

# SORPTION OF TRICHLOROETHYLENE (TCE) AND OTHER HALOGENATED ALIPHATICS ON PLANT MATERIALS

L.C. Davis, S.L. Vanderhoof, and D. Luper

*Kansas State University, Department of Biochemistry, 104 Willard Hall, Manhattan, KS 66506*

## ABSTRACT

---

Common chlorinated solvents have octanol:water partition coefficients in the range of 100-300. This significantly alters their movement through soil and plant tissues. Sorption coefficients on wood were estimated, by static equilibration techniques, for trichloroethylene (TCE), trichloroethane (TCA), chloroform and dichloromethane (DCM). For TCE and TCA the sorption to ground alfalfa and low organic sandy soil was also measured. Estimates of sorption coefficient were also determined by passing water carrying the contaminant through an intact stem section and then sectioning the stem to determine the concentration that accumulated. In the static experiments a wood:water accumulation ratio of about 7 was observed for TCE while for TCA it was only 2. For alfalfa the ratios were about 10 for TCE and 5 for alfalfa. Based on 1% organic matter the sorption of TCE in soil was about 100. Coefficients for chloroform, and DCM with wood were less than for TCA. Estimates for TCE in intact stem sections were 25 - 30 while for TCA a value of 18 was obtained. Sorption must be included in any model of contaminant movement through plants, as an important addition to exclusion from the transpiration stream.

**Key words:** *trichloroethylene, trichloroethane, chloroform, adsorption, transpiration*

---

## INTRODUCTION

It is well known that non-polar compounds are preferentially sorbed to hydrophobic surfaces and dissolve in non-polar phases. When considering potential transport of solvents such as TCE through plants, it is necessary to consider their potential partitioning to the less polar phases of the plant such as membranes, starch, primary cell walls, pectic substances, and lignin.

In our earlier studies we provided clear evidence that TCE and similar compounds do, in fact, move through plants when supplied to their water source at a concentration of 1 mM (Davis et al., 1998). We also noted that the less polar compounds show a delayed appearance in the gas phase above the plant, suggestive of sorption during the transfer process. The delay occurred even when the root system was removed from the plant, which eliminates possible partitioning at the root endodermis. Doucette et al. (1997) found little TCE movement through a plant when the exposure level was low (about 10  $\mu$ M). This suggests that there might be either a specific barrier that is overcome at high concentrations, or a strong sorption to the plant within the root zone.

We have undertaken two different kinds of experiments to try to understand TCE and other solvents' sorption in or on plant materials. The simpler of these is direct equilibration of plant material with a solution containing TCE. The alternative is to flow a solution of TCE through a segment of plant stem, observing the concentration vs time profile, and then measuring the concentration of TCE accumulated in the stem segment.

## METHODS

### *Static experiments*

Equilibration studies were done in serum-stoppered 125 mL bottles to which 10 mL of solution was added from a reservoir having the desired concentration of contaminant, TCE or other, as generally described by Gossett (1987). Replicate bottles were prepared by adding a fixed 10 mL volume of solution containing the indicated concentration of TCE from a separatory funnel capped with a septum, to a 125 mL bottle having 5 g of the indicated sorbent. Some bottles had 10 g of 4 mm glass beads to give an equivalent volume displacement comparable to 5 g of one of the following: aspen wood splints, crushed dried alfalfa, sucrose, Whatman #1 filter paper, brown kraft paper, topsoil or subsoil from the Riley County landfill area. Because identical volumes of solution and identical-sized bottles were used, sorption to septa is not a large factor in deriving relative sorption to the added sorbents.

After the solution was added, the bottles were incubated at 25°C for 8-24 hr. Gas phase concentrations of contaminant were determined by gas chromatography using a flame ionization detector. Sucrose and glass beads gave the same results as water alone. Sorption is estimated from the deficit in gas phase level of contaminant compared to these. Only wood, alfalfa, and topsoil gave consistently measurable sorption. Henry's constants used for calculations were as described in Davis et al. (1998).

### *Flow experiments*

Several approaches were tried during studies of the flow of contaminant through stem segments. Reliable results were obtained when an 8 L reservoir of contaminant solution was used and the plant stem was immersed in it, except for the portion passing through a stopper to the collection device. The flow rate through the stem was controlled by an infusion pump operating in the withdrawal mode. Positive pressure was supplied to the reservoir so that water flow was about the same without the pump as with it.

Effluent collection was the most difficult part of the entire process. Tygon (PVC) tubing was fitted to the stem end. A nested set of tubing pieces was used to adapt to the needle of a 5 mL gas-tight syringe or a 30 mL glass syringe to collect outflow at a rate of 4-5 mL/hr, which reasonably approximated the expected transpiration rate for an intact plant supported by the stem during the growing season. It was observed that a short segment (1-2 cm) of thick-walled silicone tubing allowed a significant (up to half) loss of TCE. The syringe needle was therefore inserted to within 2-3 mm of the stem end, and the tubing was changed to polyvinyl chloride material.

All studies were done with dormant stems, stored at 4°C. Usually they were removed from the intact plant just a few hours before use. Water was collected for about 30 hr, corresponding to 15-40 times the water volume of the stem segment. Stems were cut into sections weighing < 1 g and quickly transferred to 65 mL bottles sealed with Pierce Reacti-vial seals. Gas phase contami-

nant concentration was determined by GC. The stem segments were weighed wet and then after drying to determine the water content. From the level of contaminant per amount of water or dry matter, the apparent accumulation ratio or sorption coefficient could be calculated.

One test was done with a stem segment maximally exposed to air (19 cm of 21.5 cm length), in contrast to the usual technique of immersion. This permitted estimation of the loss rate from the exposed stem, by comparing the expected to the observed recovery of contaminant and the change in outflow TCE concentration when flow rate was decreased two-fold. Modeling of the profiles for contaminant movement is discussed in the paper by Jiang Hu et al. also published in this Proceedings.

## RESULTS

The figure shows equilibration results for gas phase TCE concentrations in the presence of wood or alfalfa compared to sucrose. Each data point is an experiment with at least duplicate bottles assayed in duplicate or triplicate. Table 1 provides a summary of results for several compounds on the two most tightly sorbing matrices, wood and crushed alfalfa.

To derive a sorption coefficient (wood:water) for TCE, we assume that the average decrease in TCE in the gas phase is 0.4. For a 125 mL bottle with 10 mL water and 4 mL (5 g) solids, this gives a ratio of 7.15-fold accumulation in wood relative to water. For alfalfa the sorption is somewhat stronger, with a decrease in the gas phase concentration of about 0.5 in the same series of experiments. This yields an estimated 10.8-fold accumulation ratio.

With topsoil the sorption is only 0.1 of the gas phase which yields a ratio of 1.19 soil:water. If the soil is 1% organic matter, the accumulation based on that fraction is more than 100 fold.

Comparable calculations may be done for TCA. With wood the decrease in gas phase level is only 0.2 which gives a ratio of about 2 (wood:water). For alfalfa the sorption is somewhat stronger, about 0.4 decrease in gas phase concentration. This gives a sorption ratio of 5 (alfalfa:water). For topsoil the apparent decrease in gas phase concentration is similar to that for TCE, 0.1, which gives a comparable sorption coefficient of >100 fold based on organic matter content.

For chloroform a single experiment was done with triplicates using water alone, sucrose, paper, or wood. Standard deviations were <5% of the respective mean values. The decrease in gas phase was 0.25 for wood compared to the other three. With a Henry's constant of 0.16 the calculated accumulation ratio is just 1.6, slightly lower than TCA. For dichloromethane (DCM) the decrease in gas phase concentration for four experiments at four levels of DCM was about 0.25. With the use of a Henry's constant of 0.1, the calculated ratio wood:water is 1.33, somewhat less than for chloroform.

## DISCUSSION

The static equilibration results presented here show that compounds such as TCE sorb to plant tissues in proportion to their octanol:water partition coefficients, though the sorption is not so tight as

that for soil organic matter. Control experiments with pure cellulose (paper) indicate that the sorption depends on other constituents of the plant. Hence the sorption coefficient may depend on factors such as extent of lignification. It was not possible to do experiments with a greater ratio of wood:water because the dry wood takes up close to twice its weight in water. Particularly for weakly sorbing materials like chloroform and dichloromethane, the modest depletion observed here gives a fairly large uncertainty in the weak sorption.

Our earlier work (Davis et al., 1998) showed that even cut plants, without a root system, give an apparent transpired water concentration factor less than 1, indicating that sorption must be significant for non-polar compounds such as TCE. It remains a puzzle why the transpired concentration of the contaminant appeared to reach a steady state in those experiments, despite the fairly strong sorption observed here. In those experiments it was noted that more lignified tissues, such as poplar trees, gave a greater apparent sorption than young sunflower plants. With stem segments studied here, it was observed that for the polar molecule methyl-*t*-butyl ether, the outflow concentration reached 90% of the inflow level within two aqueous volumes of the stem segment, whereas the same segment attained only half the input TCA level after 7 volumes. For TCE the lag was somewhat greater. See the paper of Jiang Hu et al. for modeling analysis of the lag phase.

The relative extent of sorption was similar over a range of TCE concentrations from about 150 to 1200  $\mu\text{M}$  in static equilibration experiments. In flow through intact stems the apparent sorption was similar at 10  $\mu\text{M}$  and 1200  $\mu\text{M}$ . It should be noted that the apparent sorption coefficient was higher for the flow experiments than for the static ones, indicating that wood splints may not contain all the strong sorption sites present in the intact plant stem. In the work described by Hu et al. the lag time for TCE through a stem was the same at 10  $\mu\text{M}$  and 1200  $\mu\text{M}$  TCE, consistent with the observed similarity of sorption coefficient. Thus any difference between transfer of TCE to the atmosphere in experiments with low vs high input concentrations of TCE may be attributed to root functions, not simple sorption (Doucette et al., 1997; Burken, 1996).

#### **ACKNOWLEDGMENT**

Although this research has been funded in part by the U.S. EPA, as project 94-27, under assistance agreement R-819653, through the Great Plains/Rocky Mountain Hazardous Substance Research Center, headquartered at Kansas State University, it has not been subjected to the agency's peer and administrative review and therefore may not necessarily reflect the views of the agency, and no official endorsement should be inferred.

## REFERENCES

- Burken, J.G. (1996). Uptake and fate of organic contaminants by hybrid poplar trees. PhD Dissertation, Dept. of Environmental Engineering, University of Iowa, Iowa City.
- 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*, 1:4, pp. 1-26 or <http://www.engg.ksu.edu/HSRC/JSHR/DAVIS1>.
- Doucette, W.J., B. Orchard, S. Hayhurst, C. Pajak, B. Bugbee, and J. Chard (1997). Quantification of TCE uptake, translocation and transpiration by plants in hydroponic systems using a high flow sealed system growth chamber. Poster presented at the 18th meeting of the Society for Environmental Toxicology and Chemistry, San Francisco, CA. Also presented at a workshop on Beneficial Effects of Vegetation in Contaminated Soils, Jan. 7-9, 1998, at Kansas State University.
- Gossett, J.M. (1987) Measurement of Henry's law constants for C1 and C2 chlorinated hydrocarbons, *Environ. Sci. Technol.*, 21, pp. 202-208.

**Table 1.** Estimated sorption coefficients for several chlorinated aliphatics on aspen wood splints or crushed dried alfalfa, with excess water present<sup>a</sup>.

Contaminant	Wood sorption ratio	Alfalfa sorption ratio
TCE	7.15	10.8
TCA	2.0	5.0
CHCl <sub>3</sub>	1.6	not done
CH <sub>2</sub> Cl <sub>2</sub>	1.33	not done

a. Sorption ratios derived from gas phase depletion in the presence of the indicated sorbent relative to an equivalent mass of sucrose or glass beads, using published values of Henry's constant, cited in Davis et al., (1998). Each value is based at least on triplicate measures. For TCE a dozen experiments were done, at several levels of TCE, as shown in the figure.

**Table 2.** Estimate of TCE & TCA sorption coefficients (wood:water) for intact poplar stem segments<sup>a</sup>.

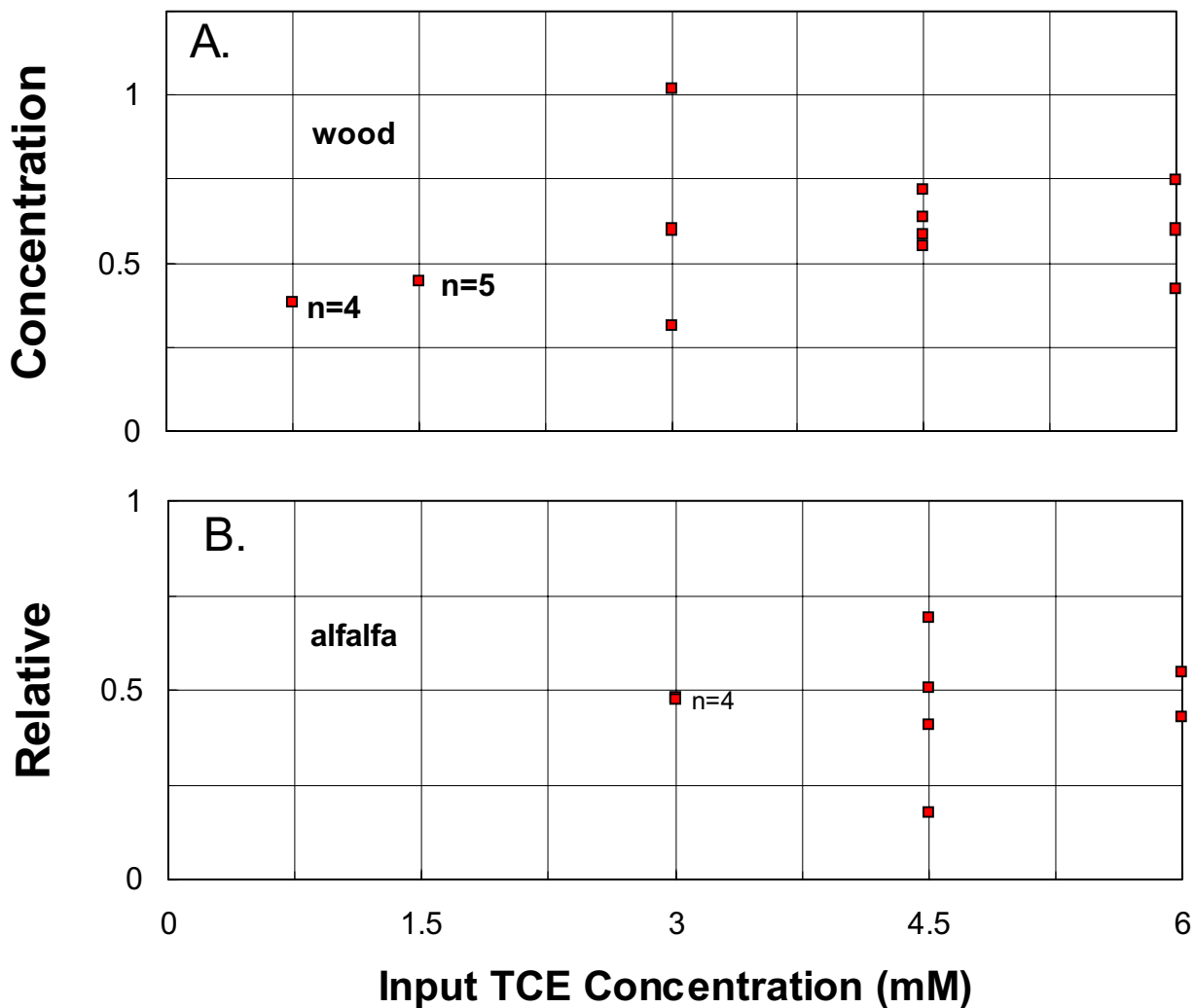
length and weight		concentration ratio
(cm)	(g)	(wood:water)
7.5	2.6	22 (TCE)
18.5	8.7	30 (TCE)
24	10.7	21 (TCE) <sup>b</sup>
30	11.3	28 (TCE)
21.5	7.0	17 (TCE) <sup>c</sup>
24	7.9	18 (TCA)

a. Derived using relative level in stem segment compared with concentration in outflow water used to approximate the internal concentration. For all but one TCE experiment, input levels of TCE were near 10 μM.

b. Done using 1200 μM TCE

c. This value may be low, 19 cm of stem was exposed to air producing about a 10 % per hr loss of TCE, based on the effect of flowrate on outflow concentration.

Figure 1. Relative gas-phase TCE concentration with sorbents added to water phase<sup>a</sup>



a. Relative concentrations were derived from the gas phase measurements on duplicate bottles for each sorbent and the sucrose control at each input concentration shown by a single data point. For wood with 0.75 mM TCE, n= 4 or 1.5 mM TCE, n=5 in the input water phase for alfalfa at 3 mM, n=4. Sucrose was not measurably different from water alone, or water with added glass beads. Final aqueous phase concentrations are calculated to be about 11-fold less than the input concentration, if there is no sorption.

