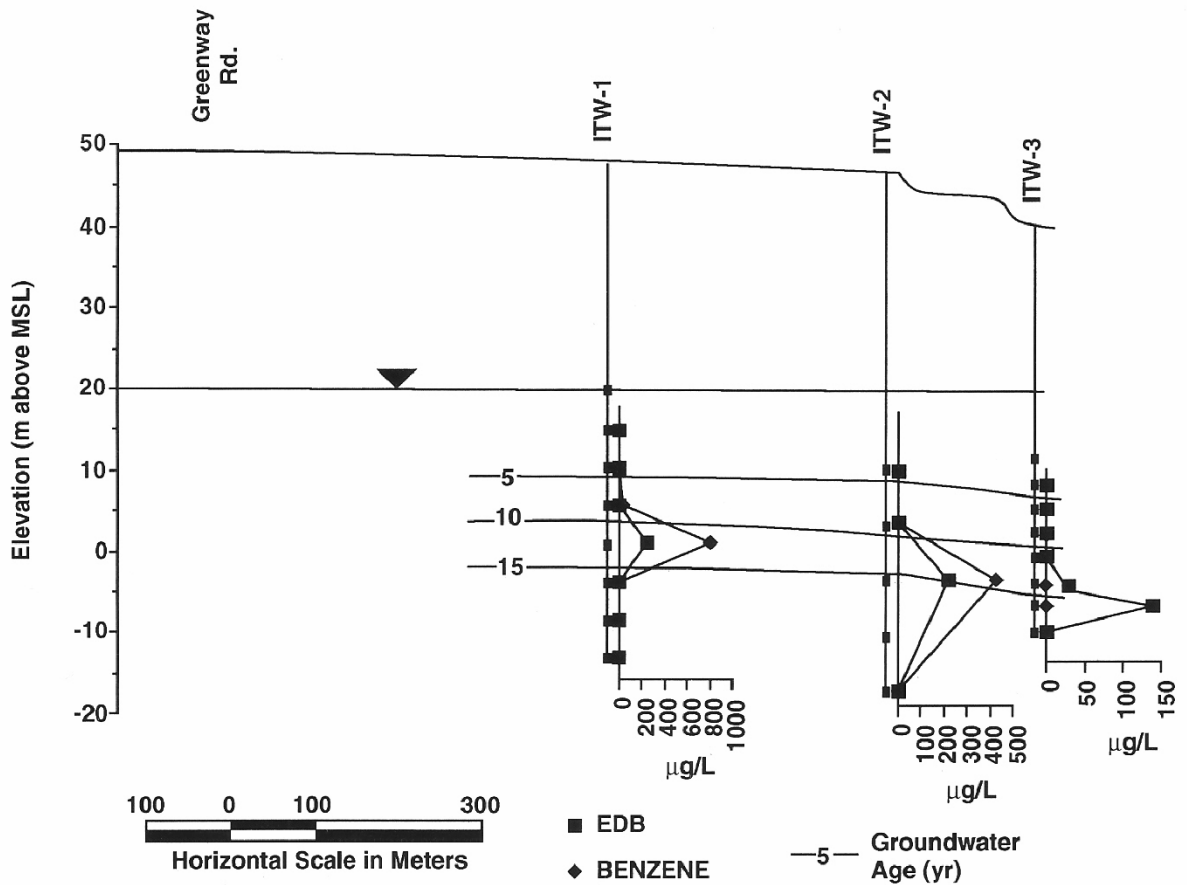


Fig. 3. Profiles of organic contaminants and ground-water age. The cross section from ITW-1 to ITW-3 is oriented along a ground-water flow line.

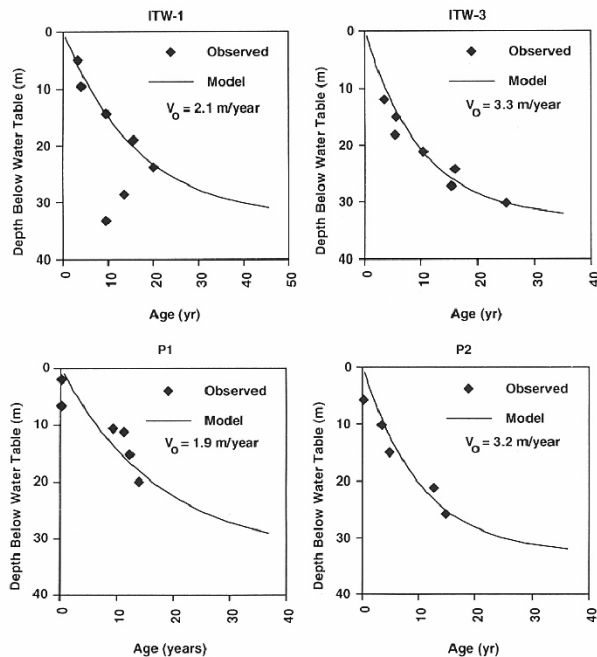


Fig. 4. Profiles of observed and simulated ground-water age. The simulated profiles were obtained by optimizing the fit between the observed and simulated age by adjusting the vertical velocity at the water table.

ship between travel time and the vertical velocity at the water table is

$$V_o = \frac{B}{t} \ln\left(\frac{B}{B-z}\right) \quad (4)$$

where B = aquifer thickness [L]; t = travel time [T]; and z = distance below the water table [L].

A nonlinear least-squares optimization procedure was developed to obtain an optimal fit of the measured age profiles to equation (4). An aquifer thickness of 33 m, which is the depth below the water table to a lower permeability silt layer, was used in the optimization routine. The fit between the modeled and observed values is generally good, as is illustrated in Figure 4. Also shown in Figure 4 are the optimized values for V_o , which range from 1.9 m/year to 3.3 m/year.

The porosity of aquifer materials in the vicinity of MMR ranges from 0.2 to 0.4 (HAZWRAP, 1989). Using a value of 0.35 for the FS-12 site, recharge rates can be computed according to equation (4) and range from 70 to 115 cm/year. Annual precipitation at the site is 122 cm, and thus recharge is 57 to 94 percent of this value. Sites P2 and ITW-3 are located in topographic depressions, and vertical velocities at these sites are greater than at P1 and ITW-1. Rain falling on top of frozen soil and snow was observed during several winter sampling trips, and it is possible that a significant amount of overland flow enhances recharge in topo-

graphically low areas. The vertical velocity determined at ITW-1 is likely to be more representative of the entire FS-12 site. Uncertainty in the effective porosity results in an uncertainty of about 20% for the estimated recharge rates.

Horizontal Velocities and Ground-Water Modeling

The horizontal uniformity of the $^3\text{H}/^3\text{He}$ age distribution suggest that flow in this system can be approximated using the Vogel (1967) model. This model assumes that the horizontal ground-water discharge across an arbitrary vertical plane is derived entirely from upstream recharge to the water table. Thus, the recharge estimates obtained from vertical age profiles can be used to estimate horizontal ground-water flow rates. A direct application of this model at the FS-12 site is complicated by the fact that the location of the flow divide has not been determined directly; however, if a contaminant plume defines a flow line, it is possible to calculate the location of the flow divide. This is possible because the orientation of each flow line is unique. It can be shown that if two points along a single flow line are known, the horizontal location of the flow line's origin (at the water table) is given by (see Appendix for a derivation),

$$\Delta X_f = \frac{\Delta X_1}{\frac{(B - Z_1)Z_2}{(B - Z_2)Z_1} - 1} \quad (5)$$

where ΔX_f = horizontal distance between the flow line's origin and the location of a known point on the flow line; ΔX_1 = horizontal distance between the two known points on the flow line; B = aquifer thickness; Z_1 = vertical coordinate of a known point on the flow line; and Z_2 = vertical coordinate of a second known point on the flow line.

Furthermore, the location of the flow divide is given by,

$$\Delta X_d = \Delta X_f \frac{B - Z_1}{Z_1} \quad (6)$$

where ΔX_d is the horizontal distance between the flow line's origin and the location of the flow divide.

Using data from ITW-1 and ITW-2 we estimate that the contaminant source and the flow divide are located 450 ± 250 m and 750 ± 300 m upgradient of ITW-1. Conventional site characterization conducted concurrent with the isotope project located a small region of fuel floating on the water table in the vicinity of Greenway Road (near the abandoned pipeline) approximately 425-475 m upgradient of ITW-1.

The horizontal ground-water velocity (V_x) at a distance of x from the flow divide is given by

$$V_x = \frac{V_o x}{B} \quad (7)$$

where V_o is the average vertical velocity at the water table between x and the flow divide. Applying the isotope-derived vertical velocities we estimate horizontal velocities that increase from about 20 ± 12 m/y near Greenway Road to 93 ± 20 m/y near ITW-3. These velocity estimates can then be combined with hydraulic gradients to estimate the average horizontal hydraulic conductivity (K_x) as

$$K_x = \frac{V_x \theta}{I} \quad (8)$$

where V_x = average horizontal velocity over the domain of interest; θ = porosity; and I = average horizontal hydraulic gradient of the domain of interest.

Considering the flow system upgradient of ITW-3 and a porosity of 0.35, the average hydraulic conductivity is 130 ± 30 m/d. A 72 hour pumping test using 11 observation wells was subsequently conducted at the FS-12 site (HAZWRAP, 1993), and yielded a mean horizontal hydraulic conductivity of about 100 m/d.

While simple, the Vogel model is extremely powerful because uncertainties in the horizontal velocity depend only on uncertainties in recharge and the model's geometry, both of which are small. In contrast, velocities based on Darcy's law depend on uncertainties in hydraulic conductivity that are typically very large. As a check on the Vogel model we developed a two-dimensional steady-state flow model for this site. The dual-formulation of flow (Frind and Matanga, 1985) was used to simulate both hydraulic potentials and stream functions using the computer code FLONET5. Figure 5 shows the model results including the simulated configuration of the water table. Also shown is the location of water at various points in time that entered the saturated zone near Greenway Road in 1975. Horizontal velocities and the travel time distribution from the flow model agree extremely well with the simple Vogel model.

Summary

Tritium and helium isotope analyses have been used to delineate ground-water ages and flow at a site contaminated with organic compounds. Vertical profiles of age and contaminant concentrations were used to estimate (1) recharge rates to the unconfined aquifer (70-110 cm/y), (2) horizontal ground-water velocities (increasing from 20 to 90 m/y from one end of the site to the other), (3) the date when contamination first reached the water table (1975 ± 3 y), (4) the location of the contaminant source (Greenway Road ± 200 m), and (5) the average hydraulic conductivity of the site (130 ± 30 m/day). Conventional site investigations revealed fuel floating on the water near the estimated source location. Furthermore, the average hydraulic conductivity determined from a 72 hr, 12 well pumping test agrees very well with the value estimated by the isotope data.

While some uncertainties exist such as the precise quantity of fuel released, the isotope and conventional characterization methods converged to the conclusion that leaks in the pipeline near Greenway Road are the source of ground-water contamination. Multiple releases with the first occurring in the early 1970s of both JP-4 and AVGAS are more consistent with observed proportions of benzene and EDB than a single release of JP-4. Differential transport and/or transformations of EDB and benzene can also explain the observed proportions of benzene and EDB qualitatively; however, these processes cannot be evaluated quantitatively due to a lack of site characterization.

Although the early investigation in 1990 attempted to identify contamination near the pipeline (through extensive

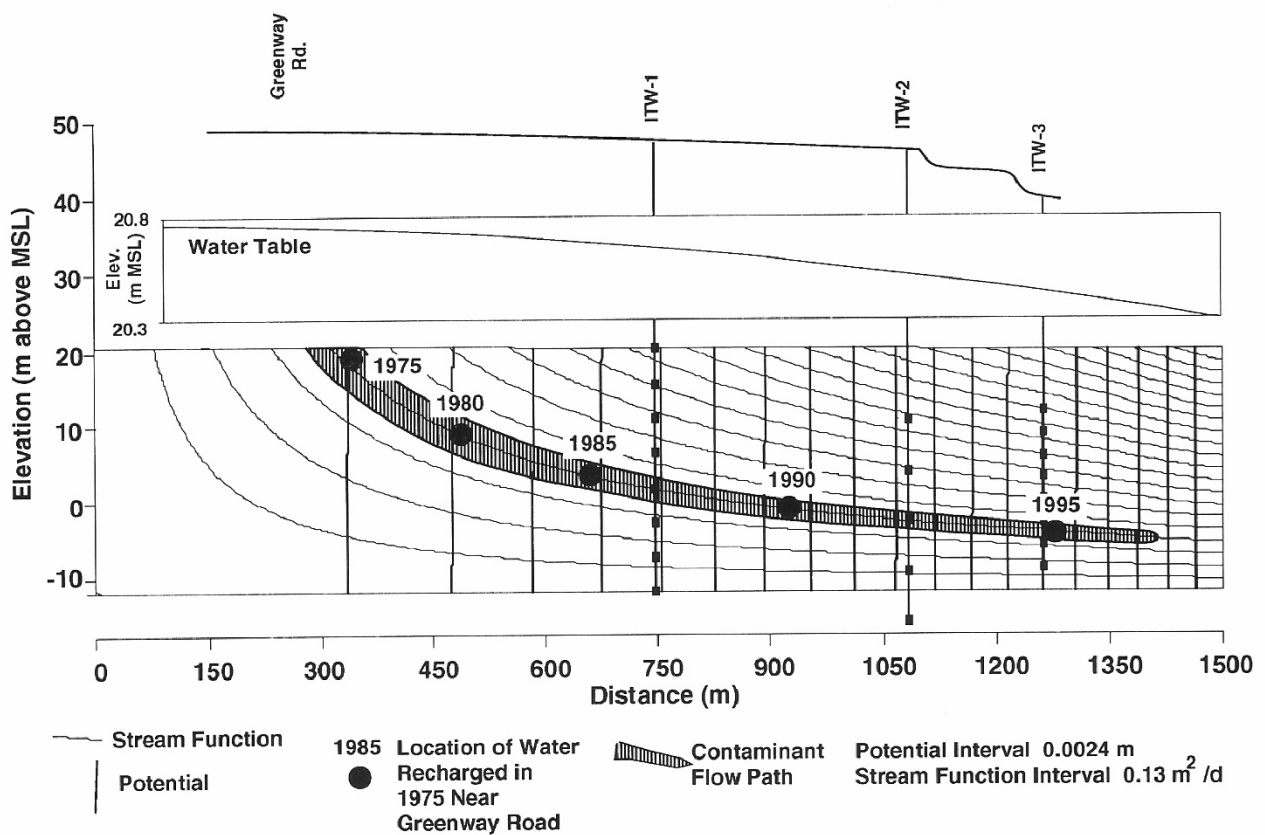


Fig. 5. Simulated stream functions, hydraulic potentials, and the configuration of the water table (note expanded scale). Also shown is the simulated location of water recharged in 1975 beneath Greenway Road at various points in time along the flow system. The shaded region highlights a flow line and does not represent a simulated contaminant plume.

drilling and a soil gas survey), the source was not located. The primary reason for this failure is that the conventional approach provides very little direct information regarding vertical fluid velocities. Near the source the vertical extent of the plume is very small. Furthermore, the source is near a flow divide where the vertical component of velocity is of comparable magnitude to the horizontal velocity and hence both components of flow are needed to estimate the contaminant trajectory.

The tritium/helium-3 ground-water dating technique provided significant insight with respect to ground-water flow at the FS-12 site. Furthermore, the integrated nature of the isotope data provide this insight in a very cost-effective manner. For example, the cost of the entire isotope project was a fraction of the pumping test alone. We anticipate that this technique will be equally useful at many other contaminated sites.

Appendix

Calculation of ^3He

To compute ground-water ages from the ^3H and He isotope data, it is necessary to separate the tritiogenic ^3He ($^3\text{He}^*$) from other components. Two methods were used depending on whether the sample was undersaturated or supersaturated with respect to atmospheric He. For samples with total He values less than $47 \mu\text{cc}/\text{kg}$ it was assumed that the below-solubility values for He resulted from gas strip-

ping during sample collection. The $^3\text{He}^*$ was computed according to (Solomon et al., 1993)

$$^3\text{He}^*_{\text{tot}} = \frac{R_o \cdot ^4\text{He}_m}{(^4\text{He}_m / ^4\text{He}_{\text{tot}})^{\alpha'}} - R_{\text{sol}} \cdot ^4\text{He}_{\text{tot}} \quad (\text{A1})$$

where $^3\text{He}^*_{\text{tot}}$ = total tritiogenic ^3He present before sample collection; $^4\text{He}_{\text{tot}}$ = total ^4He present before sample collection; $^4\text{He}_m$ = measured amount of ^4He in the sample; R_o = $^3\text{He}/^4\text{He}$ ratio in the sample at the time of collection; R_{sol} = $^3\text{He}/^4\text{He}$ ratio for water in isotopic equilibrium with the atmosphere; and α' = air-water isotope fractionation factor ($R_{\text{gas}}/R_{\text{water}}$).

For samples with total He equal to or greater than $47 \mu\text{cc}/\text{kg}$ it was assumed that the supersaturation values result from air addition. The $^3\text{He}^*$ was computed according to

$$^3\text{He}^*_{\text{tot}} = [^4\text{He}_m R_o - R_{\text{air}} (\alpha' ^4\text{He}_{\text{sol}} + ^4\text{He}_m - ^4\text{He}_{\text{sol}})] \dots (\text{A2})$$

where R_{air} = $^3\text{He}/^4\text{He}$ ratio in the atmosphere.

Flow Divide and Contaminant Source Locations

Consider an unconfined aquifer with steady flow as shown in Figure 6. If the horizontal velocity is constant with depth conservation of mass requires that

$$V_o (\Delta X_f + \Delta X_1) = Z_2 V_2 \quad (\text{A3})$$

where V_o = vertical velocity at the water table (proportional

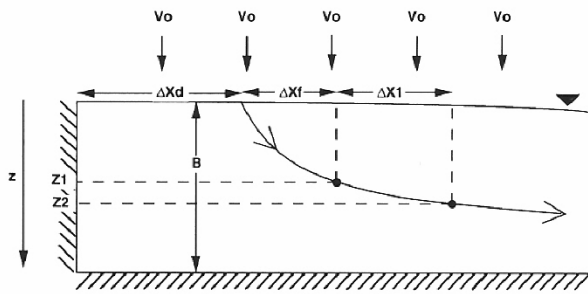


Fig. 6. Geometry of an unconfined aquifer used in the Vogel model.

to porosity); and V_2 = horizontal velocity at a distance $\Delta X_d + \Delta X_1$ from the flow divide. Also,

$$V_o \Delta X_d = (B - Z_2) V_2. \quad (A4)$$

Dividing (A3) by (A4) yields

$$\frac{\Delta X_f + \Delta X_1}{\Delta X_d} = \frac{Z_2}{B - Z_2}. \quad (A5)$$

Similarly, for a distance of $\Delta X_d + \Delta X_f$ from the flow divide

$$\frac{\Delta X_f}{\Delta X_d} = \frac{Z_1}{B - Z_1}. \quad (A6)$$

Equations (A5) and (A6) can then be solved for ΔX_f and ΔX_d .

Acknowledgments

This investigation was conducted for the Hazardous Waste Remedial Actions Program managed by Martin Marietta Energy Systems, Inc. for the U.S. Department of Energy under contract no. DE-AC05-84OR21400.

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