Guidelines for using Fenton's reagent at remedial sites

An innovative technology used to remediate dissolved gasoline constituents in groundwater involves the injection of Fenton's reagent, or hydrogen peroxide/catalyst *(Niedergang, 1997)*. Fenton's reagent can oxidize organic compounds into basically harmless substances. In 1997 a sewer and home exploded in the vicinity of a Wisconsin LUST site using this technology. Vapors from the site may have migrated along the sewer line to the house. To prevent future problems, regulators in Wisconsin and Florida developed guidelines for using product reagent. These guidelines are summarized below *(Giesfeldt, 1997)*.

The Wisconsin Department of Natural Resources recommends that a thorough site characterization be undertaken to understand the site's hydrogeology and geology *(Giesfeldt, 1997)*. **The technology should not be used in the following situations:**

- where measurable free-product or non-aqueous liquids (NAPLs) exist; once these substances are removed, it may be appropriate to use Fenton's reagent; one exception is sites with deep or contained groundwater where free-product is not floating on the groundwater and where vapor migration pathways do not exist, or where the contaminant vapor pressure is low enough not to present a vapor migration risk
- sites with a history of prior contaminant vapor migration to utility trenches, sewers, buildings or other anthropogenic features unless migration is completely controlled
- where the reaction could cause contaminant vapor migration, unless appropriate measures are taken to prevent or control migration; such measures would include:
  - efforts to identify all nearby buildings, USTs, piping and utilities, sewers, permeable soil zones and other anthropogenic or natural features that could act as vapor migration pathways; local governments, "digger's hotline" and utility companies should be contacted; unmapped and old features could be located using remote sensing techniques such as ground-penetrating radar
  - monitoring and control of all potential vapor migration pathways; this may involve using gas probes and combustible gas meters; pressure monitoring can provide useful information, since positive soil gas pressure can be an indicator of vapor migration; temperature monitoring of the subsurface may be advisable when injecting high concentrations of Fenton's reagent under pressure; soil vapor extraction systems are the preferred method to control migration in soil and utility trenches; other methods may be required for vapor control through pipes and sewers, such as forced air venting; some sites may require excavation
  - notification of nearby occupants and evaluation and/or monitoring of nearby buildings

Furthermore, workers should establish exclusion zones around the treated area. Safety measures should include the control of possible ignition sources such as switches, motors and electrical equipment and the use of intrinsically safe equipment and tools *(Giesfeldt, 1997)*.

Injection concerns

Injection of any material, under high enough pressures, can cause fracturing in the subsurface. Wisconsin DNR developed guidelines a few years ago pertaining to injection of "remedial materials". A portion of this guideline is reprinted below *(Didier and others, 1996)*.

Prior to approval, any proposal that calls for the use of a remedial infiltration system or injection well shall be reviewed to ensure the following:

- infiltration systems and injection wells are designed to operate effectively
- the infiltration or injection of a substance or a remedial material is required as part of a remedial treatment scheme and that the substance or remedial material introduced will not increase the severity of the existing contamination or permanently impair future use of the affected soil or groundwater
- the type, concentration and/or volume of the infiltrated or injected substance or remedial material is limited to the extent necessary for restoration of the contaminated soil, aquifer or groundwater
- any by-product formed as a result of remediation processes will either be recaptured or further degraded to a point where it does not constitute further risk to either human health or the environment
- environmental contaminants and all infiltrated or injected substances and remedial materials shall be controlled such that cleanup of the contaminated media is achieved and the boundaries of the impacted area are not significantly expanded during, or as a result of, the proposed remedial action
- maximum limits on soil concentration and/or water quality are established for any infiltrated or injected substances or remedial materials that are not covered under a Wisconsin Pollutant Discharge Elimination System (WPDES) permit
- monitoring of remedial activities will be sufficient to verify the performance of the infiltration or injection devices, and the effectiveness of all required contaminant containment measures

Didier and others *(1997)* also emphasize that injections of a substance or remedial material through a well or drillhole solely for the purpose of waste disposal are prohibited. In addition, this guidance also addresses specific requirements for groundwater protection and water supply protection.

New Methods for Sampling Soils for Volatile Organic Analysis: Are You Ready?

Notes from the July 15, 1998, Dinner Meeting and editorial by John Wondolleck, CHMM

Speaker: Dr. Bart Simmons, Ph.D., Hazardous Materials Laboratory - California Department of Toxic Substances Control

In the old days of sampling soil, one would drive a split spoon sampler to a designated sampling depth (which would heat up to 150 degrees F due to friction), open the spoon and sniff the core with a vapor monitor, subsample the core and place the same into a wide-mouth jar, and then ship the sample to a laboratory. Studies performed by the Army Corps of Engineers and others showed that this method of sampling could result in the loss of up to 100% of the volatile organic compounds (VOCs) originally in the soil sample. These studies also that showed up to an order of magnitude of the VOCs were lost in soil samples collected in capped sleeves due to volatilization and microbial degradation of the samples even when samples were analyzed within the "accepted" 14-day holding time. These findings led to the development of field methods that would reduce the loss of VOCs from the soil samples and provide accurate and representative site characterization data.

The latest revision to SW-846 (USEPA's Test Methods for Solid Wastes, Physical/Chemical Methods; Update III, effective December 1997) introduced Method 5035 - Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples. The SW-846 update essentially requires the preservation of soil VOC samples in the field. Three options are provided: methanol preservation, acid preservation (sodium bisulfate), and the use of an Encore-type sampler.

The benefit of the methanol and sodium bisulfate preservation methods is that the soil sample is immediately preserved in the field and placed in an air tight container complete with a magnetic stir-bar for laboratory use. The detriments of these methods are the need to measure and handle methanol and sodium bisulfate in the field, the need to provide a known quantity of soil in the container, shipping requirements for the preservatives, and the elevated detection limits caused by the methanol. In addition, sodium bisulfate cannot be used for calcareous soils due to effervescence. Other concerns are the purity of the preservative solutions related to compounds of concern. The methanol preservation method results in elevated detection limits, therefore methanol preservation cannot be used for samples at concentrations less than 200 ppb. The manner in which surrogate compounds are injected into the sample also needs to be addressed (i.e., added in the field or by the laboratory). Because different types of chemical preservative are required for low versus high concentrations of VOCs in the soil samples, and the sample concentration cannot be predetermined, collecting soil samples using both methanol and sodium bisulfate is recommended.

To subsample a soil core for preservation, the suggested method is the use of a syringe with its end cut off to collect the subsample of a specific volume. The plunger of the syringe is used to push the sample into the sample container with the preservative and the container is then immediately sealed. Equal volumes of soil and preservative are recommended by EPA; a ratio of 1 part soil to two parts preservative is recommended by DTSC.

On August 7, 1998, USEPA issued a memorandum entitled "Clarification Regarding Use of SW-846 Methods". This memorandum provides the following clarification. "The Agency recommends that all soil samples collected for volatiles be preserved in some manner, whenever possible. For low concentration samples, generally those below 200 ppb of VOCs, preservation is essential. For samples with higher concentrations of VOCs (i.e., greater than

200 ppb for VOCs), the Agency recommends that unpreserved samples be collected as a last resort, and that the rationale for not preserving the samples be clearly documented in a sampling and analysis plan that is reviewed and approved by the relevant regulatory authority." In the memorandum, USEPA requires that methanol be added to the vial by the laboratory before shipment of vials to the field. The vial then is reweighed in the field. If the difference between the two measurements is greater than 0.2 g, then the vial cannot be used. USEPA also states that if a 1:1 ratio of soil:solvent is used, the solvent must completely submerge the sample.

A third suggested method is the use of an Encore sampler. This is a hermetically sealed combined sampling tool/container used to collect and contain the sample for shipment to the laboratory. The sample container needs to be cooled to 4 degrees C and the sample extracted by the laboratory within 24 hours of collection. The Encore sampler eliminates the field responsibility of the field crew to chemically preserve the samples. Encore samplers cost $7-10 each. The lab extrudes the sample from the Encore sampler into methanol within 48 hours making the sample appropriate for high level analysis only. Two samplers must be used for each sample collected, and if moisture content is needed to be known, a third sample must also be collected. Studies are underway on the freezing of the sample container by the laboratory, which may extend the laboratory holding period prior to extraction.

All three field collection/preservative methods require that the laboratory have specialized equipment to perform the analyses. Laboratories are in the processing of purchasing and using the new equipment so USEPA and DTSC are allowing a transition period prior to enforcing the requirement that the Method 5035 be followed. DTSC will require implementation through its lab accreditation program. DTSC is considering a deadline for use of the Method 5035 in the future. At present it will be enforcing the requirements on a case by case basis. The Army Corps of Engineers is enforcing the requirement now. DTSC is not planning to reopen closed sites based on the new sampling method, even thought it is suspected that the soil VOC results are biased low. DTSC does not expect the courts to reopen any cases due to the new science.

On another note, Dr. Simmons stated that the National Laboratory Accreditation Conference will be establishing uniform national standards, replacing individual state programs for laboratory accreditation. California is a participant in this organization, thus there is a chance that California's accreditation program will be changing.

In the August 7, 1998 memorandum, USEPA states that "SW-846 contains the analytical and test methods that EPA has evaluated and found to be among those acceptable for testing under Subtitle C of RCRA. In most situations, SW-846 functions as a guidance document setting forth acceptable, although not-required, methods to be implemented by the user, as appropriate, . . ." In this statement, USEPA is recognizing that there are other means of measuring chemical and physical properties of environmental media. However, one should be cautioned that if they propose to use a method other than that presented in SW-846, Update III, the alternative method must be demonstrated to be either equal or superior to the method stated in SW-846 (if a comparable SW-846 method exists). One also must remember that USEPA has eliminated or replaced once commonly used SW-846 methods (such as 8010/8020 for VOCs) with newer and updated methods (EPA 8021) because of quality or procedural issues inherent to the older methods. Although USEPA and DTSC may still allow the use of the older methods during the transition period, one runs the risk of data being produced by the older methods being rejected by either agency. Therefore the prudent person should use only those methods stated in SW-846, Update III.

Quantification of Natural Vapor Fluxes of Trichloroethene in the Unsaturated Zone at Picatinny Arsenal, New Jersey

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The upward flux of trichloroethene (TCE) vapor through the unsaturated zone above a contaminated, water-table aquifer at Picatinny Arsenal, New Jersey, has been studied under natural conditions over a 12-month period. Vertical gas-phase diffusion fluxes were estimated indirectly by measuring the TCE vapor concentration gradient in the unsaturated zone and using Fick's law to calculate the flux. The total gas-phase flux (e.g., the sum of diffusion and advection fluxes) was measured directly with a vertical flux chamber (VFC). In many cases, the upward TCE vapor flux was several orders of magnitude greater than the upward TCE diffusion flux, suggesting that mechanisms other than steady-state vapor diffusion are contributing to the vertical transport of TCE vapors through the unsaturated zone. The measured total flux of TCE vapor from the subsurface to the atmosphere is approximately 50 kg/yr and is comparable in magnitude to the removal rate of TCE from the aquifer by an existing pump-and-treat system and by discharge into a nearby stream. The net upward flux of TCE is reduced significantly during a storm event, presumably due to the mass transfer of TCE from the soil gas to the infiltrating rainwater and its subsequent downward advection. Several potential problems associated with the measurement of total gas-phase fluxes are discussed.

Introduction

Many processes contribute to the fate and transport of organic pollutants in groundwater. These include physical transport processes such as advection and diffusion, biochemical processes such as biodegradation and hydrolysis, and interphase mass-transfer processes such as sorption and volatilization. This latter process, e.g., the natural volatilization of pollutants from groundwater into the unsaturated-zone soil gas and eventual transport to the atmosphere, has received relatively little attention in the scientific literature, probably because of the general belief that it is not a significant transport process relative to other processes. Unlike volatilization from surface waters, the concentration gradient that drives mass transfer from groundwater to soil gas is comparatively small because of transport limitations in both the saturated and the unsaturated zone. However, many common groundwater contaminants have relatively high Henry's law constants, and the upper surface area of many groundwater plumes may be significant relative to the total volume of contaminated groundwater. Consequently, volatilization may be a significant transport process given the large interfacial area available for phase transfer of the pollutant.

In recent years, several studies have quantified the concentration of volatile organic compounds in unsaturated-zone soil gas above contaminated aquifers (*1*–*6*) and have correlated these soil-gas concentrations with the concentration of the contaminants in shallow groundwater (*1*, *3*, *4*). Based on vapor concentrations in the unsaturated zone that increase linearly with depth (*2*, *4*, *6*) and the relatively large diffusion coefficients for VOCs in air relative to water, many researchers have suggested that diffusion, rather than advection, is the dominant transport process for VOCs in the unsaturated zone (*3*, *4*, *7*–*10*). Although several researchers have recently studied the advective transport of VOCs in unsaturated-zone soil gas, almost all these investigations have been in the context of induced air-venting systems for the remediation of gasoline spills or similar contamination problems (*11*–*19*). Only a few studies have discussed the possible importance of advective pollutant transport under natural conditions (*20*–*22*).

The objective of this study is to determine if diffusion alone can explain the fluxes of TCE vapor through the unsaturated zone at a contaminated field site and to determine the importance of TCE vapor fluxes relative to other contaminant sinks, including the removal of TCE by an existing pump-and-treat groundwater remediation system.

Description of Field Site

The field site chosen for this study is the Picatinny Arsenal in Morris County, New Jersey (Figure 1). In 1986, this site was selected by the U.S. Geological Survey as a national research site for the study of the fate, transport, and remediation of chlorinated solvents in groundwater. As a result of this action, the site has been carefully characterized and studied for the past decade (*23*). It is located in a glaciated valley on top of 50–65 m of stratified and unstratified drift, which overlies a weathered bedrock surface. The unconsolidated sediments form three major hydrogeologic units: a 15–21-m-thick unconfined sand and gravel aquifer, an 8–21-m-thick confining layer composed of fine sand, silt, and clay, and an 8–35-m-thick confined sand and gravel aquifer (*24*). The water table is located 2–4 m below land surface over most of the study

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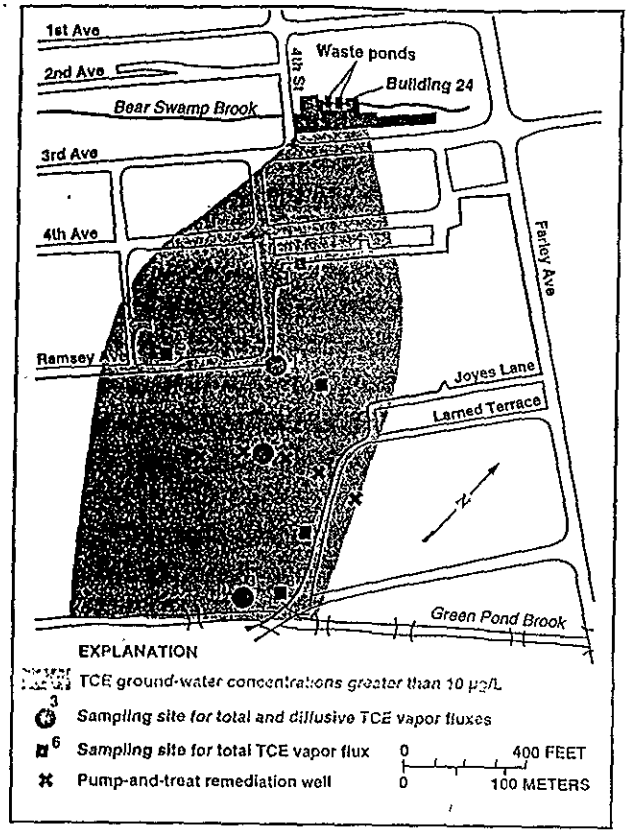

FIGURE 1. Map of field site at Picatinny Arsenal showing the location of trichloroethene (TCE) groundwater contamination, sampling sites, and withdrawal wells for the pump-and-treat remediation system.

area shown in Figure 1. The generalized direction of groundwater flow in the unconfined aquifer is from Building 24 to Green Pond Brook. The horizontal hydraulic conductivity ranges from 0.02 to 0.13 cm/s, and the average groundwater velocity is approximately 0.3 m/day (*25*).

From 1960 to 1983, Building 24 at Picatinny Arsenal (Figure 1) was used for metal plating, cleaning, and degreasing. The primary solvent used for degreasing was TCE. Wastewater from these processes was discharged into two unlined lagoons and an unlined overflow dry well adjacent to Building 24, with a combined volume of about 2.1×10^5 L (*4*). These disposal practices resulted in a contaminant plume in the unconfined aquifer extending about 500 m from Building 24 to Green Pond Brook. Although the exact mass of TCE released into the subsurface is unknown, approximately 46 000 L of TCE was purchased for use at Building 24 between 1974 and 1984. Additional TCE was likely purchased and used prior to 1974, but purchasing records are no longer available. The shaded area in Figure 1 identifies the part of the aquifer with aqueous TCE concentrations greater than 10 µg/L and is based on a synoptic sampling of 38 wells screened in the unconfined aquifer during October and November 1991 (*26, 27*). TCE concentrations as high as 44 mg/L have been measured in water samples collected from the aquifer using purge-and-trap gas chromatography/mass spectrometry (*28*). Because Green Pond Brook (Figure 1) acts as the discharge point for the water-table aquifer in the valley, no TCE has been detected in groundwater on the southeast side of Green Pond Brook. The unsaturated zone is 2–4 m thick over most of the study area (*24*), and TCE has been detected in the unsaturated-zone water and soil gas at the site (*4, 6, 24*).

In September 1992, a pump-and-treat system was installed to remediate the contaminated groundwater. The pump-and-treat system consists of five withdrawl wells screened in the unconfined aquifer at the locations indicated in Figure 1. From September 1992 to February 1995, the combined average rate of water withdrawl from the five wells was approximately 230 L/min, and the average TCE concentration was approximately 1.5 mg/L. TCE is removed from the water by air stripping followed by activated carbon adsorption. The treated water is discharged into Green Pond Brook downstream from its intersection with the groundwater plume.

Materials and Methods

The net vertical flux of TCE vapor in the unsaturated zone at Picatinny Arsenal was measured using a vertical flux chamber (VFC) that is depicted schematically in Figure 2. The VFC is similar to the emission flux chambers described by Eklund et al. (*29*), Hwang (*30*), and Batterman et al. (*31*) and used to measure the emission rates of volatile organic compounds from contaminated field sites to the atmosphere.

The VFC (Figure 2) consists of a stainless steel cylindrical drum that is open at one end. The drum is 18 cm deep and 60 cm in diameter. Two Carbotrap 300 (Supelco, Inc.)

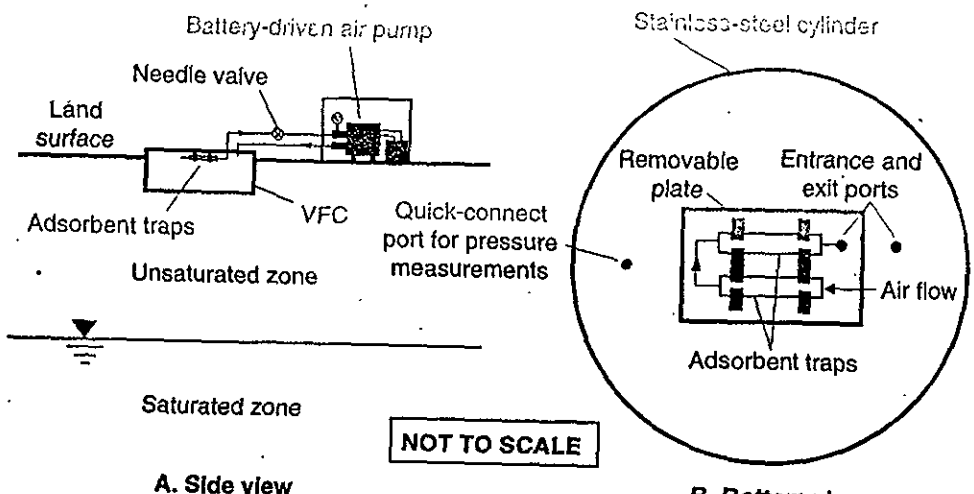

FIGURE 2. Schematic diagram of the vertical flux chamber (VFC) used to measure the total flux of TCE vapor through the unsaturated zone.

adsorbent "traps" are connected in series and mounted to a removable plate in the top of the cylinder. The Carbotrap 300 adsorbent traps are glass tubes with an 11.5 cm length, 6 mm outer diameter, and 4 mm inner diameter. Each tube contains 300 mg of 20/40 Carbotrap C, 200 mg of 20/40 Carbotrap B, and 125 mg of 60/80 Carbosieve S-III (Supelco., Inc.). These proprietary adsorbents are well suited for the adsorption of volatile organic compounds from the air. The adsorbent traps are connected by 6 mm o.d. Teflon tubing and Cajon ultra-torr fittings with O-ring seals. The O-ring fittings allow easy connection and removal of the adsorbent tubes. The first adsorbent tube is open to the atmosphere on one end and connected to the second adsorbent tube on the other. The second adsorbent tube is connected by Teflon tubing to a battery-driven air pump through the removable plate on the top of the cylinder. The VFC is installed by using a shovel to excavate soil to form a hole that is 15 cm deep and 60 cm in diameter. The top 1 cm of soil in the hole was then loosened with the shovel to ensure that any soil that was packed down during excavation did not reduce the soil's natural air permeability. Approximately 30 min after excavation of the hole is completed, the VFC is emplaced into the hole and sealed so that the top of the cylinder is approximately 3 cm above land surface. When in place, the space inside the cylinder is only filled with air, not soil. To insulate the chamber against significant temperature fluctuations, it was covered with the excavated soil and grass during operation.

Once in place, the air pump draws air from inside the cylinder through the adsorbent traps at a rate of 30 mL/min and then returns the air to the inside of the cylinder. The airflow rate can be regulated with a stainless steel needle valve. Air is circulated through the first trap, and any TCE vapor that has been transported through the unsaturated zone and into the cylinder will be removed from the airstream by adsorption to the trap. The second trap is in place to detect any breakthrough of TCE from the first trap. For any measurement, if the mass of TCE on the second trap was greater than 2% of the mass on the first trap in the series, the measurement was repeated. This configuration allows for air within the cylinder to be circulated through the traps and for maintenance of an approximate zero TCE vapor concentration at land surface with a negligible change in air pressure within the cylinder. Under certain circumstances, the TCE concentration in the air in the cylinder may be significantly above a zero concentration, and this point is addressed in the Discussion section. A Dwyer inclined manometer with oil (specific gravity = 0.826) was periodically used to determine the air pressure in the cylinder relative to atmospheric pressure during operation of the VFC. In all cases, there was no measurable deviation in pressure between the atmosphere and the interior of the cylinder. One or more flux measurements using the VFC were performed at all eight sampling locations indicated in Figure 1. The time period that the VFC was emplaced into the soil ranged from 1 to 12 h, depending on the magnitude of the TCE vapor flux.

The mass of TCE adsorbed to the traps was quantified by thermal desorption/gas chromatography using a Dynatherm thermal desorption unit and a Perkin-Elmer gas chromatograph with a calibrated flame-ionization detector and a 0.53 mm i.d. megabore capillary column. Detector response was recorded with a Perkin-Elmer 1020 computerized data acquisition and analysis system. The TCE quantification limit was 10 ng.

Samples of unsaturated-zone soil gas were collected to determine the vertical concentration profile of TCE. The soil-gas samples were collected through permanently installed "vapor probes" that have been described previously (6). Briefly, the vapor probes are constructed of either 0.64 or 0.32 cm outer diameter stainless steel tubing. Slots are cut into one end of the tubing over an interval of approximately 15 cm, and this interval is covered with fine-mesh stainless steel screening to prevent soil particles from clogging the probe. A hole is augered in the ground, and several probes of different depths are installed into the same hole. The probes are generally 0.5–0.7 m apart in the vertical dimension and are separated by a 5-cm layer of bentonite to prevent preferential vertical air flow during sampling. The remainder of the borehole is filled with native soil. In this manner, soil-gas samples can be collected from different vertical locations but at the same areal location. The depth of probes used in this study range from 0.5 m to 2.8 m. Nests of vapor probes were installed at sites 1, 2, and 3 (Figure 1). All vapor probes are capped when not in use.

To extract soil gas from the vapor probes, an Amtek Alpha-2 air sampler and Carbotrap 300 adsorbent traps (Supelco, Inc.) were used. One end of the adsorbent trap is connected directly to the top of the vapor probe, and the other end is connected to the air pump with a section of silicone tubing. The air sampling pump is turned on, and the flow rate (approximately 20 mL/min) is measured in triplicate with a bubble flow meter. Depending on the anticipated TCE concentration in the soil gas, the soil gas is allowed to pass over the adsorbent trap for time periods ranging from 15 to 60 min. The adsorbent traps are again analyzed by thermal desorption/gas chromatography. The mass of TCE collected on each trap is determined, and the TCE vapor concentration in the soil gas can be calculated by dividing by the volume of soil gas passed through the adsorbent trap. The concentrations at different depths can then be used to calculate the vertical concentration gradient. For a subset of the samples collected as described above, a second adsorbent trap was placed in series with the first adsorbent trap to determine if TCE was breaking through the first trap. In all cases, no detectable levels of TCE were measured on the second adsorbent trap.

A test was also performed to compare the performance of the above-described sampling methodology to the methodology described previously by Smith et al. (4) and Cho et al. (6) that involves the collection of a soil-gas sample in a 125-mL glass sampling bulb with Teflon stopcocks at the inflow and outflow ports of the sampling bulb. The two methods showed good agreement, with TCE concentration differences typically less than 5%. The adsorbent trap method was adopted for use in this study because of a longer allowable sample holding time [4 weeks for the adsorbent traps (see below) versus 8 h for the glass sampling bulbs (4)] and because the sensitivity of the method could be controlled by varying the sample collection time.

Following analysis, all adsorbent traps used in this investigation were desorbed for a minimum of 4 min at 370 °C to remove any residual contamination and prepare the traps for subsequent samplings. Trip blanks, consisting of clean adsorbent traps that were carried to and from the field but were not directly used for TCE measurements, were analyzed and found to contain nondetectable levels of TCE, indicating that the storage procedure did not cause contamination of the adsorbent traps. Immediately after

sampling, all adsorbent traps were stored in the dark at approximately 5 °C. Laboratory experiments indicated that traps stored in this fashion showed no measureable losses of TCE over a 4-wk period. All field samples were analyzed within 1 wk of sample collection, and most samples were analyzed within 24 h.

Soil moisture content was measured as a function of depth using time domain reflectometry (TDR) (*32*). This method uses the dependence of the apparent dielectric constant on the volumetric water content of the soil. Topp et al. (*32*) developed an empirical relation between volumetric moisture content and apparent dielectric constant that applies to most soils. A single relation can be used because the procedure is not sensitive to variations in bulk density, temperature, salinity, and mineral composition.

The TDR probes were installed at sites 1–3. Each probe consists of an aluminum plate connected to two or three 30-cm stainless steel rods (0.64 cm diameter). A plexiglass plate lies between the rods and the aluminum plate and acts as an insulator. The rods are connected with stainless steel bolts to 50-Ω cable. They are installed in the subsurface at the desired depth by augering a hole and then driving the probe into the undisturbed earth at the bottom of the hole. The hole is then filled with native soil, and the cable is brought to land surface. The cable from the probe is connected to a Tektronix 1502B metallic TDR cable tester, which produces an electronic signal. The signal travels the length of the probe and is returned to the cable tester. The apparent length of the probes, l_{app}, is determined from the graphical signal on the cable tester. This value can then be used to calculate the apparent dielectric constant and the volumetric moisture content (*32*).

Results

A total of 39 net vertical flux measurements were made using the VFC at the eight locations in Figure 1 from August 1993 to August 1994. In some cases, multiple measurements were made on the same day. The fluxes (in $\mu g\ m^{-2}\ h^{-1}$) were calculated from the experimental data by dividing the mass of TCE on the adsorbent trap by the product of the cross-sectional area of the VFC (in m^2) and the time period (in h) of the measurement. These fluxes ranged in magnitude from nondetectable to 1200 $\mu g\ m^{-2}\ h^{-1}$ and are listed in Table 1 with their corresponding locations and sampling dates.

The vertical concentration profile of TCE in the unsaturated-zone soil gas was quantified at a total of 25 different points in time at locations 1–3. In some cases, more than one concentration profile was measured per day. Figure 3 presents the results of these concentration measurements for site 1. For the majority of the synoptic measurements, the TCE vapor concentration increased approximately linearly with depth. This observation is consistent with concentration profiles measured previously at the site (*4*, *6*). However, during the more comprehensive sampling reported here, distinctly nonlinear concentration gradients were also observed (e.g., June 1994).

Volumetric soil moisture content was measured at sites 1–3 each time the vertical TCE concentration profile was measured. All moisture contents measured as part of this study were between 10 and 23%. Soil moisture contents, in combination with vertical TCE concentration profiles, were used to calculate TCE diffusion fluxes with the following relation:

TABLE 1

Total and Diffusive Trichloroethene Vapor Fluxes through the Unsaturated Zone at Picatinny Arsenal, New Jersey

site	date	total flux ($\mu g\ m^{-2}\ h^{-1}$)	diffusive flux ($\mu g\ m^{-2}\ h^{-1}$)
1	8/23/93		0.08
1	8/24/93		0.3
1	10/7/93	0.044	0.1
1	10/8/93	0.062	0.06
1	10/9/93	0.15	
1	4/14/94	1.1	0.01
1	4/14/94	0.55	nonlinear[a]
1	4/15/94	no detect	
1	4/15/94	no detect	
1	6/9/94	4.8	nonlinear
1	6/9/94	1.8	0.01
1	6/9/94	2.5	nonlinear
1	6/10/94		nonlinear
1	6/10/94		nonlinear
1	6/10/94		0.01
1	6/10/94		nonlinear
1	7/21/94	0.17	0.1
1	7/21/94	0.30	
1	7/21/94	0.046	
1	7/21/94	0.11	
1	8/5/94	0.31	
1	8/5/94	0.22	
1	8/5/94	0.20	
1	8/5/94	0.065	
1	8/5/94	0.057	
2	6/28/94	14.	0.004
2	6/28/94	13.	nonlinear
2	6/28/94	17.	0.002
2	6/28/94		nonlinear
2	8/2/94	300	0.2
2	8/2/94	470	
2	8/2/94	1,200	
2	8/2/94	410	
3	10/8/93	0.015	nonlinear
3	10/9/93	0.52	0.02
3	6/29/94	86.	nonlinear
3	6/29/94	64.	nonlinear
3	6/30/94		0.004
3	8/3/94	12.	0.1
3	8/3/94	17.	
4	10/16/94	1.0	
5	8/6/94	0.22	
6	10/15/94	no detect	
7	10/16/94	59.	
8	8/4/94	0.93	
8	8/5/94	0.36	
8	8/5/94	0.23	

[a]Vertical trichloroethene concentrations were nonlinear with depth, preventing calculation of a concentration gradient and a diffusive flux.

$$J_d = D_{eff}\frac{\partial C}{\partial z} \quad (1)$$

where J_d is the diffusive TCE flux ($\mu g\ m^{-2}\ h^{-1}$), D_{eff} is the effective diffusion coefficient, m^2/h, and C is the TCE vapor concentration at some location z in the unsaturated zone. The effective diffusion coefficient was calculated from the following expression:

$$D_{eff} = D\tau_g \quad (2)$$

where D is the diffusion coefficent for TCE in air and τ_g is the gas-phase tortuosity factor. The diffusion coefficient of TCE in air (0.076 cm^2/s) was calculated from the Wilkes–Lee modification of the Hirschfelder–Bird–Spotz method as described in Treybal (*33*). The tortuosity was calculated

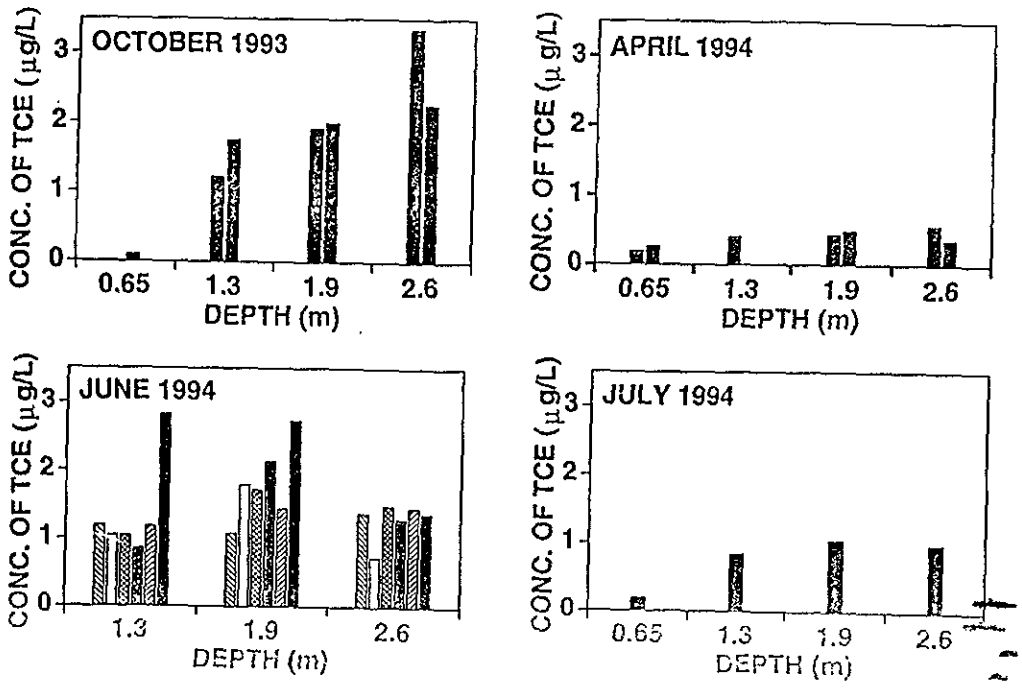

FIGURE 3. Trichloroethene (TCE) vapor concentrations at different depths and times at site 1. Bars with identical patterns in the same graph correspond to a single synoptic sampling. TCE was nondetectable at a depth of 0.65 m during all samplings in June 1994.

from the empirical relation given by Currie (34):

$$\tau_g = \frac{\theta_g^4}{\phi^{5/2}} \qquad (3)$$

where θ_g is the volumetric gas content and ϕ is porosity (approximately equal to 0.3). The volumetric gas content was calculated by subtracting the depth-averaged volumetric water content (measured in the field) from the porosity. The concentration gradient in eq 1, $\partial C/\partial z$, was determined by linear regression of the vertical TCE vapor concentrations measured in the field. For the case of distinctly nonlinear vertical concentration data, no diffusion flux was calculated. The diffusion fluxes calculated using the field data and eqs 1–3 are listed in Table 1 along with the previously described total flux data. It should be noted that several empirical and theoretical relations for predicting tortuosity factors for porous media have been presented in the literature (e.g., refs 8 and 34–37). Depending on soil porosity and moisture content, tortuosity estimates can vary with the choice of the empirical relation used. However, none of the differences between any of the above-mentioned tortuosities will account for the significant differences in diffusive and total fluxes discussed later in this paper. The above-mentioned tortuosity relations also assume that macropores are not present in the soil. The presence of macropores could increase the effective diffusion coefficient over the calculated values. Because of the inherent uncertainties in predicting effective diffusion coefficients for moist soils, calculated diffusion fluxes are only reported to one significant figure and probably should only be considered order of magnitude estimates. The calculated diffusion fluxes range from 0.002 to 0.3 $\mu g\ m^{-2}\ h^{-1}$.

On August 5, 1994, the total TCE vapor flux was measured immediately before and during a natural precipitation event at site 1. Atmospheric pressure and soil moisture content were also measured before and during the precipitation event. The measured values of soil moisture content as a function of depth and time are shown in Figure 4. The moisture content for a depth of 0.65 m and the measured total fluxes are shown as a function of time in Figure 5. The precipitation began at a time corresponding to the value of 1 h in Figures 4 and 5. The first flux measurement was made from 0 to 1 h. The second flux measurement was made from 1 to 4 h. The third flux measurement was made from 4 to 7 h. For all three flux measurements, the midpoint of the sampling interval was used for the abscissa value in Figure 5. The measured precipitation from 1 to 4 h and from 4 to 7 h was 0.2 in and 0.05 in, respectively. At times of 1 and 4 h, the atmospheric pressure was 29.1 in Hg. At 7 h, the atmospheric pressure was 29.2 in Hg.

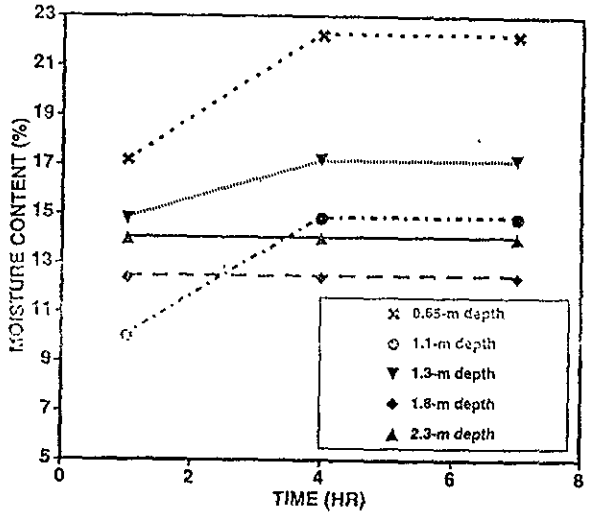

FIGURE 4. Moisture content at different depths as a function of time at site 1 on August 5, 1994.

Discussion

One of the most striking conclusions of this field study is the generally large differences between the total and diffusive TCE vapor fluxes in Table 1. A total of 16 attempts

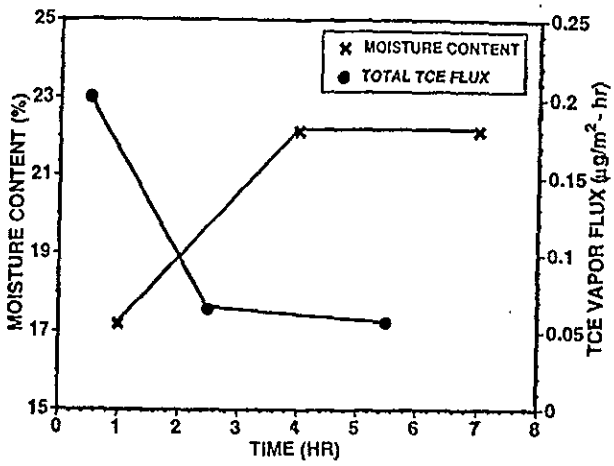

FIGURE 5. Moisture content (at a 0.65-m depth) and total TCE vapor flux as a function of time at site 1 before and during a natural precipitation event on August 5, 1994. Precipitation began at time = 1 h.

were made to simulaneously measure the diffusive and total TCE vapor fluxes at a given site during the course of this study. For seven of these measurements, the diffusive flux could not be reliably estimated because of a distinctly nonlinear concentration gradient (Table 1). Of the remaining eight pairs of measurements, the total and diffusive fluxes are comparable in magnitude only three times (site 1 on 10/7/93, 10/8/93, and 7/21/94). In most cases, the total flux is 1−4 orders of magnitude greater than the diffusive flux. The largest diffusive flux in Table 1 is 0.3 $\mu g\ m^{-2}\ h^{-1}$. Of the 39 total flux measurements made, 24 had greater total TCE fluxes than this maximum value. This suggests that many of the other total flux measurements may have been greater in magnitude than the diffusive flux if the latter could have been quantified.

Comparison of the total and diffusive fluxes in Table 1 suggests that other mechanisms may be contributing to the transport of TCE vapor in the unsaturated zone at Picatinny Arsenal. One possible mechanism is the advection of TCE vapors in response to changes in atmospheric pressure and/or temperature. As the atmospheric pressure decreases, air in the unsaturated zone will flow upward until the air pressure just above the capillary fringe equals the air pressure at land surface. The airflow will cause upward advection of TCE. Conversely, as the atmospheric pressures increases, TCE vapors will be advected downward.

The above conclusion is consistent with the frequent observation of nonlinear and time-varying TCE concentration gradients in the unsaturated zone (e.g., Table 1, Figure 3). In Figure 3, the data from June 1994 show that the vertical concentrations are nonlinear with depth and, for a given depth, are changing over a time period of several hours. Given the slow rate of groundwater flow, it is unlikely that the groundwater TCE concentration is changing significantly over this time period. Similarly, the TCE vapor concentration at land surface is constant and approximately equal to zero (*4*). Therefore, the nonlinear and time-varying TCE vapor concentrations in the unsaturated zone shown in Figure 3 cannot be explained with a steady, diffusive transport model, which would require a linear increase in TCE vapor concentration with depth.

At first thought, it may appear that the net effect of cyclic barometric pressure fluctuations would result in a net zero advective flux. Increases in atmospheric pressure would cause downward TCE advection whereas decreases in atmospheric pressure would cause corresponding upward advection of TCE. These fluxes would "balance out" over long time periods. However, due to the limitation of TCE transport across the capillary fringe (e.g., the diffusion coefficient for TCE in water is approximately 4 orders of magnitude less than in air) and the fact that air entering the unsaturated zone has essentially a zero TCE concentration, the effect of this cyclic pressure/temperature variation would be a net flux of TCE to the atmosphere. It should be noted that atmospheric pressure changes can be localized daily fluctuations or longer-term changes resulting from regional weather patterns.

Several other studies provide support for the hypothesis that advective transport of TCE in the unsaturated zone is contributing to many of the measured total fluxes. In a theoretical study of gas transport in porous media, Thorstenson and Pollock (*20*) demonstrated that pressure gradients as low as 1 Pa/m can result in advective fluxes greater than diffusion fluxes. Using temporal variations in barometric pressure measurements, Massmann and Farrier (*21*) simulated airflow in unsaturated porous media. They concluded that natural pressure-driven airflow can be significant and that air from above land surface can migrate several meters into the subsurface during natural fluctuations in atmospheric pressure. Using a model that accounted for advective and diffusive pesticide transport in the unsaturated-zone soil gas, Chen et al. (*22*) successfully simulated the vapor flux of 1,3-dichloropropene from the subsurface to the atmosphere in response to atmospheric pressure changes.

Although the total TCE fluxes measured in this study are likely influenced by gas-phase advection, it is also possible that mass transfer of TCE between the gas and water phases and between the water and soil phases in the unsaturated zone also affects the total flux of TCE to the atmosphere. TCE vapor can partition into soil organic matter, dissolve into unsaturated-zone water, and adsorb to air-water interfaces (*31, 38−43*). Smith et al. (*4*) measured the *in situ* distribution of TCE between the unsaturated-zone gas and soil at Picatinny Arsenal. They determined that the TCE soil concentrations were significantly higher than values predicted based on equilibrium with the gas-phase TCE concentrations. Cho et al. (*6*) determined that the desorption of TCE from the unsaturated zone soil could not be described by a mathematical model that assumed a local sorption equilibrium. Therefore, desorption of TCE from the unsaturated-zone soil to the soil water and soil gas may be an additional, long-term source of TCE that contributes to the total TCE vapor flux.

There are two other possible explanations for the discrepancies between total and diffusive fluxes that relate to the design of the VFC. First, because soil is excavated to a depth of approximately 15 cm below land surface and because the VFC is designed to maintain a zero or near-zero TCE vapor concentration at this surface, it is possible that some TCE vapor is being transported horizontally toward the VFC. This occurs because the upper zero-concentration boundary may have been lowered up to 15 cm relative to the surrounding soil. The calculated total fluxes assume that TCE vapor is only transported vertically. This effect would cause an overestimation of the total TCE flux, but would not account for the one or more order of magnitude differences between diffusive and total fluxes reported in Table 1.

Second, disturbing the shallow soil by excavation to a depth of 15 cm may temporarily increase the rate of TCE desorption from soil and/or soil water. If significant amounts of TCE are released by disturbing the soil by emplacement of the VFC, this could potentially result in measured total fluxes that are significantly higher than fluxes occurring under natural conditions (e.g., in the absence of soil excavation). Although this study has not explicitly attempted to quantify this process, there is information in Table 1 that suggests that this is not a significant source of error.

In Table 1, total fluxes reported for a single date and for a single location were measured with a single excavation of soil. In other words, the soil was excavated, the VFC was installed, and after some period of time, the metal plate at the top of the VFC was removed; the adsorbent traps were replaced with new traps, the metal plate was replaced onto the top of the VFC, and the next measurement was begun. This process was repeated to yield as many as five measurements of total flux in a single day. Table 1 lists these measured total fluxes in the order in which they were collected for a given site. If soil excavation increased the release of TCE to the air phase relative to natural conditions, and if this increased release was the cause for the discrepancy between total and diffusive fluxes, TCE fluxes would be expected to decrease with time for a given soil excavation. The data in Table 1 do not consistently exhibit this trend. In some cases, the total flux remains relatively constant (e.g., site 2 on 6/28/94), in other cases, the total flux increases with time (e.g., site 2 on 8/2/94), and in still other cases, the total flux decreases with time (e.g., site 1 on 8/5/94, although these measurements may also have been affected by a rain storm, as discussed later). Furthermore, if excavation of soil causes an increase in the rate of TCE desorption and this increase was large relative to natural diffusive fluxes, total flux measurements at the same site but for different excavations (all within a 2-m radius) would be expected to have similarly high, erroneous total flux values. Again, this trend is not always evident from the data in Table 1. For example, flux measurements at site 1 range over 2 orders of magnitude (from 0.044 to 4.8 $\mu g\ m^{-2}\ h^{-1}$).

During infiltration events, vapor-phase TCE can partition into rainwater and be advected downward in the aqueous phase (*6*, *44*). In addition, increased moisture contents will reduce the gas-phase diffusion flux by decreasing the effective diffusion coefficient of the porous media (*6*, *44*). The data in Figures 4 and 5 are consistent with these observations. As a result of infiltration beginning at time = 1 h, the moisture content increases at depths of 0.65, 1.1, and 1.3 m, with the largest increases occurring at the shallowest depths (Figure 4). After 3 h of infiltration, the moisture content at all depths appears to be at steady state. As the soil moisture content increases, there is a corresponding decrease in the measured flux of TCE vapor from 0.2 to 0.06 $\mu g\ m^{-2}\ h^{-1}$ (Figure 5). As rainwater with essentially a zero TCE concentration enters the subsurface, a concentration gradient is created that results in a net transfer of TCE from the vapor phase to the aqueous phase. TCE in the aqueous phase is then advected downward with the infiltrating rainwater. Vapor-phase concentrations of TCE are reduced because of the mass transfer into the aqueous phase, and the increased moisture content increases the gas-phase tortuosity factor for TCE, thereby reducing the effective diffusion coefficient and the gas-phase flux.

The average annual vapor flux of TCE from the unsaturated zone above the groundwater plume can be calculated using the data in Table 1 and Theissen polygons (*45*). This graphical technique, which is commonly used to estimate watershed precipitation based on unevenly distributed rainfall measurements, is implemented by dividing the shaded area in Figure 1 into a series of eight polygons. The polygon containing each sampling site is constructed by connecting the sampling site to every other site with a straight line. Perpendicular bisectors for each of these lines are then constructed, and the area of the resulting polygon formed by the perpendicular bisectors is estimated. This procedure is repeated for each sampling site. The average flux, J_{av}, for the shaded area in Figure 1 can then be calculated with the following relation:

$$J_{av} = \frac{\sum_{i=1}^{8} A_i J_i}{\sum_{i=1}^{8} A_i} \qquad (4)$$

where A_i is the area of the polygon containing site i, and J_i is the mean of the total fluxes measured at site i. The average flux calculated in this manner is 54 $\mu g\ m^{-2}\ h^{-1}$. The area associated with groundwater TCE concentrations greater than 10 $\mu g/L$ (Figure 1) is approximately 115 000 m^2. Therefore, the average annual TCE flux from the subsurface to the atmosphere is approximately 50 kg/yr. In a similar manner, the average diffusion flux obtained using Theissen polygons and the data in Table 1 is 0.05 $\mu g\ m^{-2}\ h^{-1}$. This corresponds to an average annual TCE diffusion flux of approximately 0.05 kg/yr.

To place these values in perspective, it is useful to compare them to other TCE sinks in the aquifer. From September 1992 to February, 1995, the pump-and-treat system at Picatinny Arsenal extracted approximately 3×10^8 L of groundwater with an average TCE concentration of 1.5 mg/L. This corresponds to a TCE removal rate of approximately 180 kg/yr, which is comparable in magnitude to the total TCE vapor flux from the subsurface. In a recent publication, Imbrigiotta et al. (*27*) has quantified the flux of TCE entering Green Pond Brook prior to the start of pump-and-treat remediaton (e.g., under nonstressed, natural flow conditions). Using estimates of the groundwater flow velocity and the measured TCE concentrations in the aquifer, and assuming that the dispersion and diffusion fluxes of TCE were negligible relative to the advective flux, these researchers calculated that approximately 50 kg/yr was removed from the aquifer by groundwater discharge into Green Pond Brook. This value is equal to the TCE vapor flux from the unsaturated zone. These comparisons indicate that the total TCE vapor flux may be a significant transport mechanism that should be accounted for in any prediction of TCE fate and transport in the subsurface. By contrast, the TCE vapor diffusion flux is small relative to the fluxes caused by groundwater discharge into Green Pond Brook and extraction of groundwater by the pump-and-treat system.

The data and analyses presented in this paper do not definitively identify advective TCE vapor fluxes as the cause of the relatively high total fluxes measured with the VFC.

However, it provides information that suggests that TCE vapor advection is a potentially important transport process and that further research is needed to address the explicit effect of subsurface pressure fluctuations on the transport of TCE vapors in the unsaturated zone.

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