# MODELING CONTAMINANT TRANSPORT IN PLANTS

J. Hu[1], L.C. Davis[2], and L.E. Erickson[1]

*Chemical Engineering[1] and Biochemistry[2] Departments, Kansas State University, Manhattan, KS 66506; Phone: (785) 532-4313, Fax: (785) 532-7372*

## ABSTRACT

In order to predict the fate of contaminant transport in plants, experiments were conducted and simple models were used to simulate the processes. Diffusion experiments were carried out to estimate contaminant diffusivity within plant roots, while adsorption experiments were used to investigate the adsorption of contaminant in plant stems. We found that plants can enhance the removal of trichloroethylene (TCE) by adsorbing it on the plant biomass and by transporting it upward into the vadose zone where it may diffuse into soil and escape to the atmosphere. The measured diffusivity of TCE in plant roots is in the range of $10^{-7}$ $cm^2/sec.$ to $10^{-6}$ $cm^2/sec.$ The adsorption coefficient for TCE is in the range of 20 to 35; for 1,1,1-trichloroethane (TCA), it is about 15. Experiments show that there is little or no adsorption of methyl-tert-butyl ether (MTBE) in plant stems.

***Key words:*** *trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), methyl-tert-butyl-ether (MTBE), diffusion, adsorption*

## INTRODUCTION

Phytoremediation, the use of vegetation for the in situ treatment of contaminated soils and sediments, is a novel technology that promises effective and inexpensive cleanup of certain hazardous waste sites (Schnoor et al., 1995; Burken and Schnoor, 1997). This technology has already been shown to be effective in a number of experiments. Previous study by Wang and Jones (1994) reported the uptake of chlorobenzenes (CBs) by carrots. Recent work by Newman et al. (1997) demonstrated that hybrid poplars have the capability to uptake and degrade the chlorinated solvent TCE. Studies by our group also show that alfalfa and hybrid poplar have the capability to take up and transpire organic contaminants (Davis et al., 1998).

In order to predict the fate of contaminant transport in plants, some models were developed to simulate the contaminant transport processes within the plant (Davis et al., 1998; Trapp and McFarlane, 1995); however, model parameters, such as diffusivity of contaminant in roots and adsorption coefficient of contaminant on the plant biomass, are needed.

In this study, two experiments were conducted. One is to estimate the diffusivity of TCE within plant roots, while the other is used to measure the adsorption coefficient of TCE, TCA, and MTBE for solutions moving through plant stems.

## EXPERIMENTAL MATERIALS AND METHODS

### *Diffusion Experiment*

Soybean seeds were grown on moist paper for 4-8 days and then the roots were cut into sections; cottonwood seedlings and alfalfa were grown in soil. Roots were bound loosely into a bundle and sealed in a 500 ml container. Then 10 ml TCE as liquid was injected and roots were allowed to come to equilibrium with the gas phase TCE for at least one hour. The TCE concentration in the gas phase at equilibrium was sampled with a 1 ml syringe and measured using gas chromatography (GC) on Porapak R with flame ionization detection. The roots were transferred very quickly to another empty container, 71.5 ml in volume, which was quickly sealed. The gas phase TCE concentration was sampled every 10 seconds within the first minute, and then sampled every 1-2 minutes until the system reached equilibrium. The experimental schematic is shown in Figure 1.

### *Adsorption Experiment*

Contaminated water containing TCE, TCA, or MTBE as indicated in Table 2 was used as the source of water to the poplar stem section. The major part of the stem section was immersed in 8 L of contaminated water. The jar was sealed by a rubber stopper. The outside stem end was sealed by Tygon PVC tubing which was used to collect the outflow water. A small amount of air was injected through the needle into the jar at the beginning of the experiment to maintain a positive pressure in the jar. Outflow water was collected by a syringe controlled by a Harvard infusion pump, and contaminant concentration was measured by GC as headspace gas in a container of known volume. The experimental schematic is shown in Figure 2.

## MODELING STUDY

### *Assumptions*

- There are no transport processes except for passive processes such as diffusion and advection (in the transpiration stream). This means that any active transport, e. g., with carriers, is excluded.
- Plants are well adapted and tolerant to the hazardous contaminants present in the soil and groundwater at the concentration used.
- Plant sections are assumed to be in uniform cylindrical form.
- Contaminants present in plants are dissolved in the liquid phase and adsorbed to plant biomass.
- There is no metabolism of contaminants in plants.

### *Model Development*

*Mass Balance on Plant Element*

Rate of change of contaminant in plant element = Rate of contaminant flux into plant element - Rate of contaminant flux out of plant element

*Root Diffusion Model:*

Based on the experimental conditions, we assume there is no convective flow in the axial direction; only radial diffusion is considered. The governing equation is:

$$\frac{\partial C_{rw}}{\partial t} = Con \frac{\partial}{r \partial r}\left( r \frac{\partial C_{rw}}{\partial r} \right); \quad Con = \frac{D_{rw}\theta_{rw}}{\theta_{rw} + (1.0 - \theta_{rw})K}$$

B. C. is:

$$C_{rw} = C_o \quad at \quad t = 0;$$
$$\frac{\partial C_{rw}}{\partial t} = 0 \quad at \quad r = 0;$$
$$C_{rw} = C_g \quad at \quad r = R;$$

where:

$C_{rw}$ is TCE concentration in root liquid phase;
$D_{rw}$ is the TCE diffusivity in root;
$\theta_{rw}$ is root water content;
K is the adsorption coefficient;
$C_o$ is the initial TCE concentration;
$C_g$ is the measured TCE concentration in gas phase;
R is the root radius.

*Stem Adsorption Model:*

Based on the experimental conditions, we assume there is no diffusion across the stem wall; only axial convective flow is considered. The tanks-in-series model, shown in Figure 3, is used. The governing equation for stage N is:

$$V_N Const \frac{dC_N}{dt} = V_w A\left(C_{N-1} - C_N\right)$$
$$Const = \left[\theta_w + (1.0 - \theta_w)K\right]$$
$$A = \pi R^2$$
$$V_N = \frac{AL}{N}$$

where:

K is the adsorption coefficient of contaminant to stem; it is defined as the ratio of contaminant concentration in stem biomass to the contaminant concentration in the liquid phase.
$\theta_w$ is the water content in stem;
$V_N$ is the volume of tank N;

$V_w$ is the velocity of water;

A is the cross section area of stem;

R is the radius of stem;

L is the total length of stem;

N is total number of tanks.

The analytical solution for the above equations for $C_o$=1 is:

$$C_N = 1 - \sum_{i=1}^{N} \frac{\tau^{i-1} e^{-\tau}}{(i-1)!}; \quad \tau = \frac{q}{\left[\theta_w + (1.0 - \theta_w)K\right]V_N}$$

where q = $V_w$At, which is the volume of water coming out of the tank N.

## RESULTS AND DISCUSSION

Table 1 presents values of root radius, root water content, and effective diffusivity for TCE in plant roots. For 8-day-old soybean roots, TCE diffusivity is $9.8*10^{-7}$ cm$^2$/sec. For 3-month cottonwood seedling roots, it is $8.123*10^{-7}$ cm$^2$/sec. For 1-year alfalfa root, it is $5.23*10^{-7}$ cm$^2$/sec. The results indicate that TCE diffusivity is smaller in older and bigger roots, which means it is easy for TCE to approach equilibrium with the TCE in the soil in small roots, while it takes longer in bigger roots. Previous study (Hu et al., 1998) showed that for small roots, 0.1 mm in diameter, time constants are less than 1 minute, while for large roots, 2.0 mm in diameter, time constants can exceed 1 hour.

Table 2 contains values of stem length, tank number, and adsorption coefficient for studies of plant stems. The results show the adsorption coefficient for TCE is within the range from 27 to 32. For TCA, it is about 15; for MTBE, it is less than 0.1. These results are in reasonable agreement with log $K_{ow}$, log $K_{oc}$ and log $K_{om}$ values (shown in Table 3), which indicates the higher the values are, the larger the adsorption coefficient for a specific contaminant compound. In general the $K_{om}$ values from the literature are larger than the experimental values found in this work.

The number of completely mixed stages in the model varies with stem length from 1 to 3. For a stem length of 7.5 cm, one stage fits the data, while for 30 cm, three stages provided the best fit. The per-stage length and stage volume were relatively constant for the different experiments.

Figure 4 shows the relative concentration of TCE in roots (8-day soybean) versus time with root radius 0.55 mm. The simulation results have a good fit with the experimental data when TCE diffusivity equals $9.8*10^{-7}$ cm$^2$/sec. The difference between the experimental data and simulation result when the experiment approaches equilibrium is caused by the assumption of infinite diffusion volume in the diffusion model.

Figures 5 and 6 show the experimental data and simulation results for contaminated water flowing through plant stems for low and high TCE concentrations. With K equal to 27, the simulation results are in good agreement with experimental data. The linear isothermal adsorption model gives a reasonable fit.

Figures 7 and 8 show the TCA and MTBE relative concentrations with respect to outflow water volumes. Appropriate values of K are 15 for TCA and 0.1 for MTBE.

## CONCLUSIONS

From experiments shown here, we can conclude that plants may enhance the removal of TCE by adsorbing it on the plant biomass and by acting as a transport pathway by which TCE moves into plant roots with water and is transported upward into the vadose zone where it may diffuse into soil and escape to the atmosphere.

During transport, TCE in small roots approaches equilibrium with TCE in soil in a very short time, while in bigger roots it may take a longer time. The diffusivity of TCE in plant roots is in the range of $10^{-7}$ $cm^2/sec.$ to $10^{-6}$ $cm^2/sec.$ The adsorption coefficient for TCE is in the range of 27 to 32; for TCA, it is about 15. Experiments show there is little or no adsorption of MTBE on plants. These sorption coefficients are in reasonable agreement with estimated values for the same compounds.

## ACKNOWLEDGEMENT

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**Table 1.** Values of root radius, water content, and effective diffusivity for roots. (K=28)

| Root Species | Root Radius (mm) | Water Content (dimensionless) | TCE Diffusivity ($cm^2$/sec.) |
|---|---|---|---|
| 8-day soybean | 0.55 | 0.955 | $9.8*10^{-7}$ |
| 3-month cottonwood seedling | 0.59 | 0.72 | $8.142*10^{-7}$ |
| 1-year alfalfa | 0.33 | 0.7 | $5.23*10^{-7}$ |

**Table 2.** Values of stem length, tank number, and adsorption coefficient for TCE, TCA, and MTBE in plant stems.

| Contaminant | Initial Contaminant Concentration (µm) | Stem Length (cm) | Tank Numbers | Adsorption Coefficient (dimensionless) |
|---|---|---|---|---|
| TCE | 7 | 7.5 | 1 | 32 |
| TCE | 8 | 30 | 3 | 27 |
| TCE | 7 | 18.5 | 2 | 32 |
| TCE | 1150 | 24 | 2 | 27 |
| TCA | 15 | 24 | 2 | 15 |
| MTBE | 100 | 24 | 2 | 0.01 |

**Table 3.** Values of molecular weight (M.W.), solubility (S), log $K_{ow}$[a], log $K_{om}$[b], and log $K_{oc}$[c] for TCE, TCA, and MTBE. (Squillace et al., 1994, and Knox et al., 1993)

| Contaminant | M.W. | S(mol/l) | log $K_{ow}$ | log $K_{om}$ | $K_{om}$ | log $K_{oc}$ |
|---|---|---|---|---|---|---|
| TCE | 131 | 0.0084 | 2.53 | 1.51 | 32.4 | 2.03 |
| TCA | 133 | 0.012 | 2.47 | 1.40 | 25.1 | 2.18 |
| MTBE | 88 | 0.57 | 1.20 | 0.179 | 1.51 | - |

[a] $K_{ow}$ is the octanol water particion coefficient;
[b] $K_{om}$ is the partition coefficient for 100% organic matter; it is estimated from log $K_{om}$ = -0.729logS + 0.001 (Knox et al., 1993);
[c] $K_{oc}$ is the adsorption coefficient for soil organic carbon.

**Figure 1.** Diffusion experimental schematic. The experiment was done in two steps. In step 1, we set the system to equilibrium with TCE for 1 ~ 2 hrs in a 500 ml container with 10 µl (14.7 mg) TCE inside. In step 2, we transferred roots to a 71.5 ml clean container, and measured the gas phase TCE concentration periodically (10 sec. until equilibrium).

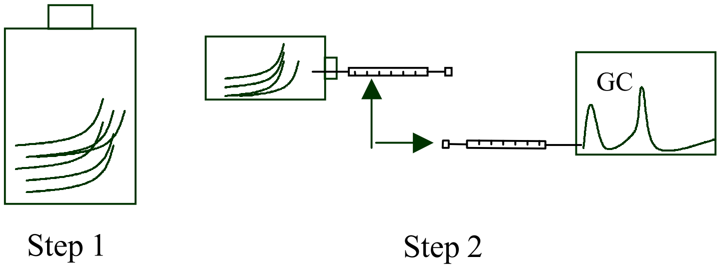

**Figure 2.** Adsorption experimental schematic. The stem section is immersed in a jar with 8 L contaminated water, and the outside stem end is sealed by a short pipe of Tygon tubing which is used to collect the outflow water.

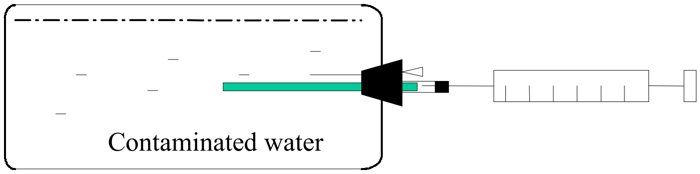

**Figure 3.** Tanks-in-series schematic. 1, 2, N-1, N stand for tank number; $C_1$, $C_2$, $C_{N-1}$, $C_N$ stand for the dimensionless contaminant concentration in the tank.

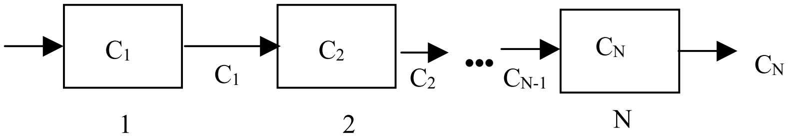

**Figure 4.** TCE relative concentration in roots as function of time. (Root radius is 0.55 mm, TCE diffusivity is $9.8*10^{-7}$ cm$^2$/sec., and K is 28.)

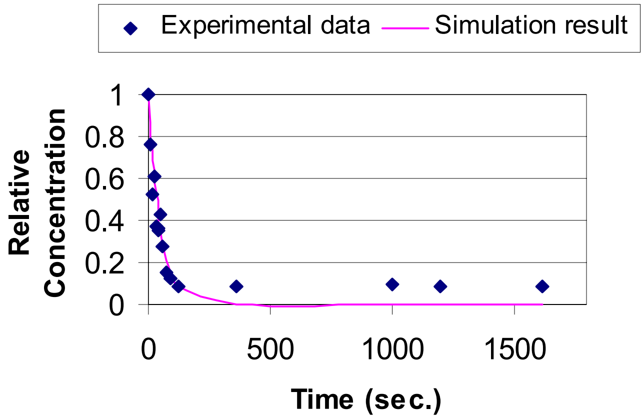

**Figure 5.** Outflow TCE relative concentration as function of outflow water volume. (Stem section length is 30 cm; original TCE concentration is 7 µM.)

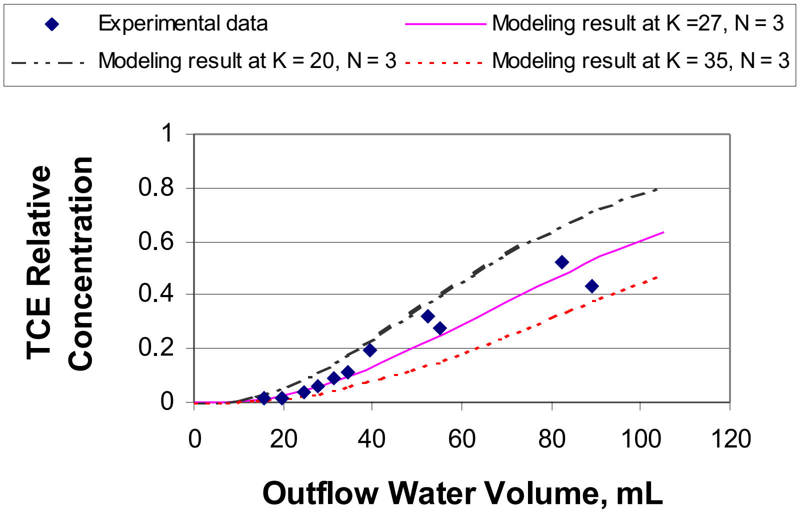

**Figure 6.** Outflow TCE relative concentration as function of outflow water volume. (Stem section length is 24 cm; original TCE concentration is 1.15 mM.)

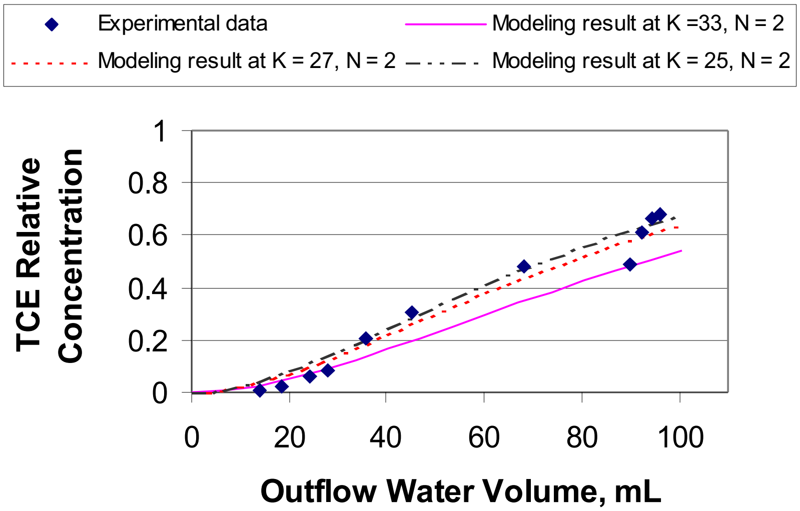

**Figure 7.** Outflow TCA relative concentration as function of outflow water volume. (Stem section length is 24 cm; original TCA concentration is 15 µM.)

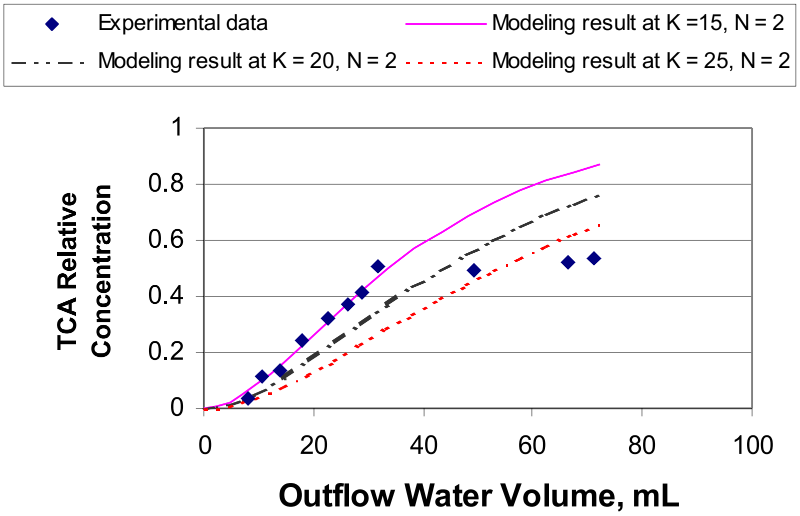

**Figure 8.** Outflow MTBE relative concentration as function of outflow water volume. (Stem section length is 24 cm; original MTBE concentration is 100 µM.)