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Preliminary Investigation of Processes that Affect Source Term Identification

D. S. Wickliff
D. K. Solomon
N. D. Farrow

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Environmental Restoration Division
ORNL Environmental Restoration Program

Preliminary Investigation of Processes that Affect Source Term Identification

D. S. Wickliff
D. K. Solomon
N. D. Farrow

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EXECUTIVE SUMMARY

An important component of risk assessment is the source term, defined as the release rate of contaminants as a function of time and space. The source terms associated with burial areas on the Oak Ridge Reservation (ORR) are difficult to quantify because the disposal records are deficient and the hydrogeochemical system is complex. It may be possible to define the source term of an area hydrochemically, using water quality data from streams, storm flow, and groundwater. However, this approach requires an understanding of major processes that control subsurface contaminant transport.

Subsurface systems at the ORR consist of discrete fractures within a matrix of porous rock. When a contaminant is first introduced into fractured porous media, very large concentration gradients can occur between fractures and the surrounding porous matrix. Because of molecular diffusion, dissolved species can migrate into the porous matrix, even when no net transfer of fluid between fractures and matrix occurs. When the volume of matrix water is large relative to the volume of fracture water, this process, known as matrix diffusion, can result in substantial dilution and attenuation of migrating contaminants. However, once primary contaminant sources (i.e., waste trenches) diminish in strength, contaminants can diffuse out of the porous matrix into fracture pathways, resulting in secondary contaminant sources.

Solid Waste Storage Area (SWSA) 5 is known to be a significant source of tritium (^3H) to the White Oak Creek (WOC) watershed. Because ^3H mobility is not attenuated significantly by geochemical processes, the sustained ^3H discharge many years after disposal began suggests that matrix diffusion is an important process in SWSA 5. An area on the southeastern edge of SWSA 5, where a known contaminant plume exists, was selected for investigation to gain understanding of processes (particularly matrix diffusion) that may be affecting contaminant transport from primary waste sources to streams.

Tritium activities in the groundwater and soil core samples increase with depth with the highest activities found at the greatest depth below the water table. The vertical distribution of ^3H is very smooth, unlike what might be expected in a fractured and heterogeneous environment. There was also little difference between ^3H activities in groundwater samples and activities in pore water extracted from soil cores. Both the distribution and the agreement between groundwater and pore water activities suggest that diffusion, rather than advection through hydraulically active fractures, dominates contaminant transport mechanisms over the interval (0–3 m) sampled in this study.

The ^3H activity in stormflow is much less than observed in groundwater, indicating that storm flow is not as significant as groundwater in transporting ^3H from the burial ground to the stream in this area of SWSA 5. However, ^{90}Sr activities suggest that subsurface storm flow is more important for ^{90}Sr. Peak ^{90}Sr values do not coincide with peak ^3H values, which may indicate that ^{90}Sr and ^3H come from physically distinct primary sources.

Using graphical stream hydrograph separation, Solomon et al. (1991) estimated that 16% of the total ^3H release in Melton Branch for 1988 resulted from quick flow; thus, 84% entered as base flow via the saturated groundwater system. The occurrence of highest ^3H

activities in the deeper groundwater and core samples from the southeast portion of SWSA 5 is consistent with their results. The agreement between our results and the streamflow results is important in that it places considerable confidence in the ability to distinguish groundwater from storm flow discharge into streams by using graphical hydrograph separation methods.

The observed ^{3}H and ^{90}Sr values from SWSA 5 have been used to formulate a working hypothesis of contaminant transport, the role of matrix diffusion, and the existence of primary and secondary sources. The vertical profile of ^{3}H may be a result of upward diffusion from a hydraulically dominant fracture (or fractured zone) coupled with a small amount of lateral advective transport within the matrix. A hydraulically dominant fracture of high ^{3}H activity existing beneath the interval sampled would suggest that there is still a source upgradient supplying ^{3}H to the subsurface system and that the contaminant release from SWSA 5 to the stream will continue to increase until that source is depleted. This hypothesis is tentative, and additional data are required to make definitive statements.

A simple mathematical model was used to examine the general effects of matrix diffusion on contaminant transport in SWSA 5. The model accounts for one-dimensional transport along parallel fractures coupled with one-dimensional diffusion into and out of the surrounding matrix. The effects of matrix diffusion on contaminant transport are largely controlled by the flux of water in fractures relative to the mass of water stored in the porous matrix. Expected parameter values that bracket the range of fracture water flux relative to water mass in the matrix for SWSA 5 were used in the simulations. Simulations of the ^{3}H profile resulting solely from molecular diffusion bear a striking resemblance to the observed ^{3}H profiles in the study area, suggesting that diffusive processes are important at SWSA 5.

Although preliminary analysis of the ^{3}H data from SWSA 5 suggests that primary sources are still active (and thus the ^{3}H discharge to streams may continue to rise for some time), existing data do not allow a prediction of the response of the systems resulting from proposed remedial actions. For example, transport simulations (for nonsorbing contaminants) indicate that if the specific discharge is 5 m/year, the remediation of primary sources would result in improved water quality within several months and secondary sources could be removed by natural flushing within about 10 years. However, if the specific discharge is 1 m/year, improvements in water quality could lag remedial actions by more than 10 years and secondary sources by natural flushing could take more than 70 years. Additional sampling at greater depths (to determine the vertical extent of ^{3}H migration) along with point dilution and borehole measurements (to determine the specific discharge more precisely) will greatly enhance our ability to predict the system's response to proposed remedial actions.

The process of matrix diffusion has many far-reaching implications for environmental restoration on the ORR. The short-term effectiveness of remedial actions aimed at reducing the discharge of contaminants from subsurface to surface water systems depends critically on the mass of contaminants presently stored within the porous matrix (i.e., the strength of secondary sources relative to primary sources). If the contaminant mass within the matrix is small, source-level remediation such as grouting, compaction, and in situ vitrification would reduce contaminant discharge shortly after remediation. If the contaminant mass in the matrix is large, only remediations that eliminate both primary sources (e.g., trench leachate) and secondary sources (i.e., diffusion out of the matrix) will effectively reduce contaminant

discharge. However, if the secondary source is located below the water table, even techniques for hydrologic isolation such as local capping and French drains may be unsuccessful because groundwater will continue to move through the secondary source area.

1. INTRODUCTION

Solid Waste Storage Area (SWSA) 5 is known to be a significant source of contaminants, especially tritium (^3H), to the White Oak Creek (WOC) watershed. For example, Solomon et al. (1991) estimated the total ^3H discharge in Melton Branch (most of which originates in SWSA 5) for the 1988 water year to be 1210 Ci. A critical issue for making decisions concerning remedial actions at SWSA 5 is knowing whether the annual contaminant discharge is increasing or decreasing. Because (1) the magnitude of the annual contaminant discharge is highly correlated to the amount of annual precipitation (Solomon et al., 1991) and (2) a significant lag may exist between the time of peak contaminant release from primary sources (i.e., waste trenches) and the time of peak discharge into streams, short-term stream monitoring by itself is not sufficient for predicting future contaminant discharges. In this study we use ^3H to examine the link between contaminant release from primary waste sources and contaminant discharge into streams. By understanding and quantifying subsurface transport processes, realistic predictions of future contaminant discharge, along with an evaluation of the effectiveness of remedial action alternatives, will be possible.

Both primary and secondary contaminant sources exist in SWSA 5. Primary sources are original burial trenches in which contaminants are leached and begin to migrate through the subsurface. Secondary sources develop as contaminants migrate through the subsurface along permeable pathways and then diffuse into low permeability regions. Secondary sources become active as primary sources are removed (or diminish in strength) and contaminants begin to diffuse out of low permeability regions back into permeable pathways. The diffusive exchange between regions of high and low permeability is known as matrix diffusion and is discussed in detail in subsequent sections of this report. The selection of remedial actions depends critically on the relative contributions of primary vs secondary sources. For example, if primary sources have been depleted by natural flushing or biochemical transformations, remedial actions aimed at individual trenches (e.g., grouting, compacting, and vitrifying) will not be effective at reducing contaminant discharge.

While matrix diffusion will result in secondary sources once primary sources begin to decline, initially contaminant migration rates are highly attenuated by this process. As a result, maximum contaminant concentrations are reduced, but the total time required to remove contaminants by flushing increases substantially because of matrix diffusion. Thus, matrix diffusion can be considered beneficial during the early periods of contaminant release and migration but, in theory, can result in very long-term contaminant discharge. Waste disposal in SWSA 5 began in 1959, and the majority of disposal was completed by 1970. Because ^3H mobility is not attenuated significantly by geochemical processes, the sustained ^3H discharge some 30 years after disposal began suggests that matrix diffusion is an important process in SWSA 5.

The objectives of this study are (1) to characterize the subsurface movement of contaminants (primarily ^3H) with an emphasis on the effects of matrix diffusion, (2) to determine the relative strength of primary vs secondary sources, and (3) to establish a methodology capable of determining whether the ^3H discharge from SWSA 5 to streams is increasing or decreasing.

2. STUDY SITE CHARACTERISTICS

Most of SWSA 5 is moderately sloping, grass-covered hillsides draining into White Oak Creek (WOC) to the west and to Melton Branch and the Melton Branch tributary to the south and east (Fig. 1). SWSA 5 is underlain by the Conasauga Group, consisting of shaley limestones and shales striking generally east-west. Trenches were often located at right angles to the bedding strike to minimize collapse of the trench walls. As a result, most of the trenches are located parallel to the slope (Fig. 1).

Previous investigations found that the transport of ^{3}H and subsequent discharge to the streams surrounding SWSA 5 during periods of baseflow was spatially discrete. Stream transect sampling in 1988 along Melton Branch and Melton Branch tributary during baseflow conditions indicated that approximately 30% of the ^{3}H mass flow in Melton Branch was entering along a 61-m (200-ft) reach on Melton Branch and approximately 44.5% was entering along a 122-m (400-ft) reach on Melton Branch tributary (Fig. 1). Most of the ^{3}H in the Melton Branch tributary reach was found to be entering at a seep in the stream channel with low discharge but very high ^{3}H activity (370 μCi/L).

Lateral subsurface storm flow can form as a result of transient saturated conditions in shallow macropores (depth 1–2 m) during and following storms (Moore, 1988). During storm events, ^{3}H and ^{90}Sr discharges in Melton Branch increase dramatically. For example, the ^{3}H and ^{90}Sr mass flow in Melton Branch changed from 7.2 and 0.0026 Ci/d during base flow to 42 and 0.015 Ci/d at the hydrograph peak during a January 1988 storm (Solomon et al., 1991). Graphical hydrograph separation was used by Solomon et al. (1991) who found that during storms as much as 60% of the ^{3}H and 75% of the ^{90}Sr mass flow in Melton Branch resulted from quick flow (which is probably roughly equivalent to storm flow). However, on an annual basis Solomon et al. (1991) estimated that only about 16% of the ^{3}H and 27% of the ^{90}Sr discharge resulted from quick flow. Thus, both shallow storm flow and groundwater discharge are important transport pathways in SWSA 5.

In 1989 a survey of ^{3}H concentrations in evapotranspired water was conducted in the grassy southeast portion of SWSA 5. Elevated levels of ^{3}H were present over the whole area, with the highest activities found near the end of two long trenches (near Site 5, Fig. 2). The area between these trenches and the seep was selected to investigate the contaminant plume and to gain understanding of processes (particularly matrix diffusion) that may be affecting the transport of contaminants (primarily ^{3}H) from the burial grounds to streams.

In order to define the vertical profile and extent of ^{3}H, soil core and groundwater samples were collected from various depths at three locations (Fig. 2). One location, Site 5, is just below the trenches on the very edge of the grassy burial ground. Site 2 is downgradient in a wooded area, and Site 3 is on the floodplain of Melton Branch tributary approximately 10 m (33 ft) from the seep.

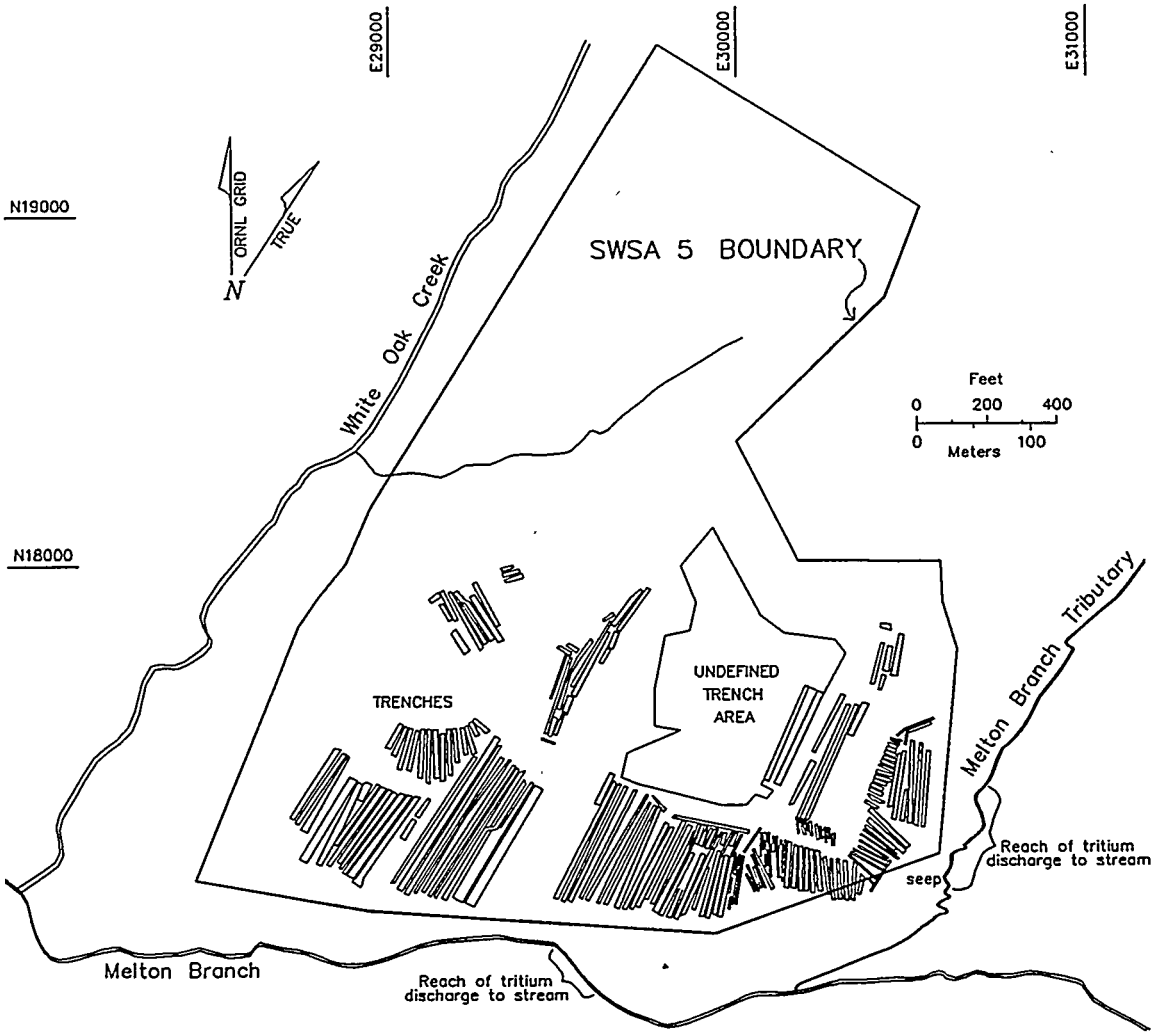

Fig. 1. Map of Solid Waste Storage Area (SWSA) 5.

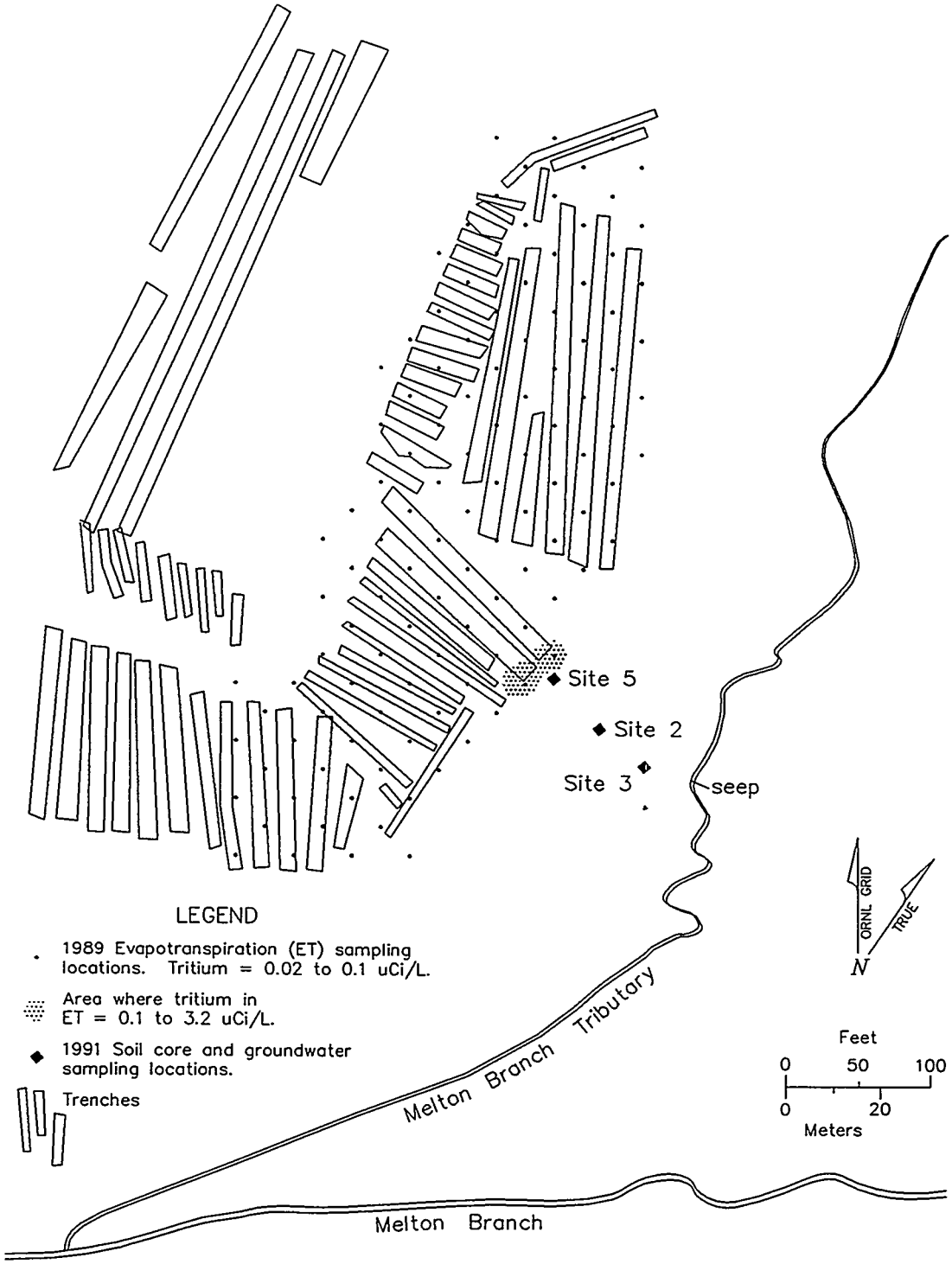

Fig. 2. Map of study area in southeast portion of SWSA 5.

3. METHODS

3.1 SAMPLE COLLECTION

3.1.1 Groundwater

Groundwater samples were collected in March and April 1991 from the saturated zone at each location using temporary drive point wells. The wells consisted of standard drill rods and a penetrometer point assembly. The points were modified with a groove near the top that served as a friction point to hold the point in place as the surrounding rod was withdrawn 10 cm to expose the screen for sampling (Fig. 3). A 61-cm (2-ft) stainless steel tube (1.3 cm OD) with rows of holes served as the screen. The drive points were driven to the first sample depth, the screen was exposed, the well was allowed to equilibrate, a water sample was collected, and then the device was driven to the next sample depth. This process was repeated until refusal depth (~3 m) was reached. A cluster of three or four individual wells was generally driven to two different sampling depths at each location. Individual wells at a given location were placed <60 cm apart.

An air-operated heavy-duty post driver, Rhino (trade name) model PD-135, weighing 136 lb, supported by a boom, was used to install wells at the various depths (Fig. 4). The air-operated driver uses 64 cfm with air pressure at 100 psi and delivers up to 1700 blows per minute. Sampling depths were determined from measurements of the point assembly and drill rods relative to a predetermined reference point.

A 0.76 cm (1/4 in.) OD polypropylene tube was inserted into the screen of each well, and a small peristaltic pump with silicon tubing was used to sample the wells. Generally, wells were pumped dry, allowed to recover partially, and then sampled. Sample volumes for ^{3}H analysis varied from 10 to 100 mL depending on the amount of water in the well. When possible, 20- to 100-mL samples were also collected for ^{90}Sr analysis. Samples for ^{90}Sr analysis were either filtered in the field using in-line filters (0.45 μm) as the water was pumped from the wells or filtered (0.45 μm) in the laboratory soon after collection. Samples for ^{90}Sr analysis were acidified (pH <2) with HCl after filtration.

After the initial sampling at each location, the drive point wells were removed with the exception of one well (2-C) at Site 2 and one well (5-D) at Site 5. These wells have been equipped with pressure transducers connected to a data logger in order to measure water level responses during and following rain events. Additional samples were collected from these wells following a rain event in June 1991.

3.1.2 Soil Cores

Most soil cores were collected using a 8.9-cm-diam (3.5-in.-diam) soil tube with a polyvinyl chloride (PVC) liner. The soil tubes were either 61 cm (2 ft) or 122 cm (4 ft) in length attached to 152-cm (5-ft) drill rods. At the upper location, Site 5, a smaller split barrel sampler (5.1 cm diam) with liner was also used to sample at greater depths. The Rhino, air-operated driver was used to drive the core tubes and split barrel sampler to the appropriate depths. Depth of penetration (assumed to be the bottom of the core) was determined from measurements relative to the same reference point used for the drive point wells.

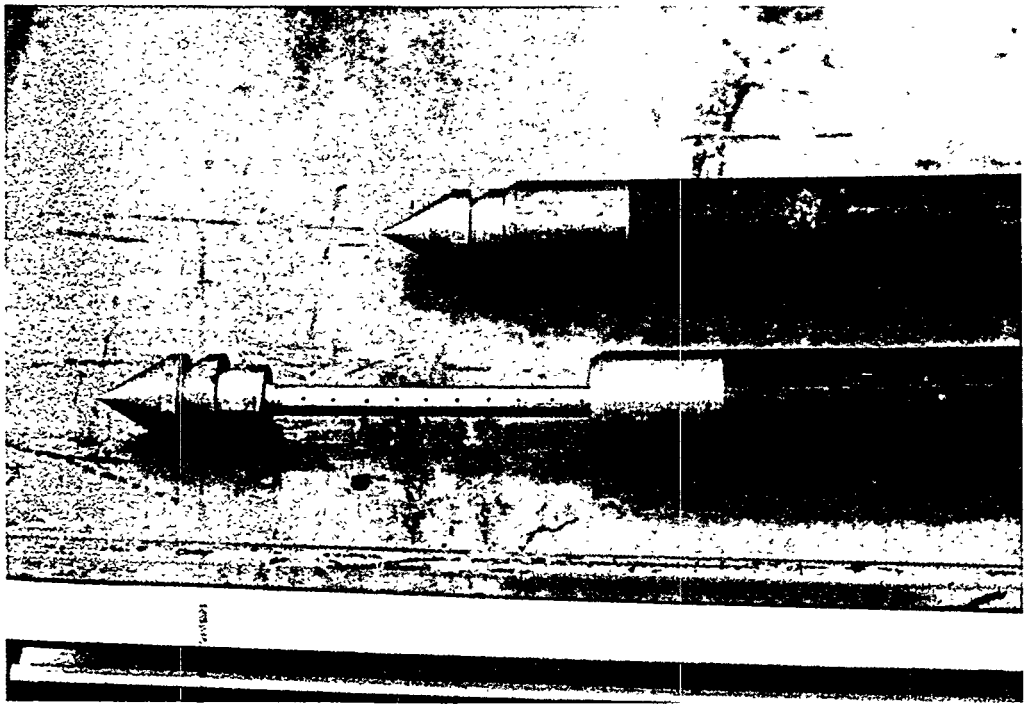

Fig. 3. Photo of drive point wells.

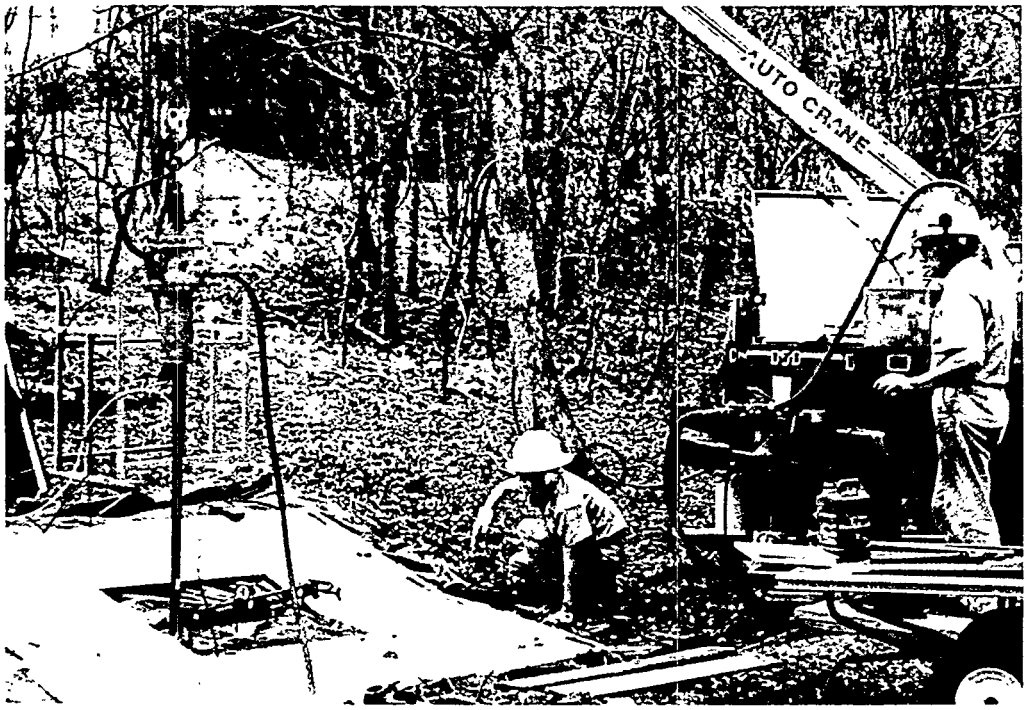

Fig. 4. Photo of drive point well installation at Site 2.

The liner and soil core were removed from the tube and sectioned into lengths typically 10 to 20 cm after corrections for compaction and fall-in had been made. Specific sample intervals were removed from the liner and saved by wrapping them tightly in parafilm and then placing them in airtight plastic jars.

3.1.3 Subsurface Storm Flow

Storm flow tube collectors were installed to collect shallow subsurface storm flow at discrete depths as it moves laterally and downward in the soil. Each collector is a small well containing a reservoir that holds the sample until the time of collection. Three storm flow collectors with sampling intervals at 20–30, 50–60, and 80–90 cm were installed in core holes at each location (Fig. 5). The bottom of the core hole, and up to 5 cm below the screened interval, was filled with bentonite. Sand was then packed from 5 cm below to 5 cm above the screened interval. Additional bentonite was added, and then a bentonite/soil mixture was packed in near the ground surface.

Storm flow samples for ^{3}H analysis and occasional ^{90}Sr analysis were collected from the reservoirs by using a small peristaltic pump. When storm flow tubes were below the water table, samples were collected following the same procedures used for groundwater collection from the drive point wells.

3.2 SAMPLE ANALYSIS

3.2.1 Tritium

Because of the high ^{3}H activity, groundwater samples were usually diluted by a factor of 10 prior to analysis. A procedure adapted from Environmental Protection Agency (EPA) Method 906.0 (EPA 1980) was used for the groundwater samples. A 100-mL aliquot was distilled in an alkaline permanganate solution. Water was extracted from the soil core samples by heating 30 to 40 g of soil and condensing and collecting the distillate. Wet and dry weight measurements were made so that soil moisture could be determined. The soil core distillates were often diluted because of the high ^{3}H activity.

Aliquots of 8 mL of the groundwater and diluted soil core distillates were mixed with 12 mL of Insta-Gel liquid scintillation cocktail and counted for 100 min on a Packard 4640 liquid scintillation counter. A series of three EPA standards of known activity and a blank were distilled and counted using a quench-corrected efficiency curve. The ratio of the blank-corrected average of the known activities and the activities calculated from the efficiency curve served as a calibration factor for relating the instrument efficiency curve and the distillation procedure.

3.2.2 Strontium-90

Cerenkov radiation counting was used to analyze the groundwater samples for ^{90}Sr (Ross, 1969). This technique utilizes the high energetic beta particle emitted during the decay of ^{90}Y, which is the daughter of ^{90}Sr. Aliquots of 20 mL of each sample were placed into plastic scintillation vials and analyzed in a liquid scintillation counter for 100 min (Larsen, 1981).

The ^{90}Sr activity in each sample was calculated by comparing the net count rate of the sample to that of a ^{90}Sr-^{90}Y standard after correcting for background blanks.

The presence of ^{60}Co or ^{137}Cs produces Compton electrons which can cause interference and produce a false-positive signal in the ^{90}Sr analyses (Larsen, 1981). A few of the groundwater samples, filters, and soil cores were scanned for gamma-emitting radionuclides primarily to determine whether or not ^{60}Co or ^{137}Cs was present. Soil cores had detectable but low ^{137}Cs activity. However, it was assumed that there was no interference with the ^{90}Sr analyses, because ^{60}Co and ^{137}Cs activities were not detected in the groundwater samples or the filters.

Soil cores samples were not analyzed for ^{90}Sr but may be in the future. Soil cores are being preserved at 4°C in parafilm and airtight containers.

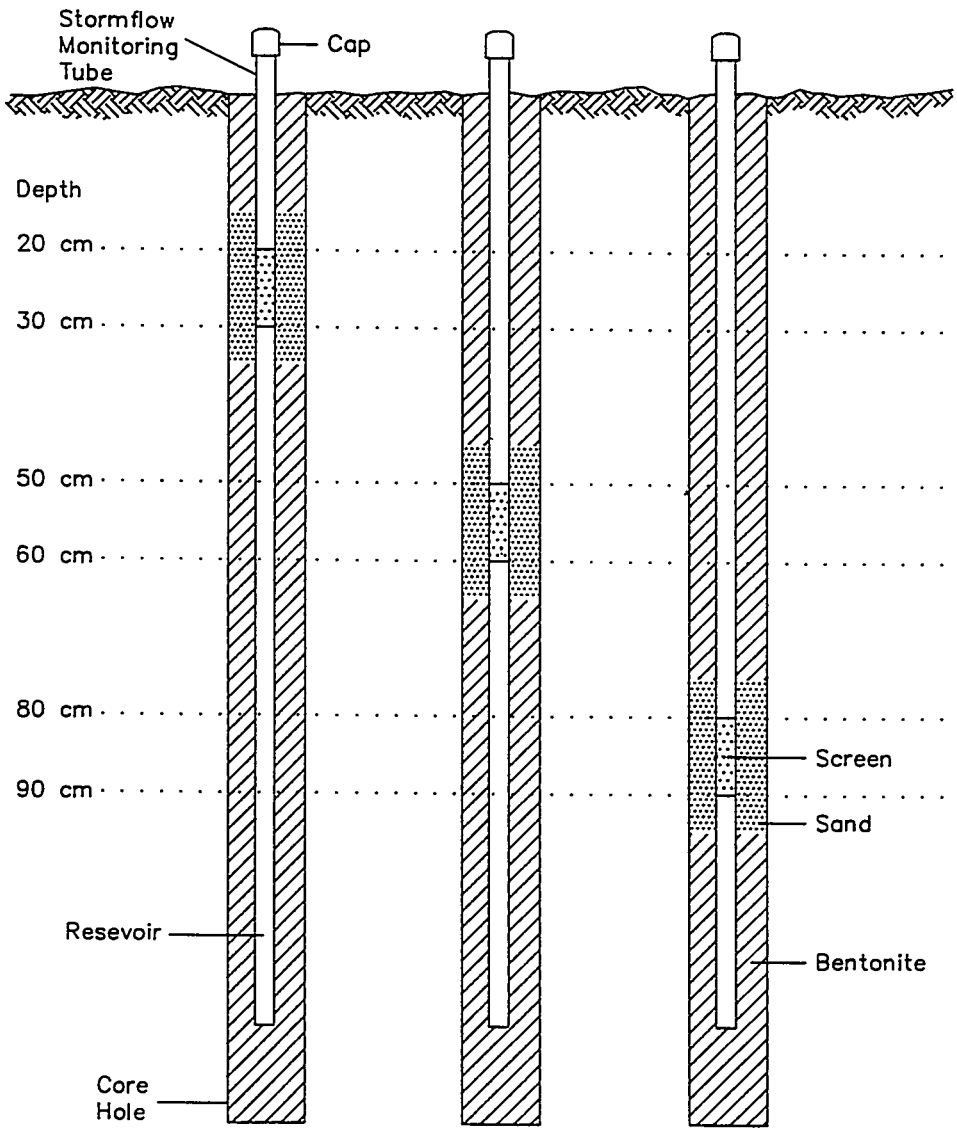

Fig. 5. Diagram of stormflow monitoring tubes.

4. RESULTS

4.1 FIELD OBSERVATIONS

Most of the background radiation (primarily beta) in the area seemed to be a result of radionuclides (probably ^{90}Sr) concentrated in the vegetation and leaf litter on the ground surface. The ground surface around Site 2 read about 700 cpm on a radiation survey meter. Soil cores at Site 2 ranged from about 350 cpm in the top 20 cm to about 80 cpm in the deeper cores. Cores at Site 5, nearest the trench, had elevated counts in the deeper samples.

Table 1 lists the soil core intervals that were collected from each location for ^{3}H analysis and soil moisture determination. During the time of coring at Site 2, the water table was only about 58 cm (1.9 ft) below ground surface so that most of the samples were from the saturated zone. The middle core intervals were quite clayey, and the last two samples were mostly weathered shale.

The depth of soil core collection at Site 3 was limited because the water table was essentially at ground surface and the saturated conditions made it difficult to retain the core within the sampling tubes. When trying to collect deeper samples, cores would slide downward back into the hole. The use of a piston coring device should solve this problem for future sampling. The deepest soil core sample (110–120 cm) contained some shale. Soil cores were mostly bluish gray clay, suggesting fairly anaerobic conditions. An orange precipitant formed in the groundwater samples collected from all sites that were not acidified, indicating that reducing conditions exist below the water table. Later when sampling storm flow tubes at Site 3, an odor that may have been hydrogen sulfide was noticed. Because of the shallow water table at Site 3, storm flow sampling tubes simply collect groundwater rather than separate subsurface storm flow. A difference in hydraulic heads was measured in drive point wells at different depths at Site 3, and an upward hydraulic gradient of 1.4 was calculated.

The 80- to 90-cm core sample from Site 5 was very clayey. The 140- to 150-cm and the 203- to 208-cm core samples were relatively dry orange-colored clay, and the deepest two samples were mostly weathered shale.

There was a significant difference between filtering groundwater samples and filtering shallow subsurface storm flow samples. Apparently, the shallow subsurface storm flow carries more small suspended particles or colloids which clog the 0.45-μm filters. Therefore, storm flow may be important in transporting radionuclides that are adsorbed to fine particles.

4.2 TRITIUM DISTRIBUTION

Tritium activities in the groundwater samples collected at the time of coring increase with depth and range from 47 to 279 μCi/L (Fig. 6). The highest concentrations were found at Site 3, where samples were collected at the greatest depth (~170 cm) below the water table. Tritium activities in water extracted from the soil cores also increased with depth (Fig. 7). The vertical distribution of ^{3}H at each location is shown in Figs. 8 through 10.

Table 1. Soil core samples collected from SWSA 5

Location	Interval depth (cm)	Date	Elevation of sample (ft)	% Soil Moisture
Site 2	0 - 20	26 Mar 91	781.58 - 780.92	36
	20 - 40		780.92 - 780.27	28
	40 - 60		780.27 - 779.61	30
	60 - 80		779.61 - 778.96	31
	80 - 90		778.96 - 778.63	29
	90 - 100		778.63 - 778.30	28
	100 - 110		778.30 - 777.97	28
	136 - 146		777.12 - 776.79	32
	166 - 176		776.13 - 775.81	31
	196 - 206		775.15 - 774.82	23
	213 - 223		774.59 - 774.26	18
Site 3	0 - 10	9 Apr 91	777.43 - 777.10	54
	10 - 20		777.10 - 776.77	37
	20 - 30		776.77 - 776.45	*
	50 - 60		775.79 - 775.46	*
	80 - 90		774.81 - 774.48	33
	90 - 100		774.48 - 774.15	33
	100 - 110		774.15 - 773.82	33
	110 - 120		773.82 - 773.49	36
Site 5	20 - 30	23 Apr 91	787.10 - 786.78	36
	50 - 60		786.12 - 785.79	24
	80 - 90		785.14 - 784.81	29
	110 - 120		784.15 - 783.82	29
	140 - 150		783.17 - 782.84	23
	203 - 208		781.10 - 780.94	29
	274 - 279		778.77 - 778.61	33
	320 - 330	24 Apr 91	777.26 - 776.93	19

* not determined

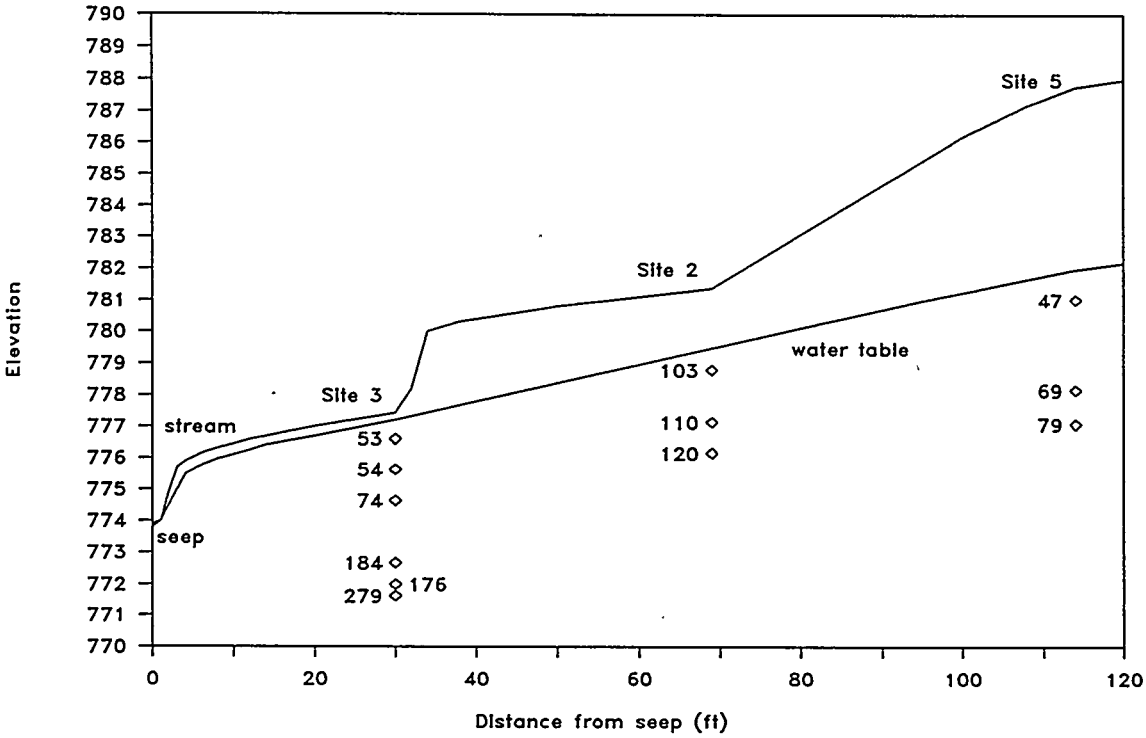

Fig. 6. Distribution of ^3H activity (μCi/L) in groundwater samples.

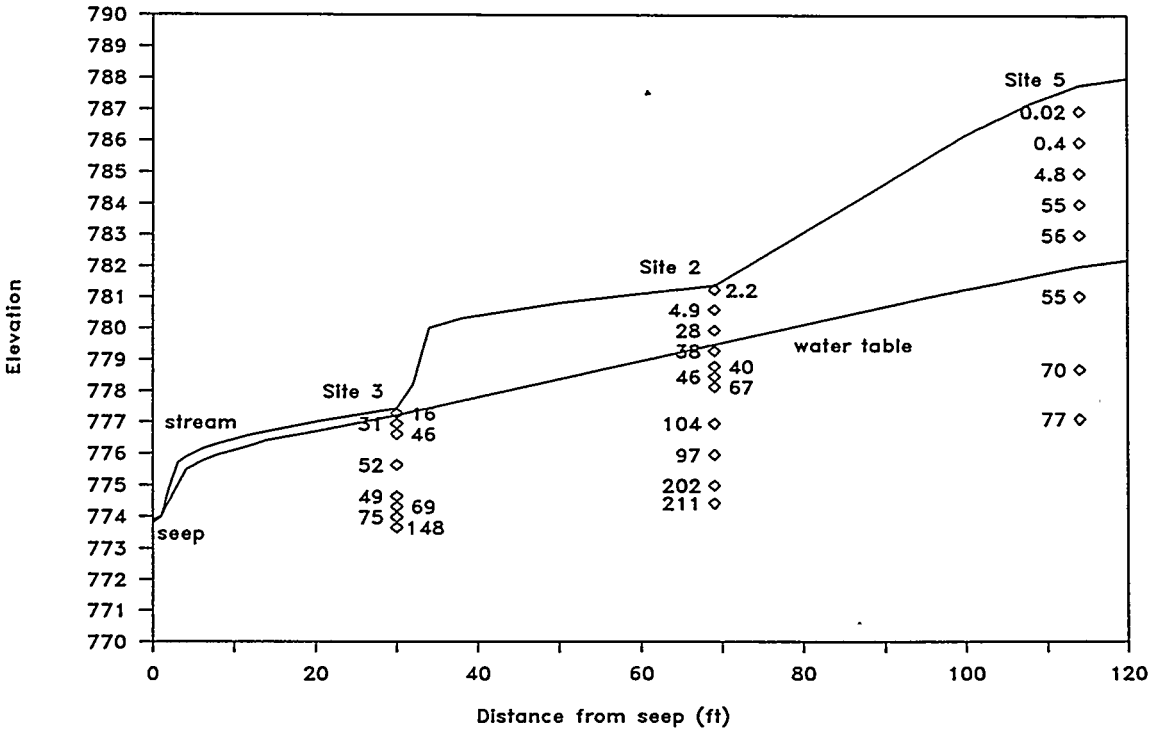

Fig. 7. Distribution of ^3H activity (μCi/L) in water extracted from soil core samples.

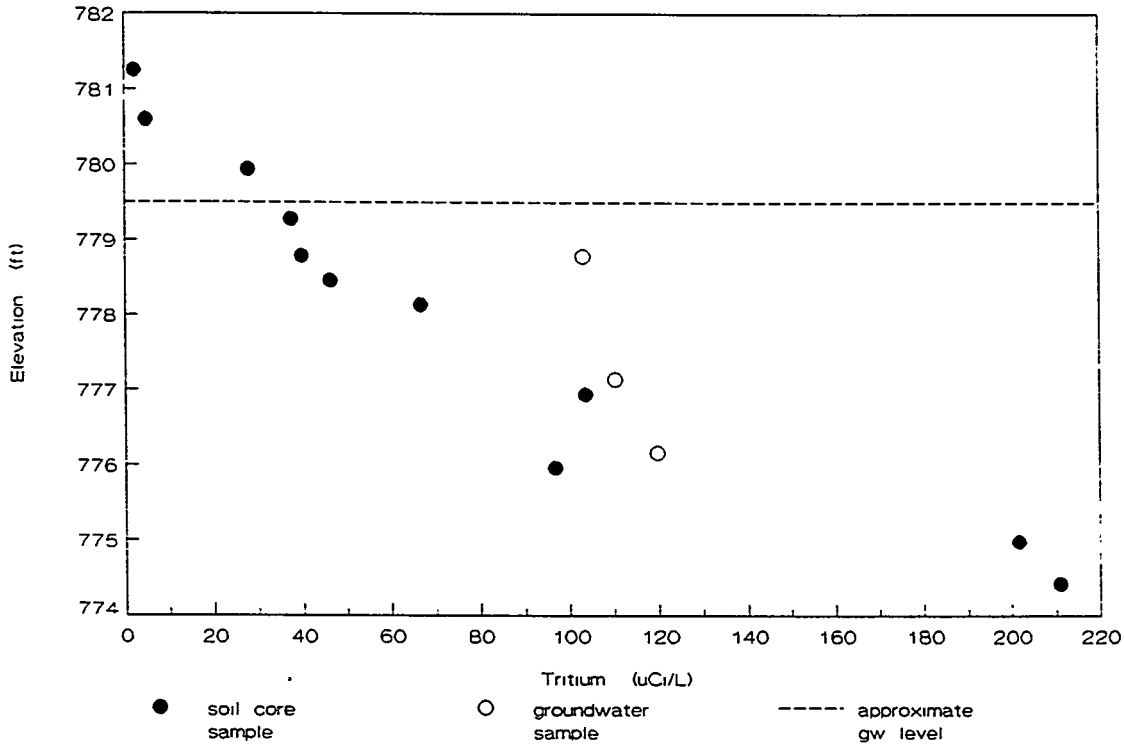

Fig. 8. Vertical distribution of ^3H at Site 2.

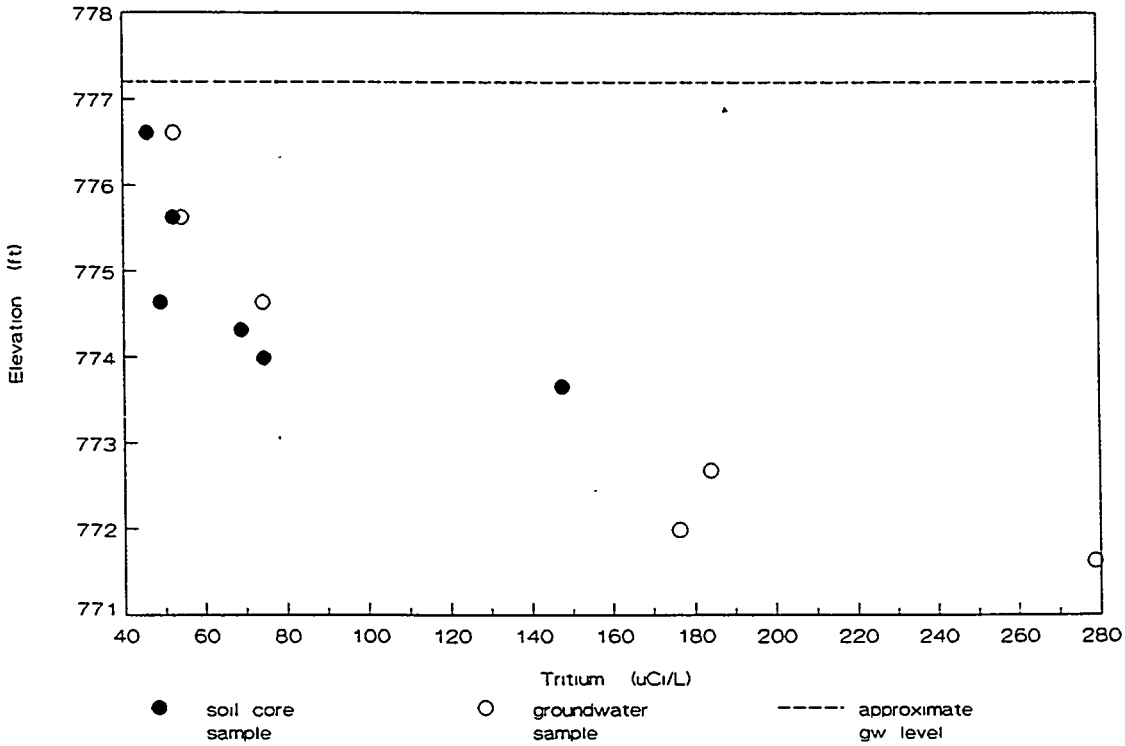

Fig. 9. Vertical distribution of ^3H at Site 3.

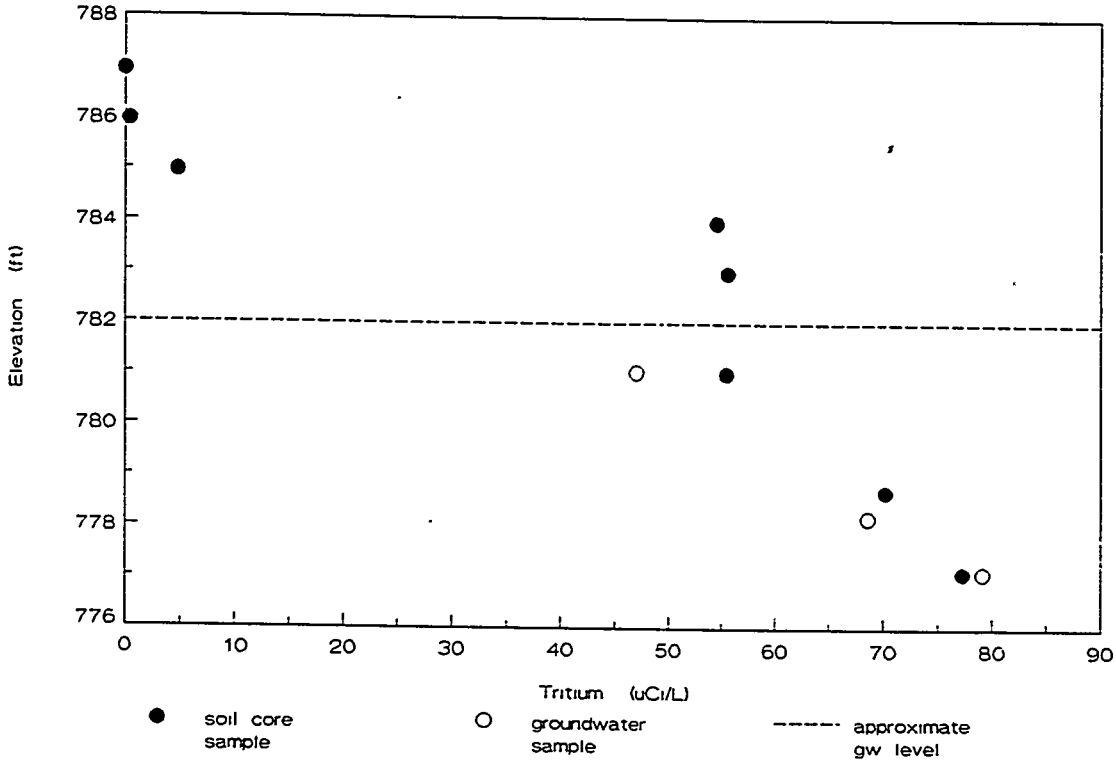

Fig. 10. Vertical distribution of ^3H at Site 5.

Samples were collected for ^{3}H from wells at Site 2 before, during, and after a 5.8-cm (2.3-in.) rain occurring on March 28 and 29, 1991. Samples were also collected from the three storm flow monitoring tubes. The deepest storm flow tube (80- to 90-cm depth) was below the water table even before the rain. Water levels were not monitored during the rain but likely rose to the level of the other two tubes. Tritium activities in samples from the upper two storm flow tubes ranged from about 5 to 10 μCi/L. These values are an order of magnitude lower than values from the saturated zone (Fig. 11). The decrease in ^{3}H activities in the shallower wells also suggests that rainwater was recharging and diluting the upper portion of the saturated system (Fig. 11). Activities in the deepest well, however, increased in the three days following the rain.

Storm flow at Site 5 occurred only in the top 30 cm and had a ^{3}H activity of <0.1 μCi/L. The deeper storm flow tubes remained dry during the rain.

4.3 STRONTIUM-90 DISTRIBUTION

The distribution of ^{90}Sr (Fig. 12) in the groundwate r from the study site was quite different from the ^{3}H distribution. The highest concentrations were found at Site 5 closest to the trench and ranged from 15.3 to 18.7 nCi/L (Table 2). Lower ^{90}Sr activities were found at Sites 2 and 3, with near-background activities in samples collected from the greatest depths below the water table (Fig. 12 and Tables 2 and 3). Storm flow samples from 20- to 30-cm depth at Site 5 had relatively low activities compared with storm flow samples collected further downgradient at Sites 2 and 3 (Tables 2 and 3). The water table at Site 3 is essentially at ground surface; therefore, the samples from the storm flow tubes are really representative of shallow groundwater and not a separate perched water. Maximum groundwater levels monitored at Site 2 during rains on June 14 and 26, 1991 (Table 3), indicate that samples from the storm flow tubes at Site 2 probably represent a mixing between the groundwater and subsurface storm flow.

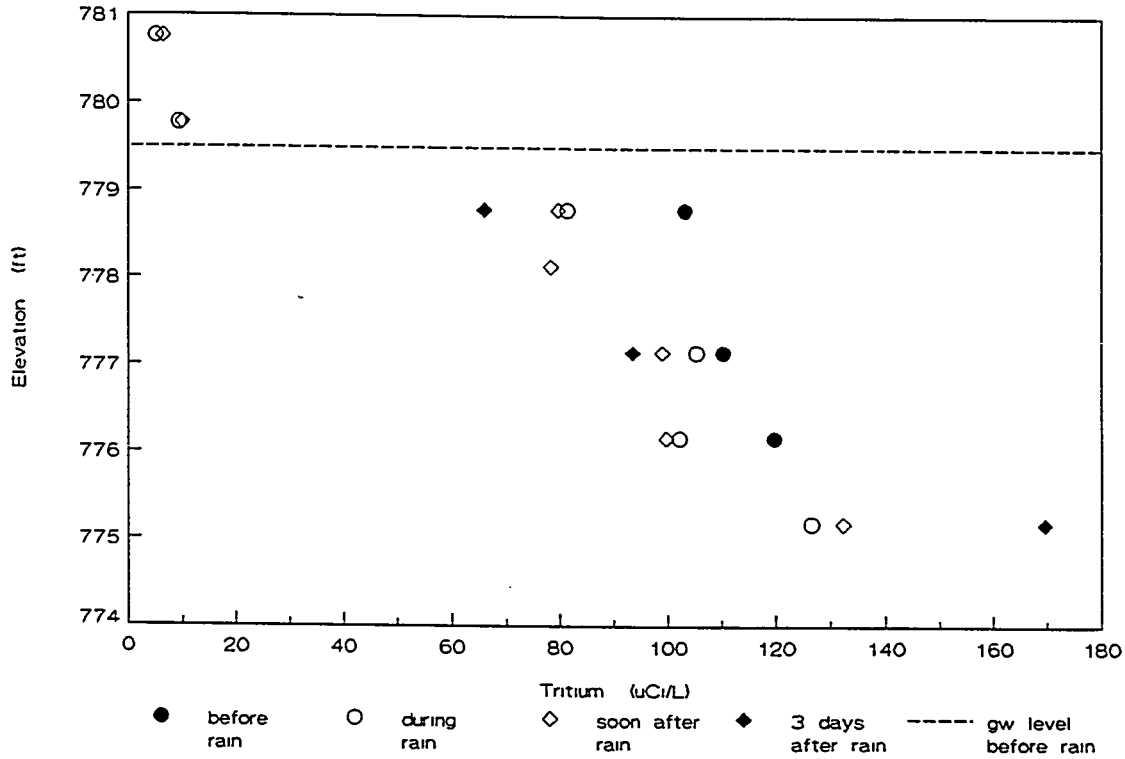

Fig. 11. Vertical distribution of ^{3}H at Site 2 before, during, and after rain.

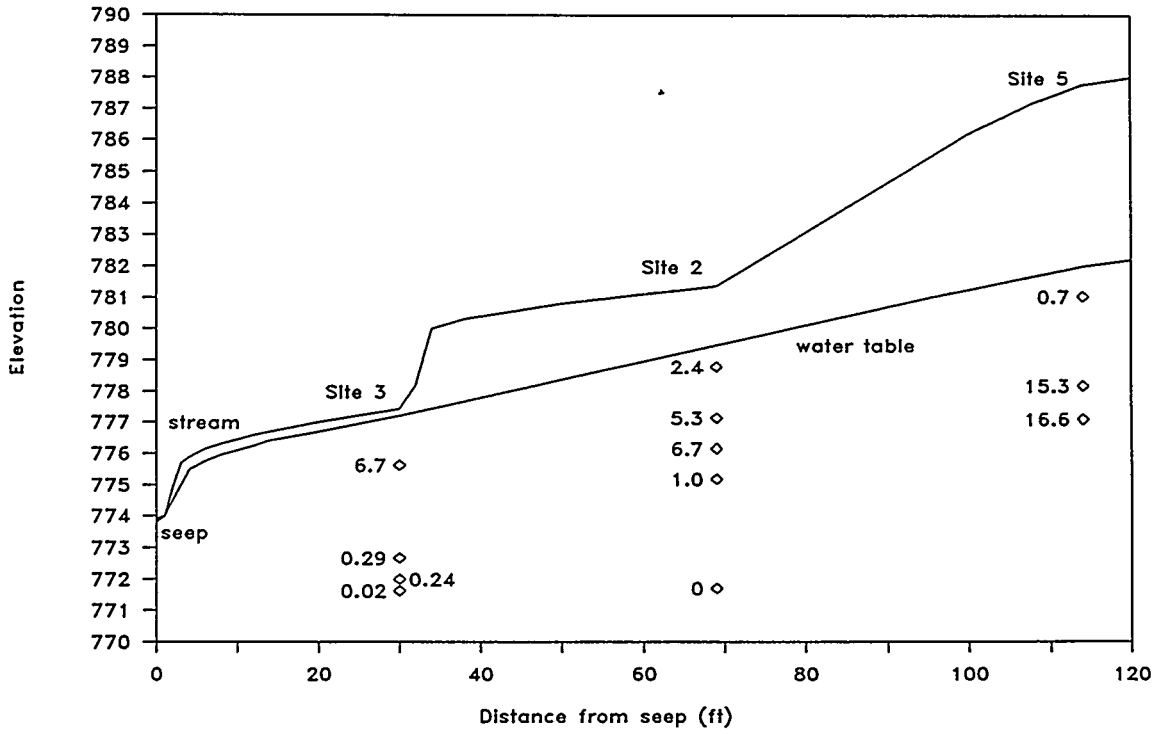

Fig. 12. Distribution of ^{90}Sr activitiy (ηCi/L) in groundwater samples.

Table 2. Strontium-90 activity (ηCi/L) in groundwater samples at Sites 3 and 5

Well No.	Interval depth (cm)	Elevation of sample (ft)	11Apr91	26Apr91	14Jun91[a]	26Jun91[b]
3-S	20 - 30	776.77 - 776.45			6.36	6.66
3-S	50 - 60	775.79 - 775.46	6.74		7.67	7.50
3-S	80 - 90	774.81 - 774.48			8.35	8.42
3-A	140 - 150	772.84 - 772.51	0.29			
3-B	161 - 171	772.15 - 771.82	0.24			
3-C	172 - 182	771.79 - 771.46	0.02			
5-S	20 - 30	787.10 - 786.78			0.1	0.09
5-B	200 - 210	781.20 - 780.87		0.66		
5-D	287 - 297	778.34 - 778.02		15.33		18.69
5-C	320 - 330	777.26 - 776.93		16.59		

[a] Sampled after 5.1 cm rain.
[b] Sampled after 4.2 cm rain.

Table 3. Strontium-90 activity (ηCi/L) in groundwater samples at Site 2

Well No.	Interval depth (cm)	Elevation of sample (ft)	29Mar91[a]	2Apr91[b]	14Jun91[c]	26Jun91[d]
2-S	20 - 30	780.92 - 780.60	3.01		0.64	1.12
2-S	50 - 60	779.94 - 779.61			1.9	2.92
2-S	80 - 90	778.96 - 778.63		2.41	3.45	3.16
2-C	130 - 140	777.31 - 776.99	5.64	5.31		3.99
2-D	160 - 170	776.33 - 776.00	6.72			
2-A	190 - 200	775.35 - 775.02	1.56	1.00		
2-B	296 - 306	771.87 - 771.54		0.00		

[a] Sampled during 5.8 cm rain
[b] Sampled 3 days after 5.8 cm rain
[c] Sampled after 5.1 cm rain. Water table = 779.2 ft (max. = 780.5 ft)
[d] Sampled after 4.2 cm rain. Water table = 780.2 ft (max. = 780.7 ft)

5. DISCUSSION

5.1 MATRIX DIFFUSION

The classical description of solute transport through porous media assumes that the solid portions of the subsurface are not porous. In granular porous media this assumption is often adequate because the primary porosity of solid particles (i.e., sand grains) is small. In contrast to granular porous media, subsurface systems on the Oak Ridge Reservation consist of discrete fractures within a matrix of porous rock. Because the permeability of discrete fractures is much greater than the rock matrix, the majority of fluid flow occurs through fractures; however, because the rock matrix is porous, the majority of fluid mass resides within the porous rock matrix. Although the bulk movement of fluid between fractures and matrix is probably small, molecular diffusion can transfer dissolved contaminants between fractures and the matrix. This process, known as matrix diffusion, is now commonly cited in research papers but is seldom recognized in applied studies.

When a contaminant is first introduced into a fractured porous media, very large concentration gradients can occur between fractures and the surrounding porous matrix. Because of molecular diffusion, dissolved species can migrate into the porous matrix, even when no net transfer of fluid between fractures and matrix occurs. When the volume of matrix water is large relative to the volume of fracture water, the diffusive exchange can result in substantial dilution of migrating contaminants. Because the majority of contaminant transport occurs through fractures, one effect of matrix diffusion is to reduce contaminant mobility. This apparent retardation is greatest when contaminants are first introduced and continually declines as matrix water becomes more and more concentrated with contaminants.

The effects of matrix diffusion on contaminant transport depend on a variety of parameters that are illustrated in Fig. 13. The matrix porosity (θ_m) is defined as the volume of pores contained within a specified volume of porous matrix. Included in this definition is the porosity that results from dead-end fractures. The fracture fluid velocity (V_f) is defined as the average velocity within hydraulically active fractures, and the matrix fluid velocity (V_m) is the average linear velocity within the matrix. The matrix fluid velocity is often negligible compared with the fracture fluid velocity. The specific discharge for the bulk porous media is defined as the fluid discharge per unit area of bulk porous media and includes flow through both fractures and matrix. This includes both the cross-sectional area of fractures and the matrix (Fig. 13). If flow through the matrix is insignificant, the specific discharge is related to the fracture fluid velocity by

$$q = V_f \theta_e$$

where θ_e is the effective porosity. When the fracture spacing and aperture are spatially constant, the effective porosity is given by

$$\theta_e = \frac{2b}{2B}$$

where $2b$ is the fracture aperture and $2B$ is the fracture spacing. Since fracture apertures are generally much less than fracture spacings, the effective porosity can be small, giving rise to

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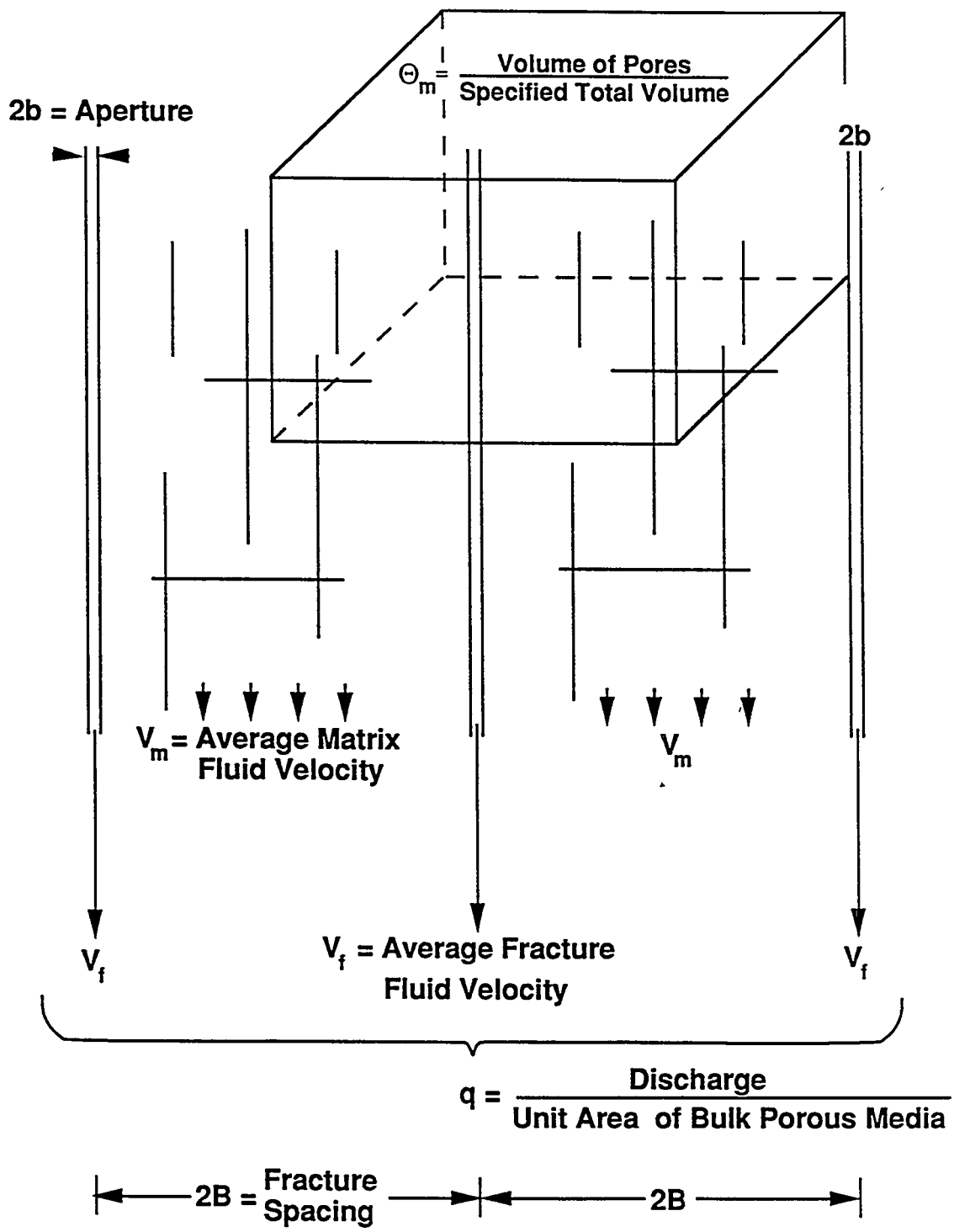

Fig. 13. Definition of several important parameters for groundwater flow and contaminant transport in fractured systems.

large fluid velocities even when the bulk specific discharge is small. For example, assuming a fracture aperture of 1 mm, a fracture spacing of 1 m, and a specific discharge of 1 m/year, we calculate a fracture fluid velocity of 1000 m/year.

Although fracture fluid velocities can be very large, the total water mass within fractures is generally insignificant compared with the water mass within the matrix. For example, if we assume a matrix porosity of 20%, a 1-mm fracture aperture, and a 1-m fracture spacing, a unit volume of bulk porous media would contain 200 parts matrix water to 1 part fracture water. Thus, diffusive transfer between fractures and matrix can result in a substantial dilution of contaminants being transported through fractures.

As contaminants first enter a fractured porous media, large concentration gradients exist because fractures contain a finite contaminant concentration while the matrix is at zero concentration. If the contaminant source is removed and uncontaminated water begins to flow through the fractures, contaminants will begin to diffuse from the matrix back into fractures, resulting in secondary contaminant sources. However, the concentration gradient for diffusing out of the matrix can never be as large as the concentration gradient that existed when the contaminant was entering the matrix. Thus, the time required to remove contaminants by outward diffusion can be substantially longer than the time required to enter the matrix.

5.2 PRELIMINARY EVALUATION OF RESULTS FROM SWSA 5

The observed ^{3}H and ^{90}Sr values have been used to formulate a working hypothesis of contaminant transport, the role of matrix diffusion, and the existence of primary and secondary sources in SWSA 5. Although this hypothesis is consistent with most of our data, alternative explanations are possible and additional data are required in order to make definitive statements. Thus, the interpretations presented in this section are subject to change and should not be considered final.

The vertical distribution of ^{3}H at each monitoring site (Figs. 8 through 10) is very smooth, unlike what might be expected in a fractured and heterogeneous environment. There was little difference between ^{3}H activities in the samples from piezometers (that were collected between rain events) and pore water extracted from soil cores. When piezometers are screened in zones with hydraulically active fractures, water samples will consist primarily of fracture water. Although pore water extracted from cores includes both matrix and fracture water, the mass of water in the matrix is large relative to the fracture water, and thus water extracted from cores effectively represents matrix water. If subsurface contaminant transport is occurring predominantly along fractures, the distribution of ^{3}H would vary depending on whether the wells intercepted fractures or whether they sampled less-permeable zones. The close agreement between samples from piezometers and samples from cores suggests that advective transport is subordinate to diffusion over the intervals sampled in this study.

Unlike advective transport in heterogeneous systems, diffusive transport can result in a relatively smooth contaminant distribution. Diffusion is much less sensitive to physical heterogeneities than is advective transport because the mean free path of molecules in thermal motion is much smaller than the radii of pores in the subsurface (Hillel, 1980, pp.

277). Thus, the relatively smooth ^3H profiles suggest that diffusion is an important transport mechanism in SWSA 5.

Samples from piezometers were also collected before, during, and after a rain event that occurred in March 1991 (Fig. 11). The ^3H activity of samples near the water table declined while the ^3H activity of the deepest sample increased as a result of the rain event. The general trend of increasing ^3H activity with depth did not change during or after the event; however, the observed temporal variations suggest that at least a small amount of advective transport occurs within the sampled interval.

The observed temporal and spatial ^3H distributions may be a result of upward diffusion from a hydraulically dominant fracture (or fractured zone) coupled with a small amount of lateral advective transport within the matrix. This scenario is illustrated schematically in Fig. 14 in which we envision principal fracture pathways that connect primary sources to discharge points in the stream. If primary ^3H sources are still active, the ^3H activity in fracture water would be greater than in the surrounding soil matrix. However, if the primary source has been depleted, fractures would then be transporting water with lower activity and flushing ^3H from the soil matrix. Thus, a comparison of the ^3H activity in the most hydrologically active regions with the ^3H activity in the matrix can be used to determine whether or not primary sources are still active. Unfortunately, it was not possible to collect samples from deeper depths with the coring technique used in this study; however, deeper samples can be collected with a different technique as outlined in Sect. 6 of this report. The ^3H activity measured in the seep in Melton Branch tributary in 1988 (370 μCi/L) was greater than that measured in any of the groundwater or pore water samples, suggesting that a hydraulically dominant fracture of high ^3H activity may exist beneath the interval sampled in this study. This suggests that there is still an upgradient source supplying ^3H to the subsurface system and that the contaminant release from SWSA 5 to the stream will continue to increase until that source is depleted. However, this hypothesis is tentative, and confirmation requires additional work as outlined in Sect. 6.

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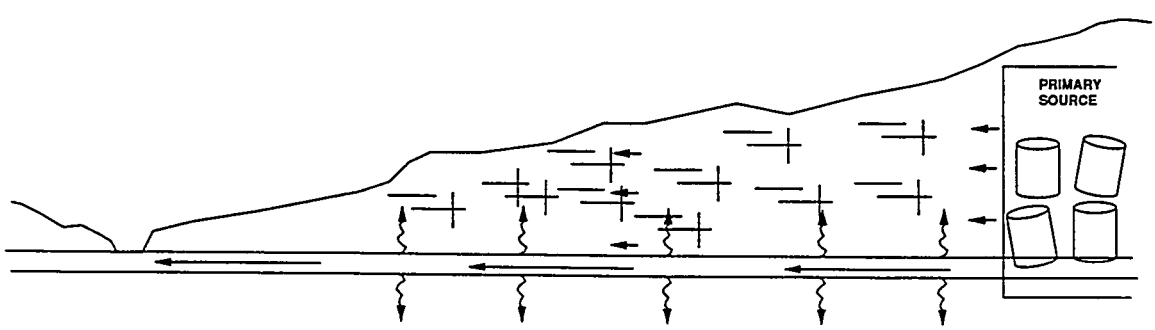

Fig. 14. Conceptual model of groundwater flow and contaminant transport at SWSA 5 study area.

Although a perched water table, indicating the presence of storm flow, was observed at Site 5 and possibly Site 2, the ^3H activity in storm flow is much less than that observed in groundwater. Thus, storm flow does not appear to be as significant as groundwater in transporting ^3H from the burial ground to the stream in this area of SWSA 5. This observation does not preclude the possibility that a large water flux occurs in the storm flow zone. The occurrence of high ^3H activities in groundwater is consistent with the results of Solomon et al. (1991). Using graphical stream hydrograph separation, they estimated that 16% of the total ^3H release in Melton Branch for 1988 resulted from quick flow; thus, 84% entered as base flow via the saturated groundwater system. The agreement between the subsurface results from this study and the streamflow results from Solomon et al. (1991) is important in that it places considerable confidence in our ability to distinguish groundwater from storm flow discharge into streams by using graphical hydrograph separation methods.

Strontium-90 activities in samples from the storm flow monitoring tubes (Tables 2 and 3) suggest that subsurface storm flow is more important for ^{90}Sr transport than for ^3H. At each monitoring site, peak ^{90}Sr values occur near the water table, and the highest values were observed at Site 5, which is the closest to burial trenches. Peak ^{90}Sr values do not coincide with peak ^3H values, which may indicate that ^{90}Sr and ^3H come from physically distinct primary sources (i.e., the ^{90}Sr source may be shallow in nearby trenches, whereas the ^3H source may be more distant and at greater depth). The observed ^{90}Sr distribution may be a result of a small amount of advective transport within the sampled interval. The higher activities near the trenches reflect ^{90}Sr being attenuated by sorption onto clay. Bioaccumulation of ^{90}Sr by trees, shrubs, and other plants may also play an important role in the transport and attenuation of ^{90}Sr.

5.3 MODELING RESULTS

We have investigated the effects of matrix diffusion on contaminant transport in SWSA 5 by using a simple mathematical model that accounts for one-dimensional transport along parallel fractures coupled with one-dimensional diffusion into and out of the surrounding matrix. The geometry of the modeled system is shown in Fig. 15, in which it is assumed that a system of parallel fractures intersects primary contaminant sources and conducts water and contaminants to discharge points in streams. Neglecting hydrodynamic dispersion, contaminant transport in the fracture is governed by (Sudicky and Frind, 1982)

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial Z} + \lambda C - \frac{\theta_m D\tau}{b}\frac{\partial C}{\partial X}\Big|_{x=b} = 0 \qquad (1)$$

subject to

$$C(Z,0) = 0 \qquad 0 \le Z < \infty \qquad (1a)$$

$$C(0,t) = C_o(t) \qquad (1b)$$

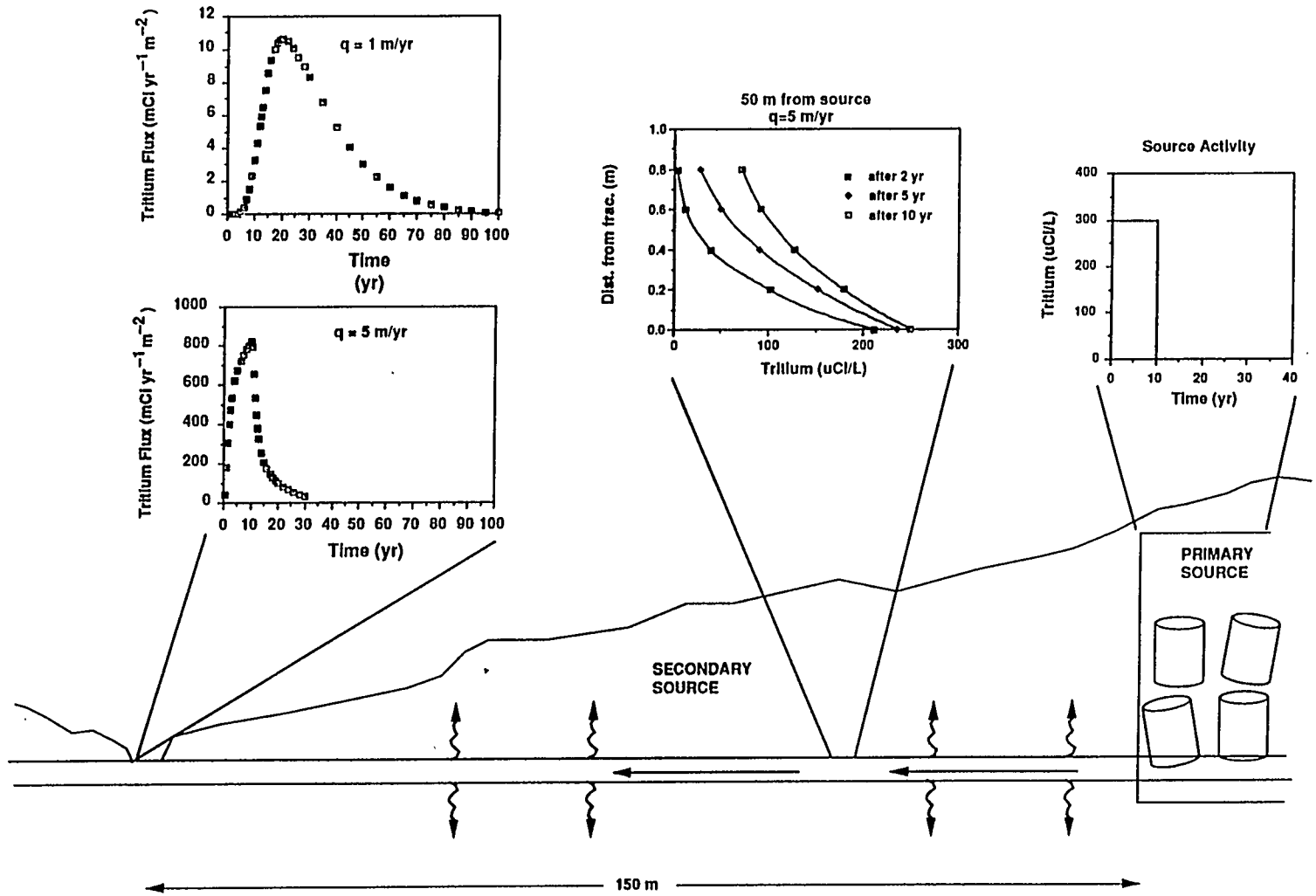

Fig. 15. Contaminant transport modeling results. (See text for discussion).

where

C = concentration in the fracture,
t = time,
V = fluid velocity,
θ_m = matrix porosity,
D = effective molecular diffusion coefficient in water,
τ = tortuosity for diffusion in the matrix,
Z = spatial coordinate along the axis of the fracture,
X = spatial coordinate perpendicular to the fracture,
b = one half the fracture aperture,
λ = decay constant,
$\frac{\partial C}{\partial X}\Big|_{x=b}$ = concentration gradient at the fracture-matrix interface.

The concentration gradient at the fracture-matrix interface is governed by Fick's second law of diffusion (Crank, 1975) which is

$$\frac{\partial C^*}{\partial t} - \frac{D\tau\partial^2 C^*}{\partial X^2} + \lambda C^* = 0 \qquad (2)$$

subject to

$$\frac{\partial C^*}{\partial X}\Big|_{x=B,Z,t} = 0 \qquad (2a)$$

$$C^*(b,Z,t) = C(Z,t) \qquad (2b)$$

$$C^*(X,Z,0) = 0 \qquad (2c)$$

where

C^* = concentration in the matrix,
B = one half the spacing between fractures.

Eqs. (1) and (2) have been solved by applying the Laplace transform to remove the temporal derivative. Inversion to real time was done numerically by using the quotient difference method (Crump, 1976). The Laplace transform of the time-dependent input function was performed by first representing the continuous curve as a series of finely discretized Heaviside step functions in time and then transforming each step function. Thus, in Laplace p-space, the input function is approximated as

$$\overline{C}_0(p) = \frac{\dot{C}_1}{p} + \frac{1}{p}\sum_{i=2}^{nc}(C_i - C_{i-1})\exp(-pt_i) \tag{3}$$

where

C_1 = concentration at time t_1 [M L^{-3}],
C_i = concentration at time t_i [M L^{-3}],
nc = number of discrete activity values,
p = Laplace transform variable.

Precise values for parameters such as fracture apertures, fracture spacings, and fluid velocities are not available for SWSA 5. Although we have utilized parameters that are consistent with independent observations on the Oak Ridge Reservation (e.g., borehole flow meter measurements to define fracture spacings), predictive simulations will be possible only when relevant physical parameters have been measured independently. Thus, the simulations presented in this report are being used to examine the general effects of matrix diffusion in the context of environmental restoration at SWSA 5, rather than to simulate actual field conditions.

The effects of matrix diffusion on contaminant transport are largely controlled by the flux of water in fractures relative to the mass of water stored in the porous matrix. For example, if fracture apertures and fluid velocities are large (resulting in a large water flux in fractures) and the matrix porosity and fracture spacings (of hydraulically active fractures) are small (resulting in a small mass of water stored in the porous matrix), contaminant migration will be controlled by advective transport through fractures, and the effects of matrix diffusion will be minimal. In contrast, when small apertures and small fluid velocities combine with large fracture spacings and large matrix porosities, matrix diffusion is a dominant transport mechanism.

We have investigated matrix diffusion by using parameter values that bracket the range of fracture water flux relative to water mass in the matrix expected for SWSA 5. The simulations assume that the ^3H activity at time zero at primary sources is 300 μCi/L and is constant for a period of 10 years. At the beginning of the tenth year the ^3H activity in primary sources is assumed to be zero (i.e., the source is removed instantaneously). Figure 15 shows the ^3H flux at a distance of 150 m from the primary source as a function of time for two values of the bulk specific discharge. The bulk specific discharge is defined as the water discharge per unit area of the bulk porous media, which includes both fractures and matrix. Table 4 lists the parameter values used in the simulations. Because water flow occurs almost entirely within fractures, the fracture fluid velocities are very large (2500 and 500 m/year for specific discharges of 5 and 1 m/year, respectively). If ^3H were not being attenuated by diffusion into the matrix, the ^3H flux at 150 m would be equal to the flux at the source (1500 and 300 mCi $year^{-1}$ m^{-2} for specific discharges of 5 and 1 m/year, respectively) in <4 months. Furthermore, with no diffusion, the flux at 150 m would be reduced to zero within 4 months after removing the primary source (at time = 10 year). As shown in Fig. 15, the peak ^3H fluxes at 150 m (800 and 11 mCi $year^{-1}$ m^{-2}) are substantially less than the fluxes at the source. This is especially true for a specific discharge of 1 m/year where the ^3H flux at 150 m is about 30 times less than at the source.

Table 4. Parameters used in matrix diffusion transport model

Parameter	Units	Case 1 (specific discharge = 5 m yr^{-1})	Case 2 (specific discharge = 1 m yr^{-1})
V Fluid Velocity	m yr^{-1}	2500	500
2b Fracture Aperture	m	0.004	0.004
2B Fracture Sapcing	m	2	2
θ_m Matrix Porosity	dimensionless	0.4	0.4
τ Tortuosity	dimensionless	0.4	0.4
Diffusion Coefficient	m^2yr^{-1}	0.0767	0.0767
Half-life	yr	12.4	12.4

Several very important differences exist between the two simulations shown in Fig. 15. When the specific discharge is 5 m/year, advective transport in the fracture is large and dominates ^3H migration. As a result, the ^3H flux at 150 m begins to decline shortly after the primary source is removed. Matrix diffusion does result in a secondary source that remains active for about 20 years after the primary source is removed; however, the strength of the secondary source declines rapidly during the first 5 years after the primary source is removed. When the specific discharge is 1 m/year, matrix diffusion begins to dominate ^3H migration. The peak ^3H flux is greatly attenuated relative to the flux at the primary source (11 vs 300 mCi $year^{-1}$ m^{-2}) and occurs 10 years after the primary source is removed. The secondary source remains active for more than 80 years. The simulation with a specific discharge of 1 m/year is particularly important to environmental restoration because it demonstrates that (1) contaminant discharge could continue to increase due to secondary sources long after primary sources are removed, and (2) stream monitoring by itself is not sufficient to ascertain whether or not primary sources are still active.

While our preliminary analysis of the ^3H data from SWSA 5 suggests that primary sources are still active (and thus the ^3H discharge to streams may continue to rise for some time), existing data do not allow a prediction of the response of the systems resulting from proposed remedial actions. For example, if the specific discharge is 5 m/year, remediating primary sources would result in improved water quality within several months; however, if the specific discharge is 1 m/year, improvements in water quality could lag remedial actions by more than 10 years. Section 6 of this report provides recommendations for data collection that could improve predictive capabilities.

Also shown in Fig. 15 are profiles of ^3H activity 50 m from the primary source and perpendicular to the fracture axis. Results are shown for 2, 5, and 10 years after releases from primary sources began. The profiles correspond to a specific discharge of 5 m/year. Because the model assumes that no advective transport occurs between fractures, the ^3H profiles results solely from molecular diffusion. As shown, the model predicts that ^3H can penetrate more than 0.8 m into the matrix after only 2 years. Although the simulations are not intended to mimic the field data, the ^3H profiles shown in Fig. 15 bear a striking resemblance to the observed ^3H profiles shown in Figs. 8 through 10.

5.4 IMPLICATIONS FOR ENVIRONMENTAL RESTORATION

The process of matrix diffusion has many far-reaching implications for environmental restoration on the Oak Ridge Reservation. Because matrix diffusion results in a strong retardation of contaminants, the average contaminant residence time can be many times greater than if matrix diffusion was not operative. When contaminant sources, such as trench leachate, are of finite duration, matrix diffusion can result in a very significant attenuation of peak concentrations at discharge points. In essence, matrix diffusion acts as a buffering mechanism in which peak contaminant fluxes are lowered and contaminant release is spread out over a longer period of time. If contaminants are not transformed by processes such as radioactive decay or biodegradation, the total contaminant release for a given source function (the source function defined as temporal variations in contaminant flux leaving waste sources) is not affected by matrix diffusion; however, if time-dependent contaminant transformations occur, the added residence time afforded by matrix diffusion can substantially reduce the total contaminant release.

As previously indicated, when contaminant sources are removed or decline in strength, it is possible for contaminants to diffuse out of the matrix and into fractures. This process, however, is slow because outward concentration gradients can never be as large as inward concentration gradients at an equivalent point in time. As a result, the removal of contaminants by remediation techniques such as "pump and treat" can be difficult. Since pump and treat technology in low-permeability systems typically enhances fluid velocities by less than a factor of 5, contaminant removal time is not likely to be significantly less than the time over which contaminants were diffusing into the matrix and could be substantially longer. Thus, for many waste sites on the Oak Ridge Reservation, contaminant removal by pump and treat could require more than 50 years of operation.

The short-term effectiveness of remedial actions aimed at reducing the discharge of contaminants from subsurface to surface water systems depends critically on the mass of contaminants that are presently stored within the porous matrix (i.e., the strength of secondary sources relative to primary sources). If the contaminant mass within the matrix is small, source-level remediation such as grouting, compaction, in situ vitrification, etc. would result in reduced contaminant discharge shortly after remediation. If the contaminant mass in the matrix is large, only remediations that eliminate both primary sources (e.g., trench leachate) and secondary sources (i.e., diffusion out of the matrix) will effectively reduce contaminant discharge. However, if the secondary source is located below the water table, even techniques for hydrologic isolation such as local capping and French drains may be unsuccessful because groundwater will continue to move through the secondary source area.

Ultimately, remediation decisions depend on the potential risk of a given waste site. Very large uncertainties exist in potential contaminant releases from primary sources because of inadequate knowledge of inventories and an incomplete understanding of leaching and container failure rates. Such uncertainties result in large risk. The risk associated with uncertainties in release rates is reduced when transport mechanisms can buffer catastrophic releases from waste sources that may currently be inactive. Since matrix diffusion provides a buffering, and though monitoring permits early warning of catastrophic failures, the risk associated with large uncertainties in potential contaminant releases is reduced because of matrix diffusion.

6. RECOMMENDATIONS FOR FUTURE WORK

To complete the ^{3}H profile, groundwater samples should be collected at greater depths until the vertical extent of the ^{3}H plume is determined. In order to completely interpret the results (i.e., evaluate the ^{3}H source term in SWSA 5), it is necessary to determine the locations of the most permeable zones in the subsurface. A multilevel sampling device that extends into bedrock should be installed. Point dilution tests and measurements using a bore hole flow meter should be made at various depths to determine zones of greater water flux. Additional information about the dynamics of the system could be obtained by using transducers in wells connected with a data logger to collect groundwater level measurements over an extended period of time. Seasonal variability in ^{3}H and ^{90}Sr concentrations should be determined by monthly monitoring of drive point wells in the area. Monthly samples should also be collected from the seep in the Melton Branch tributary where the contaminated groundwater discharges.

To further characterize the movement and to determine lateral extent of ^{3}H in the southeast portion of SWSA 5 (i.e., determine how discrete the ^{3}H plume is), groundwater samples should be collected in a line parallel to Melton Branch tributary downgradient of the trenches.

7. SUMMARY

The rate of contaminant transport (i.e., the source term) from waste trenches in burial grounds on the Oak Ridge Reservation is difficult to quantify because of deficient disposal records and the complexity of the hydrogeochemical system. Subsurface systems consist of discrete fractures within a matrix of porous rock. When a contaminant is first introduced into a fractured porous media, very large concentration gradients can occur between fractures and the surrounding porous matrix. Because of molecular diffusion, dissolved species can migrate into the porous matrix, even when no net transfer of fluid between fractures and matrix occurs. When the volume of matrix water is large relative to the volume of fracture water, this process, known as matrix diffusion, can result in substantial dilution and attenuation of migrating contaminants.

Because ^{3}H mobility is not attenuated significantly by geochemical processes, the sustained ^{3}H discharge some 30 years after disposal began suggests that matrix diffusion is an important process in SWSA 5. An area on the southeast edge of SWSA 5, where a known contaminant plume exists, was selected for investigation to gain understanding of processes (particularly matrix diffusion) that may be affecting contaminant transport from primary waste sources to streams.

Tritium activities in the groundwater and soil core samples increase with depth, with the highest activities found at the greatest depth below the water table. The vertical distribution of ^{3}H is very smooth, unlike what might be expected in a fractured and heterogeneous environment, and suggests that diffusion is an important transport mechanism in SWSA 5. There was little difference between ^{3}H activities in the groundwater samples and activities in pore water extracted from soil cores. This close agreement suggests that diffusion, rather than advection through hydraulically active fractures, dominates contaminant transport over the intervals sampled in this study.

The ^{3}H activity in storm flow is much less than that observed in groundwater, indicating that storm flow does not appear to be as significant as groundwater in transporting ^{3}H from the burial ground to the stream in this area of SWSA 5. However, ^{90}Sr activities suggest that subsurface storm flow is more important for ^{90}Sr transport than for ^{3}H. Peak ^{90}Sr values do not coincide with peak ^{3}H values, which may indicate that ^{90}Sr and ^{3}H come from physically distinct primary sources. The observed ^{90}Sr distribution may be a result of a small amount of advective transport within the sampled interval.

The occurrence of high ^{3}H activities in groundwater is consistent with the results of Solomon et al. (1991). Using graphical hydrograph separation, they estimated that 16% of the total ^{3}H release in Melton Branch for 1988 resulted from quick flow; thus, 84% entered as base flow via the saturated groundwater system. The agreement between the subsurface and streamflow results is important in that it places considerable confidence in our ability to distinguish groundwater from storm flow discharge into streams by using graphical hydrograph separation methods.

The observed ^{3}H and ^{90}Sr values have been used to formulate a working hypothesis of contaminant transport, the role of matrix diffusion, and the existence of primary and secondary sources in SWSA 5. The vertical profile of ^{3}H may be a result of upward diffusion

from a hydraulically dominant fracture (or fractured zone) coupled with a small amount of lateral advective transport within the matrix. A hydraulically dominant fracture of high ^3H activity existing beneath the interval sampled would suggest that there is still a source upgradient supplying ^3H to the subsurface system and that the contaminant release from SWSA 5 to the stream will continue to increase until that source is depleted. This hypothesis is tentative, and additional data are required in order to make definitive statements.

A simple mathematical model was used to examine the general effects of matrix diffusion on contaminant transport in SWSA 5. The model accounts for one-dimensional transport along parallel fractures coupled with one-dimensional diffusion into and out of the surrounding matrix. The effects of matrix diffusion on contaminant transport are largely controlled by the flux of water in fractures relative to the mass of water stored in the porous matrix. Expected parameter values that bracket the range of fracture water flux relative to water mass in the matrix for SWSA 5 were used in the simulations. Simulations of the ^3H profile resulting solely from molecular diffusion bear a striking resemblance to the observed ^3H profiles in the study area, suggesting that diffusive processes are important at SWSA 5.

The short-term effectiveness of remedial actions aimed at reducing the discharge of contaminants from subsurface to surface water systems depends critically on the mass of contaminants that is presently stored within the porous matrix (i.e., the strength of secondary sources relative to primary sources). Although preliminary analysis of the ^3H data from SWSA 5 suggests that primary sources are still active (and thus the ^3H discharge to streams may continue to rise for some time), existing data do not allow a prediction of the response of the systems resulting from proposed remedial actions. For example, if the specific discharge is 5 m/year, remediating primary sources would result in improved water quality within several months; however, if the specific discharge is 1 m/year, improvements in water quality could lag remedial actions by more than 10 years.

Because matrix diffusion results in a strong retardation of contaminants, the average contaminant residence time can be many times greater than if matrix diffusion was not operative. When contaminant sources, such as trench leachate, are of finite duration, matrix diffusion can result in a very significant attenuation of peak concentrations at discharge points. In essence, matrix diffusion acts as a buffering mechanism in which peak contaminant fluxes are lowered and contaminant release is spread out over a longer period of time. If time-dependent contaminant transformations occur (such as radioactive decay or biodegradation), the added residence time afforded by matrix diffusion can substantially reduce the total contaminant release.

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