
MOVEMENT OF CHLORINATED SOLVENTS AND OTHER VOLATILE ORGANICS THROUGH PLANTS MONITORED BY FOURIER TRANSFORM INFRARED (FT-IR) SPECTROMETRY

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ABSTRACT

Plants have a large capacity to transfer water from soil to the atmosphere. Soluble contaminants may be carried with that water, with a relative extent of transfer that depends on their octanol-water or organic matter-water partition coefficient. We measured the transfer rate for several solvents that vary in volatility and solubility, including trichloroethylene, trichloroethane, chloroform, dichloromethane, diethyl ether, and methyl-t-butyl ether. We tested them alone and in several combinations. An extractive Fourier Transform Infrared (FT-IR) Spectrometer (Gasmeter, produced by Temet Instruments) was used to measure concentrations in the gas phase above plants which had their root system immersed in water containing the contaminant. Deuterated water was used to trace transpiration rate. Hybrid poplars (*Populus deltoides x nigra*) and saltcedar (*Tamarix parviflora*) gave similar results, indicating relatively free movement of the indicated solvents, alone or in combinations. Alfalfa (*Medicago sativa*) also permitted transfer of those compounds that were tested.

Key words: *volatile contaminants, FT-IR, plants, transpiration, phytoremediation*

INTRODUCTION

Successful plant-based bioremediation depends on the ability of plants to survive in the presence of contaminants. In alternative strategies, plants might be used to volatilize, metabolize, or exclude contaminants, depending on whether volatilization to the atmosphere is an acceptable fate. We have recently reviewed many alternative scenarios (Davis et al., 1998). Plants are usually able to provide nutrient supplementation to microbes that can accelerate contaminant degradation. Plants may increase vertical contaminant transport by drawing water from soil if the ground water is contaminated. Water use by plants often exceeds 1 cm per day (100,000 L/ha/day) during the summer (Jensen and Haise, 1963). Such water usage leads to intermedia transfer, i.e. from water to air, of those volatile contaminants that can enter the plant. For non-volatile contaminants that are not excluded by the root system, there may be accumulation within the plant. There is also exposure of plant roots to higher concentrations of those contaminants that are relatively non-volatile and that are also partially excluded by the plant root system, because water removal must lead to an increased contaminant concentration in the residual water. Such accumulation in the root zone can lead to toxicity. Earlier studies indicated that for trichloroethylene (TCE) or similar materials, with a vapor pressure of >75 mm Hg at room temperature, the volatile compound rapidly escapes from the aqueous phase to the atmosphere in unsaturated soil (Narayanan et al., 1996, 1997a,b). If the compound is dissolved in water as it approaches the plant root zone, then its flux to the atmosphere at steady

state is regulated by the water flux from the saturated zone to the plant. Plants may be useful to enhance the flux of water, and hence the movement of contaminants such as TCE. The concentration of contaminant remains acceptably low in the atmosphere because there is rapid gas phase dispersion and the low equilibrium concentration of water in air limits the water flux to the atmosphere.

Although Briggs et al. (1982) measured a transpiration stream concentration factor (TSCF) for a number of nonvolatile organic compounds of varying octanol-water partition coefficient, there is little experimental data showing that this relationship applies to volatile solvents that constitute a large fraction of organic ground water contaminants (Burken, 1996). Therefore, we devised a system to measure directly the transfer of chlorinated or other volatile solvents from water through the roots of plants into the gas phase surrounding the tops of the plants.

Briggs et al. (1982) measured accumulation of non-volatile chemicals in small barley seedlings at intervals of 24 and 48 hours. The amount accumulated was proportional to time. When the transpiration rate is known, the accumulation can be used to infer the TSCF, assuming that the chemical sorption to the root reaches a steady state quickly. Hsu et al. (1990) measured chemical concentrations in xylem sap of decapitated plants, allowing a direct measure of the TSCF once the sorption of chemical onto the root had attained a steady state. With a volatile compound, the rate of efflux from the top of the plant might not equal the rate of intake by the xylem of the roots, if there is significant metabolism within the plant leading to non-volatile products. Thus what we are calling the TSCF might better be termed the transpired water concentration factor. It represents a minimum estimate of the TSCF described by earlier workers. Also, if a steady state is not attained, the estimated TSCF will be a low estimate.

According to the work of Briggs et al. (1982) the values of $\log K_{ow}$ from 0 - 5 span a range of TSCFs from about 0.3 to 0.8, with the highest TSCF for compounds of intermediate polarity ($\log K_{ow}$ about 2). Highly polar or highly nonpolar compounds ought to be transported less effectively than those of intermediate polarity according to the proposal of Briggs et al. (1982), who suggested that membranes and cell cytoplasm of the endodermis may be sites of effective partitioning. Strong root sorption complicates interpretation of TSCF, if significant depletion of the aqueous phase concentration occurs, or if sorption is to sites not part of the water uptake pathway. Briggs et al. (1982) discussed this problem and clearly distinguished the root concentration factor (RCF) from the TSCF. It is the TSCF that is of interest in considering intermedia transfer, whereas RCF may be more important in determining toxicity to the plant in some cases.

Fourier transform infrared spectrometry (FT-IR) can be done with a long path length extractive instrument (Gasmeter, by Temet Instruments), which allows detection of many volatile materials at levels below 1 ppm (v/v). This instrument has previously been used by other groups to monitor air contaminants (Chaffin et al. 1994) and chemical reactions (Hakuli et al. 1995). We examined the movement of common soluble chlorinated aliphatics through two species of intact woody plants,

hybrid poplars (*Populus deltoides x nigra*) and saltcedar (*Tamarix parviflora*). Both species are rapidly growing and hence use large amounts of water. A limited number of experiments were done with alfalfa (*Medicago sativa*). In each experiment 0.8% deuterated water (D₂O) was used to provide an FT-IR detectable marker (DOH) for the rate of transpiration through the plants. Some experiments with aliphatic and aromatic hydrocarbons were briefly described previously (Makepeace et al., 1996). More detailed results will be reported elsewhere (manuscript in preparation).

MATERIALS AND METHODS

Chemicals

Solvents for study were purchased from Fisher or Aldrich. D₂O (>98%) used as a tracer was from Bio-Rad. Nutrient solutions for culture were reagent grade purchased from commercial sources.

Instrumentation

Gas chromatography was conducted as previously described (Narayanan et al., 1995). A short (90 cm) column of Porapak R was used at 200° C with N₂ carrier gas and flame ionization detection. The FT-IR system was previously used by Makepeace et al. (1996). It is an extractive instrument, produced by Temet Instruments Oy, Helsinki, Finland. Applications and limitations of the instrument are given in Hakuli et al. (1995). Calibrations of the FT-IR system and gas chromatograph were done by making measured dilutions, detailed for the FT-IR in Makepeace et al. (1996).

Culture Conditions

Poplar and saltcedar plants were grown hydroponically in individual bottles partially filled with Hoagland's solution (Hoagland and Arnon, 1950). For poplars, a half-strength solution was supplied. This was renewed at intervals of a week to 10 days. Water level was restored daily. The poplars (*Populus deltoides x nigra*, Imperial Carolina cultivar) were a gift of Dr. J. Schnoor, University of Iowa. The saltcedar (*Tamarix parviflora*) was propagated from cuttings obtained on this campus and identified at the university herbarium. Plants were maintained in a room with a temperature of 25 +/- 2°C under continuous lighting provided by 40-watt, cool white fluorescent lights, at a density of 10 four ft tubes per m².

For some experiments with severed plants, poplars were grown outside in pots with regular garden soil fertilized as needed and watered daily. Wild sunflowers (*Helianthus annuus*) were garden grown and cut fresh as needed.

Alfalfa (*Medicago sativa*, cv. Kanza) plants were grown in 1 L aspirator bottles with a mixture of perlite and vermiculite. They received a nutrient solution as described by Wacek and Brill (1976), without added nitrogen, or sucrose. Each plant was more than two years old when transferred to the bottle and was maintained for several months under the same lighting and temperature conditions as for the poplar plants prior to exposure to a contaminant.

Plant Treatment

Contaminants were supplied to the root system in a closed aspirator flask with an equilibrated

headspace (Diagram 1). A foil-covered cork, appropriately notched to fit around the stem, was used to close the flask. Then a layer of soft wax (Gouda cheese coating wax) was used to cover the top of the cork and to seal fully around the stem of the plant. Silicone rubber sealant, though used by some authors (c.f. Nair et al., 1993) is highly permeable to nonpolar molecules (~10x more than natural rubber) and consequently provides a relatively poor seal (Stancell, 1971). The side-arm of the aspirator flask was closed with a rubber vaccine bottle stopper placed over it. Then enough contaminant was added and allowed to volatilize to give the gas phase concentration that would be in equilibrium with the chosen liquid phase concentration. A separatory funnel was equilibrated with appropriate amounts of contaminant and water to yield the final chosen concentration in the liquid phase, usually 1 mM. The equilibrated solution was transferred from the separatory funnel through a tube placed in the side-arm. Gas phase was allowed to escape to give atmospheric equilibrium pressure. Unless otherwise noted, 250 mL of liquid was used within a 600 mL flask, to provide some oxygen for the respiratory demands of the roots. For calculations needed to set up the treatment flasks, Henry's constant (H = dimensionless ratio of gas to liquid concentration) values were used as given in Table 1. Roots have sufficient suction capacity that withdrawal of water could continue even if the flask were perfectly sealed. In practice, air leaked into the flask to compensate for water withdrawal. Samples were taken for gas chromatographic analysis of the head-space of the flask at the initiation and termination of the experiment.

Depending on water use and H value, the concentration of the contaminant in the flask is expected to change in a predictable though complex way as water is withdrawn. For compounds that are excluded from the plant root system, concentration in the remaining aqueous phase in the flask will increase as water is withdrawn. For compounds with $H = 1$, and a TSCF of 1, removing water will simply dilute the flask material in proportion to the amount of water replaced by air in the flask. For those compounds with $H \ll 1$, the effect of water removal will be much smaller in the gas phase than for those with H near 1. In most experiments, the measured gas phase concentration of contaminant in the flask decreased 10-30% over about a day. This effect is larger than anticipated solely from water use for compounds with $H < 0.25$ and TSCF < 0.8 .

During experiments, the concentration in the gas phase of the plant root treatment flask was monitored by gas chromatography and changes in the gas phase were assumed to represent proportional changes in the liquid phase. For volatile compounds such as were studied here, the gas and liquid phases are assumed to equilibrate rapidly. The half-life for loss of these compounds from stirred water to the atmosphere is on the order of 20 min (Dilling, 1977), and the reverse reaction should also be rapid. If compounds are sorbed to the roots of the plant, the measured concentration within the flask could decline over time without leakage from the flask.

Gas Phase Containment

The top portion of the plants was completely isolated from the root system and enclosed in a 78.5 L closed rectangular chamber (about 30 cm deep by 40 cm wide by 70 cm long) from which air

was drawn by a pump through the FT-IR instrument at about 1 L/min. Exact rates are specified for each experiment, derived as the half-time for mixing within the chamber, treating it as a stirred reactor. A small opening at the place where the sampling tube entered the chamber, but more than 20 cm from the tube orifice, provided for replenishment of the chamber air supply. Refrigerated coils along the lower perimeter of the chamber condensed water, allowing accumulation of contaminant to a concentration above that which would be associated with transfer of the amount of water required to saturate the chamber. This is an essential part of the measurement process because the level of water needed to saturate air at 25° is only about 1 mM (18 mg/L). A contaminant introduced at 1 mM into 55 M water necessarily becomes diluted to about 1/20 mmolar in the gas phase, which in turn means a concentration below 1 ppm (v/v). The CO₂ requirement for photosynthesis limited the contaminant concentration ratio that could be achieved by lowered air sampling rate with water condensation.

To prevent chilling of the plants, another centrally suspended rectangular coil system (9 x 18 x 60 cm) surrounded the plants and had water at 30°C circulated through it. A small fan assured that the time averaged temperature was relatively constant and that air circulated effectively throughout the chamber from plants to condenser and back to plants. The chamber was designed to hold up to four plants but most experiments were done with just one or two. The optimal rate of transpiration from all the introduced plants together was empirically determined to be about 5 - 10 mL/h (liquid), which allowed accumulation of contaminant without depleting the CO₂ below about half of atmospheric levels. Actual CO₂ levels were monitored for each experiment.

During the entire course of the experiment, the chamber was sealed with a glass plate over the top. Illumination was provided by six fluorescent tubes, five cm above the glass, giving a light intensity very comparable to the normal growing conditions of the plants, with the difference being interposition of a glass plate which kept some plant leaves further from the lights than during usual maintenance. The glass also reflects some light. Water usage rates in the enclosed chamber were quite similar to those determined in the open air. In open air, water use varied day to day with the relative humidity, whereas within the closed chamber, the relative humidity was fixed by the temperature of the refrigeration coils, ratio of transpiration to condensation, and chamber temperature.

Transpiration within the chamber is driven by a temperature gradient between the plants and the condensing coils such that more water is soluble in air near the plants. Both heat input from the lights and the heated water coil system, set at 30°C and surrounding the plants, contribute to maintaining the gradient. At the surface of the cooling coils, the temperature was sometimes as low as 0°C, allowing formation of frost, but in most cases the temperature of the large circulating bath was about 5°C, and the temperature of the coils themselves must have been somewhat higher. A thermometer was suspended amidst the plants to assure that they remained in the range of 22-25°C.

Gas sampling and analysis

The relative gas extraction rate from the chamber was checked by injecting a known compound

that did not significantly interfere with spectral detection of the tested contaminant of interest. Generally methane or another chlorinated aliphatic solvent was used. The decrease in concentration of this marker also accounted for any diffusive leakage from the chamber at the seals around the plants, which were foil-covered cork, or elsewhere. Water flux from plants to the chamber was derived by measuring water in the flask surrounding the plant roots before and after the experiment.

The measured gas extraction rate of the FT-IR and the water (+ contaminant) flux rate into the chamber were used to derive an expected level of contaminant during steady state operation. We did this by solving the following contaminant mass balance equation for a constant rate of extraction from a well mixed chamber with a single input. Let $B=CAV$ where B is the input rate; C is the contaminant concentration; A equals $0.693/\text{half-time}$ observed for decay of a pulsed input; and V is the chamber volume. The gas flow rate from the chamber was assumed to be equal to AV .

First, we measured the observed concentration at a particular time, approximating a steady state, and solved for the predicted input rate needed to produce the observed concentration at the measured gas flow rate. Then we used the known water flux rate measured over the entire time of the experiment and the measured initial concentration to derive the predicted steady state gas phase concentration that would be obtained in the chamber if the contaminant moved as freely as water through the plants. Water use was assumed to remain constant over the time of the experiment because we could only measure water volumes accurately at the beginning and end of the experiment with a variable extent of root immersion displacing water in the root flask. The ratio of observed to expected steady state concentration indicates the apparent transpiration stream concentration factor (TSCF). The DOH concentration profile was used to verify that water transport occurred and to estimate the exchangeable water pool of the plant. The lag between first appearance of DOH and first appearance of the contaminant in the gas phase indicated the extent to which the contaminant was adsorbed to plant components during its passage through the plant.

The Gasmet FT-IR instrument has a pathlength of 8.4 m in a White Cell of approximately 4 L internal volume. Thus there is a significant mixing time within the detection cell which affects the response time of the instrument. With a 1 L/min sampling rate, about 90% completion of equilibration is attained within 20 min. As presently configured, the Gasmet FT-IR accumulates 1 spectral sample every 100 msec with a resolution of 8 cm^{-1} over the range 900 to 4000 cm^{-1} . In a 10 min accumulation time, it therefore obtains and averages 6000 spectra. Adequate spectra were obtained in shorter times but the response of the plants required a long time course and optimum instrument use was obtained when spectra were accumulated for 10 min, out of every 15 min. As seen below, the mixing time of the instrument is much faster than the response time of most plants so that it does not influence the observed pattern of contaminant transfer.

The FT-IR is a single beam spectrometer in which a baseline must be generated while the sampling cell is appropriately purged with an inert gas. Because of the long path length, the instrument is very sensitive to traces of residual gas from previous analyses. In particular, water may be

sorbed to surfaces within the instrument and only slowly desorbed during purging with dry nitrogen gas. In some figures there are apparently negative concentration values shown for a few compounds at the start of the experiment. This indicates that a trace of the same or similar compound might have been present when the reference baseline spectrum was obtained. So long as sufficient spectra are obtained at the start and end of the experiment, this has little effect on estimating the change in contaminant concentration produced by evapotranspiration through a plant.

To derive the concentrations of contaminant in the gas phase, it is necessary to construct a "Method" in which standard spectra and concentrations are supplied for the compounds of interest, e.g. water, DOH, methane or other marker, and a contaminant (Hakuli et al., 1995). The Gasmet then uses proprietary software to derive a linear least squares fit of the unknown spectrum to the input reference spectra over some defined spectral region. Errors can arise if a compound is present but not specified in a "Method," or if the instrument does not have a representative spectrum of the contaminant to use in the spectral fitting routine. Noise limits of detection are considerably below 1 ppm v/v of the gas phase for the compounds being studied in this project. However, estimates for very similar compounds may not always be unambiguous if the compounds have very similar spectra in the region being used to determine their concentrations (Hakuli et al., 1995). This effect can be seen in spectra reported elsewhere (Makepeace et al., 1996), where TCE produced a spurious contribution to the hydrocarbon spectral region which is also a water overtone (2900-3200 cm^{-1}). Comparison of residual spectra with and without a compound in the "Method" can be used to obtain apparent spectra for that compound. With the chlorinated compounds studied here, spectral interpretation was straightforward. More details on the production of standard spectra can be found in the M.S. thesis of Makepeace (1996).

Contaminant Sorption

The adsorption of chlorinated compounds to various materials was studied directly by partitioning in closed containers. Bottles with a capacity of about 1 L (965-975 mL) were sealed with a septum for gas sampling. The contaminant of interest was injected and then allowed to equilibrate with a mass of adsorbant for a period of time after which gas samples were taken for measurement of concentration. Usually methane was used as a non-sorbing marker and a sufficient mass of sorbent was present so that a significant fraction of the added contaminant was removed from the gas phase. To confirm that the sorption process was within a responsive range, one or more additional doses of the same contaminant were added and again allowed to equilibrate. Whatman 3MM paper was used to represent the cellulose fraction of cell walls; wooden splints of Canadian aspen were used to represent lignified wood tissues; and crushed alfalfa was used to represent leafy biomass. The gas phase volume was corrected for the displacement by the added sorbent, assuming a density of 1.35.

RESULTS AND DISCUSSION

More than 25 experiments have been done with the chlorinated solvents, alone or in combination with one another or with other solvents. Table 2 is a summary of calculated TSCF values, derived as discussed in Methods above. Figure 1 provides an example of the accumulation curves for DOH and TCA with a vigorously growing poplar tree. At the start of the experiment, a pulse of TCE was introduced into the chamber. The observed initial gas phase concentration gave excellent agreement with the predicted value of 35.5 mL/L (v/v). From the exponential decrease in TCE concentration over time, the half-time of extraction was derived. This, in turn, allowed calculation of the flowrate from the chamber. Using this flowrate, the known volume of the chamber, and the observed steady state concentration during the experiment, we estimated the contaminant input to the chamber, which is the amount moving through the plant. The lag-time to first appearance of TCA is about 45 min in this experiment, which corresponds to water transpiration of about 12 mL. The accumulation of DOH is somewhat slower because of the larger mixing volume within the plant, i.e., all the water within and between cells, not just that along the main transport pathway.

The CO₂ concentration in the chamber fell from 350 to 125 ppm by 500 min. This depletion is a function of the relative rate of gas exchange in the chamber compared to the CO₂ uptake for photosynthesis. Efforts were made in all experiments to keep the CO₂ depletion to less than half, but highly active plants sometimes produced greater depletion than desirable from a photosynthetic standpoint. After a steady state accumulation level was attained, the gas extraction rate was increased twofold, leading to a decrease in the observed TCA concentration in the gas phase of somewhat less than twofold. The decrease in concentration was less than 50% perhaps because of adsorption to vegetation in the chamber and equilibration of contaminant dissolved in the condensed water, or because a true steady state level for the later extraction rate had not been reached before ending the experiment.

Another experiment, shown in Fig. 2, provides a comparison of the rates of movement of TCE and TCA. The lag before increase in the gas phase is greater for TCE than that for TCA, and the slope of the rise is slightly lower, consistent with its greater adsorption to the plant during passage. The gas-phase TCE concentration attained in steady state is somewhat lower than that for TCA. It should be noted that because of the low air exchange rate in the chamber surrounding the plant, CO₂ was severely depleted, from more than 300 ppm to about 50 ppm by 400 min. The effect, if any, of operating near the photosynthetic compensation point is unknown.

In Fig. 3 the movement of a polar volatile contaminant is shown. Two plants were used for this experiment with ether, at >1.2 mM in the aqueous phase. An initial vs final baseline offset limits the determination of gas phase ether concentration to a precision of about 0.5 ppm. The CO₂ level fell to 150 ppm and remained steady, giving no indication of plant distress during exposure to this level of contaminant.

Toluene, a compound less volatile and slightly more nonpolar than TCA, was directly compared

as shown in Fig. 4. Two plants were tested together. As observable in the figure, toluene came through more slowly and at a lower rate than TCA. The steady state accumulation in the gas phase responded to a change in the gas exchange rate as expected for TCA, with an approximately twofold increase in exchange rate, giving a significant decrease in TCA concentration observed in the chamber. (Measured $t_{1/2}$ was 125 and 65 min.) Contaminant levels had probably not attained a steady state before the change of gas exchange was made so that the accumulation level estimated in the initial period may be somewhat low. This leads to a low estimate of the transpiration stream concentration factor. The CO_2 level declined to 150 ppm during the first collection phase and rebounded to 225 ppm in the second, indicating that the plants were not very limited for photosynthetic carbon assimilation, and were still responsive after contaminant exposure.

To eliminate the partitioning through roots as a factor in the differential movement of TCE and TCA, cut stems of poplar were used (Fig. 5). These had been grown outside under natural daylight and temperature conditions and had ceased elongation and new leaf production for the season. When plants were first introduced to the chamber, the CO_2 levels declined a bit lower than desired and the contaminant appeared to have reached a high level, so the rate of gas exchange was increased. The calculated TSCF at the higher gas exchange rate was higher for TCA than for TCE. The estimated TSCF for both would be lower if the earlier exchange rate were assumed. The CO_2 level reached 90 ppm in the first interval before 550 min and returned to 170 ppm by 800 min. It slowly rose thereafter, as the observed level of contaminant declined. The TSCF calculation is made assuming a constant water usage throughout the experiment. If water flux declines over time, the estimated TSCF is overestimated somewhat in initial stages and underestimated in later times, in proportion to the change in water use rate.

To make a comparison of a plant less woody than poplar, annual sunflowers were used. These possess a very high photosynthetic rate and can tolerate maintenance in water without roots for some days, until conducting vessels become plugged. Lag times for the initial rise of contaminant level are shorter in this experiment (Fig. 6) than for most, but see Fig. 1 for comparison of poplars with a comparable water use rate. The rise of contaminants relative to DOH is more rapid here than observed in Fig. 5. The observed TSCF is near unity for both contaminants (Table 2). The CO_2 depletion was similar to the first portion of the experiment with cut poplars, reaching 120 ppm at the lowest. Later the CO_2 level rose to 150 ppm as the contaminant concentrations declined, suggesting that the plants were becoming less active. There is no practical way to reliably monitor water usage without disrupting the experiments and we can only infer photosynthetic activity from the steady state depletion of CO_2 . Both the rise in CO_2 and the decline in contaminant concentration are consistent with a 25% decrease in plant transpirational activity toward the end of the experiment.

Saltcedar responded similarly to poplars but generally with greater apparent adsorption of most contaminants. The plants used for experiments shown here had been maintained in hydroponic culture for about 18 months and had relatively thick stems, approaching 6-8 mm in diameter over

the lower 20 cm. Fig. 7 is an example with methyl-*t*-butyl ether used as a highly polar contaminant and TCA as a more readily sorbed one. The effect of changing gas exchange rate is dramatically evident for the ether with a decline in concentration consistent with the changing gas exchange rate. Little effect was observed for the TCA, an observation for which we have no good explanation other than release from a sorbed reservoir within the plant. The CO₂ level declined to about 125 ppm, indicating a strong rate of photosynthesis.

From the known water use rate for each experiment, the gas flow rate, the measured initial contaminant concentration in the flask, and the steady state gas phase concentration in the chamber, we derived a ratio corresponding to the transpiration stream concentration factor. Both intact poplars and saltcedars were tested with several chlorinated solvents. Table 2 provides a summary of the apparent TSCF for a number of compounds. If two values are shown for a single compound in the table, they represent estimates based on different gas extraction rates (Figs. 1, 4, 5, 7). In the case of intact plants, one might expect to see a relationship similar to that observed by Briggs et al. (1982), which postulates that permeation through the roots to the xylem is a function of the log K_{ow} . However, for cut plants this cannot be the situation and the observed TSCF, if less than 1.0, must represent a partitioning that occurs somewhere within the plant's transpiration stream. Cut plants of sunflower and poplar were examined with several of the solvents alone and in combination.

Diethyl ether was used as an easy-to-study, relatively soluble, and volatile compound. A gasoline additive oxygenate, methyl-*t*-butyl ether, was also tested. Ethyl ether moved rapidly through the plant and appeared to have a TSCF close to unity (Table 2). The methyl-*t*-butyl ether showed a similar rapid transfer through the plant. This compound, which is quite soluble in water, has recently been found at relatively high levels in groundwater samples at several sites. It is suggested that because of its solubility, it may enter groundwater through rainfall in areas where it is used as an oxygenate additive, and that it may persist in the atmosphere for a relatively long time, with a half-life of over a year (LeClair, 1997).

Cut plants of sunflower gave the expected free transfer of several compounds to the atmosphere, whereas cut poplar stems appeared to give lower TSCFs with the chlorinated compounds (Table 2). In terms of total dry matter or height, the poplars and sunflowers were not greatly different. In various experiments the mass of sunflower varied from 11-16 g, while the poplars varied from 16-25 g. Plant heights were 35-55 cm in either case but the poplars had more and smaller diameter stems per experiment. The annual sunflowers may have been less lignified, which could affect adsorption properties of the compounds.

Methanol, ethanol, and propanol were tested alone or in combination with chlorinated compounds, with intact plants. Their water miscibility, combined with low volatility, apparently caused them to partition to the collected water in the chamber so that valid numbers for their TSCF could not be derived. In one example shown in Table 2, a relatively low TSCF for TCE was obtained in the presence of methanol. In other cases in the presence of the alcohols, we could not detect the expected

TCE, suggesting that perhaps it codissolved with the alcohol or was sorbed in the plant. The plants were able to tolerate exposure to relatively high levels of all three of the alcohols which were used at 1.6-2.0 mM.

Experiments with alfalfa were done with a number of compounds. They are hard to interpret quantitatively because the plants had not been grown hydroponically, but rather in a perlite-vermiculite medium to which water was added. Thus there was an unavoidable dilution of the added contaminants by water stored in the growth medium. Using the known weight of the planting container and medium, it was possible to estimate the amount of water to which the added contaminant was partitioning but the amount of plant dry weight could not be determined without destroying the plant. The steady state level of DOH that accumulated in the growth chamber provided an additional indication of the extent of dilution because it was used as a tracer at the same level for alfalfa as for the other plants. A lower steady state level of DOH indicated that a significant portion of the transpired water was contributed by an unlabeled source.

Some results with alfalfa are shown in Table 2. For both TCA and dichloromethane, it was obvious that the compound moves freely through alfalfa. Getting a reliable estimate of the TSCF was not possible given the constraints on measurement of liquid phase partitioning within the rooting container. Values given must be regarded as approximate, because the solution within the container was not stirred; potentially sorbing matrix material was present; and the available gas phase had to be estimated for addition of contaminant to equilibrate that phase. If roots preferentially drew water from newly added contaminated water or the added gas phase contaminant ended up near the active roots, apparent TSCFs would be overestimated.

Dichloromethane was difficult to study in any plant because other compounds such as TCE or methane, that might be used as markers for the exchange time of the chamber, have overlapping peaks that interfere with reliable determination of very low levels of DCM, and hence were omitted from the experiments. Experiments done with saltcedar at both 1 mM and 3 mM DCM showed that it moved freely through the plant. The calculated TSCF was greater than one if the exchange rate of the chamber was assumed to be similar to that in other experiments. Essential parameters for deriving the half-time of chamber sampling by alternate means were not recorded.

Preliminary estimates of adsorption of some contaminants were determined as described in Methods. Much more detailed studies are needed to determine binding isotherms for modeling transfer through plants. Adsorption was significant. For instance, 100 g dry alfalfa in a 976 mL bottle adsorbed more than 3/4 of an input 100 mL of TCE. Whatman 3MM filter paper at 200 g/bottle bound half the input amount. Wood (50 g fully saturated with water) bound half of the input. The same amount of dry wood sorbed 3/4 of the input; wetting it to saturation after equilibration decreased the sorption to the same level as prewetted wood. The difference between paper and wood is presumably due to the lignin content of wood. The sorption of TCE is considerably stronger than that of TCA, despite the greater $\log K_{ow}$ of TCA (c.f. Figs. 2 & 6). This was not expected, but has been

confirmed in binding studies to be reported elsewhere (Vanderhoof and Davis, unpublished).

If one assumes that a plant of 50 g dry weight is half wood and is equilibrated with the contents of a 600 mL flask, it is not unreasonable to expect that it could sorb half of the input TCE. Because the measured initial concentration in the flask was used to calculate the values of TSCF shown in Table 2, any preferential sorption to roots, which lowers the aqueous phase concentration in the flask, would cause an underestimate of the TSCF. Sorption to the plant stem through which the solution flows would lengthen the time required to reach a steady state, but should not alter the true steady state rate of contaminant emission. However, if the sorption is very strong, a steady state might not be attained for many hours, perhaps even beyond the practical time of the experiments. Both of these effects would tend to lower the estimated TSCF.

It should be noted that the apparent concentration of DOH serves only as an indicator of the approach to steady state. The input level of D₂O was 0.8% by volume in the water to be transpired through the plant. This concentration is diluted as the DOH passes through the plant and exchanges with various pools of exchangeable protons. The largest of these is obviously water, between and within cells. For a series of experiments with cut plants, approximating the size of the intact plants, water within the plants was 25-40 mL, giving a minimum of 4- 6 hours for its replacement from the contaminant-containing flask at the rate of water usage observed here. Dispersion of the replacement curve depends on the various pool sizes and the architecture of the plant. More sophisticated modeling is needed to describe the process in greater detail.

After exit from the plant, the DOH is further diluted by water drawn into the plant chamber at the indicated sampling rate. The solubility of water in air is on the order of 1 mM (18 mg/L), giving 25,000 mL/L (v/v). The total amount of water in the gas phase was maintained nearly constant by the refrigeration coils installed in the plant chamber around the lower portion of the outside walls. For a plant transpiring 6 mL/h, its contribution per minute would be roughly fivefold greater than the incoming air at an exchange rate of 1 L/min. On a very warm humid day, the incoming air would make a somewhat bigger contribution, while on a dry day it would make a lesser contribution. Typical levels of water in air at reasonable room temperatures are 15-30 mg/L. Diurnal cycles of relative humidity obviously affect this. Changing the air exchange rate would also have an effect on the observed steady state DOH concentration. With a chamber operating at an effective temperature of below 20° with saturating water vapor, in a room cooled to 25° and below saturating relative humidity, the net effect of input air is variable. The overall effect is quite small, a fraction of a mL/hr liquid water condensed or removed.

The observed time to accumulate DOH is somewhat longer than would occur by simple displacement because the DOH must exchange with the initially transpired, unlabeled water within the chamber, as well as the unlabeled water brought in by the gas exchange process. A freely mobile contaminant could appear to move to the gas phase more rapidly than DOH because of this dilution process, which leads to an apparent lag in the rise of DOH concentration. However, contaminants

arriving in the gas phase more slowly than DOH could be a consequence of adsorption within the plant. Thus the lag time to appearance of contaminant can be used diagnostically if not quantitatively.

In order to accumulate higher levels of contaminant than would be present directly in the transpired water in the measuring chamber, it is necessary to use condensing coils to trap out the transpired water and maintain the transpirational driving force. The condensed water may dissolve a portion of the released contaminant. At the temperature of the cooling coils (5-10° C), the vapor pressure of contaminants is significantly lower than at a room temperature of 25° and consequently the dimensionless Henry constant is smaller. For instance, Gossett determined the H value of TCE and TCA over a range of temperatures down to 9.6°. Extrapolating the change of H vs T to 0°, to consider a worst case estimate, gives about 0.075 for the H of TCE and 0.1 for the H of TCA. When 200 mL of water has been condensed, it will serve as a reservoir of contaminant equivalent to increasing the gas volume of the chamber by about 2 L for TCA and 3 L for TCE. This leads to a very small correction of the calculated TSCF derived from observed steady state gas phase concentration because in any short interval the condensed water already has accumulated contaminant in equilibrium with the gas phase, though it has an observable effect on the response to a change in gas flow rate. If the plant contains a significant volume of water which condenses in the chamber, this contributes a “once only” dilution of the chamber gas phase concentration. Again, at steady state this is a negligible effect, though it lengthens the time to attain steady state.

With an ether which has a much higher aqueous phase solubility than TCE, the correction is larger. The vapor pressure of ethyl ether at 0° is about half that at room temperature while the solubility increases less than 2-fold (Merck Index values), yielding an estimated H value on the order of 0.01 near 0°. During a one-hour interval, there might be an input of 10 mL (0.01 L) water as transpiration while there is removal of 60 L of air from the chamber. The concentration of contaminant in that 60 L is perturbed by the amount of contaminant that must remain with the transpired water as it condenses. In this instance the effect is a 1/60 error in the steady state TSCF. Mathematically, we can write this as follows, using the same notation found in Methods above. Let $B = (HAV + w)C$, where B is the input concentration; C is the liquid phase concentration; w is the transpiration rate (L/hr); H is the Henry constant; and AV is the rate of gas extraction (L/hr). For the instance of ether, at steady state, $B = (0.01 \times 60 + 0.01)C$.

Briggs et al. (1982) used an equation of the following form to fit data obtained with a non-homologous series of volatile compounds of varied polarity: $TSCF = 0.784 \exp[-(\log K_{ow} - 1.78)^2 / 2.44]$. This gives a Gaussian curve centered on $\log K_{ow} = 1.78$, with a maximum TSCF of 0.784. The compounds used in their experiments were O-methylcarbamoyloximes and substituted phenyl ureas and the plants were barley seedlings. Hsu et al. (1990) studied a different homologous series of compounds related to cinmethylin and obtained a similar curve but centered about a $\log K_{ow}$ of 3.07 with a maximum TSCF of 0.7. They used a root pressure chamber and detopped soybeans as an

experimental system. The two experimental approaches and plant material were rather different in the studies cited above. Briggs cited additional studies of other compounds and experimental techniques, some of which agreed well with their equation but others which could have been fitted equally well by the equation of Hsu et al. Burken (1996) found a value intermediate between these two groups, for a range of volatile and semi-volatile contaminants. The reasonable agreement amongst a variety of studies suggests that the response of plants to compound polarity is a general one. For the compounds that we have studied here, with $\log K_{ow}$ values relatively narrowly clustered between 0.8 and 2.7, TSCF values are thus expected to be between 0.4 and 0.8, if the relations reported by the cited authors hold for highly volatile compounds. We observed somewhat lower TSCFs than expected, possibly because of sorption to the plants, or losses of contaminant from the root exposure flask. Sorption to exposed leaf surfaces of plants would result in a lag in attainment of steady state. If such sorption is strong and the binding isotherm is linear over the concentration of interest, it will also give a somewhat lower, free steady state concentration of the contaminant. For a small amount of plant material (<50 g fresh wt) in a large container (~78 L), the error introduced by this effect would not be large.

It must also be recognized that with strongly sorbing compounds, we may not have allowed the transpiration process to come to steady state. Decisions must be made in real time and it is only after detailed analysis of graphs that it becomes apparent in some cases that the compound has not attained a steady state of movement. Such an effect is observable in some of the figures for some compounds. For instance, for Fig. 4, a change of extraction rate was made after 10 hours to increase photosynthetic rate, but neither TCA nor toluene had achieved steady state levels. The lower TSCF estimate shown in Table 2 for each of these was obtained from this portion of the curve. In Fig. 7, the same effect is observable for TCA, though not for MTBE as shown by the TSCF values reported in Table 2.

CONCLUSIONS

Volatile contaminants of the chlorinated hydrocarbon series move readily through plants. As expected from their octanol:water partition coefficient, they are partially rejected or sorbed within the plant resulting in a transpiration stream concentration less than that of the input solution (Burken, 1996). By contrast, the ethers are only slightly excluded or sorbed. Less polar gasoline constituents are more strongly excluded or sorbed than TCE (Makepeace et al., 1996, Makepeace, 1997 and unpublished).

So long as the contaminant is transferred through the plant in proportion to water flow, the levels achieved in the gas phase above the plant are relatively low. They should not cause concern about air quality in most places because there is massive dilution by normal air circulation. For instance, groundwater fully saturated with TCE at 1.5 g/L would only produce a 5 ppm (v/v) level in an enclosed container during steady state movement up through the soil column until the aboveground gas phase was water-saturated. Such a level in the root solution would be toxic to the

plant and would not be translocated (Q. Zhang, unpublished obs). Poplars have been grown for relatively long periods of time with up to 50 mg/L TCE in groundwater below the trees (Newman et al., 1997) and transpirational release of TCE is observed from these trees. The amounts reported are quite small and cannot be directly related to the input levels because of technical difficulties in the transpiration measurement.

According to Leeson and Hinchee (1996), bioventing systems, where air is deliberately injected into the soil to come out elsewhere, are not generally considered to release significant amounts of contaminant. They quote a 1993 U.S. EPA document, (EPA 451/R-93-003) *Estimation of Air Impacts for Bioventing Systems Used at Superfund Sites*, which indicates that emissions during the injection mode are thought to be minimal. A plant-based system is totally passive so that air flux rates will be considerably less than in a bioventing scheme. Only if plants completely remove the water layer overlying a dense nonaqueous-phase liquid would there be the possibility of contaminant fluxes greater than that of the water soluble portion (Narayanan et al., 1997a,b). For a fuller discussion of flux rates dependent on plants, see Davis et al. (1998). Plant based systems should have large economic advantages over other bioremediation approaches including bioventing (c.f. Cookson, 1995) because the maintenance requirements are similar to those of agriculture and forestry and the materials costs are quite modest.

The results presented in this paper indicate that the contaminants of interest do move relatively freely through plants, when their roots are exposed to them at concentrations near 1 mM. Sorption without much transfer could occur at low concentrations. The real issue for potential intermedia transfer of contaminants by plants is what concentration of contaminant is present at the surface of the root. Studies by Narayanan et al. (1997a,b) and Russell et. al (1996) indicate that there is rapid loss of contaminants to the gas phase in the region of soil just above the capillary fringe. Thus for most plants growing in real soils, their exposure to contaminants will be much lower than that found in the bulk groundwater, perhaps 10 to 100-fold less. Only with fully saturated soils would the contaminant level at the root be comparable to that in the groundwater.

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Table 1. Dimensionless Henry's constants, octanol-water partition coefficients and vapor pressures for compounds used in plant experiments.*

Compound	Henry's Constant	log K_{ow}	vapor pressure (25°) mm Hg
ethyl ether; C ₄ H ₁₀ O	0.03	0.8	534
methyl- <i>t</i> -butyl ether; C ₅ H ₁₂ O	0.02	1.8 (est)	276
Dichloromethane; CH ₂ Cl ₂	0.10	1.25	350
Chloroform; CHCl ₃	0.16	1.95	350
TCE; C ₂ HCl ₃	0.39	2.3	75
1,1,1-TCA; C ₂ H ₃ Cl ₃	0.70	2.5	125
toluene; C ₇ H ₈	0.25	2.7	29

*Values for Log K_{ow} are taken from Hansch and Leo (1979), while vapor pressures are derived from data and equations given in Yaws (1992). Values of H were derived for 25°C from data in Yaws (1992) for dichloromethane, chloroform, and toluene, and from Gossett (1987) for TCE and 1,1,1-TCA. Values for the ethers were calculated directly from solubility and vapor pressure. There are other H values in the literature for many of these compounds but a recent critical review by Staudinger and Roberts (1996) gives "best" values that are consistent with those used here.

Table 2. Estimated values of transpiration stream concentration factors (TSCF).

Plant & condition*	chemical treatment	TSCF for named compound
2 saltcedar	1 mM TCE	0.26 TCE
1 saltcedar	1 mM TCE	0.10 TCE
1 poplar (Fig. 1)	1 mM TCA	0.26-0.31 TCA
1 poplar (yr 1)	1 mM TCA	0.84 TCA
1 saltcedar (yr 1)	1 mM TCA	0.72-1.0 TCA
2 saltcedar	1 mM TCA	0.25 TCA
1 poplar (Fig. 2)	1 mM TCE & TCA	0.64 TCA, 0.58 TCE
2 poplar (Fig. 3)	>1.2mM ethyl ether	0.9 ether
1 poplar	1 mM TCA & >1.2mM ethyl ether	0.83 TCA, 0.67 ether
1 poplar	1 mM toluene	0.25 toluene
2 poplar (Fig. 4)	1 mM TCA & toluene	0.72-0.81 TCA, 0.25-0.4 toluene
2 saltcedar (Fig. 7)	1 mM TCA & 1.35 mM methyl- <i>t</i> -butyl ether	0.18-0.36 TCA, 0.62-0.64 MTBE
2 poplar	1 mM dichloromethane	0.49 DCM
1 poplar	1 mM chloroform	0.27 CHCl ₃
1 poplar	1 mM TCE & chloroform	0.22 CHCl ₃
1 poplar	1 mM TCE & methanol	0.1 TCE
2 cut sunflower (Fig. 6)	0.5 mM TCE & TCA	1.04 TCA, 0.9 TCE
2 cut sunflower	>1.2 mM ethyl ether	1.0 ether
2 cut poplar	>1.2 mM ethyl ether	0.7-0.8 ether
2 cut poplar (Fig. 5)	1 mM TCE & TCA	0.44-0.55 TCA, 0.2-0.35 TCE
2 cut poplar	0.5 mM TCA, 1 mM toluene	0.38 TCA, 0.1 toluene
2 cut poplar	1 mM dichloromethane	0.74 DCM
2 alfalfa (yr 1)	1.6 mM TCA	2 TCA
2 alfalfa (yr 1)	1 mM dichloromethane	1.2 DCM

* (yr 1) indicates experiments done in 1995, all others 1996. Figure numbers shown in parentheses for those cases where original data are shown in this paper. Values calculated for TSCF are shown to two places but cannot be considered reliable to better than 20% of the observed value. Measured gas phase concentrations have absolute errors of up to +/- 0.5 ppm associated with them as seen in the figures. For contaminants attaining only a low gas phase concentration of 2.5 ppm, this is a significant percentage uncertainty (c.f. toluene in Fig. 4). Measured water use for a single plant is valid to only about 5 mL because of variable water retention on the root system. This results in estimated water use having an error of near 10% when two plants each use 50 mL during the course of a one-day experiment. Sampling and analysis of the gas phase in the root flask is not better than 10%.

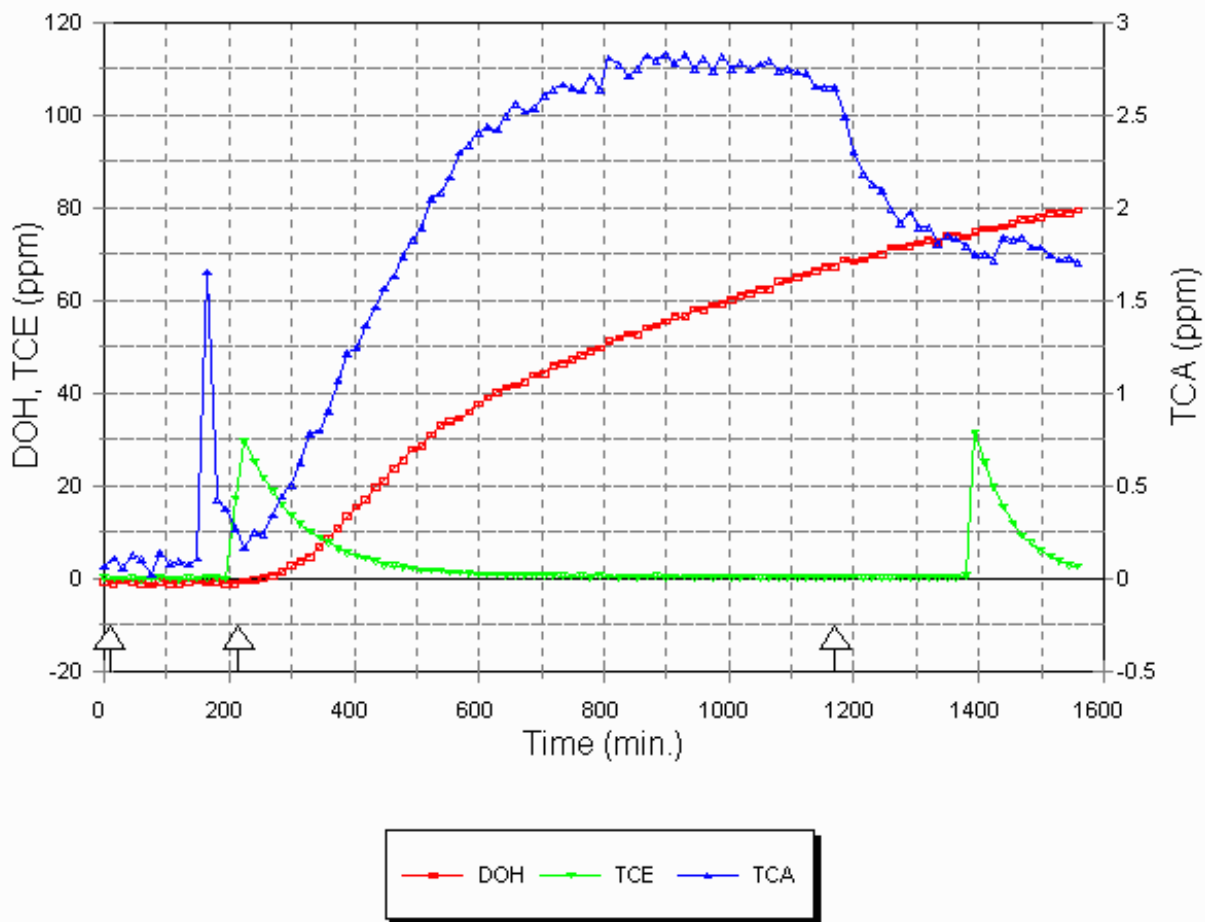


Figure 1. Migration of TCA through a poplar tree. A single large poplar was used on July 31, 1996. Prior to treatment it transpired 16.5 mL/hr. It transpired 16.3 mL/hr of water during the course of the experiment (374 mL in 23 hr). The experiment was done with an initial 504 mL in a 604 mL flask. A dozen scans of room air were acquired before the plant was placed in the chamber. A 25 cm long capillary tube was used to control the gas extraction rate through the Gasmeter. The spike of TCA at 165 min is a room contaminant that occurred during setup of the experimental plant. The actual time of starting the experiment was 180 min on the graph shown. The TCA concentration began to increase 45 min later at 225 min. Pulses of TCE were injected to the chamber at 195 and 1395 min to determine mixing half-times with two different rates of gas extraction. After the contaminant flux approached a steady state, the gas sampling rate was altered as indicated by the change to a 6 cm constriction capillary at 1170 min. Half-times were 82 min and 43 min for the two extraction rates. Note the 40-fold difference in scales for TCA and DOH gas phase concentrations, used so that both can be graphed together.

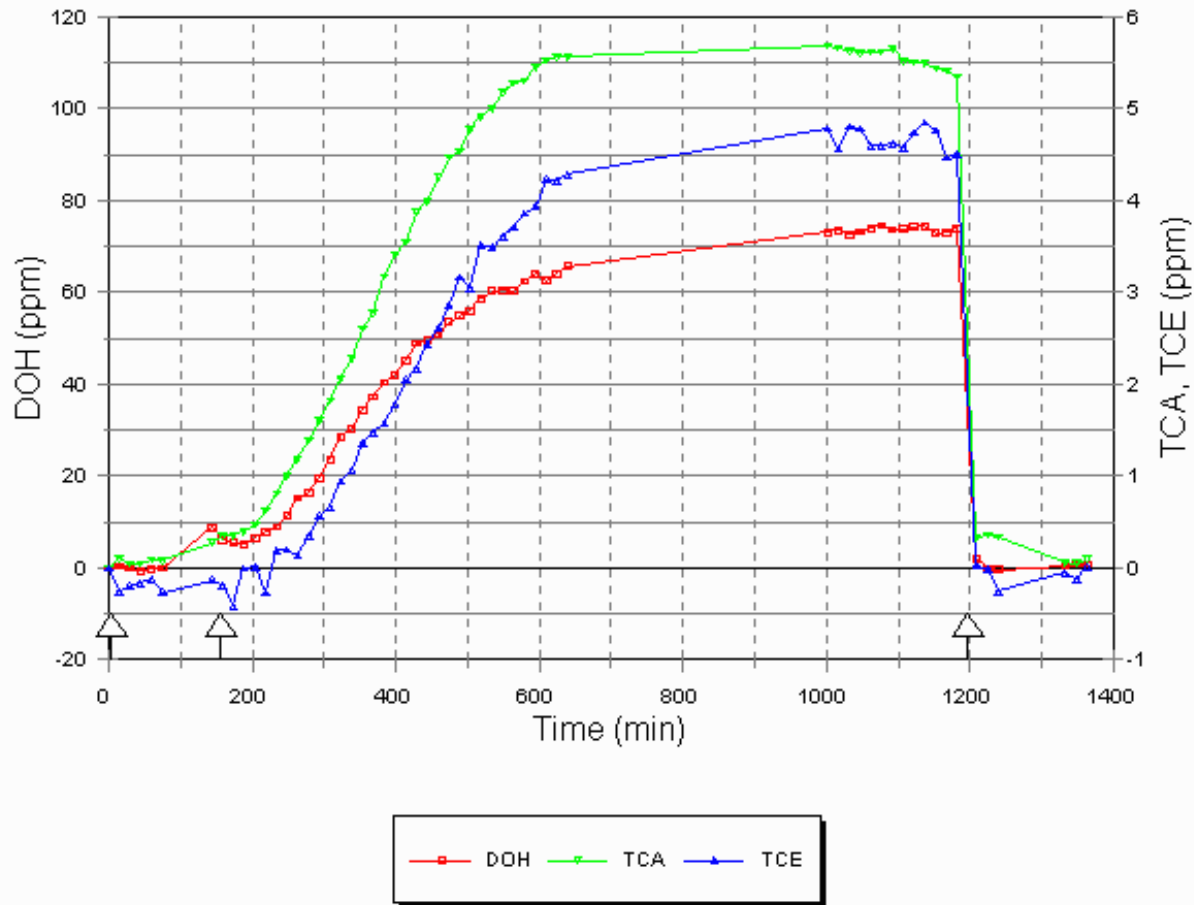


Figure 2. Comparison of migration rates of TCE and TCA. A single poplar transpiring about 12.7 mL/hr prior to treatment was used for this experiment (Aug 15, 1996) with both TCA and TCE present at 1 mM in the aqueous phase. There was about 30 min delay between adding contaminant to plants and transferring plants to the accumulation chamber. During the course of the experiment (18 hr), the gas phase concentrations of contaminant declined by 1/3 to 1/2 while about 2/3 of the water (164 mL) was removed, increasing the available gas phase from 350 to 514 mL (48%). Transpiration during treatment was 9.1 mL/hr. The chamber extraction half-time was 124 min with a 50 cm constriction line, which was used starting at 144 min. At 1200 min, room air was collected with a 12 cm constriction line, as indicated by the arrow.

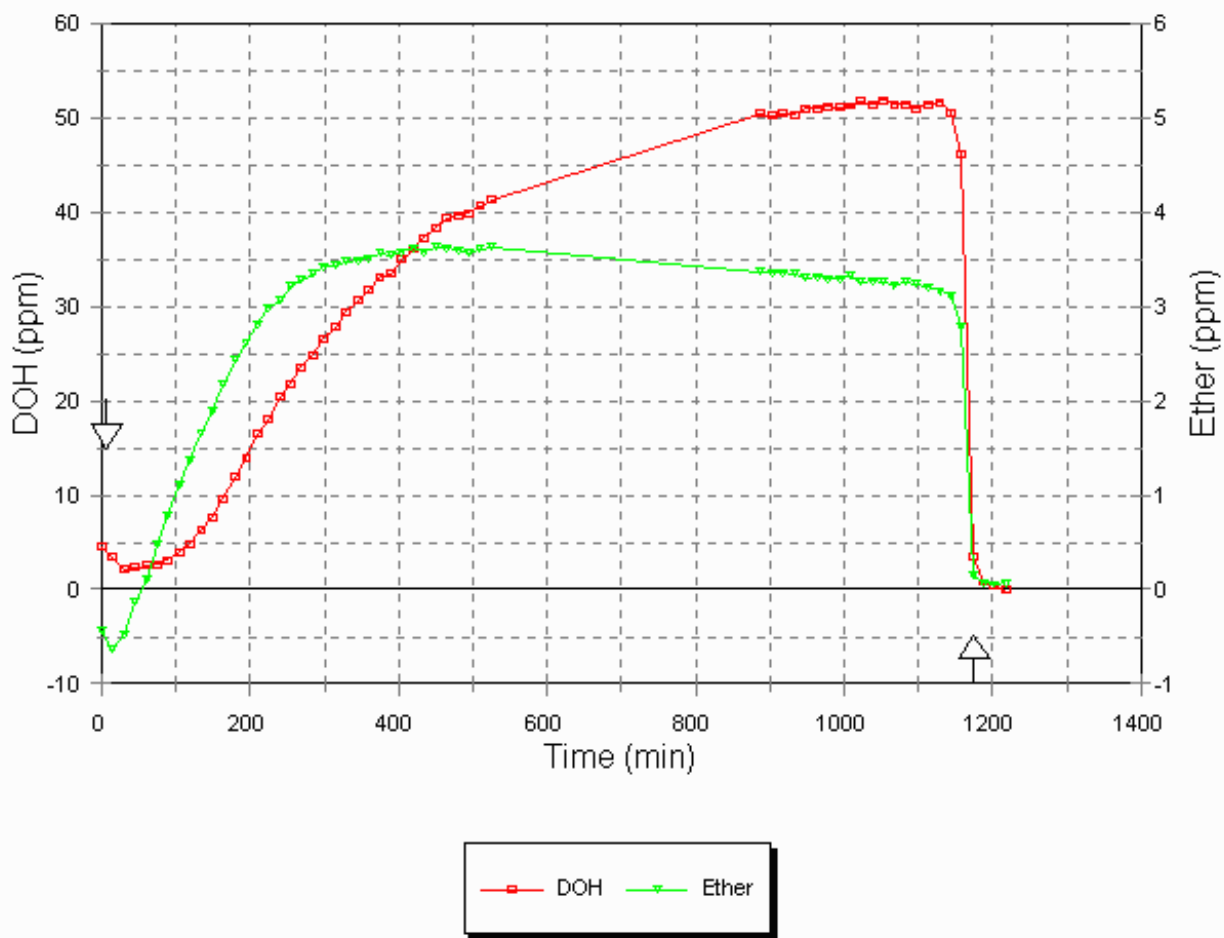


Figure 3. Movement of ether through poplars. Two trees were used in separate flasks for this experiment, Aug 1, 1996. They used 3.25 and 3.4 mL/hr with >1.2 mM ether during exposure. Total water transpired was 68 mL and 72 mL. Prior to exposure each used 4 mL/hr. Ether concentration in the gas phase of the root flasks did not decline during the 21-hr course of this experiment. The half-time of chamber extraction was 62 min with a 25 cm constriction hose, begun at 15 min as indicated by the arrow. At 1158 min, collection was switched to room air.

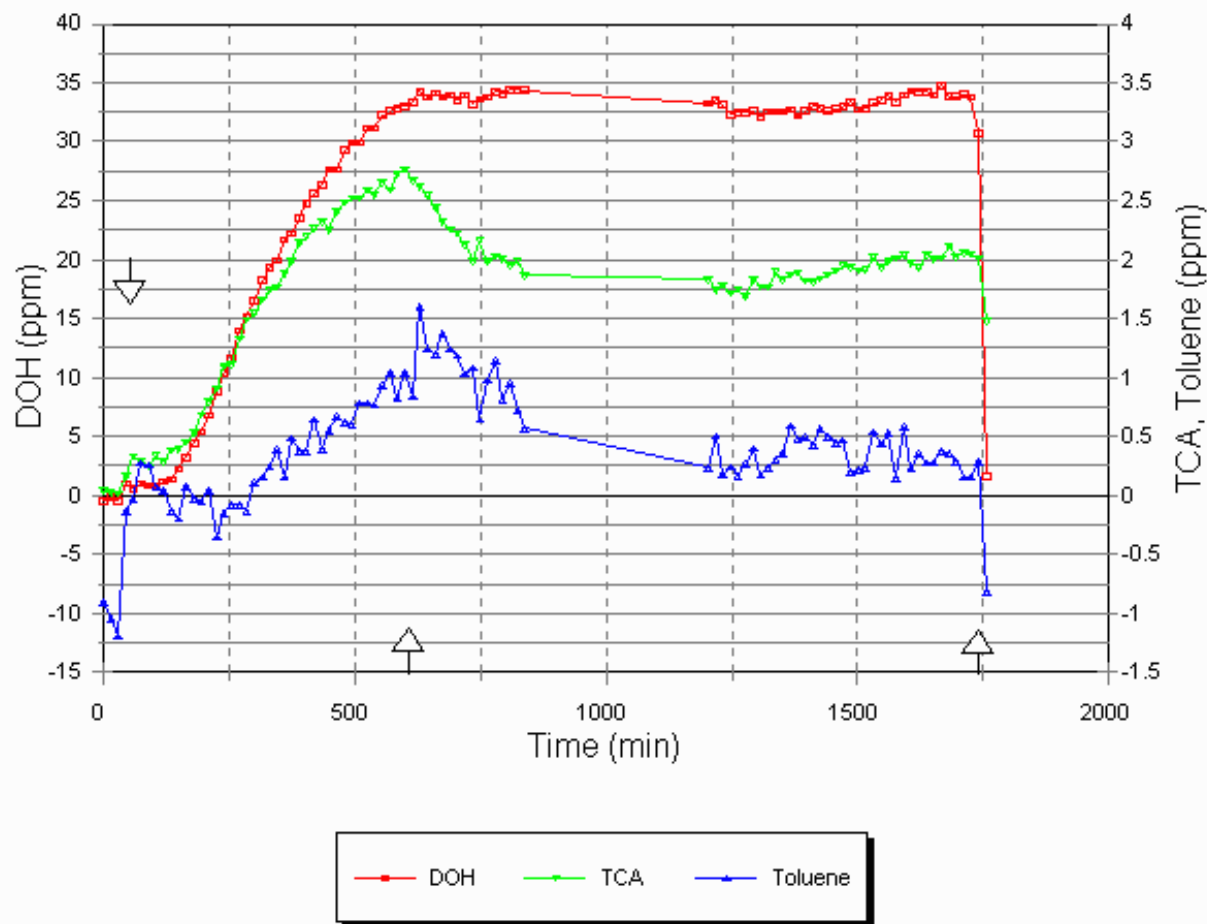


Figure 4. Comparison of movement of toluene and TCA through poplars. Two trees in separate flasks used 1.7 and 2.0 mL/hr during exposure of each to 1 mM TCA and toluene, Aug 17, 1996. Prior to exposure each used 3 mL/hr. There was no decrease in root flask contaminant concentrations for this experiment, while water use was only 40 mL of the input 250 mL. The chamber extraction half-times were 125 min with a 50 cm line and 65 min with a 25 cm line. As indicated by the arrows, a 50 cm constriction line was introduced at 45 min, a 25 cm line at 630 min, and a 12 cm line for room air collection at 1742 min. The first three scans shown here are of room air collected with a 25 cm constriction line.

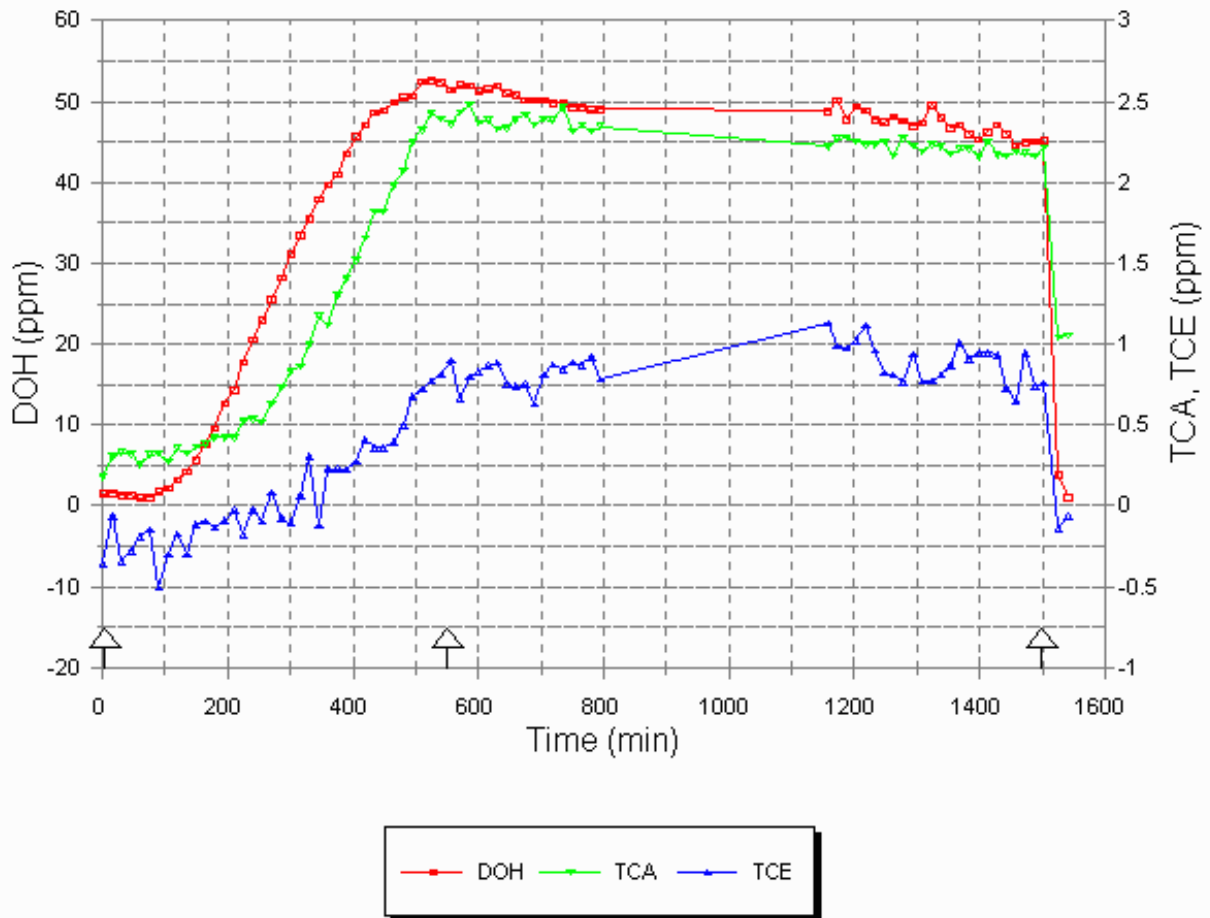


Figure 5. Comparative movement of TCA and TCE through cut poplars. Four stems (two each in two containers) were used for this experiment, Aug 24, 1996, with 1mM of each of the contaminants. Water use was just over 6 mL/hr for the four together, which were similar in size and number of leaves. The plants had been grown outdoors under natural daylight and temperature conditions and had ceased elongation and new leaf production for the season. Plants were brought indoors 14 hr prior to cutting stems. For one pair of cut stems the rate of water use immediately after cutting was 4 mL/ 1.5 hr, under the lighting conditions used for laboratory plant growth. The other two stems were cut immediately prior to treatment with contaminants. For one flask the contaminant loss in the gas phase was 1/3 and for the other 1/2 over the time of the experiment while water use was about 1/3 of the input (80 and 84 mL in 26 hours for the two flasks). The half-time for chamber extraction was 116 min with a 50 cm line and 71 min with a 25 cm line. As indicated by the arrows, the switch to a 25 cm line was made at 540 min and the change to collection of room air was made at 1525 min.

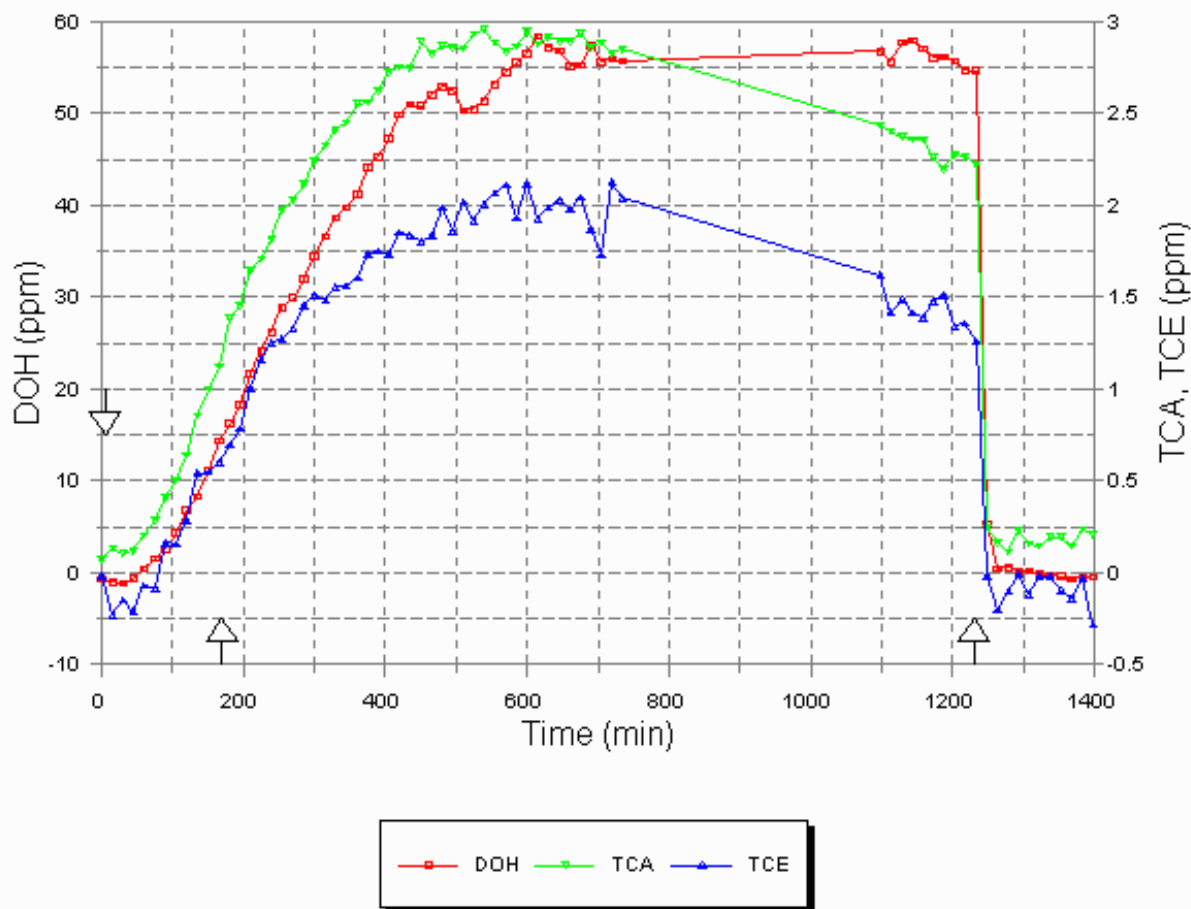


Figure 6. Comparative movement of TCA and TCE through cut sunflower plants. Three cut stems, two in one container and one in another, were used with 0.5 mM of TCA and TCE in the aqueous phase. Plants were cut in the morning of Aug 22, 1996, and immediately placed in water and transported to the laboratory. Water use was 45 mL in 2.5 hr (18 mL/hr) under the laboratory lighting conditions for the three plants all together. They used 8.0 & 8.6 mL/hr for each container, during treatment, for a total of 164 and 178 mL during the course of the experiment. The chamber half-time was 63 min with the 12 cm line and 66 min with the 25 cm line. As indicated by the arrows the 12 cm line was introduced at 150 min and room air was sampled at 1248 min.

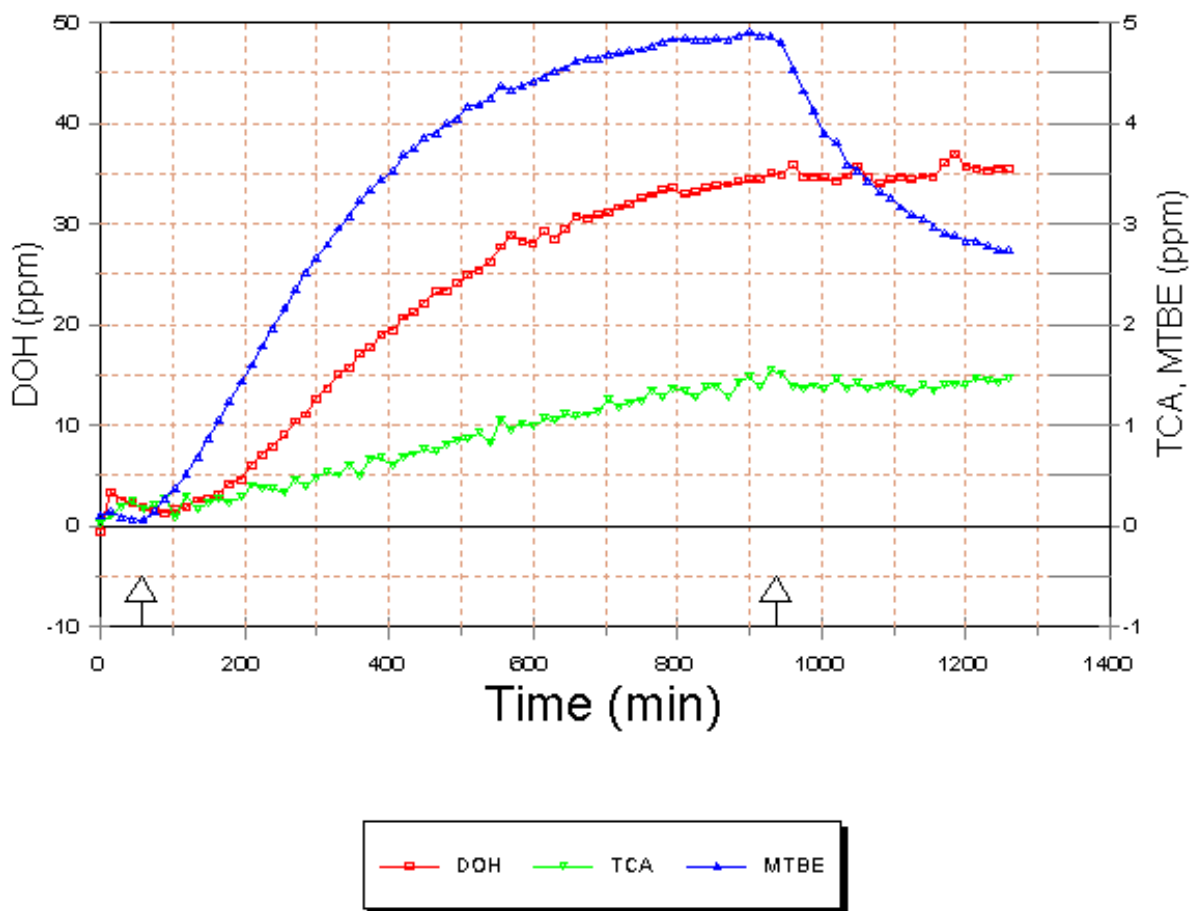


Figure 7. Comparative movement of TCA and methyl-*t*-butyl ether through saltcedar plants. Contaminants were present at 1mM (TCA) and 1.35 mM (MTBE) in the aqueous phase. Two saltcedar plants using 5.5 mL/hr together (2.7 & 2.8 mL each), were used for this experiment, Aug 18, 1996. Total water use was 60 and 64 mL (1/4 of input) during the course of the experiment. There was a decrease of less than 1/3 of TCA in one container and 60% in the other. The chamber extraction half-time was 123 min with the 50 cm line and 65 min with the 25 cm line. The first spectrum was room air obtained with a 25 cm constriction line. As indicated by arrows, the 50 cm line was used with the chamber from 15 min until a change at 930 min back to a 25 cm line.

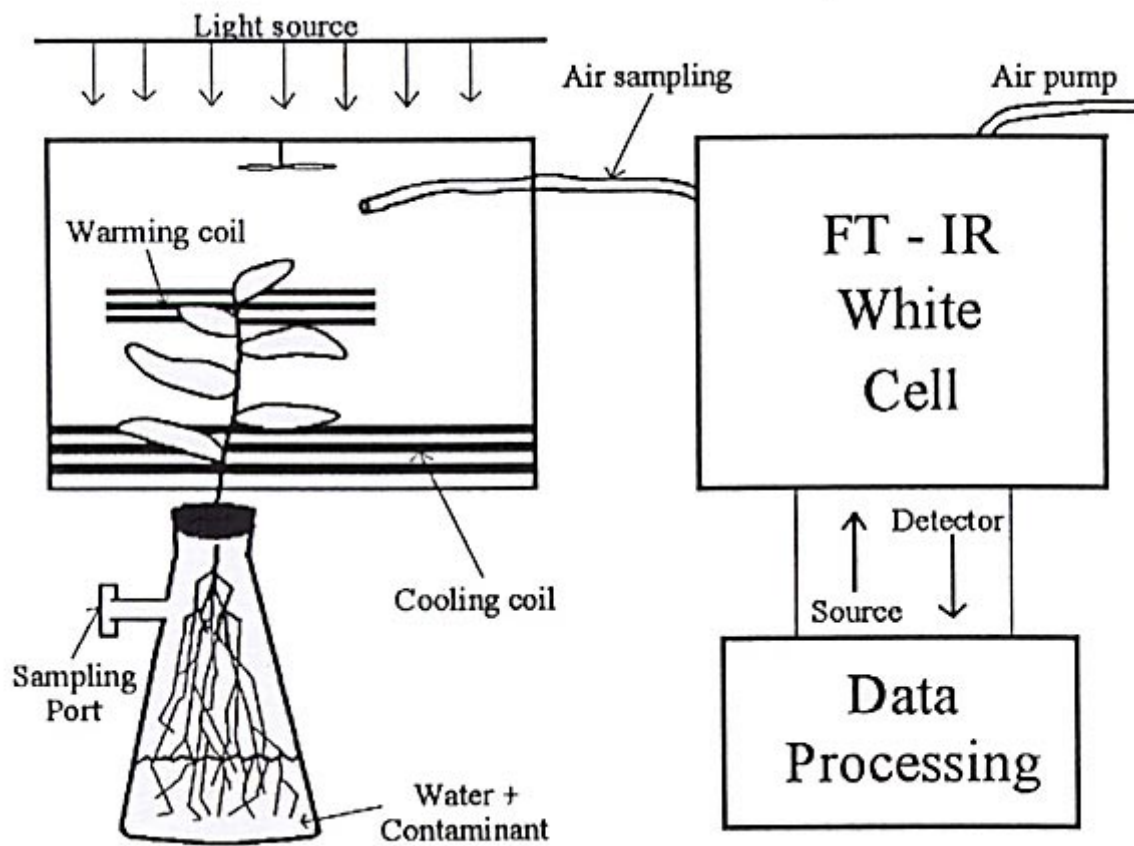


Diagram 1. Block diagram showing essential components of transpiration monitoring system.