
EXPERIMENTAL AND MODELING STUDIES OF THE FATE OF TRICHLOROETHYLENE IN A CHAMBER WITH ALFALFA PLANTS

M. Narayanan¹, N.K. Russell², L.C. Davis³, and L.E. Erickson^{1}, Departments of ¹Chemical Engineering, ²Chemistry, and ³Biochemistry, Kansas State University, Manhattan, KS, 66506*

ABSTRACT Experiments were performed in a laboratory chamber to investigate the influence of alfalfa plants on the fate and transport of trichloroethylene (TCE) fed at 200 µl/l concentration in the entering ground water. Concentrations of TCE in the aqueous and gas phases were regularly monitored in the chamber. Evapotranspirational fluxes of TCE were also reported from the soil to the headspace of the chamber. Numerical modeling of the fate of TCE in the vertical direction of this chamber was carried out using the Galerkin finite element approach. In this model, the partitioning of TCE between solid, aqueous, and gas phases was represented as rate-independent physical equilibrium processes. The boundary condition at the surface was modified to account for free volatilization of TCE to the headspace of the chamber across a thin atmospheric boundary layer. The simulation results were compared with experimental data on the transport of TCE. Results indicated that the water and air content distribution in the soil significantly impact the transport of TCE in subsurface soils.

KEYWORDS: volatile organics, trichloroethylene, gas phase diffusion, phytoremediation

INTRODUCTION

Trichloroethylene (TCE) is a frequently detected pollutant at Superfund sites. TCE is a dense non-aqueous phase liquid (DNAPL) and is also relatively volatile in nature. Trichloroethylene contamination beyond the maximum contamination limits (1-5 µg/l) in ground water used for drinking purposes is of major concern because of the potential carcinogenic nature of this pollutant. This is the reason for the enormous attention by the environmental research community on remediation of TCE. Industrial wastes and landfill leachates are sources of TCE in contaminated soils and ground water [1]. The attenuating mechanism of TCE in contaminated soils and ground water may be due to transport related processes involved in the subsurface, adsorption onto soil particles, and microbial transformation.

Trichloroethylene is relatively recalcitrant to direct biotransformation by indigenous soil microorganisms; however, the loss of TCE through the transport pathway is significant and has not been fully investigated in soil environments [1-9].

Mass transport phenomena

In contaminated soils and ground water, TCE is often present in the soil gas due to the partitioning of TCE from the polluted ground water. To investigate the migration of TCE, subsurface related transport phenomena in the liquid and gas phases need to be considered. Several researchers have studied and modeled contaminant transport with a uniform volume fraction of the liquid and gas phases and hence a constant contribution of transport phenomena in each phase in the soil environment [2, 3]. However, in the actual situation, soils

*Corresponding author (Phone: 913-532-4313, FAX: 913-532-7372).

usually comprise of water saturated and unsaturated zones sandwiching the tension-saturated zone. In the saturated and tension-saturated zones, the transport mechanisms governing mass transfer are convection and dispersion. However, in the unsaturated zone mass transport is governed by gas diffusion as well because of the existence of air in the void spaces. The rate of partitioning of TCE among the different phases may also affect the transport of TCE in contaminated soils. Researchers have modeled the partitioning as rate-limited nonequilibrium sorption or volatilization [4]. However, simple rate-independent phase equilibrium is assumed in this study.

Plant-assisted phenomena

Plants in general help in the attenuation mechanism of organic compounds contaminating soils and ground water. Several review papers and articles in books published recently highlight the escalating attention that plant-based bioremediation is receiving. Vegetation plays a significant role in bioremediating contaminated soils and ground water [1, 5-7].

In plant-soil environments, vegetation can act as a solar driven pump-and-treat system which pumps contaminated water economically during the regular photosynthetic process. Plants such as cottonwood, poplar, and alfalfa that are drought resistant and viable in contaminated soils penetrate their roots to reach ground water and draw up contaminated water to the vadose zone and rhizosphere (root zone of plants) [6]. In other words, they play a significant role in the determination of water-content profiles in actual plant-soil systems. Plant roots, in particular, may be responsible for rapid depletion of water from soil zones and create unsaturated zones of soil. Hence, the air-content profiles in

vegetated soils are closely related to the pumping and photosynthetic processes of established vegetation, and suction pressures in roots as well. The objectives of this research are to investigate and model the transport processes involved for TCE in the vertical direction from the ground water table to the surface of soil in the experimental chamber [1].

EXPERIMENTAL STUDY

A chamber with two identical U-shaped channels each 10 cm wide, approximately 1.8 m in axial flow length, and 35 cm in depth was employed for the study [1]. The design, construction, and feeding operation of TCE to this chamber are already described in Erickson, *et al.* [7], and Narayanan, *et al.* [1]. The various analytical techniques involved for determining the ground water concentration of TCE, headspace concentration of TCE, and aqueous phase concentration of TCE in the various zones of soil are also described in Narayanan, *et al.* [1].

MATHEMATICAL MODEL

The development of the mathematical model used to investigate vertical transport of TCE in the experimental chamber is well explained by Narayanan, *et al.* [9]. The governing differential equation used for TCE transport in the experimental chamber is shown below:

$$\begin{aligned} (\theta_w + \theta_a H + \rho K_d) \frac{\partial}{\partial t} (C_w) = D_w \frac{\partial}{\partial z} \left(\theta_w \frac{\partial}{\partial z} (C_w) \right) \\ - V_w \frac{\partial}{\partial z} (C_w) + HD_a \frac{\partial}{\partial z} \left(\xi \frac{\partial}{\partial z} (C_w) \right) - \theta_w k C_w \end{aligned} \quad (1a)$$

where

$$\xi = \frac{\theta_a^{10}}{\eta^2}. \quad (1b)$$

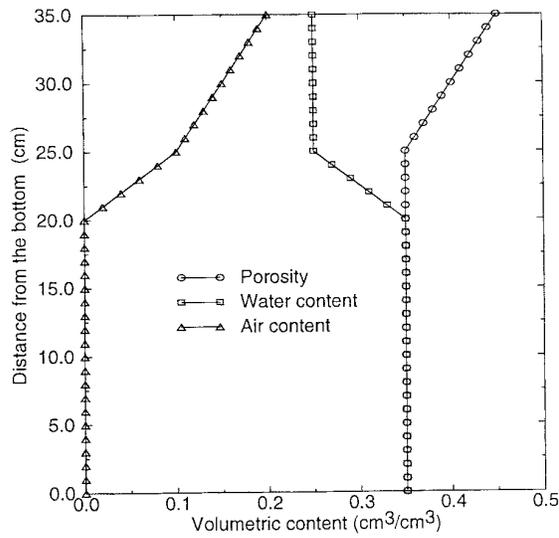


FIGURE 1. PROFILES OF POROSITY, WATER CONTENT, AND AIR CONTENT ASSUMED FOR THE CHAMBER.

Assumptions

The following are significant assumptions that were employed in developing the above TCE contaminant transport equation:

1. Convective gas phase transport was assumed to be negligible in the vadose zone. Gas phase transport was, therefore, assumed to occur only by diffusive mechanism.
2. Water pressure heads do not significantly change with time during steady state operation in the plant-soil experimental chamber. In other words, the Darcy's velocity in aqueous phase is considered to be constant and affected only by evapotranspiration.
3. Rate-independent equilibrium sorption and volatilization exists between the solid, water, and vapor phases in the experimental chamber.
4. Decay rate is of first order and relatively insignificant for TCE.

5. Porosity and water content profiles in the vegetated soil vary along the vertical direction of the soil as shown in Figure 1.

Boundary and initial conditions

Model Equation 1 is a partial differential equation with respect to C_w . To completely solve Equation 1, we need to specify the boundary conditions for the contaminant. At the bottom boundary of the chamber ($z = 0$) the concentration of TCE is assumed to be the ground water concentration:

$$C_w|_0 = \text{Concentration in ground water.} \quad (2a)$$

However, for the boundary condition at soil surface ($z = L$) free volatilization of TCE is considered. To account for free volatilization of TCE at the soil surface, a stagnant boundary layer of thickness d is assumed to exist at the ground surface due to vegetation and surface roughness. Then, the flux of the contaminant from the soil surface to the atmosphere across this boundary layer is essentially the total flux of contaminant occurring from the subsurface to the soil surface of the chamber through the gas or liquid phases. The upper boundary condition may then be represented as a Robin's kind of boundary condition:

$$\left[-\theta_w D_w \frac{\partial}{\partial z} (C_w) \Big|_L + V_w C_w \Big|_L - \xi H D_a \frac{\partial}{\partial z} (C_w) \Big|_L \right] = \frac{D_a}{d} (H C_w \Big|_L - C_{air}) \quad (2b)$$

where C_{air} , concentration in headspace atmosphere, is usually assumed to be zero as the atmosphere acts as an infinite sink for the contaminant. For the initial conditions, the steady state simulation results were employed as initial conditions for Equation 1; that is Equation 1 was solved with the left-hand-side set equal to zero to obtain initial conditions for the simulation.

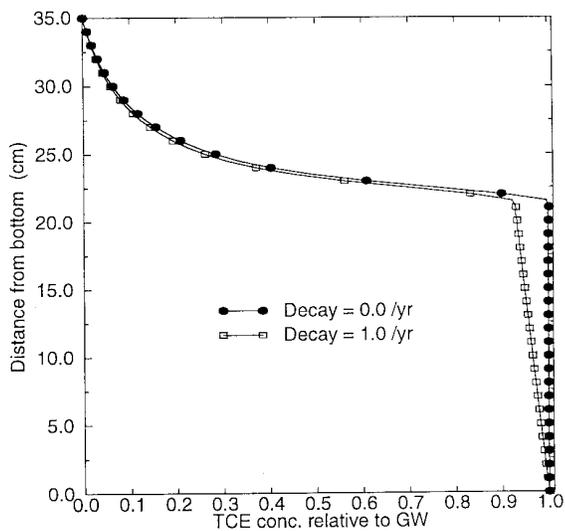


FIGURE 2. CONCENTRATION PROFILES OF TCE SIMULATED FOR DIFFERENT FIRST ORDER DECAY COEFFICIENTS IN THE SYSTEM.

COMPUTATIONAL METHOD

The governing Equation 1 was solved for one-dimensional vertical soil column using weighted residuals Galerkin finite element technique. Linear shape functions were assumed over the element for weak form of Galerkin's formulation of Equation 1. For representing the time derivative, Crank-Nicholson's method was used with a weighting parameter equal to 0.5.

DISCUSSION OF RESULTS

To simulate the solute transport in aqueous and gas phases, the distribution shown in Figure 1 was assumed based on collected data [9]. Porosity in soil was assumed to increase in the top 10 cm of soil due to the generation and degeneration of plants' roots. Figure 2 shows the TCE concentration profile in the soil at different depths for two values of the decay constants. The concentration profile shown for a decay constant of 1.0/year was obtained after 1 year of simulation. This is shown in comparison to a concentration profile

obtained with no degradation in the experimental system. It can be seen from Figure 2 that the difference in concentration profiles of TCE below 20 cm is significant relative to the difference in concentration profiles of TCE above 25 cm. This is because the degradation was assumed to occur in the aqueous phase of the chamber. Due to lower water content in the unsaturated zone of soil, a lower degradation rate was occurring in the top 10 cm of the soil.

However, it may be noted that the gradient in concentration of TCE in the aqueous phase at depth of 10 cm to 15 cm is very significant. This is because of the drop in water content in the chamber soil. A steep transition in water saturation of the soil at a depth of 10 cm to 15 cm was actually observed. This was due to significant water extraction by roots of actively growing alfalfa plants. The concentration of TCE in the water phase rapidly dropped to 30% of the ground water concentration for either value of the decay constant. This rapid gradient in TCE concentration in the aqueous phase was because of the decrease in water phase and appearance of the air phase in the top 15 cm of soil (Figure 1). Since trichloroethylene is highly volatile in nature, rapid partitioning from the water phase into the air fraction of the subsurface soil occurs. Consequently, migration of TCE occurred in the gas phase in the upward direction through a diffusional transport mechanism. This results in a rapid drop in concentration of TCE in the aqueous phase.

Figure 3 shows the concentration profiles of TCE in the aqueous phase in the vertical direction for different surface water contents (θ_s). The different values for (θ_s) were based on the experimental observations at different periods of operation of the plant-soil chamber. A (θ_s) value of 0.25 was used to

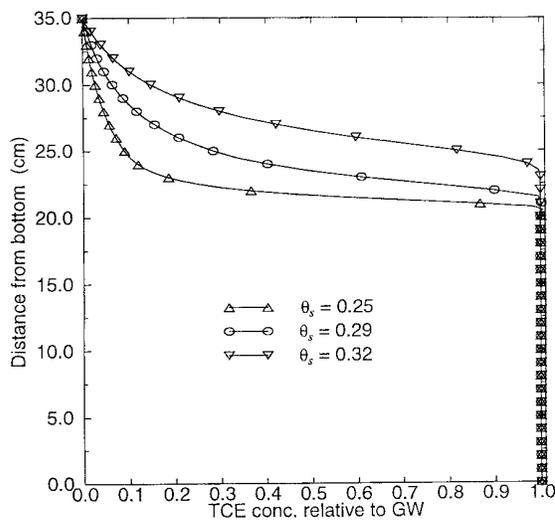


FIGURE 3. TCE PROFILES IN THE SYSTEM FOR DIFFERENT WATER CONTENTS IN THE TOP SOIL OF THE CHAMBER.

represent the period of operation of the chamber when the surface soil was relatively dry. A (θ_s) value of 0.32 represented the scenario when the surface soil was relatively wet and had a high water content. Volumetric surface water content of 0.29 was mostly the typical water content value measured in the top 10 cm of soil of this experimental chamber during the steady-state feeding operation.

It was observed in Figure 3 that the concentration of TCE in the aqueous phase was higher in the top soil of the chamber with relatively water-saturated soil ($\theta_s = 0.32$) as compared to an unsaturated soil ($\theta_s = 0.25$). Moreover, the difference in concentration of TCE in the two profiles at the zone of soil depth between 10 cm and 15 cm was significant. For example, at a depth of 10 cm from the surface of the soil, the relative concentration of TCE in the aqueous phase changed from 10% for dried and relatively unsaturated soil condition to about 90% for wet and relatively saturated soil condition. Consequently, in an interacting

plant-soil field environment where the water content profile may be continuously varying due to either seasonal changes or fluctuations in ground water table, the concentration of TCE in the aqueous phase would also significantly change in the unsaturated zone. It must, however, be emphasized that the concentration of TCE in the aqueous phase in the top 5 cm of soil surface is always less than 20% of the ground water concentration in the chamber. Therefore, plant roots that grow actively in the top 5 cm of vegetated soil would observe contaminant concentration in the water phase that is relatively low and less phytotoxic. Consequently, it may be possible to manage active vegetation as a solar-driven pumping system on the top of a highly contaminated soil without detrimental effects to the plants.

Figure 4 shows a comparison of relative concentration of TCE in the water phase between experimental measured data and numerically simulated data. The experimentally measured data was obtained at intervals of 2 cm along the soil depth from the top surface of the soil. Data from Table 1 was used to numerically simulate the profile of TCE shown in Figure 4. The surface water content (θ_s) was assumed to be 0.29 and the decay constant was assumed to be zero in this case. A reasonably good comparison between the numerical and experimental observations was obtained in the top 16 cm of the chamber soil. It may be noted that at a soil depth near 10 cm, the experimental data obtained from the two channels showed large variation. This may be attributed to differences in the water content distribution in the two channels of the system. Also, in comparison to Figure 3, it may be seen that the profiles of TCE with higher and lower surface water contents in Figure 3 served as boundary estimates of experimentally observed TCE concentration

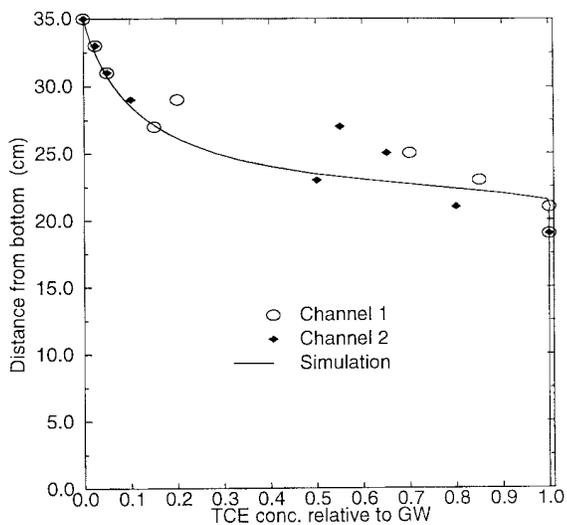


FIGURE 4. COMPARISON OF EXPERIMENTALLY-MEASURED TCE CONCENTRATION TO SIMULATED PROFILE FOR $\theta_s = 0.29$ IN TOP SOIL AND DECAY RATE = 0.0.

in the aqueous phase of the channels. This reiterates the fact that a change in water content of the soil could significantly impact the migration of TCE in the subsurface soil environment.

In both chambers, the experimental and simulated concentrations of TCE at the soil

surface ($z = L$) are very small. The concentration of TCE in the gas phase above the soil surface was below the detection limit in the open chamber but measurable when the chamber was closed [1]. Thus, the assumption that the TCE concentration in the headspace atmosphere is zero appears to be appropriate.

CONCLUSIONS

Trichloroethylene is a highly volatile contaminant which results in substantial partitioning and migration of TCE by a gaseous phase diffusion mechanism in the vertical upward direction in the unsaturated zone. Consequently, the distribution of water and air content profiles in the system significantly impacts the migration of TCE in the subsurface soil environment. Moreover, due to significant partitioning of TCE to soil gas of subsurface soils, the actual concentration of the TCE contaminant experienced by plant roots may be considerably lower than hazardous ground water concentrations. In vegetated systems, the soil porosity may increase in the top soil due to the actively growing root masses and, hence, enhance the possibility of TCE

TABLE 1. THE VARIOUS PARAMETERS AND VALUES EMPLOYED FOR THE SIMULATION STUDY OF VOLATILIZATION OF TCE FROM CHANNEL SOILS (@ 26°C).

Soil Parameters	
Porosity	0.35
Bulk density	1.5 g/cm ³
Dispersivity	0.1 cm
Darcy's flux	0.01 cm/hr
Organic carbon content	1%
Surface water content	0.29
TCE Parameters	
Organic carbon-water partition coefficient	1.08 X 10 ² cm ³ /g
Dimensionless Henry's law constant	0.38
Gas phase diffusivity	300 cm ² /hr
Decay rate	0.0
Surface boundary layer thickness	1 cm

migration in the air phase of the subsurface soil environment.

A model developed based on local physical equilibrium concepts was used to simulate subsurface transport of TCE in the experimental chamber. Gaseous diffusional transport of TCE was modeled using the Millington-Quirk equation. The model predicted the observed TCE concentration in the vegetated soil of the chamber. Other simulation studies indicated that flux of TCE from the surface soil to the headspace atmosphere increases with upward movement of water from the subsurface due to the evapotranspiration phenomenon associated with actively growing alfalfa plants. However, the emission flux rates are always below the allowable limits of the air quality of the environment. Quantification of the extent of uptake and losses of TCE through plant pathway in comparison to the extent of loss of TCE through soil pathway would be of future interest in a vegetated system though our earlier studies indicated that major loss of TCE is through the volatilization mechanism from the soil. Vegetation-mediated bioremediation is limited to relatively shallow unconfined aquifer systems in actual field environments.

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NOMENCLATURE

C_w	concentration of contaminant in aqueous phase (g/cm^3)
d	boundary layer existing at the soil surface (cm)
D_a	gas phase diffusion coefficient of contaminant (cm^2/hr)
D_w	hydrodynamic dispersion coefficient in water phase (cm^2/hr)
H	Henry's law constant of contaminant ($\text{g}/\text{cm}^3/\text{g}/\text{cm}^3$) (dimensionless)
k	first order decay constant for TCE (1/hr)
K_d	adsorption coefficient of contaminant onto soil particles (cm^3/g)
L	distance of the soil surface from the bottom of the chamber (cm)
t	time (hr)
V_w	convective volumetric flux in the upward direction (cm/hr)
z	Cartesian coordinate for vertical direction (cm)

Greek

α_w	dispersivity in the aqueous phase in the upward direction (cm)
η	soil porosity (cm^3/cm^3) (dimensionless)
θ_a	volumetric gas porosity (cm^3/cm^3) (dimensionless)
θ_w	volumetric soil-water content (cm^3/cm^3) (dimensionless)

- θ_s volumetric surface soil-water content
(cm^3/cm^3) (dimensionless)
- ρ bulk density of soil (g/cm^3)
- ξ tortuosity factor for gas phase
diffusion in the soil

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