TRANSPORT OF TRICHLOROETHYLENE THROUGH LIVING PLANT TISSUES

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ABSTRACT

Poplar and willow trees grown hydroponically accumulated TCE within the stem. Measured concentrations decreased with distance from the source indicating that radial diffusive loss is significant. The estimated half-time for loss from stems of less than 1 cm diameter was variable, depending on the water flow rate. Diffusivity estimates based on transit time and stem radius indicated a diffusivity of about 10^{-6} cm^2/s. When 4-8 mm diam. poplar stems were loaded with TCE contaminant by immersion and then allowed to equilibrate to the atmosphere, half-times were several hours. A model describing the diffusive process indicates a diffusivity (D) of 3×10^{-7} cm^2/s gives a good fit to the experimental data. It is suggested from comparison of intact and peeled stems that the cambial layer is more resistant than the underlying tissue for which a D nearer 10^{-6} cm^2/s is found. If all of the resistance were in an outer layer of 0.5 mm thickness, the D for that layer would be about 1×10^{-7} cm^2/s. Sunflowers growing in contaminated soil showed a gradient of contaminant distribution within the stem. The estimated radial diffusivity was similar to that of willows and poplars.

Key words: *diffusion, trichloroethylene, hybrid poplar*

INTRODUCTION

There is much interest in the possible intermedia transfer of contaminants from water/soil to air via plants. Burken and Schnoor (1997) showed that a predictive relationship based on the octanol:water partition coefficient could account for transfer of a number of contaminants through small poplar trees. Recently Vroblesky et al. (1999) measured chlorinated ethenes within the trunks of mature trees growing on contaminated soil at the Savannah River site. We have shown that transfer of chlorinated solvents occurs with several species of plants including poplars, willows, and sunflowers (Davis et al., 1998), generally in agreement with the work of Burken and Schnoor(1997). Recent studies by Hu in this laboratory (Hu, 1998) have extended this work to include measurement of sorption to plant tissues and estimation of the radial diffusivity of contaminants while moving through the stem of a plant. More detailed measurements and analyses are presented here.

METHODS

Vigorously growing, hydroponically cultured poplar or corkscrew willow trees of about 50 g fresh weight with a water usage of 5 - 10 mL/hr were exposed to low concentrations (~10 mM) of trichloroethylene (TCE). After 1-2 days exposure time, the plants were dissected from the top down, rapidly transferring 1-2 g pieces of stem to 65 mL bottles which were closed with mininert valves. At intervals, or after long-term equilibration, samples were analyzed by gas chromatography. Fresh and dry weights were determined for the plant segments. From these data, a profile of the TCE distribution within the plant could be derived.

Assuming steady state transport, knowing the water usage (mL/hr) and stem cross section (cm^2), one can calculate the linear superficial velocity (cm/ hr) of water from the stem base to any point within the stem below the leaves. The transit time through a given segment distance, derived from the linear velocity, assumes that the entire aqueous content of a stem segment is in equilibrium. Actual water content varied from 55-75%; for convenience a value of 66% was used in calculations. The plants used for these experiments had multiple shoots arising from upper portions of the stem, so for estimating water fluxes within these shoots, it had to be assumed that water transport was proportional to the relative cross-section of each shoot. When there were leaves on the shoot section being analyzed, it had to be assumed that the leaves on that segment and below it used only a small portion of the total water. More than 3/4 of the leaves were located above the sections analyzed.

During the winter dormancy period, long-stem segments were removed from hybrid poplar trees and either used immediately or stored for a few days under refrigeration. The stem segments were immersed in a large volume (13 L) of water containing a low concentration of TCE (~13 µM). At intervals, the stems were removed, blotted briefly, and snipped into pieces which were treated and analyzed as above. End segments concentrations were discarded from the analysis to avoid end effects. This provided a measure of the inward diffusion rate of TCE into the plant tissue.

To estimate the outward diffusivity of TCE, stem segments (25-30 cm long) were immersed in the same conditions for 3 days and then removed, blotted briefly, and placed into a large (0.97 or 1.3 L) bottle. Short pieces of the stem ends were cut off for separate analysis in smaller bottles sealed with mininert valves. Gas samples were withdrawn at intervals up to 24 hr to measure the outward diffusive flux of TCE.

Small sunflower seedlings were transplanted to a cylinder packed with soil from near the former Riley County landfill. The cylinder was watered from below with a solution containing 25 µL/L of TCE. After the plants had grown to ~25 cm, they were rapidly harvested from the top down and contaminant concentration was determined as for the poplar and willow stems.

Results from the influx or efflux experiments were plotted as log functions to derive a slope for the 1st-order transfer process, from which a half-time could be estimated. Knowing the dimensions of the stem segments, it is possible to calculate a diffusivity assuming a uniform cylindrical shape and composition. This is derived from the relationship given by Rose (1981) where the characteristic of the half-time for the entire cylinder is $0.0631 = Dt_{1/2}/r^2$.

The same relationship given above can be used to estimate a diffusivity for the data acquired with actively transpiring plants if one assumes that the linear velocity of water flow is a function of cross sectional area and volume transported per unit time. As a simple approximation, assuming a steady state flow and sorption equilibrium, the concentration decrease as the water moves up the stem is due entirely to radial diffusive losses during that movement. Knowing the radial dimension of the stem and the transit time between two points, one can use the observed concentration decrease to predict a diffusivity in the radial direction.

RESULTS

Table 1 shows calculated diffusivities for stem segments taken from two intact, actively transpiring willow and two poplar trees. In each case, stems were cut into segments for analysis and the results were graphed as concentration of TCE in µg/g dry weight of stem tissue. A best visual fit to the change of concentration as a function of distance along the stem was determined, to estimate the change in relative concentration along a portion of the stem represented by several segments. Details are given in the M.S. thesis of J. Hu (1998). Assuming that the radius of the stem does not change appreciably over the interval being analyzed, and knowing the water usage by the plant, it is possible to calculate the linear velocity of water within the plant stem and hence the residence time of a packet of water moving from the base toward the top. The diffusive loss outward was assumed to be equivalent to the diffusive loss which would occur if a stem segment of the same cylindrical cross section were exposed to uncontaminated air during a static incubation, as described by Rose (1981). If the radius decreases over a long interval of stem length, the estimated diffusivity will be somewhat misestimated by this procedure, depending on what is chosen as a best estimate of the average radius.

As may be seen in Table 1, the diffusivity estimates agree rather well, within about 3-fold, despite a greater than 10-fold difference in stem cross-sectional areas. As expected, for similar transit times, smaller stems lost a larger fraction of the input TCE. A necessary assumption is that the observed concentration of TCE is a steady-state concentration. Each plant transpired several times its mass of water. The main stem, which contains a small fraction of the total plant volume, had ~20 equivalent volumes or more passed through it. Earlier studies showed that this is sufficient to reach the steady state when a contaminated solution is pumped through a long-stem segment (Hu, 1998).

Figure 1 shows a typical efflux experiment, using a stem segment from a mature, dormant tree, in this instance for a peeled stem. The line shown is from a 1st-order regression based on a log plot of the data. In all experiments there was a very rapid release of 10-20% of the total amount contained in the stem; this was presumably the result of a thin layer of trapped solution on the surface of the stem. Because the stems used for these studies had matured in the autumn and dropped their leaves, they may not have a permeability comparable to that of actively growing shoots examined above, which generally were green, more succulent, and presumably metabolically active.

Table 2 summarizes the diffusivities derived from fitting the influx and efflux experiments with winter-harvested stems. The technique of immersing the stem section in water contaminated with

TCE would necessarily result in production of a thin liquid film on the surface of the stem, and possibly within lenticels and small cracks in the young bark. We may anticipate that diffusivities derived in this type of experiment may be somewhat lower than those obtained with shoots that had not been wetted. The magnitude of the effect depends on the relative degree of air permeability of actively growing and dormant stems.

Sunflower seedlings were grown on TCE-contaminated soil under conditions in which all of the TCE was converted to DCE at depth. The DCE concentration within plants at the base was lower than that observed in the soil several cm deep. Within the stem, the DCE concentration decreased in samples taken higher up the plant. Plants had a stem radius of less than ~2.5 mm and a length of ~30 cm. With an estimated water use of 1-2 mL/h/plant, the transit time and the half-time for contaminant loss was near an hour. Table 3 provides examples for two plants. For both plants a diffusivity of less than 10^{-6} gives a reasonable fit to the extent of contaminant loss over the distance between midpoints of two stem segments.

CONCLUSIONS

TCE and DCE pass relatively quickly through stems in the radial direction. The loss can be measured in intact plants. This loss has important implications for any study of the intermedia transfer of TCE or other volatile organics from soil to atmosphere. One must monitor not only the transpiration water of the plant but also the atmosphere surrounding the stems, particularly the smaller stems near the newly growing, leafy portions of the tree or other plant.

REFERENCES

Bird, R.B., W.E. Stewart, and E.N. Lightfoot, 1960. Transport Phenomena, John Wiley and Sons, New York. p. 548.

Burken, J.G., and J.L. Schnoor, 1998. Predictive relationships for uptake of organic contaminants by hybrid poplar trees, Environ. Sci. Technol., 32 pp. 3379-3385.

Davis, L.C., S. Vanderhoof, J. Dana, K. Selk, K. Smith, B. Goplen, and L.E. Erickson, 1998. Chlorinated solvent movement through plants monitored by Fourier transform infrared (FT-IR) spectrometry, Journal of Hazardous Substance Research Vol 1 # 4, pp. 1-26.

Hu, J., 1998. Study on fate and transport of contaminants in plants, M.S. Thesis, Kansas State University, Dept. of Chemical Engg.

D.A. Rose, 1981. Gas exchange in leaves, in *Mathematics and Plant Physiology*, D.A. Rose and D.A. Charles-Edwards (eds.) Academic Press pp. 67-78.

Vroblesky, D.A., C.T. Nietsch, and J.T. Morris, 1999. Chlorinated ethenes from groundwater in tree trunks, Environ. Sci. Technol. 33 pp. 510-515.

Table 1. Transfer and loss of TCE in intact poplar and willow trees.

Plant Part	**Radius**	**Interval**	**Linear velocity**	**Transit**	**Loss**	**Diffusivity**	**Water use and time**
	(cm)	(cm)	(cm/hr)	time (hr)	(%)	(x 10^{-6} cm^2/sec)	
poplar #1 stem	0.34	9	45	.2	35	>3	268 mL/23 hr.
branch 1	0.19	25	68	0.37	50	2	
branch 2	0.16	26	68	0.38	62	1.5	
branch 3	0.12	15	68	0.22	85	3	
Poplar #2 stem	0.31	7	35	0.2	10	3	299 mL/42 hr.
branch 3	0.2	15	30	0.49	34	1	
Willow #1 stem	0.5	22	8.5	2.59	62	3	211 mL/48 hr
branch	0.2	39	54	0.72	38	2	
Willow #2 stem	0.35	10	36	0.28	14	1.5	393 mL/42 hr
branch 1	0.2	14	55	0.25	52	3	
branch 2	0.2	1955	55	.35	56	2.5	

Poplar # 1, 40 g fresh wt, used 268 mL in 25 hr; poplar # 2, 55 g fresh wt, used 299 mL in 42 hr; willow # 1, 60 g fresh wt, used 211 mL in 48 hr; willow # 4, 50 g fresh wt, used 383 mL in 42 hr.

Table 2. Radial diffusion of TCE through poplar stems.

Experiment date and treatment	**Radius** (cm)	**D from half-life**[1] (x 10^{-7} cm^2/s)	**D, thin film**[2] (x 10^{-7} cm^2/s)
1/7/99, with bark	0.25	3.3	1.3
12/24/98, with bark	0.31	2.7	0.7
1/7/99, with bark	0.43	7.5	0.4
1/18/99, no bark, new	0.36	9.5	N/A
1/18/99, no bark, dead	0.31	6.0	N/A
12/21/98, inward diff[3]	0.33	2.7	ND

N/A = not applicable; ND = not determined

1. Based on the method and equations provided by Rose (1981)
2. From an equation in Bird et al. (1960) assuming 0.5 mm film
3. Seven stem segments were pulled from a reservoir of contaminated water at various times (1/2, 1,2,3,5,7 & 22 hr) and the concentration of TCE within the stems was derived from levels observed in bottles closed with mininert valves, after equilibration.

Table 3. Contaminant loss in stems of soil-grown sunflowers.

Experiment/position	**Segment length (cm)**	**Weight (g)**	**Relative GC peak height per weight**
#1 Top[1]	7.9	0.7	5.7
2nd	7.5	0.8	7.4
3rd	6.2	0.8	12.4
Bottom	6.8	1.1	18.3
#2 Top (+petioles)	2.5	2.1	5.8
2nd	7.5	1.8	20
3rd	5.7	1.2	34
Bottom	4.6	1.2	36

1. In experiment # 1, an 8-cm segment of the top was quickly transferred to a small bottle of water to estimate water usage over the next hour. This indicated a water use rate of 2 mL/hr. This was a wild sunflower.
2. For experiment #2, water use was 1.2 mL/hr, estimated for the planted cylinder prior to plant harvest. This was a domestic confectionary seed selection.

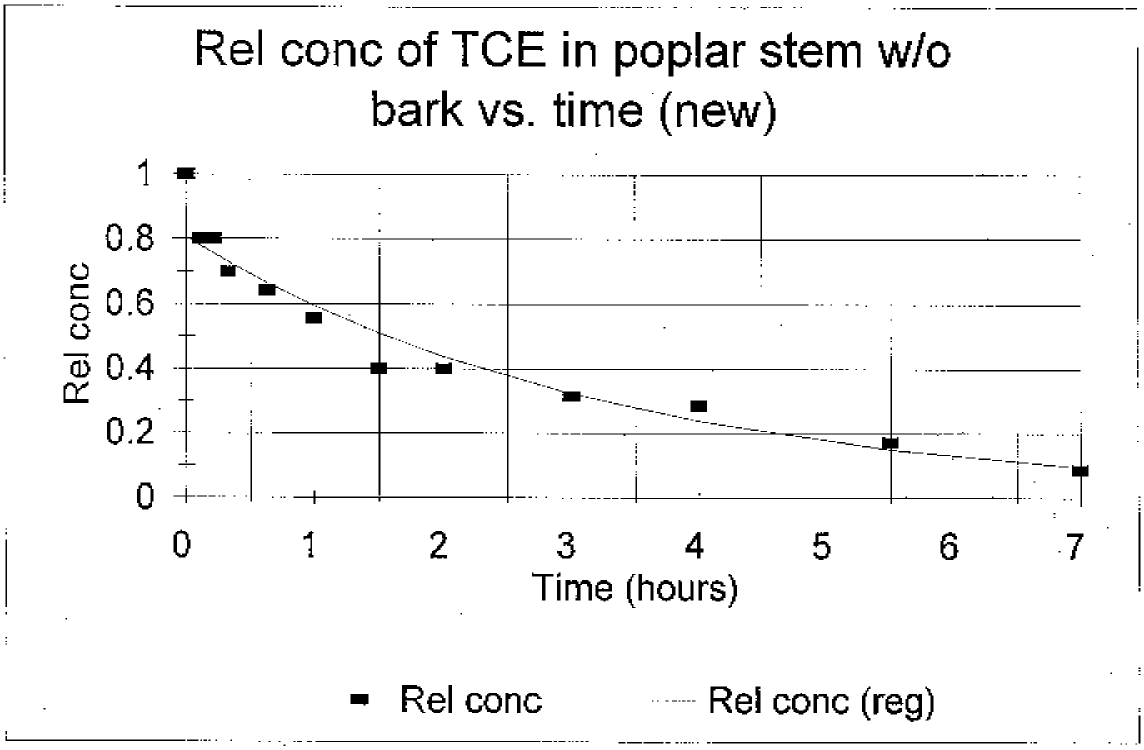

Figure 1. Relative concentration of TCE in poplar stem without bark versus time (new).