



HENRY'S CONSTANT, DARCY'S LAW, AND CONTAMINANT LOSS

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ABSTRACT

A six-channel system was used to determine how differences of Henry's law constant and vertical water velocity affect the diffusive loss of contaminants from a sandy soil. Two channels (10 cm wide x 110 cm long x 65 cm deep) were each fed with methyl *tert*-butyl ether, dichloromethane, or trichloroethylene in groundwater. After steady state was attained, vertical concentration gradients were measured in unplanted (inlet end) and planted (outlet end) halves of each channel. An analytical model was used to describe contaminant movement in soil of different porosity and fractional water saturation. Changing the two parameters for Henry's law constant (different compounds) and vertical Darcy water velocity (planted vs unplanted end) provided a good qualitative fit to the different observed distributions. Calculated profiles were also sensitive to soil porosity and fractional water saturation. The chosen compounds span much of the observed range of Henry's law constants for volatile compounds (0.02 to 0.4) and the measured Darcy velocities represent most of those likely to be encountered in natural settings for unsaturated soils. Thus we can use the model to predict volatilization losses for a wide range of compounds, if they are being released from soil water.

Key words: methyl *tert*-butyl ether, dichloromethane, trichloroethylene, volatilization, modeling

INTRODUCTION

Henry's law constant and porosity

Air quality depends on soil contamination in a complex fashion. Whether one is concerned with radon entry into subsurface structures or evaporation of a gasoline spill, it is necessary to deal with the wide variability in molecular movement produced by differing soil porosity and moisture content (Washington et al., 1994; Gidda et al., 1999). *In situ* measurements are not easy to conduct in a quantitative way and may be difficult to interpret (Smith et al., 1996), so for most purposes simple approximations and estimations are applied. As the experimental database has increased, more refined estimations have become possible. These in turn allow more precise determination of where contaminant leakage is likely to significantly impact air quality.

When we attempted to model the movement of a soluble contaminant from groundwater to the atmosphere, we found that the value of Henry's law constant had a large impact on estimations of contaminant concentration distribution within the soil (Narayanan et al., 1999 and unpubl. obs.). Two similar substances differing only in Henry's law constant could be predicted to show very different steady state vertical distribution profiles within the soil, despite identical input contaminant concentration and rate of vertical water movement. Conversely, two different rates of water movement in the vertical direction could lead to rather different soil distributions for a single contaminant, if it had a fairly small Henry's law constant (H).

For a compound that is both volatile and very soluble in water, as methyl *t*-butyl ether

(MTBE) is, both aqueous and gaseous phase diffusion must be considered in the capillary fringe and unsaturated soil; whereas for a contaminant such as radon, only the gas-phase diffusion is pertinent, because it is scarcely soluble in water at all. Most volatile compounds of interest fall between these two in their H value. We thus concluded that further examination of this problem was necessary if we were to correctly understand the potential exposure of soil organisms to contaminants such as MTBE. If the organisms of interest are plants and associated rhizosphere micro-organisms, variation in exposure alters the potential for remediation. More volatile compounds with large Henry's law constants are more likely to pass through the gas phase to the atmosphere without opportunity for degradation.

Temperature effects

Washington (1996) used a strictly thermodynamic approach to derive an estimate of the importance of temperature and water content on the partitioning of contaminants between gas, liquid, and solid phases of soil. His specific interest was the use of soil gas surveys as an indicator of contamination, and to predict how results might vary depending on the temperature and moisture content of the soil. For some compounds, the published H value increased by less than one-third between 10 and 20 °C, while for others it nearly doubled. Thus the relative tendency for a substance to depart from the soil depends in a complicated way on temperature, which increases diffusivity in a regular way, and usually increases H but to a different extent for different substances. Re-

cently Dewulf et al. (2000) determined the effect of temperature on H values for 20 compounds, few of which were considered by Washington. They showed that for several rather soluble compounds, the temperature effect can actually decrease H with increase of T; that is, it may enhance the solubility more than the vapor pressure. Washington (1996) mapped out climatic regimes that indicated the likelihood of volatilization losses over the annual cycle for a particular compound in different regions of the U.S. Obviously, the predicted seasonal response patterns depend on how the compound responds to changing temperature and soil water content, as well as seasonally varying evapotranspiration rates and the relative porosity of the soil. Some substances may volatilize appreciably in summer but not in winter.

Dynamic estimations

Earlier workers considered the dynamics of how porosity and H interact to permit loss of contaminant from unplanted soil. The modeling work of Jury et al. (1990) considered two fixed values of water loss, zero or 0.1 cm/d, with two soil types, sandy and clayey. They examined 32 compounds with a wide range of solubility and partition properties, and sizes from chloromethane to dioxin. However, all compounds were assumed to have the same diffusion coefficients, $4.3 \times 10^3 \text{ cm}^2/\text{d}$ in air and $0.43 \text{ cm}^2/\text{d}$ in water. These correspond to values for a compound with a molecular weight above 200 (c.f. McCarthy and Johnson, 1993) and may underestimate the relative diffusive loss of smaller compounds. A 1-m deep soil layer which covered a contaminated zone of 0.3 m

was assumed to have a constant permeability throughout the 1 m covering the contaminant source, and a fixed-water content based on the soil type. This may be a reasonable approximation when a soil cap is applied over a buried contaminant layer.

Biodegradation within the overlying layer of soil was considered as part of the loss process by Jury et al. (1990), and when one examines the results of their modeling, it is apparent that the estimated half-life for degradation is the key variable determining the relative potential to escape for compounds of similar H. For instance, chloroform and trichloromethane (the same compound) both appear in the data set, with two-fold different values for half-life and sorption coefficient assigned to them, which results in a more than three-fold difference in the predicted volatilization loss from a sandy soil. A planted soil with an active rhizosphere could shorten the half-life appreciably (Anderson and Walton, 1995), but it would also increase soil water movement, decreasing the residence time available for degradation. It is difficult to predict which factor might dominate in determining the overall loss rate.

As a screening level tool, a simple model like that of Jury et al. (1990) may be useful to identify compounds that might be likely to escape a soil cap, assuming that the half-lives and sorption coefficients were well estimated. This assumption is critical. Thus benzene, which was initially assumed to have a half-life of a year, had a much greater predicted tendency to be lost by volatilization than did toluene with an assumed half-life of five days. A later short

publication (Jury et al., 1992) used new data and re-estimated the tendency for compounds to escape. They showed that when a more realistic half-life was assigned to benzene (the same as for toluene), it was not more fugitive than toluene. Later work (Jin et al., 1994) suggested that for toluene, the half-life might be on the order of a few hours, not days, which in turn would reduce the chance for volatilization loss still further.

In the work of Jury et al. (1990), a few compounds were identified to vary several-fold in their net volatilization loss as a function of water flux. These were compounds for which the predicted half-life was rather long, so that residence time in the soil was important for degradation. The second factor critical to escape was sorption to organic matter in the soil. Strong sorption resulted in slow release. The derivations of equations of Jury et al. (1990) have been corrected recently (Robinson, 2000), but for our purposes the corrections introduce few changes. It is the estimated half-lives and sorption coefficients that are most critical.

McCarthy and Johnson (1993) experimentally examined the impact of variable water saturation on contaminant distribution profiles for trichloroethylene (TCE). Then they modeled the predicted vertical TCE transfer rate that could account for the observed profiles, in the absence of water movement. Their experimental system represents a real-life soil condition at a contaminated site better than the assumption of Jury et al. (1990) that the soil is uniformly moist. TCE, with a dimensionless $H = 0.38$ at 25°C ,

escaped primarily via the gas phase and rapidly was lost above the capillary fringe because the effective diffusivity increased nearly 1000-fold in moving from saturated to less saturated soil. McCarthy and Johnson (1995) experimentally examined in more detail the effect of relative air-filled porosity on TCE diffusion through column segments. They showed that the effective diffusion coefficient changed 100-fold over the capillary fringe because of changing air-filled porosity.

Our work with TCE in a planted mesocosm confirmed their finding of the relative importance of gas-phase diffusion and water saturation. A finite element model was developed originally for toluene (Narayanan et al., 1998a,b), to consider both horizontal flow of groundwater and vertical movement under the influence of evapotranspiration. It fitted the data for distribution of TCE with depth very well. An analytical solution was also derived for comparison of TCE profiles in the vertical direction. Details have been published for a modeling of TCE movement in a planted system, considering water movement and variable soil saturation as well as microbial degradation (Narayanan et al., 1999). With TCE, most of the contaminant loss was due to diffusion through the gas-phase soil pores. Total TCE loss from the system was limited by the flux of water up through the capillary fringe, as expected on the basis of McCarthy and Johnson's (1993) work.

For simplicity of calculation, we have used the analytical one-dimensional model to determine the parameter sensitivity for TCE and other contaminant movement, when the varied

parameters are water velocity and Henry's law constant. In this paper, we show both calculated and experimentally measured results for contaminant distribution within the soil of a mesocosm.

Experimental methods

The experimental chamber system has been described several times previously (cited in Zhang et al., 2001) and has been in use for several experiments since Nov. 1995. In brief, it consists of six channels, each 10 cm wide x 110 cm long x 65 cm deep. Water enters at the bottom of one end and leaves at the other, while the depth of the water table is controlled by the height of the outlet line. Each channel is packed with a sandy soil from near a contaminated site and planted with alfalfa. The soil organic matter content is about 1 to 1.5% in the top layer of soil and below 0.5 % in lower layers (Davis et al., 1993, unpubl. obs.). For this experiment, only the latter half of each channel had plants, providing two distinct upward water flow regimes. The six channels are placed side by side under a bank of 12 4-foot, 40-watt fluorescent lights (cool white deluxe). The average light intensity of $>160 \mu\text{mol}/\text{m}^2/\text{s}$ is maintained continually. Water is supplied to the inlet container at a rate of 1 L/d. Two channels received MTBE at 100 $\mu\text{L}/\text{L}$; two received dichloromethane at 50 $\mu\text{L}/\text{L}$; and two received TCE at 50 $\mu\text{L}/\text{L}$ during the experiment reported here.

Contaminant concentrations in the input and output water were routinely measured by gas chromatography of headspace gas of samples to determine the extent of contaminant loss from the saturated zone during passage of

water through the 1-m channel. Diffusive contaminant loss from the soil was measured by placing a container of known volume over a portion of the soil surface, then sampling the gas in that container through a septum to measure the rate of accumulation. Losses through plants were determined as described by Zhang et al. (2001) by sampling the plants and quickly placing them in bottles to equilibrate. From the water use rate and concentration-per-unit water in the plant stem at ground level, the flux through the plant may be estimated. Only a small fraction of the contaminant passes through the plants to above the soil surface. The concentration of MTBE in plant water at the ground surface is about one-eighth that of the inlet water. MTBE is the contaminant most effectively carried with the water; for TCE, the concentration in plant water of above-ground parts was near zero.

Soil sampling was done by digging a hole at the boundary between the planted and unplanted portions of a channel. After excavation to 10 cm, samples were taken by boring horizontally into either the planted or unplanted region as appropriate. Further excavation to 20 cm was followed by additional sampling. After excavating and sampling to the final depth of 30 cm, the excavated soil was repacked in the same order in which it was removed. Each horizontal sample was about 6-8 g of moist soil, placed in a bottle sealed with a Mininert stopper to equilibrate. Aqueous phase concentration was determined by gas chromatography of the headspace to measure the total mass of contaminant, and then drying and weighing to determine the water content of the soil. Esti-

mates were not corrected for the fraction of contaminant sorbed to soil organic matter, as only relative profiles were of interest.

The excavation method provided good vertical resolution but was semi-destructive of the planted channel. On several other occasions, soil samples were obtained by boring vertically from the soil surface in increments of ~8 cm. Typically, three depths of sample were obtained and analyzed. This gave less vertical resolution but allowed comparison of planted and unplanted channels on repeated occasions.

Calculational methods

The analytical solution for vertical contaminant and water movement as described by Narayanan et al. (1999a) uses Bessel functions and a piecewise solution. The deepest portion of the vertical soil column is assumed to be fully saturated with water. Above that is a capillary fringe where the relative saturation decreases linearly. At the top is a region of constant partial saturation. Changing the relative saturation gradient and saturation fraction in the top section alters the derived profiles somewhat, but the essential trends remain. We have chosen to assume soil properties like those of a fine sand soil which closely approximates our experimental system. It is similar to the column used by McCarthy and Johnson (1995) but with a less uniform grain size than they had; they used # 8 quartz sand.

The Henry's law constant is most conveniently expressed for our purposes as the ratio of concentration in the gas phase to concentration in the liquid phase, both in units of molar.

Thus, it is written

$$H = \frac{\text{mol} / L(\text{air})}{\text{mol} / L(\text{water})}$$

The units of these concentrations cancel to give a simple dimensionless value. Henry's law constant is also defined by the vapor pressure in air divided by the solubility in water, both in appropriate units, corrected for non-ideality (Washington, 1996).

The range of H values for compounds of environmental concern is very large. Some materials like atrazine are scarcely volatile yet are fairly water soluble, while others like hexane are highly volatile and scarcely soluble in water. If we want to consider both water movement and chemical partitioning, we have to devise practical limits for modeling calculations, because the analytical solution uses a limited number of terms in the Bessel function. When considering water as a carrier of contaminants in the unsaturated zone, for practical purposes we can ignore the insoluble hydrocarbons and the fixed gases including N₂O or radon, all with H values above 10, because over the range of real water movement rates in the vertical direction, they are very little affected by water flow.

Instead their movement depends almost entirely on the air-filled porosity of the soil. A practical upper limit of H to consider in modeling might be about 1, because diffusion through air is 10,000 times faster than through water. Thus when the gas phase is a significant fraction of total porosity, most contaminant movement occurs through the gas phase (McCarthy and Johnson, 1995). The accessibility of the gas phase for diffusion varies as approximately the

cube of the air-filled porosity (Narayanan et al., 1999a).

The lower limit for H is harder to define, but *t*-butyl alcohol, a common contaminant of MTBE, might be near the limit of what we need to consider as a volatile partitioning between air and water. It has an H value 40-fold below that of MTBE, less than 0.001, so it stays mostly in the water phase under almost all conditions. Its gas-phase diffusion will contribute little to its movement in the soil. If the water moves, it moves.

The ambient temperature affects H by altering both solubility and volatility, so for instance, MTBE may have an H value of 0.01 at 10° C and H = 0.05 at near 30° C (Callender and Davis, 2001). This response to temperature is more extreme than any reported by Dewulf et al. (1999) over the same temperature range. As we show below, depending on water velocity, this variation in H with temperature can have a large effect on relative fraction of the contaminant remaining with the water as it moves to the surface. For MTBE, which is much more water preferring than TCE (H ~0.02 vs 0.4 at 25° C), the water flux is critical in determining how close to the soil surface the aqueous phase concentration of MTBE is significant (say 10% of the groundwater input concentration). This in turn determines whether organisms in the soil are exposed to MTBE at high concentrations in the aqueous phase.

Darcy's law may be applied to fluids including air or water. It states that the flux of fluid is related to the quantity of fluid passing through a specified area per unit time. For

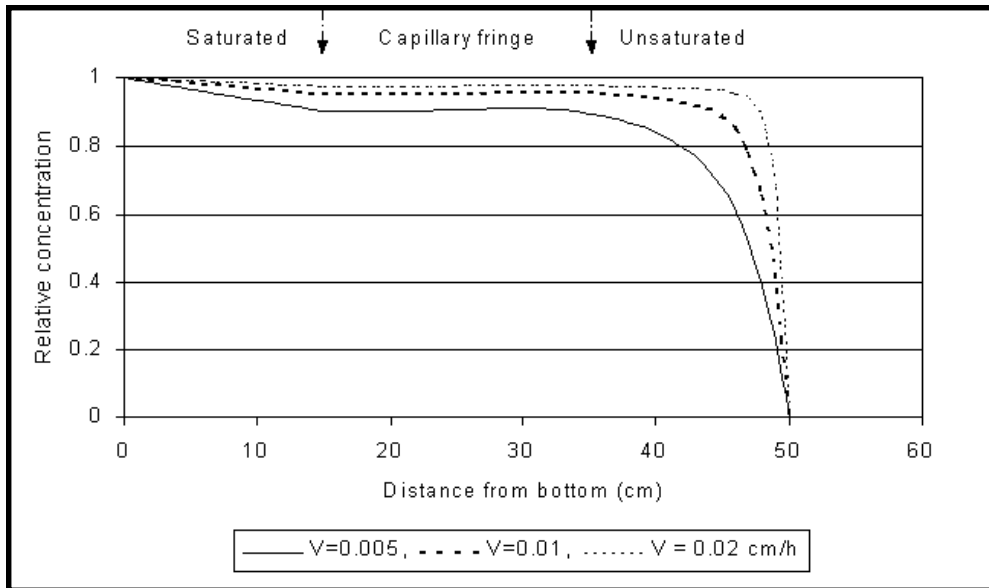


Figure 1a. Contaminant concentration profiles, $H = 0.01$.

convenience, we deal with cm^3/d passing across an area of cm^2 , which gives a velocity in cm/d .

The quantity that passes depends on a hydraulic conductivity, which is a property of the transmitting medium, and the pressure gradient applied.

In the particular case of interest to us, vertical transport, the driving force for water movement is the vapor-pressure deficit either due to simple surface evaporation or by plant transpiration.

The upward Darcy velocity of water from a unit area of soil surface may range from near zero on a damp day to several cm/d when a strong sun and wind are combined to draw water from a large surface area of plant leaves. During an irrigation event or rainfall, the velocity is in the downward direction. Flow downward is potentially much faster than upward because gravity favors downward movement and only chemical potential differences drive the upward movement. Note that the actual linear velocity of some water within the soil (seepage velocity), or

within a plant xylem, may be many fold greater than the Darcy velocity. Within a plant, the Darcy velocity equivalent is the superficial velocity, the volume of water movement per cross-sectional area of stem per time.

In modeling, we used a reasonable estimate of diffusion coefficient for a molecule of molecular weight around 100. The estimate of McCarthy and Johnson (1999), $300 \text{ cm}^2/\text{h}$, was used for the gas phase. For the aqueous phase, dispersion was assumed to be negligible in comparison.

RESULTS AND DISCUSSION

We have made use of the analytical solution (Narayanan et al., 1993) for one dimension to determine sensitivity of the input parameters including H and water movement (Darcy velocity). The graphs (Figures 1 and 2) show how for constant H , the water velocity alters the equilibrium distribution of contaminant in the soil, and how for constant velocity,

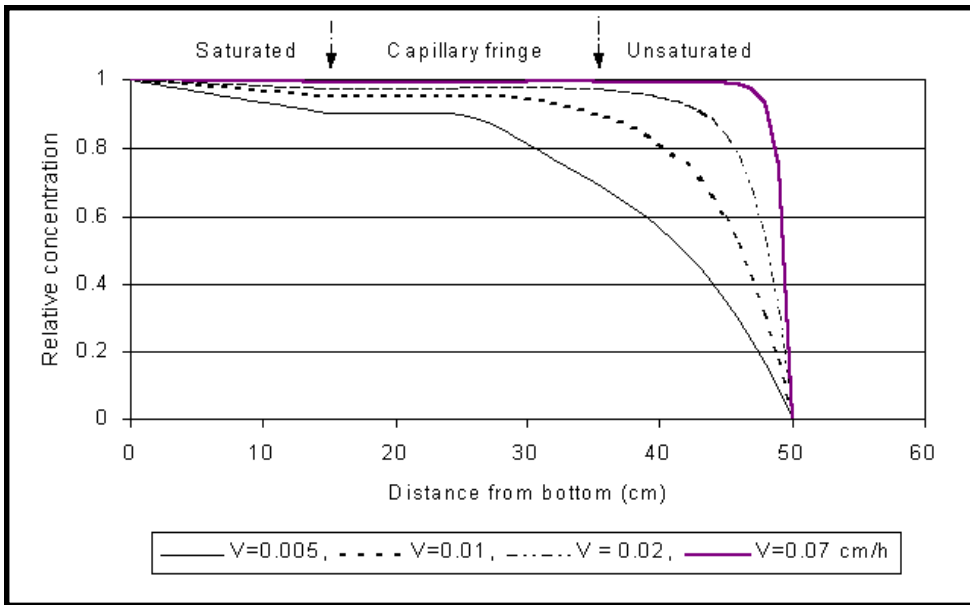


Figure 1b. Contaminant concentration profiles, $H = 0.03$.

compounds with different H may respond. For a given compound, changing temperature usually has an appreciable effect on H . We have not modeled the effect of temperature on values for D ; D values for both water and air increase as temperature increases.

These simulated profiles are consistent with experimentally determined concentrations in soil water. The results of Figure 3 were obtained at a single time for each of three channels treated with a different contaminant for several months. The planted and unplanted portions of the channel were sampled simultaneously so that the observed gradients differ primarily because of different vertical water movements. However, the unplanted portion of the channel has a measurable Darcy velocity of more than 0.1 cm/d, which is the high velocity considered by Jury et al. (1990). Thus the loss rates for contaminant might be higher than they estimated, primarily because bacterially mediated degradation would have less time to

operate. The water fluxes in the planted portion are up to 1 cm/d, thus the contaminated groundwater is moved up to the root zone up to 10 times faster when plants are present. One might expect that a very large fraction of the inlet contaminant might be lost through the soil surface if neither bacterial nor plant metabolic processes were able to degrade it. In fact, for MTBE, we find that after the system has time to adapt for some months, a large fraction of all inlet contaminant is degraded by soil bacteria and only a little escapes through the plants (L. Davis, unpubl. obs.).

Figure 2a shows an upward water velocity similar to that observed in the unplanted portion of the channel. Experimental data from the unplanted portions of the channels (Figure 3) have been plotted assuming that the soil surface is at 50 cm from the bottom of the channel. Figure 2c shows an upward water velocity similar to that observed in the planted portion of the channels. Experimental data from the

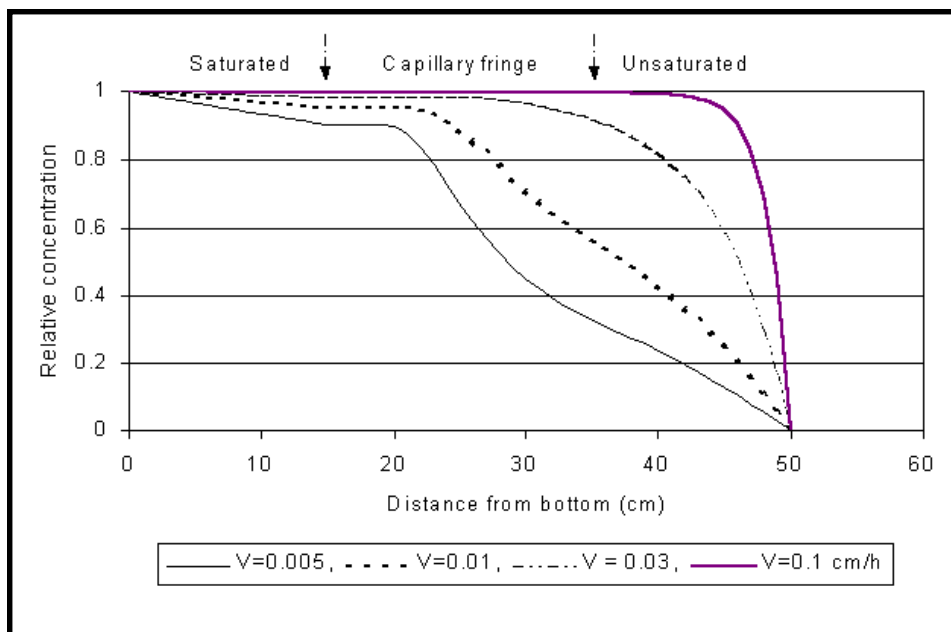


Figure 1c. Contaminant concentration profiles, $H = 0.1$.

planted portions of the channels (Figure 3) have been plotted, as for Figure 2a. At a room temperature of 25-27 °C, the H value for TCE is near 0.4; that for DCM is about 0.15 (Jury et al., 1990) and that of MTBE is 0.03-0.04 (Callender and Davis, 2001).

There is reasonable agreement between simulated and experimental data in Figure 2, if one considers that the model uses a single porosity and water content for the upper portion of the soil. Narayanan et al. (1999a) used a finite element model with porosity increasing near the soil surface to fit experimental results with TCE as contaminant. The increased air content makes escape of all compounds easier (varying with the cube of air-filled porosity) as they approach the surface, consistent with the experimental observations. In addition, there is strong evidence that after longer treatment of the soil, biodegradation becomes a significant factor in disappearance of MTBE (Davis, unpubl.

obs.). It may have made a lesser contribution in this experiment. Long-term treatment with DCM also seems to induce degradation; surface fluxes went to zero after several months (Davis, unpubl. obs.).

Whether or not the contaminant is degraded by soil bacteria, quite often most of the roots of the plants will not be exposed to concentrations nearly so high as those in the groundwater. As soon as a volatile contaminant reaches the unsaturated zone, it will partition to the gas phase to a large extent. If the soil is fine enough to allow significant capillary rise, but not so tightly packed as to have a low total porosity, only those roots deep in the soil will contact a relatively high contaminant level. In other work (Hu et al., 1998), we have shown that contaminants diffuse freely from roots. Thus the contaminant will partition from the root to the gas phase during water movement toward the stem.

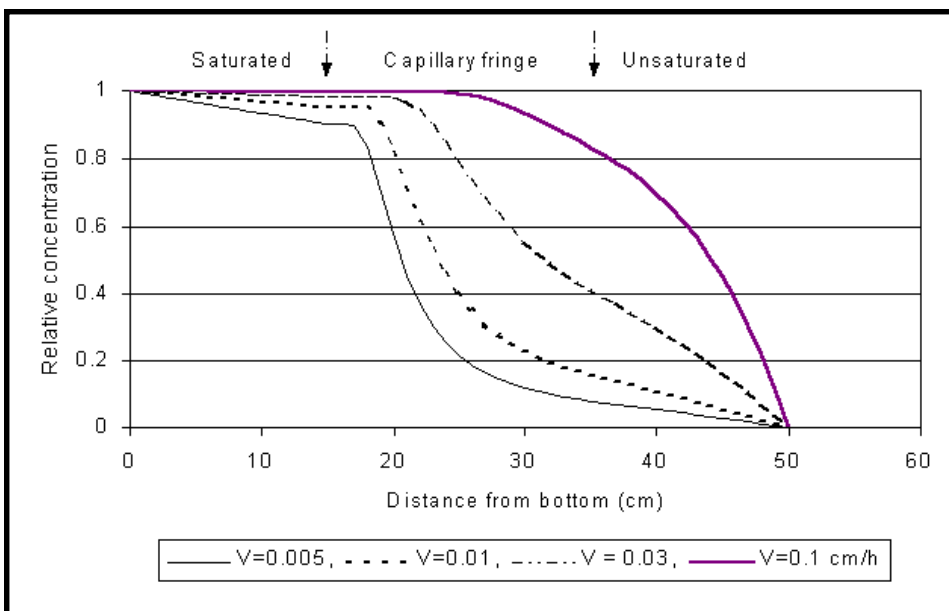


Figure 1d. Contaminant concentration profiles, $H=0.5$.

Previously we had shown that for TCE in an unplanted system maintained for a long time in the laboratory, there is no loss from the surface under the influence of evaporation (Davis, 2000). Instead, the TCE is degraded via *cis*-dichloroethylene when the saturated zone is close to the surface. With the present system having a deep unsaturated zone overlying the few cm saturated zone, we have not reproducibly detected formation of DCE after more than a year of exposure to TCE.

To add further complexity, or perhaps a saving grace, when contaminants have to move through a saturated or near-saturated soil, the losses will be limited primarily by the rate of water movement out of the soil times the dissolved concentration of contaminant in the saturated zone (Narayanan et al., 1999b). The concentration in the saturated zone is depleted only by microbial action, not by diffusion (McCarthy and Johnson, 1995; Narayanan et al., 1999a). This property of water-saturated

soil provides a large factor of protection for air quality because water, the carrier of contaminant, is relatively insoluble in air. We can visualize this graphically. About 15-25 μL (mg) of water, a cube ~ 2.5 mm on a side, disperses as vapor in 1 L (10^3 mL, 10^6 μL), a cube 10 cm on a side. So we get a protection of about 50,000-fold dilution compared to what is in the groundwater. Of course turbulent mixing in the atmosphere in Kansas leads to a rapid further dissipation. This protection factor is not applicable for a directly spilled volatile source like gasoline at the pump (Gidda et al., 1995), but it is important for phytoremediation efforts, for instance when contaminated groundwater is produced by flowing past a leaking underground storage tank. This is more fully discussed in Narayanan et al. (1999b).

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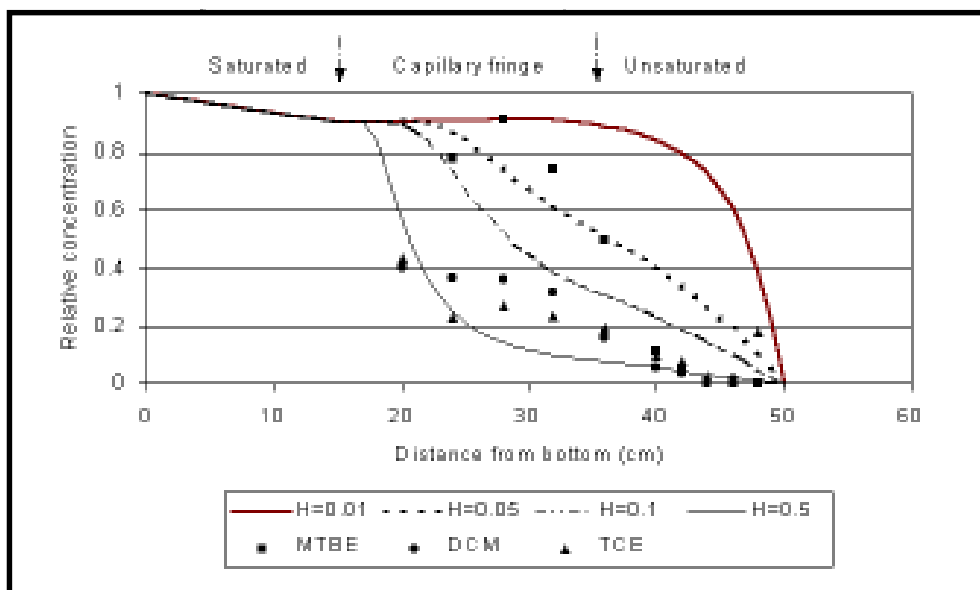


Figure 2a. Contaminant concentration profiles, $V = 0.005$ cm/h.

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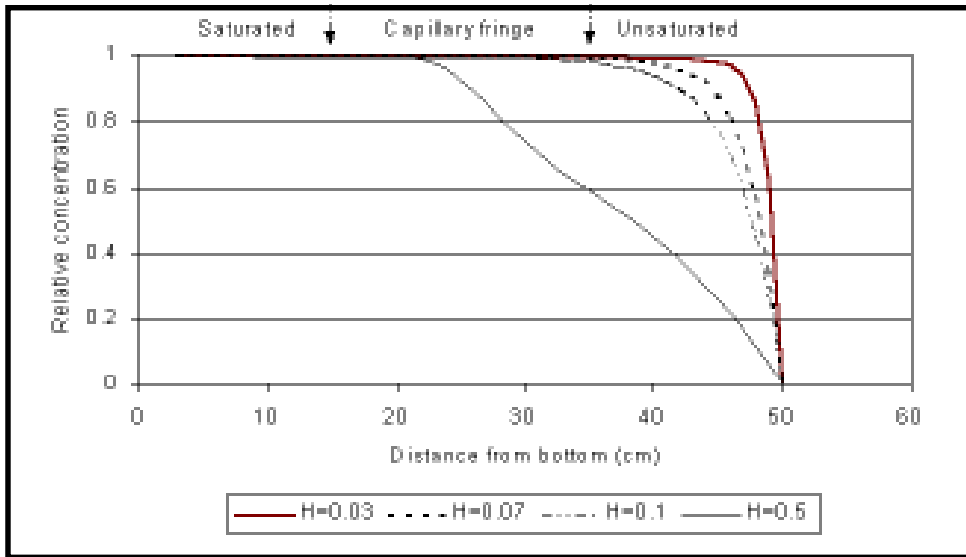


Figure 2b. Contaminant concentration profiles, $V = 0.05$ cm/h.

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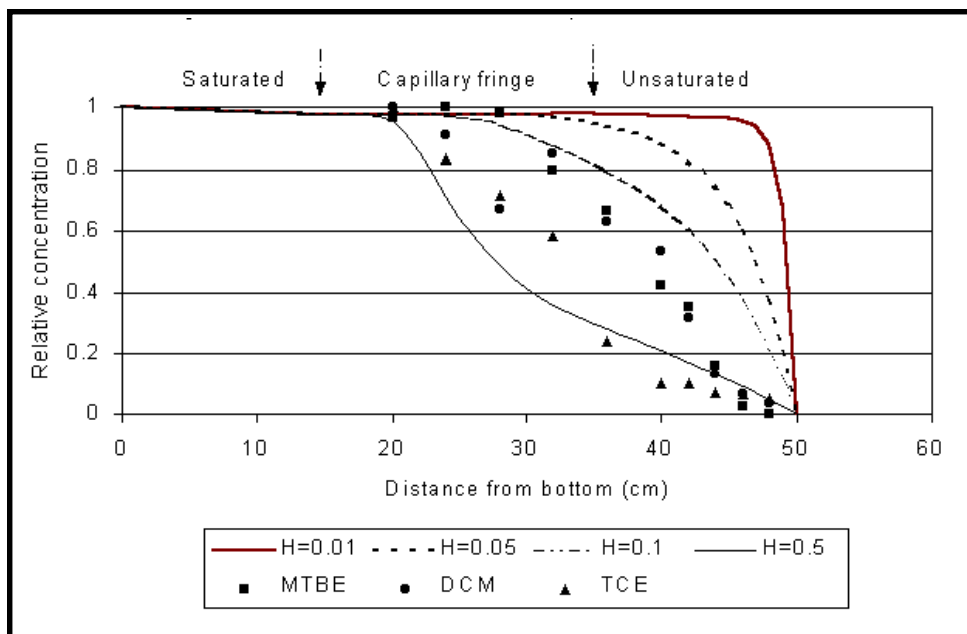


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LEGENDS

Figure 1. Calculated effect of varied upward vertical water velocity at different fixed H. In each case, soil from 0 to 15 cm was below the water table; 15 to 35 cm was in the variably saturated fringe where the saturation decreased to a limiting value maintained constant between 35 to 50 cm. Total porosity was assumed to be 0.35 and the limiting water content was 0.1, giving an air-filled porosity of 0.25 in the upper 15 cm.

Figure 2. Calculated effect of varied H at different fixed upward vertical water velocities. All conditions as in Figure 1. Part a. Simulated contaminants concentration profiles for $V = 0.005$ cm/h and different H values. Experimental data for unplanted portions of channels are included. \blacktriangle =TCE; \blacksquare = MTBE; \bullet = DCM. Part b. Simulated profiles for $V = 0.05$ cm/h. Part c. Simulated profiles for $V = 0.02$ cm/h,

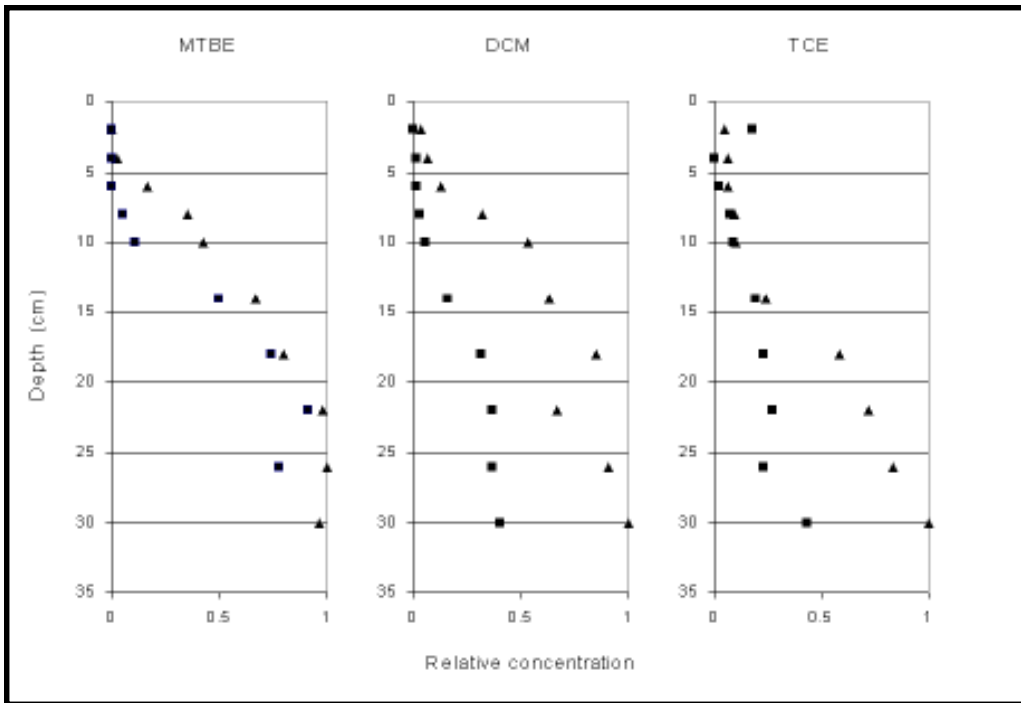


Figure 3. Experimental data for planted (▲) and unplanted (■) portions.

with experimental results from planted portions of channels. Symbols are as in part a.

Figure 3. Comparison of relative contaminant distributions in soil with and without plants present. In each part, the experimentally determined concentration of contaminant in the soil water is plotted after normalizing to the highest observed concentration sampled. This is not identical to the input concentration because sampling did not proceed to the water table and sorption occurs. For MTBE, the concentration at 30 cm is the same as the input water. For

DCM, the observed level at 30 cm is about two-thirds that in the inlet water. We do not know if this low value represents degradation or losses during sampling, but it is likely to indicate degradation because the outlet water samples have consistently given lower concentrations of DCM than the inlet water. For TCE, the observed level is about 25% above that of the inlet water because a significant fraction of TCE was sorbed to soil organic matter. During measurement of TCE in the soil sample, this sorbed portion is measured as part of the total.