
MEASURING CONTAMINANT FLUX THROUGH PLANTS BY FOURIER TRANSFORM INFRARED (FT-IR) SPECTROMETRY

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ABSTRACT Plants have a large capacity to transfer water and associated contaminants from soil to atmosphere. We measured the transfer rate for a range of constituents of gasoline that vary in volatility, solubility, and octanol/water partition coefficient. We tested benzene, toluene, ethyl benzene, *meta*-xylene, 1,2,4-trimethyl benzene, cyclohexene, *n*-pentane, ethyl ether, *n*-propyl ether, and *t*-butyl methyl ether. Aliphatic hydrocarbon constituents of gasoline were either not water soluble to sufficiently high concentration for study or they are too volatile to handle conveniently (e.g., butane). An extractive Fourier Transform Infrared Spectrometer 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 as a monitor for transpiration rate. The relative rate of transfer for different compounds was reasonably consistent with the work of Briggs, *et al.* [1], which relates their movement in plants to the log of their octanol/water partition coefficient ($\log K_{ow}$). For the ethers it appeared that they moved more rapidly than expected based on $\log K_{ow}$.

KEYWORDS: volatile contaminants, FT-IR, plants

INTRODUCTION

Plant-based bioremediation depends on the ability of plants to survive in the presence of contaminants, to metabolize or exclude contaminants, and to provide nutrient supplementation to microbes that can accelerate contaminant degradation. Plants facilitate transport of contaminants by drawing water from soil. Rates of water use may commonly exceed 1 cm per day (100,000 l/ha/day) during the summer. This water usage in turn could lead to intermedia transfer of volatile contaminants and exposure of plants to high concentrations of the contaminants that are relatively non-volatile and that are also partially excluded by the plant root system. Earlier studies have indicated that for compounds with a volatility similar to that of trichloroethylene, with a vapor pressure of >50 mm Hg at room

temperature, the compound rapidly escapes from the aqueous phase to the atmosphere whenever the soil is unsaturated [2]. If the compound is initially dissolved in water, then at steady state its rate of flux to the atmosphere is regulated by the rate of water flux. For a spill in dry soil the flux rate will depend on soil properties and vapor pressure. Plants may be useful to enhance the flux rate of water, and hence of contaminants, while assuring that the concentration of contaminant remains acceptably low in the atmosphere.

Cookson [3] indicates that gasoline contains more than 50 constituent compounds. A wide range of octanol-water partition coefficients similar to that of gasoline is represented by the series chosen here, from about $\log K_{ow}$ 0.8 to 3.4. According to the work of Briggs, *et al.* [1], these K_{ow} values

span a range of transpiration stream concentration factors (TSCF) from about 0.3 to 0.8, with the highest TSCF for compounds of intermediate polarity like toluene. 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.*

Fourier transform infrared spectrometry (FT-IR), with a long path length extractive instrument (Gasmeter, by Temet Instruments), allows detection of many common volatile materials at levels below 1 ppm (v/v). We examined the movement of common soluble, volatile gasoline constituents through two species of woody plants, hybrid poplars (*Populus deltoides x nigra*) and salt-cedar (*Tamarix parviflora*). Both species are rapidly growing, water consumptive, and drought resistant. In each case 1% deuterated water was used to provide an FT-IR-detectable marker for the rate of transpiration through the plants.

MATERIALS AND METHODS

We tested benzene, toluene, ethyl benzene, *meta*-xylene, 1,2,4-trimethyl benzene, cyclohexene, *n*-pentane, ethyl ether, *n*-propyl ether, and *t*-butyl methyl ether. Aliphatic hydrocarbon constituents of gasoline were either not water soluble to sufficiently high concentration for study or they are too volatile to handle conveniently (e.g., butane).

Contaminants were supplied to the root system in a closed flask with an equilibrated headspace. The top portion of each plant was completely isolated from the root system and enclosed in a 78.5 liter closed chamber from which air was drawn by a pump through the FT-IR instrument at about 1 l/min. Refrigerated coils condensed water, allowing accumulation of contaminant above

the amount that would be associated with water required for saturating the air in the chamber. The need to supply CO₂ (from room air) for photosynthesis limited the maximum concentration ratio that could be achieved.

The relative gas extraction rate was checked by injecting a known compound that did not significantly interfere with detection of the tested contaminant of interest. Generally trichloroethylene (TCE) was used. From the gas extraction rate of the FT-IR and the water (+ contaminant) flux rate into a chamber of known size it is possible to derive an expected level of contaminant steady state accumulation. The ratio of observed peak height to expected peak height indicates the apparent TSCF for the particular compound. The DOH peak is used to verify that water transport has occurred and is at a steady state rate during the time of monitoring.

The FT-IR accumulates 1 spectral sample every 100 msec with a resolution of 8 cm⁻¹ over the range 900 to 4,000 cm⁻¹. During the usual 10 min accumulation time it, therefore, obtains and averages 6,000 spectra.

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, i.e., water, DOH, TCE, and a contaminant. The Gasmeter then uses proprietary software to derive a simple least squares best 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

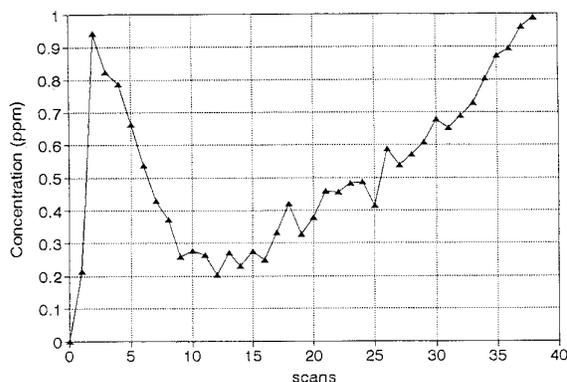


FIGURE 1a. POPLAR:ETHYL BENZENE ANALYTE. JULY 10, 1995; ETHYL BENZENE TREATMENT.

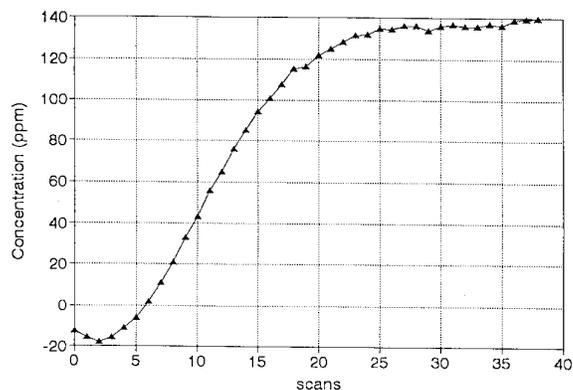


FIGURE 1c. POPLAR:DOH ANALYTE. JULY 10, 1995; ETHYL BENZENE TREATMENT.

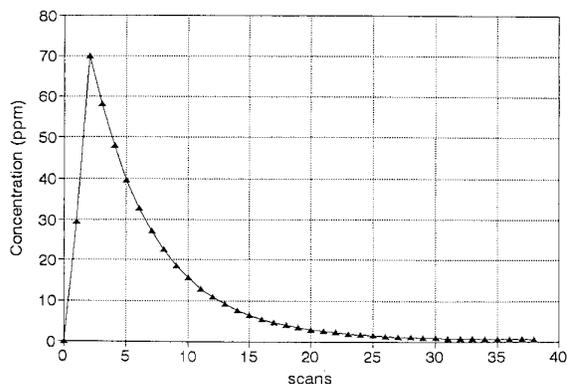


FIGURE 1b. POPLAR:TCE ANALYTE. JULY 10, 1995; ETHYL BENZENE TREATMENT.

phase for the compounds being studied in this project. However, comparison 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. Comparison of residual spectra with and without a compound in the “Method” was used to obtain apparent spectra for that compound. The spectra were then compared to authentic spectra to verify the identification process.

RESULTS

Ethyl benzene, xylene, and trimethyl benzene (least polar) were often toxic to the

plants at the initial concentration of ~1 mM. Other compounds were tolerated at levels up to 2 mM in the aqueous phase surrounding the root system. The least polar compounds, which also have unfavorable TSCF values, were difficult to detect in the gas phase surrounding the plant tops for two reasons. First, they were expected to move into the plants to very low levels based on their TSCF, which is a function of their K_{ow} . Second, their strongest accessible absorption peak lies immediately over a water overtone in the infrared. This makes reliable determination of baselines more difficult than for compounds that absorb in a water “window.” Other compounds with higher water solubility were detectable at levels related to water flux and TSCF. Examples of several compounds are shown in the figures that follow.

The first figure (Figures 1a-1c) provides an example of a plant showing a steady state transpiration rate. This plant was treated with ethylbenzene for 9.5 hours (four scans/hr). TCE used for measuring the chamber mixing half-time gives rise to a spurious peak identified as ethylbenzene in this instance. In this instance a small error in the estimated concentration of TCE (~1%) shows up as a large error in the estimation of

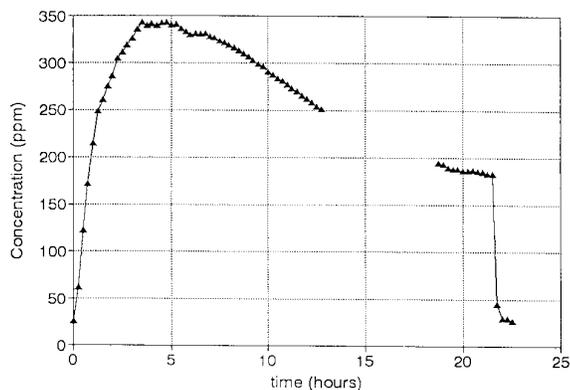


FIGURE 2. POPLAR:DOH ANALYTE. JULY 17, 1995; 1,2,4-TRIMETHYLBENZENE TREATMENT.

a compound present at a very low relative concentration (Figure 1a). The estimated concentration of TCE itself is well determined over a different spectral region and shows no irregular fluctuations such as those seen in the ethylbenzene (Figure 1b). The relative noisiness in the ethylbenzene peak is produced by the necessity to mathematically subtract a large contribution from water overtones and from TCE in instances when it is present. Note that there is a considerable lag between arrival of DOH and contaminant in the chamber (Figure 1c). Such a lag is anticipated for a hydrophobic compound that adsorbs to plant tissue.

Figure 2 provides an example of an injured plant showing the decline of transpiration after the initial phase. No detectable contaminant (trimethyl benzene) left the plant. Spectra were acquired as for the study shown in Figure 1, but the graph is presented as a function of time rather than scan number. The length of time required for a plant to reach a steady state of transpiration depends on the size of the plant and its photosynthetic activity.

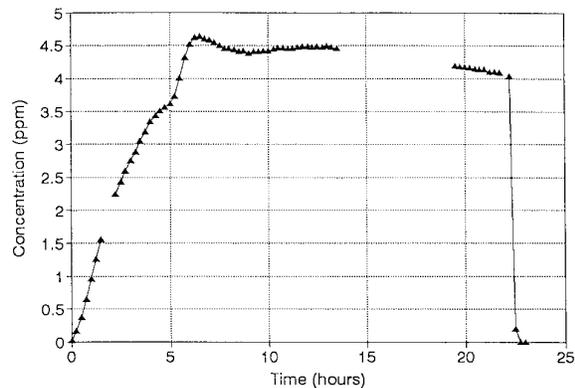


FIGURE 3a. POPLAR:ETHYL ETHER ANALYTE. JULY 27, 1995; ETHYL ETHER TREATMENT.

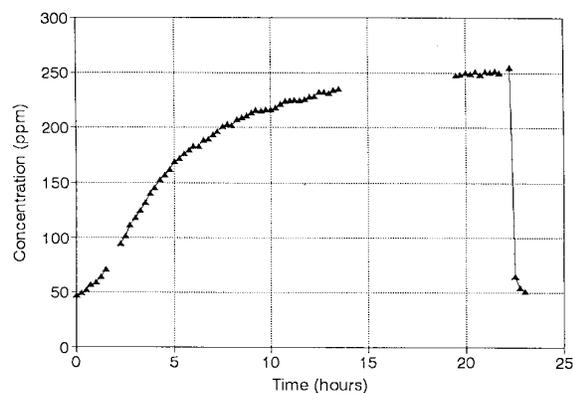


FIGURE 3b. POPLAR:DOH ANALYTE. JULY 27, 1995; ETHYL ETHER TREATMENT.

The third figure (Figures 3a and 3b) shows a plant with increased transpiration after reaching a steady state. Ethyl ether rises to a steady state and then slowly declines while the DOH concentration continues to rise. A comparable result was observed with propyl ether. These profiles indicate that there is a complex interaction between transpiration rate and the compound to which the plant is exposed and the duration of exposure. Note that both the DOH and the ethyl ether concentrations returned to their starting values after the sampling was discontinued at 22 hours.

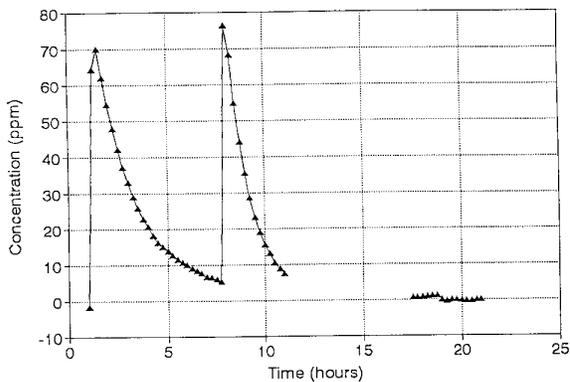


FIGURE 4a. POPLAR:TCE ANALYTE. JUNE 26, 1995; BENZENE TREATMENT.

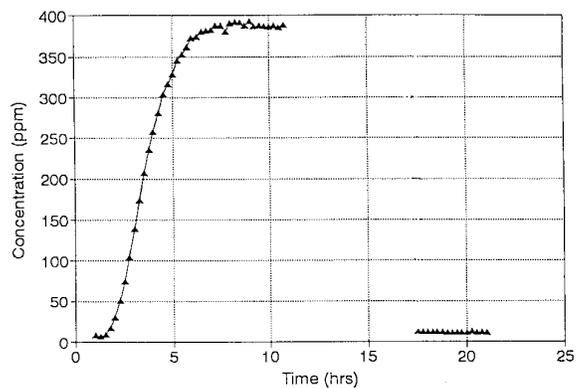


FIGURE 4c. POPLAR:DOH ANALYTE. JUNE 26, 1995; BENZENE TREATMENT.

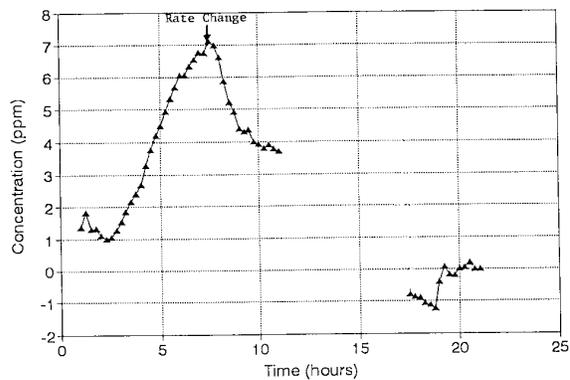


FIGURE 4b. POPLAR:BENZENE ANALYTE. JUNE 26, 1995; BENZENE TREATMENT.

Calculation of the apparent transpiration stream concentration factor depends on assuming that water flux is constant over the time of the entire experiment, and that the contaminant does not lag significantly behind the water in moving through the plant. With the ethers, water flux rates apparently increased over time. Hence the predicted contaminant flux should also increase, which would decrease the discrepancy between the observed and expected steady state accumulations.

Influence of sampling rate on steady state concentrations of DOH and contaminant may be observed in the fourth figure (Figure 4a-4c), showing an experiment with benzene. Two plants were present in the

chamber simultaneously. The extraction rate was altered after 7.5 hours. The TCE profiles indicate the change of half-time for mixing produced by this change of extraction rate (@ 1.6 fold) (Figure 4a). As expected the steady state benzene level declines as extraction rate is increased (Figure 4b). Concentration of CO₂, which had been significantly reduced at the low extraction rate, increased upon increasing the exchange rate. The DOH concentration remains unchanged when the extraction rate is changed, because DOH is a constant fraction of all the water entering the chamber; the plants, rather than the room air, are the main source of water (Figure 4c). With condensing coils present, the air is saturated with water vapor so that changing the extraction rate has no effect on the apparent concentration. When the sampling line was disconnected at 17 hours, observed concentrations of benzene, DOH, and TCE returned to zero, indicating that the "Method" used here was correctly calculating concentrations and that the baseline was stable.

TECHNICAL CHALLENGES TO BE MET

1. Water flux should be measured over multiple discrete time intervals. This is not simply the observed DOH concentration which represents a time-averaged rate, with plant size, relative humidity, and chamber mixing constant interacting.
2. Contaminant disappearance and aqueous phase concentration change as a function of time should be accounted for. This includes leakage, exclusion from the plant, and plant uptake.
3. Role of contaminant adsorption to plant biomass should be accounted for. Large plants might adsorb a significant fraction of contaminant both in the root system and stem and leaves. This can result in a long lag to the steady state release into the observation chamber.

CONCLUSIONS

We conclude that volatile hydrocarbon contaminants can move through plants, much like nonvolatile pesticides of varying polarity. We observed higher than expected mobility for the most polar compounds, the ethers. Only compounds of intermediate or high polarity move through plants sufficiently well to be detected by FT-IR. Nonpolar compounds like trimethylbenzene are poorly transported and/or toxic to plants. Studies of chlorinated hydrocarbons having different polarities will be reported elsewhere. In future, other species of plant can be examined, the role of plant mass can be explored, and mixed contaminants can be monitored.

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