Passive Volatilization of Gasoline from Soil

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ABSTRACT: Gasoline spills were simulated in the laboratory with three air-dried soils, using a synthetic gasoline and unsaturated soil to quantify passive volatilization over a period of up to 16 d. The total and individual gasoline components were monitored as a function of time and depth in the soil.

   The time required to deplete the overall gasoline concentration in the soil to 40% of the initial concentration ranged from 0.25 to 10 d for the three soils. Sand was the fastest, followed by loamy sand and silt loam. The volatilization rate of gasoline from soil was found to be dependent on soil, chemical type, and depth. Observation of individual components indicated that a wicking mechanism contributed to the gasoline flux toward the surface.

KEY WORDS: evaporation, petroleum hydrocarbons, unsaturated zone.

I. INTRODUCTION

Gasoline is stored and used extensively throughout society, and invariably it will spill or leak into soil. The USEPA (1988) reports that 25% of all underground storage tanks (USTs) are leaking, whether at commercial, industrial, or government facilities. Once released into the soil, gasoline has the potential to contaminate the atmosphere through volatilization and the groundwater through subsurface migration. Many gasoline components pose a health risk; thus, it is imperative that gasoline spills are minimized or promptly remediated after a spill occurrence.

   Gasoline-contaminated sites are frequently remediated via volatilization in either a passive or active mode. However, in either mode, the rate of gasoline volatilization is not easily quantified or predicted. Factors making this prediction uncertain include the impact of soil type and conditions and the state of the gasoline. To address the lack of information, laboratory experiments were conducted using a synthetic gasoline spiked as an immiscible phase into three air-dried soils: Ottawa Sand, Delhi Loamy Sand, and Elora Silt Loam. This paper describes the behavior of the various chemical compounds comprising the synthetic gasoline, and presents the time for 40% of the gasoline to volatilize for the soils and

conditions studied. The paper also discusses the impact passive volatilization has on site remediation.

II. BACKGROUND

Gasoline spilled into unsaturated soil migrates into the subsurface under the influence of gravity until the entire volume is dispersed into the soil pores (Zytner *et al.*, 1993). This gasoline remains in the soil until it volatilizes into the atmosphere, is transported further into the subsurface by infiltrating water, or is biologically degraded. To minimize the occurrence of vapor migration and solute transport, prompt remediation should occur.

Numerous options for the cleanup of gasoline-contaminated surface soils exist (Kostecki and Calabrese, 1989). Options include soil vapor extraction (Khan and Cruse, 1990), chemical degradation (Khan and Cruse, 1990), excavation and landfill, *in situ* bioremediation (Dean-Ross *et al.*, 1992; English and Loehr, 1991), bioventing (Dupont, 1993), surfactant flushing (Zalidis *et al.*, 1991), and passive volatilization. Passive volatilization describes the natural evaporation of the contaminant from soil and includes the following engineered modifications: covering excavations to facilitate venting and excavating the soil and land-spreading it (Donaldson *et al.*, 1992).

Passive volatilization is an inexpensive remediation option, as natural mechanisms are used to remove the bulk of gasoline. The gasoline migrates to the soil surface by convection due to bulk gasoline concentration gradients and due to diffusion in the gaseous or liquid gasoline due to individual component concentration gradients. However, limited information is available in the literature on the volatilization rates.

III. MATERIALS AND METHODS

A synthetic gasoline was used in this study to improve consistency and to simplify sample and data analysis. It contained six petroleum hydrocarbons: toluene, ethylbenzene, *m*-xylene, *n*-heptane, *n*-octane, and *n*-hexadecane with the compositions provided in Table 1. The alkanes, *n*-heptane, and *n*-octane were used as the bulk portion of the gasoline, while the aromatic components — toluene, ethylbenzene, and *m*-xylene — were present at levels consistent with commercial gasolines. *n*-Hexadecane was added as a low-volatility control (tracer) for experimental purposes.

Three soils were selected for the experiments: Ottawa Sand (OS), Delhi Loamy Sand (DLS), and Elora Silt Loam (ESL). Table 2 provides each soil's characteristics. The OS was used as received, whereas, the DLS and ESL were sieved (2 mm) to remove large particles and then suitably mixed to produce consistency.

TABLE 1
Synthetic Gasoline Composition

Component	Composition (wt%)	Vapor pressure[a] (Pa @ 20°C)
n-Heptane	40	4500
Toluene	9	2900
n-Octane	40	1400
Ethylbenzene	2	940
m-Xylene	4	820
n-Hexadecane	5	0.05

[a] Zwolinski, B. J. and Wilhoit, R. C. 1971. Handbook of Vapor Pressures and Heat of Vapori*zation of Hydrocarbons and Related Compounds.* AP144-TRC, Publications in Science and Engineering, College Station, TX.

TABLE 2
Soil Characteristics

Soil Type	Percent				Hydraulic conductivity (sat'd, m/s)	Bulk density (g/cm^3)	Retention capacity[a] ($g_{gasoline}/g_{soil}$)
	Sand	Silt	Clay	OM			
Ottawa Sand	98.8	1.2	0.0	0.0	3.6×10^{-4}	1.7	0.068
Delhi Loamy Sand	86.5	9.0	4.5	1.2	3.8×10^{-5}	1.5	0.170
Elora Silt Loam	34.0	50.1	15.9	2.5	3.7×10^{-6}	1.5	0.238

[a] After 24 h of free drainage.

All three soils were air dried prior to use, resulting in 0.0, 0.7, and 2.2 % moisture content, respectively, for OS, DLS, and ESL.

The experimental apparatus consisted of a cubic galvanized steel box measuring 250 mm on each side. This box was subdivided into 25 50 × 50 mm segments by a galvanized steel dividing grid.

The experimental procedure involved filling the soil box (without the grid in place) with contaminated soil. To provide uniform gasoline distribution in the soil box, the contaminated soil was prepared by mixing 12 batches of clean air-dry soil with gasoline in a sealed glass container. The mass of gasoline added to the soil was 80% (by wt) of the soil's retention capacity, as determined in preliminary experiments (Table 2). Retention capacity is defined as the maximum concentration of gasoline that can be retained under the influence of gravity at a specific moisture content. The 80% (by wt) was selected to provide a significant nonaqueous phase of gasoline and yet minimize liquid drainage during setup. As the batches of soil

were prepared, they were sequentially added to the apparatus in layers and manually compacted using vibration to achieve the desired bulk density (Table 2).

Sample cores taken at time 0 h provided a means of checking whether the initial gasoline was indeed uniform and whether any liquid drainage was occurring. Based on the total gasoline concentration of these samples vs. depth, the standard deviation observed was less than 25% in all cases, and this was judged to be reasonable.

Once the box was filled, the dividing grid was hammered into place. The soil box was then placed in a fume hood. To assist in keeping a uniform air velocity across the soil surface, a portable fan was placed level with the top of the box. The air velocity was measured at 1 m/s (3.6 km/h) at a height of 5 cm above the soil surface, which is in the low wind speed range in comparison to a field situation. Over the course of the experiments, the room temperature was $19 \pm 2°C$.

Immediately after placing the apparatus in the fume hood, one of the segments was randomly selected and sampled. A core sample was removed by a custom soil coring sampler measuring 300 mm in length, which allowed "undisturbed sampling". Following the initial sample, 24 further cores were taken at different time intervals covering a time span of 16 d. Each core was analyzed by taking 4 g of soil approximately every 50 mm in length from the core removed by the coring sampler. Care was required in measuring depth location, as some compaction occurred when the sampler was driven into the soil. Each soil sample was extracted with methanol in a 40-ml borosilicate glass vial with a teflon-lined cap.

The volatilization experiments with OS and DLS were completed once, while replicate experiments were conducted only for the ESL. The final ESL values were then averaged, as the differences in gasoline mass remaining between the two experiments ranged from 2 to 35%.

In addition to the soil volatilization experiments, wicking experiments were conducted using the same apparatus. In these wicking experiments, only the bottom 75 mm of the soil box had soil contaminated with gasoline. The remaining 175 mm of soil (placed on the top of 75 mm of gasoline-contaminated soil) were initially clean. The surface of the soil box was sealed with aluminum foil to minimize volatilization during the wicking experiments. Soil samples were collected as before: six samples over 14 d for DLS and six samples over 28 d for ESL. Visual observations as to the location of the gasoline wetting front were also recorded when the soil core was removed.

A single volatilization experiment was also performed in which a shallow pool of synthetic gasoline was volatilized from a tray at a room temperature of 18.5°C. The gasoline thickness in the tray was approximately 7 mm. The tray rested on an electronic balance to allow mass measurements to be read at the same time as gasoline samples were collected by syringe for gas chromatographic analysis. The portable fan was again used to provide a constant air flow.

All samples were analyzed by a Hewlett Packard 5890 Series II Gas Chromatograph (GC) equipped with a flame ionization detector. A DB-5 J&W capillary

column of dimensions 30 m × 0.32 mm with a 1-μm film stationary phase was used. The temperature program was 6 min at 40°C, a ramp of 20°C/min to 140°C, then 25°C/min to 260°C, with a final hold time of 2 min. Calibration was by means of external standards.

IV. **RESULTS AND DISCUSSION**

Figure 1 shows the fraction remaining relative to the initial mass in the gasoline for the six components vs. time for the tray experiment. As expected, *n*-heptane with the largest vapor pressure (Table 1) volatilized first, followed by toluene, *n*-octane, ethylbenzene, and *m*-xylene. *n*-Hexadecane, which was added as a conservative tracer, also behaved as expected. The near-linear relationship is consistent with the observations of Stiver *et al.* (1989). The evaporation rate from a tray in the absence of any soil provides a reference point for comparing the soil-based evaporation studies.

Figure 2 is a typical plot for the behavior of the gasoline at a depth of 50 mm for the soils tested. The ordinate is the concentration of compound *i* in the soil (milligrams of *i* per gram of soil) relative to the initial concentration of *i* in the soil, both at a particular depth in the soil (50 mm in this case). As expected, the most
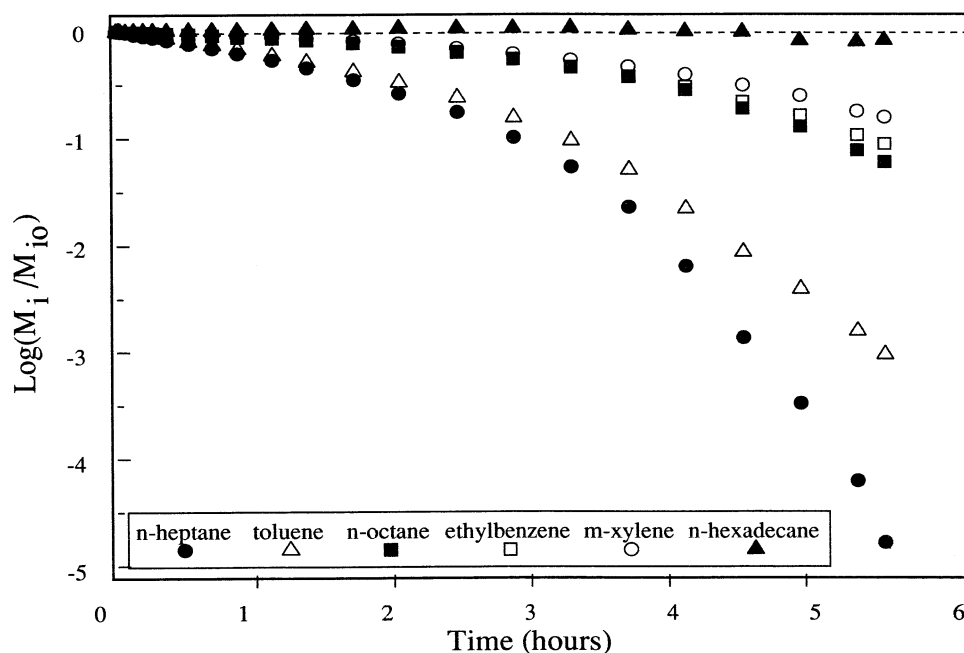

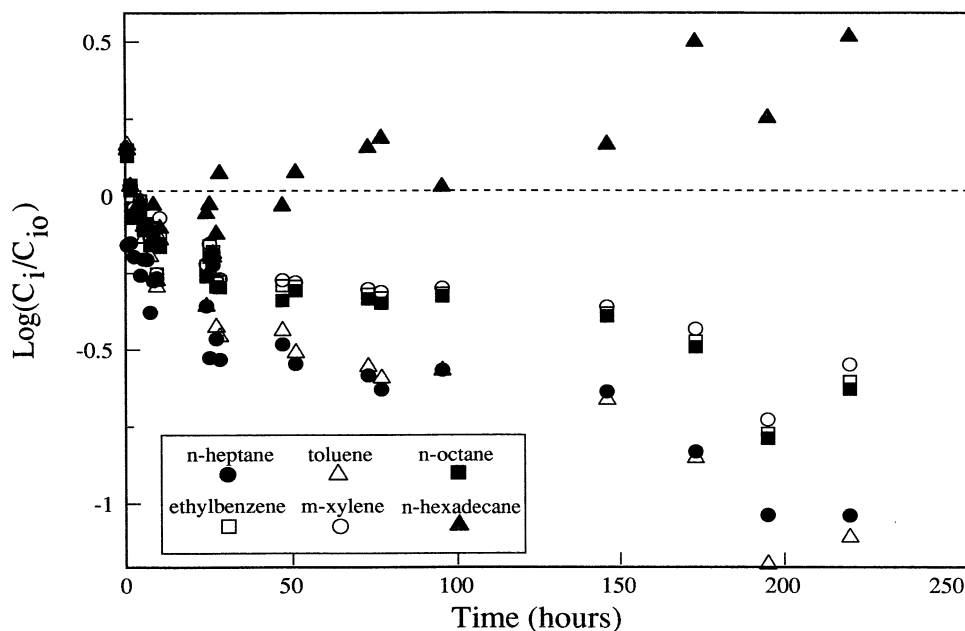**FIGURE 1.**   Volatilization of synthetic gasoline from a pool thickness of 7 mm.

FIGURE 2. Volatilization by component in DLS soil at a depth of 50 mm.

volatile components diminish the most rapidly at this depth. However, *n*-hexadecane (the relatively nonvolatile tracer) increases in soil concentration with time, as indicated by an ordinate value above 1. This accumulation of *n*-hexadecane at the surface of the soil requires a source. The source could only be the air above the soil or the soil further below the surface. It is unlikely that the air above the soil is sufficiently contaminated with *n*-hexadecane to contribute the quantities observed, leaving the deeper soil as the source.

The tracer *n*-hexadecane can be transported to the surface from the deeper soil by one of three mechanisms: diffusive transport through the immiscible gasoline mixture, diffusive transport through the soil-air followed by condensation at the surface, or convective transport with a bulk gasoline flow toward the surface. Diffusive transport from the deeper soil to the surface soil requires an appropriate concentration gradient in the soil. The observed *n*-hexadecane concentration gradient shows higher concentrations at the surface, with lower concentrations in the deeper soil, thus precluding diffusive transport as the mechanism of *n*-hexadecane moving to the surface.

The driving force required for a convective flux of bulk gasoline from the deeper soil to the surface is a lower total gasoline content at the surface than in the deeper soil. The observed gasoline content with depth is consistent with this required driving force. Thus, the increasing n-hexadecane content at the surface is the result of a convective flow of bulk gasoline to the surface. In essence, capillary forces in

the soil create a wicking behavior toward the surface which will then contribute to volatilization rates.

Comparison of Figure 1 with Figure 2 shows the net effect of the soil on gasoline volatilization rates. Although the soil allows for a wicking process that contributes to volatilization rates, the overall volatilization rate is substantially slower in the presence of soil. The observed volatilization rates from soil are estimated to be more than 100-fold slower. Part of this difference can be attributed to the fact that the soil experiments involve a quantity of gasoline that is several times greater than the tray experiments; three times for OS, six times for DLS, and ten times for ESL. The remainder of the difference between the rates can be attributed to mass transfer limitations within the soil structure.

The wicking behavior also affects the loss rates of gasoline components as a function of depth in soil. In a strictly evaporative process, one would expect volatilization rates to be faster for gasoline at shallow depths than at deeper soil depths. Figure 3 illustrates that this is indeed the observed behavior for toluene from DLS. However, Figure 4 illustrates that not all of the compounds follow this trend. Figure 4 is the behavior of n-octane in ESL. It seems that the most volatile components are controlled and behave in a manner consistent with a strictly evaporative process. However, the less volatile components are controlled by a combination of evaporative and convective processes. A strictly convective process
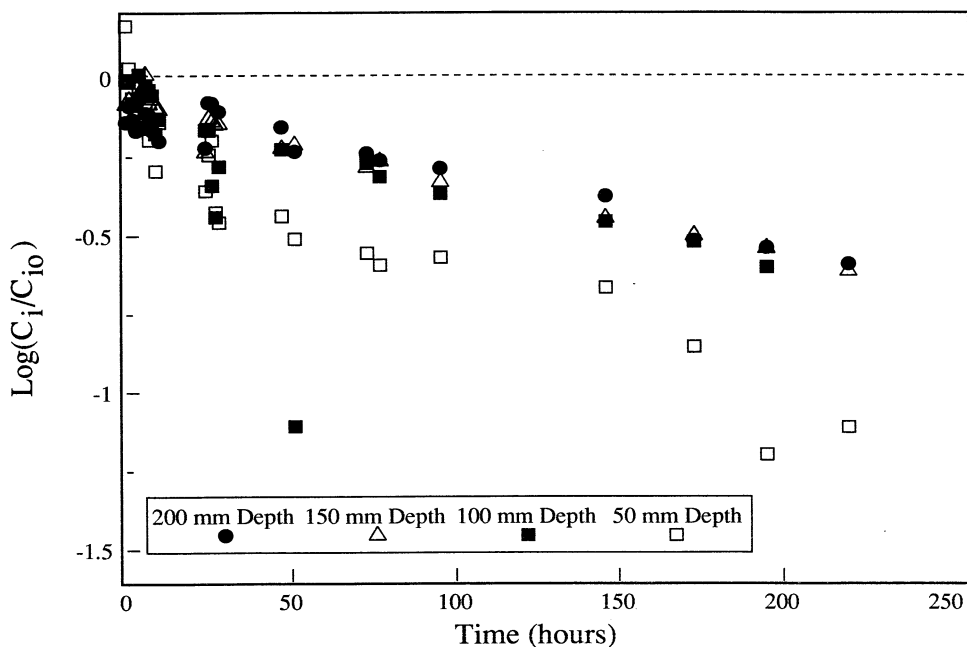

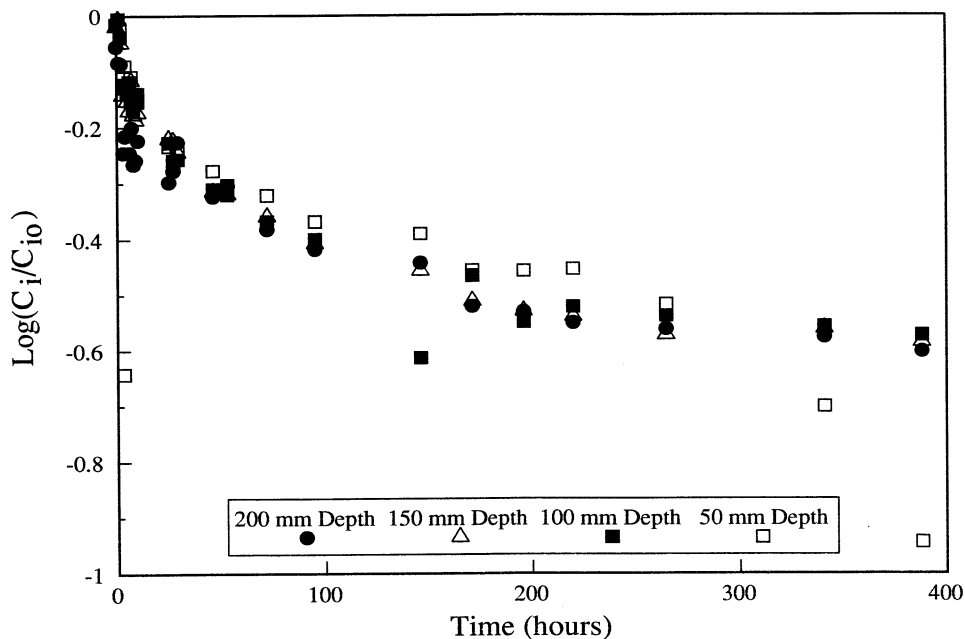**FIGURE 3.** Volatilization of toluene in DLS soil as a function of depth.

FIGURE 4. Volatilization of *n*-octane in ESL as a function of depth.

would lose contaminants at greater depths first. A strictly convective process, in an overall sense, cannot occur, as it is the evaporative process that creates the driving force for the convective process. However, an individual low vapor pressure component of the gasoline could be controlled by the convective process.

As a further confirmation of the existence of a significant convective flow through soil, a separate wicking experiment was conducted for each soil. In these experiments the bottom 75 mm of soil was contaminated and the top 175 mm started clean. In addition, the surface was sealed to minimize the evaporative process. Figure 5 illustrates the gasoline's behavior in this experiment for the ESL soil. It is apparent that a substantial fraction of the gasoline may indeed migrate under convective forces over the time span of a few hundred hours (the time span of the volatilization experiments). The observed wetting front paralleled the total gasoline migration as depicted in Figure 5. The observation of a condensed phase moving upward rules out the possibility that the gasoline reached the surface in the wicking process by a volatilization mechanism. A final check confirming the convective flow was that the composition of the gasoline near the surface was similar to the composition in the deeper soils. If volatilization was significant, a separation of components as a function of depth would have been observed.

The effect of soil type on volatilization is shown by Figure 6. Figure 6 clearly shows that *n*-heptane volatilizes first from OS, followed by DSL and ESL. This
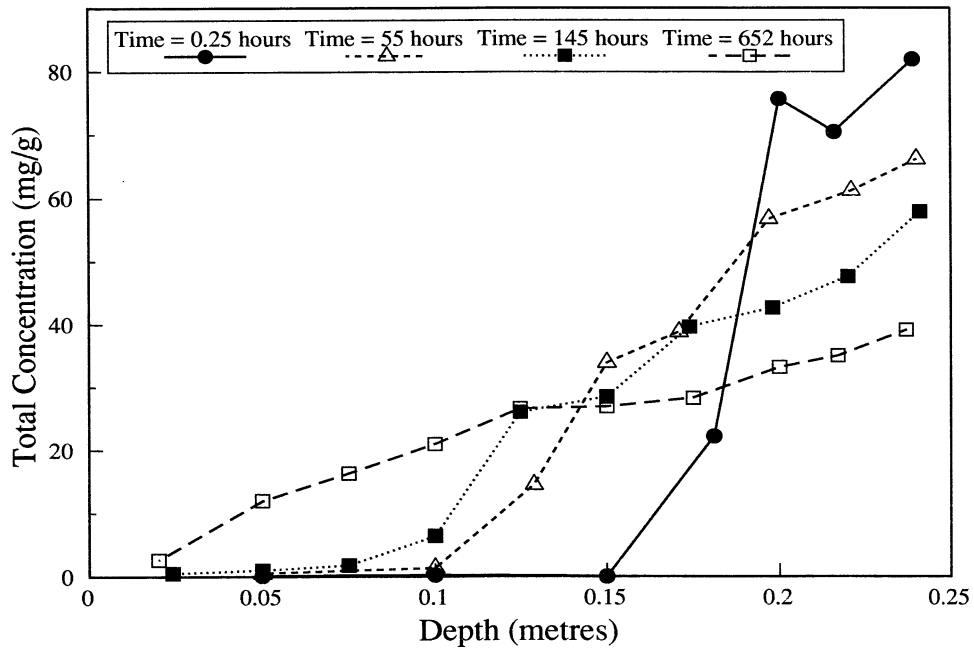
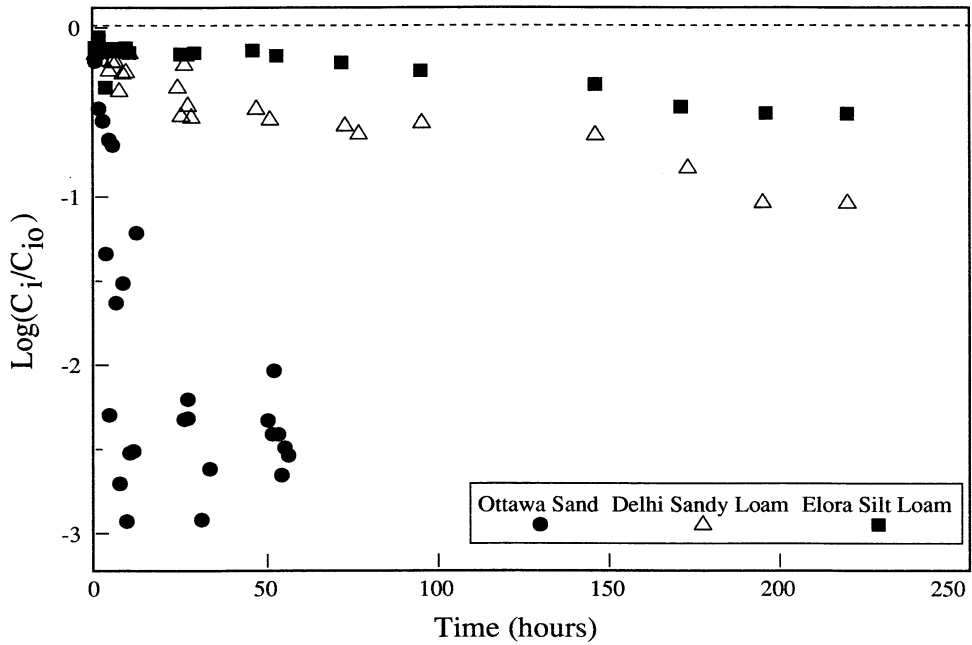**FIGURE 5.** Gasoline wicking front position vs. time in ESL soil.

FIGURE 6. Volatilization of *n*-heptane in OS, DLS, and ESL soils at a depth of 50 mm.

trend is consistent for all the gasoline components tested. The soil characteristics in Table 2 show that volatilization preferences are consistent with the changes in soil texture and hydraulic conductivity. That is, as the particle sizes decreased (lower hydraulic conductivity) and as the clay content and organic matter content increased, the volatilization rate decreased. However, further experiments are necessary with a wider range of soils to quantify the dependence on textural characteristics.

In this study, the effect of soil type on volatilization rates is obscured somewhat by the differing initial gasoline content of the three soils. The initial starting concentration of 80% (by wt) of the retention capacity was chosen to reflect levels that are likely following a leakage or spill in each of the three soils. However, these differing levels result in varying soil-air contents in the soil, which has an effect on evaporation. Further work should be conducted involving differing initial gasoline contents in soil to quantify the effects of the soil-air fraction on volatilization rates.

Finally, the basis for comparison can alter the interpretation. The ESL soil appears to be evaporating more slowly when considering the fraction of gasoline remaining as the measure. However, considering the mass flux at the soil surface, the rates of evaporation are nearly the same for the ESL and DLS soils.

To aid in the comparison of volatilization in the various soils tested with literature data, the time required for the gasoline to reach 40% of the initial concentration was determined. The calculated times are summarized in Table 3 and confirm the volatilization preferences stated earlier.

Comparison of the times in Table 3 to values reported in the literature shows that they are consistent. Galen *et al.* (1990a) reported that it took 240 h for kerosene to reach 40% of its initial concentration at a depth of 75 mm in loamy sand. The kerosene consisted of heavier hydrocarbons (C_9 to C_{15}) as opposed to the lighter hydrocarbons comprising the synthetic gasoline (80% of C_7 and C_8). Galin *et al.* (1990b) observed decreasing volatilization rates in going from coarse to fine sand. Donaldson *et al.* (1990) reported that 32 d were required for petrochemical hydrocarbons to reach 61% of the initial concentration in sandy loam at a depth of 180

TABLE 3
Time to Reach 40% of Initial Gasoline Concentration (hours)

Soil	Overall	Depth			
		50 mm	100 mm	150 mm	200 mm
Tray	2.5	—	—	—	—
Ottawa Sand	6	0.88	1.4	4.9	16
Delhi Loamy Sand	160	110	140	160	200
Elora Silt Loam (average of two runs)	240	200	210	240	280

to 200 mm. Dominguez Laseca *et al.* (1990) found that 64% of gasoline evaporated from beach sand after 25 min. Anderson *et al.* (1990) found that the half-lives of volatile components in soil ranged from 2 to 11.3 d.

Attempts to generate simple empirical correlations proved difficult. Simple expressions of volatilization rates as a function of vapor pressure, soil type, and/ or soil depth proved to be disappointing. Further attempts with more complex functionalities are warranted but, if successful, may not be user friendly.

Given the apparent importance of both a convective and an evaporative process, successful modeling of behavior for predictive means may well require a mechanistic structure. However, many parameters necessary for such a model are not readily available. In particular, the conductivity and capillary potential characteristics of gasoline in soil as a function of gasoline content, soil type, and moisture content are needed. The effect of increasing water content on the passive volatilization of gasoline from DLS has been observed by Smith *et al.* (1994). Research in support of these needs is ongoing and will ultimately allow for a rigorous modeling of multicomponent volatilization from unsaturated soil.

V. **APPLICATIONS**

The effectiveness of passive volatilization as a remediation technique has been shown to be a function of soil, depth of contamination, and time. Based on the available information, passive volatilization is effective for sandy soils having shallow contamination. The data also suggest that deeper contaminated soils be mixed at regular intervals.

The ability to quantify passive volatilization rates also has benefits in the assessment of the various risks associated with a contaminated site. Based on the mass of gasoline that has volatilized into the atmosphere, the atmospheric concentrations can be calculated. This allows determination of the impact on a local community's air quality and health risks of the spill-response team. This study suggests that the greatest concern is with sandy soils, including when contaminated soil at lower levels (e.g., 3 m) is exposed through excavation.

The wicking process identified here can occur whenever an immiscible phase concentration gradient is present. Consequently, wicking can impact other removal methods such as soil venting or groundwater pump and treat. The ability to quantify immiscible phase velocity based on the concentration gradient produced would be valuable for modeling immiscible phase movement during remediation.

VI. **SUMMARY**

The experimental results presented in this paper indicate that the volatilization rate of gasoline is dependent on the soil and chemical type, wicking behavior,

and depth of gasoline in the soil. Wicking is a significant mechanism. Based on the results:

1. The volatilization rate decreases as depth of contamination in soil increases.

2. Volatilization (based on fraction remaining) occurs fastest in OS (6 h), followed by DLS (160 h) and ESL (240 h).

3. The volatilization rate increases with increasing vapor pressure (*n*-heptane, followed by toluene, *n*-octane, ethylbenzene, *m*-xylene, and *n*-hexadecane).

ACKNOWLEDGEMENTS

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