

FUNDAMENTAL PROCESSES OF PLANTS AND SOILS

Transport of Contaminants in Plant and Soil Systems

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Abstract

The transport of contaminants in soil and plant systems depends on the properties of the contaminant, aqueous phase flow, soil properties, and size and growth of the plants. There is convective flow of the aqueous phase in soil, plant roots, and plant stems because of differences in the pressure of water or matrix potential as a function of position. Significantly larger quantities of water are lost to the atmosphere through evapotranspiration when growing plants are present. Contaminants are transported to the soil surface in plant roots and in the soil.

Contaminants such as trichloroethylene (TCE) and methyl-tert-butyl ether (MTBE) diffuse through the walls of roots and stems. Volatile compounds such as TCE diffuse through the gas phase in unsaturated soil into the atmosphere. In small roots, TCE transported upward in the aqueous phase may diffuse out through the walls of the roots into the unsaturated soil and to the atmosphere. In large mature trees, TCE has been found in the xylem in locations where the groundwater is contaminated with TCE. The concentration of TCE decreases with height because the TCE diffuses out

through the plant cells between the xylem and bark of the trees.

Since MTBE is more soluble in water and less volatile than TCE, it is transported through the roots into plant stems of alfalfa. The loss of MTBE through the walls of the stems appears to be limited by diffusion through the plant cells in the stem wall. This process has been modeled with a transport model.

Introduction

The fate and transport of water and contaminants in soil with growing vegetation has been the subject of research in our laboratories for more than nine years. Since much of the information contained in the oral presentation is available in other manuscripts and publications, the primary purpose of this manuscript is to identify these publications and provide information on the significant transport processes which have been observed in our investigations.

Methods

Most of the experimental research has been conducted using plant growth chambers in a laboratory setting. These chambers include two identical U-shaped channels, each 10 cm wide, 35 cm deep, and approximately 180 cm in axial length (Narayanan et al, 1995a and 1995b; Narayanan et al., 1999a) and a six channel system (Zhang et al, 1998a; Zhang et al, 1999). Each of the six channels was 10 cm wide, 110 cm long and 65 cm deep with 60 cm of soil. Measurements have been made of the contaminant concentration in the inlet and outlet groundwater, the gas phase leaving the surface, and at points within the chambers. Experiments have been conducted with toluene, phenol, trichloroethylene, and methyl tert-butyl ether.

Models have been developed and computer simulation has been used to provide additional information on the processes that are affecting the fate of the contaminants.

Results

The fate and transport of organic contaminants depends on the physical and chemical properties of the contaminants. In the early work with toluene and phenol, biodegradation in the soil appeared to be the primary mode

of disappearance. Toluene degradation appeared to be limited to aerobic conditions (Davis et al., 1994; Erickson et al., 1994; Narayanan et al., 1995a; Narayanan et al., 1998a and 1998b). Phenol may have been biodegraded anaerobically as well as aerobically. There was no evidence that toluene and phenol were lost to the atmosphere (Davis et al., 1994).

In the research with trichloroethylene (TCE), biodegradation was observed in the early research (Narayanan et al., 1995b), but it did not appear to be significant in the later research (Narayanan et al., 1999a). Experiments were conducted to investigate the diffusion of TCE in plant systems (Davis et al., 1999). Values of diffusivity of TCE in plants were found to be about 0.1 to 0.3 of the value of the diffusivity of TCE in liquid water. For small roots, TCE which moves upward with soil water in plant roots may move out of the roots near the soil surface by diffusion. Narayanan et al. (1999a) has shown that the concentration of TCE is very low at the soil surface because of gas phase diffusion in unsaturated soil. With alfalfa plants in TCE contaminated soil, there is little evidence of TCE moving up into the plant stem; however, Vroblesky et al. (1999) has shown that TCE does move up into large trees. While the estimated diffusivity for TCE is similar in the trees, the radial distances are larger and thus, the concentrations of TCE in the xylem are detectable and significant.

Plants impact transport by removing water from the soil. The gas phase diffusion in the unsaturated zone varies with the fraction of gas phase volume. As plants remove water from the soil, they increase the fraction of gas phase volume in the surface soil which enhances the transport of oxygen and volatile contaminants. When plants are present the movement of contaminants and the drying rate following precipitation are different than when plants are not present.

When methyl tert-butyl ether (MTBE) is the contaminant, there is a greater tendency for the contaminant to be found in the plant because of the greater solubility in water and the lower value of the Henry constant compared to TCE. In our research with MTBE, values of diffusivity for MTBE in plant stems were found to be about two orders of magnitude smaller than those for MTBE in water (values were about 0.008 to 0.02 of those for MTBE in liquid water) (Zhang et al., 2000; Zhang, 1999).

The loss of volatile contaminants to the atmosphere has been investigated experimentally and through modeling and simulation (Davis et al., 1994; Davis et al., 1998b; Narayanan et al., 1999b). If the contaminant is transformed rapidly in the atmosphere and if the degradation products are environmentally acceptable, phytovolatilization may be a desirable process to move the contaminants from the soil and groundwater into the atmosphere. Narayanan et al. (1999b) has shown that volatile organic concentrations in the atmosphere are usually well below the threshold limit values where health concerns become significant. The rate at which

contaminants are moved from the soil to the atmosphere is limited by the dissipation of water vapor into the atmosphere. Thus, when the contaminant and water move upward together, the rate is limited by the rate of evapotranspiration which is limited by the dissipation of the soil water into the air. For example, for TCE in soil water at a concentration of 1 mmol/L or 131 mg/L, the corresponding concentration for TCE in water saturated air is 0.56 ppm by volume at 25 C. There is a significant dilution because of the expectation that all of the transpired water must be dissipated into the air.

The volume of water that is transpired by plants is significant (Davis et al., 1998a). When the roots can find adequate water, alfalfa, poplars and willows may use as much as 2 meters of water in one year (2 cubic meters per square meter of area). Zhang (1999) has shown that water use in planted chambers is significantly greater than that in the unplanted chamber (Zhang et al., 1998b and 1999). There is significant interest in using plants as solar driven pumps to contain plumes and the vegetation as the treatment system. While the degree of treatment depends on the contaminant, it has been shown that for many contaminants, plants may be used as part of a pump-and-treat system (Davis et al., 1998a; Erickson et al., 1997; Narayanan et al., 1999b).

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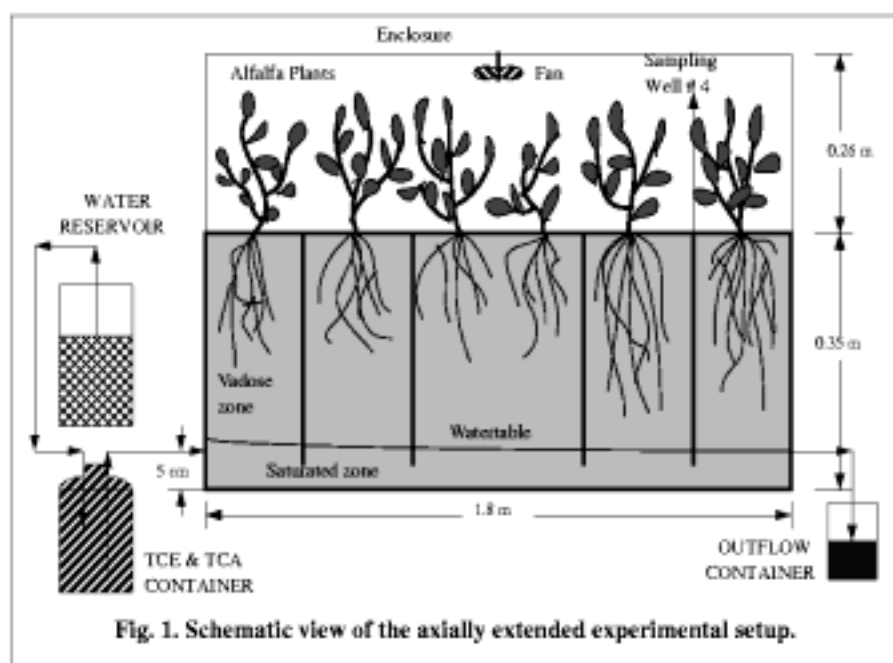


Table 2: Mass balance for contaminant carbon (mmol/day).

Compound	Inflow carbon (mmol)	Outflow carbon (mmol)	Carbon disappearing (mmol)
Toluene	34.0	8.2	25.8
Phenol	27.0	0.3	26.7

Table 3: FTIR estimates of CO₂ in the headspace of the chamber (mmol/day).

CO ₂ with C feed (mmol)	CO ₂ without C feed (mmol)	CO ₂ due to Contaminant Degradation (mmol)
85.0	57.0	28.0

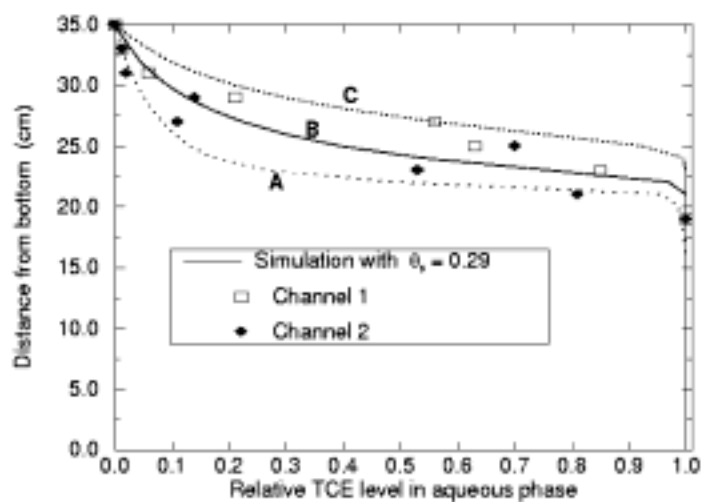
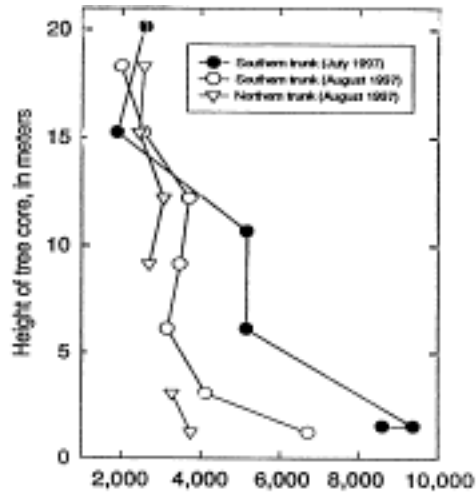


Fig. Experimentally measured and numerically simulated TCE conc. profiles in the system. Lines **A**, **B**, and **C** are TCE profiles for $\theta_s = 0.25$, 0.29 , and 0.32 , respectively. Experimentally measured profiles in the aqueous phase are shown as hollow squares and filled diamonds.



Trichloroethene concentration in tree cores, in nanomoles of gas per liter of core water

Trichloroethene concentration in cores along the trunk of tree 7 (bald cypress). Cores from the northern trunk were not collected in July 1997.

(From Vroblesky et al., Environ. Sci. & Technol., 33: 510 (1999).)

Estimated values of diffusivity for trichloroethylene in trees

Tree	Diffusivity cm ² /s	Source of data
Poplar	1.6×10 ⁻⁶	Hu
	1 × 10 ⁻⁶	Davis <i>et al.</i>
	2 × 10 ⁻⁶	Davis <i>et al.</i>
	3 × 10 ⁻⁶	Davis <i>et al.</i>
Willow	1.6 × 10 ⁻⁶	Hu
	1.5 × 10 ⁻⁶	Davis <i>et al.</i>
	2 × 10 ⁻⁶	Davis <i>et al.</i>
	3 × 10 ⁻⁶	Davis <i>et al.</i>
Bald Cyprus	3 × 10 ⁻⁶	Vroblesky <i>et al.</i>

Diffusivity of trichloroethylene in water is 1 × 10⁻⁵ cm²/s.

Comparison of confined and unconfined gas phase concentrations of trichloroethylene (TCE) for several different concentrations in ground water at 25°C and 1 atmosphere.

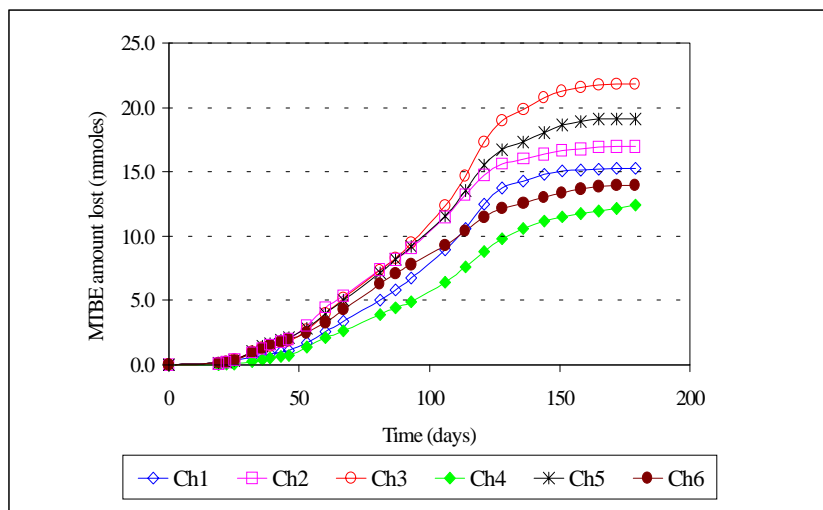
Concentration in ground water		Concentration in gas phase		
mmol/L	mg/L	Confined,* ppmv	TCE in water** vapor, ppmv	TCE in water** saturated air, ppmv
1.0	131	9,100	18	0.56
0.1	13.1	910	1.8	0.056
0.01	1.31	91	0.18	0.0056
0.001	0.131	9.1	0.018	0.00056

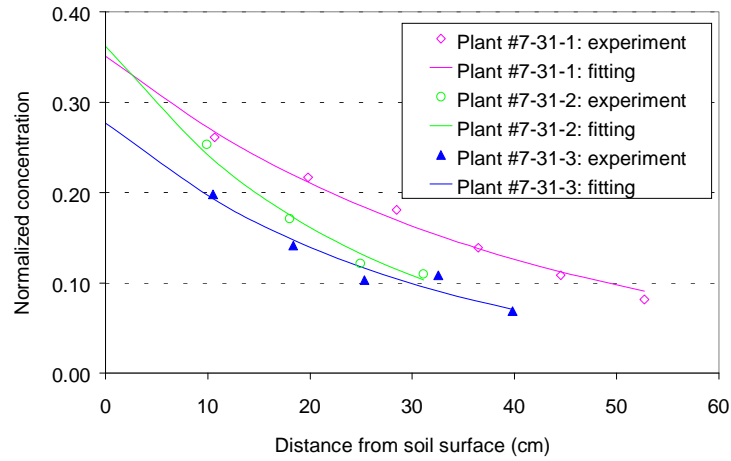
ppmv = parts per million by volume.

* Confined gas phase concentrations are assumed to be in equilibrium with the liquid phase.

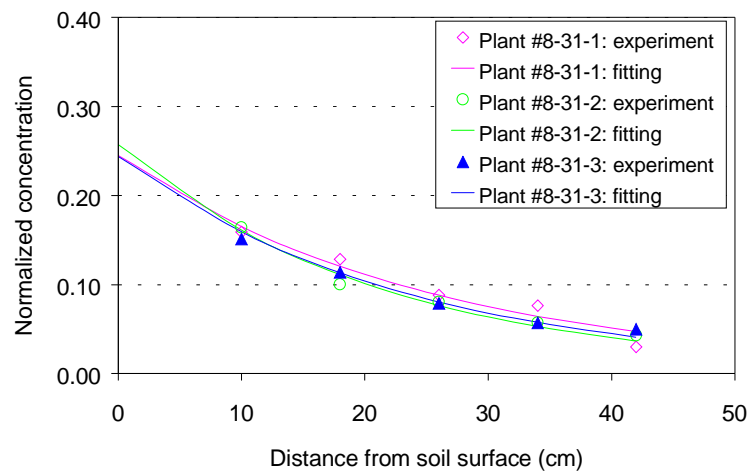
**Unconfined gas phase concentrations are based on evaporation of water vapor and TCE together.

Integrated amount of MTBE lost to the atmosphere over time from the soil surface of six channels.

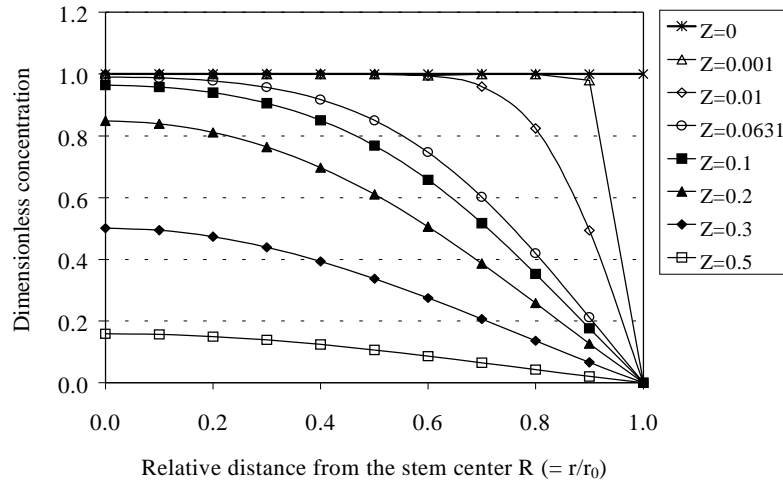




MTBE concentration in plant water as a function of stem position from the soil surface. The points are experimental data and the solid lines are the exponential fittings of form $c = c_0 \exp(-\alpha z)$. The concentration is normalized to the inlet concentration (0.844 mM).



MTBE concentration in plant water as a function of stem position from the soil surface. The points are experimental data and the solid lines are the exponential fittings of form $c = c_0 \exp(-\alpha z)$. The concentration is normalized to the inlet concentration (0.844 mM).



Concentration distribution within the plant stem as a function of the characteristic distance $Z (= \frac{\theta_w D z}{u r_0^2})$, with uniform concentration at $Z = 0$.
 Concentration is reduced to the overall concentration at $Z = 0$.

J. R. Philip (1958) &

D. A. Rose (1981):

diffusion between an individual cell and a large body of solution in which it was placed

$$\tau_{1/2} = \frac{Dt_{1/2}}{r_0^2} = 0.0631$$

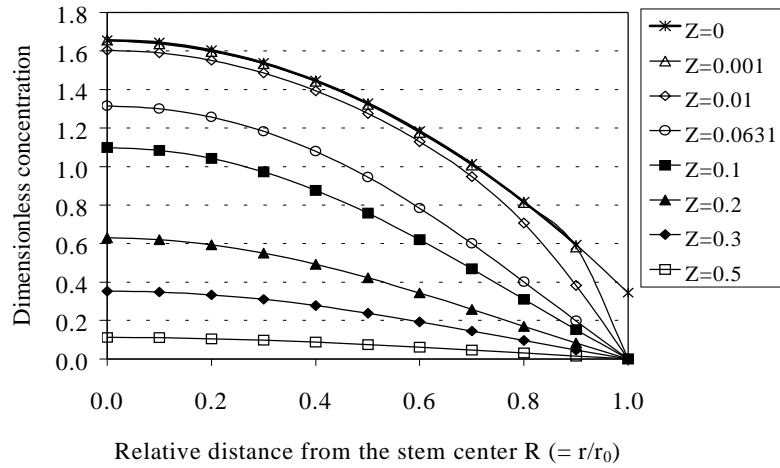
Our Results:

diffusion between a porous plant stem and the atmosphere

$$Z_{1/2} = \frac{\theta_w D z_{1/2}}{u r_0^2} = 0.0631$$

MTBE diffusion coefficient D (with uniform concentration at $Z = 0$):

$$5.88 \times 10^{-8} \sim 1.11 \times 10^{-7} \text{ (cm}^2\text{/sec)}$$



Concentration distribution within the plant stem as a function of $Z (= \frac{\theta_w D_z}{ur_0^2})$ for plant #7-31-1, with non-uniform concentration at $Z = 0$.
 Concentration reduced to the overall concentration at $Z = 0$.

Results--for non-uniform starting conditions

$$Z'_{1/2} = \frac{\theta_w D' z_{1/2}}{ur_0^2} = 0.0919$$

MTBE diffusion coefficient D' :

$$8.57 \times 10^{-8} \sim 1.62 \times 10^{-7} \text{ (cm}^2\text{/sec)}$$

Comparison of Standard Deviations of Two Model Solutions from the Experimental Data

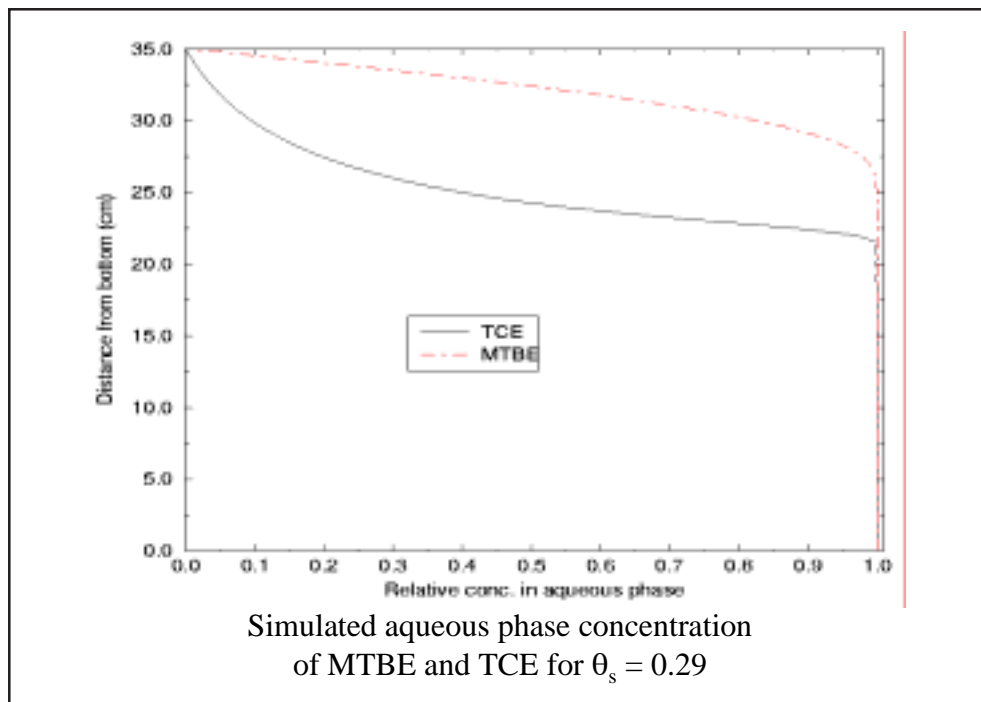
Plant#	7-31-1	7-31-2	7-31-3	8-31-1	8-31-2	8-31-3
uniform	0.0753	0.0782	0.0748	0.0929	0.0771	0.0676
non-uniform	0.0452	0.0524	0.0519	0.0608	0.0373	0.0253

Mass balance of water and estimated fraction of MTBE transpired by plants during the three- months test period.

Channel #, description	1, planted and aerated	2, planted but not aerated	3, planted but not aerated	4, unplanted and not aerated	5, planted but not aerated	6, planted and aerated
Total water added (L)	186	192	191	185	199	197
Evapotranspired water (ET) (L)	81	116	109	37*	106	108
Estimated average plant uptake of MTBE (fraction)	0.015	0.029	0.024	0.0**	0.032	0.035
Estimated greatest plant uptake of MTBE (fraction)	0.035	0.068	0.056	0.0**	0.075	0.080
Corrected recovery	0.78	0.69	0.80	1.0	0.85	0.71
Recovery with average plant uptake	0.80	0.72	0.82	1.0	0.88	0.75

* There was only evaporation of water in this unplanted channel.

**No plant uptake for this channel.



Key Publications

1. Zhang, Qizhi, L.C. Davis, and L.E. Erickson. "Effect of Vegetation on Transport of Groundwater and Nonaqueous Phase Liquid Contaminants," *Journal of Hazardous Substance Research*, Vol. 1, No. 8 (1998), <http://www.engg.ksu.edu/HSRC>.
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